Active CLP RAS Lab Addresses

As of February 2009

A4 Scientific, Inc.
1544 Sawdust Road
Suite 505
The Woodlands, TX 77380
Lab Code: A4
Phone: 281-292-5277
FAX: 281-292-2481

Contract Number(s):
EPW05036 (Organic Multi - SOM01.2)
EPW08063 (Inorganic Multi - ILM05.4)

Bonner Analytical Testing Co.
2703 Oak Grove Road
Hattiesburg, MS 39402
Lab Code: BONNER
Phone: 601-264-2854
FAX: 601-268-7084

Contract Number(s):
EPW08064 (Inorganic Multi - ILM05.4)

ChemTech Consulting Group
284 Sheffield Street
Mountainside, NJ 07092
Lab Code: CHEM
Phone: 908-789-8900
FAX: 908-789-8922

Contract Number(s):
EPW08065 (Inorganic Multi - ILM05.4)

Datachem Laboratories, Inc.
960 West LeVoy Drive
Salt Lake City, UT 84123
Lab Code: DATAC
Phone: 801-266-7700
FAX: 801-268-9992

Contract Number(s):
EPW05026 (Organic Multi - SOM01.2)
EPW08066 (Inorganic Multi - ILM05.4)

KAP Technologies, Inc.
9391 Grogans Mill Road
Suite A-2
The Woodlands, TX 77380
Lab Code: KAP
Phone: 281-367-0065
FAX: 281-367-6772

Contract Number(s):
EPW05032 (Organic Multi - SOM01.2)

Liberty Analytical Corporation
501 Madison Avenue
Cary, NC 27513
Lab Code: LIBRTY
Phone: 919-379-4100
FAX: 919-379-4040

Contract Number(s):
EPW05028 (Organic Multi - SOM01.2)
EPW08067 (Inorganic Multi - ILM05.4)

Mitkem Corporation
175 Metro Center Boulevard
Warwick, RI 02886
Lab Code: MITKEM
Phone: 401-732-3400
FAX: 401-732-3499

Contract Number(s):
EPW05030 (Organic Multi - SOM01.2)

Active CLP RAS Lab Addresses

As of February 2009

Shealy Environmental
106 Vantage Point Drive
West Columbia, SC 29172
Lab Code: SHEALY
Phone: 803-791-9700
FAX: 803-791-9111

Contract Number(s):
EPW05031 (Organic Multi - SOM01.2)

SVL Analytical, Inc.
One Government Gulch
Kellogg, ID 83837
Lab Code: SVL
Phone: 208-784-1258
FAX: 208-783-0891

Contract Number(s):
EPW08068 (Inorganic Multi - ILM05.4)

TestAmerica Laboratories, Inc.
30 Community Drive
Suite 11
South Burlington, VT 05403
Lab Code: STLV
Phone: 802-660-1990
FAX: 802-660-1919

Contract Number(s):
EPW07057 (Organic Multi - SOM01.2)

OSWER 9240.0-44
EPA 540-R-07-06

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Office of Superfund Remediation and Technology Innovation

Contract Laboratory Program Guidance for Field Samplers

Foreword

The intent of the Contract Laboratory Program (CLP) Guidance for Field Samplers is to replace the CLP Samplers Guide. This guidance document is designed to provide users with general information regarding environmental sample collection for the United States Environmental Protection Agency's (USEPA) Contract Laboratory Program (CLP). This document provides minimum CLP requirements, an explanation of the general sampling process sequence of events, and any related information. The appendices contain useful reference information and checklists to aid in planning and documenting sampling activities.

CLP users also are encouraged to review the Introduction to the Contract Laboratory Program document that contains a general overview of the CLP, how it works, and how to access the program. The CLP requires samplers to use the functionality provided by the Field Operations Records Management System (FORMS) II Lite™ software, which is the preferred means of creating CLP sample documentation. For guidance in using the software to record and submit sampling data, users should reference the FORMS II Lite User's Guide.

Both the Introduction to the Contract Laboratory Program and the Contract Laboratory Program Guidance for Field Samplers can be downloaded from the CLP Web site at the following address:

http://www.epa.gov/superfund/programs/clp/guidance.htm

The FORMS II Lite User's Guide can be downloaded from the CLP Web site at the following address:

http://dyncsdao1.fedcsc.com/itg/forms2lite/doc.html

For more information regarding the CLP or this guide, please contact Elizabeth Holman via email at Holman.Elizabeth@epa.gov or via telephone at (703) 603-8761.

Key Information

Text in blue and underlined indicates an external link to information outside of this document.

The images below are located throughout the document to draw attention to important information and each are labeled accordingly:

Important

Note

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ASB	Analytical Services Branch
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CLP	Contract Laboratory Program
CLP PO	CLP Project Officer
CRQL	Contract Required Quantitation Limit
CVAA	Cold Vapor Atomic Absorption
DOT	Department of Transportation
DQO	Data Quality Objective
dbf	Database File
ET	Eastern Time
FORMS II Lite™	Field Operations Records Management System II Lite
FSP	Field Sampling Plan
HCN	Hydrocyanic acid
IATA	International Air Transport Association
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
MS	Matrix Spike
MSD	Matrix Spike Duplicate
$NAHSO_4$	Sodium Bisulfate
NPL	National Priorities List
OSC	On-scene/on-site Coordinator
OSHA	Occupational Safety and Health Administration
OSRTI	Office of Superfund Remediation and Technology Innovation
OSWER	Office of Solid Waste and Emergency Response
PCBs	Polychlorinated Biphenyls
PE	Performance Evaluation
PM	Program Manager
ppb	Parts-Per-Billion
ppt	Parts-Per-Trillion
PRP	Potentially Responsible Party
PT	Proficiency Testing
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl Chloride
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QASPER	Quality Assurance Sampling Plan for Environmental Response
QATS	Quality Assurance Technical Support
QC	Quality Control
RAS	Routine Analytical Services
RPM	Remedial Project Manager
RSCC	Regional Sample Control Center Coordinator
RSM	Regional Site Manager
SAM	Site Assessment Manager
SAP	Sampling Analysis Plan
SARA	Superfund Amendments and Reauthorization Act
SDG	Sample Delivery Group
SMC	System Monitoring Compound
SMO	Sample Management Office
SOP	Standard Operating Procedure
SOW	Statement of Work
SVOA	Semivolatile Organic Analyte
TR/COC	Traffic Report/Chain of Custody
txt	Text File
UN	United Nations
USEPA	United States Environmental Protection Agency
VOA	Volatile Organic Analyte
XML	eXtensible Markup Language

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1.0 INTRODUCTION

1.1 About this Guide

This document describes the important organizational roles and responsibilities for those who plan and conduct environmental sample collection projects for analysis through the Superfund's Contract Laboratory Program (CLP). This chapter introduces the structure and purpose of this document. Chapter 2, *Pre-field Activities*, addresses pre-field planning activities that the sampling team could complete prior to the actual sampling event. Chapter 3, *In-field Activities*, addresses those activities that need to be completed during the sampling event.

Appendix A describes the functions within a sampling project which are taken from the Quality Assurance Project Plan requirements. Appendix B and Appendix C contain the sample collection guidelines for Volatile Organic Analytes (VOAs) in soil and in water. Appendix D recommends sampling techniques. Appendix E contains checklists to help the sampler ensure that all necessary steps are completed.

A project and site-specific Quality Assurance Project Plan (QAPP) providing Regional guidance will override guidance given within this document.

1.2 Overview of the CLP

The CLP is a national program of commercial laboratories under contract to support the USEPA's nationwide effort to clean up designated hazardous waste sites by supporting its Superfund program. The Superfund program was originally established under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 and presently exists under the Superfund Amendments and Reauthorization Act (SARA) of 1986.

The CLP uses state-of-the-art technology to provide users with analytical services. The program provides data of known and documented quality to support USEPA enforcement activities or other user needs. To achieve this goal, the CLP has established strict Quality Control (QC) procedures and detailed documentation requirements. Current CLP users include the USEPA Regions, States and Tribal governments, and other Federal agencies. CLP users also are encouraged to review the *Introduction to the Contract Laboratory Program* document that contains a general overview of the CLP, how it works, and how to access the program.

1.2.1 Key Players Within the CLP

In coordinating Superfund sampling efforts, the Analytical Services Branch (ASB) is supported by the Sample Management Office (SMO) contractor, the Regional CLP Project Officers (CLP POs), the Regional Sample Control Center Coordinators (RSCCs), and the Regional Site Managers (RSMs), including Site Assessment Managers (SAMs), On-scene/On-site Coordinators (OSCs), and Remedial Project Managers (RPMs). Samplers may work directly with the RSCC and/or RSM (or equivalent), and/or an OSC from the Field Support Section during a sampling event. See Table 1-1 for a brief description of the functions performed by key participants (functions may vary by Region).

Table 1-1. Participants in the CLP Sampling Process

Participants	Responsibilities
Analytical Services Branch	USEPA ASB directs the CLP from within the Office of Superfund Remediation and Technology Innovation (OSRTI) in the Office of Solid Waste and Emergency Response (OSWER). ASB responsibilities include: • Development of the Statements of Work (SOWs) that define required analytical methods (including QC, detection/quantitation limits, and holding times) for the analytical services procured under the CLP; • Development and implementation of policies and budgets for Superfund analytical operations; • Development of information management policies and products for analytical data; • Management of SMO and Quality Assurance Technical Support (QATS) contracts; • National administration, evaluation, and management of the CLP; and • Direction of CLP Quality Assurance (QA) activities in coordination with overall OSWER QA activities. To obtain the most current ASB contact list, refer to the following Web site: http://www.epa.gov/superfund/programs/clp/contacts.htm#ASB
CLP Sample Management Office	The contractor-operated SMO provides necessary management, operations, and administrative support to the CLP. SMO receives Regional analytical requests, coordinates and schedules sample analyses, and tracks sample shipments. SMO also receives and checks data for completeness and compliance, processes laboratory invoices, and maintains a repository of sampling records and program data.
CLP Contract Laboratories	The contractor-operated laboratories within CLP provide necessary analytical services for the isolation, detection, and quantitation of the CLP's target compounds and analytes.
Regional CLP Project Officer	The CLP PO monitors the technical performance of the contract laboratories in each Region. The CLP PO works closely with ASB Program Managers (PMs) to identify and resolve laboratory technical issues, and leads laboratory on-site evaluations. To obtain the most current CLP PO contact list, refer to the following Web site: http://www.epa.gov/superfund/programs/clp/polist.htm
Regional Sample Control Center Coordinator	In most Regions, the RSCC coordinates sampling efforts and serves as the central point-of-contact for sampling questions and problems. The RSCC works with SMO to schedule sample shipments to laboratories. In addition, the RSCC's activities may include: informing SMO of sample shipment, cancellations, special instructions, and sampling issues. To obtain the most current RSCC contact list, refer to the following Web site: http://www.epa.gov/superfund/programs/clp/rscclist.htm
Regional Site Manager	The RSM Coordinates the development of acceptance or performance criteria and oversees project-specific contractors, state officials, or private parties conducting site sampling efforts. The RSM could be the SAM, the OSC, or the Remedial Project Manager (RPM).
Field Support Section	The Field Support Section consists of personnel such as the OSC, SAM, and RPM. In most Regions, the Field Support Section develops Standard Operating Procedures (SOPs) for field sampling and related procedures, and assists sampling teams in following those SOPs. The sampling team determines what type(s) of CLP services will be required for a particular sampling event. The Field Support Section reviews Sampling Analysis Plans (SAPs) prepared by sampling teams and oversees sampling teams in the field. The Field Support Section may also prepare their own SAPs, perform sampling activities in the field, and analyze and report the results of their sampling events to the RSM.

1.3 Overview of the Sampling Process

At–a-Glance:
Overview of the Sampling Process

- ✓ Procedures must be consistent.
- ✓ Analytical data must be accurate and defensible.
- ✓ Procedures must meet minimum requirements.

Once USEPA has determined that physical, chemical, and/or biological testing of a site is necessary, samples of material from the site area must be collected. The type of material that must be collected and the analytical method to be used depends upon the physical location of the site, detection level(s), site history (previous sampling), and known or unknown conditions and contaminants. The sampling process includes carefully planned and consistently applied procedures that produce accurate and legally defensible data. The sampling team should consider the procedures and plans presented in this guide as minimum sampling process guidelines to maintain sample integrity and identity. Samples should be collected according to the approved project and site-specific QAPP and SAP. This document does not define specific sampling procedures because specific sampling protocols depend on individual site conditions, Regional requirements, and acceptance and performance criteria. Since Regions may have their own specific requirements for individual sampling programs, they are responsible for generating Region-specific sampling SOPs.

1.3.1 Procedures Must be Consistent

The purpose of sampling is to collect representative portions from a suspected contaminated site. Sample collection is critical to determining the presence, type, concentration, and extent of environmental contamination by hazardous substances, thus it is a crucial part of every sampling and environmental testing effort. Sampling procedures must be consistently written and followed to mitigate risk of error and the expense of re-sampling.

Failure to follow proper sampling and shipping procedures could result in samples that are contaminated, broken, mislabeled, lost during shipping, or unusable because of a missed holding time. If procedures are inconsistently or improperly followed, any resultant analytical data may be inaccurate and may not be defensible in a court of law.

If re-sampling is needed due to improper sampling, the sampling team may incur the cost.

1.3.2 Analytical Data Must be Accurate and Defensible

The data gathered during sampling activities helps to accurately characterize contaminated waste sites so that the impact on human health and the environment can be properly evaluated. Acquiring accurate and defensible data that will be accepted in a court of law is the CLP's primary objective; therefore, the sampler must collect samples according to strict sampling procedures, plans, and guidelines. USEPA and many other Federal agencies use data resulting from analytical testing of soil/sediment/aqueous samples to:

- Determine if a site is contaminated with organic and/or inorganic compounds;
- Identify pollution sources and Potentially Responsible Parties (PRPs);
- Validate remedial design methodologies;
- Assess response and remedial priorities;
- Assess risk to human health and the environment;
- Determine appropriate cleanup actions; and
- Determine cleanup achievements.

1.3.3 Sampling Procedures and Guidelines Must Meet Minimum Requirements

It is imperative that samplers be aware of the minimum CLP and Regional requirements that directly impact and define how a sampling event will take place. It is important to note that the procedures and guidelines set forth in this document are considered minimum CLP requirements. Samplers should reference the following sections within this document that specifically address important requirements that must be met for a successful sampling event:

- Section 1.4.1 CLP Documentation Requirements;
- Section 2.4.1 Request Scheduling of Analysis, SMO-assigned Case Numbers, CLP Sample Numbers, and Laboratory Contact Information;
- Section 2.7 Comply with Transportation and Shipping Requirements;
- Section 2.8 Provide Shipment Notification;
- Section 3.1 Collect Samples; and
- Section 3.2 Complete Documentation.

1.4 Overview of Sampling Documentation Requirements

The sampler must properly document samples collected for analysis in order to uniquely identify each sample and ensure adequate chain-of-custody procedures. When collecting samples, the sampler should always keep in mind that any samples collected may be used in future litigation. This is especially important when samples are from privately owned property. If sampling on privately owned property, samplers should also provide the property owner with a receipt for samples collected and removed from that owner's property. Samplers may also be required by a Region to use a sample label, sample tag, or field operations records documenting information such as daily activities, equipment and materials used, personnel involved, site security, etc. These types of documentation help ensure proper sample identification and provide additional chain-of-custody records.

The documentation required by a Region for a sampling event is outlined in project plans such as the QAPP, SAP, and Field Sampling Plan (FSP).

At–a-Glance:
Overview of the Sampling Document Requirements

- ✓ Must use FORMS II Lite to create sample documentation. Analytical data must be accurate and defensible.
- ✓ CLP documentation requirements:
  - CLP Sample Number
  - SMO-assigned Case Number
  - Traffic Report/Chain of Custody (TR/COC) Record
  - Sample Labels
  - Sample Tags
  - Custody Seals
  - Field Operation Records

Under no circumstances should the site name appear on any documentation that is sent to the laboratory (for the CLP).

1.4.1 CLP Documentation Requirements

Samplers must:

1) Record the CLP Sample Number on each sample bottle;
2) Complete the Traffic Report/Chain of Custody (TR/COC) Record using the FORMS II Lite software, making sure to indicate on the TR/COC Record if the samples require the use of a Modified Analysis;
3) Complete and attach sample labels;
4) Complete and attach sample tags to meet Regional requirements;
5) Complete and attach custody seals to meet Regional requirements; and
6) Complete field operations records, as necessary.

Please contact your RSCC (see Table 1-1) for information regarding CLP Sample Numbers, SMO-assigned Case Numbers, TR/COC Records, and chain-of-custody seals for sampling events.

For information regarding using FORMS II Lite to create and complete a TR/COC Record, refer to the following Web site:

http://www.epa.gov/superfund/programs/clp/f2lite.htm

1.4.1.1 CLP Sample Number

A CLP Sample Number is unique per sampling location and is used to identify and track samples throughout the sampling and analytical processes and is recorded on many types of sampling documentation (e.g., TR/COC Records, sample labels, and sample tags). CLP Sample Numbers are provided to samplers by their RSCC or SMO.

Samplers must contact their RSCC (or their designee) to obtain CLP Sample Numbers for their sampling event. Samplers must correctly assign the CLP Sample Numbers to the appropriate sample bottle or container. Please refer to Section 3.2.1 for more detailed information regarding the use of CLP Sample Numbers.

If the sampler has any questions regarding the assignment of CLP Sample Numbers, they should contact their RSCC.

1.4.1.2 SMO-assigned Case Number

SMO-assigned Case Numbers are used to track groups of samples throughout the sampling and analytical processes and are recorded on many types of sampling documentation (e.g., TR/COC Records, sample labels, and sample tags). Samplers must correctly assign the SMO-assigned Case Number to the appropriate sample bottle or container. To obtain a SMO-assigned Case Number, samplers must contact their RSCC (or their designee).

1.4.1.3 Laboratory Assignment

Samplers are responsible for shipping samples to the appropriate SMO-assigned laboratory for analysis. Samplers must contact their RSCC (or their designee) to obtain their laboratory assignment or they may be provided by SMO.

1.4.1.4 TR/COC Record

The TR/COC Record is used as physical evidence of sample custody and functions as a permanent record of each sample collected.

Per CLP documentation requirements, each cooler must contain a TR/COC Record that lists all the samples contained therein.

In an effort to automate sample documentation in the field, ASB has developed a stand-alone, Windows-based software application that samplers can use to automatically create and generate sample documentation. The FORMS II Lite software allows users to enter information prior to and during sampling events. It allows users to multi-task and electronically create, edit, and print documentation associated with sampling activities. Users can customize data entry screens throughout the entire documentation process. Users can also customize the format and content of sample labels based on specific requirements.

The program simplifies and accelerates the tedious manual sample documentation process by reducing the generation of handwritten documents by almost 70%. The FORMS II Lite software enables samplers to:

- Increment CLP Sample Numbers or manually assign their own unique, project-specific non-CLP Sample Numbers;
- Input the SMO-assigned Case Number into the appropriate field;
- Create sample labels, sample tags, TR/COC Records, Sample Weight forms, and receipts for samples taken from a site;
- Track samples from the field to the laboratory;

- Electronically capture sample information into databases; and
- Export electronic data as a database File (.dbf), Text (.txt), or eXtensible Markup Language (.xml) file.

USEPA requires samplers to use the FORMS II Lite software for all CLP sampling efforts. For assistance with obtaining or using the FORMS II Lite software, please contact the FORMS II Lite Help Desk at 703-818-4200 from 9:00 AM - 5:00 PM Eastern Time (ET). For additional information regarding FORMS II Lite use and training, please refer to the following Web site:

http://www.epa.gov/superfund/programs/clp/f2lite.htm

1.4.1.5 Chain-of-Custody Seals

A chain-of-custody seal is any adhesive label or tape that can be used to seal a sample bottle, container, plastic bag, or shipping cooler such that if it is opened or tampered with, the seal will be broken. Custody seals must be placed on each sample bottle, container, or bag (as appropriate) and each shipping cooler or container. The custody seal is an excellent means of maintaining a record of chain-of-custody, as well as guarding against possible sample contamination or tampering during shipping.

1.4.1.6 Sample Labels

A sample label is a sticker attached to a sample bottle or container that contains a sample. Sample labels are affixed to each sample container as samples are collected in the field or affixed prior to going in the field. A sample label must contain, at a minimum, a CLP Sample Number so that they can be associated with, and listed on, the associated TR/COC Record. The sample label may also include the required analysis/fraction and preservative used (to eliminate confusion at the laboratory). Samplers should refer to their project plans for Region-specific sample label requirements.

1.4.1.7 Sample Tags

A sample tag identifies a sample bottle or container that contains a sample. The tag also provides specific analytical direction and proof that a sample existed. To support the use of sample data in potential enforcement actions, samples with other than in situ measurements (e.g., pH, temperature, conductivity) can be identified with a sample tag. A CLP Sample Number and SMO-assigned Case Number must be recorded on a sample tag to indicate that the sample container comprises the whole sample in the case where there is just one container of sample, or part of the indicated sample in the case of multiple containers of sample. Samplers should refer to their project plans for Region-specific sample tag requirements.

1.4.1.8 Field Operation Records

Samplers should maintain complete, accurate, and legible field operations records as they perform a sampling activity. The following records are included: Field Logbooks; Corrective Action Reports; Sampling Trip Reports; supplemental standardized forms; logs; and records such as maps or photographs that document each step of the work performed in the field. Samplers should refer to their project plans for Region-specific field operations record requirements. These records are very important tools because they are considered part of the official project file when legal issues arise.

1.4.1.9 Weight Logs

A sample weight log identifies the tared, sample and final weights per bottle for VOA samples. In order to support Method 5035 for VOAs, samplers should enter tared and final weights per bottle in the CLP Sample Weight Log.

2.0 PRE-FIELD ACTIVITIES

This chapter provides instructions for completing the suggested pre-field activities that samplers could complete prior to performing sampling activities. These important pre-field activities will save time and help the sampler to better prepare for the sampling event. Samplers should be aware of issues routinely arise during the sampling process so that samplers can avoid making the same mistakes or having the same problems that could adversely affect their sampling event. Samplers are also expected to review all pertinent project plans and meet both CLP and Regional requirements that directly impact the structure and purpose of a sampling event.

At-a-Glance:
Pre-field Activities

- ✓ Prepare for and communicate during a sampling event.
- ✓ Review project plans containing Regional requirements.
- ✓ Plan to meet documentation requirements.
- ✓ Obtain any necessary permits, licenses, and clearances.
- ✓ Identify and obtain sampling materials.
- ✓ Comply with transportation and shipping requirements.
- ✓ Provide shipment notification.
- ✓ Perform Readiness Review/Run-through.

The project plans provide information such as the types and numbers of samples to be collected, the analytical methods to be used based on the desired level of quantitation, and the necessary equipment and supplies. The plans also describe the sampling method which may require different specific sample volumes/masses, containers, preservation, shipping, and handling to maintain the integrity of the samples without degradation or contamination.

In addition to reviewing project plans, samplers should determine if the sampling site is privately or publicly owned and obtain the necessary permission to access the sampling site. If the site is privately owned, samplers should make sure to have receipts for available samples to provide to the owner for all samples collected and removed from their property. Samplers must also prepare to identify and obtain sampling materials, prepare to meet documentation requirements by obtaining and learning to use the required software, comply with transportation and shipping requirements, and perform a readiness review/dry run of the sampling process.

2.1 Prepare for a Sampling Event

Samplers must prepare to meet CLP and Regional requirements for a sampling event, appropriately use the CLP Sample Number and SMO-assigned Case Number, complete the TR/COC Record using the FORMS II Lite software, and complete and attach the custody seal(s). It is very important that the sampler include the correct CLP Sample Number on each sample. It is also imperative that the TR/COC Record be accurately completed and submitted with the sample(s). Finally, the sampler must accurately and legibly complete and attach a custody seal to each sample container, or plastic sample bag (as appropriate), and each shipping cooler or container.

However, meeting the sampling requirements requires more than just the proper application of a CLP Sample Number on each sample, completion of the TR/COC Record, and use of a custody seal. The actual collection of samples, packaging, and shipping of those samples are equally important to a successful sampling event.

For example, if a sampler collects an insufficient volume of a sample, the laboratory may not be able to perform the requested analysis. Insufficient sample volumes may also result in a laboratory being unable to perform laboratory quality control, such as Matrix Spike (MS), Matrix Spike Duplicate (MSD), and Duplicate sample analysis. Additionally, if the laboratory receives a sample that is either unpreserved or the sample pH is outside of the required range, the sample cannot be properly analyzed.

Unfortunately, improper shipping and labeling processes and procedures often result in:

- Samples being shipped to the wrong laboratory;
- Broken or empty samples being received at the laboratory; and
- Custody seals or sealant tape that is missing or broken on sample bottles, containers, plastic bags, or shipping coolers shipped to the laboratories.

The importance of completing the paperwork associated with a sampling event cannot be overemphasized. Samplers must make a conscientious effort to accurately complete the TR/COC Record since this is the main document used to derive vital information about a particular sample. The person completing a TR/COC Record

must be careful to avoid errors such as the appropriate sample(s) not being listed, or the wrong samples being listed. In an effort to eliminate such errors and the confusion that can be associated with handwritten TR/COC Records, samplers must use the FORMS II Lite software to complete the TR/COC Record and other associated sampling documentation.

It is extremely important that QC samples, including field sample duplicates, field samples for Matrix Spike and Matrix Spike Duplicate analyses, and Proficiency Testing (PT) samples, also known as Performance Evaluation (PE) samples, be designated and labeled per Regional guidance by samplers in the field. Mislabeling of QC samples can result in improper and/or inaccurate analysis of a sample at the laboratory.

2.2 Communicate During a Sampling Event

Communication is a key element in planning, administrating, and conducting a sampling event. It is extremely important that all parties involved in a sampling event be in contact throughout the sampling process. The procedures and recommendations outlined in this guide are based on more than 20 years of experience. It has been demonstrated that approximately 50% of all sampling efforts have been negatively affected by incorrect sampling procedures and poor communication among participants.

The key elements of communication for a sampling event include the relationship between the RSCC, SMO, the samplers in the field, and the laboratories who will be accepting the samples. For instance, the samplers must contact the RSCC to start the process for setting up a sampling event. The RSCC will in turn contact SMO who will schedule the sampling event, establish laboratory availability, and arrange for the laboratory to accept projected samples. SMO will then communicate the laboratory assignment to the Region and possibly the sampler.

The sampler should contact the RSCC (per Regional guidelines) and allow enough time for the RSCC to contact SMO at least a week prior to the sampling event.

SMO provides SMO-assigned Case and CLP Sample Numbers in time for the sampling event. SMO also schedules a laboratory and makes sure the laboratory will not have any capacity problems. Communication is also important because if there is a change in the sampling event due to a cancellation or an increase or decrease in the number of samples that will be sent to the laboratory, the sampler can contact the RSCC who can work with SMO to remedy potential capacity, availability, or overbooking problems.

2.3 Review Project Plans Containing Regional Requirements

In addition to meeting CLP requirements, the sample collection process must fulfill numerous Regional requirements. These requirements are determined by a variety of factors that affect how samples should be collected for an individual sampling event. These factors include:

- The type of samples being collected (organic/inorganic, water, soil/sediment, etc.);
- The method by which the samples will be analyzed;
- The acceptance or performance criteria (i.e., Data Quality Objectives [DQOs]); and
- The type of data needed.

The QAPP for each sampling project is written to meet requirements outlined in the documents *EPA Requirements for Quality Assurance Project Plans* (QA/R-5), *EPA Guidance on Quality Assurance Project Plans* (G-5), and Regional QAPP preparation documents. The QAPP is prepared in advance of field activities and is used by samplers to develop any subsequent plans such as the Sampling SAP or the FSP. Samplers should review the QAPP and any subsequent project plans for information outlining the basic components of a sampling activity. QAPP and project plans should be finalized and approved by appropriate Regional QA personnel, the OSC, SAM, or the RPM before providing them to the sampling team. This should be done prior to the start of field activities. Appendix A explains the functions within a sampling project (as these functions relate to a sampling event) and the elements of that function as described in a typical QAPP. Copies of all project plans and relevant SOPs should be maintained in the field for the duration of the sampling project.

2.4 Plan to Meet Documentation Requirements

At-a-Glance:
Plan to meet documentation requirements.

- ✓ Request SMO-assigned Case and CLP Sample Numbers.
- ✓ Prepare sample cooler return documentation.
- ✓ Prepare to use the FORMS II Lite software.

Sampling events require a variety of accurate and complete documentation. Samplers should review their project plans to determine the types of documentation that must be completed for a sampling project and to ensure that the appropriate documentation will be on-hand in the field. The CLP documentation requirements include the CLP Sample Number, the SMO-assigned Case Number, the TR/COC Record, sample labels, sample tags, custody seals, and field operations records (as necessary). Samplers need to request SMO-assigned Case and CLP Sample Numbers for each sampling event prior to starting field activities. Samplers also need to make sure that the correct TR/COC Records (Organic TR/COC Record for organic analysis or Inorganic TR/COC Record for inorganic analysis) are being used within the FORMS II Lite software. Finally, samplers should be prepared to complete the appropriate shipping cooler return documentation.

Since samplers are required to use the FORMS II Lite software to prepare and submit sampling project documentation and maintain sample chain-of-custody, software users must be familiar with all emergency back up procedures that should be followed in the event of a system failure. Samplers must have access to FORMS II Lite-generated TR/COC Records at sampling events. If problems are experienced while using the FORMS II Lite software, please contact the FORMS II Lite Help Desk at 703-818-4200 from 9:00 AM - 5:00 PM ET.

In the event of a system crash, samplers must have backup hardcopies of FORMS II Lite TR/COC Records. For information regarding emergency backup procedures, please refer to the following Web site:

http://www.epa.gov/superfund/programs/clp/trcoc.htm

2.4.1 Request Scheduling of Analysis, SMO-assigned Case Numbers, CLP Sample Numbers, and Laboratory Contact Information

SMO-assigned Case Numbers are assigned based on a request for CLP Routine Analytical Services (RAS), which is processed though the RSCC (or his/her designee). The sampler must request the RSCC to schedule CLP RAS analysis. The CLP does have the capacity to schedule sampling on an emergency basis, however the sampler must contact the RSCC (or his/her designee) to obtain details regarding how to handle such a situation. When scheduling a sampling event that will last for more than one week, it is recommended that the sampler contact the RSCC (or his/her designee) on a weekly basis to provide updates. This contact between the sampler, the RSCC (or his/her designee), and SMO is very important because it will ensure better availability of laboratory capacity.

In addition to SMO-assigned Case and CLP Sample Numbers, samplers should make sure to have accurate laboratory contact information, such as:

- Laboratory name;
- Laboratory address;
- Contact name; and
- Laboratory phone number.

This information is used for both TR/COC Records and chain-of-custody documentation and shipping paperwork such as address labels and airbills.

The SMO-assigned Case Number is used to track groups of samples throughout the sampling and analytical processes. Samplers must correctly indicate the assigned Case Number on the appropriate sample bottle or container.

The RSCC (or his/her designee) provides the CLP Case Numbers and Sample Numbers for each sampling event to samplers. Once the CLP Sample Numbers have been provided to the sampler, the sampler can use FORMS II Lite to print them onto sample labels.

The following characters are not to be used in generating CLP Sample Numbers and should never appear on any paperwork submitted to the laboratory: I, O, U, and V.

A CLP *Sample Number* is defined **as** a number that is unique per sampling location and identifies each CLP sample (see Section 1.4.1.1). Since samples must be identified per analytical program (either organic or inorganic), there are two types of TR/COC Records and two letter codes to denote organic vs. inorganic analysis.

A CLP *sample* is defined as one discrete portion of material to be analyzed that is contained at one concentration level, from one station location for each individual or set of analytical fractions -- provided the fractions are all requested for the same CLP analytical service (i.e., organic or inorganic), and identified by a unique Sample Number.

When samples are collected from several station locations to form a composite sample, the composite sample should be assigned either a number from one of the station locations used during collection, or a unique number that represents the composite sample for tracking purposes. The numbering scheme used internally at a sampling event for identifying composite samples should also be documented appropriately (e.g., in the field logs).

Organic CLP Sample Numbers begin with the Regional letter code, followed by four letters and/or numbers. Inorganic CLP Sample Numbers begin with "M", followed by the Regional letter code and then four letters and/or numbers. See Table 2-1 for Region and letter codes for each sample type (i.e., organic or inorganic).

Table 2-1. CLP Sample Number Letter Codes

Region	Letter Code	
	Organic	Inorganic
1	A	MA
2	B	MB
3	C	MC
4	D	MD
5	E	ME
6	F	MF
7	G	MG
8	H	MH
9	Y	MY
10	J	MJ

According to CLP guidelines, each individual inorganic water sample may be analyzed for total metals or dissolved metals, but not both. Therefore, water samples collected for total metal and dissolved metal analyses from the same sampling location must be assigned separate (unique) CLP Sample Numbers. A sampler can use the same CLP Sample Number for an inorganic soil or water sample collected for total metals, mercury and cyanide analyses.

Organic soil and water samples may be collected for analysis under the SOM01 SOW to detect:

- Aroclors;
- Semivolatile Organic Analytes (SVOAs);
- Pesticides;
- Volatile Organic Analytes (VOAs); and/or
- Trace Volatile Analytes

Inorganic soil and water samples may be collected for analysis for cyanide, and for metals using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and Cold Vapor Atomic Absorption (CVAA), under the ILM05.X SOW.

Inorganic water only samples may be collected for analysis for cyanide, and for metals using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and CVAA, under the ILM05 SOW.

2.4.2 Prepare Sample Cooler Return Documentation

CLP laboratories must routinely return sample shipping coolers to the appropriate sampling office within 14 calendar days following receipt of shipment from the sampler. For sample coolers to be returned, the

sampler must complete the appropriate cooler documentation and work with Regions and government agencies to provide a cost-effective mechanism for laboratories to return the empty coolers to the appropriate sampling office. The sampling cooler return documentation can be prepared in advance and provided to samplers before field activities begin. **The sampler (not the CLP laboratory) is responsible for paying for return of the cooler and should also include shipping airbills bearing the sampler's account number, as well as a return address to allow for cooler return.**

To maintain consistency among cooler transportation programs, samplers should:

- Minimize the use of multiple transportation carriers to avoid confusion;
- Use multiple-copy labels so the laboratory and the sampling team can each retain a copy for their records;
- Prepare labels in advance so that the laboratory can simply affix a completed shipping label on the cooler;
- Include third-party billing information (i.e., their shipping account number) on labels so the laboratory will not be billed by the transportation carrier;
- Confirm that the laboratory knows which transportation carrier to use; and
- Include the SMO-assigned Case Number on return information.

2.5 Obtain Municipal Permits, Licenses, and Clearances

Before starting a sampling event, samplers must make sure to obtain the proper municipal permits, accesses to the property, and any government clearances, if required. The sampler must also contact any appropriate utility companies to ascertain where any underground pipes, cables, etc., may be located.

At-a-Glance:
Obtain permits, licenses, and clearances.

- ✓ Request access to County, State, Tribal, military, and/or Federal property.
- ✓ Contact private property owner(s).
- ✓ Contact utility companies.

2.5.1 Request Access to County, State, Tribal, Military, and/or Federal Property

Proper access to perform sampling activities is important not only for legal reasons, but also to eliminate delays in work and possible refusal to allow sampling to take place. It is crucial that the appropriate permits, licenses, and clearances be secured to obtain access for sampling activities that will be performed on County, State, Tribal, military, and/or Federal property. The sampler must contact the appropriate government offices or personnel well in advance to determine what kinds of approval are required. Pre-approval may be required for specific types of sample collection such as drilling or excavation. For example, drilling on a military base requires pre-approval. Base security may require clearances for all members of the sampling team, including subcontractors. This process may take two or more days.

If arrangements are not made in advance, the team may not be allowed to enter the site until their clearances are processed and the team has been approved to drill. As a result, the sampling schedule is delayed, costing extra time and money.

2.5.2 Contact Private Property Owners

The sampler must obtain written permission from the private property owner(s) before sampling on their property, even if verbal permission has been granted. It is recommended that samplers obtain verbal permission prior to their arrival at the sampling location, but written permission can be obtained on the day of sampling. If a property owner refuses to grant access to their property, it may be necessary for sampling participants to contact the appropriate authorities for assistance.

2.5.3 Contact Utility Companies

The sampler should contact local utility companies (e.g., power, phone, gas, cable, sanitation, etc.) at least one week prior to the sampling event to have underground cables, lines, and pipes flagged and marked. This is required by law. A national one-call directory can be found at:

http://www.digsafely.com/contacts.htm.

This will eliminate potential safety hazards and service disruption. For example, soil sampling in a residential area may require digging below the soil's surface. It is very important to know where utility lines and pipes are located so that samplers do not hit live electrical wires or rupture gas lines. Samplers should follow Regional or other appropriate program procedures for the procurement of such services. The utility service(s) disruption dates should be confirmed at least two days prior to sampling activities.

Pre-payment of survey fees to local utility companies may be required.

2.6 Identify and Obtain Sampling Materials

Samplers must make sure to be prepared for a sampling project with the appropriate sampling materials (equipment, supplies, sample containers, packing materials, and shipping materials). The equipment and supplies must be properly cleaned, calibrated, and tested as necessary to meet the needs of the sampling project.

At-a-Glance:
Identify and obtain sampling materials.

- ✓ Procure appropriate equipment and supplies.
- ✓ Procure sample containers.
- ✓ Procure shipping supplies.

2.6.1 Procure Appropriate Equipment and Supplies

Each sampling event requires the procurement of equipment and materials to collect, document, identify, pack, and ship samples. The proper field sampling equipment is vital to a successful sample collection. Regional or other samplers should obtain, and arrange in advance, all of the equipment and supplies required for each sampling event. Samplers should review the project plans to verify that the proper equipment is being used for sample collection.

At a minimum, the following materials are generally required during a sampling event:

- Sample storage containers;
- Packing material;
- Sample containers;
- Shipping containers;
- Access to the FORMS II Lite software for creating sample labels, stickers, tags, and TR/COC Records;
- Custody seals; and
- Sampling equipment such as bowls, augers, pumps, etc.

Sampling events may also require specific items such as:

- Cooler temperature blanks;
- Trip blanks for VOA analysis;
- Preservation supplies (e.g., ice or acid); and
- Specially prepared sample vials (e.g., for SW-846 Method 5035A).

2.6.2 Procure Sample Containers

The analytical protocol(s) to be used for sample analysis often requires the use of a particular type of sample container. The type of container also may depend on the sample matrix and analysis. It is recommended that samplers use borosilicate glass containers, which are inert to most materials, when sampling for pesticides and/or other organics. Conventional polyethylene is recommended when sampling for metals because of the lower cost and absorption rate of metal ions.

Using the wrong container may result in breakage, gathering of an insufficient volume needed to perform sample analysis, or the container material may interfere with the analysis. Therefore, samplers should identify and use the correct sample containers for each sampling event.

Containers procured for a sampling event are usually pre-cleaned and shipped ready-for-use from the manufacturer to the sampling site. Regardless of the type of container used, samplers must ensure that the containers have been analyzed or certified clean to levels below concern for the project. These containers must meet the USEPA container type specifications listed in Table 2-2.

Table 2-2. Container Type Specifications

Reference Number	Container Type	Specifications	
		Closure	Septum
1	40 mL amber glass vial, 24 mm neck finish.	Polypropylene or phenolic, open-top screw-cap, 15 cm opening, 24-400 size.	24 mm disc of 0.005 in. Polytetrafluoroethylene (PTFE) bonded to 0.120 in. silicone for total a thickness of 0.125 in.
2	1 L high density polyethylene, cylinder-round bottle, 28 mm neck finish.	Polyethylene cap, ribbed, 28-410 size; F217 polyethylene liner.	N/A
3	8 oz short, wide mouth, straight-sided, glass jar, 70 mm neck finish.	Polypropylene or phenolic cap, 70-400 size; 0.015 in. PTFE liner.	N/A
4	4 oz (120 mL) tall, wide mouth, straight-sided, glass jar, 48 mm neck finish.	Polypropylene or phenolic cap, 48-400 size; 0.015 in. PTFE liner.	N/A
5	1 L amber round glass bottle, 33 mm pour-out neck finish.	Polypropylene or phenolic cap, 33-430 size; 0.015 in. PTFE liner.	N/A
6	500 mL high density polyethylene, cylinder-round bottle, 28 mm neck finish.	Polypropylene cap, ribbed, 28-410 size; F217 polyethylene liner.	N/A
7	Coring tool used as a transport device (e.g., 5 g Sampler).	Has built-in closing mechanism.	N/A
8	250 mL high density polyethylene, cylinder-round bottle, 28 mm neck finish.		N/A

The information contained in this table is also cross-referenced in the sample collection parameters discussed in Chapter 3. The container Reference Numbers are used in Tables 3-2 and 3-3 under the Containers column. For example, samples collected for low-level soil VOA analysis using SW-846 Method 5035A may require the sampler to use pre-prepared, tared closed-system purge-and-trap vials with a preservative (refer to Appendix B).

Have extra containers readily available for each sampling event in case of breakage, loss, or contamination.

2.6.3 Procure Shipping Supplies

Samples should be correctly packaged into the appropriate shipping containers to reduce the risk of breakage or leakage, and the shipping containers should be appropriately prepared for shipment. Before heading into the field, samplers should refer to the appropriate project plans to determine the types of samples that will be taken during the sampling project so that samplers will have the proper packaging materials at the site for all pertinent samples container types and sample matrices. Samplers should also make sure to obtain the appropriate shipping paperwork (e.g., shipping forms required by the delivery service).

2.7 Comply with Transportation and Shipping Requirements

Samplers are expected to review the applicable project plans to be aware of all State, Federal, Department of Transportation (DOT), and International Air Transport Association (IATA) regulations governing environmental and hazardous sample packaging. The person who ships the samples is responsible for being in compliance with applicable packaging, labeling, and shipping requirements.

Samplers should request and receive sample permits for outside the continental United States, prior to shipping.

Additional information can be obtained on Hazardous Materials Safety Program regulations from the DOT's Research and Special Programs Administration. Federal transportation regulations can be found in 49-CFR Parts 100-185, are available on the Internet at:

http://www.myregs.com/dotrspa/

2.8 Provide Shipment Notification

Some Regions may require that samplers notify their RSCC (or his/her designee) when samples are shipped. Some Regions allow samplers to contact SMO directly to provide shipment notification. It is recommended that samplers contact the RSCC of sample origin to verify if such notification is necessary. If samplers are shipping samples after 5:00 PM ET, samplers must notify the RSCC (or designee) or SMO by 8:00 AM ET on the following business day.

For Saturday delivery at the laboratory, samplers MUST contact the RSCC (or designee) or SMO so that SMO will receive the delivery information by 3:00 PM ET on the Friday prior to delivery.

2.9 Perform Readiness Review/Dry Run

A readiness review/dry run is a test run of the proposed sampling event. This is a recommended practice since it gives samplers a chance to check all plans, documentation software (i.e., FORMS II Lite), and equipment lists for accuracy and completeness prior to sampling activities. It also provides an opportunity to consult with sampling team members to make sure all the elements are in place and everyone understands their tasking before actually going out to the field. Sampling project managers should provide the test or dry run dates and schedules to samplers so that samplers can prepare accordingly.

3.0 IN-FIELD ACTIVITIES

This chapter addresses the in-field activities a sampler will focus on during a sampling event such as: determining the type of samples to be collected; collecting the samples; meeting volume, preservation, and holding time requirements; completing documentation; and packing and shipping samples.

When performing a sampling event, the sampler is expected to follow prescribed sampling techniques. The sampler should also be aware of any special sampling considerations, contamination issues, and sample compositing and mixing methods that could affect their sampling efforts. Please refer to Appendix D for more detailed information.

At-a-Glance:
In-field Activities

- ✓ Collecting samples
- ✓ Completing documentation
- ✓ Sampling considerations
- ✓ Procuring shipping supplies

Appropriate Regional guidance and procedures should be consulted for detailed sample collection, preservation, handling and storing, equipment decontamination, and QA/QC procedures.

3.1 Collect Samples

CLP RAS are generally used to analyze samples from Superfund sites. The matrices can be water, soil, or sediment. In some instances, a mixed-matrix sample may be collected which contains either a supernate (for a sediment/soil sample) or a precipitate (for a water sample). In this event, samplers should consult their management plans and/or discuss the required procedures with the RSM or their designee.

A CLP sample consists of all sample aliquots (portions):

- for each individual or set of analytical fractions;
- from one station location;
- for one sample matrix;
- at one concentration level;
- for one laboratory; and
- for one analytical program;

provided that the fractions are all requested from the same CLP analytical service.

In general, it is recommended that two individual samples be collected by separating the aqueous layer from the solid/precipitate layer at the point of collection. They may be assigned two different sample IDs (e.g., Sample IDs ABC124 and ABC125 for Sample ID ABC123), along with a note in the field sample log or tracking system that the sample IDs are derived or related to the same sample ID, to ensure correct follow-up upon receipt of results from the laboratory. Alternatively, they may be assigned the same sample ID, along with a notation of each individual sub-sample or fraction (e.g., Sample IDs ABC123-1 and ABC123-2 or Sample ID ABC123 Fraction 1 and Sample ID ABC123 Fraction 2 for Sample ID ABC123).

3.1.1 Determine Types of Samples to be Collected

Samplers may be required to take several types of samples or sample aliquots during a sampling event. They should refer to their project plans to determine the types of samples or aliquots to be taken, the volumes needed of each sample or aliquot, and the preservation needed for each sample. For an explanation of the various sample types and the requirements for collecting and submitting each particular type, refer to Table 3-1.

Table 3-1. QC Sample Types and CLP Submission Requirements

Sample Type	Purpose	Collection[1]	CLP Sample Number
Field Duplicate	To check reproducibility of laboratory and field procedures. To indicate non-homogeneity.	Collect from areas that are known or suspected to be contaminated. Collect one sample per week or 10% (Regions may vary) of all field samples per matrix, whichever is greater.	Assign two separate (unique) CLP Sample Numbers (i.e., one number to the field sample and one to the duplicate). Submit blind to the laboratory.
Field Blanks	To check cross-contamination during sample collection, preservation, and shipment, as well as in the laboratory. Also to check sample containers and preservatives.	Collect for each group of samples of similar matrix per day of sampling. Organics - Use water (demonstrated to be free of the contaminants of concern). Inorganics - Use metal-free (deionized or distilled) water.	Assign separate CLP Sample Numbers to the field blanks.
Trip Blank (Volatile Organic Analysis Only)	To check contamination of VOA samples during handling, storage, and shipment from field to laboratory.	Prior to going into the field, prepare and seal one sample per shipment per matrix using water demonstrated to be free of the contaminants of concern (deionized water is appropriate). Place this sample in the cooler used to ship VOA samples.	Assign separate CLP Sample Numbers to the trip blanks.
Equipment Blank or Rinsate Blank	To check field decontamination procedures.	Collect when sampling equipment is decontaminated and reused in the field or when a sample collection vessel (bailer or beaker) will be used. Use blank water (water demonstrated to be organic-free, deionized or distilled for inorganics) to rinse water into the sample containers.	Assign separate CLP Sample Numbers to the equipment blanks.
Matrix Spike (MS) and Duplicate (MSD)[2] (Organic Analysis Only)	To check accuracy and precision of organic analyses in specific sample matrices.	Collect from areas that are known or suspected to be contaminated. For smaller sampling events (i.e., 20 samples or less), MS/MSD additional volume should be collected in the first round of sampling and included in the first shipment of samples to the laboratory. Collect double or triple volume[3] for aqueous samples and soil VOA samples designated for MS/MSD analyses. Additional sample volume is not required for soil samples requiring SVOA, Pesticide, and/or Aroclor analysis. See Appendix B for VOA collection volumes.	Assign the same CLP Sample Number to the field sample and the extra volume for MS/MSD. Identify the sample designated for MS/MSD on the TR/COC Record.
Matrix Spike (MS) and Duplicate (MSD) (Inorganic Analysis Only)	To check accuracy and precision of inorganic analyses in specific sample matrices.	Collect from areas that are known or suspected to be contaminated. For smaller sampling events (i.e., 20 samples or less), Matrix Spike and Duplicates should be collected in the first round of sampling and included in the first shipment of samples to the laboratory. Additional sample volume may be required for inorganic analysis.[4]	Assign the same CLP Sample Number to the field sample and extra volume (if collected). Identify the sample(s) designated for Matrix Spike and Duplicates on the TR/COC Record.
PE Samples	Specially-prepared QC samples used to evaluate a laboratory's analytical proficiency.	The PE samples contain analytes with concentrations unknown to the laboratory. Designated Regional or authorized personnel (depending on Regional policy) arrange for Case-specific CLP PE samples to be prepared and shipped by the QATS contractor. The PE samples can be shipped to the site, or shipped per Regional direction. QATS provides the appropriate preparation instructions and chain-of-custody materials.	Samplers have no direct interaction with the PE sampling process, but should be aware that such samples do exist within the CLP sampling process. Samplers must, however, order PE samples and ship them to the laboratory if required by the Region.

[1] Consult Regional or Project Manager Guidance for field QC sample frequencies; laboratory QC sample frequencies are generally fixed in the laboratory subcontracts or specified in analytical methods. Current frequency for MS/MSD (organic) and MS/duplicate (inorganic) for the CLP is one sample per twenty field sample of similar matrix.

[2] Samples sent under the Organic SOW (SOM01) do not require an MS or MSD for Trace VOA, VOA and BNA fractions, but the Region may opt to send them at their discretion.

[3] Example of double volume: An aqueous sample for SVOA analysis would require the field sampler to collect at least 2 L of field sample and at least 1 L each for the MS and MSD samples for a total volume of 4 L. If Pesticide or Aroclor MS/MSD analyses are required for the same sample, an additional 4 L must be collected. Double volume is the MINIMUM allowable volume for samples designated for MS/MSD analysis. Triple volume may be sent for MS/MSD samples to allow for sufficient volume for these analyses in the event sample volume is lost as a result of samples breaking, leaking, or laboratory accidents.

[4] Double volume may be sent for inorganic aqueous MS and MSD samples to allow for sufficient volume for these analyses in the event sample volume is lost as a result of samples breaking, leaking or laboratory accidents.

3.1.1.1 Collect Field QC Samples

Samplers can collect field QC samples and laboratory QC samples to verify that sample quality is maintained during a sampling project.

Field QC samples are designed to assess variability of the media being sampled and to detect contamination and sampling error in the field. The types of field QC samples that are generally collected include field duplicates and field blanks (such as equipment, trip, or rinse blanks). Generally, field duplicate samples should remain "blind" to the laboratory (i.e., they should have separate CLP Sample Numbers).

3.1.1.2 Collect Laboratory QC Samples

A laboratory QC sample is an additional analysis of a field sample, as required by the laboratory's contract. There are three types of laboratory QC samples:

- MS [for organic and inorganic samples];
- MSD [for organic samples only]; and
- Duplicates [for inorganic samples only].

Samplers should obtain Regional guidance regarding the collection of MS and MSD samples (especially for organics analyses).

Samplers should select one sample per matrix per 20 samples as a "laboratory QC" sample. Designated organic laboratory QC samples should be noted on the Organic TR/COC Record. Designated inorganic laboratory QC samples should be noted on the Inorganic TR/COC Record. The laboratory QC sample must not be designated only in the "Field QC Qualifier" column on either the Organic or Inorganic TR/COC Records. Make sure that the laboratory QC sample is included in TR/COC Record samples to be used for the Laboratory QC field.

The sampler should select a field sample as the laboratory QC sample. If the sampler does not select a field sample as the laboratory QC sample, then it is possible that the laboratory could select the field blank (e.g., an equipment or rinsate blank) sample to meet contractual QC requirements. The use of field blanks for laboratory MS/MSD/Duplicate analysis reduces the usability of the data to assess data quality.

In the event of multiple sample shipments during a sampling event, it is recommended that the sampler submit laboratory QC samples in the first sample shipment.

3.1.2 Meet Volume, Preservation, and Holding Time Requirements

Samplers should refer to their project plans to obtain the specific sample volumes to be collected, the preservation needed for those samples, and the technical holding times under which they must submit samples to the scheduled CLP laboratory. Sample collection parameters (to include sample volumes, preservatives, and technical holding times) for organic collection and analysis are listed in Tables 3-2 and 3-3. Sample collection parameters for inorganic analysis and collection are listed in Table 3-4.

3.1.2.1 Collect Sample Volume

Collecting sufficient sample volume is critical. There must be sufficient physical sample volume for the analysis of all required parameters and completion of all QC determinations. The type of analytical procedure(s) to be performed will often dictate the sample volume to collect. For example, each water sample collected for VOA analysis by CLP SOW SOM01 or ILM05 requires a minimum of three vials, each filled completely to a 40 mL capacity. See Appendix C for information regarding the collection of VOAs in water. It is extremely important that samplers refer to their specific project plans to identify and collect the correct sample volume during each sampling event.

When sampling for VOAs in soils, samplers must use SW-846 Method 5035A guidelines included in Appendix B.

3.1.2.2 Preserve Samples

Degradation of some contaminants may occur naturally (e.g., VOAs). The sampler must chemically preserve some water samples for certain analytes before shipping them to the laboratory. The sampler should preserve and immediately cool all samples to 4°C (±2°C) upon collection and samples should remain cooled until the time of analysis (do not freeze water samples). Preservation techniques vary among Regions so the sampler should obtain Region-specific instructions and review the appropriate project plans and SOPs. See Appendix C for information regarding the collection of VOAs in water.

3.1.2.3 Ship within Holding Times

Samplers should ship samples to scheduled CLP laboratories as soon as possible after collection. Daily shipment of samples to CLP laboratories is preferred whenever possible. If samples cannot be shipped on a daily basis, they must be properly preserved and maintained to meet CLP-specified temperatures, holding times, and custody requirements.

The technical holding times are the maximum time allowed between a sample collection and the completion of the sample extraction and/or analysis. In contrast, contractual holding times are the maximum lengths of time that the CLP laboratory can hold the sample prior to extraction and/or analysis. These contractual holding times are described in the appropriate CLP SOW. Contractual holding times are shorter than the technical holding times to allow for sample packing and shipping.

If samplers are shipping samples after 5:00 PM ET, they must notify the RSCC (or designee) or SMO by 8:00 AM ET on the following business day. When making a Saturday delivery, samplers shall contact the RSCC (or designee) or SMO by 3:00 PM ET on the Friday prior to delivery.

Table 3-2. Sample Collection Requirements for CLP SOW SOM01 (VOAs)

Matrix	Container Type	Sample Type	Minimum Number of Containers Needed				Minimum Volume/ Mass	Important Notes	Preservative	Technical Holding Time
			with Water	Dry	% Moisture	TOTAL				
Water	See Table 2-2, Reference Number 1.	Samples Only	-	-	-	**3**	Fill to capacity	Containers/vials must be filled to capacity with no headspace or air bubbles. Refer to Appendix C for samples requiring QC analyses.	Preserve to a pH of 2 with HCl and cool to 4°C (±2ºC) immediately after collection. DO NOT FREEZE water samples.	14 days
		Samples with SIM	-	-	-	**4**				
		Samples with MS/MSD	-	-	-	**6**				
		Samples with SIM and MS/MSD	-	-	-	**8**				
Soil/ Sediment	**OPTION 1** Closed-system Vials See Table 2-2, Reference Number 1.	Samples Only	-	3	1	**4**	5g	Place samples on side prior to being frozen. Refer to Appendix B for samples requiring QC analyses.	Frozen (-7°C to -15°C) or iced to 4° (±2°C).	14 days
		Samples with MS/MSD	-	9	1	**10**				48 hours
	OPTION 2 Closed-system containing Vials Water See Table 2-2, Reference Number 1.	Samples Only	2	1	1	**4**	5g	Containers/vials must be filled to capacity with no headspace or air bubbles. Place samples on side prior to being frozen. Refer to Appendix B for samples requiring QC analyses.	Frozen (-7°C to -15°C) or iced to 4° (±2°C). DO NOT FREEZE water samples.	14 days
		Samples with MS/MSD	6	1	5	**12**				48 hours
	OPTION 3 See Table 2-2, Reference Number 7.	Samples Only	-	3	1	**4**	5g	Refer to Appendix B for samples requiring QC analysis.	Frozen (-7°C to -15°C) or iced to 4°C (±2°C).	48 hours
		Samples with MS/MSD	-	9	1	**10**				48 hours

Notes

[1] Minimum volume/mass to be collected in order to ensure sample analysis can be performed.

[2] Check Regional guidance regarding use of acid as a preservative of samples that may contain carbonates, residual chlorine, and other oxidants.

[3] This technical holding time is calculated from the time of sample collection to sample extraction. Sample extracts are to be analyzed within 40 days of extraction. It is recommended that samplers ship samples to the laboratory on the same day that they are collected, or as soon as possible thereafter.

[4] Check Regional guidance regarding use of acid preservatives when testing for carbonates, residual chlorine, and other oxidants.

Table 3-3. Sample Collection Requirements for CLP SOW SOM01 (SVOAs, Pesticides and Aroclors)

Analysis	Matrix	Containers	Minimum Volume/ Mass	Important Notes	Preservative	Technical Holding Time
Semivolatile Analytes	Water	See Table 2-2, Reference Number 5.	2L	If amber containers are not available, the samples should be protected from light.	Cool all samples to 4°C (±2°C) immediately after collection. DO NOT FREEZE water samples.	7 days
	Soil/ Sediment	See Table 2-2, Reference Numbers 3 and 4.	Fill to capacity		Cool all samples to 4°C (±2°C) immediately after collection.	14 days
Pesticides/ Aroclors	Water	See Table 2-2, Reference Number 5.	2L	If amber containers are not available, the samples should be protected from light.	Cool all samples to 4°C (±2°C) immediately after collection. DO NOT FREEZE water samples.	7 days
	Soil/ Sediment	See Table 2-2, Reference Numbers 3 and 4.	Fill to capacity		Cool all samples to 4°C (±2°C) immediately after collection.	14 days

Notes

[1] Minimum volume/mass to be collected in order to ensure sample analysis can be performed.
[2] Check Regional guidance regarding use of acid as a preservative of samples that may contain carbonates, residual chlorine, and other oxidants.
[3] This technical holding time is calculated from the time of sample collection to sample extraction. Sample extracts are to be analyzed within 40 days of extraction. It is recommended that samplers ship samples to the laboratory on the same day that they are collected, or as soon as possible thereafter.
[4] Check Regional guidance regarding use of acid preservatives when testing for carbonates, residual chlorine, and other oxidants.

Table 3-4. Sample Collection Requirements for CLP SOW ILM05

Analysis	Matrix	Containers	Minimum Volume/ Mass[1]	Important Notes	Preservative	Technical Holding Time[4]
Metals/ICP-AES and/or Mercury by CVAA	Water	See Table 2-2, Reference Number 2.	1L	If collecting for both ICP-AES AND ICP-MS methods, a separate 1L volume of sample must be collected for each method per sample location.	Acidify to pH < 2 with HNO_3 and cool to 4°C (±2°C) immediately after collection.[2] DO NOT FREEZE water samples.	6 months for all metals except Mercury (28 days)
	Soil/ Sediment	See Table 2-2, Reference Number 3.	Fill to capacity		Cool to 4°C (±2°C) immediately after collection.	6 months
Cyanide/ Spectrophotometric Determination[3]	Water	See Table 2-2, Reference Number 2.	1L		To neutralize residual chlorine, immediately upon collection, add 0.6 g ascorbic acid for each liter of sample collected. Add NaOH until pH >12 and cool to 4°C (±2°C) immediately after collection.[5] DO NOT FREEZE water samples.	14 days
	Soil/ Sediment	See Table 2-2, Reference Number 3.	Fill to capacity		Cool to 4°C (±2°C) immediately after collection.	14 days

Notes

1 Minimum volume/mass to be collected in order to ensure sample analysis can be performed.

2 Check Regional guidance regarding use of acid as a preservative of samples that may contain carbonates, residual chlorine, and other oxidants.

3 Samplers must test for sulfide and oxidizing agents (e.g., chlorine) in aqueous samples in the field upon collection. Please refer to the SAP and Appendix C for guidance. Sulfides adversely affect the analytical procedure. The following can be done to test for and neutralize sulfides. Place a drop of the sample on lead acetate test paper to detect the presence of sulfides. If sulfides are present, treat 25 mL more of the sample than that required for the cyanide determination with powdered cadmium carbonate or lead carbonate. Yellow cadmium sulfide or black lead sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complication or occlusion of cyanide on the precipitated material. Sulfide removal should be performed in the field, if practical, prior to pH adjustment with NaOH.

4 This technical holding time is calculated from the time of sample collection to sample extraction. Sample extracts are to be analyzed within 40 days of extraction. It is recommended that samplers ship samples to the laboratory on the same day that they are collected, or as soon as possible thereafter.

3.2 Complete Documentation

Samplers must complete all documentation, including the recording of the CLP Sample Number on the sample container or bottle, sample labels, and chain-of-custody seals (as appropriate), the completion of the TR/COC Record, and the completion of field operations records (as necessary).

Samplers should use the FORMS II Lite software to create and print sample labels and the TR/COC Record. Samplers can create and print out two copies of a sample label and attach one to the sample container or bottle, and place the other on the sample tag that may be attached to the sample container or bottle.

Samplers are expected to review their project plans to determine what documentation they are expected to include during a sampling event. It is highly recommended that samplers provide documentation, even if the Region does not require it.

Note: Under no circumstances should the site name appear on any documentation being sent to the laboratory.

An example of a packaged sample is shown in Figure 3-1. A description of each type of documentation and instructions for accurate completion are included in the following sections.

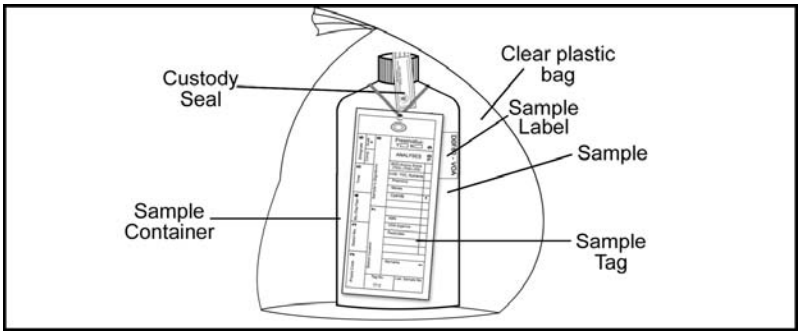


Figure 3-1. Packaged Sample with Identification and Chain-of-Custody Documentation (Excluding TR/COC Record)

3.2.1 Identify a Sample with a CLP Sample Number and SMO-assigned Case Number

The CLP Sample Number and SMO-assigned Case Number **must** be recorded on each sample taken during a sampling event (see Section 1.4.1.1). Samplers can record these numbers on the sample bottle or container using permanent ink. The numbers must also be recorded on the sample tag, if required.

Note: Dissolved metal samples and total metal samples taken from the same sampling location cannot have the same CLP Sample Number because two different sets of data will be generated.

3.2.2 Complete TR/COC Records

A Traffic Report is used as physical evidence of sample custody and as a permanent record for each sample collected. A chain-of-custody record documents the exchange and transportation of samples from the field to the laboratory.

The ASB requires samplers to use the FORMS II Lite software to create documentation for all CLP sampling efforts. For assistance with obtaining or using the FORMS II Lite software, please contact the FORMS II Lite Help Desk at 703-818-4200 from 9:00 AM - 5:00 PM ET.

To meet CLP sample documentation and chain-of-custody requirements, the sampler must attach a separate TR/COC Record to each cooler they ship. The TR/COC Record must document each sample within the cooler. Samples shipped in other coolers should not be documented. This practice maintains the chain-of-custody for all samples in case of incorrect shipment.

If more than one TR/COC Record is used for the samples within one cooler, all of the records must have complete header information and original signatures. Samplers are responsible for the care and custody of samples from the time of collection to the time of shipment to the laboratories for analysis. A sample is considered under custody if:

- It is in possession or in view after being in possession;
- It was in possession and then secured or sealed to prevent tampering; or
- It was in possession when placed in a secured area.

Each time the custody of samples is turned over to another person, the TR/COC Record must be signed off by the former custodian and accepted by the new custodian. Samplers are, therefore, responsible for properly completing any forms or other Region-required documentation used to establish the chain-of-custody for each sample during a sampling event.

3.2.2.1 Complete a TR/COC Record Using the FORMS II Lite Software

Once the sampler inputs sample collection information into FORMS II Lite, a TR/COC Record will be generated electronically. The software automatically displays only the information to be entered by the sampler. FORMS II Lite then generates a laboratory and a Regional copy of the TR/COC Record (see Figures 3-2 through 3-5). The sampler can print out multiple copies of the TR/COC Record as necessary. The sampler must sign and submit original copies of the TR/COC Record as appropriate.

An electronic TR/COC Record created using the FORMS II Lite software contains basic header information; however, the sampler can also include some additional detailed information. For example, not only is the sample matrix listed on the electronic TR/COC Record, but the name of the sampler taking the sample can also be entered. Samplers should note that certain information will not appear on the electronic TR/COC Record (e.g., matrix and preservative descriptions).

3.2.2.2 Indicate Modified Analysis on FORMS II Lite TR/COC Records

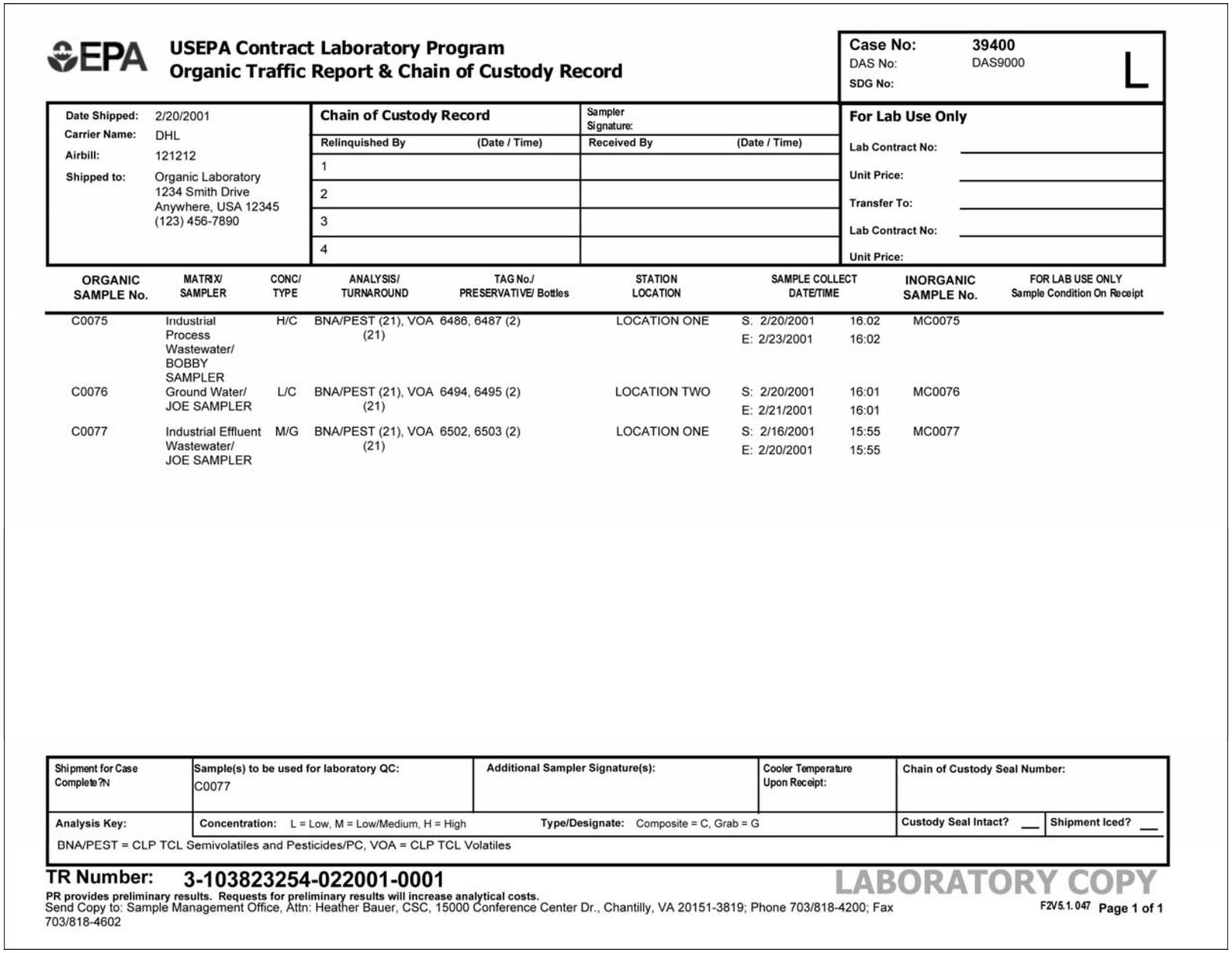
When completing a TR/COC Record using FORMS II Lite, the sampler should identify any samples that will be analyzed using a CLP Modified Analysis. Samplers should indicate use of a Modified Analysis by creating a new analysis within the FORMS II Lite Wizard or through the FORMS II Lite Reference Tables. This newly-created analysis should contain the Modification Reference Number within the name assigned to the analysis. For example, if a Region submits a Modified Analysis for an additional analyte, and SMO assigns the Modification Reference Number 1301.0, the FORMS II Lite analysis could be named "VOA by M.A. 1301.0". The associated abbreviation for this analysis could be "VOA M.A.". If you have any questions regarding identification of Modified Analysis using FORMS II Lite, please contact the FORMS II Lite Help Desk at 703-818-4200 from 9:00 AM - 5:00 PM ET.

3.2.2.3 Make Manual Edits to Printed FORMS II Lite TR/COC Records

If a FORMS II Lite TR/COC Record has been printed and deletions or edits need to be made by the sampler, the following procedures must be followed:

- If making a deletion, manually cross out the information to be disregarded from the TR/COC Record, initial and date the deletion.
- If making an addition, enter the new information and initialsign and date the newly added information.

All modifications made on a printed TR/COC Record must be initialed and dated.



USEPA Contract Laboratory Program
Organic Traffic Report & Chain of Custody Record

Case No: 39400
DAS No: DAS9000
SDG No:
L

Date Shipped:	2/20/2001
Carrier Name:	DHL
Airbill:	121212
Shipped to:	Organic Laboratory 1234 Smith Drive Anywhere, USA 12345 (123) 456-7890

Chain of Custody Record

Relinquished By	(Date / Time)	Received By	(Date / Time)
1			
2			
3			
4			

Sampler Signature:

For Lab Use Only
Lab Contract No:
Unit Price:
Transfer To:
Lab Contract No:
Unit Price:

ORGANIC SAMPLE No.	MATRIX/ SAMPLER	CONC/ TYPE	ANALYSIS/ TURNAROUND	TAG No./ PRESERVATIVE/ Bottles	STATION LOCATION	SAMPLE COLLECT DATE/TIME		INORGANIC SAMPLE No.	FOR LAB USE ONLY Sample Condition On Receipt
C0075	Industrial Process Wastewater/ BOBBY SAMPLER	H/C	BNA/PEST (21), VOA (21)	6486, 6487 (2)	LOCATION ONE	S: 2/20/2001 E: 2/23/2001	16:02 16:02	MC0075	
C0076	Ground Water/ JOE SAMPLER	L/C	BNA/PEST (21), VOA (21)	6494, 6495 (2)	LOCATION TWO	S: 2/20/2001 E: 2/21/2001	16:01 16:01	MC0076	
C0077	Industrial Effluent Wastewater/ JOE SAMPLER	M/G	BNA/PEST (21), VOA (21)	6502, 6503 (2)	LOCATION ONE	S: 2/16/2001 E: 2/20/2001	15:55 15:55	MC0077	

Shipment for Case Complete?N	Sample(s) to be used for laboratory QC:	Additional Sampler Signature(s):	Cooler Temperature Upon Receipt:	Chain of Custody Seal Number:	
	C0077				
Analysis Key:	**Concentration:** L = Low, M = Low/Medium, H = High	**Type/Designate:** Composite = C, Grab = G		**Custody Seal Intact?** ___	**Shipment Iced?** ___

BNA/PEST = CLP TCL Semivolatiles and Pesticides/PC, VOA = CLP TCL Volatiles

TR Number: 3-103823254-022001-0001

LABORATORY COPY

PR provides preliminary results. Requests for preliminary results will increase analytical costs.
Send Copy to: Sample Management Office, Attn: Heather Bauer, CSC, 15000 Conference Center Dr., Chantilly, VA 20151-3819; Phone 703/818-4200; Fax 703/818-4602

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Figure 3-2. Organic Traffic Report & Chain of Custody Record (Laboratory Copy)

USEPA Contract Laboratory Program
Inorganic Traffic Report & Chain of Custody Record

Case No: 39400
DAS No: DAS9000
SDG No:
L

Date Shipped:	2/20/2001
Carrier Name:	DHL
Airbill:	121212
Shipped to:	Inorganic Laboratory 1234 Smith Drive Anywhere, USA 12345 (123) 456-7890

Chain of Custody Record

Relinquished By	(Date / Time)	Received By	(Date / Time)
1			
2			
3			
4			

Sampler Signature:

For Lab Use Only
Lab Contract No:
Unit Price:
Transfer To:
Lab Contract No:
Unit Price:

INORGANIC SAMPLE No.	MATRIX/ SAMPLER	CONC/ TYPE	ANALYSIS/ TURNAROUND	TAG No./ PRESERVATIVE/ Bottles	STATION LOCATION	SAMPLE COLLECT DATE/TIME		ORGANIC SAMPLE No.	FOR LAB USE ONLY Sample Condition On Receipt
MC0075	Industrial Process Wastewater/ BOBBY SAMPLER	H/C	Al (21), Ba (21), Ca (21), Cr (21), TM/CN (21)	6481, 6482, 6483, 6484, 6485 (5)	LOCATION ONE	S: 2/20/2001 E: 2/23/2001	16:02 16:02	C0075	
MC0076	Ground Water/ JOE SAMPLER	L/C	Al (21), Ba (21), Ca (21), Cr (21), TM/CN (21)	6489, 6490, 6491, 6492, 6493 (5)	LOCATION TWO	S: 2/20/2001 E: 2/21/2001	16:01 16:01	C0076	
MC0077	Industrial Effluent Wastewater/ JOE SAMPLER	M/G	Al (21), Ba (21), Ca (21), Cr (21), TM/CN (21)	6497, 6498, 6499, 6500, 6501 (5)	LOCATION ONE	S: 2/16/2001 E: 2/20/2001	15:55 15:55	C0077	

Shipment for Case Complete?N	Sample(s) to be used for laboratory QC:	Additional Sampler Signature(s):	Cooler Temperature Upon Receipt:	Chain of Custody Seal Number:	
	MC0077				
Analysis Key:	**Concentration:** L = Low, M = Low/Medium, H = High	**Type/Designate:** Composite = C, Grab = G		**Custody Seal Intact?** ___	**Shipment Iced?** ___

Al = Aluminum, Ba = Barium, Ca = Calcium, Cr = Chromium, TM/CN = CLP TAL Total Metals and Cyanide

TR Number: 3-103823254-022001-0003

LABORATORY COPY

PR provides preliminary results. Requests for preliminary results will increase analytical costs.
Send Copy to: Sample Management Office, Attn: Heather Bauer, CSC, 15000 Conference Center Dr., Chantilly, VA 20151-3819; Phone 703/818-4200; Fax 703/818-4602

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Figure 3-3. Inorganic Traffic Report & Chain of Custody Record (Laboratory Copy)

USEPA Contract Laboratory Program
Organic Traffic Report & Chain of Custody Record

Case No: 39400 R
DAS No: DAS9000

Region:	3	Date Shipped:	2/20/2001	Chain of Custody Record	Sampler Signature:
Project Code:	QW-123	Carrier Name:	DHL	Relinquished By (Date / Time)	Received By (Date / Time)
Account Code:	ACCT000	Airbill:	121212	1	
CERCLIS ID:		Shipped to:	Organic Laboratory 1234 Smith Drive Anywhere, USA 12345 (123) 456-7890	2	
Spill ID:	ID3			3	
Site Name/State:	REAL SITE, UT			4	
Project Leader:	DAN SAMPLER				
Action:	Other				
Sampling Co:	SMITH CO.				

ORGANIC SAMPLE No.	MATRIX/ SAMPLER	CONC/ TYPE	ANALYSIS/ TURNAROUND	TAG No./ PRESERVATIVE/ Bottles	STATION LOCATION	SAMPLE COLLECT DATE/TIME	INORGANIC SAMPLE No.	QC Type
C0075	Industrial Process Wastewater/ BOBBY SAMPLER	H/C	BNA/PEST (21), VOA (21)	6486, 6487 (2)	LOCATION ONE	S: 2/20/2001 16:02 E: 2/23/2001 16:02	MC0075	--
C0076	Ground Water/ JOE SAMPLER	L/C	BNA/PEST (21), VOA (21)	6494, 6495 (2)	LOCATION TWO	S: 2/20/2001 16:01 E: 2/21/2001 16:01	MC0076	Spike
C0077	Industrial Effluent Wastewater/ JOE SAMPLER	M/G	BNA/PEST (21), VOA (21)	6502, 6503 (2)	LOCATION ONE	S: 2/16/2001 15:55 E: 2/20/2001 15:55	MC0077	--

Shipment for Case Complete? N	Sample(s) to be used for laboratory QC: C0077	Additional Sampler Signature(s):	Chain of Custody Seal Number:
Analysis Key:	Concentration: L = Low, M = Low/Medium, H = High	Type/Designate: Composite = C, Grab = G	Shipment Iced? _____
BNA/PEST = CLP TCL Semivolatiles and Pesticides/PC, VOA = CLP TCL Volatiles			

TR Number: 3-103823254-022001-0001

REGION COPY

PR provides preliminary results. Requests for preliminary results will increase analytical costs.

Send Copy to: Sample Management Office, Attn: Heather Bauer, CSC, 15000 Conference Center Dr., Chantilly, VA 20151-3819; Phone 703/818-4200; Fax 703/818-4602

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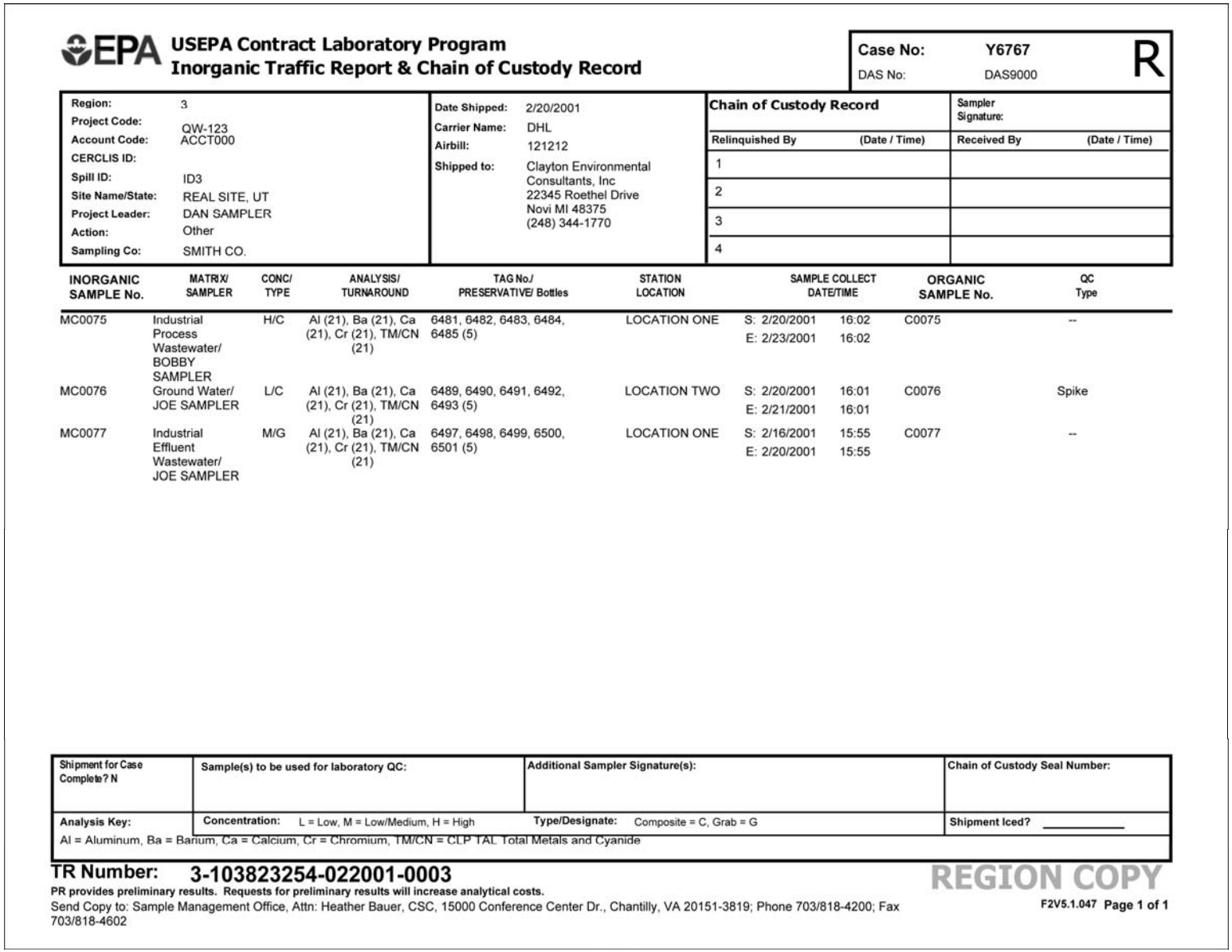
Figure 3-4. Organic Traffic Report & Chain of Custody Record (Region Copy)



EPA **USEPA Contract Laboratory Program**
Inorganic Traffic Report & Chain of Custody Record

Case No: Y6767 **R**
DAS No: DAS9000

Region:	3	**Date Shipped:**	2/20/2001
Project Code:	QW-123	**Carrier Name:**	DHL
Account Code:	ACCT000	**Airbill:**	121212
CERCLIS ID:		**Shipped to:**	Clayton Environmental Consultants, Inc 22345 Roethel Drive Novi MI 48375 (248) 344-1770
Spill ID:	ID3		
Site Name/State:	REAL SITE, UT		
Project Leader:	DAN SAMPLER		
Action:	Other		
Sampling Co:	SMITH CO.		

Chain of Custody Record

Relinquished By	(Date / Time)	Received By	(Date / Time)
1			
2			
3			
4			

Sampler Signature:

INORGANIC SAMPLE No.	MATRIX/ SAMPLER	CONC/ TYPE	ANALYSIS/ TURNAROUND	TAG No./ PRESERVATIVE/ Bottles	STATION LOCATION	SAMPLE COLLECT DATE/TIME	ORGANIC SAMPLE No.	QC Type
MC0075	Industrial Process Wastewater/ BOBBY SAMPLER	H/C	Al (21), Ba (21), Ca (21), Cr (21), TM/CN (21)	6481, 6482, 6483, 6484, 6485 (5)	LOCATION ONE	S: 2/20/2001 16:02 E: 2/23/2001 16:02	C0075	--
MC0076	Ground Water/ JOE SAMPLER	L/C	Al (21), Ba (21), Ca (21), Cr (21), TM/CN (21)	6489, 6490, 6491, 6492, 6493 (5)	LOCATION TWO	S: 2/20/2001 16:01 E: 2/21/2001 16:01	C0076	Spike
MC0077	Industrial Effluent Wastewater/ JOE SAMPLER	M/G	Al (21), Ba (21), Ca (21), Cr (21), TM/CN (21)	6497, 6498, 6499, 6500, 6501 (5)	LOCATION ONE	S: 2/16/2001 15:55 E: 2/20/2001 15:55	C0077	--

Shipment for Case Complete? N	Sample(s) to be used for laboratory QC:	Additional Sampler Signature(s):	Chain of Custody Seal Number:
Analysis Key:	Concentration: L = Low, M = Low/Medium, H = High	Type/Designate: Composite = C, Grab = G	Shipment Iced? _____
Al = Aluminum, Ba = Barium, Ca = Calcium, Cr = Chromium, TM/CN = CLP TAL Total Metals and Cyanide			

TR Number: 3-103823254-022001-0003

REGION COPY

PR provides preliminary results. Requests for preliminary results will increase analytical costs.

Send Copy to: Sample Management Office, Attn: Heather Bauer, CSC, 15000 Conference Center Dr., Chantilly, VA 20151-3819; Phone 703/818-4200; Fax 703/818-4602

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Figure 3-5. Inorganic Traffic Report & Chain of Custody Record (Region Copy)

3.2.3 Complete and Attach Custody Seals

Custody seals are usually pre-printed stickers that are signed (or initialed) and dated by the sampler after sample collection and placed on sample bottles or containers and/or shipping coolers or containers (see Figure 3-6). The custody seals document who sealed the sample container and verifies that the sample has not been tampered with. The seals must be placed such that they will break if the sample bottle or container or the shipping cooler or container is tampered with or opened after leaving custody of samplers. Custody seals can also be used to maintain custody of other items such as envelopes containing videotapes of the sample collection process.

Custody seals should never be placed directly onto a coring tool used as a transport device (e.g., 5 g Sampler) or tared, 40 mL closed-system vials. The seals must be placed on the bag for the coring tool used as a transport device, or on the bag used to enclose the vials. Refer to Appendix B for details.

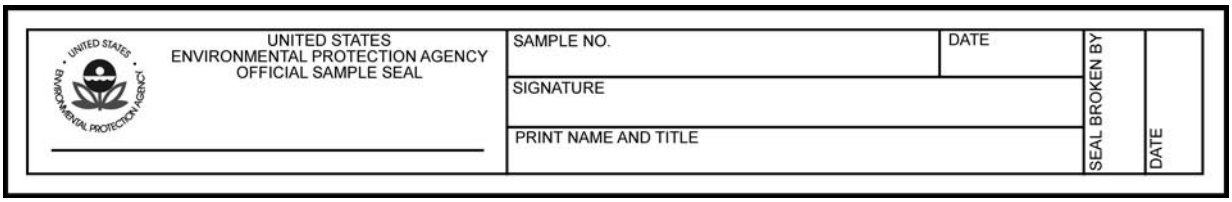

Figure 3-6. Custody Seal

Instructions for completing and attaching a custody seal are included in Table 3-5.

Table 3-5. Completing and Attaching a Custody Seal

Step	Action	Important Notes
1	Record the CLP Sample Number.	The space for the CLP Sample Number does not need to be completed on custody seals being placed on the opening of a cooler, only on those being placed on the opening of sample bottles or containers.
2	Record the month, day, and year of sample collection.	
3	Sign the seal in the Signature field.	
4	Print your name and title in the Print Name and Title field.	
5	Place the custody seal over the edge of the sample bottle or container such that it will break if tampered with.	Custody seals can be placed directly on any sample container except for coring tools used as a transport device (e.g., 5 g Samplers) and tared VOA bottles. If packing coring tools used as a transport device or tared VOA bottles, place them in a clear plastic bag and place the custody seal on the outside of the bag.
6	If possible, cover the custody seal with clear plastic tape to protect it.	Take special care to not place the protective tape over the seal in such a way that it can be removed and then re-attached without signs of tampering.

The use and type of custody seals can vary by Region or collecting organization. Samplers should obtain the appropriate custody seals and specific instructions for correctly attaching them from the RSCC.

3.2.4 Complete and Attach Sample Labels

Samplers affix sample labels to each sample container. A sample label must contain the associated CLP Sample Number (either written or pre-printed), SMO-assigned Case Number, and the preservative used. It must also denote the analysis/fraction. Samplers may also include additional information such as the station location or the date/time of collection. Samplers should use FORMS II Lite to create and print sample labels. The sampler can print two labels and attach one to the sample container or bottle, and place the other label on the sample tag that should also be attached to the sample container or bottle. The

labels should then be covered with clear packaging tape to protect the label and maintain legibility. If handwriting a sample label, the sampler should complete the label information using waterproof ink, place the label on the outside of the sample bottle or container, then cover the label with clear packaging tape to protect the label and maintain legibility (see Figure 3-1).

Do not attach labels to tared VOA sample vials. A label should already be pre-attached to the tared vial.

3.2.5 Complete and Attach Sample Tags

To support use of sample data in potential enforcement actions, sample characteristics other than on-site measurements (e.g., pH, temperature, conductivity) can be identified with a sample tag. Typically, site-specific information is written on the tags using waterproof ink. The use and type of sample tags may vary by Region. For each sampling event, samplers should receive the required sample tags and type of information to include from the RSCC. The sampler can use FORMS II Lite to create and print out multiple sample labels, one of which can be attached to the sample tag and then covered with clear packaging tape to protect the label and maintain legibility. If FORMS II Lite-created sample labels are not available, a detailed set of instructions for completing and attaching a handwritten sample tag are included in Table 3-6.

The use and type of sample tags may vary among Regions.

Table 3-6. Completing and Attaching a Handwritten Sample Tag

Step	Action	Important Notes
1	Under the "Remarks" heading, record the CLP Sample Number and SMO-assigned Case Number.	Make sure to record the correct CLP Sample Number and SMO-assigned Case Number in a legible manner.
2	Record the project code (e.g., Contract Number, Work Assignment Number, Interagency Agreement Number, etc.) assigned by USEPA.	
3	Enter the station number assigned by the sampling team coordinator.	
4	Record the month, day, and year of sample collection.	
5	Enter the military time of sample collection (e.g., 13:01 for 1:01 PM).	
6	Identify the designate and place an "X" in either the "Comp." or "Grab" box if the sample is either a composite or grab sample.	
7	Record the station location.	
8	Sign the sample tag in the Signature area.	
9	Place an "X" in the box next to Yes or No to indicate if a preservative was added to the sample.	
10	Under "Analyses", place an "X" in the box next to the parameters for which the sample is to be analyzed.	
11	Leave the box for "Laboratory Sample Number" blank.	
12	It is recommended that the sample tag be attached to the neck of the sample bottle or container using regular string, stretch string, or wire (see Figure 3-1).	Do **NOT** use wire to attach a sample tag to a metals sample.

An example of a completed sample tag is included in Figure 3-7 below:

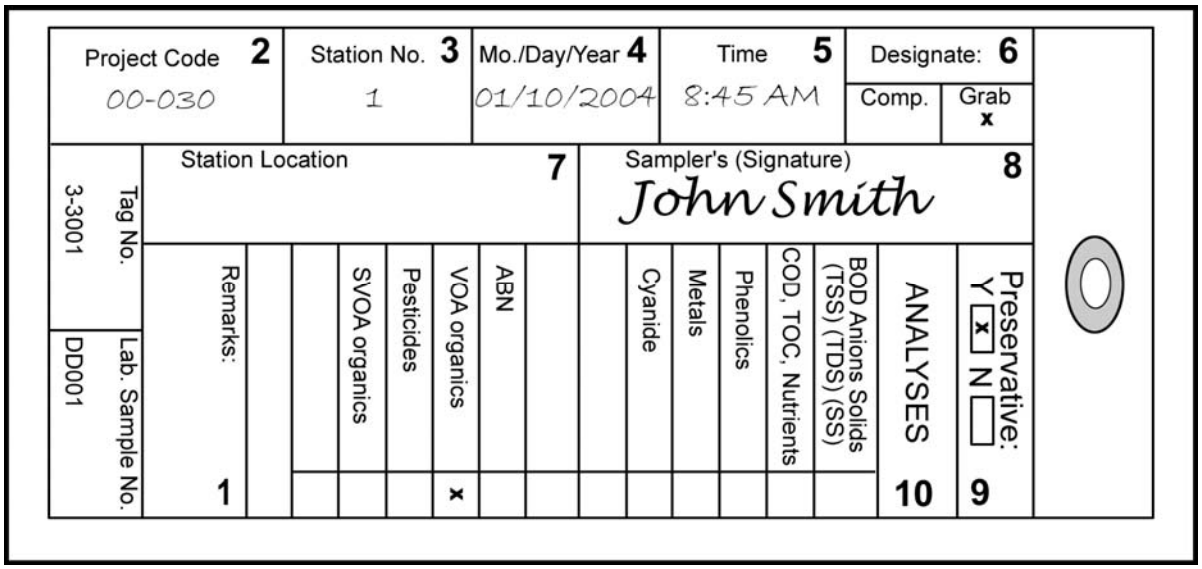

Figure 3-7. Completed Sample Tag

3.3 Provide Sample Receipt

After samples have been taken from private property, the sampler should prepare a receipt for these samples and provide this receipt to the property owner. This is especially important when sampling on private property since these samples could be used during future litigation and the receipt will verify that the owner granted approval for the removal of the samples from the property. An example of a sample receipt created using FORMS II Lite is shown in Figure 3-8.

EPA Region 3
U.S. ENVIRONMENTAL PROTECTION AGENCY

RECEIPT FOR SAMPLES

PROJECT NO.	PROJECT NAME	NAME & LOCATION OF FACILITY/SITE
QW-123		EXAMPLE SITE
SAMPLERS: (SIGNATURES)		

STATION NO.	LOCATION/DESCRIPTION	DATE	TIME	Comp/Grab	NO. OF EPA CONTAINERS	SPLIT SAMPLE Y OR N	EPA SAMPLE TAG NO.'S
STATION ONE	LOCATION ONE	2/20/2001	15:55	G	11	Yes	112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122
STATION ONE	LOCATION TWO	2/20/2001	16:01	C	11	Yes	123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133
STATION TWO	LOCATION ONE	2/20/2001	16:02	C	11	Yes	134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144

SPLIT SAMPLES TRANSFERRED BY: (PRINT)	DATE	SPLIT SAMPLES RECEIVED BY ☐ OR DECLINED BY ☐ (PRINT)	DATE/TIME
(SIGN)	TIME	(SIGN)	TELEPHONE
		TITLE	

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Figure 3-8. Sample Receipt Created Using the FORMS II Lite Software

3.4 Pack and Ship Samples

Once the samples have been collected, it is very important that the sampler properly package the samples for shipment and ensure that the samples are sent to the appropriate laboratory as quickly as possible. Prompt and proper packaging of samples will:

- Protect the integrity of samples from changes in composition or concentration caused by bacterial growth or degradation from increased temperatures;
- Reduce the chance of leaking or breaking of sample containers that would result in loss of sample volume, loss of sample integrity, and exposure of personnel to toxic substances; and
- Help ensure compliance with shipping regulations.

3.4.1 Sample Containers

Once samples are collected, they must be stored in conditions that maintain sample integrity. All samples should be placed in shipping containers or other suitable containers with ice to reduce the temperature as soon as possible after collection. Ideally, all samples should be shipped the day of collection for overnight delivery to the laboratory. If samples cannot be shipped on the day of collection, the sample temperature should be maintained at 4°C (±2°C) until they are shipped to the laboratory.

One CLP RAS sample may be contained in several bottles and vials. For example, one soil sample may consist of all containers needed for three of the analytical fractions available under this service (i.e., SVOA fraction, Pesticide fraction, and Aroclor fraction), even though the fractions are collected in separate containers. Therefore, the analysis to be performed and the matrix type will determine the type of container(s) that will be used, as well as the volume that must be collected for that particular sample fraction.

3.4.2 Inventory of Samples and Documentation

Prior to shipment, samplers should conduct an inventory of the contents of the shipping cooler or container against the corresponding TR/COC Record when packing for shipment to laboratories. An inventory will ensure that the proper number of containers have been collected for each analysis of the samples, that the required PE and QC samples and cooler temperature blanks are included, and the correct Sample Numbers and fractions have been assigned to each sample.

3.4.3 Shipping Regulations

Sample shipping personnel are legally responsible for ensuring that the sample shipment will comply with all applicable shipping regulations. For example, hazardous material samples must be packaged, labeled, and shipped in compliance with all IATA Dangerous Goods regulations or DOT regulations and USEPA guidelines. Refer to Appendix B for detailed shipping guidelines when using SW-846 Method 5035A to preserve and ship samples.

3.4.4 Sample Packaging for Shipment

Samplers are responsible for the proper packaging of samples for shipment. To ensure that samples are appropriately packaged (e.g., to avoid breakage and/or contamination) the sampler should consult their respective project plans to determine the proper packing and shipping procedures. The sampler must determine the sample type, pack the shipping containers correctly, include necessary paperwork, label and seal shipping containers or coolers, and ship the samples.

3.4.4.1 Determine the Sample Type and Container

Samplers should know what kinds of samples they are handling to ensure proper packaging. Samplers should refer to their appropriate project plans to determine which type of sample container should be used for each type of sample being taken during the sampling event.

Please follow Regional guidance with reference to samples containing dioxin or radioactive waste.

3.4.4.2 Pack Shipping Containers

It is imperative that samples are correctly and carefully packed in shipping containers to prevent the sample containers from breaking or leaking. Samplers must prepare and pack a shipping cooler or container according to the instructions outlined in Table 3-7.

Table 3-7. Packing Samples for Shipment

Step	Action	Important Notes
1	Seal all drain holes in the shipping container, both inside and out, to prevent leakage in the event of sample breakage.	
2	Check all lids/caps to make sure the samples are tightly sealed and will not leak.	
3	Seal samples within a clear plastic bag.	Custody seals can be placed directly on any sample container except for coring tools used as a transport device (e.g., 5 g Samplers) and tared VOA bottles. If packing coring tools used as a transport device or tared VOA bottles, place them in a clear plastic bag and place the custody seal on the outside of the bag.
4	Fully chill samples to 4°C (±2°C) prior to placement within suitable packing materials.	
5	Prior to placing samples within the shipping cooler, it is recommended that samplers line shipping containers with non-combustible, absorbent packing material.	
6	Place samples in CLEAN, sealed, watertight shipping containers (metal or hard plastic coolers).	
7	Conduct an inventory of the contents of the shipping cooler/container against the corresponding TR/COC Record.	
8	Cover samples in double-bagged ice to prevent water damage to packing materials.	Do NOT pour loose ice directly into the sample cooler. The ice is used to maintain the temperature of the samples within the shipping cooler.
9	It is recommended a temperature blank be included within each cooler being shipped.	The temperature blank is generally a 40 L vial filled with water and labeled “temperature blank” but does not have a Sample Number.
10	Ensure that the site name or other site-identifying information does not appear on any documentation being sent to the laboratory.	The laboratory should not receive any site-identifying information.

3.4.4.3 Include Necessary Paperwork

Samplers must properly place the necessary paperwork in the shipping cooler. All paperwork must be placed in a plastic bag or pouch and then secured to the underside of the shipping cooler lids (see Figure 3-9).

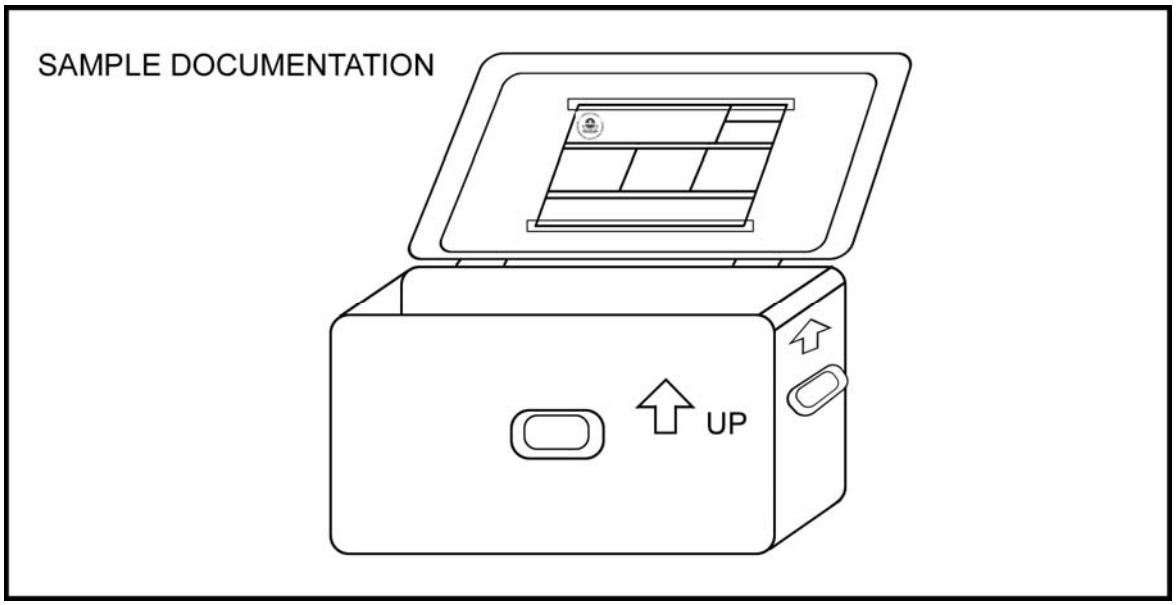

Figure 3-9. Sample Cooler with Attached TR/COC Record and Cooler Return Documentation

Necessary paperwork includes TR/COC Records and sample weight logs (see Figure 3-10), if required (for VOA samples). Samplers should contact their RSCC (or designee) for specific paperwork requirements.

USEPA Contract Laboratory Program
Sample Weight Log

Shipped to: AAA Testing Laboratory
1700 Mill Avenue
Houston TX 77099
(281) 983-1234

Case No. 39563
DAS No. DAS34
Date Shipped: 9/29/2003

Sample No.	Matrix	Analysis	Preservative	Bottle/ Tag Number	Tared Weight (g)	Final Weight (g)	Sample Weight (g)	Laboratory Weight	Traffic Report No.
C0036	Subsurface Soil (>12")	CLP TCL Volatiles	Ice Only	199548	32.80	37.20	4.40		3-103018225-092903-0001
C0036	Subsurface Soil (>12")	CLP TCL Volatiles	Ice Only	199547	32.10	38.30	6.20		3-103018225-092903-0001
C0036	Subsurface Soil (>12")	CLP TCL Volatiles	Ice Only	199549	31.20	38.60	7.40		3-103018225-092903-0001
C0037	Surface Soil (0"-12")	CLP TCL Volatiles	Ice Only	199552	32.00	36.90	4.90		3-103018225-092903-0001
C0037	Surface Soil (0"-12")	CLP TCL Volatiles	Ice Only	199551	32.40	37.10	4.70		3-103018225-092903-0001
C0037	Surface Soil (0"-12")	CLP TCL Volatiles	Ice Only	199550	31.90	35.90	4.00		3-103018225-092903-0001

Completed By:	Date:

All weights are measured in grams

Figure 3-10. Sample Weight Log

3.4.4.4 Return Sample Shipping Coolers

CLP laboratories must routinely return sample shipping coolers within 14 calendar days following shipment receipt. Therefore, the sampler should also include cooler return instructions with each shipment. The sampler (not the CLP laboratory) is responsible for paying for return of the cooler and should also include shipping airbills bearing the sampler's account number, as well as a return address to allow for cooler return.

3.4.4.5 Label and Seal Sample Shipping Coolers

After samples are packaged within shipping coolers, samplers must carefully secure the top and bottom of the coolers with tape, place return address labels clearly on the outside of the cooler, and attach the required chain-of-custody seals (see Figure 3-11).

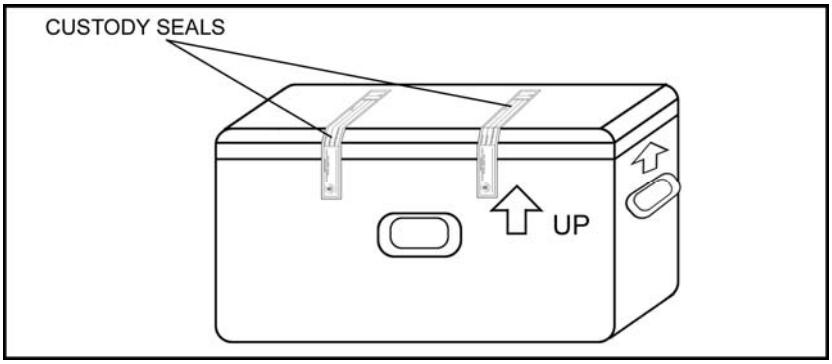

Figure 3-11. Shipping Cooler with Custody Seals

If more than one cooler is being delivered to a laboratory, samplers should mark each cooler as "1 of 2", "2 of 2", etc. In addition, samplers must accurately complete and attach shipping airbill paperwork for shipment of the samples to the laboratory. An airbill, addressed to the Sample Custodian of the receiving laboratory, should be completed for each cooler shipped. Samplers should receive the correct name, address, and telephone number of the laboratory to which they must ship samples from the RSCC or SMO. To avoid delays in analytical testing, samplers should make sure they are sending the correct types of samples to the correct laboratory when collecting samples for multiple types of analysis. For example, inorganic samples may be shipped to one laboratory for analysis, while organic samples may need to be shipped to another laboratory.

3.4.4.6 Ship Samples

The sampling contractor should ensure that samplers know the shipping company's name, address, and telephone number. In addition, they should be aware of the shipping company's hours of operation, shipping schedule, and pick-up/drop-off requirements.

Overnight Delivery

It is imperative that samples be sent via overnight delivery. Delays caused by longer shipment times may cause technical holding times to expire, which in turn may destroy sample integrity or require the recollection of samples for analysis.

Saturday Delivery

For shipping samples for Saturday delivery, the sampler MUST contact the RSCC (or their designee) or SMO so that SMO will receive the delivery information by 3:00 PM ET on the Friday prior to delivery.

3.4.5 Shipment Notification

When samples are shipped to CLP Laboratories, samplers **must immediately** report all sample shipments to the RSCC (or their designee) or to SMO. **Under no circumstances should the sampler contact the laboratory directly.** If samplers are shipping samples after 5:00 PM ET, they must notify the RSCC (or

designee) or SMO by 8:00 AM ET on the following business day. Samplers should receive the name and phone number of the appropriate SMO coordinator to contact from the Region/RSCC.

Samplers must provide the following information to the RSCC (or their designee) or to SMO:

- Name and phone number at which they can easily be reached (preferably closest on-site phone number if still in the field);
- SMO-assigned Case Number (see Section 2.4.1);
- Number, concentration, matrix and analysis of samples being shipped;
- Name of laboratory (or laboratories) to which the samples were shipped;
- Airbill number(s);
- Date of shipment;
- Case status (i.e., whether or not the Case is complete);
- Problems encountered, special comments, or any unanticipated issues;
- When to expect the next anticipated shipment; and
- An electronic export of the TR/COC Record (must be sent as soon as possible after sample shipment). For information regarding electronic export of TR/COC Records, refer to the following Web site:

http://www.epa.gov/superfund/programs/clp/f2lsubmit.htm

For Saturday delivery, samplers MUST contact the RSCC (or their designee) or SMO so that SMO will receive the delivery information by 3:00 PM ET on the Friday prior to delivery.

Samplers should be aware if their Region requires them to notify the RSCC (or designee) and/or SMO of sample shipment.

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Appendix A: Functions within a Sampling Project

The following table describes Quality Assurance Project Plan (QAPP) requirements taken from *EPA Requirements for Quality Assurance Project Plans* (EPA QA/R-5).

Functions Within a Sampling Project	Elements of that Function
Project Management	
Project/Task Organization	Identifies the individuals or organizations participating in the project and defines their specific roles and responsibilities.
Problem Definition/Background	States the specific problem to be solved or decision to be made and includes sufficient background information to provide a historical and scientific perspective for each particular project.
Project/Task Description	Describes the work to be performed and the schedule for implementation to include: • Measurements to be made during the course of the project; • Applicable technical, regulatory, or program-specific quality standards, criteria, or objectives; • Any special personnel and equipment requirements; assessment tools needed; and • A work schedule and any required project and quality records, including types of reports needed.
Quality Objectives and Criteria	Describes the project quality objectives and measurement performance criteria.
Special Training/Certification	Ensures that any specialized training for non-routine field sampling techniques, field analyses, laboratory analyses, or data validation should be specified.
Documents and Records	• Itemizes the information and records that must be included in the data report package and specifies the desired reporting format for hard copy and electronic forms, when used. • Identifies any other records and/or documents applicable to the project such as audit reports, interim progress reports, and final reports that will be produced. • Specifies or references all applicable requirements for the final disposition of records and documents, including location and length of retention period.
Data Generation and Acquisition	
Sampling Process Design (Experimental Design)	• Describes the experimental design or data collection design for the project. • Classifies all measurements as critical or non-critical.
Sampling Methods	• Describes the procedures for collecting samples and identifies sampling methods and equipment. Includes any implementation requirements, support facilities, sample preservation requirements, and materials needed. • Describes the process for preparing and decontaminating sampling equipment to include the disposal of decontamination by-products, selection and preparation of sample containers, sample volumes, preservation methods, and maximum holding times for sampling, preparation, and/or analysis. • Describes specific performance requirements for the method. • Addresses what to do when a failure in sampling occurs, who is responsible for corrective action, and how the effectiveness of the corrective action shall be determined and documented
Sample Handling and Custody	• Describes the requirements and provisions for sample handling and custody in the field, laboratory, and transport, taking into account the nature of the samples, the maximum allowable sample holding times before extraction and analysis, and the available shipping options and schedules. • Includes examples of sample labels, custody forms, and sample custody logs.

Analytical Methods	• Identifies the analytical methods and equipment required, including sub-sampling or extraction methods, waste disposal requirements (if any), and specific method performance requirements. • Identifies analytical methods by number, date, and regulatory citation (as appropriate). If a method allows the user to select from various options, the method citations should state exactly which options are being selected. • Addresses what to do when a failure in the analytical system occurs, who is responsible for corrective action, and how the effectiveness of the corrective action shall be determined and documented. • Specifies the laboratory turnaround time needed, if important to the project schedule. • Specifies whether a field sampling and/or laboratory analysis Case Narrative is required to provide a complete description of any difficulties encountered during sampling or analysis.
Quality Control (QC)	• Identifies required measurement QC checks for both the field and laboratory. • States the frequency of analysis for each type of QC check, and the spike compounds sources and levels. • States or references the required control limits for each QC check and corrective action required when control limits are exceeded and how the effectiveness of the corrective action shall be determined and documented. • Describes or references the procedures to be used to calculate each of the QC statistics.
Instrument/Equipment Testing, Inspection, and Maintenance	• Describes how inspections and acceptance testing of environmental sampling and measurement systems and their components will be performed and documented. Identifies and discusses the procedure by which final acceptance will be performed by independent personnel. • Describes how deficiencies are to be resolved and when re-inspection will be performed. • Describes or references how periodic preventative and corrective maintenance of measurement or test equipment shall be performed. • Identifies the equipment and/or system requiring periodic maintenance. • Discusses how the availability of spare parts identified in the operating guidance and/or design specifications of the systems will be assured and maintained.
Instrument/Equipment Calibration and Frequency	• Identifies all tools, gauges, instruments, and other sampling, measuring, and test equipment used for data collection activities affecting quality that must be controlled, and at specific times, calibrated to maintain performance within specified limits. • Identifies the certified equipment and/or standards used for calibration. • Describes or references how calibration will be conducted using certified equipment and/or standards with known valid relationships to nationally recognized performance standards. If no such standards exist, documents the basis for calibration. • Indicates how records of calibration shall be maintained and traced to the instrument.
Inspection/Acceptance of Supplies and Consumables	• Describes how and by whom supplies and consumables shall be inspected and accepted for use in the project. • States acceptance criteria for such supplies and consumables.
Non-direct Measurements	• Identifies any types of data needed for project implementation or decision-making that are obtained from non-measurement sources (e.g., computer databases, programs, literature files, historical databases). • Describes the intended use of data. • Defines the acceptance criteria for the use of such data in the project. • Specifies any limitations on the use of the data.
Data Management	• Describes the project data management scheme, tracing the data path from generation in the field or laboratory to their final use or storage. • Describes or references the standard record-keeping procedures, document control system, and the approach used for data storage and retrieval on electronic media.

Appendix B: CLP Sample Collection Guidelines for VOAs in Soil by SW-846 Method 5035A

A. Preferred Options for the Contract Laboratory Program (CLP) are Options 1, 2, and 3:

Soil samples must be placed on their sides prior to being frozen.

Option 1.

Closed-system Vials:

Container - tared or preweighed 40 mL VOA Vials containing a magnetic stir bar.

Collect 5 g of soil per vial (iced or frozen in the field).

Regular Samples	3 Vials - Dry (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 4 Total Vials
Regular Samples Requiring QC Analysis	9 Vials - Dry (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 10 Total Vials

Option 2.

Closed-system Vials Containing Water:

Container - tared or pre-weighed 40 mL VOA vials containing a magnetic stir bar and 5 mL water.

Collect 5 g of soil per vial (iced or frozen in the field).

Regular Samples	2 Vials with water added (5 g soil and 5 mL water per vial) 1 Vial - Dry (5 g soil in vial) 1 Vial - Dry (filled with soil, no headspace) 4 Total Vials (2 with water and 2 dry)
Regular Samples Requiring QC Analysis	6 Vials with water added (5 g soil and 5 mL water per vial) 5 Vials - Dry (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 12 Total Vials (6 with water and 6 dry)

Option 3.

Coring Tool used as a Transport Device

Container - 5 g Samplers or equivalent.

All Samplers should be iced or frozen in the field and bagged individually.

Regular Samples	3 Samplers (5 g soil per Sampler) 1 Vial - Dry (filled with soil, no headspace) 4 Total (3 Samplers and 1 Vial)
Regular Samples Requiring QC Analysis	9 Samplers (5 g soil per Sampler) 1 Vial - Dry (filled with soil, no headspace) 10 Total (11 Samplers and 1 Vial)

B. Options 4, 5, and 6 are NOT preferred options for the CLP:

Option 4.

Closed-system Vials:

Container - tared or preweighed 40 mL VOA Vials containing a magnetic stir bar and preservative.

Collect 5 g of soil per vial and add Sodium bisulfate ($NaHSO_4$) preservative (5 mL water + 1 g $NaHSO_4$) - iced or frozen in the field.

Caution: This option is NOT a Preferred Option for the CLP because:

NaHSO4 preservation creates low pH conditions that will cause the destruction of certain CLP target analytes (e.g., vinyl chloride, trichloroethene, trichlorofluoromethane, cis- and trans-1,3-dichloropropene). Projects requiring the quantitation of these analytes should consider alternative sample preservation methods. NaHSO4 also cannot be used on carbonaceous soils. Check the soil before using this method of collection! Soil can be checked by placing a test sample in a clean vial, then adding several drops of NaHSO4 solution. If the soil bubbles, use Option 4b and note this issue on the TR/COC Record.

Option 4a. Samples preserved in the field

Regular Samples	2 Vials with $NaHSO_4$ preservative added (5g soil per vial) 1 Vial without $NaHSO_4$ preservative added (5g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 4 Total Vials (2 with $NaHSO_4$ preservative and 2 without)
Regular Samples Requiring QC Analyses	4 Vials with $NaHSO_4$ preservative added (5g soil per vial) 5 Vials without $NaHSO_4$ preservative added (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 10 Total Vials (4 with $NaHSO_4$ and 6 without)

Option 4b. Samples are preserved by the laboratory (No $NaHSO_4$ preservative is added to these samples in the field).

Regular Samples	3 Vials - Dry (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 4 Total Vials
Regular Samples Requiring QC Analyses	9 Vials - Dry (5 g soil per vial) 1 Vial - Dry (filled with soil, no headspace) 10 Total Vials

Option 5.

Methanol Preservation (medium-level analysis only):

Container - tared or pre-weighed 40 mL VOA vials containing 5-10 mL methanol.

Collect 5 g of soil per vial (iced in the field).

Caution: This is NOT a preferred option for the CLP because:

Samples preserved with methanol can only be analyzed by the medium-level method. Low-level Contract Required Quantitation Limit (CRQLs) cannot be achieved when samples are preserved this way.

Additional problems associated with use of methanol as a preservative in the field include:

- Possible contamination of the methanol by sampling-related activities (e.g., absorption of diesel fumes from sampling equipment);
- Leakage of methanol from the sample vials during shipping, resulting in loss of VOAs prior to analysis.

Regular Samples	2 Vials (5 g soil and 5-10 mL methanol per vial) 1 Vial - Dry (filled with soil, no headspace) 3 Total Vials (2 with methanol and 1 dry)
Regular Samples Requiring QC Analysis	6 Vials (5 g soil and 5-10 mL methanol per vial) 1 Vial -Dry (filled with soil, no headspace) 7 Total Vials (6 with methanol and 1 dry)

If shipping samples containing methanol as a preservative, a shipping label must be used to indicate methanol. This label must also contain the United Nations (UN) identification number for methanol (UN 1230), and indicate Limited Quantity.

Option 6.

Glass Containers filled with sample - No Headspace:

Container - 4 oz Glass Jars.

Glass container filled with soil with no headspace and iced.

Caution: This is NOT a preferred option for the CLP because:

Samples collected in this manner lose most of their volatile analytes prior to analysis when the sample containers are opened and sub-sampled in the laboratory. This option is only available due to Regional requirements.

Regular Samples	2 Glass Jars (4 oz) filled with sample, no headspace 1 Vial - Dry (filled with soil, no headspace) 3 Total Containers
Regular Samples Requiring QC Analysis	2 Glass Jars (4 oz) filled with sample, no headspace 1 Vial - Dry (filled with soil, no headspace) 3 Total Containers

C. Caution:

1. Extreme care must be taken to ensure that frozen samples do not break during shipment.
2. Before adding soil to pre-weighed vials containing a stir bar, weigh the vials to confirm the tared weight. If the weight varies by more than 0.1 g, record the new weight on the label and the sample documentation. Do NOT add labels to these vials once the tared weight has been determined/confirmed.

D. Dry Samples:

All options include taking a sample in a dry 40 mL VOA vial (or a 4 oz wide mouth jar) with no headspace. No additional water, $NaHSO_4$, or methanol is added to this sample. This sample is taken to determine moisture content; therefore, it does not need to be tared or have a stir bar.

E. Iced or Frozen Samples:

1. Iced means cooled to 4°C (±2°C) immediately after collection.
2. Frozen means cooled to between -7°C and -15°C immediately after collection.

F. Sample Delivery:

CLP strongly recommends that all samples reach the laboratory by COB the next day after sample collection.

G. Notes:

1. For Option 4, samples can be preserved with $NaHSO_4$ either:
   - In the field; or
   - In the laboratory upon receipt. In this case, the sampler should put the following information in the Preservation Column of the TR/COC Record - "To be preserved at lab with $NaHSO_4$". This Regional Request should also be communicated to SMO so that the laboratory can be notified.
2. Regional QAPPs may require the use of Option 5. Please note that this option is for medium-level analysis ONLY.
3. If water, methanol, or $NaHSO_4$ preservative is added to the vials in the field, a field blank containing the appropriate liquid used in the vials should be sent to the laboratory for analysis.

H. Number of Containers Rationale:

The rationale for the number of containers (vials or samplers) required for the field sample and the required laboratory QC for each option is given as follows:

Option 1.

Rationale for Regular Vials:	1 vial for low-level analysis (water purge) 1 vial for backup low-level analysis 1 vial for medium-level analysis (methanol extraction)
Rationale for QC Vials:	2 vials for MS and MSD low-level analysis 2 vials for MS and MSD medium-level analysis 2 vials for backup (MS and MSD) low-level or medium-level analysis

Option 2.

Rationale for Regular Vials:	1 vial for low-level analysis (water purge) 1 vial for back up low-level analysis 1 vial dry for medium-level analysis (methanol extraction)
Rationale for QC Vials:	2 vials for MS and MSD low-level analysis 2 vials for MS and MSD medium-level analysis 2 vials for backup (MS and MSD) low-level or medium-level analysis
Medium-level: Analysis	Methanol will be added in the laboratory

Option 3.

Rationale for Regular Samples:	1 sampler for low-level analysis (water purge) 1 sampler for back up low-level analysis 1 sampler for medium-level analysis (methanol extraction)
Rationale for QC Samples:	2 samplers for MS and MSD low-level analysis 2 samplers for backup MS and MSD low-level analysis 2 samplers for MS and MSD medium-level analysis 2 samplers for backup MS and MSD medium-level analysis

Option 4a ($NaHSO_4$ added in the field).

Rationale for Regular Vials:	1 vial with water for low-level analysis (water purge) 1 vial with water for backup low-level analysis 1 vial dry for medium-level analysis (methanol extraction)
Rationale for QC Vials:	2 vials with water for MS and MSD low-level analysis 2 vials dry for MS and MSD medium-level analysis 2 vials for backup (MS and MSD) low-level or medium-level analysis

Option 4b ($NaHSO_4$ added in the laboratory).

Rationale for Regular Vials:	1 vial for low-level analysis (water purge) 1 vial for backup low-level analysis 1 vial for medium-level analysis (methanol extraction)
Rationale for QC Vials:	2 vials for MS and MSD low-level analysis 2 vials for MS and MSD medium-level analysis 2 vials for backup (MS and MSD) low-level or medium-level analysis

Option 5.

Rationale for Regular Samples:	1 vial for regular medium-level analysis 1 vial for back up medium-level analysis
Rationale for QC Samples:	2 samples for MS and MSD 2 samples for backup MS and MSD

Option 6.

In this option, all Regular and QC samples for both low-level and medium analysis are taken as subsamples from the same container.

Rationale for Regular Analysis	1 glass jar for low-level analysis and medium-level analysis **1 glass jar for backup low-level analysis and medium-level analysis**
Rationale for QC Analysis:	1 glass jar for low-level analysis and medium-level analysis **1 glass jar for backup low-level analysis and medium-level analysis**

Appendix C: General CLP Sample Collection Guidelines VOAs in Water

Regional guidance and/or specific Project Plan requirements will supersede the guidelines listed below.

Collect the following:

- At least two 40 mL glass containers with polytetrafluoroethylene (PTFE)-lined septa and open top screw-caps that are filled to capacity with no air bubbles, preserved to a pH of 2 with HCl, and cooled to 4°C (±2°C) immediately after collection. DO NOT FREEZE THE SAMPLES.
- If Selected Ion Monitoring (SIM) analysis is requested, at least two additional 40 mL glass containers with PTFE-lined septa and open top screw-caps that are filled to capacity with no air bubbles, preserved to a pH of 2 with HCl, and cooled to 4°C (±2°C) immediately after collection.

Test for Carbonates, Residual Chlorine, Oxidants, and Sulfides:

- It is very important that samplers obtain Regional guidance when testing and ameliorating for:
  - Carbonates;
  - Residual chlorine (e.g., municipal waters or industrial waste waters that are treated with chlorine prior to use or discharge); or
  - Oxidants.
- VOA samples containing carbonates react with the acid preservative causing effervescence (due to formation of carbon dioxide), which can cause loss of volatile analytes.
- Residual chlorine present in VOA samples can continue to react with dissolved organic matter. This continuous reaction may lead to inaccurate quantitation of certain analytes present in the sample at the time of collection.
- Residual chlorine and oxidants present in VOA samples can cause degradation of certain volatile analytes (e.g., styrene).

Perform the following for *Pre-Preserved* Vials:

1. Pour the sample slowly down the edge of the sample vial to avoid excess aeration or agitation of the sample during filling.
2. Fill the vial completely so that a reverse (convex) meniscus is present and ensure that there are no air bubbles present (either in the body or especially at the top of the vial).
3. Place the septum on the vial so that the PTFE side is in contact with the sample, and then firmly tighten the cap.
4. Gently flip the vial a few times to ensure that the sample is mixed with the acid preservative.
5. While holding the vial upright, gently tap the sample to check for air bubbles (either in the body or especially at the top of the vial).
6. If air bubbles are present, discard the sample and select a new vial in which to recollect a new sample. Repeat Steps 1 - 5 above.
7. Do NOT mix or composite samples for VOAs.
8. Cool sample to a temperature of 4°C (±2°C). Samplers should begin the cooling process in the field as samples are being collected. Double-bagged ice should be used. DO NOT FREEZE WATER SAMPLES.
9. Immediately transfer the vial to the sample shuttle (device that contains a "set" of VOA vials) once it has been collected. Do NOT allow ice to touch the vials.

Perform the Following for *Empty* Vials:

1. Rinse the vial with sample water prior to actual sample collection and preservation.

Regions vary in their approach to pre-rinsing and/or re-using sample vials (e.g., some Regions do not recommend pre-rinsing and/or re-use of pre-cleaned containers using sample water). Be sure to follow Regional guidance.

2. Add 1-2 mL of acid preservative to the vial. Check to ensure that the sample you are collecting requires a preservative (follow Regional guidance).
3. Pour the sample slowly down the edge of the sample vial to avoid excess aeration and agitation of the sample.
4. Fill the vial completely so that a reverse (convex) meniscus is present and ensure that there are no air bubbles present (either in the body or especially at the top of the vial).
5. Place the septum on the vial so that the PTFE side is in contact with the sample, and then firmly tighten the cap.
6. Gently flip the vial a few times to ensure that the sample is mixed with the acid preservative.
7. While holding the vial upright, gently tap the vial to check for air bubbles (either in the body or especially at the top of the vial).
8. If air bubbles are present, discard the sample and recollect a new sample using the same sample vial. Repeat Steps 1 - 7 above.
9. Check the recollected sample for air bubbles. If air bubbles are present, additional sample water may be added to the vial to eliminate air bubbles. If there are air bubbles after three consecutive attempts to eliminate air bubbles by the addition of sample water, the entire sample and sample vial should be discarded and a new sample collected.
10. Do NOT mix or composite samples for VOAs.
11. Cool sample to a temperature of 4°C (±2°C). Samplers should begin the cooling process in the field as samples are being collected. Double-bagged ice should be used. DO NOT FREEZE WATER SAMPLES.
12. Immediately transfer the vial to the sample shuttle (device which contains a "set" of VOA vials) once it has been collected. Do NOT allow ice to touch the vials.

Things to Remember:

- Samples must be shipped as soon as possible, preferably on the same day as sample collection to avoid exceeding sample holding times. If overnight transit is not possible, samples should be maintained at 2 - 4°C until they are shipped to the laboratory.
- If samples are not preserved (a requirement for certain analytes), the technical holding time is shortened to 7 days.

Appendix D: Sampling Techniques and Considerations

During a sampling event, the sampler is expected to follow prescribed sampling techniques. The sampler should also be aware of any special sampling considerations, contaminant issues, and sample compositing and mixing methods that could affect their sampling efforts.

Regional guidance will take precedence over any of the techniques and considerations listed below.

D.1 General Sampling Techniques

Information regarding surface water, sediment, soil, and groundwater sampling can be found in many documents including, but not limited to, the following sources:

- Compendium of ERT Surface Water and Sediment Sampling Procedures, EPA/540/P-91/005;
- Compendium of ERT Soil Sampling and Surface Geophysics Procedures, EPA/540/P-91/006;
- Compendium of ERT Groundwater Sampling Procedures, EPA/540/P-91/007;
- Quality Assurance Sampling Plan for Environmental Response (QASPER) software, Version 4.1, ERT; and
- *Requirements for the Preparation of Sampling and Analysis Plans*; United States Army Corps of Engineers, February 1, 2001, EM 200-1-3.

When working with potentially hazardous materials, samplers should follow USEPA and OSHA requirements, specific health and safety procedures, and DOT requirements.

D.2 Special Sampling Considerations

Samplers should refer to Regionally-developed SOPs to obtain specific procedures for properly collecting and preserving samples in the field. For additional guidance regarding sampling for VOAs in soil and water, see Appendices B and C. Samplers should obtain Regional guidance when testing and ameliorating for:

- Carbonates in VOA soil and water;
- Residual chlorine in VOA soil and water, or cyanide water;
- Oxidants in VOA soil and water; or
- Sulfides in cyanide.

D.3 Contaminant Sampling

Certain compounds can be detected in the parts-per-billion (ppb) and/or parts-per-trillion (ppt) range. Extreme care MUST be taken to prevent cross-contamination of these samples. The following precautions should be taken when trace contaminants are a concern:

- Disposable gloves should be worn each time a different location is sampled.
- When collecting both surface water and sediments, surface water samples should be collected first. This reduces the chance of sediment dispersal into surface water, and the resulting loss of surface water sample integrity.
- Sampling should occur in a progression from the least to the most contaminated area, if this information is known to the sampling team.
- Samplers should use equipment constructed of PTFE, stainless steel, or glass that has been properly pre-cleaned for collection of samples for trace organic and/or inorganic analyses. Equipment constructed of plastic or polyvinyl chloride (PVC) should NOT be used to collect samples for trace organic compound analyses.
- Equipment constructed of stainless steel should NOT be used to collect samples for trace metals analysis.

D.4 Sample Compositing

Sample compositing is a site-specific activity that must be conducted according to the SAP. Compositing is typically used for large sites under investigation to improve the precision (i.e., lower the variance) of the estimated average contaminant concentrations. **Samples for VOA analysis should NOT be composited to minimize loss of VOAs/analytes.**

Composite samples consist of a series of discrete grab samples that are mixed together to characterize the average composition of a given material. The discrete samples are usually of equal volume, but may be weighted to reflect an increased flow or volume. Regardless, all discrete samples must be collected in an identical manner and the number of grab samples forming a composite should be consistent. There are several compositing techniques that may be required such as:

- Flow-proportioned – Collected proportional to the flow rate during the compositing period by either a time-varying/constant volume or a time-constant/varying volume method. This technique is usually associated with wastewater or storm water runoff sampling.
- Time – Composed of a varying number of discrete samples collected at equal time intervals during the compositing period. This technique is typically used to sample wastewater and streams, and in some air sampling applications.
- Areal – Collected from individual grab samples collected in an area or on a cross-sectional basis. Areal composites are comprised of equal volumes of grab samples where all grabs are collected in an identical manner. This technique is typically used for estimating average contaminant concentrations in soils or sediments. This technique is useful when contaminants are present in nugget form (i.e., TNT chunks, lead shot, etc.), thus exhibiting large differences in concentration over a small sample area.
- Vertical – Collected from individual grab samples but taken from a vertical cross section. Vertical composites are comprised of equal volumes of grab samples where all grab samples are collected in an identical manner. Examples would include vertical profiles of a soil borehole or sediment columns.
- Volume – Collected from discrete samples whose aliquot volumes are proportional to the volume of sampled material. Volume composites are usually associated with hazardous waste bulking operations where the sample represents combined or bulked waste.

When compositing solid samples (i.e., sediment, soil, or sludge) for analysis of compounds present in trace quantities, use a stainless steel or PTFE bowl and spatula.

D.5 Sample Mixing and Homogenizing

Mixing of the sample for the remaining parameters is necessary to create a representative sample media. It is extremely important that solid samples be mixed as thoroughly as possible to ensure that the sample is as representative as possible of the sample location. Please refer to the project-specific SAP regarding instructions on removal of any extraneous materials (e.g., leaves, sticks, rocks, etc.). The mixing technique will depend on the physical characteristics of the solid material (e.g., particle size, moisture content, etc.). The mixing container should be large enough to hold the sample volume and accommodate the procedures without spilling. Both the mixing container (generally a bowl or tray) and the mixing implement should be properly decontaminated before use. Samples should be homogenized according to procedures listed in the project-specific SAP.

Samples for VOA analysis should not be mixed to minimize loss of volatile analytes.

Table D-1 provides a short procedure for mixing a soil sample with a small particle size (less than 1/4 in) and filling sample containers in the field.

Table D-1. Mixing a Sample and Filling Sample Containers

Step	Action
1	Roll the contents of the compositing container to the middle of the container and mix.
2	Quarter the sample and move to the sides of the container.
3	Mix each quarter individually, then combine and mix OPPOSITE quarters, then roll to the middle of the container.
4	Mix the sample once more, and then quarter the sample again.
5	Mix each quarter individually, then combine and mix ADJACENT corners, then roll to the middle of the container. The goal is to achieve a consistent physical appearance before sample containers are filled.
6	Flatten piled material into an oblong shape.
7	Using a flat-bottomed scoop, collect a strip of soil across the entire width of the short axis and place it into a sample container.
8	Repeat Step 7 at evenly-spaced intervals until the sample containers are filled.
9	Record the approximate quantity of each subsample in the field log book.

Appendix E: Sampling Checklists

Appendix E-1: Personnel Preparation Checklist

(Page 1 of 1)

Personnel Briefing	Yes	No	Comments:
1. Did you review sampling team responsibilities and identify individual(s) responsible for corrective actions?			
2. Did you ensure that you have met the appropriate personal safety and protection requirements?			
3. Did you identify sampling locations and receive permission to access them, as appropriate?			
4. Did you contact the appropriate utility companies PRIOR to the start of sampling?  By law, utility companies must be contacted prior to the start of digging/sampling so that any underground utilities (gas lines, water lines, electrical lines, etc.) can be marked. A list of one-call centers for each state may be found at: http://www.digsafely.com/contacts.htm.			
5. If sampling on private property, do you have sample receipts to provide to the property owner for all samples taken and removed from the property?			
6. Have you determined the number and type of samples to be collected?			
7. Did you review sample collection methods?			
8. Have you reviewed sample container requirements?			
9. Did you review decontamination requirements, procedures, and locations?			
10. Did you determine holding times and conditions?			
11. Did you determine Performance Evaluation (PE) and Quality Control (QC) sample requirements?			
12. Have you obtained shipping cooler temperature blanks, if required?			
13. Did you review sample label and tag requirements?			
14. Did you review Traffic Report/Chain of Custody (TR/COC) Record and custody seal requirements?			
15. Have you obtained the laboratory name, shipping addresses, and telephone number?			
16. Did you review cooler return instructions?			
17. Have you obtained shipping company information (name, telephone number, account number, pickup schedule)?			
18. Have you obtained shipping schedules?			
19. Did you review shipment reporting requirements and the appropriate contact names and telephone numbers for reporting?			
20. Have you included any sampler comments regarding sampling issues (e.g., low volumes, matrix, suspected concentrations based on field measurements)?			

Appendix E-2: General Sample Collection Checklist

(Page 1 of 1)

General Sample Collection	Yes	No	Comments:
1. Did you identify and mark the sampling location with buoys, flags, or stakes according to the sampling plans, maps, and grids?			
2. If the sampling location is inaccessible, did you contact the appropriate field or Regional personnel for instructions?			
3. Did you use the correct sampling equipment?			
4. Did you follow the correct decontamination procedures?			
5. Did you follow the correct collection procedures?			
6. Did you use the correct sample containers for each sample collected?			
7. Did you collect the correct volume for each sample?			
8. Did you collect the correct type of sample, including primary samples and Quality Control (QC) samples?			
9. Did you properly preserve each sample collected?			
10. Did you correctly document and label each sample with all necessary information?  Under no circumstances should the site name appear on any documentation being sent to the laboratory.			
11. If sampling on private property, did you provide a sample receipt to the owner of the property for all samples taken and removed from the property?			

Appendix E-3: Completing Field Logbook Checklist

(Page 1 of 1)

Completing Field Logbook	Yes	No	Comments:
1. Did you use waterproof ink when writing in the field logbook?			
2. Did you document sampling project information such as: • Project name, ID, and location; • Names of samplers; • Geological observations, including maps; • Atmospheric conditions; • Field measurements; and • Sampling dates, times, and locations?  Under no circumstances should the site name appear on any documentation being sent to the laboratory.			
3. Did you record sampling activity information such as: • Sampling dates and times; • Sample identifications; • Sample matrices; • Sample descriptions (e.g., odors and/or colors); • Number of samples taken; • Sampling methods/equipment; and • Description of QC samples?			
4. Did you document any and all deviations from the sampling plan?			
5. Did you document any and all difficulties in sampling and/or any unusual circumstances?			
6. Were all errors corrected by crossing a line through the error, initialing the error, dating the error, and then adding the correct information?			

Appendix E-4: Completing Handwritten Sample Labels Checklist

(Page 1 of 1)

Completing Handwritten Sample Labels	Yes	No	Comments:
1. Did the Region provide CLP Sample Numbers and SMO-assigned Case Numbers?			
2. If additional CLP Sample Numbers were needed, did you contact the appropriate Regional personnel?			
3. Were the CLP Sample Numbers and SMO-assigned Case Numbers on the labels correct? Organic CLP Sample Numbers begin with the Regional letter code, followed by letters and numbers. Inorganic CLP Sample Numbers begin with "M", followed by the Regional letter code, and then letters and numbers.  The following characters are not used in generating CLP Sample Numbers and should never appear on any paperwork send to the laboratory: I; O; U; and V. Also, the last character of a CLP Sample Number will never be a letter.			
4. Were samples uniquely numbered and designated to only one sample?  Samples collected for total metal and dissolved metal analyses must receive separate, unique, CLP Sample Numbers.			
5. Were Quality Control (QC) samples numbered accordingly?			
6. Were the specific requirements followed for total and dissolved metals analysis, QC and Performance Evaluation (PE) samples, and SW-846 Method 5035A?			
7. Were all temperature blanks labeled with "TEMPERATURE BLANK"?			
8. Was a sample label containing the CLP Sample Number, SMO-assigned Case Number, location, concentration, preservative, and the fraction/analysis, attached to each sample bottle or container as the sample was collected?  Under no circumstances should the site name appear on any documentation being sent to the laboratory.			
9. Was clear tape placed over the sample labels to protect the labels from moisture and to help the labels adhere to the sample bottle?			
10. Were all errors corrected by crossing a line through the error, initialing the error, dating the error, and then adding the correct information?			

Appendix E-5: Completing Handwritten Sample Tags & Custody Seals Checklists

(Page 1 of 1)

Completing Handwritten Sample Tags	Yes	No	Comments:
1. Was waterproof ink used on the sample tags?			
2. If Regionally required for individual sample containers, was the project code on the sample tag completed?			
3. Was the station number on the sample tag completed?			
4 Was the date filled in using the format MM/DD/YYYY?			
5. Was the time of sample collection indicated in military time format HH:MM?			
6. Was the box checked indicating composite or grab sample?			
7. Was the station location on the sample tag completed?			
8. Did you indicate whether or not the sample was preserved by checking "yes" or "no?"			
9. Was the appropriate analysis indicated on the sample tag?			
10. Were the appropriate CLP Sample Number and SMO-assigned Case Number indicated and cross-referenced with the numbers on the sample label?			
11. Did you sign the sample tags?			
12 Did you attach the sample tag to the neck of the sample bottle with striang, stretch string, or wire (recommended method)?  Do **NOT** use wire to attach a sample tag to a metal sample.			
13. Were all errors corrected by crossing a line through the error, initialing the error, dating the error, and then adding the correct information?			

Completing Custody Seals	Yes	No	Comments:
1. Did you sign and date the custody seal?			
2. Did you attach a completed custody seal to the sample bottle, container, or plastic bag, placing the seal over the cap or lid of each sample bottle or container or on the bag opening such that it will be broken if the sample bottle, container, or bag is opened or tampered with?			
3. As appropriate, did you attach the completed custody seal to the sample shipping container or cooler, placing the seal such that it will be broken if the container or cooler is opened or tampered with?			
4. Were all errors corrected by crossing a line through the error, initialing the error, dating the error, and then adding the correct information?			

Appendix E-6: Packing Sample Container Checklist

(Page 1 of 1)

Packing Sample Container	Yes	No	Comments:
1. Did you follow all State, Federal, Department of Transportation (DOT), and International Air Transportation Association (IATA) regulations governing the packaging of environmental and hazardous samples?  If samples contain methanol preservation (e.g., samples to be analyzed by SW-846 Method 5035A), refer to the packaging instructions in Appendix A.			
2. Were all CLP Sample Numbers, SMO-assigned Case Numbers, fractions/analyses, labels, tags, and custody seals attached to the correct sample containers?			
3. Was an inventory conducted of CLP Sample Numbers, SMO-assigned Case Numbers, fractions/analyses, and containers, and verified against the TR/COC Records?			
4. Were the correct number and type of Performance Evaluation (PE) and Quality Control (QC) samples collected?			
5. Were all sample containers sealed in clear plastic bags with the sample label and tag visible through the packaging?			
6. Were all soil/sediment samples known to contain dioxin securely enclosed in metal cans (e.g., paint cans) with the lids sealed?			
7. Was suitable absorbent packing material placed around the sample bottles or containers?			
8. Were the outsides of metal containers labeled properly with the CLP Sample Number, SMO-assigned Case Number, and the fraction/analysis of the sample inside?			

Appendix E-7: Packing Shipping Container Checklist

(Page 1 of 1)

Packing Shipping Container	Yes	No	Comments:
1. Were you shipping samples in a clean waterproof metal or hard plastic ice chest or cooler in good condition?			
2. Were all non-applicable labels from previous shipments removed from the container?			
3. Were all inside and outside drain plugs closed and covered with suitable tape (e.g., duct tape)?			
4. Was the inside of the cooler lined with plastic (e.g., large heavy-duty garbage bag)?			
5. Was the lined shipping cooler packed with noncombustible absorbent packing material?			
6. Were sample containers placed in the cooler in an upright position not touching one another?			
7. Was a sample shipping cooler temperature blank included in the cooler?			
8. Did the documentation in the cooler only address the samples in that cooler?			
9. Was the site name absent from all documentation?  Under no circumstances should the site name appear on any documentation being sent to the laboratory.			
10. Was there sufficient packing material around and in between the sample bottles and cans to avoid breakage during transport?			
11. If required, was double-bagged ice placed on top and around sample bottles to keep the samples cold at 4°C (± 2° C)?  Do Not Pack Loose Ice Into the Cooler!			
12. Was the top of the plastic liner fastened and secured with tape?			
13. Was a completed custody seal placed around the top of the fastened plastic liner (if required by the Region)?			
14. Were all sample documents enclosed within the cooler (e.g., TR/COC Record and cooler return instructions) in a waterproof plastic bag?			
15. Was the plastic bag, containing the documentation, taped to the underside of the cooler lid?			
16. Were cooler return instructions and airbills, if required, taped to the underside of the cooler lid?			
17. Was the return address of the cooler written with permanent ink on the underside of the cooler lid?			
18. Was tape placed around the outside of the entire cooler and over the hinges?			
19. Were the completed custody seals placed over the top edge of the cooler so the cooler cannot be opened without breaking the seals?			
20. Was the return address label attached to the top left corner of the cooler lid?			
21. Were instructional labels attached to the top of the cooler, as necessary (e.g., "This End Up," "Do Not Tamper With," or "Environmental Laboratory Samples")?			
22. If shipping hazardous samples, were the correct labels attached to the cooler (e.g., "Flammable Liquids", "Caution", or "Poison")?			
23. If shipping samples containing methanol as a preservative (e.g., samples to be analyzed by SW-846 Method 5035A), was a label used to indicate methanol, the United Nations (UN) identification number for methanol (UN 1230), and Limited Quantity?			

Appendix E-8: Shipping & Reporting CLP Samples Checklist

(Page 1 of 1)

Shipping CLP Samples	Yes	No	Comments:
1. Did you follow all State, Federal, Department of Transportation (DOT), and International Air Transportation Association (IATA) regulations governing the shipment of environmental and hazardous samples?			
2. Was a separate airbill filled out for each cooler being shipped?			
3. Was the airbill filled out completely, including correct laboratory name, address, and telephone number, identification of recipient as "Sample Custodian," and appropriate delivery option (e.g., overnight or Saturday)?			
4. Was the completed airbill attached to the top of the cooler with the correct laboratory address?			
5. If more than one cooler was being shipped to the same laboratory, were they marked as "1 of 2," "2 of 2," etc.?			
6. Were the samples being shipped "overnight" through a qualified commercial carrier?			
Reporting CLP Samples	**Yes**	**No**	**Comments:**
1. Did you contact the Contract Laboratory Program Sample Management Office (SMO) on the same day samples were shipped?			
2. If the samples were shipped after 5:00 PM Eastern Time (ET), were they reported to the RSCC (or designee) or to SMO by 8:00 AM ET the following business day?			
3. Did you notify the RSCC (or designee) or SMO so that SMO will receive the delivery information by 3:00 PM ET on Friday for sample shipments that will be delivered to the laboratory on Saturday?			
4. Did you provide the RSCC (or designee) or SMO with: • Your name, phone number, and Region number; • Case Number of the project; • Exact number of samples, matrix(ces), concentration(s), and type of analysis; • Laboratory(ies) to which the samples were shipped; • Carrier name and airbill number; • Date of shipment; • Date of next shipment; and • Any other information pertinent to the shipment?			

Appendix F: Glossary

Analyte -- The element, compound, or ion that is determined in an analytical procedure; the substance or chemical constituent of interest.

Analytical Services Branch (ASB) -- Directs the Contract Laboratory Program (CLP) from within the United States Environmental Protection Agency's (USEPA's) Office of Superfund Remediation and Technology Innovation (OSRTI) in the Office of Solid Waste and Emergency Response (OSWER).

Aroclor -- Polychlorinated biphenyls (PCBs) or a class of organic compounds with 1 to 10 chlorine atoms attached to biphenyl and a general chemical formula of $C_{12}H_{10-x}Cl_x$. PCBs, commercially produced as complex mixtures containing multiple isomers at different degrees of chlorination, were marketed in North America under the trade name Aroclor.

Case -- A finite, usually predetermined, number of samples collected over a given time period from a particular site. Case Numbers are assigned by the Sample Management Office (SMO). A Case consists of one or more Sample Delivery Groups (SDGs).

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) -- Initiated in December 1980, CERCLA provided broad federal authority to respond directly to the release or possible release or hazardous substances that may endanger human health or the environment. CERCLA also established a trust fund to provide for cleanup when no responsible party could be identified; hence CERCLA is commonly referred to as "Superfund".

Contract Laboratory Program (CLP) -- A national program of commercial laboratories under contract to support the USEPA's nationwide efforts to clean up designated hazardous waste sites by providing a range of chemical analytical services to produce environmental data of known and documented quality. This program is directed by USEPA's Analytical Services Branch (ASB).

Contract Laboratory Program Project Officer (CLP PO) -- Monitors technical performance of the contract laboratories in each Region.

Contract Laboratory Program Sample Management Office (CLP SMO) -- A contractor-operated facility operated under the CLP, awarded and administered by the USEPA, which provides necessary management, operations, and administrative support to the CLP. SMO coordinates and schedules sample analyses, tracks sample shipments and analyses, receives and tracks data for completeness and compliance, and processes laboratory invoices.

Custody Seal -- An adhesive label or tape that is used to seal a sample bottle or container that maintains chain-of-custody and that will break if the sample bottle or container is opened or tampered with.

Cyanide (Total) -- Cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

Data Quality Objective (DQO) -- The requirements established to maintain the quality of the data being collected.

Data Validation -- Data validation is based on Region-defined criteria and limits, professional judgment of the data validator, and (if available) the Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP).

Equipment Blank -- A sample used to check field decontamination procedures. See Field Blank.

Field Blank -- Any blank sample that is submitted from the field. Each field blank is assigned its own unique USEPA Sample Number. A Field Blank checks for cross-contamination during sample collection, sample shipment, and in the laboratory. A field blank includes trip blanks, rinsates, equipment blanks, etc.

Field Duplicate -- Checks reproducibility of laboratory and field procedures and indicates non-homogeneity.

Field Operations Reporting Management System (FORMS) II Lite -- A stand-alone, Windows-based software application that enables samplers to automatically create and generate sample documentation both prior to and during a sampling event.

Field QC Sample -- Used to detect for contamination or error in the field.

Field Sample -- Primary sample material taken out in the field from which other samples, such as duplicates or split samples are derived. A field sample can be prepared in the field and sent for analysis in one or multiple containers, and is identified by a unique EPA Sample Number.

Field Sampling Plan (FSP) -- Developed to outline the actual steps and requirements pertaining to a particular sampling event, and explains, in detail, each component of the event to all involved samplers.

Holding Time -- The elapsed time expressed in hours, days, or months from the date of collection of the sample until the date of its analysis.

> **Contractual** -- The lengths of time that the CLP laboratory must follow to comply with the terms of the contract, and are described in the CLP analytical services Statements of Work (SOWs).
>
> **Technical** -- The maximum lengths of time that samples may be held from time of collection to time of preparation and/or analysis and still be considered valid.

Laboratory Blank -- See Method Blank.

Laboratory Duplicate -- A sample required by the laboratory's contract to check the precision of inorganic analyses.

Laboratory QC Sample -- An additional volume of an existing sample, as required by the laboratory's contract, used to detect contamination or error in the laboratory's practices.

Matrix -- The predominant material of which a sample to be analyzed is composed.

Matrix Spike (MS) -- Sample required by the laboratory's contract to check the accuracy of organic and inorganic analyses. It is an aliquot of a sample (water or soil) that is fortified (spiked) with known quantities of a specific compound and subjected to the entire analytical procedure. See Matrix Spike Duplicate.

Matrix Spike Duplicate (MSD) -- Sample required by the laboratory's contract to check the accuracy and precision of organic analyses. It is a second aliquot of the same matrix as the Matrix Spike (MS) that is spiked to determine the precision of the method. See Matrix Spike.

Method Blank -- An analytical control consisting of all reagents, internal standards and surrogate standards [or System Monitoring Compounds (SMCs) for volatile organic analysis], that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination, also referred to as laboratory blank when defining the level of laboratory contamination.

Performance Evaluation (PE) Sample -- A sample of known composition provided by the USEPA for contractor analysis. Used by USEPA to evaluate contractor performance.

Pesticides -- Substances intended to repel, kill, or control any species designated a "pest", including weeds, insects, rodents, fungi, bacteria, and other organisms. Under the CLP, only organochlorine pesticides are analyzed (e.g., DDT, Dieldrin, Endrin, etc.).

Polychlorinated Biphenyls (PCBs) -- A group of toxic, persistent chemicals used in electrical transformers and capacitors for insulating purposes, and in gas pipeline systems as a lubricant. The sale and new use of PCBs were banned by law in 1979.

Quality Assurance (QA) -- An integrated system of management activities involving planning, implementation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality needed and expected by the customer.

Quality Assurance Project Plan (QAPP) -- Document written to meet requirements outlined in the document *EPA Guidance for Quality Assurance Project Plans* (EPA QA/R-5). Prepared in advance of field activities and used by samplers to develop any subsequent plans such as the Sampling Analysis Plan (SAP) or the Field Sampling Plan (FSP).

Quality Control (QC) -- The overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality.

Regional Sample Control Center (RSCC) Coordinator -- In most Regions, coordinates sampling efforts and serves as the central point-of-contact for sampling questions and problems. Also assists in coordinating the level of Regional sampling activities to correspond with the monthly projected demand for analytical services.

Regional Site Manager -- Coordinates the development of data quality objectives and oversees project-specific remedial or removal contractors, State officials, or private parties conducting site sampling efforts.

Rinse Blank -- A sample used to check decontamination procedures. Also see Field Blank.

Routine Analytical Service (RAS) -- The standard inorganic and organic analyses available through the CLP.

Sample -- A discrete portion of material to be analyzed that is contained in single or multiple containers, and identified by a unique Sample Number.

Sample Delivery Group (SDG) – A unit within a sample Case that is used to identify a group of samples for delivery. An SDG is defined by the following, whichever is most frequent:

- Each Case of field samples received; or
- Each 20 field samples (excluding PE samples) within a Case; or
- Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).

In addition, all samples and/or sample fractions assigned to an SDG must have been scheduled under the same contractual turnaround time. Preliminary Results have no impact on defining the SDG. Sample may be assigned to SDGs by matrix (e.g., all soil samples in one SDG, all water samples in another) at the discretion of the laboratory.

Sample Label -- An identification label attached to a sample bottle or container to identify the sample.

Sample Number -- A unique number used to identify and track a sample. This number can be recorded on a sample label or written on the sample bottle or container using indelible ink.

Sample Tag -- A tag attached to a sample that identifies the sample and maintains chain-of-custody.

Sampling Analysis Plan (SAP) -- A document that explains how samples are to be collected and analyzed for a particular sampling event.

Semivolatile Organic Analyte (SVOA) -- A compound amenable to analysis by extraction of the sample using an organic solvent.

Statement of Work (SOW) -- A document that specifies how laboratories analyze samples under a particular Contract Laboratory Program (CLP) analytical program.

Superfund -- The program operated under the legislative authority of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and Superfund Amendments and Reauthorization Act (SARA) that funds and carries out USEPA removal and remedial activities at hazardous waste sites. These activities include establishing the National Priorities List (NPL), investigating sites for inclusion on the list, determining their priority, and conducting and/or supervising cleanup and other remedial actions.

Superfund Amendments and Reauthorization Act (SARA) -- The 1986 amendment to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

Traffic Report/Chain of Custody (TR/COC) Record -- A record that is functionally similar to a packing slip that accompanies a shipment of goods. Used as physical evidence of sample custody and functions as a permanent record for each sample collected.

Trip Blank -- A sample used to check for contamination during sample handling and shipment from field to laboratory. Also see Field Blank.

Volatile Organic Analyte (VOA) -- A compound amenable to analysis by the purge-and-trap technique. Used synonymously with the term purgeable compound.

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EXHIBIT D

INTRODUCTION TO ANALYTICAL METHODS

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Exhibit D - Analytical Methods

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1.0 INTRODUCTION

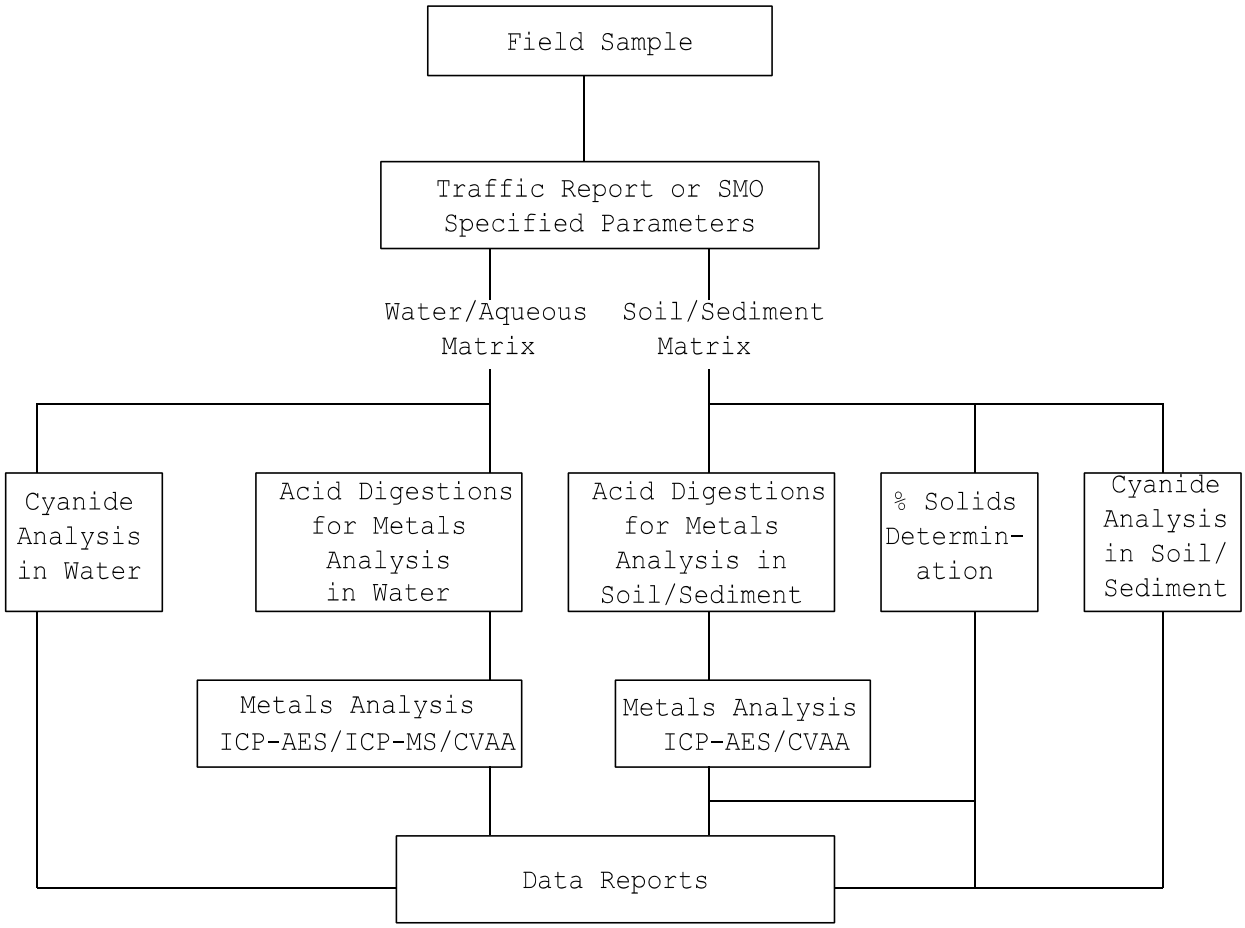
The inorganic analytical service provides a contractual framework for laboratories. This framework applies USEPA Contract Laboratory Program (CLP) analytical methods for the isolation, detection, and quantitative measurement of 23 metals (including mercury) and cyanide in water/ aqueous and/or soil/sediment samples.

The analytical methods that follow are designed to analyze water and sediment/soil from hazardous waste sites for the presence of inorganic analytes contained on the Inorganic Target Analyte List (TAL) (see Exhibit C). The inorganic methods include alternative analysis procedures for some analytes, multiple preparation procedures, and Quality Control (QC) requirements. Analytical techniques in the inorganic methodologies include Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), Cold Vapor Atomic Absorption Spectroscopy, and Spectrophotometry. Graphite Furnace Atomic Absorption (GFAA) may be requested by the modified analysis clause in the contract.

1.1 Inorganic Methods Flow Chart

Figure 1 outlines the general analytical scheme the Contractor shall follow in performing standard trace metals and cyanide analyses under this contract.

1.2 Figure 1 - Inorganic Methods Flow Chart



1.3 Glassware Cleaning

Lab glassware to be used within the metals analysis must be acid cleaned according to USEPA's manual, Methods for Chemical Analysis of Water and Wastes or an equivalent procedure. An electronic version can be found via USEPA's National Environmental Publications Internet Site (NEPIS) at http://www.epa.gov/cincl.

1.4 Standard Stock Solutions

Stock solutions to be used for preparing instrument or method standards may be purchased or prepared as described in the individual methods of Exhibit D, Section 7 (Reagents and Standards).

1.5 Verification of Aqueous Sample Preservation

1.5.1 At the time of sample receipt, the Contractor shall check the pH of the sample and note in a preparation log if the pH is less than 2 for metals. In addition, it should be noted if the pH is greater than 12 for a cyanide sample. Unless instructed by the USEPA Regional CLP Project Officer (CLP PO), the Contractor shall not perform any pH adjustment action if the sample has not been properly preserved. If the sample has not been properly preserved, contact Sample Management

Office (SMO) for further instructions before proceeding with the preparation and analysis. The Contractor may adjust the pH of a sample for metals if SMO provides written documentation to the Contractor from the USEPA Regional CLP PO or USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB) Inorganic Program Manager (ASB PM) authorizing the adjustment.

1.5.2 Before preparation is initiated for an aqueous cyanide sample, the Contractor shall test for the presence of sulfides and oxidizing agents (e.g., residual chlorine). The test for sulfides shall be performed by placing a drop of the sample on a strip of lead acetate paper (which has been pre-moistened with pH 4 acetate buffer solution). If the test strip turns black, the Contractor shall treat the total volume of sample with powdered cadmium carbonate or lead carbonate. Yellow cadmium sulfide precipitates when the sample contains sulfide. This operation shall be repeated until a drop of the treated sample solution does not darken the lead acetate test paper. The solution shall be filtered through a dry filter paper into a dry beaker, and the volume of sample to be used for analysis shall be measured from the filtrate. It is recommended that the Contractor avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. The test for oxidizing agents shall be performed by placing a drop of the sample on a strip of potassium iodide - starch test paper (KI - starch paper). If the test strip turns blue, the Contractor shall contact SMO for further instructions from the Region before proceeding with sample preparation and analysis. The Contractor shall document the presence of sulfides or oxidizing agents in the Sample Delivery Group (SDG) Narrative.

1.6 Percent Solids Determination Procedure

1.6.1 Immediately following the weighing of the sample to be processed for analysis, add 5-10 g of sample to a tared weighing dish. Weigh and record the weight to the nearest 0.01 g.

1.6.2 Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven maintained at 103-105°C. Sample handling and drying should be conducted in a well-ventilated area.

1.6.3 Dry the sample overnight (12-24 hours) but no longer than 24 hours. If dried less than 12 hours, it must be documented that constant weight was attained.[1] Remove the sample from the oven and cool in a desiccator with the weighing dish cover in place before weighing. Weigh and record weight to nearest 0.01 g. Do not analyze the dried sample.

1.6.4 Duplicate percent solids determinations are required at the same frequency as other analytical determinations. Duplicate results are to be recorded on Form VI-IN.

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[1]Drying time is defined as the elapsed time in the oven; thus raw data must record time in and out of the oven to document the 12-hour drying time minimum. In the event it is necessary to demonstrate the attainment of constant weight, data must be recorded for a minimum of two repetitive weigh/dry/desiccate/weigh cycles with a minimum of 1-hour drying time in each cycle. Constant weight would be defined as a loss in weight of no greater than 0.01 g between the start weight and final weight of the last cycle.

1.6.5 For the duplicate percent solids determination, designate one sample aliquot as the "original" sample and the other aliquot as the "duplicate" sample. Calculate dry weight using the results of the "original" sample aliquot.

1.6.6 Calculate percent solids by the formula below. The value thus obtained will be reported on the appropriate Forms I and, where applicable, Forms VA-IN and VI-IN. This value will be used for calculating analytical concentration on a dry weight basis.

EQ. 1 Percent Solids

$$\% \text{ Solids} = \frac{\text{Sample Dry Weight}}{\text{Sample Wet Weight}} \times 100$$

1.6.7 If the sample contains less than 50% solids, the Contractor shall notify SMO immediately of the samples impacted. After notification to SMO, the Contractor shall proceed with sample analysis and document the issue in the SDG Narrative.

1.7 Insufficient Sample Volume

If insufficient sample volume (less than the required amount) is received to perform the analysis, the Contractor shall contact the SMO to apprise them of the problem. SMO will contract the Region for instructions. The Region will either approve that no sample analysis be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analysis will be permitted. SMO will notify the Contractor of the Region's decision. The Contractor shall document the Region's decision in the SDG Narrative.

1.8 Sample Mixing

Unless instructed otherwise by the USEPA Regional CLP PO, all samples shall be mixed thoroughly prior to aliquoting for digestion. There is no specific procedure provided herein for homogenization of soil/ sediment samples; however, an effort should be made to obtain a representative aliquot.

1.9 Undiluted Analysis

1.9.1 All samples shall be run undiluted for multi-analyte analysis (i.e., the final product of the sample preparation procedure) unless the dilution adjusted detection limits for all analytes are below the CRQL. When an analyte concentration exceeds the calibrated or linear range, appropriate dilution (but not below the CRQL) and re-analysis is required. The Contractor shall use the least dilution necessary to bring the analyte(s) instrument reading within the upper 75% of the calibrated or linear range and report the highest valid value for each analyte as measured from the undiluted and diluted analyses. Unless the Contractor can submit proof that dilution was required to obtain valid results, both diluted and undiluted sample measurements must be contained in the raw data.

1.9.2 For single analyte analysis, a diluted sample analysis may be the only sample analysis performed if the analyte's instrument result is in the upper 75% of the calibrated or linear range. An undiluted sample analysis does not have to be performed in this case. The sample and its associated matrix spike and duplicate shall initially be run at the same dilution.

1.9.3 All sample dilutions shall be made with reagent water appropriately acidified (except for cyanide) to maintain constant acid strength.

1.10 Dissolved Metals

1.10.1 If dissolved metals are requested by USEPA Regional Offices, the Contractor shall follow the instructions provided on the Traffic Report(s)/Chain of Custody Record(s). If there are no instructions on the Traffic Report/Chain of Custody Record, the Contractor shall digest the samples designated as dissolved metals.

1.10.2 If the Regional Office indicates on the Traffic Report/Chain of Custody Record that a digestion is not to be performed when analyzing field samples for dissolved metals, then a aqueous Laboratory Control Sample (LCSW) and a post-digestion spike sample (hardcopy Form VB-IN and diskette QC codes PDO and PDF) are not required.

1.11 Replicate Exposure

If the Contractor analyzes samples using multiple injections or exposures, the Contractor must use the data obtained from all injections or exposures to calculate the final sample result even if more than the minimum number of injections or exposures are taken.

1.12 Raw Data Requirements

The Contractor is reminded and cautioned that the collection and provision of raw data may or may not be referred to within the individual methods of Exhibit D or the Quality Assurance (QA) protocol of Exhibit E. The raw data deliverable requirements are specified in Exhibit B, Section 2.5.2.3. Raw data collected and provided in association with the performance of analyses under this contract shall conform to the appropriate provisions of Exhibit B.

1.13 Quality Control Samples

If the Sampler designated two (or more) samples as QC for the same matrix, and the QC samples are not specifically labeled with the analysis they are to be used for (dissolved metals and total metals), then the Contractor is to contact SMO to report the issue. SMO shall then contact the Region and notify the Contractor of the Regional decision.

1.14 Safety

The toxicity or carcinogenicity of each reagent used in this SOW has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of chemicals specified in this method. A reference file of material handling data sheets should also be made available to all personnel involved in the chemical analysis.

1.15 Pollution Prevention

1.15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, USEPA recommends recycling as the next best option.

1.15.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington D.C., 20036, (202) 872-4477.

1.16 Waste Management

USEPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 1.15.2.

EXHIBIT D - PART A

ANALYTICAL METHODS
FOR
INDUCTIVELY COUPLED PLASMA -
ATOMIC EMISSION SPECTROSCOPY

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Exhibit D - Analytical Methods for ICP-AES

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1.0 SCOPE AND APPLICATION

The following method is an inductively coupled atomic plasma-atomic emission spectroscopy procedure that is used to analyze water, sediment, sludge, and soil samples taken from hazardous waste sites. All metals (except mercury) which are contained in the Inorganic Target Analyte List (TAL) in Exhibit C are quantitated by this Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) method.

2.0 SUMMARY OF METHOD

Water and soil samples are treated with acids and heat or microwave energy to solubilize the metals present. These digestates are then analyzed for trace metals by an atomic emission optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to a plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed and the intensities of the lines are monitored by a photosensitive device. The signals from the photosensitive device are processed by a computer. A background correction technique is required to compensate for variable background contribution to the spectra of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

Several types of interference effects may contribute to inaccuracies in the determination of trace elements in water and soil/sediments. To prevent this, appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 milligrams per Liter (mg/L) and when total elements are determined after the appropriate digestion procedures are performed. Several types of interferences are summarized below:

4.1 Spectral Interferences

Spectral interferences can be categorized as: overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena, and/or background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data. This would require the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array.

4.2 Physical Interferences

Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may minimize these interferences. If these types of interferences are present, they must be reduced by dilution of the sample.

Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution has been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

4.3 Chemical Interferences

Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES) technique; however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, and by matrix matching. These types of interferences can be highly dependent on matrix type and the specific analyte element.

5.0 SAFETY

See Section 1.14 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Glassware/Labware

6.1.1 250 milliliter (mL) beaker or other appropriate vessel

6.1.2 Watch glasses

6.1.3 Funnels

6.1.4 Graduated cylinders

6.1.5 Various volumetric flasks (Type A)

6.1.6 Thermometer that covers a range of 0-200°C

6.1.7 Whatman No. 42 filter paper or equivalent

6.1.8 Hot plate, block digester, or other heating source

6.1.9 Equipment and supplies for microwave digestion

6.1.9.1 Whatman No. 41 filter paper (or equivalent)

6.1.9.2 Disposable polypropylene filter funnel

6.1.9.3 Polyethylene bottles, 125 mL, with caps

6.1.9.4 Microwave oven with programmable power settings up to at least 600 watts.

6.1.9.5 The system must use PTFE PFA digestion vessels (120 mL capacity) capable of withstanding pressure of up to 110 (±10) pounds per square inch (psi) [7.5 (±0.7 atm)]. These vessels are capable of controlled pressure relief at pressures exceeding 110 psi.

6.1.9.6 A rotating turntable must be used to ensure homogeneous distribution of microwave radiation within the oven. The speed of the turntable must be a minimum of 3 revolutions per minute (rpm).

6.1.10 Balances - Analytical Balance, 300 gram (g) capacity, and minimum ±0.01 g.

6.2 Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES) consisting of a computer controlled atomic emission spectrometer with background correction, a radio frequency generator, and a supply of Argon gas, welding grade or better.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-77). Use this preparation for all reagents, standards, and dilutions of solutions.

7.1.2 Acetic acid - Concentrated (specific gravity 1.06).

7.1.3 Hydrochloric acid - Concentrated (specific gravity 1.19).

7.1.4 Hydrochloric acid, (1+1) - Add 500 milliliters (mL) conc. HCl (specific gravity 1.19) to 400 mL reagent water and dilute to 1 Liter (L).

7.1.5 Nitric acid - Concentrated (specific gravity 1.41).

7.1.6 Nitric acid, (1+1) - Add 500 mL conc. HNO_3 (specific gravity 1.41) to 400 mL reagent water and dilute to 1 L.

7.1.7 Hydrogen peroxide (30%)

7.1.8 Nitric acid, 5% (v/v) - Add 50 mL conc. HNO_3 to 500 mL reagent water; dilute to 1 L.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 8.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.2 Stock Standard Solutions

7.2.2.1 Stock standard solutions may be purchased or prepared from reagent grade chemicals or metals. All salts must be dried for 1 hour at 105°C unless otherwise specified.

(CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling) Typical stock solution preparation procedures follow.

7.2.2.2 Aluminum solution, stock (1 mL = 100 µg Al) - Dissolve 0.100 grams (g) of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1+1) HCl and dilute to 1000 mL with reagent water.

7.2.2.3 Antimony solution, stock (1 mL = 100 µg Sb) - Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in reagent water, add 10 mL (1+1) HCl and dilute to 1000 mL with reagent water.

7.2.2.4 Arsenic solution, stock (1 mL = 100 µg As) - Dissolve 0.1320 g of As_2O_3 in 100 mL of reagent water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.5 Barium solution, stock (1 mL = 100 µg Ba) - Dissolve 0.1516 g $BaCl_2$ (dried at 250°C for 2 hours) in 10 mL reagent water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1000 mL with reagent water.

7.2.2.6 Beryllium solution, stock (1 mL = 100 µg Be) - Do not dry. Dissolve 1.966 grams (g) $BeSO_4 \bullet 4H_2O$, in reagent water, add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.7 Cadmium solution, stock (1 mL = 100 µg Cd) - Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.8 Calcium solution, stock (1 mL = 100 µg Ca) - Suspend 0.2498 g $CaCO_3$ dried at 180°C for 1 hour before weighing in reagent water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.9 Chromium solution, stock (1 mL = 100 µg Cr) - Dissolve 0.1923 g of CrO_3 in reagent water. When solution is complete acidify with 10 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.10 Cobalt solution, stock (1 mL = 100 µg Co) - Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3. Add 10.0 mL (1+1) HCl and dilute to 1000 mL with reagent water.

7.2.2.11 Copper solution, stock (1 mL = 100 µg Cu) - Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.12 Iron solution, stock (1 mL = 100 µg Fe) - Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1+1) HCl and 2 mL of conc. HNO_3. Cool, add an additional 5 mL of conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.13 Lead solution, stock (1 mL = 100 µg Pb) - Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 mL of conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.14 Magnesium solution, stock (1 mL = 100 µg Mg) - Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.15 Manganese solution, stock (1 mL = 100 µg Mn) - Dissolve 0.1000 g of manganese metal in the acid mixture, 10 mL conc. HCl and 1 mL conc. HNO_3, and dilute to 1000 mL with reagent water.

7.2.2.16 Nickel solution, stock (1 mL = 100 µg Ni) - Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO_3, cool and dilute to 1000 mL with reagent water.

7.2.2.17 Potassium solution, stock (1 mL = 100 µg K) - Dissolve 0.1907 g KCl, dried at 110°C, in reagent water. Dilute to 1000 mL.

7.2.2.18 Selenium solution, stock (1 mL = 100 µg Se) - Do not dry. Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in reagent water and dilute to 1000 mL.

7.2.2.19 Silver solution, stock (1 mL = 100 µg Ag) - Dissolve 0.1575 g $AgNO_3$ in 100 mL of reagent water and 10 mL conc. HNO_3. Dilute to 1000 mL with reagent water.

7.2.2.20 Sodium solution, stock (1 mL = 100 µg Na) - Dissolve 0.2542 g NaCl in reagent water. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.21 Thallium solution, stock (1 mL = 100 µg Tl) - Dissolve 0.1303 g $TlNO_3$ in reagent water. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.22 Vanadium solution, stock (1 mL = 100 µg V) - Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.23 Zinc solution, stock (1 mL = 100 µg Zn) - Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.3 Secondary Dilution Standards

7.2.3.1 Mixed Secondary Dilution Standards

Prepare mixed secondary dilution standard solutions by diluting the appropriate volumes of stock standards with acidified reagent water to obtain the final volume. Mixed secondary dilution standard solutions may be purchased. The purchased standards shall meet the requirements in Section 7.2.1.

7.2.4 Working Standards

7.2.4.1 The calibration blank is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to 100 mL with reagent water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

7.2.4.2 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

The concentration of the analytes in the CRI shall be at the respective CRQLs. Information regarding the CRI shall be reported on Form IIB-IN.

7.2.4.3 Interference Check Sample (ICS) Solution

The ICS consists of two solutions: Solution A (ICSA) and Solution AB (ICSAB). ICSA consists of the interferents and ICSAB consists of the analytes mixed with the interferents.

7.2.4.4 Method Detection Limit (MDL) Solution

The MDL solution shall be at a concentration of 3 to 5 times the expected MDL.

7.2.4.5 Mixed Calibration Standard Solutions

7.2.4.5.1 Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Sections 7.2.4.5.2 through 7.2.4.5.7). Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl and dilute to 100 mL with reagent water (see Note in Section 7.2.4.5.6). Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and

stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change with aging. Although not specifically required, some typical calibration standard combinations follow.

7.2.4.5.2 Mixed standard solution I - manganese, beryllium, cadmium, lead, and zinc.

7.2.4.5.3 Mixed standard solution II - barium, copper, iron, vanadium, and cobalt.

7.2.4.5.4 Mixed standard solution III - arsenic and selenium.

7.2.4.5.5 Mixed standard solution IV - calcium, sodium, potassium, aluminum, chromium, and nickel.

7.2.4.5.6 Mixed standard solution V - antimony, magnesium, silver and thallium.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of reagent water and warm the flask until the solution clears. Cool and dilute to 100 mL with reagent water. For this acid combination, the silver concentration should be limited to 2 milligrams per Liter (mg/L). Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

7.2.4.5.7 Protect all standards from light. Samples, sample digestates, and standards must be stored separately.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All samples must be collected in glass or polyethylene containers. Water/aqueous samples must be preserved with nitric acid to pH less than 2 immediately after collection. All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until digestion.

8.1.1 Dissolved Metals

For the determination of dissolved metals, the sample must be filtered through a 0.45 micrometer (µm) pore diameter membrane filter at the time of collection or as soon as possible. Use a portion of the sample to rinse the filter flask, discard this portion, and collect the required volume of filtrate. Preserve the filtrate with nitric acid to pH less than 2 immediately after filtration.

8.2 Procedures for Sample Storage

The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days the samples may be disposed of in a manner that complies with all applicable regulations.

8.3 Procedure for Sample Digestate Storage

Sample digestates must be stored until 365 days after delivery of a complete, reconciled data package to USEPA.

8.4 Contract Required Holding Time

The maximum holding time for metals is 180 days from Validated Time of Sample Receipt (VTSR).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. The Method Detection Limit (MDL), precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where correction factors are valid. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 Microwave Calibration Procedure

9.2.1 The calibration procedure is a critical step prior to the use of any microwave unit. The microwave unit must be calibrated every six months. The data for each calibration must be available for review during on-site audits. In order that absolute power settings may be interchanged from one microwave unit to another, the actual delivered power must be determined.

9.2.2 Calibration of a laboratory microwave unit depends on the type of electronic system used by the manufacturer. If the unit has a precise and accurate linear relationship between the output power and the scale used in controlling the microwave unit, then the calibration can be a two-point calibration at maximum and 40% power. If the unit is not accurate or precise for some portion of the controlling scale, then a multiple-point calibration is necessary. If the unit power calibration needs a multiple-point calibration, then the point where linearity begins must be identified. For example: a calibration at 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% power settings can be applied and the data plotted. The non-linear portion of the calibration curve can be excluded or restricted in use. Each percent is equivalent to approximately 5.5-6 watts and becomes the smallest unit of power that can be controlled. If 20-40 watts are contained from 99-100%, that portion of the microwave calibration is not controllable by 3-7 times that of the linear portion of the control scale and will prevent duplication of precise power conditions specified in that portion of the power scale.

9.2.3 The power available for heating is evaluated so that the absolute power setting (watts) may be compared from one microwave to another. This is accomplished by measuring the temperature rise in 1 kilogram (kg) of water exposed to microwave radiation for a fixed period of time. The water is placed in a PTFE beaker (or a beaker that is made of some other material that does not absorb microwave energy) and stirred before measuring the temperature. Glass beakers absorb microwave energy and may not be used. The initial temperature of the water must be between 19 and 25°C. The beaker is circulated continuously through the field for at least two minutes at full power. The beaker is removed from the microwave, the water is stirred vigorously, and the final temperature is recorded. The final reading is the maximum temperature reading after each energy exposure. These measurements must be accurate to ±0.1°C and made within 30 seconds of the end of heating. If more measurements are needed, do not use the same water until it has cooled down to room temperature. Otherwise, use a fresh water sample.

The absorbed power is determined by the following formula:

EQ. 1 Absorbed Power

$$P = \frac{(K)\ (C_p)\ (m)\ (DT)}{t}$$

WHERE, P = The apparent power absorbed by the sample in watts (joules per second).

K = The conversion factor for thermochemical calories per second to watts (=4.184).

C_p = The heat capacity, thermal capacity, or specific heat (cal. g^{-1} $°C^{-1}$) of water (=1.0).

m = The mass of the sample in grams (g).

DT = The final temperature minus the initial temperature (°C).

t = The time in seconds (s).

Using 2 minutes and 1 kg of reagent water, the calibration equation simplifies to:

$$P = (DT)\ (34.87)$$

The microwave user can now relate power in watts to the percent power setting of the microwave.

9.3 Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES) Instrument Calibration Procedure

9.3.1 Instruments shall be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time shall be included in the raw data.

9.3.2 The calibration standards shall be prepared as in Section 7.2.4.5.

9.3.3 Calibrate the ICP-AES instruments according to instrument manufacturer's recommended procedures. At least two standards shall be used for ICP-AES calibration. One of the standards shall be a blank.

9.3.4 Any changes or corrections to the analytical system shall be followed by recalibration.

9.4 Initial Calibration Verification (ICV)

9.4.1 Immediately after each of the ICP-AES systems have been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of the ICV solution(s) at each wavelength used.

9.4.2 Only if the ICV solution(s) is(are) not available from USEPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a

concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration.

9.4.3 The ICV solution(s) shall be run at each wavelength used for analysis. The values for the ICV shall be reported on Form IIA-IN.

9.5 Continuing Calibration Verification (CCV)

9.5.1 To ensure calibration accuracy during each analysis run, one of the following standards is to be used for the CCV and shall be analyzed and reported for every wavelength used for the analysis of each analyte, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard shall also be analyzed and reported for every wavelength used for analysis at the beginning of the run and after the last analytical sample. The analyte concentrations in the CCV standard shall be different than the concentration used for the ICV and shall be one of the following solutions at or near one-half of the calibration standard:

- USEPA Solutions
- NIST Standards
- A Contractor-prepared standard solution

The same CCV standard shall be used throughout the analysis runs for a Sample Delivery Group (SDG) of samples received.

9.5.2 Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses, and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it, as well as the difference in time between the CCV and the analytical sample immediately preceding it, may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

9.5.3 Information regarding the CCV shall be reported on Form IIA-IN.

9.6 Initial and Continuing Calibration Blank (ICB/CCB)

A calibration blank shall be analyzed at each wavelength used for analysis immediately after every ICV and CCV, at a frequency of 10% or every 2 hours during the run, whichever is more frequent. The blank shall be analyzed at the beginning of the run and after the last analytical sample.

NOTE: A CCB shall be analyzed immediately after the last CCV, and the last CCV shall be analyzed immediately after the last analytical sample of the run. The results for the calibration blanks shall be reported on Form III-IN.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to inform them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample and analyze one or more of the phases, separately. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do any of the following:

- Separate the phases and analyze the phase(s) that is(are) amenable to analysis. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Water/Aqueous Sample Preparation

10.1.3.1 Preparation Method/Code (HW1) (USEPA Method 200.7, December 1982)

Shake sample and transfer 50-100 milliliter (mL) of well-mixed sample to a 250 mL heating vessel, add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample. Cover with watch glass or similar cover and heat on a hot plate, block digester, or equivalent heating source which is adjustable and capable of maintaining a temperature of 92-95°C for 2 hours or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material.

NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

Adjust sample volume to 50-100 mL with reagent water. The sample is now ready for analysis. Concentrations so determined shall be

reported as "total". If volumes less than 100 mL are used, all other reagents shall be reduced appropriately (e.g., if 50 mL is used, reduce reagent volumes by one-half). The final volume of the digestate must equal the initial volume of the sample aliquot.

10.1.3.2 Preparation Method/Code (MW1) (USEPA SW-846 Method 3015)

10.1.3.2.1 A 45 mL aliquot of the sample is measured into PTFE digestion vessels.

10.1.3.2.2 5 mL of concentrated HNO_3 is added to the digestion vessels.

10.1.3.2.3 The caps with the pressure release valves are placed on the vessels hand tight and then tightened, using constant torque, to 12 ft/lbs. The weight of each vessel is recorded to 0.02 gram (g).

10.1.3.2.4 Place 5 sample vessels in the carousel, evenly spaced around its periphery in the microwave unit. Venting tubes connect each sample vessel with a collection vessel. Each sample vessel is attached to a clean, double-ported overflow vessel to collect any sample expelled from the sample vessel in the event of over pressurization. Assembly of the vessels into the carousel may be done inside or outside the microwave.

10.1.3.2.5 This procedure is energy balanced for five 45 mL water samples (each with 5 mL of acid) to produce consistent conditions. When fewer than five samples are digested, the remaining vessels must be filled with 45 mL of tap, deionized, or reagent water and 5 mL of concentrated nitric acid.

10.1.3.2.6 Newer microwave ovens may be capable of higher power settings which may allow a larger number of samples. If the analyst wishes to digest more than 5 samples at a time, the analyst may use different power settings as long as they result in the same time temperature conditions defined in the power programming for this method.

10.1.3.2.7 The initial temperature of the samples should be 24°C (±1°C). The Preparation Blank (PB) must have 45 mL of deionized water and the same amount (5 mL) of acid that is added to the samples.

10.1.3.2.8 The microwave unit first-stage program must be set to give 545 watts for 10 minutes and the second-stage program to give 344 watts for 10 minutes. This sequence brings the samples to 160°C (±4°C) in 10 minutes and permits a slow rise to 165-170°C during the second 10 minutes.

10.1.3.2.9 Following the 20 minute program, the samples are left to cool in the microwave unit for 5 minutes, with the exhaust fan on. The samples and/or carousel may then be removed from the microwave unit. Before opening the vessels, let cool until they are no longer hot to the touch.

10.1.3.2.10 After the sample vessel has cooled, weigh the sample vessel and compare to the initial weight as reported on the preparation log. Any sample vessel exhibiting a less than or equal to 0.5 g loss into the overflow vessel must have any excess sample from the associated collection vessel added to the original sample vessel before proceeding with the sample preparation.

Any sample vessel exhibiting a greater than 0.5 g loss must be identified in the preparation log and the sample redigested.

10.1.3.2.11 Sample Filtration - The digested samples are shaken well to mix in any condensate within the digestion vessel before being opened. The digestates are then filtered into 50 mL glass volumetric flasks through Whatman No. 41 (or equivalent) filter paper and diluted to 50 mL (if necessary). The samples are now ready for analysis. The sample results must be corrected by a factor of 1.11 in order to report final concentration values based on an initial volume of 45 mL. Concentrations so determined shall be reported as "total".

10.1.3.3 Preparation Method/Code (MW2) (ASTM Standard D4309-91)

10.1.3.3.1 A 50 mL aliquot of the sample is measured into PTFE digestion vessels.

10.1.3.3.2 3 mL of concentrated HNO_3 and 2 mL of concentrated HCl is added to the digestion vessels.

10.1.3.3.3 Proceed as in Preparation Method/Code "MW1", Sections 10.1.3.2.3 through 10.1.3.2.11.

10.1.3.3.4 Sample Filtration - The digested samples are shaken well to mix in any condensate within the digestion vessel before being opened. If necessary, the digestates are then filtered through filter paper and diluted to 55 mL. The samples are now ready for analysis. The sample results must be corrected by a factor of 1.1 in order to report final concentration values based on an initial volume of 50 mL. Concentrations so determined shall be reported as "total".

10.1.4 Soil/Sediment Sample Preparation

10.1.4.1 Preparation Method/Code (HS1) (USEPA Method 200.7, December 1982)

10.1.4.1.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 to 1.5 g portion of sample and transfer to a beaker.

10.1.4.1.2 Add 10 mL of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 92-95°C on hot plate or block digester, and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, as appropriate, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the heating vessel.

10.1.4.1.3 After the second reflux step has been completed and the sample has cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return the heating vessel to the heat source for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the heating vessel.

Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

10.1.4.1.4 Add 5 mL of 1:1 HCl and 10 mL of reagent water, return the covered heating vessel to the heat source, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with reagent water.

NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

The sample is now ready for analysis.

10.1.4.2 Preparation Method/Code (HS2) (USEPA SW-846 Method 3050B)

10.1.4.2.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 to 2.0 g portion of sample and transfer to a beaker.

10.1.4.2.2 Add 10 mL of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 92-95°C on hot plate, block digester, or equivalent heating source, and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, as appropriate, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the heating vessel. Add an additional 5 mL of concentrated HNO_3 and reflux. Repeat this step until sample oxidation is complete (no brown fumes generated).

10.1.4.2.3 After the reflux steps have been completed and the sample has cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return the heating vessel to the heat source for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the heating vessel.

10.1.4.2.4 Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

10.1.4.2.5 Add 10 mL of concentrated HCl and return the covered heating vessel to the heat source and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with reagent water.

NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

The sample is now ready for analysis.

10.1.4.3 Preparation Method/Code (MS1) (USEPA SW-846 Method 3051)

10.1.4.3.1 Add a representative 0.50 g (±0.01 g) of sample to the PTFE PFA vessel.

10.1.4.3.2 Add 10 mL of concentrated nitric acid. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel.

10.1.4.3.3 Cap the vessel, then tighten using constant torque to 12 ft/lbs, according to the manufacturer's direction.

10.1.4.3.4 Connect the sample vessel to the overflow vessel using PTFE PFA tubing.

10.1.4.3.5 Weigh the vessel assembly to the nearest 0.01 g.

10.1.4.3.6 Place sample vessels in groups of 2 sample vessels or 6 sample vessels in the carousel, evenly spaced around its periphery in the microwave unit. If fewer than the recommended number of samples are to be digested (i.e., 3 samples plus 1 blank) then the remaining vessels must be filled with 10 mL of nitric acid to achieve the full complement of vessels.

10.1.4.3.7 Each sample vessel must be attached to a clean, double-ported vessel to collect any sample expelled from the sample vessel in the event of over pressurization. Assembly of the vessels into the carousel may be done inside or outside the microwave. Connect the overflow vessel to the center well of the oven.

10.1.4.3.8 The PB must have 0.5 mL of reagent water and the same amount (10 mL) of acid that is added to the samples. The PB must later be diluted to 50 mL in the same manner as the samples.

10.1.4.3.9 Irradiate the 2 sample vessel group at 344 watts for 10 minutes, or the 6-sample vessel group at 574 watts for 10 minutes.

10.1.4.3.10 This program brings the samples to 175°C in 5.5 minutes; the temperature remains between 170-180°C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atmospheres (atm) for most samples. The pressure may exceed these limits in the case of high concentrations of carbonate or organic compounds. In these cases, the pressure will be limited by the relief pressure of the vessel to 7.5 (±0.7 atm).

10.1.4.3.11 Allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave unit, with exhaust fan on. Allow the vessels to cool to room temperature before opening. The vessels must be carefully vented and uncapped in a fume hood.

10.1.4.3.12 Weigh each vessel assembly. If the weight of acid plus the sample has decreased by more than 10% from the original weight, discard the digests. Determine the reason for the loss. Losses typically are attributed to use of digestion time longer than ten minutes, using too large of a sample, or having improper heating conditions. Once the source of the losses has been corrected, prepare a new set of samples for digestion.

10.1.4.3.13 Sample Filtration: Shake the sample well to mix in any condensate within the digestion vessel before being opened.

Filter the digestion vessel into a 50 mL glass volumetric flask through filter paper. Rinse the sample digestion vessel, cap, connecting tube, and (if venting occurred) the overflow vessel into the 50 mL glass flask. Dilute to 50 mL. The samples are now ready for analysis. Concentrations so determined shall be reported as "total".

10.1.5 Non-Prepared Samples

10.1.5.1 Preparation Method/Code (NP1)

10.1.5.1.1 This code shall be used to report samples that are not digested prior to analysis (e.g., dissolved metal samples that the Contractor was instructed not to digest).

10.1.5.1.2 This Preparation Method/Code shall also be used to report the non-prepared Method Detection Limit (MDL). The concentration of this MDL shall be used to determine the appropriate concentration qualifier for the results of non-prepared samples and instrument Quality Control (QC) analyses.

10.2 Microwave Digestion Cleaning Procedure

10.2.1 Initial Cleaning of the PTFE PFA Digestion Vessels

10.2.1.1 Prior to first use - new vessels must be annealed before they are used. A pretreatment/cleaning procedure must be followed. This procedure calls for heating the vessels for 96 hours at 200°C. The vessels must be disassembled during annealing and the sealing surfaces (the top of the vessel or its rim) must not be used to support the vessel during annealing.

10.2.1.2 Rinse in reagent water.

10.2.1.3 Immerse in 1:1 HCl for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.

10.2.1.4 Rinse in reagent water.

10.2.1.5 Immerse in 1:1 HNO_3 for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.

10.2.1.6 The vessels are then rinsed with copious amounts of reagent water prior to use for any analyses under this contract.

10.2.2 Cleaning Procedure between Sample Digestions

10.2.2.1 Wash entire vessel in hot water using laboratory-grade non-phosphate detergent.

10.2.2.2 Rinse with 1:1 nitric acid.

10.2.2.3 Rinse 3 times with reagent water.

10.3 Sample Analysis

10.3.1 Set up the instrument with proper operating parameters established in Section 9.1. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 minutes of operation prior to calibration.

10.3.2 Initiate appropriate operating configuration of computer.

10.3.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using mixed calibration standard solutions such as those described in Section 7.2.4.5.1.

10.3.4 A minimum of two replicate exposures is required for standardization and all QC and sample analyses. The average result of the multiple exposures for the standardization and all QC and sample analyses shall be used.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Water/Aqueous Sample Calculation

The concentrations determined in the digestate are to be reported in units of microgram per Liter (µg/L):

EQ. 2 Aqueous Sample Concentration

$$\text{Concentration (µg/L)} = C \times \frac{V_f}{V_i} \times DF$$

WHERE,
- C = Instrument value in µg/L
- V_f = Final digestion volume (mL)
- V_i = Initial digestion volume (mL)
- DF = Dilution Factor

11.2 Soil Sample Calculation

The concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample, in units of milligrams per kilogram (mg/kg):

EQ. 3 Soil Sample Concentration

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S} \times DF$$

WHERE,
- C = Concentration (mg/L)
- V = Final sample volume in Liters (L)
- W = Wet sample weight (kg)
- S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6).
- DF = Dilution Factor

11.3 Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation

To calculate the adjusted MDL or adjusted CRQL for water/aqueous samples, substitute the value of the MDL (µg/L) or CRQL (µg/L) into the "C" term in Equation 2 above.

Calculate the adjusted MDL or adjusted CRQL for soil samples as follows:

EQ. 4 Adjusted Soil MDL/Adjusted Soil CRQL Concentration

$$\text{Adjusted Concentration (dry wt.)(mg/kg)} = C \times \frac{W_M}{W_R} \times \frac{V_R}{V_M} \times \frac{1}{S} \times DF$$

WHERE,

C	=	MDL or CRQL concentration (mg/kg)
W_M	=	Minimum method required wet sample weight (g)
W_R	=	Reported wet sample weight (g)
V_M	=	Method required final sample volume (mL)
V_R	=	Reported final sample volume (mL)
S	=	% Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6).
DF	=	Sample Dilution Factor

12.0 QUALITY CONTROL (QC)

12.1 Initial Calibration Verification (ICV)

The ICV standard shall be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier. If measurements exceed the control limits of 90% (low) and 110% (high), the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. Information regarding the ICV shall be reported on Form IIA-IN.

12.2 Continuing Calibration Verification (CCV)

The CCV standard shall be prepared by combining compatible elements at a concentration equivalent to the mid-points of their respective calibration curves. If the deviation of the CCV is greater than the control limits specified of 90% (low) and 110% (high), the analysis shall be stopped, the problem corrected, the instrument recalibrated, the calibration verified, and the re-analysis of preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification shall be performed for the analytes affected. Information regarding the CCV shall be reported on Form IIA-IN.

12.3 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

12.3.1 To verify linearity near the CRQL, a standard at the CRQL (CRI) shall be prepared, in the same acid matrix as the calibration standards, and analyzed at the beginning (immediately following the ICV/ICB) and end of each sample analysis run, immediately preceding the Interference Check Sample (ICS) analyses. In addition, the Contractor shall analyze the CRI at a frequency of not less than once per 20 analytical samples[1] per analysis run. These analyses of the CRI sample shall be immediately followed by the ICS analyses. [That is, the analytical run sequence shall be CRI, ICS Solution A (ICSA), ICS Solution AB (ICSAB), CCV and Continuing Calibration Blank (CCB), in that order].

12.3.2 The CRI shall be run for every wavelength used for analysis, except those for Al, Ba, Ca, Fe, Mg, Na, and K. Information regarding the CRI shall be reported on Form IIB-IN.

12.3.3 If the percent recovery of the CRI falls outside the control limits of 70-130% (50-150% for antimony, lead, and thallium) for one or more analytes, the CRI shall be re-analyzed immediately for those analytes only. If the results of the re-analysis for those analytes fall within the control limits, no further corrective action is required. If the results of the re-analysis for those analytes do not fall within the control limits, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the CRI analyzed, and the samples associated with the CRI re-analyzed.

12.4 Blank Analyses

There are two different types of blanks required by this method. The calibration blank is used in establishing the analytical curve while the Preparation Blank is used to monitor for possible contamination.

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[1]As defined in Exhibit G, CRI is an analytical sample.

12.4.1 Initial and Continuing Calibration Blank (ICB/CCB)

The ICB and CCB are prepared with acids and reagent water. If the absolute value of the calibration blank (ICB/CCB) result exceeds the CRQL (see Exhibit C), the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration blank shall be performed for the elements affected.

12.4.2 Preparation Blank (PB)

12.4.2.1 The PB shall contain all the reagents and in the same volumes as used in processing the samples. The PB shall be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

12.4.2.2 At least one PB, consisting of reagent water processed through each sample preparation and analysis procedure (see Section 10), shall be prepared and analyzed with every Sample Delivery Group (SDG), or with each batch[2] of samples digested, whichever is more frequent.

12.4.2.3 The first batch of samples in an SDG is to be assigned to Preparation Blank one, the second batch to Preparation Blank two, etc. (see Form III-IN). Each Sample Data Package shall contain the results of all PB analyses associated with the samples in that SDG.

12.4.2.4 The PB is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

12.4.2.4.1 If the absolute value of the concentration of the blank is less than or equal to the CRQL (see Exhibit C), no further action is required.

12.4.2.4.2 If any analyte concentration in the blank is above the CRQL, the lowest concentration of that analyte in the associated samples shall be greater than or equal to 10 times the blank concentration. Otherwise, all samples associated with the blank, with the analyte concentration less than 10 times the blank concentration and above the CRQL, shall be redigested and re-analyzed with appropriate new Quality Control (QC) for that analyte. The only exception to this shall be an identified field blank. The sample concentration is not to be corrected for the blank value.

12.4.2.4.3 If the concentration of the blank is below the negative CRQL, then all samples reported below 10 times the CRQL associated with the blank, shall be redigested and re-analyzed with appropriate new QC.

12.4.2.4.4 The values for the PB shall be reported on Form III-IN.

12.5 Interference Check Sample (ICS)

12.5.1 The ICS is prepared by the analyst or obtained from USEPA, if available.

[2]A group of samples prepared at the same time.

12.5.2 To verify interelement and background correction factors, the Contractor shall analyze and report the results for the ICS, for all elements on the Target Analyte List (TAL) and for all interferents (target and non-target), at the beginning and end of each analysis run, but not before the ICV. In addition, the Contractor shall analyze and report the results for the ICS at a frequency of not less than once per 20 analytical samples[3] per analysis run. These analyses of the ICS shall be immediately followed by the analysis of a CCV/CCB pair. The ICS solutions shall be obtained from USEPA, if available, and analyzed according to the instructions supplied with the ICS. The Contractor shall not dilute the ICS more than is necessary to meet the linear range values of the instrument.

12.5.3 The ICS consists of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively, starting with Solution A.

12.5.4 The analytical results of ICS Solution A (ICSA) shall fall within the control limit of ±2 times the CRQL of the analyte's true value or ±20% of the analyte's true value, whichever is greater (the true value shall be zero unless otherwise stated) in the ICSA. For example, if the analysis result(s) for Arsenic (CRQL = 10 µg/L, ICSA true value = 0 µg/L) in the ICSA analysis during the run is 19 µg/L, then the analytical result for Arsenic falls within the ±2 times the CRQL window for Arsenic in the ICSA. If the analytical results of the ICSA do not fall within the control limits, the analysis shall be terminated, the problem corrected, the instrument recalibrated, and re-analysis of the analytical samples analyzed since the last compliant ICSA shall be performed. For analytes with CRQLs less than 5000 µg/L, the ICSA results shall be reported from an undiluted sample analysis.

12.5.5 Results for the ICS Solution AB (ICSAB) during the analytical runs shall fall within the control limit of ±2 times the CRQL of the true value or ±20% of the true value, whichever is greater, for the analytes included in the ICSAB. If the analytical results of the ICSA do not fall within the control limits, the analysis shall be terminated, the problem corrected, the instrument recalibrated, and re-analysis of the analytical samples analyzed since the last compliant ICSAB shall be performed.

NOTE: The control limits and concentrations for the ICSAB are being monitored. These may be adjusted to provide greater control of interferences.

12.5.6 If true values for analytes contained in the ICS are not supplied with the solutions, the mean shall be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination shall be made during an analytical run where the results for the previously supplied ICS met all contract specifications. Additionally, the results of this initial mean determination shall be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted). Only if the ICS solutions are not available from USEPA, independent Check Samples shall be prepared with interferent and analyte concentrations at the levels specified in Table 1 - Interferent and Analyte Elemental Concentrations Used for ICP-AES Interference Check Sample (ICS). The mean value and standard deviation shall be established by

[3]As defined in Exhibit G, ICSA and ICSAB are analytical samples.

initially analyzing the Check Samples at least five times repetitively for each parameter on Form IVA-IN. Results shall fall within the control limit of ±2 times the CRQL of the established mean value or ±20% of the established mean value, whichever is greater. The mean and standard deviation shall be reported in the raw data. Results from the ICS analyses shall be reported on Form IVA-IN for all Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) analytes.

12.6 Spike Sample Analysis

12.6.1 The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and/or measurement methodology. If a digestion is performed, the spike is added before the digestion (i.e., prior to the addition of other reagents). At least one spike sample analysis (matrix spike) shall be performed on each group of samples of a similar matrix type (i.e., water, soil) or for each SDG.[4]

12.6.2 If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.7). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for spiked sample analysis. USEPA may require that a specific sample be used for the spike sample analysis.

12.6.3 The analyte spike shall be added in the amount given in Table 2 - Spiking Levels for Spike Sample Analysis, for each element analyzed.

NOTE: See Table 2 footnotes for concentration levels and applications.

12.6.4 If the spike recovery is not at or within the limits of 75-125%, the data of all samples received and associated with that spike sample shall be flagged with the letter "N" on Forms IA/IB-IN and VA-IN. An exception to this rule is granted when the sample concentration exceeds the spike added concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

12.6.5 When the matrix spike recovery falls outside the control limits and the sample result does not exceed four times the spike added, a post-digestion spike shall be performed for those elements that do not meet the specified criteria (exception: Ag). Note that if a post-digestion spike analysis is required for an analyte, the same EPA sample that was used for the matrix spike analysis shall be used for the post-digestion spike analysis. Spike the unspiked aliquot of the sample at two times the indigenous level or two times the CRQL, whichever is greater. Results of the post-digestion spike shall be reported on Form VB-IN.

12.6.6 In the instance where there is more than one spike sample per matrix per SDG, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix and method in the SDG. Individual component percent recoveries are calculated as follows:

[4]USEPA may require additional spike sample analyses, upon USEPA Regional CLP Project Officer (CLP PO) request.

EQ. 5 Spike Percent Recovery

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

WHERE, SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

12.6.7 When sample concentration is less than the Method Detection Limit (MDL), use SR = 0 only for purposes of calculating percent recovery. The Spike Sample Results (SSRs), Sample Results (SRs), Spike Added (SA), and percent recovery (positive or negative) shall be reported on Form VA-IN.

12.6.8 The units used for reporting SSRs will be identical to those used for reporting sample results on Form IA-IN.

12.7 Duplicate Sample Analysis

12.7.1 One duplicate sample shall be analyzed from each group of samples of a similar matrix type (i.e., water, soil) or for each SDG.[5] Duplicates cannot be averaged for reporting on Form IA-IN.

12.7.2 Duplicate sample analyses are required for percent solids. Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. USEPA may require that a specific sample be used for duplicate sample analysis. The Relative Percent Difference (RPD) for each component is calculated as follows:

EQ. 6 Duplicate Sample Relative Percent Difference

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

WHERE, RPD = Relative Percent Difference

S = Sample Result (original)

D = Duplicate Result

12.7.3 The results of the duplicate sample analyses shall be reported on Form VI-IN. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to five times the CRQL (see Exhibit C). A control limit of the CRQL value shall be entered in the "Control Limit" column on Form VI-IN if either the sample or duplicate value is less than five times the CRQL. If the sample and duplicate values are greater than or equal to five times the CRQL, or if the sample and duplicate values are less than the CRQL, the "Control Limit" field is left empty.

12.7.4 If one result is above five times the CRQL level and the other is below, use the CRQL criteria to determine if the duplicate analysis is in control. If both sample and duplicate values are less than the

[5]USEPA may require additional duplicate sample analyses, upon USEPA Regional CLP PO request.

MDL, the RPD is not calculated on Form VI-IN. For solid sample or solid duplicate results less than five times the CRQL, enter the value of the CRQL, corrected for sample weight and percent solids, (i.e., original, not duplicate sample weight and percent solids), in the "Control Limit" column. If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on Forms IA/IB-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix in the SDG. The percent difference data will be used by USEPA to evaluate the long-term precision of the methods for each element. Specific control limits for each element will be added to Form VI-IN at a later date based on these precision results.

12.8 Laboratory Control Sample (LCS) Analysis

12.8.1 Water/aqueous and solid LCS shall be analyzed for each analyte using the same sample preparations, analytical methods, and Quality Assurance/Quality Control (QA/QC) procedures employed for the EPA samples received.

12.8.1.1 The aqueous LCS solution (LCSW) shall be obtained from USEPA [if unavailable, the ICV solution(s) may be used]. One LCSW shall be prepared and analyzed for every group of aqueous samples in a SDG, or for each batch of aqueous samples digested, whichever is more frequent.

12.8.1.2 The USEPA provided solid LCS (LCSS) shall be prepared and analyzed using each of the procedures applied to the solid samples received (exception: percent solids determination not required). If the USEPA LCSS is unavailable, other USEPA QC Check Samples or other certified materials may be used. The control limits for these materials and samples must be documented. One LCSS shall be prepared and analyzed for every group of solid samples in a SDG, or for each batch of samples digested, whichever is more frequent.

12.8.2 All LCS and percent recovery results shall be reported on Form VII-IN. If the percent recovery for the LCSW falls outside the control limits of 80-120% (exception: Ag and Sb), the analyses shall be terminated, the problem corrected, and the samples associated with that LCSW redigested and re-analyzed with appropriate new QC.

12.8.3 If the results for the LCSS fall outside the control limits established by USEPA, the analyses shall be terminated, the problem corrected, and the samples associated with that LCSS redigested and re-analyzed with appropriate new QC.

12.9 ICP-AES Serial Dilution Analysis

12.9.1 Prior to reporting concentration data for the analyte elements, the Contractor shall analyze and report the results of the ICP-AES serial dilution analysis. The ICP-AES serial dilution analysis shall be performed on a sample from each group of samples of a similar matrix type (i.e., water, soil) or for each SDG, whichever is more frequent. Samples identified as field blanks and PE samples shall not be used for serial dilution analysis.

12.9.2 If the analyte concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample), the serial dilution (a five fold dilution) shall then agree within 10% of the original determination after correction for dilution. If the dilution

analysis for one or more analytes is not within a control limit of 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received and associated with that serial dilution must be flagged with an "E" on Form VIII-IN and Forms IA/IB-IN.

12.9.3 The percent differences for each component are calculated as follows:

EQ. 7 Serial Dilution Percent Differences

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

WHERE, I = Initial Sample Result (Instrument reading)

S = Serial Dilution Result (Instrument reading x5)

12.9.4 In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within contract criteria, flag all the samples of the same matrix in the SDG. Serial dilution results and "E" flags shall be reported on Form VIII-IN.

12.10 Method Detection Limit (MDL) Determination

12.10.1 Before any field samples are analyzed under this contract, the MDLs shall be determined for non-prepared analyses (Preparation Method/Code "NP1"), each digestion procedure and instrument used, prior to the start of contract analyses, and annually thereafter, and shall meet the levels specified in Exhibit C.

An MDL study shall be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions to verify the current sensitivity of the analysis.

12.10.1.1 To determine the MDLs, the Contractor shall run MDL studies following the procedures given in 40 CFR, Part 136. The Contractor shall prepare the MDL samples by each digestion procedure used and shall analyze these samples on each instrument used. The Contractor shall also analyze the non-prepared MDL samples on each instrument used.

12.10.1.2 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C.

12.10.1.3 The concentration of the non-prepared MDL (Preparation Method/Code "NP1") shall be used to determine the appropriate concentration qualifier for the results of non-prepared samples and instrument QC analyses.

12.10.1.4 The results of the MDL determination studies shall be forwarded to the USEPA Regional CLP PO, Sample Management Office (SMO), and Quality Assurance Technical Support (QATS).

12.10.1.5 The MDL results shall be reported on Form IX-IN.

12.11 Interelement Corrections

12.11.1 Before any field samples are analyzed under this contract, the interelement correction factors shall be determined prior to the start of contract analyses and at least quarterly thereafter. Correction factors for spectral interference due to Al, Ca, Fe, and Mg shall be determined for all ICP-AES instruments at all wavelengths

used for each analyte reported by ICP-AES. Interelement correction factors shall also be reported for any other elements (including those on the TAL) that have been determined to interfere with the requested target analyte(s).

NOTE: Depending on sample matrix and interferences, it may be necessary to analyze interelement correction factors at a frequency greater than quarterly and/or at multiple concentrations comparable to the sample interferent levels.

12.11.2 If the instrument was adjusted in any way that may affect the ICP-AES interelement correction factors, the factors shall be redetermined and the results submitted for use. In addition, all data used for the determination of the interelement correction factors shall be available to the USEPA during an on-site laboratory evaluation. Results from interelement correction factors determination shall be reported on Form XA-IN and Form XB-IN for all ICP-AES analytes.

12.12 Linear Range Standard (LRS)

12.12.1 Before any field samples are analyzed under this contract, the linear ranges shall be determined and reported prior to the start of contract analyses, and at least quarterly thereafter by the analysis of a linear range verification check standard, for each element on Form XI-IN. The standard shall be analyzed during a routine analytical run performed under this contract. The analytically determined concentration of this standard shall be within 5% of the true value. This concentration is the upper limit of the ICP-AES linear range beyond which results cannot be reported under this contract without dilution of the analytical sample.

12.13 Example Analytical Sequence for ICP-AES

S0
S
ICV
ICB
CRI
ICSA
ICSAB
CCV
CCB
10 samples
CCV
CCB
7 samples
CRI
ICSA
ICSAB
CCV
CCB
10 samples, etc.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 1.15 in Exhibit D - Introduction to Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 1.16 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 200.7. December 1982.

16.2 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Method 3050B. Third Edition, Update III. December 1996.

16.3 American Society for Testing and Materials. Standard Practice for Sample Digestion Using Closed Vessel Microwave Heating Technique for the Determination of Total Recoverable Metals in Water. D4309-91. October 1991.

16.4 US Government Printing Office. 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

16.5 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Method 3015. Third Edition, Update II. September 1994.

16.6 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Method 3051. Third Edition, Update II. September 1994.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1: Interferent and Analyte Elemental Concentrations Used for ICP-AES Interference Check Sample (ICS)

Analytes	(mg/L)	Interferents	(mg/L)
Ag	0.2	Al	250
As	0.1	Ca	250
Ba	0.5	Fe	100
Be	0.5	Mg	250
Cd	1.0		
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	0.05		
Sb	0.6		
Se	0.05		
Tl	0.1		
V	0.5		
Zn	1.0		

NOTE: ICS Solution A (ICSA) contains the interferents at the indicated concentrations. The ICSA may be analyzed at twice the concentration indicated when interferences are present at higher concentrations in the sample. ICS Solution AB (ICSAB) contains all of the analytes and interferents listed above at the indicated concentrations.

TABLE 2: Spiking Levels for Spike Sample Analysis

Element	Water (µg/L)	Soil[(1)] (mg/kg)	Element	Water (µg/L)	Soil[(1)] (mg/kg)
Aluminum	2,000	*	Magnesium	*	*
Antimony	100	20	Manganese	500	100
Arsenic	40	8	Nickel	500	100
Barium	2,000	400	Potassium	*	*
Beryllium	50	10	Selenium	50	10
Cadmium	50	10	Silver	50	10
Calcium	*	*	Sodium	*	*
Chromium	200	40	Thallium	50	10
Cobalt	500	100	Vanadium	500	100
Copper	250	50	Zinc	500	100
Iron	1,000	*			
Lead	20	4			

[*]No spike required. NOTE: Elements without spike levels, and not designated with an asterisk, shall be spiked at appropriate levels.

[1]The levels shown indicate concentrations in the spike sample when the wet weight of 1 gram of sample is taken for analysis. Adjustment shall be made to maintain these spiking levels when the weight of sample taken deviates by more than 10% of these values. Appropriate adjustment shall be made for microwave digestion procedures where 0.5 grams of sample or 50 mL (45 mL of sample plus 5 mL of acid) or 55 mL (50 mL of sample plus 5 mL of acid) of aqueous sample are required for analysis.

EQ. 8 Spiking Level Adjustment

$$\text{mg/kg} = \text{µg/L} \times \frac{\text{final volume (L)}}{\text{sample weight (g)}}$$

EXHIBIT D - PART B

ANALYTICAL METHODS FOR INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

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Exhibit D - Analytical Methods for ICP-MS

Table of Contents

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1.0 SCOPE AND APPLICATION

This method provides procedures for the use of Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) to determine the concentration of dissolved and total recoverable elements in water/aqueous samples taken from hazardous waste sites. This method is applicable to all metals in the Target Analyte List (TAL) for ICP-MS in Exhibit C.

2.0 SUMMARY OF METHOD

This method describes the multi-element determination of trace elements by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). Sample material in solution is introduced by nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio. The separated ions are detected and the ion information processed by a data handling system. Interferences related to the technique must be recognized and corrected. Such corrections may include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from plasma gas, reagents, or sample matrix. Instrumental drift, as well as suppressions or enhancements of instrument response, must be corrected for the use of internal standards.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

Several types of interferences may cause inaccuracies in the determination of trace elements by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). To prevent this, appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. Possible interferences are in Sections 4.1 through 4.5.

4.1 Isobaric Elemental Interferences

Isobaric Elemental Interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio, and which cannot be resolved by the mass spectrometer. All elements determined by this method have, at minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method, only selenium-82 (krypton) has an isobaric elemental interference. If alternative analytical isotopes having higher natural abundances are selected, in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios should be established prior to the application of any corrections.

4.2 Abundance Sensitivity

Abundance Sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and mass filter operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution should be adjusted to minimize.

4.3 Isobaric Polyatomic Ion Interferences

These are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified and are listed in Table 1 - Isobaric Molecular-Ion Interferences, with the target analytes affected. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence, since the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

4.4 Physical Interferences

These are associated with the physical processes which govern the transport of the sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during

the excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute to deposits of material on the extraction and/or skimmer cones. Deposits can reduce the effective diameter of the orifices and therefore ion transmission. Dissolved solid levels not exceeding 0.2% (w/v) have been recommended to reduce such effects. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards ideally should have similar analytical behavior to the elements being determined.

4.5 Memory Interferences

Memory Interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects, or carryover, can result from sample deposition on the sampler and skimmer cones, as well as from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples (see Section 7.3.3). The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element should be estimated prior to analysis. This may be achieved by aspirating a standard, containing the elements corresponding to ten times the upper end of the linear range for a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of ten of the Method Detection Limit (MDL) should be noted. Memory interferences may also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect, and should examine the analyte concentration in the previous sample to identify if it was high. If a memory interference is suspected, the sample should be re-analyzed after a long rinse period.

5.0 SAFETY

See Section 1.14 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Glassware/Labware

6.1.1 250 milliliter (mL) beaker or other appropriate vessel (glass or plastic)

6.1.2 Watch glasses (glass or plastic)

6.1.3 Funnels

6.1.4 Graduated cylinders

6.1.5 Various volumetric flasks (Type A)

6.1.6 Thermometer that covers range of 0-200°C

6.1.7 Whatman No. 42 filter paper or equivalent

6.1.8 Hot plate, block digester, or other heating source capable of maintaining 92-95°C.

6.1.9 Balances - Analytical Balance, 300 gram (g) capacity, and minimum ±0.1 milligram (mg).

6.2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) consisting of:

- An instrument capable of scanning the mass range 5-250 atomic mass unit (amu) with a minimum resolution capability of 1 amu peak width at 5% peak height and either a conventional or extended dynamic range detector.
- A radio-frequency generator compliant with Federal Communications Commission (FCC) regulations.
- A high purity (99.99%) argon gas supply.
- A variable speed peristaltic pump to deliver sample solution to the nebulizer.
- A mass-flow controller on the nebulizer gas supply is required.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagents may contain elemental impurities that might affect the integrity of analytical data. Owing to the high sensitivity of Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), high-purity reagents should be used whenever possible. Suitable acids are available from a number of manufacturers or may be prepared by sub-boiling distillation. Nitric acid is preferred for ICP-MS in order to minimize polyatomic ion interferences. Several polyatomic ion interferences result when hydrochloric acid (HCl) is used, however, it should be noted that HCl is required to maintain stability in solutions containing antimony and silver. When HCl is used, corrections for the chloride polyatomic ion interferences must be applied to all data.

7.1.1 Reagent Water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-77). Use this preparation for all reagents, standards, and dilutions of solutions.

7.1.2 Nitric Acid - Concentrated (specific gravity 1.41).

7.1.3 Nitric acid (1+1) - Add 500 milliliters (mL) conc. HNO_3 to 400 mL of reagent water and dilute to 1 Liter (L).

7.1.4 Nitric acid (1+9) - Add 100 mL conc. nitric acid to 400 mL of reagent water and dilute to 1 L.

7.1.5 Hydrochloric acid - Concentrated (specific gravity 1.19).

7.1.6 Hydrochloric acid (1+1) - Add 500 mL conc. HCl to 400 mL of reagent water and dilute to 1 L.

7.1.7 Hydrochloric acid (HCl) (1+4) - Add 200 mL conc. HCl to 400 mL reagent water and dilute to 1 L.

7.1.8 Ammonium hydroxide - Concentrated (specific gravity 0.902).

7.1.9 Tartaric acid - (CASRN 87-69-4).

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 8.0. The Contractor must be able to verify that the standards are certified. Manufacturer’s certificates of analysis must be retained by the Contractor and presented upon request.

7.2.2 Stock Standard Solutions

7.2.2.1 Stock standard solutions may be purchased from a reputable commercial source or prepared from reagent grade chemicals or metals (99.99-99.999% pure). All salts should be dried for 1 hour at 105°C unless otherwise specified. Stock solutions should be stored in Fluorinated Ethylene Propylene (FEP) fluorocarbon bottles. Note that some metals, particularly those which form surface oxides, require cleaning prior to being weighed. This may be achieved by pickling the surface of the metal in acid. An amount in excess of the desired weight should be pickled

repeatedly, rinsed with water, dried and weighed until the desired weight is achieved.

7.2.2.2 Aluminum solution, stock [1 mL = 1000 micrograms (µg) Al] - Pickle aluminum metal in warm (1+1) HCl to an exact weight of 0.100 g. Dissolve in 10 mL conc. HCl and 2 mL conc. nitric acid, heating to effect solution. Continue heating until the volume is reduced to 4 mL. Cool and add 4 mLs of reagent water. Heat until volume is reduced to 2 mL. Cool and dilute to 100 mL with reagent water.

7.2.2.3 Antimony solution, stock (1 mL = 1000 µg Sb) - Dissolve 0.100 g antimony powder in 2 mL (1+1) nitric acid and 0.5 mL conc. HCl, heating to effect solution. Cool, add 20 mL reagent water and 0.15 g tartaric acid. Warm the solution to dissolve the white precipitate. Cool and dilute to 100 mL with reagent water.

7.2.2.4 Arsenic solution, stock (1 mL = 1000 µg As) - Dissolve 0.1320 g As_2O_3 in a mixture of 50 mL reagent water and 1 mL conc. ammonium hydroxide. Heat gently to dissolve. Cool and acidify solution with 2 mL conc. nitric acid. Dilute to 100 mL with reagent water.

7.2.2.5 Barium solution, stock (1 mL = 1000 µg Ba) - Dissolve 0.1437 g $BaCO_3$ in a solution mixture of 10 mL reagent water and 2 mL conc. nitric acid. Heat and stir to effect solution and degassing. Dilute to 100 mL with reagent water.

7.2.2.6 Beryllium solution, stock (1 mL = 1000 µg Be) - Dissolve 1.965 g $BeSO_4 \bullet 4H_2O$ (DO NOT DRY) in 50 mL reagent water. Add 1 mL conc. nitric acid. Dilute to 100 mL with reagent water.

7.2.2.7 Bismuth solution, stock (1 mL = 1000 µg Bi) - Dissolve 0.1115 g Bi_2O_3 in 5 mL conc. nitric acid. Heat to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.8 Cadmium solution, stock (1 mL = 1000 µg Cd) - Pickle cadmium metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.9 Chromium solution, stock (1 mL = 1000 µg Cr) - Dissolve 0.1923 g CrO_3 in a solution mixture of 10 mL reagent water and 1 mL conc. nitric acid. Dilute to 100 mL with reagent water.

7.2.2.10 Cobalt solution, stock (1 mL = 1000 µg Co) - Pickle cobalt metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.11 Copper solution, stock (1 mL = 1000 µg Cu) - Pickle copper metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.12 Indium solution, stock (1 mL = 1000 µg In) - Pickle indium metal in (1+1) nitric acid to an exact weight of 0.100 g. Dissolve in 10 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.13 Lead solution, stock (1 mL = 1000 µg Pb) - Dissolve 0.1599 g $PbNO_3$ in 5 mL (1+1) nitric acid. Dilute to 100 mL with reagent water.

7.2.2.14 Magnesium solution, stock (1 mL = 1000 µg Mg) - Dissolve 0.1658 g MgO in 10 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.15 Manganese solution, stock (1 mL = 1000 µg Mn) - Pickle manganese flake in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.16 Nickel solution, stock (1 mL = 1000 µg Ni) - Dissolve 0.100 g nickel powder in 5 mL conc. nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.17 Scandium solution, stock (1 mL = 1000 µg Sc) - Dissolve 0.1534 Sc_2O_3 in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.18 Selenium solution, stock (1 mL = 1000 µg Se) - Dissolve 0.1405 g SeO_2 in 20 mL reagent water and dilute to 100 mL with reagent water.

7.2.2.19 Silver solution, stock (1 mL = 1000 µg Ag) - Dissolve 0.100 g silver metal in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water. Protect from the light.

7.2.2.20 Terbium solution, stock (1 mL = 1000 µg Tb) - Dissolve 0.1176 g Tb_4O_7 in 5 mL conc. nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.21 Thallium solution, stock (1 mL = 1000 µg Tl) - Dissolve 0.1303 g $TlNO_3$ in a solution mixture of 10 mL reagent water and 1 mL conc. nitric acid. Dilute to 100 mL with reagent water.

7.2.2.22 Vanadium solution, stock (1 mL = 1000 µg V) - Pickle vanadium metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.23 Yttrium solution, stock (1 mL = 1000 µg Y) - Dissolve 0.1270 g Y_2O_3 in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.24 Zinc solution, stock (1 mL = 1000 µg Zn) - Pickle zinc metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.3 Secondary Dilution Standards

Prepare mixed secondary dilution standard solutions by diluting the appropriate volumes of stock standards with acidified reagent water to obtain the final volume. Originating stock standards should be checked for the presence of impurities which might influence the accuracy of the standard. Freshly prepared standards should be transferred to acid-cleaned, not previously used, FEP fluorocarbon bottles for storage and monitored periodically for stability. Mixed secondary dilution standard solutions may be purchased. The purchased standards shall meet the requirements in Section 7.2.1.

7.2.4 Working Standards

7.2.4.1 Mixed Calibration Standard Solutions

Care must be taken in the preparation of mixed calibration standards to ensure that the elements are compatible and stable. Fresh calibration standards should be prepared from mixed standard solutions every two weeks or as needed. Dilute the mixed standards to levels appropriate to the operating range of the instrument using reagent water containing 1% (v/v) nitric acid. The element concentrations in the calibration standards should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. If the direct addition procedure is being used, add internal standards.

7.2.4.2 Internal Standard Solution

Prepare mixed standard by diluting 10 mL each of the chosen element's stock standards to 100 mL with reagent water. Use this solution for additions to blanks, calibration standards, and samples, or dilute by an appropriate amount using 1% (v/v) nitric acid if the internal standards are being added by a peristaltic pump.

7.2.4.3 Tuning Solution

This solution is used for instrument tuning and mass calibration prior to analysis. Prepare mixed standard by diluting beryllium, magnesium, cobalt, indium, and lead stock standards to 100 µg/L with 1% (v/v) nitric acid. Do not add internal standard to this solution.

7.2.4.4 Interference Check Sample (ICS)

The ICS consists of two solutions: Solution A (ICSA) and Solution AB (ICSAB). ICSA consists of the interferents and ICSAB consists of the analytes mixed with the interferents. If the direct addition procedure is being used, add internal standards.

7.2.4.4.1 Solution A - Contains 100 milligrams per Liter (mg/L) of aluminum, calcium, iron, magnesium, potassium, sodium, phosphorus (as orthophosphate), sulfur (as sulfate), 200 mg/L carbon, 1000 mg/L chloride, and 2 mg/L molybdenum and titanium.

7.2.4.4.2 Solution AB - Contains all of the elements in Solution A plus all target analytes at a concentration of 20 µg/L.

7.2.4.5 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

The concentrations of the analytes in the CRI shall be at the CRQL. Information regarding the CRI shall be reported on Form IIB-IN.

7.2.4.6 Method Detection Limit (MDL) Solution

The MDL solution shall be at a concentration of 3 to 5 times the expected MDL.

7.3 Blanks

Three types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the Preparation Blank (PB) (see Section 12.5.2) is used to assess possible contamination

from the sample preparation procedure and to assess spectral background, and the rinse blank is used to flush the instrument between samples in order to reduce memory interferences.

7.3.1 Calibration Blank - Consists of 1% (v/v) nitric acid in reagent water. If the direct addition procedure is being used, add internal standards.

7.3.2 Preparation Blank - Must contain all the reagents in the same volumes as used in preparing the samples. The PB must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

7.3.3 Rinse Blank - Consists of 2% (v/v) nitric acid in reagent water.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All samples must be collected in glass or polyethylene containers. Water/aqueous samples must be preserved with nitric acid to pH less than 2 immediately after collection. All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until digestion.

8.1.1 Dissolved Metals

For the determination of dissolved metals, the sample must be filtered through a 0.45 micrometer (µm) pore diameter membrane filter at the time of collection or as soon as possible. Use a portion of the sample to rinse the filter flask, discard this portion, and collect the required volume of filtrate. Preserve the filtrate with nitric acid to pH less than 2 immediately after filtration.

8.2 Procedures for Sample Storage

The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after the delivery of a complete, reconciled data package to USEPA. After 60 days the samples may be disposed of in a manner that complies with all applicable regulations.

8.3 Procedure for Sample Digestate Storage

Sample digestates must be stored until 365 days after delivery of a complete, reconciled data package to USEPA.

8.4 Contract Required Holding Time

The maximum holding time for metals is 180 days from Validated Time of Sample Receipt (VTSR).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. The Method Detection Limit (MDL), precision, linear dynamic range, and interference effects must be investigated and established for each individual element on that particular instrument. All measurements must be within the operational range of the instrument where corrections are valid. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) Instrument Calibration Procedure

9.2.1 Precalibration routine - The following precalibration routine must be completed prior to calibrating the instrument.

Set up the instrument with proper operating parameters established in Section 9.1. The instrument must be allowed to become stable prior to calibration. Conduct any necessary mass calibration and resolution routines to bring peak width within the manufacturer's specifications and adjust mass calibration to within 0.1 amu over the range of 6 to 210 amu.

Demonstrate instrument stability and precision by analyzing the tuning solution a minimum of five times consecutively. This may be carried out as five separate analyses or as a single analysis with at least five integrations. The percent relative standard deviation of the absolute signals for all analytes in the tuning solution must be less than 5%.

9.2.2 Internal Standardization

Internal standardization must be used in all analyses (except the tuning solution) to correct the instrument drift and physical interferences. A list of acceptable internal standards is provided in Table 4 - Internal Standards. For full range mass scans, a minimum of five internal standards shall be used. The masses of the internal standards shall bracket the masses of the analyte. The internal standards selected for a run must be consistent throughout the entire run. Internal standards shall be present in all samples, standards, and blanks (except the tuning solution) at identical levels. This may be achieved by directly adding an aliquot of the internal standards solution to each sample, standard, and blank, or by mixing with the sample solution prior to nebulization using a second channel of the peristaltic pump and mixing coil. The concentration of the internal standard should be sufficiently high for good precision and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. Depending on the sensitivity of the instrument, a concentration range of 20 µg/L to 200 µg/L of each internal standard is recommended. Internal standards should be added to samples, standards, and blanks in a similar manner, in order for dilution effects to be disregarded.

9.2.3 Calibration

Instruments shall be calibrated daily, once every 24 hours, or each time the instrument is set up. The instrument standardization date and time shall be included in the raw data. Calibration standards shall be prepared as in Section 7.2.4.1. Calibrate the instrument with at least two standards, one of which must be a blank standard. A minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.

NOTE: Any changes or corrections to the analytical system shall be followed by recalibration.

9.3 Initial Calibration Verification (ICV)

9.3.1 Immediately after each instrument has been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of the ICV solution(s) for each mass used to report final results.

9.3.2 Only if the ICV solution(s) is(are) not available from USEPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source other than those used in the standards for instrument calibration.

9.3.3 The ICV solution(s) shall be run at each mass used for reporting final results. The values for the ICV shall be reported on Form IIA-IN.

9.4 Continuing Calibration Verification (CCV)

9.4.1 To ensure calibration accuracy during each analysis run, one of the following standards shall be used for the CCV for each mass used for reporting final results for each element, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard shall also be analyzed and reported for each mass used for reporting final results for each element at the beginning of the run and after the last analytical sample. The analyte concentrations in the CCV standard(s) shall be different from the concentrations for the ICV and shall be one of the following solutions at or near one-half of the calibration standard:

- USEPA Solutions
- NIST Standards
- A Contractor-prepared standard solution

The same CCV standard shall be used throughout the analysis runs for a Sample Delivery Group (SDG) of samples received.

9.4.2 Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses, and other related operations which may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it, as well as the difference in

time between the CCV and the analytical sample immediately preceding it, may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

9.4.3 Information regarding the CCV shall be reported on Form IIA-IN.

9.5 Initial and Continuing Calibration Blank (ICB/CCB)

A calibration blank shall be analyzed for each mass used for reporting final results for each element immediately after every ICV and CCV, at a frequency of 10% or every 2 hours during the run, whichever is more frequent. The blank shall be analyzed at the beginning of the run and after the last analytical sample.

NOTE: A CCB shall be analyzed immediately after the last CCV, and the last CCV shall be analyzed immediately after the last analytical sample of the run. The results of the calibration blanks shall be reported on Form III-IN.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to inform them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analysis be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analysis will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample and analyze one or more of the phases, separately. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do any of the following:

- Separate the phases and analyze the phase(s) that is(are) amenable to analysis. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Sample Preparation Procedures

10.1.3.1 Preparation Method/Code (HW2)

Shake and transfer a 100 mL aliquot of the sample to a 250 mL heating vessel, add 2 mL (1+1) nitric acid and 1 mL of (1+1) hydrochloric acid (HCl) to the sample. Cover with a ribbed watch glass and heat on either a hot plate, block digester, or equivalent heating source which is adjustable and capable of maintaining a temperature of 92-95°C for 2 hours, or until the sample volume is reduced to about 20 mL (DO NOT BOIL). Cover with a watch glass to prevent additional evaporation and reflux for 30 minutes. Cool sample, transfer to a 50 mL volumetric flask, and adjust sample volume to 50 mL with reagent water. Mix and allow any solids present to settle by gravity overnight or centrifuge (if after settling or centrifuging, the sample contains suspended solids, a portion of the sample may be filtered prior to analysis).

10.1.3.1.1 Prior to analysis, adjust the chloride concentration by pipetting 20 mL of the digestate into a 50 mL volumetric flask and dilute to volume with reagent water and mix. If the direct addition method is being used, add internal standards and mix. The sample is now ready for analysis.

10.1.3.2 Preparation Method/Code (HW3)

Shake sample and transfer 50-100 mL of well-mixed sample to an appropriate polytetrafluoroethylene (PTFE), polypropylene, or polyethylene heating vessel. Add 2 mL of (1+1) nitric acid and 1 mL of (1+1) hydrochloric acid to the vessel. Cover with a ribbed watch glass or similar cover and heat on a hot plate, block digester, or equivalent heating source that is adjustable and capable of maintaining a temperature of 92-95°C until the sample volume has been reduced by half. Cover with a watch glass or similar cover to prevent further evaporation and reflux for an additional 30 minutes. Cool sample and filter to remove insoluble material.

NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

Adjust volume to 50-100 mL with reagent water. The sample is now ready for analysis. If volumes less than 100 mL are used, all other reagents shall be reduced appropriately (e.g., if 50 mL is used, reduce reagent volumes by one-half). The final volume of the digestate must equal the initial volume of the sample aliquot.

10.2 Sample Analysis

10.2.1 For every new or unusual matrix, it is highly recommended that a semi-quantitative analysis be carried out to screen for high element concentrations. Information gained from this may be used to prevent potential damage to the detector during sample analysis and to identify elements which may be higher than the linear range. Matrix screening may be carried out by diluting the sample by a factor of 500 and analyzing in semi-quantitative mode. The sample should also be screened for background levels of all elements chosen for use as internal standards in order to prevent bias in the calculation of analytical data.

10.2.2 Initiate instrument operating configuration. Tune and calibrate the instrument for the analytes of interest. Establish instrument software run procedures for quantitative analysis. For all sample analyses, a minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for data reporting.

10.2.3 The rinse blank should be used to flush the system between samples. Allow sufficient time to remove traces of the previous sample or a minimum of one minute. Samples should be aspirated for a sufficient period of time to obtain a stable response prior to the collection of data.

10.2.4 Samples having concentrations higher than the established linear dynamic range should be diluted into range and re-analyzed. The sample should first be analyzed for the trace elements, protecting the detector from the high concentration elements, if necessary, by the selection of appropriate scanning windows. The sample should then be diluted for the determination of the remaining elements. Alternatively, the dynamic range may be adjusted by selecting an alternative isotope of lower natural abundance, provided QC data for that isotope have been established. The dynamic range must not be adjusted by altering instrument conditions to an uncharacterized state.

10.2.5 All masses which might affect data quality must be monitored during the analytical run. At a minimum, those masses prescribed in Table 2 - Mass Choices for Elements that Must Be Monitored During the Analytical Run, must be monitored in the same scan that is used for the collection of the data. This information should be used to correct the data for identified interferences.

10.2.6 During the analysis of samples, the laboratory must comply with the required QC described in Section 12. For the determination of dissolved analytes when the Region has specified that no preparation is required, the Preparation Blank (PB) and Laboratory Control Sample (LCS) are not required.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Recommended Elemental Equations

Elemental expressions recommended for sample data calculations are listed in Table 3 - Recommended Elemental Expressions for Isobaric Interferences. Do not report element concentrations below the determined Method Detection Limit (MDL).

11.2 Data Value Corrections

Data values should be corrected for instrument drift or sample matrix induced interferences by the application of internal standardization. Corrections for characterized spectral interferences should be applied to the data. Chloride interference corrections should be made on all samples, regardless of the addition of hydrochloric acid (HCl), as the chloride ion is a common constituent of environmental samples.

11.3 Multiple Monitored Isotopes

If an element has more than one monitored isotope, examination of the concentration calculated for each isotope or the isotope ratios will provide useful information in detecting a possible spectral interference. Consideration should therefore be given to both primary and secondary isotopes in the evaluation of sample concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

11.4 Prepared Sample Analysis (HW2)

EQ. 1 Prepared Sample Concentration by Method HW2

$$\text{Concentration } (\mu g/L) = C \times \frac{V_f}{V_i} \times \frac{V_f}{20} \times DF$$

WHERE,

- C = Instrument value in µg/L (The average of all replicate integrations).
- V_f = Final digestion volume (50 mL)
- V_i = Initial digestion volume (100 mL)
- DF = Dilution Factor

11.5 Prepared Sample Analysis (HW3)

EQ. 2 Prepared Sample Concentration by Method HW3

$$\text{Concentration (g/L)} = C \times \frac{V_f}{V_i} \times DF$$

WHERE,

- C = Instrument value in µg/L (The average of all replicate integrations).
- V_f = Final digestion volume (mL)
- V_i = Initial digestion volume (mL)
- DF = Dilution Factor

11.6 Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation

To calculate the adjusted CRQL or adjusted MDL, multiply the value of the CRQL (µg/L) or MDL (µg/L) by the sample dilution factor.

12.0 QUALITY CONTROL (QC)

12.1 Tune Standard

The Tune Standard shall be prepared in the same acid matrix as the calibration standards and analyzed at least 5 times consecutively. Analyses may be carried out as five separate analyses or as a single analysis with at least five integrations. If the mass calibration is not within 0.1 amu over the range of 6 to 210 amu, or the percent Relative Standard Deviation (%RSD)of the absolute signals of the analytes exceeds 5%, the analysis shall be terminated, the problem corrected, and the instrument re-tuned. All sample results reported must be associated with an instrument tune that meets these requirements.

12.2 Initial Calibration Verification (ICV)

The ICV Standard shall be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier. If measurements exceed the control limits of 90% (low) and 110% (high), the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. Information regarding the ICV shall be reported on Form IIA-IN.

12.3 Continuing Calibration Verification (CCV)

The CCV standard shall be prepared by combining compatible elements at a concentration equivalent to the mid-points of their respective calibration curves. If the deviation of the CCV is greater than the specified control limits of 90% (low) and 110% (high), the analysis shall be stopped, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification shall be performed for the elements affected. Information regarding the CCV shall be reported on Form IIA-IN.

12.4 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

12.4.1 To verify linearity near the CRQL, a standard at the CRQL (CRI) shall be prepared, in the same acid matrix as the calibration standards, and analyzed at the beginning (immediately following the ICV/ICB and immediately preceding the Interference Check Sample (ICS) analyses). In addition, the contractor shall analyze the CRI at the end of each sample analysis run and at a frequency of not less than once per 20 analytical samples[1] per analysis run. These subsequent analyses of the CRI shall be immediately followed by CCV/CCB analyses.

12.4.2 The CRI shall be run for every required isotope used for the analysis of all Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) analytes. Information regarding the CRI shall be reported on Form IIB-IN.

12.4.3 If the percent recovery of the CRI falls outside the control limits of 70-130% (50-150% for cobalt, manganese, and zinc) for one or more analytes, the CRI shall be re-analyzed immediately for those analytes only. If the results of the re-analysis for those analytes fall within the control limits, no further corrective action is required. If the results of the re-analysis for those analytes do not fall within the control limits, the analysis shall be terminated, the

[1]As defined in Exhibit G, CRI is an analytical sample.

problem corrected, the instrument recalibrated, the CRI analyzed, and the samples associated with the CRI re-analyzed.

12.5 Blank Analyses

There are two different types of blanks required by this method. The calibration blank is used in establishing the analytical curve while the preparation blank is used to monitor for possible contamination.

12.5.1 Initial and Continuing Calibration Blank (ICB/CCB)

The ICB and CCB are prepared with acid and reagent water. If the absolute value of the calibration blank (ICB/CCB) result exceeds the CRQL (see Exhibit C), the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration blank shall be performed for the elements affected.

12.5.2 Preparation Blank (PB)

12.5.2.1 The PB shall contain all the reagents and in the same volumes as used in processing the samples. The PB shall be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

12.5.2.2 At least one PB, consisting of reagent water processed through each sample preparation and analysis procedure (see Section 10), shall be prepared and analyzed with every Sample Delivery Group (SDG), or with each batch[2] of samples digested, whichever is more frequent.

12.5.2.3 The first batch of samples in an SDG is to be assigned to Preparation Blank one, the second batch to Preparation Blank two, etc. (see Form III-IN). Each Sample Data Package shall contain the results of all PB analyses associated with the samples in that SDG.

12.5.2.4 The PB is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

12.5.2.4.1 If the absolute value of the concentration of the blank is less than or equal to the CRQL (see Exhibit C), no further action is required.

12.5.2.4.2 If the analyte concentration in the blank is above the CRQL, the lowest concentration of that analyte in the associated samples shall be greater than or equal to 10 times the blank concentration. Otherwise, all samples, associated with the blank, with the analyte concentration less than 10 times the blank concentration and above the CRQL, shall be redigested and re-analyzed with appropriate new Quality Control (QC) for that analyte. The only exception to this shall be an identified field blank. The sample concentration is not to be corrected for the blank value.

12.5.2.4.3 If the concentration of the blank is below the negative CRQL, then all samples reported below 10 times the CRQL associated

[2]A group of samples prepared at the same time.

with the blank, shall be redigested and re-analyzed with appropriate new QC.

12.5.2.4.4 The values for the PB shall be reported on Form III-IN.

12.6 Interference Check Sample (ICS)

12.6.1 The ICS is prepared by the analyst or obtained from USEPA, if available.

12.6.2 To verify corrections for elemental and polyatomic isobaric interferences, the Contractor shall analyze and report the results for the ICS for all elements on the Target Analyte List (TAL) and analyze for all interferents, at the beginning of each analysis run, but not before the ICV. This analysis of the ICS shall be immediately followed by analysis of a CCV/CCB pair. The ICS solutions shall be obtained from USEPA, if available, and analyzed according to instructions supplied with the ICS. The Contractor shall not dilute the ICS (for the higher concentration elements) more than is necessary to meet the linear range values of the instrument.

12.6.3 The ICS consists of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively, starting with Solution A.

12.6.4 The analytical results of ICS Solution A (ICSA) shall fall within the control limit of ±3 times the CRQL of the analyte's true value or ±20% of the analyte's true value (the true value shall be zero unless otherwise stated) in the ICSA, whichever is greater. If not, the analysis shall be terminated, the problem corrected, the instrument recalibrated, and re-analysis of the analytical samples analyzed since the last compliant ICSA shall be performed. The ICSA results for these analytes shall be reported from an undiluted sample analysis.

12.6.5 Results for the ICS Solution AB (ICSAB) during the analytical runs shall fall within the control limit of ±3 times the CRQL of the true value or ±20% of the true value, whichever is greater, for the analytes included in the ICSAB. If not, the analysis shall be terminated, the problem corrected, the instrument recalibrated, and re-analysis of the analytical samples analyzed since the last compliant ICSAB shall be performed.

NOTE: The control limits and concentrations for the ICSAB are being monitored. These may be adjusted to provide greater control of interferences.

12.6.6 If true values for analytes contained in the ICS are not supplied with the solutions, the mean shall be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination shall be made during an analytical run where the results for a previously supplied ICS met all contract specifications. Additionally, the results of this initial mean determination shall be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted). Only if the ICS solutions are not available from USEPA, independent Check Samples shall be prepared with interferent and analyte concentrations at the levels specified in Sections 7.2.4.4.1 and 7.2.4.4.2. The mean value and standard deviation shall be established by initially analyzing the Check Samples at least five times repetitively for each analyte listed on Form IVB-IN. Results shall fall within the control limit of ±3 times the CRQL of the established mean value or ±20% of the

established mean value, whichever is greater. The mean and standard deviation shall be reported in the raw data. Results from the ICS analyses shall be reported on Form IVB-IN for all ICP-MS parameters.

12.7 Spike Sample Analysis

12.7.1 The spike sample analysis is designed to provide information about the effect of sample matrix on the digestion and/or measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents). At least one spike sample analysis (matrix spike) shall be performed for each SDG[3].

12.7.2 If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated "original sample" (see Section 12.8). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for spiked sample analysis. USEPA may require that a specific sample be used for the spike sample analysis.

12.7.3 The analyte spike shall be added in the amount given in Table 5 - Spiking Levels for Spike Sample Analysis, for each element analyzed.

12.7.4 If the spike recovery is not at or within the limits of 75-125%, the data for all samples received and associated with that spike sample and shall be flagged with the letter "N" on Forms IA/IB-IN and VA-IN. An exception to this rule is granted when the sample concentration exceeds the Spike Added (SA) concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

12.7.5 When the matrix spike recovery falls outside the control limits and the sample result does not exceed four times the spike added, a post-digestion spike shall be performed for those elements that do not meet the specified criteria. Note that if a post-digestion spike analysis is required for an analyte, the same EPA sample that was used for the matrix spike shall be used for the post-digestion spike analysis. Spike an unspiked aliquot of the digestate at two times the indigenous level or two times the CRQL, whichever is greater. Results of the post-digestion spike shall be reported on Form VB-IN.

12.7.6 In the instance where there is more than one spike sample per matrix per SDG, if one spike sample recovery is not within contract criteria, flag all the samples in the SDG. Individual component percent recoveries are calculated as follows:

EQ. 3 Spike Percent Recovery

$$\%\text{Recovery} = \frac{SSR - SR}{SA} \times 100$$

WHERE, SSR = Spike Sample Result

SR = Sample Result

SA = Spike Added

[3]USEPA may require additional spike sample analyses, upon USEPA Regional CLP Project Officer (CLP PO) request.

12.7.7 When sample concentration is less than the Method Detection Limit (MDL), use SR = 0 only for purposes of calculating percent recovery. The Spike Sample Results (SSRs), Sample Results (SRs), Spike Added (SA), and percent recovery (positive or negative) shall be reported on Form VA-IN.

12.7.8 The units used for reporting SSRs will be identical to those used for reporting sample results on Form IA-IN.

12.8 Duplicate Sample Analysis

12.8.1 One duplicate sample shall be analyzed for each SDG[4]. Duplicates cannot be averaged for reporting on Form IA-IN.

12.8.2 Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. USEPA may require that a specific sample be used for duplicate sample analysis. The Relative Percent Difference (RPD) for each analyte is calculated as follows:

EQ. 4 Duplicate Sample Relative Percent Difference

$$RPD = \frac{|S-D|}{(S+D)/2} \times 100$$

WHERE, RPD = Relative Percent Difference

S = Sample Result (original)

D = Duplicate Result

12.8.3 The results of the duplicate sample analyses shall be reported on Form VI-IN. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to five times the CRQL (see Exhibit C). A control limit equal to the CRQL shall be entered in the "Control Limit" column on Form VI-IN if either the sample or duplicate value is less than five times the CRQL. If the sample and duplicate values are greater than or equal to five times the CRQL, or if the sample and duplicate values are less than the CRQL, the "Control Limit" field is left empty.

12.8.4 If one result is above five times the CRQL level and the other is below, use the CRQL criteria to determine if the duplicate analysis is in control. If both sample and duplicate values are less than the MDL, the RPD is not calculated on Form VI-IN. If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on Forms IA/IB-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples in the SDG. The percent difference data will be used by USEPA to evaluate the long-term precision of the methods for each element. Specific control limits for each element may be added to Form VI-IN at a later date based on these precision results.

[4]USEPA may require additional duplicate sample analyses, upon USEPA Regional CLP PO request.

12.9 Laboratory Control Sample (LCS) Analysis

12.9.1 A water/aqueous LCS (LCSW) shall be analyzed for each analyte using the same sample preparations, analytical methods, and Quality Assurance/Quality Control (QA/QC) procedures employed for USEPA samples received.

12.9.2 The LCSW solution must be obtained from USEPA (if unavailable, the ICV solution(s) may be used). One aqueous LCS shall be prepared and analyzed for each group of samples in an SDG, or for each batch of samples digested, whichever is more frequent.

12.9.3 All LCSW and percent recovery results shall be reported on Form VII-IN. If the percent recovery for the LCSW falls outside the control limits of 80-120%, the analyses shall be terminated, the problem corrected, and the samples associated with that LCSW redigested and re-analyzed with appropriate new QC.

12.10 ICP-MS Serial Dilution Analysis

12.10.1 Prior to reporting concentration data for the analyte elements, the Contractor shall analyze and report the results of the ICP-MS serial dilution analysis. The ICP-MS serial dilution analysis shall be performed on a sample from each SDG. Samples identified as field blanks and PE samples shall not be used for serial dilution analysis.

12.10.2 If the analyte concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not within a control limit of 10%, and the internal standards in the original sample met the contract criteria, an interference effect must be suspected, and the data for all affected analytes in the samples received and associated with that serial dilution must be flagged with an "E" on Forms IA/IB-IN and VIII-IN.

12.10.3 The percent differences for each component are calculated as follows:

EQ. 5 Serial Dilution Percent Difference

$$\%\text{Difference} = \frac{|I - S|}{I} \times 100$$

WHERE, I = Initial Sample Result (Instrument Reading)

S = Serial Dilution Result (Instrument Reading x5)

12.10.4 In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within the contract criteria, flag all samples in the SDG. Serial dilution results and "E" flags shall be reported on Form VIII-IN.

12.10.5 If the internal standard responses for the field sample chosen for serial dilution analysis are not within the limits and the appropriate corrective action (two-fold dilution and reanalysis) is taken, the following shall apply to the serial dilution analysis: if the internal standard responses of the field sample reanalysis are within the limits, the serial dilution results are to be reported

from a five-fold dilution of the reanalyzed sample. If the internal standard responses of the field sample reanalysis are not within the limits, the serial dilution results are to be reported from a five-fold dilution of the original sample.

12.11 Internal Standards

12.11.1 The analyst shall monitor the responses from the internal standards throughout the sample set being analyzed. Ratios of the internal standard responses between isotopes should also be routinely monitored. This information may be used to correct potential problems caused by mass dependent drift, errors incurred in adding the internal standards or increases in the concentrations of individual internal standards caused by background contributions from the sample. The absolute response of any one internal standard must not deviate more than 60-125% of the original response in the calibration blank. If deviations greater than these are observed in field samples, matrix spikes, or duplicate samples, the original sample shall be diluted by a factor of two, internal standards added, and the sample re-analyzed. If the internal standard responses for the diluted sample analysis are within the limits, report the results of this analysis on the appropriate Summary Form. If the internal standard responses for the diluted sample analysis are not within the limits, note this in the SDG Narrative and report the results of the undiluted original sample analysis on the appropriate Summary Form.

12.12 Method Detection Limit (MDL) Determination

12.12.1 Before any field samples are analyzed under this contract, the MDLs shall be determined for each instrument used, prior to the start of contract analyses, and annually thereafter, and shall meet the levels specified in Exhibit C.

An MDL study shall be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions to verify the current sensitivity of the analysis.

12.12.2 To determine the MDLs, the Contractor shall run MDL studies following the procedures given in 40 CFR, Part 136. The Contractor shall prepare the MDL samples by each digestion procedure used and shall analyze these samples on each instrument used. The Contractor shall also analyze non-prepared MDL samples on each instrument used.

12.12.3 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C.

12.12.4 The direct analysis MDL (Preparation Method/Code "NP1") shall be used to determine the appropriate concentration qualifier for the results of instrument QC.

12.12.5 The results of the MDL determination studies shall be forwarded to the USEPA Regional CLP PO, Sample Management Office (SMO), and Quality Assurance Technical Support (QATS).

12.12.6 The MDL results shall be reported on Form IX-IN.

12.13 Linear Dynamic Range (LDR)

12.13.1 Before any field samples are analyzed under this contract, the upper limit of the linear calibration range shall be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range, prior to the start of contract analyses

and at least quarterly thereafter. The linear calibration range used for the analysis of samples shall be determined from the resulting data. The upper LDR limit shall be an observed signal no more than 10% below the level extrapolated from lower standards. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and re-analyzed. The LDRs must be verified whenever a change in instrument hardware operating conditions indicate they should be redetermined, or verified quarterly.

12.14 Example Analytical Sequence for ICP-MS

Tune
S0
S
ICV
ICB
CRI
ICSA
ICSAB
CCV
CCB
10 samples
CCV
CCB
7 samples
CRI
CCV
CCB
10 samples, etc.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 1.15 in Exhibit D - Introduction to Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 1.16 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry. Method 200.8. Revision 5.4. 1994.

16.2 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Method 6020A. Third Edition, Update IV-A. 1986.

16.3 US Government Printing Office. 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

16.4 US Environmental Protection Agency. Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry. Method 200.8. Revision 5.4. 1994. Modified for the Contract Laboratory Program.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1. Isobaric Molecular-Ion Interferences

Analyte	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{121}Sb	PdO		AgN			AgC	
^{123}Sb	AgO		AgN	SrCl	ZrS	CdC	
^{75}As	CoO	NiOH	NiN	ArCl	CaS	CuC	
^{138}Ba	SnO	SbOH					
^{137}Ba	SbO	SnOH		MoCl			
^{136}Ba	SnO	SnOH				SnC	
^{135}Ba	SnO	SnOH		MoCl			
^{134}Ba	SnO	SnOH	SnN	MoCl		SnC	
^{132}Ba	SnO, CdO	InOH	SnN	MoCl	MoS	SnC	
^{130}Ba	CdO	CdOH	SnN, CdN	MoCl	MoS	SnC	
^{9}Be							
^{114}Cd	MoO	MoOH	MoN	SeCl	SeS		
^{112}Cd	MoO, ZrO	MoOH	MoN	SeCl, AsCl	SeS	MoC	
^{111}Cd	MoO	MoOH	MoN	GeCl			
^{110}Cd	MoO, ZrO		MoN, ZrN	GeCl, AsCl	SeS	MoC	
^{113}Cd	MoO	MoOH		SeCl, AsCl			
^{116}Cd	MoO						
^{106}Cd	ZrO		MoN, ZrN		GeS	MoC, ZrC	
^{108}Cd	MoO, ZrO	ZrOH	MoN, ZrN	GeCl	SeS, GeS	MoC, ZrC	
^{52}Cr	ArO	ClOH				ArC	
^{53}Cr	ClO	ArOH	KN	NCl, OCl		KC	
^{50}Cr	SO		ArN		SO	ArC	Mo^{++}
^{54}Cr		ClOH	ArN, CaN			CaC	
^{59}Co	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn^{++}
^{63}Cu	TiO, PO_2	TiOH	TiN	SiCl, MgCl	PS	VC	ArNa
^{65}Cu	TiO	TiOH	VN	SiCl	S_2, SO_2H	CrC	
^{208}Pb							
^{206}Pb							

Table 1. Isobaric Molecular-Ion Interferences (Con't)

Analyte	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{207}Pb							
^{204}Pb							
^{55}Mn	KO	ArOH	KN		NaS	CaC	Cd^{++}
^{202}Hg	WO						
^{200}Hg	WO	WOH	WN				
^{199}Hg	WO	WOH					
^{201}Hg		WOH					
^{198}Hg	WO	TaOH	WN			WC	
^{204}Hg							
^{196}Hg			WN			WC	
^{58}Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd^{++}, Sn^{++}
^{60}Ni	CaO	CaOH	TiN	MgCl, NaCl	SiS	TiC	Sn^{++}
^{62}Ni	TiO	ScOH	TiN	AlCl, MgCl	SiS	TiC, CrC	Sn^{++}
^{61}Ni	ScO	CaOH	TiN	MgCl	SiS	TiC	Sn^{++}
^{64}Ni	TiO	TiOH	TiN, CrN	SiCl, AlCl	S_2	CrC	
^{80}Se	ZnO	CuOH	ZnN	ScCl, CaCl	TiS	ZnC	
^{78}Se	NiO	NiOH	ZnN	CaCl, KCl	TiS	ZnC	
^{82}Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		
^{76}Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
^{77}Se	NiO	NiOH	CuN	CaCl, ArCl	ScS	CuC	
^{74}Se	NiO	FeOH	NiN	Cl_2, KCl	CaS	NiC	
^{107}Ag	ZrO	ZrOH		GeCl	AsS	MoC	
^{109}Ag		MoOH	MoN	GeCl	SeS	MoC	
^{205}Tl							
^{203}Tl		WOH					
^{51}V	ClO	SOH	ClN	ClO, ClN	FS	KC	
^{50}V	SO		ArN			ArC	Mo^{++}
^{64}Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	S_2	CrC	
^{66}Zn	TiO	TiOH	CrN	PCl, SiCl	S_2	FeC	
^{68}Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba^{++}

Table 1. Isobaric Molecular-Ion Interferences (Con't)

Analyte	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{67}Zn	VO	TiOH	CrN	SCl	ClS	MnC	Ba^{++}
^{70}Zn	FeO	CrOH	GeN	Cl_2	ArS	NiC	

NOTE: The information provided in this table does not indicate that all of the described interferences need to be tested. However, this table can be consulted if unusual samples are encountered.

Table 2. Mass Choices for Elements that Must Be Monitored During the Analytical Run

Mass	Element of Interest
121	Antimony
75	Arsenic
134, 135, 136, 137	Barium
9	Beryllium
111, 114	Cadmium
52, 53	Chromium
59	Cobalt
63, 65	Copper
206, 207, 208	Lead
24, 25, 26	Magnesium
55	Manganese
60, 61, 62	Nickel
77, 78, 80, 82	Selenium
107, 109	Silver
203, 205	Thallium
51	Vanadium
66, 67, 68	Zinc

NOTE: Underlined isotopes are preferred for measurements. Where possible, alternative isotopes are indicated. Those isotopes not listed shall not be used as a primary isotope for measurement, although they may be monitored for interference corrections if necessary.

Table 3. Recommended Elemental Expressions for Isobaric Interferences

Element	Isobaric Correction	Expression Proportional to Elemental Concentration
Sb	none	$(1.0000)(^{121}C)$
As	ArCl, Se	$(1.0000)(^{75}C) - (3.127)[(^{77}C) - (0.815)(^{82}C)]$
Ba	none	$(1.0000)(^{137}C)$
Be	none	$(1.0000)(^{9}C)$
Cd	MoO, Pd	$(1.000)(^{111}C) - (1.073)[(^{108}C) - (0.712)(^{106}C)]$
Cr	none	$(1.0000)(^{52}C)$
Co	none	$(1.0000)(^{59}C)$
Cu	none	$(1.0000)(^{63}C)$
Pb	none	$(1.0000)(^{206}C) + (1.0000)(^{207}C) + (1.0000)(^{208}C)$
Mn	none	$(1.0000)(^{55}C)$
Ni	none	$(1.0000)(^{60}C)$
Se	none	$(1.0000)(^{82}C)$
Ag	none	$(1.0000)(^{107}C)$
Tl	none	$(1.0000)(^{205}C)$
V	ClO, Cr	$(1.0000)(^{51}C) - (3.127)[(^{53}C) - (0.113)(^{52}C)]$
Zn	none	$(1.0000)(^{66}C)$
Sc	none	$(1.0000)(^{45}C)$
Y	none	$(1.0000)(^{89}C)$
Rh	none	$(1.0000)(^{103}C)$
In	Sn	$(1.0000)(^{115}C) - (0.0140)(^{118}C)$
Tb	none	$(1.0000)(^{159}C)$
Ho	none	$(1.0000)(^{165}C)$
Bi	none	$(1.0000)(^{209}C)$

C - Calibration blank subtracted counts at specified mass

The coefficients in correction equations were calculated using natural isotopic abundances, and assuming zero instrumental fractionation. For each particular instrument these coefficients must be determined experimentally.

The correction equations shall not be applied if appropriate interference check sample measurement demonstrates absence of interference above the CRQL.

Table 4. Internal Standards (must use at least five)

Internal Standard	Mass	CAS Number
Lithium	6	7439-93-2
Scandium	45	7440-20-2
Yttrium	89	7440-65-5
Rhodium	103	7440-16-6
Indium	115	7440-74-6
Terbium	159	7440-27-9
Holmium	165	7440-60-0
Lutetium	175	7439-94-3
Bismuth	209	7440-69-9

NOTE: Use of Li^6 requires enriched standard.

Table 5. Spiking Levels for Spike Sample Analysis

Analyte	Spike (µg/L)
Sb	100
As	40
Ba	2000
Be	50
Cd	50
Cr	200
Co	500
Cu	250
Pb	20
Mn	500
Ni	500
Se	10
Ag	50
Tl	50
V	500
Zn	500

EXHIBIT D - PART C

ANALYTICAL METHODS
FOR
COLD VAPOR MERCURY ANALYSIS

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Exhibit D - Analytical Methods for Cold Vapor Mercury Analysis

Table of Contents

Table of Contents (Con't)

1.0 SCOPE AND APPLICATION

The analytical method that follows is designed to analyze water, sediment, sludge, and soil samples taken from hazardous waste sites using a cold vapor technique with Atomic Absorption (AA) for total mercury.

In addition to inorganic forms of mercury, organic mercury may also be present. These organo-mercury compounds will not respond to the cold vapor AA technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but studies have shown that a number of organo-mercury compounds, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to ensure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in, or spiked to, a natural system.

The range of the method may be varied through instrument and/or recorder expansion. Using a 100 milliliters (mL) sample, a detection limit of less than 0.1 micrograms per Liter (µg/L) can be achieved.

The range of the method for soil/sediments is 0.05 milligrams per kilogram (mg/kg) to 5 mg/kg. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.

2.0 SUMMARY OF METHOD

2.1 Water by Automated and Manual Techniques

This is a physical method based on the absorption of radiation at 253.7 nanometers (nm) by mercury vapor. Free mercury atoms can exist at room temperature; therefore, mercury can be measured by Atomic Absorption (AA) without a heated sample cell. Organic compounds are oxidized, and in the cold vapor mercury technique, mercury is chemically reduced to the free atomic state by reacting the sample with a strong reducing agent like stannous chloride or sodium borohydride in a closed reaction vessel. The volatile free mercury is then driven from the reaction flask by bubbling air through the solution. Mercury atoms are carried in the air stream through tubing connected to an absorption cell, which is placed in the light path of the AA spectrophotometer. Sometimes the cell is heated slightly to avoid water condensation; otherwise the cell is completely unheated. As the mercury atoms pass into the sampling cell, measured absorbance rises indicating the increasing concentration of mercury atoms in the light path. Some systems allow the mercury vapor to pass from the absorption tube to waste, in which case the absorption peaks and then falls as the mercury is depleted. The highest absorbance observed during the measurement will be taken as the analytical signal.

2.2 Soil/Sediment by Manual Technique

2.2.1 A weighed portion of the sample is acid digested for 2 minutes at 95°C, followed by oxidation with potassium permanganate and potassium persulfate. Mercury in the digested sample is then measured by the conventional cold vapor technique.

2.2.2 An alternate digestion involving the use of an autoclave is described in Section 10.1.4.2.1.2.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Water

4.1.1 Some sea waters and wastewaters high in chlorides have shown a positive interference, and require additional permanganate [as much as 25 milliliters (mL)]. During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation at 253 nanometers (nm). Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.

4.1.2 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.

4.1.3 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 milligram per Liter (mg/L) of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

4.1.4 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on recovery of mercury from spiked samples.

4.1.5 Samples containing solids must be blended and then mixed while being sampled if total mercury values are to be reported.

4.2 Soil/Sediment

4.2.1 The same types of interferences that may occur in water samples are also possible with sediments (i.e., sulfides, high copper, high chlorides, etc.).

4.2.2 Samples containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

5.0 SAFETY

See Section 1.14 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 General Information for Water and Soils (Automated and Manual Techniques)

6.1.1 Atomic Absorption (AA) Spectrophotometer - Any AA unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the AA spectrophotometer.

NOTE: All cold vapor mercury analyzers shall be equipped with all manufactured required equipment (i.e., dryers) to ensure that the specified CRQLs are met.

6.1.2 Mercury Hollow Cathode Lamp

6.1.3 Recorder - Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

6.2 Water by Automated Technique

6.2.1 Automated Analyzer instrumentation consisting of:

6.2.1.1 Sampler with provision for sample mixing

6.2.1.2 Manifold

6.2.1.3 Proportioning Pump(s)

6.2.1.4 High temperature heating bath with distillation coil(s)

6.2.1.5 Vapor-liquid separator

6.2.1.6 Absorption cell with quartz windows

6.3 Water and Soil/Sediment by Manual Technique

6.3.1 Absorption Cell - Standard spectrophotometer cells

6.3.2 Air Pump - Any device capable of delivering 1 Liter (L) of air per minute may be used.

6.3.3 Flowmeter - Capable of measuring an air flow of 1 L per minute.

6.3.4 Aeration Tubing - Tygon tubing is used for transporting the mercury vapor from the sample bottle to the absorption cell and for its return.

6.3.4.1 Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.

6.3.5 Drying Tube - 6" X 3/4" diameter tube containing 20 grams (g) of magnesium perchlorate.

NOTE: In place of the magnesium perchlorate drying tube, a small reading lamp with a 60-watt bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient temperature.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Water by Automated Technique

7.1.1.1 Reagent Water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-77). Use this preparation for all reagents, standards, and dilutions of solutions.

7.1.1.2 Sulfuric acid, concentrated - Reagent grade.

7.1.1.2.1 Sulfuric acid, 2N - Dilute 56 milliliters (mL) of concentrated sulfuric acid to 1 Liter (L) with reagent water.

7.1.1.2.2 Sulfuric acid, 10% - Dilute 100 mL concentrated sulfuric acid to 1 L with reagent water.

7.1.1.3 Nitric acid, concentrated - Reagent grade of low mercury content.

Nitric acid, 0.5% wash solution - Dilute 5 mL of concentrated nitric acid to 1 L with reagent water.

7.1.1.4 Stannous sulfate - Add 50 grams (g) stannous sulfate to 500 mL of 2N sulfuric acid (see Section 7.1.1.2.1). This mixture is a suspension and should be stirred continuously during use.

NOTE: Stannous chloride may be used in place of stannous sulfate.

7.1.1.5 Sodium chloride-hydroxylamine sulfate solution - Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in reagent water to 1 L.

NOTE: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

7.1.1.6 Potassium permanganate ($KMnO_4$) - 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 L of reagent water.

7.1.1.7 Potassium permanganate, 0.1N - Dissolve 3.16 g of potassium permanganate in reagent water and dilute to 1 L.

7.1.1.8 Potassium persulfate - 0.5% solution, w/v. Dissolve 5 g of potassium persulfate in 1 L of reagent water.

7.1.1.9 Air scrubber solution - Mix equal volumes of 0.1N potassium permanganate (see Section 7.1.1.6) and 10% sulfuric acid (see Section 7.1.1.2.2).

7.1.2 Water and Soil/Sediment by Manual Technique

7.1.2.1 Reagent water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-77). Use this preparation for all reagents, standards, and dilutions of solutions.

7.1.2.2 Sulfuric acid, concentrated - Reagent grade.

7.1.2.2.1 Sulfuric acid, 0.5N - Dilute 14.0 mL of concentrated sulfuric acid to 1 L. (Water technique only.)

7.1.2.3 Nitric acid, concentrated - Reagent grade of low mercury content. If a high Preparation Blank (PB) is obtained, it may be necessary to distill the nitric acid.

7.1.2.4 Stannous sulfate - Add 25 g stannous sulfate to 250 mL of 0.5N sulfuric acid. This mixture is a suspension and should be stirred continuously during use.

NOTE: Stannous chloride may be used in place of stannous sulfate.

7.1.2.5 Sodium chloride-hydroxylamine sulfate solution - Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL.

NOTE: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

7.1.2.6 Potassium permanganate ($KMnO_4$) - 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

7.1.2.7 Potassium persulfate - 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 mL of reagent water.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 8.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.1.1 Stock standard solutions may be purchased or prepared from reagent grade chemicals or metals.

7.2.1.2 Stock mercury solution - Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL [1.0 mL = 1.0 milligram (mg) Hg].

7.2.1.3 Working mercury solution - Make successive dilutions of the stock mercury solution (see Section 7.2.1.2) to obtain a working standard containing 0.1 micrograms (µg) per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution, prepare standards.

7.2.2 Working Standards

7.2.2.1 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

The concentration of the CRI for mercury shall be at the CRQL. Information regarding the CRI shall be reported on Form IIB-IN.

7.2.2.2 Method Detection Limit (MDL) Solution

The MDL solution shall be at a concentration of 3 to 5 times the expected MDL.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All samples must be collected in glass or polyethylene containers. Water/aqueous samples must be preserved with nitric acid to pH less than 2 immediately after collection. All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until digestion.

8.1.1 Dissolved Metals

For the determination of dissolved metals, the sample must be filtered through a 0.45 micrometer (µm) pore diameter membrane filter at the time of collection or as soon as possible. Use a portion of the sample to rinse the filter flask, discard this portion, and collect the required volume of filtrate. Preserve the filtrate with nitric acid to pH less than 2 immediately after filtration.

8.2 Procedure for Sample Storage

The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days the samples may be disposed of in a manner that complies with all applicable regulations.

8.3 Contract Required Holding Time

The maximum holding time for mercury is 26 days from Validated Time of Sample Receipt (VTSR).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Cold Vapor Atomic Absorption (AA) Instrument Calibration Procedure

9.1.1 Instruments shall be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time shall be included in the raw data.

9.1.2 The date and time of preparation and analysis shall be given in the raw data.

9.1.3 Calibration standards shall be prepared fresh with each preparation batch. Prepare a minimum of five calibration standards (which includes a blank) in graduated amounts in the appropriate range. One of the standards must be at the Contract Required Quantitation Limit (CRQL).

9.1.4 Aspirate the standards and record the readings. Results for these standards shall be within 5% of the true value. Each standard concentration and the calculations to show that the 5% criteria has been met shall be given in the raw data. If the values do not fall within this range, recalibration is necessary. The 5% criteria does not apply to the calibration standard at the CRQL. The acceptance criteria for the initial calibration curve is a correlation coefficient more than or equal to 0.995.

9.1.5 Baseline correction is acceptable as long as it is performed after every sample or after the Continuing Calibration Verification (CCV) and Blank (CCB) check. Resloping is acceptable as long as it is immediately preceded and immediately followed by a compliant CCV and CCB.

9.2 Initial Calibration Verification (ICV)

9.2.1 Immediately after the AA system has been calibrated, the accuracy of the initial calibration shall be verified and documented for mercury by the analysis of the ICV solution at the wavelength used for analysis.

9.2.2 Only if the ICV solution is not available from USEPA, or where a certified solution of the analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analyte from a different source than that used in the standards for the instrument calibration. The value for the ICV shall be reported on Form IIA-IN.

9.3 Continuing Calibration Verification (CCV)

9.3.1 To ensure calibration accuracy during each analysis run, one of the following standards is to be used for the CCV and shall be analyzed and reported at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard shall also be analyzed and reported at the beginning of the run and after the last analytical sample. The analyte concentration in the CCV standard shall be different than the concentration used for the ICV and shall be one of the following solutions at or near the mid-range level of the calibration curve:

- USEPA Solutions
- NIST Standards
- A Contractor-prepared standard solution

The same CCV standard shall be used throughout the analysis runs for a Sample Delivery Group (SDG) of samples received.

9.3.2 Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses, and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it, as well as the difference in time between the CCV and the analytical sample immediately preceding it, may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

9.3.3 Information regarding the CCV shall be reported on Form IIA-IN.

9.4 Initial and Continuing Calibration Blank (ICB/CCB)

A calibration blank shall be analyzed at each wavelength used for analysis immediately after every ICV and CCV, at a frequency of 10% or every 2 hours during the run, whichever is more frequent. The blank shall be analyzed at the beginning of the run and after the last analytical sample.

NOTE: A CCB shall be analyzed immediately after the last CCV, and the last CCV shall be analyzed immediately after the last analytical sample of the run. The results for the calibration blanks shall be reported on Form III-IN.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to inform them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample, and analyze one or more of the phases separately. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside the scope), the Region may require the Contractor to do any of the following:

- Separate the phases and analyze the phase(s) that is (are) amenable to analysis. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Water Preparation of Standards and Samples (Manual Technique)

10.1.3.1 Standards Preparation

10.1.3.1.1 Transfer aliquots of the working mercury solution to a series of 300 milliliters (mL) BOD bottles or other suitable digestion vessels. Add enough reagent water to each bottle to make a total volume of 50-100 mL.

10.1.3.1.2 Mix thoroughly and add 5 mL of concentrated sulfuric acid (see Section 7.1.2.2) and 2.5 mL of concentrated nitric acid (see Section 7.1.2.3) to each bottle. Add 15 mL of $KMnO_4$ (see Section 7.1.2.6) solution to each bottle and allow to stand at least 15 minutes. Add 8 mL of potassium persulfate (see Section 7.1.2.7) to each bottle and heat for 2 hours in a water bath or block digester maintained at 95°C. (If an autoclave is employed, cover the BOD bottles with foil and heat in the autoclave for 15 minutes at 120°C and 15 PSI instead of heating for 2 hours in a waterbath at 95°C). Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (see Section

7.1.2.5) to reduce the excess permanganate. When the solution has been decolorized, wait 30 seconds, add 5 mL of the stannous sulfate solution (see Section 7.1.2.4) and immediately attach the bottle to the aeration apparatus to form a closed system. At this point the sample is allowed to stand quietly without manual agitation. If volumes less than 100 mL are used, all other reagents shall be reduced accordingly (e.g., if 50 mL is used, reduce reagent volumes by one-half).

10.1.3.1.3 The circulating pump, which has previously been adjusted to a rate of 1 Liter (L) per minute, is allowed to run continuously (see Note 1). The absorbance will increase and reach maximum within 30 seconds. As soon as the response levels off, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 2). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting instrument response at 253 nanometers (nm) versus micrograms (µg) of mercury.

NOTE 1: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 2: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as equal volumes of 0.1 M $KMnO_4$, and 10% H_2SO_4 or 0.25% iodine in a 3% KI solution. A specially treated charcoal that will adsorb mercury vapor is commercially available.

10.1.3.2 Sample Preparation

10.1.3.2.1 Preparation Method/Code (CW1)

10.1.3.2.1.1 Transfer 50-100 mL, or an aliquot diluted to 50-100 mL, containing not more than 1.0 µg of mercury, to a 300 mL BOD bottle or other suitable digestion vessel, and continue as described in Section 10.1.3.1.2.

NOTE: The same amount of $KMnO_4$ added to the samples should be present in standards and blanks.

10.1.3.2.1.2 Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (see Section 7.1.2.5) to reduce the excess permanganate. Purge the headspace in the BOD bottle for at least 1 minute and add 5 mL of stannous sulfate (see Section 7.1.2.4) and immediately attach the bottle to the aeration apparatus.

NOTE: Add reductant in 6 mL increments until $KMnO_4$ is completely reduced (until the color is no longer purple).

10.1.4 Soil/Sediment Preparation of Standards and Samples (Manual)

10.1.4.1 Standards Preparation

10.1.4.1.1 Transfer aliquots of the working mercury solutions (see Section 7.2.1.3) to a series of 300 mL BOD bottles or other suitable digestion vessels. Add enough reagent water to each bottle to make a total volume of 10 mL.

10.1.4.1.2 Add 5 mL of concentrated H_2SO_4 (see Section 7.1.2.2) and 2.5 mL of concentrated HNO_3 (see Section 7.1.2.3) and heat 2 minutes in a water bath or block digester at 95°C. Allow the sample to cool and add 50 mL reagent water, 15 mL of $KMnO_4$ solution (see Section 7.1.2.6) and 8 mL of potassium persulfate solution (see Section 7.1.2.7) to each bottle and return to the water bath or block digester for 30 minutes. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (see Section 7.1.2.5) to reduce the excess permanganate. Add 50 mL of reagent water (final volume of reagent water = 100 mL). Treating each bottle individually, add 5 mL of stannous sulfate solution (see Section 7.1.2.4) and immediately attach the bottle to the aeration apparatus. At this point the sample is allowed to stand quietly without manual agitation. If an autoclave is used, the standards shall be prepared in the same way as the samples (see Section 10.1.4.2.1.2).

10.1.4.1.3 The circulating pump, which has previously been adjusted to a rate of 1 L per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the response levels off, open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus µg of mercury.

10.1.4.2 Sample Preparation

10.1.4.2.1 Preparation Method/Code (CS1)

10.1.4.2.1.1 Weigh a representative 0.20 g (±0.01 g) portion of wet sample and place in the bottom of a BOD bottle. Add enough reagent water to each sample to make a total volume of 10 mL. Continue as described in Section 10.1.4.1.2.

10.1.4.2.1.2 If an autoclave is used, add 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 to the 0.20 g (±0.01 g) of sample. Add 5 mL of saturated $KMnO_4$ solution and 8 mL of potassium persulfate solution and cover with a piece of aluminum foil. The sample is autoclaved at 120°C and 15 PSI for 15 minutes. Cool, make up to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution (see Section 7.1.2.5) to reduce the excess permanganate. Purge the headspace of the sample bottle for at least one minute and continue as described under Section 10.1.4.1.2.

10.1.5 Preparation of Standards for Automated Cold Vapor Analysis Technique (Analysis Method - AV)

10.1.5.1 Standards Preparation

Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution, prepare standards.

10.2 Sample Analysis

10.2.1 Set up instrument with proper operating parameters.

10.2.2 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using calibration standard solutions mentioned in Section 9.1. Samples prepared by a certain method must be analyzed with calibration and QC standards prepared by the same method. Therefore, only one Preparation Method/Code can be associated with each run.

10.2.3 Analyze the Continuing Calibration Verification (CCV) instrument check standard and the Continuing Calibration Blank (CCB) after every 10 analytical samples.

10.2.4 Analysis of Water/Aqueous Samples by the Automated Cold Vapor Technique (AV) Preparation Method/Code (CW2)

10.2.4.1 Set up manifold.

10.2.4.2 Feed all the reagents through the system with acid wash solution (see Section 7.1.1.3) through the sample line, adjusting the heating bath to 105°C.

10.2.4.3 Turn on the Atomic Absorption (AA) Spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.

10.2.4.4 Arrange working mercury standards in sampler and start sampling. Complete loading of sample tray with unknown samples.

10.2.4.5 After the analysis is complete, put all lines except the H_2SO_4 line in reagent water to wash out system. After flushing, wash out the H_2SO_4 line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (see Section 7.1.1.4) through the sample lines followed by reagent water. This will prevent build-up of oxides of manganese.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Water/Aqueous by Automated Technique

11.1.1 Prepare a standard curve by plotting the instrumental response of processed standards against true concentration values. Use a linear regression equation to determine the concentration of field and Quality Control (QC) samples.

11.1.2 If samples were diluted for analysis, multiply the results from the linear regression by the dilution factor.

11.2 Water/Aqueous by Manual Technique

11.2.1 Determine the instrumental response of the unknown and determine the mercury value from the standard curve.

11.2.2 Calculate the mercury concentration in the sample by the formula:

EQ. 1 Aqueous Sample Concentration (Manual)

$$\text{Hg Concentration } (\mu g/L) = \frac{\mu g \text{ Hg, curve}}{\text{aliquot volume, mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

11.3 Soil by Manual Technique

11.3.1 Measure the instrumental response of the unknown and determine the mercury value from the standard curve.

11.3.2 Calculate the mercury concentration in the sample by the formula:

EQ. 2 Soil Sample Concentration (Manual)

$$\text{Hg Concentration (mg/kg)} = \text{Hg } \mu g/g = \frac{C}{W \times S} \times (0.1L)$$

WHERE, C = Concentration from curve (µg/L)

W = Wet sample weight (g)

S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6).

11.4 Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation

To calculate the adjusted MDL or adjusted CRQL for water/aqueous samples, multiply the value of the MDL (µg/L) or CRQL (µg/L) by the Dilution Factor. Calculate the adjusted MDL or adjusted CRQL for soil samples as follows:

EQ. 3 Adjusted Soil MDL/Adjusted Soil CRQL Concentration

$$\text{Adjusted Concentration (dry wt.)(mg/kg)} = C \times \frac{W_M}{W_R} \times \frac{1}{S} \times DF$$

WHERE,

C	=	MDL or CRQL concentration (mg/kg)
W_M	=	Method required wet sample weight (g)
W_R	=	Reported wet sample weight (g)
S	=	% Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6).
DF	=	Dilution Factor

12.0 QUALITY CONTROL

12.1 Initial Calibration Verification (ICV)

The ICV Standard shall be prepared in the same acid matrix as the samples and carried through the entire preparation and analysis procedure. If measurements exceed the control limits of 80% (low) and 120% (high), the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. Information regarding the ICV shall be reported on Form IIA-IN.

12.2 Continuing Calibration Verification (CCV)

The CCV Standard shall be prepared by the analyst at a concentration equivalent to the mid-point of the calibration curve and carried through the entire preparation and analysis procedure. If the deviation of the CCV is greater than the control limits of 80% (low) and 120% (high), the analysis shall be stopped, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification shall be performed. Information regarding the CCV shall be reported on Form IIA-IN.

12.3 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

12.3.1 To verify linearity near the CRQL, the Contractor shall analyze a CRI at the beginning and end of each sample analysis run, immediately following the ICV/ICB. In addition, the Contractor shall analyze and report the results for the CRI at a frequency of not less than once per 20 analytical samples[1] per analysis run. The CRI analysis shall be run immediately followed by the CCV and Continuing Calibration Blank (CCB) analyses. The CRI shall be prepared by spiking an aliquot of reagent water with mercury at the CRQL. The CRI shall be taken through the same process used to digest and analyze the associated samples.

12.3.2 CRI and percent recovery results shall be reported on Form IIB-IN. If the percent recovery falls outside the control limits of 70-130%, the CRI shall be re-analyzed immediately. If the result of the re-analysis falls within the control limits, no further corrective action is required. If the result of the re-analysis does not fall within the control limits, the analysis shall be terminated, the problem corrected, the instrument recalibrated, or the CRI and associated samples redigested and analyzed.

12.4 Blank Analyses

There are two different types of blanks required by this method. The calibration blank is used in establishing the analytical curve while the preparation blank is used to monitor for possible contamination.

12.4.1 Initial and Continuing Calibration Blank (ICB/CCB)

The ICB and CCB are prepared with acids and reagent water and carried through the entire preparation and analysis procedure. If the absolute value of the calibration blank (ICB/CCB) result exceeds the CRQL (see Exhibit C), the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical

[1]As defined in Exhibit G, CRI is an analytical sample.

samples analyzed since the last compliant calibration blank shall be performed.

12.4.2 Preparation Blank (PB)

12.4.2.1 The PB shall contain all the reagents and in the same volumes as used in processing the samples. The PB shall be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

12.4.2.2 At least one PB, consisting of reagent water processed through each sample preparation and analysis procedure (see Section 10), shall be prepared and analyzed with every Sample Delivery Group (SDG), or with each batch[2] of samples digested, whichever is more frequent.

12.4.2.3 The first batch of samples in an SDG is to be assigned to Preparation Blank one, the second batch to Preparation Blank two, etc. (see Form III-IN). Each Sample Data Package shall contain the results of all PB analyses associated with the samples in that SDG.

12.4.2.4 The PB is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

12.4.2.4.1 If the absolute value of the concentration of the blank is less than or equal to the CRQL (see Exhibit C), no further action is required.

12.4.2.4.2 If the analyte concentration in the blank is above the CRQL, the lowest concentration of the analyte in the associated samples shall be greater than or equal to 10 times the blank concentration. Otherwise, all samples associated with that blank, with the analyte concentration less than 10 times the blank concentration and above the CRQL, shall be redigested and re-analyzed with appropriate new Quality Control (QC). The only exception to this shall be an identified field blank. The sample concentration is not to be corrected for the blank value.

12.4.2.4.3 If the concentration of the blank is below the negative CRQL, then all samples reported below 10 times the CRQL and associated with the blank shall be redigested and re-analyzed with appropriate new QC.

12.4.2.4.4 The values for the PB shall be reported on Form III-IN.

12.5 Spike Sample Analysis

12.5.1 The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and/or measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents). At least one spike sample analysis (matrix spike) shall be performed on each group of samples of a similar matrix type (i.e., water, soil) or for each SDG.[3] The sample

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[2]A group of samples prepared at the same time.

[3]USEPA may require additional spike sample analyses, upon USEPA Regional CLP Project Officer (CLP PO) request.

and its associated spike sample shall initially be run at the same dilution.

12.5.2 If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.6). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for spiked sample analysis. USEPA may require that a specific sample be used for the spike sample analysis.

12.5.3 The analyte spike shall be added at 1 µg/L (water) or 0.5 mg/kg (soil). Adjustment shall be made to maintain these spiking levels when the weight of sample taken deviates by more than 10% of these values.

12.5.4 If the spike recovery is not at or within the limits of 75-125%, the data of all samples received and associated with that spike sample and determined by the same analytical method shall be flagged with the letter "N" on Forms IA-IN and VA-IN. An exception to this rule is granted when the sample concentration exceeds the spike added concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

12.5.5 In the instance where there is more than one spike sample per matrix, per method, per SDG, and one spike sample recovery is not within contract criteria, flag all the samples of the same matrix and method in the SDG. Individual component percent recoveries (%R) are calculated as follows:

EQ. 4 Spike Percent Recovery

$$\%\ \text{Recovery} = \frac{SSR - SR}{SA} \times 100$$

WHERE, SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

12.5.6 When sample concentration is less than the Method Detection Limit (MDL), use SR = 0 only for purposes of calculating percent recovery. The Spike Sample Results (SSRs), Sample Results (SRs), Spike Added (SA), and percent recovery (positive or negative) shall be reported on Form VA-IN.

12.5.7 The units used for reporting SSRs will be identical to those used for reporting sample results on Form IA-IN.

12.6 Duplicate Sample Analysis

12.6.1 One duplicate sample shall be analyzed from each group of samples of a similar matrix type (i.e., water, soil) or for each SDG.[4] Duplicates cannot be averaged for reporting on Form IA-IN. The

[4]USEPA may require additional duplicate sample analyses, upon USEPA Regional CLP PO request.

sample and its associated duplicate sample shall initially be run at the same dilution.

12.6.2 Duplicate sample analyses are required for percent solids. Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. USEPA may require that a specific sample be used for duplicate sample analysis. The Relative Percent Difference (RPD) is calculated as follows:

EQ. 5 Duplicate Sample Relative Percent Difference

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

WHERE, RPD = Relative Percent Difference

S = Sample Result (original)

D = Duplicate Result

12.6.3 The results of the duplicate sample analyses shall be reported on Form VI-IN. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to five times the CRQL (see Exhibit C). A control limit of the CRQL value shall be entered in the "Control Limit" column on Form VI-IN if either the sample or duplicate value is less than five times the CRQL. If the sample and duplicate values are greater than or equal to five times the CRQL, or if the sample and duplicate values are less than the CRQL, the "Control Limit" field is left empty.

12.6.4 If one result is above five times the CRQL level and the other is below, use the CRQL criteria to determine if the duplicate analysis is in control. If both sample and duplicate values are less than the MDL, the RPD is not calculated on Form VI-IN. For solid sample or solid duplicate results less than five times the CRQL, enter the value of the CRQL, corrected for sample weight and percent solids (i.e., original, not duplicate sample weight and percent solids), in the "Control Limit" column. If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on Forms IA-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix and method in the SDG. The percent difference data will be used by USEPA to evaluate the long-term precision of the method. Specific control limits for each element will be added to Form VI-IN at a later date based on these precision results.

12.7 Laboratory Control Sample (LCS) Analysis

12.7.1 A solid LCS (LCSS) shall be analyzed using the same sample preparations, analytical methods, and Quality Assurance (QA)/QC procedures employed for the EPA samples received.

12.7.2 The USEPA provided LCSS shall be prepared and analyzed using the procedures applied to the solid samples received (exception: percent solids determination not required). If the USEPA LCSS is unavailable, other USEPA QC Check samples or other certified materials may be used. In such a case, control limits for the LCSS must be documented and provided. One LCSS shall be prepared and

analyzed for every group of solid samples in a SDG, or for each batch of samples digested, whichever is more frequent.

12.7.3 All LCSS and percent recovery results will be reported on Form VII-IN. If the results for the LCSS fall outside the control limits established by USEPA, the analyses shall be terminated, the problem corrected, and the samples associated with that LCSS redigested and re-analyzed with appropriate new QC.

12.8 Method Detection Limit (MDL) Determination

12.8.1 Before any field samples are analyzed under this contract, the MDLs shall be determined for each digestion procedure and instrument used, prior to the start of contract analyses, and annually thereafter, and shall meet the levels specified in Exhibit C.

An MDL study shall be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions, to verify the current sensitivity of the analysis.

12.8.2 To determine the MDLs, the Contractor shall run MDL studies following the procedures given in 40 CFR, Part 136. The Contractor shall prepare the MDL samples by each digestion procedure used and shall analyze these samples on each instrument used.

12.8.3 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C.

12.8.4 The results of the MDL determination studies shall be forwarded to the USEPA Regional CLP PO, Sample Management Office (SMO), and Quality Assurance Technical Support (QATS).

12.8.5 The MDL results shall be reported on Form IX-IN.

12.9 Example Analytical Sequence for Mercury

S0
S0.2
S0.5
S1.0
S2.0
S5.0
S10.0
ICV
ICB
CRI
CCV
CCB
10 samples
CCV
CCB
9 samples
CRI
CCV
CCB
10 samples, etc.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 1.15 in Exhibit D - Introduction to Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 1.16 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 245.1. 1974.

16.2 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 245.2. 1974.

16.3 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 245.5. 1974.

16.4 US Government Printing Office. 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Not applicable.

EXHIBIT D - PART D

ANALYTICAL METHODS
FOR
TOTAL CYANIDE ANALYSIS

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Exhibit D - Analytical Methods for Total Cyanide Analysis

Table of Contents

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1.0 SCOPE AND APPLICATION

The analytical method that follows is designed to analyze various water types, sediment, sludge, and soil samples taken from hazardous waste sites, for total cyanide.

This analytical method includes the use of acid and heat to remove cyanide from the sample.

2.0 SUMMARY OF METHOD

2.1 Waters and Soils

2.1.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

2.1.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl), by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read between 570 and 580 nanometers (nm). To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

Interferences are eliminated or reduced by using the distillation procedure.

4.1 Sulfides

Sulfides adversely affect the colorimetric procedure. The sample should be tested in the field for the presence of sulfides as described in Section 8.1.1.

4.2 Surfactants

The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoam agent will prevent the foam from collecting in the condenser.

4.3 Oxidizing Agents

Oxidizing agents such as chlorine decompose most of the cyanides. The sample should be tested in the field for the presence of oxidizing agents as described in Section 8.1.1.

5.0 SAFETY

See Section 1.14 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Conventional Distillation of Water and Soils

6.1.1 Reflux distillation apparatus. The boiling flask should be of 1 Liter (L) size with an inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.1.2 Spectrophotometer suitable for measurements between 570 and 580 nanometers (nm) with a 1.0 centimeter (cm) cell or larger (for manual spectrophotometric method).

6.1.3 Automated analyzer instrumentation (for automated spectrophotometric method) including:

6.1.3.1 Sampler

6.1.3.2 Pump

6.1.3.3 Cyanide manifold

6.1.3.4 Colorimeter with 15 millimeters (mm) flow cells and 580 nm filters

6.1.3.5 Recorder

6.1.3.6 Data system (optional)

6.1.3.7 Glass or plastic tubes for the sampler

6.2 Midi Distillation of Water and Soils

6.2.1 Midi reflux distillation apparatus

6.2.2 Heating block - Capable of maintaining 125°C (±5°C).

6.2.3 Auto analyzer system with accessories:

6.2.3.1 Sampler

6.2.3.2 Pump

6.2.3.3 Cyanide cartridge

6.2.3.4 Colorimeter with 50 mm flow cells and 580 nm filter

6.2.3.5 Chart recorder or data system

6.2.4 Assorted volumetric glassware, pipets, and micropipets

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-77). Use this preparation for all reagents, standards, and dilutions of solutions.

7.1.2 Conventional Distillation and Preparation Reagents of Water and Soils

7.1.2.1 Sodium hydroxide solution, 1.25N - Dissolve 50 grams (g) of NaOH in reagent water, and dilute to 1 Liter (L) with reagent water. (Same Distillation and Preparation Reagent for Midi Distillation of Water and Soils.)

7.1.2.2 Cadmium carbonate - Powdered

7.1.2.3 Ascorbic acid - Crystals

7.1.2.4 Sulfuric acid - Concentrated

7.1.2.5 Hydrochloric acid (HCl) - Concentrated (specific gravity 1.19).

7.1.2.6 Magnesium chloride solution - Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 milliliter (mL) flask, dissolve, and dilute to 1 L with reagent water. (Same Distillation and Preparation Reagent for Midi Distillation of Water and Soils.)

7.1.3 Midi Distillation and Preparation Reagents of Water and Soils

7.1.3.1 Sodium hydroxide absorbing solution and sample wash solution, 0.25N - Dissolve 10.0 g NaOH in reagent water and dilute to 1 L.

7.1.3.2 Sulfuric acid, 50% (v/v) - Carefully add a portion of concentrated H_2SO_4 to an equal portion of reagent water.

7.1.4 Manual Spectrophotometric Reagents for Water and Soils

7.1.4.1 Acetate Buffer - Dissolve 410 g of $NaC_2H_3O_2 \cdot 3H_2O$ in 500 mL of reagent water. Add sufficient glacial acetic acid to adjust pH to 4.5 (approximately 500 mL).

7.1.4.2 Chloramine-T solution - Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of reagent water and refrigerate until ready to use. Prepare fresh weekly.

7.1.4.3 Color Reagent

7.1.4.3.1 Pyridine-barbituric acid reagent - Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough reagent water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (specific gravity 1.19), mix, and cool to room temperature. Dilute to 250 mL with reagent water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.1.5 Semi-Automated Spectrophotometric Reagents for Conventional and Midi Distillation of Water and Soils

7.1.5.1 Chloramine-T solution - Dissolve 0.40 g of chloramine-T in reagent water and dilute to 100 mL. Prepare fresh daily.

7.1.5.2 Acetate Buffer - Dissolve 410 g of $NaC_2H_3O_2 \cdot 3H_2O$ in 500 mL of reagent water. Add sufficient glacial acetic acid to adjust pH to 4.5 (approximately 500 mL).

7.1.5.3 Pyridine-barbituric acid solution - Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 mL of reagent water and swirl the flask. Add 75 mL of pyridine and mix. Add 15 mL of concentrated HCl and mix. Dilute to about 900 mL with reagent water and mix until the barbituric acid is dissolved. Dilute to 1 L with reagent water. Store at 4°C (±2°C).

7.1.5.4 Sampler wash - Dissolve 10 g of NaOH in reagent water and dilute to 1 L. (For conventional distillation of water and soils only.)

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 8.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.2 Stock Standard Solutions

7.2.2.1 Stock Standard Reagents for Water and Soils

7.2.2.1.1 Stock cyanide solution - Dissolve 2.51 g of KCN and 2 g KOH in 1 L of reagent water. Standardize with 0.0192N $AgNO_3$.

7.2.2.1.2 Standard cyanide solution, intermediate - Dilute 50.0 mL of stock (1 mL = 1 milligram (mg) CN) to 1000 mL with reagent water.

7.2.2.1.3 Standard cyanide solution - Prepare fresh daily by diluting 100 mL of intermediate cyanide solution to 1000 mL with reagent water and store in a glass stoppered bottle. 1 mL = 5.0 micrograms (µg) CN [5.0 milligrams per Liter (mg/L)].

7.2.2.1.4 Sodium hydroxide solution, 0.25N - Dissolve 10 g of NaOH in reagent water and dilute to 1 L.

7.2.2.2 Stock Standard Reagents for Midi Distillation of Water and Soils

7.2.2.2.1 Stock cyanide solution, 1000 mg/L CN - Dissolve 2.51 g of KCN and 2.0 g KOH in reagent water and dilute 1 L. Standardize with 0.0192N $AgNO_3$.

7.2.2.2.2 Intermediate cyanide standard solution, 10 mg/L CN - Dilute 1.0 mL of stock cyanide solution (see Section 7.2.2.2.1) plus 20 mL of 1.25N NaOH solution (see Section 7.1.2.1) to 100 mL with reagent water. Prepare this solution at time of analysis.

7.2.2.2.3 Sodium hydroxide solution, 0.1N - Dissolve 4 g of NaOH in reagent water and dilute to 1 L.

7.2.3 Secondary Dilution Standards

7.2.3.1 Secondary Dilution Standards

Prepare secondary dilution standard solutions by diluting the appropriate volumes of stock standards with 0.25N NaOH. The final concentration of NaOH in all standards should be 0.25N.

7.2.4 Working Standards

7.2.4.1 Method Detection Limit (MDL) Solution

7.2.4.1.1 The MDL solution shall be at a concentration of 3 to 5 times the expected MDL.

7.2.4.2 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

7.2.4.2.1 The concentration of the CRI for cyanide shall be at the CRQL. Information regarding the CRI shall be reported on Form IIB-IN.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

8.1.1 Water Sample Preservation

Collection of total cyanide must be in polyethylene or glass containers. The sample must be tested for sulfides and oxidizing agents, and preserved by the sampler immediately upon sample collection. Place a drop of the sample on lead acetate test paper (which has been pre-moistened with pH 4 acetate buffer solution) to detect the presence of sulfides. If sulfides are present (test strip turns black), the sample volume required for the cyanide determination should be increased by 25 milliliters (mL). The total volume of sample should then be treated with powdered cadmium carbonate or lead carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. If no sulfides are present, test for the presence of oxidizing agents by placing a drop of the sample on a strip of potassium iodide - starch test paper (KI - starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 gram (g) of ascorbic acid for each liter of sample volume. Preserve the sample with NaOH to pH greater than 12 and maintain at 4°C (±2°C) until distillation.

8.1.2 Soil/Sediment Sample Preservation

Samples shall be kept at 4°C (±2°C) from the time of collection until distillation.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to the USEPA. After 60 days the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.2.3 Samples, sample distillates, and standards must be stored separately.

8.3 Contract Required Holding Time

The maximum sample holding time for cyanide is 12 days from Validated Time of Sample Receipt (VTSR).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the difference between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. The analyst should follow the instructions provided by the manufacturer of the particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 General Procedure

The following general procedure applies to most semi-automated colorimeters. Set up the manifold and complete system per manufacturer's instructions. Allow the colorimeter and recorder to warm up for at least 30 minutes prior to use. Establish a steady reagent baseline, feeding reagent water through the sample line and appropriate reagents (see Section 7.1.5) through reagent lines. Adjust the baseline using the appropriate control on the colorimeter. Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations [per 250 milliliter (mL)].

9.3 Spectrophotometric Instrument Calibration Procedure

9.3.1 Instruments shall be calibrated daily or once every 24 hours, and each time the instrument is set up. The instrument standardization date and time shall be included in the raw data.

9.3.2 The date and time of preparation and analysis shall be given in the raw data.

9.3.3 Calibration standards shall be prepared fresh daily or each time an analysis is to be made and discarded after use. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. One of the calibration standards shall be at the Contract Required Quantitation Limit (CRQL). The acceptance criteria for the initial calibration curve is a correlation coefficient greater than or equal to 0.995.

9.3.4 Any changes or corrections to the analytical system shall be followed by recalibration.

9.3.5 Baseline correction is acceptable as long as it is performed after every sample or after the Continuing Calibration Verification (CCV) and Blank (CCB) check. Resloping is acceptable as long as it is immediately preceded and immediately followed by a compliant CCV and CCB.

9.4 Initial Calibration Verification (ICV)

9.4.1 Immediately after each cyanide system has been calibrated, the accuracy of the initial calibration shall be verified and documented for cyanide by the analysis of the ICV Solution at the wavelength used for analysis.

9.4.2 Only if the ICV Solution is not available from USEPA, or where a certified solution of the analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but

within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration.

9.4.3 The ICV shall be distilled. This means that an ICV must be distilled with each batch of samples analyzed and that the samples distilled with an ICV must be analyzed with that particular ICV.

9.4.4 The value for the ICV shall be reported on Form IIA-IN.

9.5 Continuing Calibration Verification (CCV)

9.5.1 To ensure calibration accuracy during each analysis run, one of the following standards is to be used for the CCV and shall be analyzed and reported at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard shall also be analyzed and reported at the beginning of the run and after the last analytical sample. The analyte concentration in the CCV standard shall be different than the concentration used for the ICV and shall be one of the following solutions at or near the mid-range level of the calibration curve:

- USEPA Solutions
- NIST Standards
- A Contractor-prepared standard solution

The same CCV standard shall be used throughout the analysis runs for a Sample Delivery Group (SDG) of samples received.

9.5.2 Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses, and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it, as well as the difference in time between the CCV and the analytical sample immediately preceding it, may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

9.5.3 Information regarding the CCV shall be reported on Form IIA-IN.

9.6 Initial and Continuing Calibration Blank (ICB/CCB)

A calibration blank shall be analyzed at the wavelength used for analysis immediately after every ICV and CCV, at a frequency of 10% or every 2 hours during the run, whichever is more frequent. The blank shall be analyzed at the beginning of the run and after the last analytical sample.

NOTE: A CCB shall be analyzed immediately after the last CCV, and the last CCV shall be analyzed immediately after the last analytical sample of the run. The results for the calibration blanks shall be reported on Form III-IN.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90%, of the required amount) is received to perform the analyses, the Contractor shall contact Sample Management Office (SMO) to inform them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multi-phase samples (e.g., two-phase liquid sample, oily sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprize them of the type of sample received. SMO will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample, and analyze one or more of the phases separately. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do any of the following:

- Separate the phases and analyze the phase(s) that is (are) amenable to analysis. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Soil samples are not dried prior to analysis. A separate percent solids determination must be made in accordance with the procedure in Exhibit D - Introduction to Analytical Methods, Section 1.6.

10.1.4 Before preparation is initiated for an aqueous sample, the Contractor shall test for the presence of sulfides and oxidizing agents (e.g., residual chlorine). The test for sulfides shall be performed by placing a drop of the sample on a strip of lead acetate paper (which has been pre-moistened with pH 4 acetate buffer solution). If the test strip turns black, the Contractor shall treat the total volume of sample with powdered cadmium carbonate or lead carbonate. Yellow cadmium sulfide precipitates when the sample contains sulfide. This operation shall be repeated until a drop of the treated sample solution does not darken the lead acetate test paper. The solution shall be filtered through a dry filter paper into a dry beaker, and the volume of sample to be used for analysis shall be measured from the filtrate. It is recommended that the Contractor avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the

precipitated material. The test for oxidizing agents shall be performed by placing a drop of the sample on a strip of potassium iodide - starch test paper (KI - starch paper). If the test strip turns blue, the Contractor shall contact SMO for further instructions from the Region before proceeding with sample preparation and analysis. The Contractor shall document the presence of sulfides or oxidizing agents in the SDG Narrative.

10.2 Water and Soil Preparation of Standards and Samples

10.2.1 Standards Preparation

10.2.1.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. The mid-range standard must be analyzed immediately after the first CCV/CCB. If the distilled standard does not agree within ±15% of the undistilled standards, the operator shall find and correct the cause of the apparent error before proceeding.

10.2.1.2 Standards for Manual Spectrophotometric Analysis of Water and Soil Samples

Prepare a minimum of three standards and a blank by pipetting suitable volumes of standard solution into 250 milliliter (mL) volumetric flasks.

NOTE: The concentration of one of the calibration standards shall be at the Contract Required Quantitation Limit (CRQL).

To each standard, add 50 mL of 1.25N NaOH and dilute to 250 mL with reagent water. The same method for color development (i.e., pyridine-barbituric acid or pyridine-pyrazolone) must be used for both the samples and standards. Standards must bracket the concentration of the samples. If dilution is required, use the blank solution.

10.2.1.3 Standards for Semi-Automated Spectrophotometric Analysis of Water and Soil Samples

Calibration standards - Prepare a blank and at least three calibration standards over the range of the analysis by pipetting suitable volumes of standard solution into volumetric flasks. One calibration standard must be at the CRQL. Add NaOH to each standard to bring the concentration of NaOH to 10 grams per Liter (g/L). Store at 4°C (±2°C).

10.2.1.4 Standards for Midi Distillation Preparation and Semi-Automated Spectrophotometric Analysis of Water and Soil Samples

Prepare a minimum of three standards and a blank by pipetting suitable volumes of standard solution into 50 mL volumetric flasks. Dilute standards to 50 mL with 0.25N NaOH.

NOTE: One calibration standard must be at the CRQL.

10.2.2 Water Samples Preparation (Distillation)

10.2.2.1 Preparation Method/Code (DW1)

10.2.2.1.1 Place 500 mL of sample in the 1 liter boiling flask. Add 50 mL of NaOH solution (see Section 7.1.2.1) to the absorbing tube and dilute if necessary with reagent water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

10.2.2.1.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

NOTE: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to re-adjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

10.2.2.1.3 Slowly add 25 mL concentrated sulfuric acid (H_2SO_4) (see Section 7.1.2.4) through the air inlet tube. Rinse the tube with reagent water and allow the airflow to mix the flask contents for three minutes. Pour 20 mL of magnesium chloride solution (see Section 7.1.2.6) into the air inlet and wash down with a stream of water.

10.2.2.1.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

10.2.2.1.5 Drain the solution from the absorber into a 250 mL volumetric flask and bring up to volume with reagent water washings from the absorber tube.

NOTE: The distillation procedure results in a two-fold concentration of the sample.

10.2.3 Water Samples Preparation (Midi-Distillation)

10.2.3.1 Preparation Method/Code (DW2)

10.2.3.1.1 The procedure described here utilizes a midi distillation apparatus and requires a sample aliquot of 50 mL or less for aqueous samples.

10.2.3.1.2 Pipet 50 mL of sample, or an aliquot diluted to 50 mL, into the distillation flask along with 2 or 3 boiling chips.

10.2.3.1.3 Add 50 mL of 0.25N NaOH (see Section 7.1.3.1) to the gas absorbing impinger.

10.2.3.1.4 Connect the boiling flask, condenser, and absorber in the train. The excess cyanide trap contains 0.5N NaOH.

10.2.3.1.5 Turn on the vacuum and adjust the gang (Whitney) valves to give a flow of three bubbles per second from the impingers in each reaction vessel.

10.2.3.1.6 After five minutes of vacuum flow, inject 5 mL of 50% (v/v) H_2SO_4 (see Section 7.1.3.2) through the top air inlet tube of the distillation head into the reaction vessel. Allow to mix for 5 minutes.

NOTE: The acid volume must be sufficient to bring the sample/solution pH to below 2.0.

10.2.3.1.7 Add 2 mL of magnesium chloride solution (see Section 7.1.2.6) through the top air inlet tube of the distillation head into the reaction flask. Excessive foaming from samples containing surfactants may be quelled by the addition of either another 2 mL of magnesium chloride solution or a few drops of a commercially available anti-foam agent. The Contractor shall document the addition of magnesium chloride solution or anti-foam agent in the SDG Narrative.

10.2.3.1.8 Turn on the heating block and set for 123-125°C. Heat the solution to boiling, taking care to prevent solution backup by periodic adjustment of the vacuum flow.

10.2.3.1.9 After one and a half hours of refluxing, turn off the heat and continue the vacuum for an additional 15 minutes. The flasks should be cool at this time.

10.2.3.1.10 After cooling, close off the vacuum at the gang valve and remove the absorber. Seal the receiving solutions and store them at 4°C until analyzed. The solutions must be analyzed for cyanide within the 12 day holding time specified in Section 8.3.

10.2.4 Soil Samples Preparation

10.2.4.1 Preparation Method/Code (DS1) (Distillation)

10.2.4.1.1 Accurately weigh a representative 1-5 gram (g) portion of wet sample and transfer it to a boiling flask. Add 500 mL of reagent water. Shake or stir the sample so that it is dispersed.

10.2.4.1.2 Add 50 mL of NaOH solution (see Section 7.1.2.1) to the absorbing tube and dilute if necessary with reagent water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the train.

10.2.4.1.3 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

NOTE: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to re-adjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

10.2.4.1.4 Slowly add 25 mL of concentrated H_2SO_4 (see Section 7.1.2.4) through the air inlet tube. Rinse the tube with reagent water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (see Section 7.1.2.6) into the air inlet and wash down with a stream of water.

10.2.4.1.5 Heat the solution to boiling, taking care to prevent the solution from backing up and overflowing into the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

10.2.4.1.6 Drain the solution from the absorber into a 250 mL volumetric flask and bring up to volume with reagent water washings from the absorber tube.

10.2.4.2 Preparation Method/Code (DS2) (Midi-Distillation)

10.2.4.2.1 The procedure described here utilizes a midi distillation apparatus and requires a sample aliquot of 1 gram for solid materials.

10.2.4.2.2 Weigh 1.0 g of sample (to the nearest 0.01 g) into the distillation flask and dilute to 50 mL with reagent water. Add 2 or 3 boiling chips.

10.2.4.2.3 Add 50 mL of 0.25N NaOH (see Section 7.1.3.1) to the gas absorbing impinger.

10.2.4.2.4 Connect the boiling flask, condenser, and absorber in the train. The excess cyanide trap contains 0.5N NaOH.

10.2.4.2.5 Turn on the vacuum and adjust the gang (Whitney) valves to give a flow of three bubbles per second from the impingers in each reaction vessel.

10.2.4.2.6 After five minutes of vacuum flow, inject 5 mL of 50% (v/v) H_2SO_4 (see Section 7.1.3.2) through the top air inlet tube of the distillation head into the reaction vessel. Allow to mix for 5 minutes.

NOTE: The acid volume must be sufficient to bring the sample/solution pH to below 2.0.

10.2.4.2.7 Add 2 mL of magnesium chloride solution (see Section 7.1.2.6) through the top air inlet tube of the distillation head into the reaction flask. Excessive foaming from samples containing surfactants may be quelled by the addition of either another 2 mL of magnesium chloride solution or a few drops of a commercially available anti-foam agent. The Contractor shall document the addition of magnesium chloride solution or anti-foam agent in the SDG Narrative.

10.2.4.2.8 Turn on the heating block and set for 123-125°C. Heat the solution to boiling, taking care to prevent solution backup by periodic adjustment of the vacuum flow.

10.2.4.2.9 After one and a half hours of refluxing, turn off the heat and continue the vacuum for an additional 15 minutes. The flasks should be cool at this time.

10.2.4.2.10 After cooling, close off the vacuum at the gang valve and remove the absorber. Seal the receiving solutions and store them at 4°C until analyzed. The solutions must be analyzed for cyanide within the 12 day holding time specified in Section 8.3.

10.2.5 Non-Distilled Analyses

10.2.5.1 Preparation Method/Code (NP1)

10.2.5.1.1 This code shall be used to report samples that are not distilled prior to analysis.

10.2.5.1.2 This Preparation Method/Code shall also be used to report the non-distilled Method Detection Limit (MDL). The concentration of this MDL shall be used to determine the appropriate concentration qualifier for the results of instrument QC analyses [except the distilled Initial Calibration Verification (ICV)].

10.3 Sample Analysis

10.3.1 Manual Spectrophotometric Determination

10.3.1.1 Allow all standards and samples to come to ambient room temperature prior to analysis. Withdraw 50 mL or less of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25N sodium hydroxide solution (see Section 7.1.3.1). Add 1.0 mL of acetate buffer (see Section 7.1.4.1) and mix. The dilution factor must be reported on Form XIII-IN.

10.3.1.2 Add 2 mL of chloramine-T (see Section 7.1.4.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (see Section 7.1.4.3.1) and mix. Dilute to mark with reagent water and mix again. Allow 8 minutes for color development then read absorbance between 570 and 580 nanometers (nm) in a 1 centimeter (cm) cell within 15 minutes.

10.3.2 Semi-Automated Spectrophotometric Determination of Distillates

10.3.2.1 Set up the manifold. Pump the reagents through the system until a steady baseline is obtained.

10.3.2.2 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks. Allow all standards and samples to come to ambient room temperature prior to analysis.

10.3.2.3 When a steady reagent baseline is obtained and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the colorimeter until the desired signal is obtained. Establish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled Quality Control (QC) samples.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Water/Aqueous Sample Calculation

11.1.1 For semi-automated colorimetric determination (Non-Midi-Distillation), measure the instrument response of the calibration standards and calculate a linear regression equation. Apply the equation to the samples and Quality Control (QC) samples to determine the cyanide concentration in the distillates. To determine the concentration of cyanide in the original sample, MULTIPLY THE RESULTS BY ONE-HALF (since the original volume was 500 milliliter (mL) and the distillate volume was 250 mL). Also correct for, and report on Form XIII-IN, any dilutions which were made before or after distillation.

11.1.2 For manual colorimetric determination, calculate the cyanide, in micrograms per Liter (µg/L), in the original sample as follows:

EQ. 1 Aqueous Sample Concentration (Manual)

$$\text{CN Concentration (µg/L)} = \frac{A \times 1000\ \text{mL/L}}{B} \times \frac{50\ \text{mL}}{C}$$

WHERE,

A	=	µg CN read from standard curve (per 250 mL)
B	=	mL of original sample for distillation (see Section 10.2.2.1.1)
C	=	mL taken for colorimetric analysis (see Section 10.3.1.1)
50 mL	=	volume of original sample aliquot (see Section 10.3.1.1)
1000 mL/L	=	conversion mL to L

The minimum value that can be substituted for A is the Method Detection Limit (MDL) value adjusted for volume.

11.2 Soil Sample Calculation

11.2.1 A separate determination of percent solids must be performed (see Exhibit D - Introduction to Analytical Methods, Section 1.6).

11.2.2 The concentration of cyanide in the sample is determined as follows:

11.2.2.1 Manual Spectrophotometric

EQ. 2 Soil Sample Concentration (Manual)

$$\text{CN Concentration (mg/kg)} = \frac{A \times \frac{50\ \text{mL}}{B}}{C \times \frac{\%\ \text{solids}}{100}}$$

WHERE,

A	=	µg CN read from standard curve (per 250 mL).
B	=	mL of distillate taken for colorimetric determination (see Section 10.3.1.1).
C	=	wet weight of original sample in g (see Section 10.2.4.1.1).
50 mL	=	standard volume taken for colorimetric determination (see Section 10.3.1.1)
% solids	=	percent solids (see Exhibit D - Introduction to Analytical Methods, Section 1.6).

11.2.2.2 Semi-Automated Spectrophotometric for Non-Midi-Distillates

If the semi-automated method is used, measure the peak heights of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the samples and QC audits to determine the cyanide concentration in the distillates.

EQ. 3 Soil Sample Concentration (Semi-automated)

$$\text{CN Concentration (mg/kg)} = \frac{A \times .25}{C \times \frac{\% \text{ solids}}{100}}$$

WHERE,

A	=	µg/L determined from standard curve.
C	=	wet weight of original sample in g (see Section 10.2.4.1.1).
.25	=	conversion factor for distillate final volume (see Section 10.2.4.1.6).
% solids	=	percent solids (see Exhibit D - Introduction to Analytical Methods, Section 1.6).

The minimum value that can be substituted for A is the MDL value.

11.3 Calculations for Midi Distillation of Waters and Soils

11.3.1 Calculations for Semi-automated Colorimetric Determination

11.3.1.1 Prepare a standard curve by plotting absorbance (peak heights, determined visually or using a data system) of standards (y) versus cyanide concentration values (total µg CN/L) (x). Perform a linear regression analysis.

11.3.1.2 Multiply all distilled values by the standardization value to correct for the stock cyanide solution not being exactly 1000 milligrams per Liter (mg/L) (see Section 7.2.2.2.1).

11.3.1.3 Using the regression analysis equation, calculate sample receiving solution concentrations from the calibration curve.

11.3.1.4 Calculate the cyanide of aqueous samples in µg/L of original sample, as follows:

EQ. 4 Aqueous Sample Concentration (Midi)

$$\text{CN Concentration (µg/L)} = \frac{A \times D \times F}{B}$$

WHERE,

A = µg/L CN of sample from regression analysis

B = volume of original sample for distillation (0.050 L) (see Section 10.2.3.1.2)

D = any dilution factor necessary to bracket sample value within standard values

F = sample receiving solution volume (0.050 L)

The minimum value that can be substituted for A is the MDL value.

11.3.1.5 Calculate the cyanide of solid samples in mg/kg of original sample, as follows:

11.3.1.5.1 A separate determination of percent solids must be performed (see Exhibit D - Introduction to Analytical Methods, Section 1.6).

11.3.1.5.2 The concentration of cyanide in the sample is determined as follows:

EQ. 5 Soil Sample Concentration (Midi)

$$\text{CN Concentration (mg/kg)} = \frac{A \times D \times F}{B \times E}$$

WHERE,

A = µg/L CN of sample from regression analysis curve

B = wet weight of original sample (see Section 10.2.4.2.2)

D = any dilution factor necessary to bracket sample value within standard values

E = % solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)

F = sample receiving solution volume (0.050 L)

The minimum value that can be substituted for A is the MDL value.

11.4 Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation

To calculate the adjusted aqueous MDL or adjusted aqueous CRQL for the manual colorimetric method, multiply the MDL (µg/L) or CRQL (µg/L) by

0.25 and substitute the result for the "A" term in Equation 1. To calculate the adjusted aqueous MDL or adjusted aqueous CRQL for all other methods, follow the instructions in Section 11.1.1 or substitute the MDL (µg/L) or CRQL (µg/L) for the "A" term in Equation 4, as appropriate.

The adjusted soil MDL or adjusted soil CRQL for all methods shall be calculated as follows:

EQ. 6 Adjusted Soil MDL/Adjusted Soil CRQL Concentration

$$\text{Adjusted Concentration (mg/kg)} = C \times \frac{W_M}{W_R} \times \frac{1}{S}$$

WHERE,

C	=	MDL or CRQL concentration (mg/kg)
W_M	=	minimum method required wet sample weight (g)
W_R	=	reported wet sample weight (g)
S	=	% Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6).

For the midi-distillation, multiply the adjusted concentration value (mg/kg) obtained in Equation 6 by any applicable dilution factor.

12.0 QUALITY CONTROL (QC)

12.1 Initial Calibration Verification (ICV)

The ICV standard shall be prepared in the same matrix as the calibration standards and in accordance with the instructions provided by the supplier. The ICV standard shall be distilled. If measurements exceed the control limits of 85% (low) and 115% (high), the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. Information regarding the ICV shall be reported on Form IIA-IN.

12.2 Continuing Calibration Verification (CCV)

The CCV standard shall be prepared by the analyst at a concentration equivalent to the mid-point of the calibration curve. If the deviation of the CCV is greater than the control limits of 85% (low) and 115% (high), the analysis shall be stopped, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification shall be performed. Information regarding the CCV shall be reported on Form IIA-IN.

12.3 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

12.3.1 To verify linearity near the CRQL, a standard at the CRQL (CRI) shall be prepared, in the same matrix as the calibration standards, and analyzed at the beginning and at the end of each sample analysis run, immediately following the ICV/ICB. In addition, the Contractor shall analyze the CRI at a frequency of not less than once per 20 analytical samples[1] per analysis run. The CRI analysis shall be run immediately followed by the CCV and Continuing Calibration Blank (CCB) analyses. The CRI shall be prepared by spiking an aliquot of reagent water with cyanide to yield a concentration in the final solution equal to the CRQL.

12.3.2 CRI and percent recovery results shall be reported on Form IIB-IN. If the percent recovery falls outside the control limits of 70-130%, the CRI shall be re-analyzed immediately. If the result of the re-analysis falls within the control limits, no further corrective action is required. If the result of the re-analysis does not fall within the control limits, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the CRI analyzed, and the samples associated with the CRI re-analyzed.

12.4 Blank Analyses

There are two different types of blanks required by this method. The calibration blank is used in establishing the analytical curve while the preparation blank is used to monitor for possible contamination.

12.4.1 Initial and Continuing Calibration Blank (ICB/CCB)

The ICB and CCB are prepared with reagents and reagent water. If the absolute value of the calibration blank (ICB/CCB) result exceeds the CRQL (see Exhibit C), the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical

[1]As defined in Exhibit G, CRI is an analytical sample.

samples analyzed since the last compliant calibration blank shall be performed.

12.4.2 Preparation Blank (PB)

12.4.2.1 The PB shall contain all the reagents and in the same volumes as used in processing the samples. The PB shall be carried through the complete procedure and contain the same concentration in the final solution as the sample solution used for analysis.

12.4.2.2 At least one PB, consisting of reagent water processed through each sample preparation and analysis procedure (see Section 10), shall be prepared and analyzed with every Sample Delivery Group (SDG), or with each batch[2] of samples distilled, whichever is more frequent.

12.4.2.3 The first batch of samples in an SDG is to be assigned to Preparation Blank one, the second batch of samples to Preparation Blank two, etc. (see Form III-IN). Each Sample Data Package shall contain the results of all the PB analyses associated with the samples in that SDG.

12.4.2.4 The PB is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

12.4.2.4.1 If the absolute value of the concentration of the blank is less than or equal to the CRQL (see Exhibit C), no further action is required.

12.4.2.4.2 If the analyte concentration in the blank is above the CRQL, the lowest concentration of the analyte in the associated samples shall be greater than or equal to 10 times the blank concentration. Otherwise, all samples associated with the blank, with the analyte concentration less than 10 times the blank concentration and above the CRQL, shall be redistilled and re-analyzed with appropriate new QC. The only exception to this shall be an identified field blank. The sample concentration is not to be corrected for the blank value.

12.4.2.4.3 If the concentration of the blank is below the negative CRQL, then all samples associated with the blank and reported below 10 times CRQL shall be reprepared and re-analyzed with appropriate new QC.

The values for the preparation blank shall be reported on Form III-IN.

12.5 Spike Sample Analysis

12.5.1 The spike sample analysis is designed to provide information about the effect of the sample matrix on the distillation and/or measurement methodology. The spike is added prior to any distillation steps. At least one spike sample analysis (matrix spike) shall be performed on each group of samples of a similar

[2]A group of samples prepared at the same time.

matrix type (i.e., water, soil) or for each SDG.[3] The sample and its associated spike sample shall initially be run at the same dilution.

12.5.2 If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.6). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for spiked sample analysis. USEPA may require that a specific sample be used for the spike sample analysis.

12.5.3 The analyte spiking solution shall be added to yield a final concentration of 100 µg/L in the final sample solution prepared for analysis (i.e., post-distillation). The final volume of the sample after distillation shall be the basis for the amount of cyanide to be added as the spike. For instance, the full volume distillation procedure will require addition of 25 µg cyanide to the sample prior to distillation [based on the final distillate volume of 250 milliliter (mL)] to meet the specified spiking level; and the midi distillation procedure requires the addition of 5 µg of cyanide to the sample prior to distillation (based on the final distillate volume of 50 mL).

12.5.3.1 For soil samples, the final sample solution prepared for analysis (i.e., the distillate) shall contain cyanide spiked at a concentration of 100 µg/L regardless of the distillation procedure employed, or the amount of sample used for distillation. The final sample volume after distillation shall be used as the basis for the amount of cyanide to add as the spike. The units for reporting soil sample cyanide results shall be mg/kg. To convert from µg/L to mg/kg, the equation below shall be used:

EQ. 7 Conversion to mg/kg

$$\text{mg/kg} = \text{µg/L} \times \frac{\text{final distillate volume (L)}}{\text{sample weight (g)}}$$

12.5.4 If the spike recovery is not at or within the limits of 75-125%, the data of all samples received and associated with that spike sample and determined by the same analytical method shall be flagged with the letter "N" on Forms IA-IN and VA-IN. An exception to this rule is granted when the sample concentration exceeds the spike added concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

12.5.5 When the matrix spike recovery falls outside the control limits and the sample result does not exceed 4 times the spike added, a post-distillation spike shall be performed. Note that if a post-distillation spike analysis is required, the same USEPA sample that was used for the matrix spike analysis shall be used for the post digestion spike analysis. Spike the unspiked aliquot of the sample at 2 times the indigenous level or 2 times CRQL, whichever is greater. Results of the post-distillation spike shall be reported on Form VB-IN.

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[3]USEPA may require additional spike sample analyses, upon USEPA Regional CLP Project Officer (CLP PO) request.

12.5.6 In the instance where there is more than one spike sample per matrix, per method, per SDG, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix and method in the SDG. Individual component percent recoveries are calculated as follows:

EQ. 8 Spike Percent Recovery

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

WHERE,

SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

12.5.7 When the sample concentration is less than the Method Detection Limit (MDL), use SR = 0 only for purposes of calculating percent recovery. The Spike Sample Results (SSRs), Sample Results (SRs), Spike Added (SA), and percent recovery (positive or negative) shall be reported on Form VA-IN.

12.5.8 The units used for reporting spike sample results will be identical to those used for reporting sample results on Form IA-IN.

12.6 Duplicate Sample Analysis

12.6.1 One duplicate sample shall be analyzed from each group of samples of a similar matrix type (i.e., water, soil) or for each SDG.[4] Duplicates cannot be averaged for reporting on Form IA-IN. The sample and its associated duplicate sample shall initially be run at the same dilution.

12.6.2 Duplicate sample analyses are required for percent solids. Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. USEPA may require that a specific sample be used for duplicate sample analysis. The Relative Percent Difference (RPD) is calculated as follows:

EQ. 9 Duplicate Sample Relative Percent Difference

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

WHERE,

RPD = Relative Percent Difference

S = Sample Result (original)

D = Duplicate Result

12.6.3 The results of the duplicate sample analyses shall be reported on Form VI-IN. A control limit of 20% for RPD shall be used for

[4]USEPA may require additional duplicate sample analyses, upon USEPA Regional CLP PO request.

original and duplicate sample values greater than or equal to five times the CRQL (see Exhibit C). A control limit of the CRQL value shall be entered in the "Control Limit" column on Form VI-IN if either the sample or duplicate value is less than five times the CRQL. If the sample and duplicate values are greater than or equal to five times the CRQL, or if the sample and duplicate values are less than the CRQL, the "Control Limit" field is left empty.

12.6.4 If one result is above five times the CRQL level and the other is below, use the CRQL criteria to determine if the duplicate analysis is in control. If both sample and duplicate values are less than the MDL, the RPD is not calculated on Form VI-IN. For solid sample or solid duplicate results less than five times the CRQL, enter the value of the CRQL, corrected for sample weight and percent solids, (i.e., original, not duplicate sample weight and percent solids), in the "Control Limit" column. If the duplicate sample results are outside the control limits, flag all the data for samples received and associated with that duplicate sample with an "*" on Forms IA-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix and method in the SDG. The percent difference data will be used by USEPA to evaluate the long-term precision of the method. Specific control limits for each element will be added to Form VI-IN at a later date based on the precision results.

12.7 Laboratory Control Sample (LCS) Analysis

12.7.1 A solid LCS (LCSS) shall be analyzed using the same sample preparations, analytical methods, and Quality Assurance (QA)/QC procedures employed for the EPA samples received. For cyanide, a distilled ICV shall be used as the aqueous LCS (LCSW).

12.7.2 The USEPA provided LCSS shall be prepared and analyzed using each of the procedures applied to the solid samples received (exception: percent solids determination not required). If the USEPA LCSS is unavailable, other USEPA QC Check samples or other certified materials may be used. In such a case, the control limits for LCSS must be documented and provided. One LCSS shall be prepared and analyzed for every group of solid samples in a SDG, or for each batch of samples distilled, whichever is more frequent.

12.7.3 All LCSS and percent recovery results will be reported on Form VII-IN. If the results for the LCSS fall outside the control limits established by USEPA, the analyses shall be terminated, the problem corrected, and the samples associated with that LCSS reprepared and re-analyzed with appropriate new QC.

12.8 Method Detection Limit (MDL) Determination

12.8.1 Before any field samples are analyzed under this contract, the MDLs shall be determined for non-distilled analyses (Preparation Method/Code "NP1") and for each distillation procedure and instrument used, prior to the start of the contract analyses, and annually thereafter, and shall meet the levels specified in Exhibit C.

An MDL study shall be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions to verify the current sensitivity of the analysis.

12.8.2 To determine the MDLs, the Contractor shall run MDL studies following the procedures given in 40 CFR, Part 136. The Contractor shall

prepare the MDL samples by each distillation procedure used and shall analyze these samples on each instrument used. The Contractor shall also analyze the non-distilled MDL samples on each instrument used.

12.8.3 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C.

12.8.4 The non-distilled MDL (Preparation Method/Code "NP1") shall be used to determine the appropriate concentration qualifier for the results of instrument QC analyses (except the distilled ICV).

12.8.5 The results of the MDL determination study shall be forwarded to the USEPA Regional CLP PO, Sample Management Office (SMO), and Quality Assurance Technical Support (QATS).

12.8.6 The MDL results shall be reported on Form IX-IN.

12.9 Example Analytical Sequence for Cyanide

S0
S10.0
S50.0
S100.0
S200.0
S400.0
ICV (distilled)
ICB
CRI
CCV
CCB
MIDRANGE
9 samples
CCV
CCB
9 samples
CRI
CCV
CCB
10 samples, etc.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 1.15 in Exhibit D - Introduction to Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 1.16 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 335.2. 1980.

16.2 American Water Works Association/American Public Health Association/Water Environment Federation. Standard Methods for the Examination of Water and Wastewater. Method 4500. 18th Edition.

16.3 US Government Printing Office. 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Not applicable.

EXHIBIT E

CONTRACT LABORATORY PROGRAM QUALITY ASSURANCE MONITORING PLAN

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Exhibit E - Contract Laboratory Program Quality Assurance Monitoring Plan

Table of Contents

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1.0 OVERVIEW

Quality Assurance (QA) and Quality Control (QC) are integral parts of the U.S. Environmental Protection Agency's (USEPA's) Contract Laboratory Program (CLP). The QA process consists of management review and oversight at the planning, implementation, and completion stages of the environmental data collection activity, and ensures that data provided are of the quality required. The QC process includes those activities required during data collection to produce the data quality desired and to document the quality of the collected data.

1.1 Quality Assurance/Quality Control (QA/QC) Activities

During the planning of an environmental data collection program, QA activities focus on defining data quality criteria and designing a QC system to measure the quality of data being generated. During the implementation of the data collection effort, QA activities ensure that the QC system is functioning effectively, and that the deficiencies uncovered by the QC system are corrected. After environmental data are collected, QA activities focus on assessing the quality of data obtained to determine its suitability to support enforcement or remedial decisions.

1.1.1 This exhibit describes the overall QA/QC operations and the processes by which the CLP meets the QA/QC objectives defined above. This contract requires a variety of QA/QC activities. These contract requirements are the minimum QC operations necessary to satisfy the analytical requirements associated with the determination of the different method analytes. These QC operations are designed to facilitate laboratory comparison by providing USEPA with comparable data from all Contractors. These requirements do not release the analytical Contractor from maintaining their own QC checks on method and instrument performance.

1.2 Incentives/Sanctions

The Contractor may anticipate incentives by <u>consistently</u> providing the following: (1) high quality, technically sound data as stipulated by the ILM05.3 contract; (2) on-time or early delivery of the Sample Delivery Group (SDG) Cover Sheet; (3) above average Quarterly Blind (QB) Performance Evaluation (PE) sample scores; (4) diskettes that pass the initial Contract Compliance Screening (CCS) acceptance criteria; and (5) SDGs delivered on-time. Samples are distributed routinely to Contractors based on the quality of work performed, as measured by the Performance Scheduling Algorithm (PSA) (see Section G of the contract for details). A Contractor that consistently meets the contract performance requirements as highlighted above, will earn a higher PSA score, thereby increasing the likelihood of receiving samples for analyses. If the Contractor fails to meet the requirements set forth in this Statement of Work (SOW) or elsewhere in the contract, USEPA may take, but is not limited to, the following actions (see Section E of the contract for details): reduction in the number of samples sent under the contract; suspension of sample shipments; data package audit(s); electronic data audit(s); on-site laboratory evaluation(s); and/or remedial PE sample(s).

2.0 INTRODUCTION

Appropriate use of data generated under the large range of analytical conditions encountered in environmental analyses requires reliance on the Quality Control (QC) procedures and criteria incorporated into the ILM05.3 Statement of Work (SOW).

The data acquired from QC procedures are used to estimate and evaluate the information content of analytical results and to determine the necessity for, or the effect of, corrective action procedures. The parameters used to estimate information content include precision, accuracy, detection limit, and other quantitative and qualitative indicators. In addition, QC procedures give an overview of the activities required in an integrated program to generate data of known and documented quality required to meet defined objectives.

2.1 Quality Assurance/Quality Control (QA/QC) Program Components

2.1.1 The Contractor's QA/QC program shall include (1) internal QC criteria that demonstrate compliant levels of performance, as determined by QA review, as well as (2) external review of data and procedures accomplished by the monitoring activities of the USEPA OSRTI Analytical Services Branch (ASB), Regional Data Users, Sample Management Office (SMO), and the Quality Assurance Technical Support (QATS) Laboratory. Each external review accomplishes a different purpose. These reviews are described in specific sections of this exhibit. Laboratory evaluation samples, electronic data audits, and data packages provide an external QA reference for the program. A Contractor on-site evaluation system is also part of the external QA monitoring. A feedback loop provides the results of the various review functions to the Contractors through direct communications with the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) and the USEPA OSRTI ASB Inorganic Program Manager (ASB PM).

2.1.2 This exhibit does not provide specific instructions for constructing QA Management Plans, QC systems, or a QA organization. It is, however, an explanation of the QA/QC requirements of CLP. It outlines minimum standards for QA/QC programs. It also includes specific items that are required in a Quality Assurance Management Plan (QAP) and by the QA/QC documentation detailed in this contract. Delivery of this documentation provides USEPA with a complete data package which will stand alone, and limits the need for contact with the Contractor or with an analyst, at a later date, if some aspect of the analysis is questioned.

2.1.3 In order to assure that the product delivered by the Contractor meets the requirements of the contract, and to improve interlaboratory data comparison, the Contractor shall:

- Prepare, and adhere to, a written approved QAP, as defined in Exhibit E, Section 5;
- Prepare and adhere to, Standard Operating Procedures (SOPs) as described in Exhibit E, Section 6;
- Adhere to the analytical methods in Exhibit D and associated QC requirements specified within Exhibit E;
- Verify and document analytical standards and retain documentation of the purity of neat materials, as well as, the purity and accuracy of solutions obtained from private chemical supply houses;

- Submit all raw data and required documentation for Regional review;

- Submit results of all analyzed laboratory evaluation samples, and adhere to corrective action procedures;

- Submit, upon request, instrument data tapes and applicable documentation for tape audits, including a copy of the Sample Data Package;

- Submit to on-site laboratory evaluations, and adhere to corrective action procedures; and

- Submit all original documentation generated during sample analyses for USEPA review.

3.0 GENERAL QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) REQUIREMENTS

The Contractor shall adhere to USEPA's Good Laboratory Practices for laboratory cleanliness with regard to glassware and apparatus. The Contractor shall also adhere to good laboratory practices with regard to reagents, solvents, and gases. For additional guidelines regarding these general laboratory procedures, see the Handbook for Analytical Quality Control in Water and Wastewater Laboratories USEPA-600/4-79-019, USEPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, September 1982.

4.0 SPECIFIC QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) MONITORING PROCEDURES

4.1 Purpose

4.1.1 The purpose of this document is to provide (1) a uniform set of procedures for the analysis of inorganic constituents of samples, (2) documentation of methods and their performance, and (3) verification of the sample data generated. Although it is impossible to address every analytical situation in one document, this exhibit defines the minimum requirements for each major step relevant to any inorganic analysis.

4.1.2 The primary function of the Contract Laboratory Program (CLP) QA/QC program is the definition of procedures for the evaluation and documentation of analytical methodologies and the reduction and reporting of data. The location and summary of the QA/QC performance based contracting methods can be found in Exhibit E, Section 15, Table 1 - Contract Laboratory Program Quality Assurance Monitoring Plan. The objective is to provide a uniform basis for sample handling, instrument and methods maintenance, performance evaluation, and analytical data gathering and reporting. In many instances where methodologies are available, specific QC procedures are incorporated into the method documentation (see Exhibit D).

4.1.3 The QA/QC procedures defined herein shall be used by the Contractor when performing the methods specified in Exhibit D. When QA/QC procedures are specified in Exhibit D, the Contractor shall follow those procedures, in addition to procedures specified here.

4.2 Laboratory Audit and Intercomparison Study Program

The Contractor is required to participate in the Laboratory Audit and Intercomparison Study Program run by USEPA. The Contractor shall be required to analyze at least one Quarterly Blind (QB) sample per calendar quarter during the contract period for inorganics.

4.3 Annual Verification of Method Detection Limits (MDLs)

The Contractor shall perform and report annual verification of MDLs by the method specified in Exhibit D, by type, matrix, and model for each instrument used on this contract, to Sample Management Office (SMO), Quality Assurance Technical Support (QATS), and the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) as specified in Exhibit B. All the MDLs shall meet the requirements specified in Exhibit C.

4.4 Quarterly Verification of Linear Ranges/Interelement Correction Factors

The Contractor shall perform and report quarterly verification of linear ranges by the method specified in Exhibit D, by type and model for each instrument used on this contract, to SMO, QATS, and the USEPA Regional CLP PO as specified in Exhibit B. The Contractor shall also report, as specified in Exhibit B, integration times. For Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) methods, the Contractor shall also report, as specified in Exhibit B, wavelengths used and all interelement correction factors.

4.5 Quality Assurance/Quality Control Measurements

4.5.1 In this Exhibit, as well as other places within this Statement of Work (SOW), the term “analytical sample” discusses the required

frequency or placement of certain QA/QC measurements. The term "analytical sample" is defined in the glossary, Exhibit G.

4.5.2 In order for the QA/QC information to reflect the status of the samples analyzed, all samples and their associated QA/QC analysis shall be analyzed under the same operating and procedural conditions.

4.5.3 If any QC measurement fails to meet contract criteria, the analytical measurement must not be repeated prior to taking the appropriate corrective action as specified in Exhibit D. The exception is the CRI analysis, which may be re-analyzed once before corrective action is necessary.

4.5.4 The Contractor shall report all QC data in the exact format specified in Exhibits B and H.

4.5.5 MDLs, precision, linear dynamic range, and interference effects shall be established for each analyte on a particular instrument. All reported measurements shall be within the instrumental linear ranges. The Contractor shall maintain QC data confirming instrument performance and analytical results.

5.0 QUALITY ASSURANCE MANAGEMENT PLAN (QAP)

5.1 Introduction

The Contractor shall establish a Quality Assurance (QA) program with the objective of providing sound analytical chemical measurements. This program shall incorporate the Quality Control (QC) procedures, any necessary corrective action, all documentation required during data collection, and the quality assessment measures performed by management to ensure acceptable data production. The Contractor shall follow the USEPA EPA Requirements for Quality Management Plans (EPA QA/R-2). An electronic version can be found at http://www.epa.gov/quality1/qa_docs.html.

5.1.1 The Contractor shall prepare a written QAP which describes the procedures that are implemented to achieve the following:

- Maintain data integrity, validity, and usability;
- Ensure that analytical measurement systems are maintained in an acceptable state of stability and reproducibility;
- Detect problems through data assessment and establish corrective action procedures which keep the analytical process reliable; and
- Document all aspects of the measurement process in order to provide data which are technically sound and legally defensible.

5.1.2 The QAP must present, in specific terms, the policies, organization, objectives, functional guidelines, and specific QA/QC activities designed to achieve the data quality requirements in this contract. Standard Operating Procedures (SOPs) pertaining to each element shall be included or referenced as part of the QAP. The QAP shall be paginated consecutively in ascending order. The QAP shall be available during on-site laboratory evaluations and shall be submitted to the designee within 7 days of written request by the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) or the USEPA OSRTI Analytical Services Branch (ASB) Inorganic Program Manager (ASB PM). Additional information relevant to the preparation of a QAP can be found in USEPA and ASTM publications.

5.2 Required Elements of a Quality Assurance Management Plan

The required elements of a laboratory's QAP are outlined in this section. This outline shall be used as a framework for developing the QAP.

A. Organization and Personnel

1. QA Policy and Objectives (the mission and quality policy of the organization)
2. QA Management (the specific roles, authorities, and responsibilities of management and staff with respect to QA and QC activities)
   a. Organization
   b. Assignment of QA/QC Responsibilities

c. Reporting Relationships (the means by which effective communications with personnel actually performing the work are assured)

d. QA Document Control Procedures

e. QA Program Assessment Procedures (the process used to plan, implement, and assess the work performed)

3. Personnel

a. Resumes

b. Education and Experience Pertinent to this Contract

c. Training Records and Progress

B. Facilities and Equipment

1. Instrumentation and Backup Alternatives

2. Maintenance Activities and Schedules

C. Document Control

1. Laboratory Notebook Policy

2. Sample Tracking/Custody Procedures

3. Logbook Maintenance and Archiving Procedures

4. Sample Delivery Group (SDG) File Organization, Preparation, and Review Procedures

5. Procedures for Preparation, Approval, Review, Revision, and Distribution of SOPs

6. Process for Revision of Technical or Documentation Procedures

D. Analytical Methodology

1. Calibration Procedures and Frequency

2. Sample Preparation Procedures

3. Sample Analysis Procedures

4. Standards Preparation Procedures

5. Decision Processes, Procedures, and Responsibility for Initiation of Corrective Action

E. Data Generation

1. Data Collection Procedures

2. Data Reduction Procedures

3. Data Validation Procedures

4. Data Reporting and Authorization Procedures

F. Quality Assurance (the process which measures the effectiveness of QA will be established and how frequently effectiveness will be measured)

1. Data Quality Assurance

2. Systems/Internal Audits

3. Performance/External Audits

4. Corrective Action Procedures (the continual improvement based on lessons learned from previous experience)

5. QA Reporting Procedures

6. Responsibility Designation

G. Quality Control

1. Solvent, Reagent, and Adsorbent Check Analysis

2. Reference Material Analysis

3. Internal QC Checks

4. Corrective Action and Determination of QC Limit Procedures

5. Responsibility Designation

5.3 Updating and Submitting the Quality Assurance Management Plan

5.3.1 The revised QAP will become the official QAP under the contract and may be used during legal proceedings. The Contractor shall maintain the QAP on file at the Contractor's facility for the term of the contract. Both the initial submission and the revised QAP shall be paginated consecutively in ascending order. The revised QAP shall include:

- Changes resulting from (1) the Contractor's internal review of their organization, personnel, facility, equipment, policy and procedures, and (2) the Contractor's implementation of the requirements of the contract, and

- Changes resulting from USEPA's review of the laboratory evaluation sample data, bidder supplied documentation, and recommendations made during the pre-award on-site laboratory evaluation.

5.3.1.1 The Contractor shall send a copy of the latest version of the QAP within 7 days of a request from a USEPA Regional CLP PO or the USEPA OSRTI ASB PM. The request will designate the recipients.

5.3.2 Subsequent Updates and Submissions. During the term of the contract, the Contractor shall amend the QAP when the following circumstances occur:

- USEPA modifies the technical requirements of the Statement of Work (SOW) or contract;

- USEPA notifies the Contractor of deficiencies in the QAP document;

- USEPA notifies the Contractor of deficiencies resulting from USEPA's review of the Contractor's performance;

- The Contractor's organization, personnel, facility, equipment, policy, or procedures change; or

- The Contractor identifies deficiencies resulting from the internal review of their organization, personnel, facility, equipment, policy, or procedures changes.

5.3.2.1 The Contractor shall amend the QAP within 14 days of when the circumstances listed in Exhibit E, Section 5.3, result in a discrepancy between what was previously described in the QAP and what is presently occurring at the Contractor's facility. When the QAP is amended, all changes in the QAP shall be clearly marked (e.g., a bar in the margin indicating where the change is found in the document, highlighting the change by underlining the change, bold printing the change, or using a different print font) and a copy is sent to the USEPA Regional CLP PO and Quality Assurance Technical Support (QATS). The amended section pages shall have the date on which the changes were implemented. The Contractor shall incorporate all amendments to the latest version of the QAP document. The Contractor shall archive all amendments to the QAP document for future reference by USEPA.

5.4 Incentives/Sanctions

The Contractor shall amend the QAP as specified within this section. The QAP describes the policies and procedures for ensuring that work processes, products, or services satisfy expectations or specifications in ILM05.3. Failure to comply with the requirements of this section may result in sanctions as described in the contract.

6.0 STANDARD OPERATING PERFORMANCE STANDARDS

6.1 Introduction

In order to obtain reliable results, adherence to prescribed analytical methodology is imperative. In any operation that is performed on a repetitive basis, reproducibility is best accomplished through the use of Standard Operating Procedures (SOPs). As defined by USEPA, an SOP is a written document which provides directions for the step-by-step execution of an operation, analysis, or action which is commonly accepted as the method for performing certain routine or repetitive tasks. The Contractor shall follow the USEPA Guidance for the Preparation of Standard Operating Procedures (SOPs) for Quality-Related Documents (EPA QA/G-6). An electronic version can be found at http://www.epa.gov/quality1/qa_docs.html.

6.1.1 SOPs prepared by the Contractor shall be functional (i.e., clear, comprehensive, up-to-date, and sufficiently detailed to permit duplication of results by qualified analysts). The SOPs shall be paginated consecutively in ascending order.

6.1.2 All SOPs shall reflect Contractor activities as they are currently performed in the laboratory. In addition, all SOPs shall be:

- Consistent with current USEPA regulations, guidelines, and the Contract Laboratory Program (CLP) ILM05.3 contract requirements.
- Consistent with instrument(s) manufacturer’s specific instruction manuals.
- Available to USEPA during an on-site laboratory evaluation. A complete set of SOPs shall be bound together and available for inspection at such evaluations. During on-site laboratory evaluations, laboratory personnel shall demonstrate the application of the SOPs if requested.
- Available to the designated recipients within 7 days, upon request by the USEPA Regional CLP Project Officer (CLP PO) or the USEPA OSRTI Analytical Services Branch (ASB) Inorganic Program Manager (ASB PM).
- Capable of providing for the development of documentation that is sufficiently complete to record the performance of all tasks required by the protocol.
- Capable of demonstrating the validity of data reported by the Contractor and explain the cause of missing or inconsistent results.
- Capable of describing the corrective measures and feedback mechanism utilized when analytical results do not meet protocol requirements.
- Reviewed regularly and updated as necessary when contract, facility, or Contractor procedural modifications are made.
- Archived for future reference in usability or evidentiary situations.
- Available at specific work stations as appropriate.

- Subject to a document control procedure which precludes the use of outdated or inappropriate SOPs.

- Reviewed and signed by all Contractor personnel performing actions identified in the SOP.

6.2 Format

The format for SOPs may vary depending upon the type of activity for which they are prepared; however, at a minimum, the following sections shall be included:

- Title page;

- Document Control;

- Scope and Applicability;

- Summary of Method;

- Definitions (acronyms, abbreviations, and specialized forms used in the SOP);

- Health & Safety;

- Personnel Qualifications;

- Interferences;

- Apparatus & Materials (list or specify; note also designated locations where found);

- Handling & Preservation;

- Instrument or Method Calibration;

- Sample Preparation and Analysis;

- Data Calculations;

- Quality Control (QC) limits;

- Corrective action procedures, including procedures for secondary review of information being generated;

- Data Management and Records Management;

- Miscellaneous notes and precautions; and

- References.

6.3 Required SOPs

The Contractor shall maintain the following SOPs:

6.3.1 Evidentiary SOPs for required chain-of-custody and document control are discussed in Exhibit F.

6.3.2 Sample Receipt and Storage

- Sample receipt and identification logbooks,
- Refrigerator temperature logbooks, and
- Security precautions.

6.3.3 Sample Preparation

6.3.3.1 Metals

6.3.3.2 Cyanide

6.3.4 Glassware Cleaning

6.3.5 Calibration (Balances, etc.)

- Procedures;
- Frequency requirements;
- Preventative maintenance schedule and procedures;
- Acceptance criteria and corrective actions; and
- Logbook maintenance authorization.

6.3.6 Analytical Procedures (for each analytical system)

- Instrument performance specifications;
- Instrument operating procedures;
- Data acquisition system operation;
- Procedures when automatic quantitation algorithms are overridden;
- QC required parameters;
- Analytical run/injection logbooks; and
- Instrument error and editing flag descriptions and resulting corrective actions.

6.3.7 Maintenance Activities (for each analytical system)

- Preventative maintenance schedule and procedures,
- Corrective maintenance determinants and procedures, and
- Maintenance authorization.

6.3.8 Analytical Standards

- Standard coding/identification and inventory system;
- Standards preparation logbook(s);
- Standard preparation procedures;

- Procedures for equivalency/traceability analyses and documentation;
- Purity logbook (primary standards and solvents);
- Storage, replacement, and labeling requirements; and
- QC and corrective action measures.

6.3.9 Data Reduction Procedures

- Data processing systems operation;
- Outlier identification methods;
- Identification of data requiring corrective action; and
- Procedures for format and/or forms for each operation.

6.3.10 Documentation Policy/Procedures

- Contractor/analyst's notebook policy, including review policy;
- Complete Sample Delivery Group (SDG) File (CSF) contents;
- Complete SDG File organization and assembly procedures, including review policy; and
- Document inventory procedures, including review policy.

6.3.11 Data Validation/Self-Inspection Procedures

- Data flow and chain-of-command for data review;
- Procedures for measuring precision and accuracy;
- Evaluation parameters for identifying systematic errors;
- Procedures to assure that hardcopy and electronic deliverables are complete and compliant with the requirements in the Statement of Work (SOW) Exhibits B and H;
- Procedures to assure that hardcopy deliverables are in agreement with their comparable electronic deliverables;
- Demonstration of internal Quality Assurance (QA) inspection procedure (demonstrated by supervisory sign-off on personal notebooks, internal laboratory evaluation samples, etc.);
- Frequency and type of internal audits (e.g., random, quarterly, spot checks, perceived trouble areas);
- Demonstration of problem identification, corrective actions, and resumption of analytical processing. Sequence resulting from internal audit (i.e., QA feedback); and
- Documentation of audit reports (internal and external), response, corrective action, etc.

6.3.12 Data Management and Handling

- Procedures for controlling and estimating data entry errors;
- Procedures for reviewing changes to data and deliverables and ensuring traceability of updates;
- Lifecycle management procedures for testing, modifying, and implementing changes to existing computing systems including hardware, software, and documentation or installing new systems;
- Database security, backup, and archival procedures including recovery from system failures;
- System maintenance procedures and response time;
- Individual(s) responsible for system operation, maintenance, data integrity, and security; and
- Specifications for staff training procedures.

6.4 Updating and Submitting SOP Requirements

6.4.1 The revised SOPs will become the official SOPs under the contract and may be used during legal proceedings. The Contractor shall maintain the complete set of SOPs on file at the Contractor's facility for the term of the contract. Both the initial submission and the revised SOPs shall be paginated consecutively in ascending order. The revised SOPs shall include:

- Changes resulting from (1) the Contractor's internal review of their procedures and (2) the Contractor's implementation of the requirements of the contract, and
- Changes resulting from USEPA's review of the laboratory evaluation sample data, bidder supplied documentation, and recommendations made during the pre-award on-site laboratory evaluation.

6.4.1.1 The Contractor shall send a complete set of the latest version of SOPs or individually requested SOPs within 7 days of a request from an USEPA Regional CLP PO or the USEPA OSRTI ASB PM. The request will designate the recipients.

6.4.2 Subsequent Updates and Submissions. During the term of the contract, the Contractor shall amend the SOPs when the following circumstances occur:

- USEPA modifies the technical requirements of the SOW or contract;
- USEPA notifies the Contractor of deficiencies in the SOP documentation;
- USEPA notifies the Contractor of deficiencies resulting from USEPA's review of the Contractor's performance;
- The Contractor's procedures change;
- The Contractor identifies deficiencies resulting from the internal review of the SOP documentation; or

- The Contractor identifies deficiencies resulting from the internal review of their procedures.

6.4.2.1 Existing SOPs shall be amended or new SOPs shall be written within 14 days of when the circumstances listed in Exhibit E, Section 6.4, result in a discrepancy between what was previously described in the SOPs and what is presently occurring at the Contractor's facility. All changes in the SOPs shall be clearly marked (e.g., a bar in the margin indicating where the change is in the document, highlighting the change by underlining the change, bold printing the change, or using a different print font) and a copy is sent to the USEPA Regional CLP PO and Quality Assurance Technical Support (QATS). The amended/new SOPs shall have the date on which the changes were implemented.

6.4.2.2 When existing SOPs are amended or new SOPs are written, the Contractor shall document the reasons for the changes and maintain the amended SOPs or new SOPs on file. Documentation of the reasons for the changes shall be maintained on file with the amended SOPs or new SOPs.

6.4.2.3 Documentation of the reason(s) for changes to the SOPs shall also be submitted along with the SOPs.

6.5 Incentives/Sanctions

The Contractor shall amend SOPs as specified within this section. The SOPs specify analytical procedures in greater detail than appear in Exhibit D. Adherence to these requirements will ensure that the procedure is conducted in a standard, reliable, and reproducible process described in ILM05.3. Failure to comply with the requirements specified herein may result in sanctions as described in the contract.

7.0 CONTRACT COMPLIANCE SCREENING (CCS) PERFORMANCE STANDARDS

7.1 Overview

7.1.1 CCS is one aspect of the Government's contractual right of inspection of analytical data. CCS examines the Contractor's adherence to the contract requirements based on the Sample Data Package delivered to USEPA.

7.1.2 CCS is performed by the Sample Management Office (SMO) under the direction of USEPA. To assure a uniform review, a set of standardized procedures has been developed to evaluate the Sample Data Package submitted by a Contractor against the technical and completeness requirements of the contract. USEPA reserves the right to add and/or delete individual checks.

7.2 CCS Results

CCS results are distributed to the Contractor and other data recipients. The Contractor has 4 business days to correct deficiencies and shall send all corrections to the Regional client and SMO. CCS results are used in conjunction with other information to measure overall Contractor performance and to take appropriate actions to correct deficiencies in performance.

7.3 CCS Trend Report

USEPA will periodically generate a CCS trend report which summarizes CCS results over a given period of time. USEPA will send the CCS trend report or discuss the CCS trend report during an on-site laboratory evaluation. In a detailed letter to the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) and USEPA Contracting Officer, the Contractor shall address the deficiencies and the subsequent corrective action implemented by the Contractor to correct the deficiencies within 14 days of receipt of the report or the on-site laboratory evaluation.

7.4 Incentives/Sanctions

7.4.1 If new Standard Operating Procedures (SOPs) are required to be written, or if existing SOPs are required to be rewritten or amended because of deficiencies and subsequent corrective action implemented by the Contractor, the Contractor shall write/amend the SOPs per the requirements listed in Exhibit E, Section 6.

7.4.2 The Contractor shall correct deficiencies and resubmit the data within 4 business days, as specified within this section. Resubmission and correction of the data will ensure that the end user is reviewing contractually compliant data described in ILM05.3. Correct resubmission of the data may also result in a reduction in overall sanctions. Specific details on incentives can be found in the contract. If the Contractor fails to adhere to the requirements listed in this section, the Contractor will be in noncompliance with the contract and may be subjected to sanctions as described in the contract.

8.0 ANALYTICAL PERFORMANCE STANDARDS REQUIREMENTS

8.1 Overview

USEPA will not supply analytical reference standards either for direct analytical measurements or for the purpose of traceability. All contract laboratories shall be required to prepare from materials or purchase from private chemical supply houses those standards necessary to successfully and accurately perform the analyses required in this protocol.

8.2 Preparation of Chemical Standards from the Neat High Purity Bulk Material

8.2.1 If the laboratory cannot obtain analytical reference standards, the laboratory may prepare their own chemical standards. Laboratories shall obtain the highest purity possible when purchasing chemical standards; standards purchased at less than 97% purity shall be documented as to why a higher purity could not be obtained.

8.2.2 The chemical standards shall be kept at manufacturer recommended conditions when not being used in the preparation of standard solutions. Proper storage of chemicals is essential in order to safeguard them from decomposition.

8.2.3 The Contractor shall be responsible for having analytical documentation proving the purity of each compound as stated. Purity confirmation, when performed, shall use appropriate techniques. Use of two or more independent methods is recommended. The correction factor for impurity when weighing neat materials in the preparation of solution standards is:

EQ. 1 Weight of Impure Compound

$$\text{weight of impure compound} = \frac{\text{weight of pure compound}}{(\text{percent purity}/100)}$$

where "weight of pure compound" is that required to prepare a specific volume of a solution standard of a specified concentration.

8.2.4 The Contractor is responsible for obtaining analytical documentation proving that all compounds used in the preparation of solution standards are correctly identified.

8.2.5 Logbooks shall be kept for all weighing and dilutions. All subsequent dilutions from the primary standard and the calculations for determining their concentrations shall be recorded and verified by a second person. All solution standards shall be refrigerated, if required, when not in use. All solution standards shall be clearly labeled as to the identity of the analyte or analytes, the standard ID number of the solution, concentration, date prepared, solvent, expiration date of the solution, special storage requirements (if any), and initials of the preparer.

8.3 Purchase of Chemical Standards Already in Solution

Solutions of analytical reference standards can be purchased by Contractors provided the solutions meet the following criteria.

8.3.1 Reference standards shall be accompanied by documentation of the purity confirmation of the material to verify the integrity of the standard solutions.

8.3.2 The quality of reference standards purchased shall be demonstrated statistically and analytically by a method of the supplier's choice. One way this can be demonstrated is to prepare and analyze three solutions: a high standard, a low standard, and a standard at the target concentration (see Sections 8.3.2.1 and 8.3.2.2). The supplier must then demonstrate that the analytical results for the high standard and low standard are consistent with the difference in theoretical concentrations. This is done by the Student's t-test in Section 8.3.2.4. If this is achieved, the supplier must then demonstrate that the concentration of the target standard lies midway between the concentrations of the low and high standards. This is done by the Student's t-test in Section 8.3.2.5. Thus, the standard is certified to be within 10% of the target concentration using the equations in Section 8.3.2.6. If the procedure above is used, the supplier must document that the following have been achieved.

8.3.2.1 Two solutions of identical concentration shall be prepared independently from neat materials. An aliquot of the first solution shall be diluted to the intended concentration (the "target standard"). One aliquot is taken from the second solution and diluted to a concentration 10% greater than the target standard. This is called the "high standard". One further aliquot is taken from the second solution and diluted to a concentration 10% less than the target standard. This is called the "low standard".

8.3.2.2 Six replicate analyses of each standard (a total of 18 analyses) shall be performed in the following sequence: low standard; target standard; high standard; low standard; target standard; high standard; etc.

8.3.2.3 The mean and variance of the six results for each solution shall be calculated:

EQ. 2 Mean

$$\text{MEAN} = \frac{Y_1 + Y_2 + Y_3 + Y_4 + Y_5 + Y_6}{6}$$

EQ. 3 Variance

$$\text{VARIANCE} = \frac{Y_1^2 + Y_2^2 + Y_3^2 + Y_4^2 + Y_5^2 + Y_6^2 - 6(\text{MEAN})^2}{5}$$

The values Y_1, Y_2, Y_3, ..., represent the results of the six analyses of each standard. The means of the low, target, and high standards are designated M_1, M_2, and M_3, respectively. The variances of the low, target, and high standards are designated V_1, V_2, and V_3, respectively. Additionally, a pooled variance, V_p, is calculated.

EQ. 4 Pooled Variance

$$V_p = \frac{\frac{V_1}{0.81} + V_2 + \frac{V_3}{1.21}}{3}$$

If the square root of V_p is less than one percent of M_2, then $M_2^2/10{,}000$ is to be used as the value of V_p in all subsequent calculations.

8.3.2.4 The test statistic shall be calculated:

EQ. 5 Low and High Standard Test Statistic

$$\text{TEST STATISTIC} = \frac{\left| \frac{M_3}{1.1} - \frac{M_1}{0.9} \right|}{\left(\frac{V_p}{3} \right)^{0.5}}$$

If the test statistic exceeds 2.13, then the supplier has failed to demonstrate a 20% difference between the high and low standards. In such a case, the standards are not acceptable.

8.3.2.5 The test statistic shall be calculated:

EQ. 6 Target Standard Test Statistic

$$\text{TEST STATISTIC} = \frac{\left| M_2 - \left(\frac{M_1}{1.8} \right) - \left(\frac{M_3}{2.2} \right) \right|}{\left(\frac{V_p}{4} \right)^{0.5}}$$

If the test statistic exceeds 2.13, the supplier has failed to demonstrate that the target standard concentration is midway between the high and low standards. In such a case, the standards are not acceptable.

8.3.2.6 The 95% confidence intervals for the mean result of each standard shall be calculated:

EQ. 7 Low Standard Interval

$$\text{Interval for Low Standard} = M_1 \pm 2.13 \left(\frac{V_p}{6} \right)^{0.5}$$

EQ. 8 Target Standard Interval

$$\text{Interval for Target Standard} = M_2 \pm 2.13 \left(\frac{V_p}{6} \right)^{0.5}$$

EQ. 9 High Standard Interval

$$\text{Interval for High Standard} = M_3 \pm 2.13 \left(\frac{V_p}{6} \right)^{0.5}$$

8.3.2.6.1 These intervals shall not overlap. If overlap is observed, then the supplier has failed to demonstrate the ability to discriminate the 10% difference in concentrations. In such a case, the standards are not acceptable.

8.3.2.6.2 In any event, the Contractor is responsible for the quality of the standards employed for analyses under this contract.

8.4 Requesting Standards from the USEPA Standards Repository

Solutions of analytical reference materials can be ordered from the USEPA Chemical Standards Repository, depending on availability. The Contractor may place an order for standards only after demonstrating that these standards are not available from commercial vendors, either in solution or as a neat material.

8.5 Documentation of the Verification and Preparation of Chemical Standards

It is the responsibility of the Contractor to maintain the necessary documentation to show that the chemical standards it has used in the performance of Contract Laboratory Program (CLP) analysis conform to the requirements previously listed.

8.5.1 Weighing logbooks, calculations, raw data, etc., whether produced by the Contractor or purchased from chemical supply houses, shall be maintained by the Contractor and may be subject to review during on-site inspection visits. In those cases where the documentation is supportive of the analytical results of data packages sent to USEPA, such documentation is to be kept on file by the Contractor for a period of one year.

8.5.2 Upon request by the USEPA Regional CLP Project Officer (CLP PO), the Contractor shall submit their most recent previous year's documentation (12 months) for the verification and preparation of chemical standards within 14 days of the receipt of request to the designated recipients.

8.5.3 USEPA will periodically generate a report discussing deficiencies in the Contractor's documentation for the verification and preparation of chemical standards. USEPA will send the report or discuss the deficiencies during an on-site laboratory evaluation. In a detailed letter to the USEPA Regional CLP PO and CLP Quality Assurance Coordinator, the Contractor shall address the deficiencies and the subsequent corrective action implemented by the Contractor to correct the deficiencies within 14 days of receipt of the report or the on-site laboratory evaluation.

8.5.4 If new Standard Operating Procedures (SOPs) are required to be written, or if existing SOPs are required to be rewritten or amended because of deficiencies and subsequent corrective action implemented by the Contractor, the Contractor shall write/amend the SOPs per the requirements listed in Exhibit E, Section 6.

8.6 Incentives/Sanctions

The Contractor shall obtain the highest purity possible when purchasing chemical standards specified within this section. The use of high purity standards will ensure a more accurate identification and quantitation of analytes described in the ILM05.3 Statement of Work (SOW). Failure to meet the requirements set forth in this section may result in sanctions as described in the contract.

9.0 DATA PACKAGE MONITORING AUDITS

9.1 Overview

Data package audits are performed by USEPA for program overview and specific Regional concerns. Standardized procedures have been established to assure uniformity of the auditing process. Data packages are periodically selected from recently received Cases. They are evaluated for the technical quality of hardcopy raw data, Quality Assurance (QA), and adherence to contractual requirements. This function provides external monitoring of program Quality Control (QC) requirements. Data package audits are used to assess the technical quality of the data and evaluate overall laboratory performance. Audits provide USEPA with an in-depth inspection and evaluation of the Case data package with regard to achieving QA/QC acceptability. A thorough review of the raw data is completed including: all instrument readouts used for the sample results, instrument printouts, and other documentation for deviations from the contractual requirements, a check for transcription and calculation errors, a review of the qualifications of the laboratory personnel involved with the Case, and a review of the latest version of all Standard Operating Procedures (SOPs) on file.

9.2 Responding to the Data Package Audit Report

9.2.1 After completion of the data package audit, USEPA will send a copy of the data package audit report to the Contractor or discuss the data package audit report on an on-site laboratory evaluation. In a detailed letter to the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) and the USEPA designated recipient, the Contractor shall discuss the corrective actions implemented to resolve the deficiencies listed in the data package audit report within 14 days of receipt of the report.

9.2.2 If new SOPs are required to be written, or if existing SOPs are required to be rewritten or amended because of deficiencies and subsequent corrective action implemented by the Contractor, the Contractor shall write/amend the SOPs per the requirements listed in Exhibit E, Section 6.

9.3 Incentives/Sanctions

The Contractor shall discuss the corrective actions implemented to resolve the deficiencies listed in the data package audit report within 14 days of receipt of the comments from USEPA, as specified within this section. The data package audits ensure that the policies and procedures identified in this Statement of Work (SOW) meet the requirements of this contract. If the Contractor fails to adhere to the requirements listed in this section, the Contractor will be in noncompliance with the contract and may be subjected to sanctions as described in the contract.

10.0 REGIONAL DATA REVIEW MONITORING

10.1 Overview

Contractor data are generated to meet the specific needs of USEPA Regions. In order to verify the usability of data for the intended purpose, each Region reviews data from the perspective of the end user, based on functional guidelines for data review which have been developed jointly by the Regions and the USEPA OSRTI Analytical Services Branch (ASB). Each Region uses these guidelines as the basis for data evaluation. Individual Regions may augment the basic guideline review process with additional review based on Region-specific or site-specific concerns. Regional reviews, like the sites under investigation, vary based on the nature of the problem under investigation and the Regional response appropriate to the specific circumstances.

10.1.1 Regional data reviews, relating usability of the data to a specific site, are part of the collective assessment process. They complement the review done at the Sample Management Office (SMO), which is designed to identify contractual discrepancies, and the review done by the USEPA OSRTI ASB, which is designed to evaluate Contractor and method performance.

11.0 QUALITY ASSURANCE (QA) PROFICIENCY MONITORING

As a means of measuring and evaluating both the Contractor's and the method's analytical performance, the Contractor shall participate in USEPA's Proficiency Testing Program. USEPA's Proficiency Testing Program involves the analysis of Case specific Performance Evaluation (PE) samples and Quarterly Blind (QB) Audits. The Contractor's analytical PE samples and QB results will be used by USEPA to assess and verify the Contractor's continuing ability to produce acceptable analytical data in accordance with the contractual requirements. The Contractor shall receive a passing score of 75% to be in compliance with the contract.

11.1 Performance Evaluation (PE) Samples

11.1.1 The PE sample(s) may be scheduled with the Contractor as frequently as on a Sample Delivery Group (SDG)-by-SDG basis. The PE samples may be sent either by the Regional client or the USEPA OSRTI Analytical Services Branch (ASB). PE samples assist USEPA in monitoring Contractor performance.

11.1.2 PE samples will be provided as either single-blinds (recognizable as a PE sample but of unknown composition), or as double-blinds (not recognizable as a PE sample and of unknown composition). The Contractor will not be informed of either the analytes/parameters or the concentrations in the PE samples.

11.1.3 The Contractor may receive the PE samples as either full volume samples or ampulated/bottled concentrates from USEPA or a designated USEPA Contractor. The PE samples shall come with instructions concerning the unique preparation procedures, if any, required to reconstitute the PE samples (i.e., the required dilution of the PE sample concentrate). PE samples are to be digested and analyzed with the rest of the routine samples in the SDG. The Contractor shall prepare and analyze the PE sample using the procedure described in the sample preparation and method analysis sections of Exhibit D. All contract required Quality Control (QC) shall be met. The PE sample results are to be submitted in the SDG deliverable package per normal reporting procedures detailed in Exhibit B.

11.1.4 In addition to PE sample preparation and analysis, the Contractor shall be responsible for correctly identifying and quantitating the analytes included in each PE sample. When PE sample results are received by USEPA, the PE sample results will be evaluated for correct analytical identification and quantitation. The PE sample evaluation will be provided to the Contractor via coded evaluation sheets, by analyte. USEPA will notify the Contractor of unacceptable performance.

11.2 Quarterly Blind (QB) Audits

11.2.1 A QB Audit is a unique analytical Case containing only PE samples (i.e., referred to as QB samples). The QB samples will be scheduled by the USEPA OSRTI ASB through the Sample Management Office (SMO). QB samples assist USEPA in monitoring Contractor performance.

11.2.2 QB samples will be provided as single-blinds (recognizable as a PE sample but of unknown composition). The Contractor will not be informed of either the analytes or the concentrations in the PE samples.

11.2.3 The Contractor may receive the QB samples as either full volume samples or ampulated/bottled concentrates from USEPA or a designated USEPA Contractor. The QB samples shall come with instructions concerning the unique preparation procedures, if any, required to reconstitute the QB samples (i.e., the required dilution of the QB sample concentrate). The Contractor shall prepare and analyze the QB samples using the procedure described in the sample preparation and method analysis sections of Exhibit D. All contract required QC shall be met, including spike and duplicate analyses. The QB sample results are to be submitted in the SDG deliverable package per normal reporting procedures detailed in Exhibit B.

11.2.4 In addition to QB sample preparation and analysis, the Contractor shall be responsible for correctly identifying and quantitating the analytes included in each QB sample. When QB sample results are received by USEPA, the QB sample results will be scored for correct analytical identification and quantitation. The QB sample scoring will be provided to the Contractor via coded evaluation sheets, by analyte. USEPA will notify the Contractor of unacceptable performance. The Contractor's QB sample performance will be assessed into one of the following three categories:

11.2.4.1 Acceptable, No Response Required: Score greater than or equal to 90%. The data meets most or all of the scoring criteria. No response is required.

11.2.4.2 Acceptable, Response Explaining Deficiencies Required: Score greater than or equal to 75%, but less than 90%. Deficiencies exist in the Contractor's performance. Corrective action response required.

11.2.4.3 Unacceptable Performance, Response Explaining Deficiencies Required: Score less than 75%. Corrective action response required.

11.2.5 In the case of Section 11.2.4.2 or 11.2.4.3, the Contractor shall describe the deficiency(ies) and the action(s) taken in a corrective action letter to the USEPA Contracting Officer, USEPA Regional Contract Laboratory Program Project Officer (CLP PO), and CLP Quality Assurance (QA) Coordinator within 14 days of receipt of notification from USEPA.

11.2.6 In the case of Section 11.2.4.2 or 11.2.4.3, if new Standard Operating Procedures (SOPs) are required to be written, or if existing SOPs are required to be rewritten or amended because of deficiencies and subsequent corrective action implemented by the Contractor, the Contractor shall write/amend the SOPs per the requirements listed in Exhibit E, Section 6.

11.2.7 The Contractor shall be notified by the USEPA Contracting Officer concerning agreement or disagreement with the proposed remedy for unacceptable performance.

11.2.8 A Remedial QB Audit is a unique analytical Case containing only QB samples. A Remedial QB Audit may be scheduled by the USEPA OSRTI ASB with the Contractor(s) for any of the following reasons: unacceptable PE sample performance, unacceptable QB sample performance, and/or major change in the laboratory (e.g., relocation, new owner, or high turn-over of key personnel). Sections 11.2.2 through 11.2.7 apply to the Remedial QB Audit process.

11.3 Incentives/Sanctions

The Contractor shall analyze PE and QB samples with acceptable analytical results in accordance with the contractual requirements as described in this section. If the Contractor fails to adhere to the requirements listed in this section, the Contractor will be in noncompliance with the contract and may be subjected to sanctions as described in the contract.

12.0 ON-SITE LABORATORY QUALITY ASSURANCE (QA) MONITORING EVALUATIONS

12.1 Overview

The USEPA Regional Contract Laboratory Program Project Officer (CLP PO) or the USEPA Contracting Officer's authorized representative will conduct an on-site laboratory evaluation. On-site laboratory evaluations are carried out to monitor the Contractor's ability to meet selected terms and conditions specified in the contract. The evaluation process incorporates two separate categories: Quality Assurance (QA) Evaluation and Evidentiary Audit.

12.2 Quality Assurance On-Site Evaluation

QA evaluators inspect the Contractor's facilities to verify the adequacy and maintenance of instrumentation, the continuity, experience and education of personnel, and the acceptable performance of analytical and Quality Control (QC) procedures for adherence to the contract requirements.

12.2.1 The Contractor shall expect that items to be monitored will include, but are not limited to, the following:

- Size, cleanliness, and organization of the facility;
- Quantity, age, availability, scheduled maintenance, and performance of instrumentation;
- Availability, appropriateness, and utilization of the Quality Assurance Management Plan (QAP) and Standard Operating Procedures (SOPs);
- Staff qualifications, experience, and personnel training programs;
- Analysis of Performance Evaluation (PE) sample(s);
- Reagents, standards, and sample storage facilities;
- Standard preparation logbooks and raw data;
- Bench sheets and analytical logbook maintenance and review; and
- Review of the Contractor's sample analysis/data package inspection/data management procedures.

12.2.2 Prior to an on-site evaluation, various documentation pertaining to performance of the specific Contractor is integrated into a profile package for discussion during the evaluation. Items that may be included are: previous on-site reports; Quarterly Blind (QB) and/or PE sample scores results; Regional review of data; Contractor performance information provided by the Region; data audit reports; results of Contract Compliance Screening (CCS); and data trend reports.

12.3 Evidentiary Audit

Evidence auditors conduct an on-site laboratory evaluation to determine if laboratory policies and procedures are in place to satisfy evidence handling requirements as stated in Exhibit F. The evidence audit comprises a procedural audit, an audit of written SOPs, and an audit of analytical project file documentation.

12.3.1 Procedural Audit. The Contractor shall perform analysis of PE sample(s) in the presence of the USEPA designated team during the procedural audit. The procedural audit will be comprised of everything from sample receipt to data package assembly and completion. This includes the review and examination of actual SOPs and accompanying documentation for the following laboratory operations: sample receiving, sample storage, sample identification, sample security, sample tracking (from receipt to completion of analysis), analytical project file organization and assembly, and proper disposal of samples and cogenerated wastes.

12.3.2 Written SOPs Audit. The written SOPs audit consists of review and examination of the written SOPs to determine if they are accurate and complete for the following laboratory operations: sample receiving, sample storage, sample identification, sample security, sample tracking (from receipt to completion of analysis), and analytical project file organization and assembly.

12.3.3 Analytical Project File Evidence Audit. The analytical project file evidence audit consists of review and examination of the analytical project file documentation. The auditors review the files to determine:

- The accuracy of the document inventory;
- The completeness of the file;
- The adequacy and accuracy of the document numbering system;
- Traceability of sample activity;
- Identification of activity recorded on the documents; and
- Error correction methods.

12.4 Discussion of the On-Site Team's Findings

The QA and evidentiary auditors discuss their findings with the USEPA Regional CLP PO prior to debriefing the Contractor. During the debriefing, the auditors present their findings and recommendations for corrective actions necessary to the Contractor personnel. A report which discusses deficiencies found during the on-site audit will be sent to the Contractor to provide further clarification of findings. In a detailed letter to the USEPA Regional CLP PO and CLP Quality Assurance Coordinator, the Contractor shall discuss the deficiencies and the subsequent corrective actions implemented by the Contractor to resolve the deficiencies within 14 days of receipt of report or the on-site laboratory evaluation.

12.4.1 If new SOPs are required to be written, or if existing SOPs are required to be rewritten or amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend the SOPs per the requirements listed in Exhibit E, Section 6.

12.5 Incentives/Sanctions

The Contractor shall submit to on-site evaluations, as specified within this section. The on-site evaluations ensure that the policies and procedures identified in this Statement of Work (SOW) meet the requirements of this contract. If the Contractor fails to adhere to the requirements listed in this section, the Contractor will be in

noncompliance with the contract and may be subjected to sanctions as described in the contract.

13.0 ELECTRONIC DATA QUALITY ASSURANCE (QA) MONITORING AUDITS

13.1 Overview

Periodically, USEPA requests the instrument electronic data from Contractors for a specific Case in order to accomplish electronic data audits. Generally, electronic data submissions and audits are requested for the following reasons.

- Program overview;
- Indication of data quality problems;
- Support for on-site audits; and
- Specific Regional requests.

13.1.1 Depending upon the reason for an audit, the instrument electronic data from a recent Case, a specific Case, or a laboratory evaluation sample may be requested. Electronic data audits provide a mechanism to assess adherence to contractual requirements and to ensure the consistency of data reported on the hardcopy/electronic deliverables with that generated on analytical instruments. This function provides external monitoring of Program Quality Control (QC) requirements and checks adherence of the Contractor to internal Quality Assurance (QA) procedures. In addition, electronic data audits enable USEPA to evaluate the utility, precision, and accuracy of the analytical methods.

13.1.2 The Contractor shall store <u>all</u> raw and processed electronic analytical data in the appropriate instrument manufacturer's format, uncompressed, and with no security codes. The data shall include all necessary data files for a complete reconstruction of the previously submitted hardcopy and electronic deliverable data package. All associated raw data files in the instrument manufacturer proprietary software format must be submitted if those files contain data or instrumental parameters regarding any analysis and or correction applied to an instrument or analytical result. This instrument electronic data shall include data for all samples and all QC samples, including but not limited to: blanks, matrix spikes, post-digestion spikes, analytical spikes, duplicates, serial dilutions, Laboratory Control Samples (LCSs), Contract Required Quantitation Limits (CRQL) Check Standards (CRIs), Interference Check Samples (ICSs), tunes, initial calibrations and verifications, and Continuing Calibration Verifications (CCVs). In addition, the Contractor shall supply raw data for the Method Detection Limit (MDL) studies and Linear Range Analyses (LRS) which are used to set the MDL and LRV values for the year/quarter in which the Sample Delivery Group (SDG) was analyzed. The Contractor shall maintain a reference logbook of data files of EPA sample number, calibration data, standards, blanks, spikes, and duplicates. The logbook shall include EPA sample numbers, identified by Case and SDG.

13.1.3 The Contractor is required to retain the instrument electronic data for three years after submission of the reconciled Complete SDG File. Electronic media shipped to the USEPA designated recipient must be fully usable by the recipient. Diskettes must be 3.5 inch, high density, 1.44 MB MS/DOS formatted and tapes must be either 4 mm or 8 mm. Alternative means for delivery of electronic data may be utilized

by the Contractor upon prior written approval by USEPA. When submitting electronic instrument data to USEPA, the following materials shall be delivered in response to the request.

13.1.3.1 All associated raw data files for all analytical samples and all QC samples. For example, files for ICP should include raw intensities and mercury and cyanide files should include raw absorbances or integrated areas.

13.1.3.2 All processed data files and quantitation output files associated with the raw data files described in Section 13.1.3.1.

13.1.3.3 All associated identification and calculation files used to generate the data submitted in the data package. This includes, but is not limited to, result files, acquisition files, calibration files, and method files.

13.1.3.4 All Contractor-generated Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES)/ICP - Mass Spectrometer (ICP-MS) interference correction files must be submitted.

13.1.3.5 A copy of the Contractor's reference logbook relating data files to EPA sample number, calibration data, standards, blanks, spikes, and duplicates. The logbook shall include EPA sample numbers and laboratory file identifiers for all samples, blanks, and standards, identified by Case and SDG.

13.1.3.6 A printout of the directory of all files in each directory, including all subdirectories and the files contained therein.

13.1.3.7 A copy (hardcopy) of the completed Sample Data Package.

13.1.3.8 A statement attesting to the completeness of the electronic instrument data submission, signed and dated by the Contractor's laboratory manager. The Contractor shall also provide a statement attesting that the data reported have not been altered in any way. These statements shall be part of a Cover Sheet that includes the following information relevant to the data submission:

- Contractor name;
- Date of submission;
- Case number;
- SDG number;
- Instrument make and model number for each instrument;
- Instrument operating software name and version number;
- Data software name and version used for acquisition, re-quantitation, and hardcopy/report generation;
- Data system computer;
- System operating software;
- Data system network;
- Data backup software;

- Data backup hardware;
- Media type and volume of data (in MB) backed up; and
- Names and telephone numbers of two Contractor contacts for further information regarding the submission.

13.2 Submission of the Instrument Electronic Data

Upon request of the USEPA Regional Contract Laboratory Program Project Officer (CLP PO), the Contractor shall send the required instrument electronic data and all necessary documentation to the USEPA designated recipient [e.g., Quality Assurance Technical Support (QATS)] within 7 days of notification.

NOTE: The instrument electronic data shall be shipped according to the procedures in Exhibit F.

13.3 Responding to the Electronic Data Audit Report

After completion of the electronic data audit, USEPA will send a copy of the electronic data audit report to the Contractor or may discuss the electronic data audit report at an on-site laboratory evaluation. In a detailed letter to the USEPA Regional CLP PO, the Contractor shall discuss the corrective actions implemented to resolve the deficiencies listed in the electronic data audit report within 14 days of receipt of the report or the on-site laboratory evaluation.

13.3.1 If new Standard Operating Procedures (SOPs) are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section 6.

13.4 Incentives/Sanctions

The Contractor shall submit to electronic data audits and adhere to the requirements specified in this section. Resubmission and correction of electronic data will ensure that the end user is reviewing contractually compliant data described in the ILM05.3 contract. If the Contractor fails to adhere to the requirements listed in this section, the Contractor will be in noncompliance with the contract and may be subjected to sanctions as described in the contract.

14.0 DATA MANAGEMENT PERFORMANCE REQUIREMENTS

14.1 Overview

14.1.1 Data management procedures are defined as procedures specifying the acquisition or entry, update, correction, deletion, storage, and security of computer readable data and files. These procedures shall be in written form and contain a clear definition for all databases and files used to generate or resubmit deliverables. Key areas of concern include: system organization (including personnel and security), documentation operations, traceability, and Quality Control (QC).

14.1.2 Data manually entered from hardcopy shall be subject to QC checks and the error rates estimated. Systems should prevent entry of incorrect or out-of-range data and alert data entry personnel of errors. In addition, data entry error rates shall be estimated and recorded on a monthly basis by re-entering a statistical sample of the data entered and calculating discrepancy rates by data element.

14.2 Documenting Data Changes

The record of changes in the form of corrections and updates to data originally generated, submitted, and/or resubmitted shall be documented to allow traceability of updates. Documentation shall include the following for each change.

- Justification or rationale for the change.
- Initials of the person making the change(s). Data changes shall be implemented and reviewed by a person or group independent of the source generating the deliverable.
- Documentation of changes shall be retained according to the schedule of the original deliverable.
- Resubmitted diskettes or other deliverables shall be re-inspected as a part of the laboratory's internal inspection process prior to resubmission. The entire deliverable, not just the changes, shall be inspected.
- The Laboratory Manager shall approve changes to originally submitted deliverables.
- Documentation of data changes may be requested by laboratory auditors.

14.3 Lifecycle Management Procedures

Lifecycle management procedures shall be applied to computer software systems developed by the Contractor to be used to generate and edit contract deliverables. Such systems shall be thoroughly tested and documented prior to utilization.

14.3.1 A software test and acceptance plan including test requirements, test results and acceptance criteria shall be developed, followed, and available in written form.

14.3.2 System changes shall not be made directly to production systems generating deliverables. Changes shall be made first to a development system and tested prior to implementation.

14.3.3 Each version of the production system will be given an identification number, date of installation, and date of last operation and will be archived.

14.3.4 System and operations documentation shall be developed and maintained for each system. Documentation shall include a user's manual and an operations and maintenance manual.

14.3.5 This documentation shall be available for on-site review and/or upon written request by the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) or the USEPA OSRTI Analytical Services Branch (ASB) Inorganic Program Manager (ASB PM).

14.4 Personnel Responsibilities

Individual(s) responsible for the following functions shall be identified.

- System operation and maintenance including documentation and training.
- Database integrity, including data entry, data updating and QC.
- Data and system security, backup and archiving.

15.0 TABLES

TABLE 1. Contract Laboratory Program Quality Assurance Monitoring Plan

SOW Reference	Performance Requirements	Performance Standards	QA Monitoring Plan
Exhibit A: Summary of Requirements	Summary of Program Requirements	Performance standards are summarized in Exhibit A, Sections 1.0 through 4.0.	QA monitoring plan is outlined in Exhibit E.
Exhibit B: Reporting and Deliverables Requirements	Reporting and Deliverable Requirements	Performance standards are outlined in Exhibit B, Sections 1.0 through 4.0.	CCS in Exhibit E, Section 7.0, and CADRE will be used to monitor reporting electronic deliverables.
Exhibit C: Inorganic Target Analyte List with Contract Required Quantitation Limits	Target Analyte List with Contract Required Quantitation Limits	Performance standards are outlined in Exhibit C, Section 1.0.	QA monitoring plan is outlined in Exhibit E.
Exhibit D: Analytical Methods	ICP-AES requirements are outlined in Exhibit D, Part A, Sections 1.0 through 8.0, 14.0, and 15.0.	Performance standards are outlined in Exhibit D, Part A, Sections 9.0 through 11.0.	QA monitoring plan is outlined in Exhibit D, Part A, Section 12.0, and Exhibit E.
	ICP-MS requirements are outlined in Exhibit D, Part B, Sections 1.0 through 8.0, 14.0, and 15.0.	Performance standards are outlined in Exhibit D, Part B, Sections 9.0 through 11.0.	QA monitoring plan is outlined in Exhibit D, Part B, Section 12.0, and Exhibit E.
	Mercury requirements are outlined in Exhibit D, Part C, Sections 1.0 through 8.0, 14.0 and 15.0.	Performance standards are outlined in Exhibit D, Part C, Sections 9.0 through 11.0.	QA monitoring plan is outlined in Exhibit D, Part C, Section 12.0, and Exhibit E.
	Cyanide requirements are outlined in Exhibit D, Part D, Sections 1.0 through 8.0, 14.0, and 15.0.	Performance standards are outlined in Exhibit D, Part D, Sections 9.0 through 11.0.	QA monitoring plan is outlined in Exhibit D, Part D, Section 12.0, and Exhibit E.
Exhibit E: Contract Laboratory Program Quality Assurance Monitoring Plan	General QA/QC Requirements	As outlined in Exhibit D, Quality Control sections.	QA Management Plan is outlined in Exhibit E, Section 5.0.

TABLE 1. Contract Laboratory Program Quality Assurance Monitoring Plan (Con't)

SOW Reference	Performance Requirements	Performance Standards	QA Monitoring Plan
Exhibit E: Contract Laboratory Program Quality Assurance Monitoring Plan (Con't)	Quality Assurance Management Plan	As outlined in Exhibit E, Sections 5.1.1 and 5.1.2, a written QA Management Plan shall be used to ensure acceptable data production of known and documented quality.	USEPA will review and approve the QA Management Plan.
	Standard Operating Procedures	Performance standards are outlined in Exhibit E, Sections 6.0 through 6.4, and must be performed as stated.	SOPs will be reviewed by USEPA during Pre-Award, on-site audits, after modifications are made and randomly, as deemed appropriate.
	Contract Compliance Screening	Performance standards are outlined in Section E.2 of the ILM05.3 IFB and must be performed as stated.	The sample data package will be evaluated against the technical and completeness requirements of the contract.
	Analytical Standards	Performance standards are outlined in Exhibit E, Sections 8.0 through 8.5, and must be performed as stated.	Randomly, USEPA will review analytical standards verification and preparation documentation, as deemed appropriate.
	Data Package Audits	Performance standards are outlined in Exhibit E, Sections 9.0 through 9.2.	Data package audits are performed by USEPA to evaluate technical quality of the hardcopy raw data, QA, and adherence to contractual requirements.
	Regional Data Review	Analytical data is reviewed by each Region from the perspective of the end user to determine the usability of the data, as outlined in Exhibit E, Section 10.0.	Regional validation and/or CADRE reports are generated for all data packages.

TABLE 1. Contract Laboratory Program Quality Assurance Monitoring Plan (Con't)

SOW Reference	Performance Requirements	Performance Standards	QA Monitoring Plan
Exhibit E: Contract Laboratory Program Quality Assurance Monitoring Plan (Con't)	Proficiency Testing	Performance standards are outlined in Exhibit E, Sections 11.0 through 11.2, and must be performed as stated.	Acceptable QB scores will assist in monitoring contractor performance as defined in Exhibit E, Sections 11.2.4.1 through 11.2.4.3, and 11.2.8.
	On-Site Laboratory Evaluations	Performance standards are outlined in Exhibit E, Sections 12.0 through 12.4.	USEPA will evaluate the results from quality assurance and evidentiary on-site audits as defined in Exhibit E, Sections 12.2.1 through 12.3.3, to assist in monitoring the contractor.
	Electronic Data Audits	Performance standards are outlined in Exhibit E, Sections 13.0 through 13.3.	CCS in Exhibit E, Section 7.0, will be used to monitor electronic deliverables.
	Data Management	Performance standards are outlined in Exhibit E, Sections 14.0 through 14.4, and must be performed as stated.	USEPA will monitor data management practices during quality assurance and evidentiary on-site audits.
Exhibit F: Chain-of-Custody, Document Control and Written Standard Operating Procedures	Standard Operating Procedures	Performance standards are outlined in Exhibit F, Sections 2.0 through 2.7.	SOPs will be reviewed by USEPA during Pre-Award, on-site audits, after modifications are made, and randomly as deemed appropriate.
	Written Standard Operating Procedures	Performance standards are outlined in Exhibit F, Sections 3.0 through 3.7.	SOPs will be reviewed by USEPA during Pre-Award, on-site audits, after modifications are made, and randomly as deemed appropriate.
Exhibit G: Glossary of Terms	Glossary of Terms	Contractors shall adhere to interpretation of SOW terms as defined within Exhibit G.	N/A

TABLE 1. Contract Laboratory Program Quality Assurance Monitoring Plan (Con't)

SOW Reference	Performance Requirements	Performance Standards	QA Monitoring Plan
Exhibit H: Data Dictionary and Format for Data Deliverables in Computer-Readable Format	Data Dictionary and Format	Performance standards are outlined in Exhibit H and Appendix A.	CCS in Exhibit E, Section 7.0, will be used to monitor electronic deliverables.
Appendix B: Modified Analysis	GFAA requirements are outlined in Appendix B, Sections 1.0 through 8.0, 14.0, and 15.0.	Performance standards are outlined in Appendix B, Sections 9.0 through 11.0.	QA monitoring plan is outlined in Appendix B, Section 12.0, and Exhibit E.

EXHIBIT F

CHAIN-OF-CUSTODY, DOCUMENT CONTROL
AND WRITTEN STANDARD OPERATING PROCEDURES

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Exhibit F - Chain-of-Custody, Document Control and
Written Standard Operating Procedures

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1.0 INTRODUCTION

A sample is physical evidence collected from a facility or from the environment. Controlling evidence is an essential part of the hazardous waste investigation effort. To ensure that U.S. Environmental Protection Agency's (USEPA's) sample data and records supporting sample-related activities are admissible and have weight as evidence in future litigation, Contractors are required to maintain USEPA samples under chain-of-custody and to account for all samples and supporting records of sample handling, preparation, and analysis. Contractors shall maintain sample identity, sample custody, and all sample-related records according to the requirements in this exhibit.

1.1 Purpose of Evidence Requirements

The purpose of the evidence requirements include:

- Ensuring traceability of samples while in possession of the Contractor;
- Ensuring custody of samples while in possession of the Contractor;
- Ensuring the integrity of sample identity while in possession of the Contractor;
- Ensuring sample-related activities are recorded on documents or in other formats for USEPA sample receipt, storage, preparation, analysis, and disposal;
- Ensuring all laboratory records for each specified Sample Delivery Group will be accounted for when the project is completed; and
- Ensuring that all laboratory records directly related to USEPA samples are assembled and delivered to USEPA or, prior to delivery, are available upon USEPA's request.

2.0 STANDARD OPERATING PROCEDURES

The Contractor shall implement the following Standard Operating Procedures (SOPs) for sample receiving, sample identification, sample security, sample storage, sample tracking and document control, computer-resident sample data control, and Complete Sample Delivery Group (SDG) File (CSF) organization and assembly to ensure accountability of USEPA sample chain-of-custody as well as control of all USEPA sample-related records.

2.1 Sample Receiving

2.1.1 The Contractor shall designate a sample custodian responsible for receiving USEPA samples.

2.1.2 The Contractor shall designate a representative to receive USEPA samples in the event that the sample custodian is not available.

2.1.3 Upon receipt, the condition of shipping containers and sample containers shall be inspected and recorded on Form DC-1 by the sample custodian or a designated representative.

2.1.4 Upon receipt, the condition of the custody seals (intact/broken) shall be inspected and recorded on Form DC-1 by the sample custodian or a designated representative.

2.1.5 The sample custodian or a designated representative shall verify and record on Form DC-1 the agreement or disagreement of information recorded on all documents received with samples and information recorded on sample containers.

2.1.6 The sample custodian or a designated representative shall verify and record the following information on Form DC-1 as samples are received and inspected:

- Presence or absence and condition of custody seals on shipping and/or sample containers;
- Custody seal numbers when present;
- Presence or absence of Traffic Reports/Chain of Custody Records or Packing Lists;
- Presence or absence of airbills or airbill stickers;
- Airbill or airbill sticker numbers;
- Presence or absence of sample tags;
- Sample tags listed/not listed on Traffic Reports/Chain of Custody Records;
- Condition of the sample bottles;
- Presence or absence of cooler temperature indicator bottle;
- Cooler temperature;
- Date of receipt;
- Time of receipt;
- EPA sample numbers;

- pH of all aqueous samples;
- Sample tag numbers;
- Assigned laboratory numbers;
- Remarks regarding condition of sample shipment, etc.;
- Samples delivered by hand; and
- Problems and discrepancies.

2.1.7 The sample custodian or a designated representative shall sign, date, and record the time on all accompanying forms, when applicable, at the time of sample receipt (e.g., Traffic Reports/Chain of Custody Records or packing lists, and airbills).

NOTE: Initials are not acceptable.

2.1.8 The Contractor shall contact the Sample Management Office (SMO) to resolve problems and discrepancies including, but not limited to: absent documents; conflicting information; absent or broken custody seals; insufficient sample volume; unsatisfactory sample condition (e.g., leaking sample container); and samples not preserved to the proper pH.

2.1.9 The Contractor shall record the resolution of all problems and discrepancies communicated through SMO.

2.2 Sample Identification

2.2.1 The Contractor shall maintain the identity of USEPA samples and prepared samples (including extracted samples, digested samples, and distilled samples) throughout the laboratory.

2.2.2 Each sample and sample preparation container shall be labeled with the EPA sample number or a unique laboratory sample identification number.

2.3 Sample Security

2.3.1 The Contractor shall demonstrate that USEPA sample custody is maintained from receiving through retention or disposal. A sample is in custody if:

- It is in your possession; or
- It is in your view after being in your possession; or
- It is locked in a secure area after being in your possession; or
- It is in a designated secure area. (Secure areas shall be accessible only to authorized personnel).

2.3.2 The Contractor shall demonstrate security of designated secure areas.

2.4 Sample Storage

The Contractor shall designate storage areas for USEPA samples and prepared samples.

2.5 Sample Tracking and Document Control

2.5.1 The Contractor shall record all activities performed on USEPA samples.

2.5.2 Titles which identify the activities recorded shall be printed on each page of all laboratory documents. (Activities include, but are not limited to: sample receipt; sample storage; sample preparation, and sample analysis.) When a document is a record of analysis, the instrument type and parameter group [e.g., ICP-AES (metals)] shall be included in the title.

2.5.3 When columns are used to organize information recorded on laboratory documents, the information recorded in the columns shall be identified in a column heading.

2.5.4 Reviewers' signatures shall be identified on laboratory documents when reviews are conducted.

NOTE: Individuals recording review comments on computer-generated raw data are not required to be identified unless the written comments address data validity.

2.5.5 The laboratory name shall be identified on preprinted laboratory documents.

2.5.6 Each laboratory document entry shall be dated with the month/day/year (e.g., 01/01/1999) and signed by the individual(s) responsible for performing the recorded activity at the time the activity is recorded.

2.5.7 Notations on laboratory documents shall be recorded in ink.

2.5.8 Corrections to laboratory data reporting forms and raw data shall be made by drawing single lines through the errors and entering the correct information. Information shall not be obliterated or rendered unreadable. Corrections and additions to information shall be signed (or initialed) and dated.

2.5.9 Unused portions of laboratory documents shall be lined-out.

2.5.10 Pages in bound and unbound logbooks shall be sequentially numbered.

2.5.11 Instrument-specific run logs shall be maintained to enable the reconstruction of run sequences.

2.5.12 Logbook entries shall be in chronological order.

2.5.13 Logbook entries shall include only one SDG per page, except in the events where SDGs "share" Quality Control (QC) samples (e.g., instrument run logs and extraction logs).

2.5.14 Each page in bound and unbound logbooks shall be dated (month/day/year) and signed (no initials) at the bottom by the individual recording the activity (if a single entry is made on a page) or by the last individual recording information on the page (if multiple entries are on the same page).

2.5.15 Information inserted into laboratory documents shall be affixed permanently in place. The individual responsible for inserting information shall sign and date across the insert and logbook page at the time information is inserted.

2.5.16 The Contractor shall document disposal or retention of USEPA samples, remaining portions of samples, and prepared samples.

2.6 Computer-Resident Sample Data Control

2.6.1 Contractor personnel responsible for original data entry shall be identified at the time of data input.

2.6.2 The Contractor shall make changes to electronic data in a manner which ensures that the original data entry is preserved, the editor is identified, and the revision date is recorded.

2.6.3 The Contractor shall routinely verify the accuracy of manually entered data, electronically entered data, and data acquired from instruments.

2.6.4 The Contractor shall routinely verify documents produced by the electronic data collection system to ensure accuracy of the information reported.

2.6.5 The Contractor shall ensure that the electronic data collection system is secure.

2.6.5.1 The electronic data collection system shall be maintained in a secure location.

2.6.5.2 Access to the electronic data collection system functions shall be limited to authorized personnel through utilization of software security techniques (e.g., log-ons or restricted passwords).

2.6.5.3 Electronic data collection systems shall be protected from the introduction of external programs or software (e.g., viruses).

2.6.6 The Contractor shall designate archive storage areas for electronic data and the software required to access the data.

2.6.7 The Contractor shall designate an individual responsible for maintaining archives of electronic data including the software.

2.6.8 The Contractor shall maintain the archives of electronic data and necessary software in a secure location. (Secure areas shall be accessible only to authorized personnel.)

2.7 Complete SDG File (CSF) Organization and Assembly

2.7.1 The Contractor shall designate a document control officer responsible for the organization and assembly of the CSF.

2.7.2 The Contractor shall designate a representative responsible for the organization and assembly of the CSF in the event that the document control officer is not available.

2.7.3 The Contractor shall maintain documents relating to the CSF in a secure location.

2.7.4 All original laboratory forms and copies of SDG-related logbook pages shall be included in the CSF.

2.7.5 Copies of laboratory documents in the CSF shall be photocopied in a manner to provide complete and legible replicates.

2.7.6 Documents relevant to each SDG including, but not limited to, the following shall be included in the CSF:

- logbook pages;
- bench sheets;
- screening records;
- preparation records;
- repreparation records;
- analytical records;
- re-analysis records;
- records of failed or attempted analysis;
- custody records;
- sample tracking records;
- raw data summaries;
- computer printouts;
- correspondence;
- FAX originals;
- library search results; and
- other.

2.7.7 The document control officer or a designated representative shall ensure that sample tags are encased in clear plastic bags before placing them in the CSF.

2.7.8 CSF documents shall be organized and assembled on an SDG-specific basis.

2.7.9 Original documents which include information relating to more than one SDG (e.g., Traffic Reports/Chain of Custody Records, calibration logs) shall be filed in the CSF of the lowest SDG number, and copies of these originals shall be placed in the other CSF(s). The document control officer or a designated representative shall record the following statement on the copies in (indelible) *dark ink*:

COPY
ORIGINAL DOCUMENTS ARE INCLUDED IN CSF _____

_____
Signature

_____
Date

2.7.10 All CSFs shall be submitted with a completed Form DC-2. All resubmitted CSFs shall be submitted with a new or revised Form DC-2.

2.7.11 Each item in the CSF and resubmitted CSFs shall be inventoried and assembled in the order specified on Form DC-2. Each page of the CSF shall be stamped with a sequential number. Page number ranges shall be recorded in the columns provided on Form DC-2. Intentional gaps in the page numbering sequence shall be recorded in the "Comments" section on Form DC-2. When inserting new or inadvertently omitted documents, the Contractor shall identify them with unique accountable numbers. The unique accountable numbers and the locations of the documents shall be recorded in the "Other Records" section on Form DC-2.

2.7.12 Before shipping each CSF, the document control officer or a designated representative shall verify the agreement of information recorded on all documentation and ensure that the information is consistent and the CSF is complete.

2.7.13 The document control officer or a designated representative shall document the shipment of deliverable packages including what was sent, to whom, the date, and the carrier used.

2.7.14 Shipments of deliverable packages, including resubmittals, shall be sealed with custody seals by the document control officer or a

designated representative in a manner such that opening the packages would break the seals.

2.7.15 Custody seals shall be signed and dated by the document control officer or a designated representative when sealing deliverable packages.

3.0 WRITTEN STANDARD OPERATING PROCEDURES

The Contractor shall develop and implement the following written Standard Operating Procedures (SOPs) for sample receiving, sample identification, sample security, sample storage, sample tracking and document control, computer-resident sample data control, and Complete Sample Delivery Group (SDG) File (CSF) organization and assembly to ensure accountability for USEPA sample chain-of-custody and control of all USEPA sample-related records.

3.1 Sample Receiving

3.1.1 The Contractor shall have written SOPs for sample receiving which accurately reflect the procedures used by the laboratory.

3.1.2 The written SOPs for sample receiving shall ensure that the procedures listed below are in use at the laboratory.

3.1.2.1 The condition of shipping containers and sample containers are inspected and recorded on Form DC-1 upon receipt by the sample custodian or a designated representative.

3.1.2.2 The condition of custody seals are inspected and recorded on Form DC-1 upon receipt by the sample custodian or a designated representative.

3.1.2.3 The presence or absence of the following documents/items accompanying the sample shipment is verified and recorded on Form DC-1 by the sample custodian or a designated representative:

- Custody seals;
- Traffic Reports/Chain of Custody Records or Packing Lists;
- Airbills or airbill stickers;
- Sample tags; and
- Cooler temperature indicator bottle.

3.1.2.4 The agreement or disagreement of information recorded on shipping documents with information recorded on sample containers is verified and recorded on Form DC-1 by the sample custodian or a designated representative.

3.1.2.5 The following information is recorded on Form DC-1 by the sample custodian or a designated representative as samples are received and inspected:

- Custody seal numbers, when present;
- Airbill or airbill sticker numbers;
- Sample tag numbers listed/not listed on Traffic Reports/Chain of Custody Records;

- Condition of sample bottles;
- Cooler temperature;
- Date of receipt;
- Time of receipt;
- EPA sample numbers;
- pH of all aqueous samples;
- Sample tag numbers;
- Assigned laboratory numbers;
- Remarks regarding condition of sample shipment, etc.;
- Samples delivered by hand; and
- Problems and discrepancies.

3.1.2.6 All accompanying forms are signed, dated, and the time is recorded, when applicable, at the time of sample receipt (e.g., Traffic Reports/Chain of Custody Records or packing lists, and airbills) by the sample custodian or a designated representative.

3.1.2.7 The Sample Management Office (SMO) is contacted to resolve problems and discrepancies including, but not limited to: absent documents; conflicting information; absent or broken custody seals; insufficient sample volume; unsatisfactory sample condition (e.g., leaking sample container); and samples not preserved to the proper pH.

3.1.2.8 The resolution of all problems and discrepancies communicated through SMO is recorded.

3.2 Sample Identification

3.2.1 The Contractor shall have written SOPs for sample identification which accurately reflect the procedures used by the laboratory.

3.2.2 The written SOPs for sample identification shall ensure that the procedures listed below are in use at the laboratory.

3.2.2.1 The identity of USEPA samples and prepared samples is maintained throughout the laboratory when:

- The Contractor assigns unique laboratory sample identification numbers, the written SOPs shall include a description of the procedure used to assign these numbers;
- The Contractor uses prefixes or suffixes in addition to laboratory sample identification numbers, the written SOPs shall include their definitions; and
- The Contractor uses methods to uniquely identify fractions/parameter groups and matrix type, the written SOPs shall include a description of these methods.

3.2.2.2 Each sample and sample preparation container is labeled with the SMO number or a unique laboratory sample identification number.

3.3 Sample Security

3.3.1 The Contractor shall have written SOPs for sample security which accurately reflect the procedures used by the laboratory.

3.3.2 The written SOPs for sample security shall include the items listed below.

3.3.2.1 Procedures which ensure the following:

- Sample custody is maintained; and
- The security of designated secure areas is maintained.

3.3.2.2 A list of authorized personnel who have access to locked storage areas.

3.4 Sample Storage

3.4.1 The Contractor shall have written SOPs for sample storage which accurately reflect the procedures used by the laboratory.

3.4.2 The written SOPs for sample storage shall describe locations, contents, and identities of all storage areas for USEPA samples and prepared samples in the laboratory.

3.5 Sample Tracking and Document Control

3.5.1 The Contractor shall have written SOPs for sample tracking and document control which accurately reflect the procedures used by the laboratory.

3.5.2 The written SOPs for sample tracking and document control shall include the items listed below.

3.5.2.1 Examples of all laboratory documents used during sample receiving, sample storage, sample transfer, sample analyses, CSF organization and assembly, and sample retention or disposal.

3.5.2.2 Procedures which ensure the following:

- All activities performed on USEPA samples are recorded;
- Titles which identify the activities recorded are printed on each page of all laboratory documents;
- Information recorded in columns is identified with column headings;
- Reviewers' signatures are identified on laboratory documents;
- The laboratory name is included on preprinted laboratory documents;
- Laboratory document entries are signed and dated with the month/day/year (e.g., 01/01/1999);
- Entries on all laboratory documents are recorded in ink;
- Corrections and additions to laboratory documents are made by drawing single lines through the errors, entering the correct information, and initialing and dating the new information;

- Unused portions of laboratory documents are lined-out;
- Pages in bound and unbound logbooks are sequentially numbered;
- Instrument-specific run logs are maintained to enable the reconstruction of run sequences;
- Logbook entries are recorded in chronological order;
- Entries are recorded for only one SDG on a page, except in the event where SDGs "share" Quality Control (QC) samples (e.g., instrument run logs and extraction logs);
- Each page in bound and unbound logbooks shall be dated (month/day/year) and signed (no initials) at the bottom by the individual recording the activity (if a single entry is made on a page) or by the last individual recording information on the page (if multiple entries are on the same page);
- Information inserted in laboratory documents is affixed permanently, signed, and dated across the insert; and
- The retention or disposal of USEPA samples, remaining portions of samples, and prepared samples is documented.

3.6 Computer-Resident Sample Data Control

3.6.1 The Contractor shall have written SOPs for computer-resident sample data control which accurately reflect the procedures used by the laboratory.

3.6.2 The written SOPs for computer-resident sample data control shall include the items listed below.

3.6.2.1 Procedures which ensure the following:

- Contractor personnel responsible for original data entry are identified;
- Changes to electronic data are made such that the original data entry is preserved, the editor is identified, and the revision date is recorded;
- The accuracy of manually entered data, electronically entered data, and data acquired from instruments is verified;
- Report documents produced by the electronic data collection system are routinely verified to ensure the accuracy of the information reported;
- Electronic data collection system security is maintained;
- Archives of electronic data and accompanying software are maintained in a secure location; and
- Off-site backup and storage of electronic data is maintained.

3.6.2.2 Descriptions of archive storage areas for the electronic data and the software required to access data archives.

3.6.2.3 A list of authorized personnel who have access to electronic data collection system functions and to archived data.

3.7 CSF Organization and Assembly

3.7.1 The Contractor shall have written SOPs for CSF organization and assembly which accurately reflect the procedures used by the laboratory.

3.7.2 The written SOPs for CSF organization and assembly shall ensure that the procedures listed below are in use at the laboratory.

- Documents relating to the CSF are maintained in a secure location.
- All original laboratory forms and copies of SDG-related logbook pages are included in the CSF.
- Laboratory documents are photocopied in a manner to provide complete and legible replicates.
- All documents relevant to each SDG are included in the CSF.
- Sample tags are encased in clear plastic bags by the document control officer or a designated representative before placing them in the CSF.
- The CSF is organized and assembled on an SDG-specific basis.
- Original documents which contain information relating to more than one SDG are filed in the CSF of the lowest SDG and copies are referenced to originals in the event that an original document contains information relating to more than one SDG.
- Each CSF is submitted with a completed Form DC-2, and resubmitted CSFs are submitted with a new or revised Form DC-2.
- Each page of the CSF is stamped with a sequential number and the page number ranges are recorded in the columns provided on Form DC-2. Intentional gaps in the page numbering sequence are recorded in the "Comments" section of Form DC-2. Inserted documents are recorded in the "Other Records" section of Form DC-2.
- Consistency and completeness of the CSF are verified by the document control officer or a designated representative.
- Shipments of deliverable packages are documented by the document control officer or a designated representative.
- Deliverable packages are shipped by the document control officer or a designated representative using custody seals in a manner such that opening the packages would break the seals.
- Custody seals are signed and dated by the document control officer or a designated representative before placing them on deliverable packages.

EXHIBIT G

GLOSSARY OF TERMS

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ABSORBANCE - A measure of the decrease in incident light passing through a sample into a detector. It is defined mathematically as:

Absorbance

$$A = -\log \frac{I}{Io}$$

WHERE,

I = Radiation intensity of a sample.
I_o = Radiation intensity of a blank.

ALIQUOT - A measured portion of a field sample, standard, or solution taken for sample preparation and/or analysis.

ANALYSIS DATE/TIME - The date and military time (24-hour clock) of the introduction of the sample, standard, or blank into the analysis system.

ANALYTE - The element or ion an analysis seeks to determine; the element of interest.

ANALYTICAL SAMPLE - Any solution or media introduced into an instrument on which an analysis is performed, excluding instrument calibration, initial calibration verification (ICV), initial calibration blank (ICB), continuing calibration verification (CCV), continuing calibration blank (CCB), and tunes. Note the following are all defined as analytical samples: undiluted and diluted samples (USEPA and non-USEPA), matrix spike samples, duplicate samples, serial dilution samples, analytical spike samples, post-digestion spike samples, Interference Check Samples (ICSs), Contract Required Quantitation Limit (CRQL) Check Standards (CRIs), Laboratory Control Samples (LCSs), Performance Evaluation (PE) samples, Preparation Blanks (PBs), Linear Range Samples (LRSs), and cyanide MIDRANGE samples.

ANALYTICAL SEQUENCE - The actual instrumental analysis of the samples from the time of instrument calibration through the analysis of the final CCV or CCB. All sample analyses during the analytical sequence are subject to the QC protocols set forth in Exhibits D and E of this contract unless otherwise specified in the individual methods.

ANALYTICAL SERVICES BRANCH (ASB) - The division of United States Environmental Protection Agency's (USEPA) Office of Superfund Remediation and Technology Innovation (OSRTI) responsible for the overall management of the Contract Laboratory Program (CLP).

ANALYTICAL SPIKE - A spike that is fortified just prior to analysis by adding a known quantity of the analyte to an aliquot of the prepared sample.

ASTM - American Society for Testing and Materials. A developer and provider of voluntary consensus standards.

AUTOZERO - Zeroing the instrument at the proper wavelength. It is equivalent to running a standard blank with the absorbance set at zero.

BACKGROUND CORRECTION - A technique to compensate for variable background contribution to the instrument signal in the determination of trace elements.

BASELINE - Analysis used to reset the baseline during mercury or cyanide runs.

BATCH - A group of samples prepared at the same time in the same location using the same method.

BLANK - An analytical sample designed to assess specific sources of contamination. See individual definitions for types of blanks.

CALIBRATION - The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type of reagents or concentration of acids as used in the sample preparation.

CALIBRATION BLANK - A blank solution containing all of the reagents and in the same concentration as those used in the analytical sample preparation. This blank is not subjected to the preparation method.

CALIBRATION STANDARDS - A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). The solutions may or may not be subjected to the preparation method but contain the same matrix (i.e., the same amount of reagents and/or preservatives) as the sample preparations to be analyzed.

CASE - A finite, usually predetermined number of samples collected over a given time period from a particular site. Case numbers are assigned by the Sample Management Office (SMO). A Case consists of one or more Sample Delivery Groups (SDGs).

CONCENTRATION LEVEL (low or medium) - For inorganics analysis, low or medium level is defined by the appropriate designation by the sampler on the Traffic Report/Chain of Custody Record.

CONTAMINATION - A component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents laboratory environment, or analytical instruments.

CONTINUING CALIBRATION VERIFICATION (CCV) - A single parameter or multi-parameter standard solution prepared by the analyst and used to verify the stability of the instrument calibration with time, and the instrument performance during the analysis of samples. The CCV can be one of the calibration standards. However, all parameters being measured by the particular system must be represented in this standard and the standard must have the same matrix (i.e., the same amount of reagents and/or preservatives) as the samples. The CCV should have a concentration in the middle of the calibration range and shall be run every 10 analytical samples or every 2 hours, whichever is more frequent.

CONTRACT COMPLIANCE SCREENING (CCS) - A screening of electronic and hardcopy data deliverables for completeness and compliance with the contract. This screening is done under USEPA direction by the SMO Contractor.

CONTRACT LABORATORY PROGRAM (CLP) - Supports the USEPA's Superfund effort by providing a range of state-of-the-art chemical analytical services of known quality. This program is directed by the Analytical Services Branch (ASB) of the Office of Superfund Remediation and Technology Innovation (OSRTI) of USEPA.

CONTRACT REQUIRED QUANTITATION LIMIT (CRQL) - Minimum level of quantitation acceptable under the contract Statement of Work (SOW).

CONTRACT REQUIRED QUANTITATION LIMIT (CRQL) CHECK STANDARD (CRI) - A single parameter or multi-parameter standard solution prepared at the CRQL and used to verify the instrument calibration at low levels.

CONTROL LIMITS - A range within which specified measurement results must fall to be compliant. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that noncompliant data be flagged.

CYANIDE (Total) - Cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

DATE - MM/DD/YYYY - Where MM = 01 for January, 02 for February, ... 12 for December; DD = 01 to 31; YYYY = 1998, 1999, 2000, 2001, etc.

DAY - Unless otherwise specified, day shall mean calendar day.

DIGESTION LOG - An official record of the sample preparation (digestion).

DIRECT ANALYSIS - Analysis of a sample, standard, or blank that has not been taken through a preparation procedure (digestion or distillation).

DISSOLVED METALS - Analyte elements in a water/aqueous sample which will pass through a 0.45 micrometer (µm) filter.

DRY WEIGHT - The weight of a sample based on percent solids. The weight after drying in an oven.

DUPLICATE - A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

FIELD BLANK - This is any sample that is submitted from the field and is identified as a blank. This includes trip blanks, rinsates, equipment blanks, etc.

FIELD QC - Any Quality Control sample submitted from the field to the laboratory. Examples include, but are not limited to: field blanks, field duplicates, and field spikes.

FIELD SAMPLE - A portion of material received to be analyzed that is contained in single or multiple containers and identified by a unique EPA sample number.

GRAPHITE FURNACE ATOMIC ABSORPTION (GFAA) - A technique for the determination of analytes in which a sample aliquot is injected into a hollow graphite tube, which is then heated to atomize the analyte. The vapor absorbs light at wavelengths characteristic of the element(s) atoms present.

HOLDING TIME - The elapsed time expressed in days from the date of receipt of the sample by the Contractor until the date of its analysis.

Holding time = (sample analysis date - sample receipt date)

INDEPENDENT STANDARD - A Contractor-prepared standard solution that is composed of analytes from a different source than those used in the standards for the calibration.

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY (ICP-AES) - A technique for the simultaneous or sequential multi-element determination of elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Characteristic atomic line emission spectra are produced by excitation of the sample in a radio frequency inductively coupled plasma.

INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (ICP-MS) - A technique for the multi-element determination of elements in solution. The basis of the technique is the detection of atomic ions produced by an ICP and sorted by mass/charge ratio.

IN-HOUSE - At the Contractor's facility.

INITIAL CALIBRATION - Analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity, and dynamic range of the instrument to target analytes.

INITIAL CALIBRATION VERIFICATION (ICV) - Solution(s) prepared from stock standard solutions, metals or salts obtained from a source separate from that utilized to prepare the calibration standards. The ICV is used to verify the concentration of the calibration standards and the adequacy of the instrument calibration. The ICV should be traceable to NIST or other certified standard sources when USEPA ICV solutions are not available.

INJECTION - Introduction of the analytical sample into the instrument excitation system for the purpose of measuring absorbance, emission or concentration of an analyte. May also be referred to as exposure.

INSUFFICIENT QUANTITY - When there is not enough volume (water/aqueous sample) or weight (soil/sediment) to perform any of the required operations: sample analysis, percent solids, etc. Exhibit D provides guidance for addressing this problem.

INTERFERENCE CHECK SAMPLE - A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors.

INTERFERENTS - Substances which affect the analysis for the element of interest.

INTERNAL STANDARD - A non-target element added to a sample at a known concentration after preparation but prior to analysis. Instrument responses to internal standards are monitored as a means of assessing overall instrument performance.

LABORATORY - Synonymous with Contractor as used herein.

LABORATORY CONTROL SAMPLE (LCS) - A control sample of known composition. Laboratory control samples are analyzed using the same sample preparation, reagents, and analytical methods employed for the USEPA samples received.

LABORATORY RECEIPT DATE - The date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and Sample Traffic Report/Chain of Custody Record. Also referred to as VTSR (Validated Time of Sample Receipt).

LINEAR RANGE, LINEAR DYNAMIC RANGE - The concentration range over which the instrument response remains linear.

MATRIX - The predominant material of which the sample to be analyzed is composed. For the purpose of this SOW, a sample matrix is either water/ aqueous or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

MATRIX EFFECT - In general, the effect of particular matrix constituents.

MATRIX SPIKE - Aliquot of a sample (water/aqueous or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

METHOD DETECTION LIMIT (MDL) - The concentration of a target parameter that, when a sample is processed through the complete method, produces a signal with 99 percent probability that it is different from the blank. For 7 replicates of the sample, the mean value must be 3.14s above the blank, where "s" is the standard deviation of the 7 replicates.

MIDRANGE - A distilled standard at a concentration approximately equivalent to the midpoint of the calibration curve used to verify the reliability of the distillation procedure.

NARRATIVE (SDG Narrative) - Portion of the data package which includes laboratory, contract, Case, sample number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution. Complete SDG Narrative specifications are included in Exhibit B.

PERCENT DIFFERENCE (%D) - As used in this SOW and elsewhere to compare two values. The difference between the two values divided by one of the values.

PERCENT SOLIDS (%S) - The proportion of solid in a soil sample determined by drying an aliquot of the sample.

PERFORMANCE EVALUATION (PE) SAMPLE - A sample of known composition provided by USEPA for Contractor analysis. Used by USEPA to evaluate Contractor performance.

PREPARATION BLANK - An analytical control that contains reagent water and reagents, which is carried through the entire preparation and analytical procedure.

PREPARATION LOG - An official record of the sample preparation (digestion or distillation).

QUALITY ASSURANCE TECHNICAL SUPPORT (QATS) LABORATORY - A Contractor-operated facility operated under the QATS contract, awarded and administered by USEPA.

REAGENT WATER - The purity of this water must be equivalent to ASTM Type II reagent water of Specification D1193-77, "Standard Specification for Reagent Water".

RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOW and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

REPRESENTATIVE - Alternate or designee who has the knowledge and authority to perform a specific task.

RESLOPE - An analysis used to re-align the calibration curve during mercury or cyanide runs.

ROUNDING RULES - If the figure is greater than or equal to 5, round up, otherwise round down. As an example, 11.443 is rounded down to 11.44 and 11.455 is rounded up to 11.46. If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures. See forms instructions (Exhibit B) for exceptions.

RUN - A continuous analytical sequence consisting of prepared samples and all associated Quality Assurance (QA) measurements as required by the contract SOW. A run begins with the instrument calibration and is to be completed within a 24-hour period.

SAMPLE - A portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

SAMPLE DELIVERY GROUP (SDG) - A unit within a sample Case that is used to identify a group of samples for delivery. An SDG is defined by the following, whichever is most frequent:

- Each Case of field samples received, or
- Each 20 field samples [excluding Performance Evaluation (PE) samples] within a Case, or
- Each 7 calendar day period (3 calendar day period for 7 day turnaround) during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).
- In addition, all samples and/or sample fractions assigned to an SDG must have been scheduled under the same contractual turnaround time. Preliminary Results have **no impact** on defining the SDG.

Samples may be assigned to SDGs by matrix (i.e., all soil samples in one SDG, all water samples in another) at the discretion of the laboratory.

SAMPLE MANAGEMENT OFFICE (SMO) - A Contractor-operated facility operated under the SMO contract, awarded and administered by USEPA.

SAMPLE NUMBER (EPA SAMPLE NUMBER) - A unique identification number designated by USEPA for each sample. The EPA sample number appears on the sample Traffic Report/Chain of Custody Record which documents information on that sample.

SENSITIVITY - The slope of the analytical curve (i.e., functional relationship between instrument response and concentration).

SERIAL DILUTION - The dilution of a sample by a factor of five. When corrected by the dilution factor, the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents.

SOIL - Synonymous with soil/sediment or sediment as used herein.

SOP - Standard Operating Procedure.

SOW - Statement of Work.

STANDARD ANALYSIS - An analytical determination made with known quantities of target analytes.

STOCK SOLUTION - A standard solution which can be diluted to derive other standards.

TARGET ANALYTE LIST (TAL) - A list of Inorganic Analytes (metals and cyanide) as designated in Exhibit C.

TIME - When required to record time on any deliverable item, time shall be expressed as Military Time [i.e., a 24-hour clock (0000-2359)].

TRAFFIC REPORT/CHAIN OF CUSTODY RECORD (TR/COC) - An USEPA sample identification form filled out by the sampler, which accompanies the sample during shipment to the laboratory and is used for documenting sample identity, sample chain-of-custody, and sample receipt by the laboratory.

TUNE - Analysis of a solution containing a range of isotope masses to establish ICP-MS accuracy, resolution, and precision prior to calibration.

USEPA OSRTI ASB INORGANIC PROGRAM MANAGER (ASB PM) - The USEPA, OSRTI ASB Official who manages the CLP Inorganic Program.

USEPA REGIONAL CLP PROJECT OFFICER (CLP PO) - The Regional USEPA official responsible for monitoring laboratory performance and/or requesting analytical data or services from a CLP laboratory.

VALIDATED TIME OF SAMPLE RECEIPT (VTSR) - The date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and Sample Traffic Report/Chain of Custody Record.

WET WEIGHT - The weight of a sample aliquot including moisture (undried).

10% FREQUENCY - A frequency specification during an analytical sequence allowing for no more than 10 analytical samples between required calibration verification measurements, as specified by the contract SOW.

EXHIBIT H

DATA DICTIONARY AND FORMAT
FOR DATA DELIVERABLES IN
COMPUTER-READABLE FORMAT

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Exhibit H - Data Dictionary and Format for Data Deliverables
in Computer-Readable Format

Table of Contents

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1.0 USEPA AGENCY STANDARD IMPLEMENTATION

1.1 Format Characteristics

The following constitutes an implementation of the USEPA Agency Standard for Electronic Data Transmission based upon analytical results and ancillary information required by the contract. All data generated by a single analysis are grouped together, and the groups are aggregated to produce files that report data from a Sample Delivery Group (SDG). Because this implementation is only a subset of the USEPA Agency Standard, some fields have been replaced by delimiters as place holders for non-Contract Laboratory Program (CLP) data elements.

1.1.1 This implementation includes detailed specifications for the required format of each record. The position in the record where each field is to be contained relevant to other fields is specified, as well as the maximum length of the field. Each field's required contents are specified as literal (contained in quotes), which must appear exactly as shown (without quotes), or as a variable for which format and/or descriptions are listed in the format/contents column. Options and examples are listed for most fields. For fields where more than three options are available, a list and description of options are supplied following the record descriptions. Fields are separated from each other by the delimiter "|" (ASCII 124). Fields that do not contain data should be zero length or a blank field (empty with no space or additional delimiters between the delimiters before and after the field) with the delimiter as a place holder. For the purposes of Section 9 of this Exhibit, wherever "blank" is given as an option under the "Format/Contents" column, it refers to a blank field as explained above.

1.1.2 Numeric fields may contain numeric digits, a decimal place, and a leading minus sign. A positive sign is assumed if no negative sign is entered in a numeric field and must not be entered into any numeric field. Values that exceed the maximum length allowed shall be reported to the maximum possible, maintaining the specified decimal place and maximum field length restrictions.

1.1.3 Requirements for significant figures and number of decimal places are specified in Exhibit B. The numeric field lengths are specified such that all possible numeric values can be written to the file. The size of the numeric field indicates the maximum number of digits, including a decimal place and negative sign, if appropriate, that can appear in the field at the same time. Therefore, the number reported may need to be rounded (using rounding rules described in Exhibit B) to fit into the field. The rounding must maintain the greatest significance possible providing the field length limitation. In addition, the rounded number that appears on the form, and therefore the field in the diskette file, must be used in any calculation that may result in other numbers reported on the same form or other forms in the SDG. Field lengths should only be as long as necessary to contain the data; packing with blanks is not allowed.

1.1.4 USEPA is currently developing a data delivery strategy that may be used as an alternative to the requirements stated in Exhibit H. This strategy's intent is to provide a neutral data delivery structure to the Contractor that will further facilitate the exchange of analytical information generated under this analytical protocol. The proposed strategy is intended to accommodate laboratories that generate data transmission files under multiple data formats. Upon implementation of this alternate electronic data delivery strategy by the USEPA and prior to submission of data in alternate format(s), the

Contractor must first demonstrate its ability to provide electronic data as stated in this Exhibit H and obtain written permission from the USEPA for the submission of data in alternate format(s). The Contractor will receive a written response to its request within 90 calendar days. However, until the implementation of this alternate electronic data delivery strategy by the USEPA, all electronic data deliverables must be provided as specified in this Exhibit H.

2.0 RECORD TYPES

2.1 Specifications

The USEPA Agency Standard consists of variable length ASCII records. Maximum field length specifications match the reporting requirements in Exhibit B. The last two bytes of each record must contain "carriage return" and "line feed", respectively.

2.1.1 This implementation consists of twelve record types that can be summarized in four groups, designated by the first record type in each group:

Type	Type ID	Contents
Run Header	10	Information pertinent to a group of samples processed in a continuous sequence; usually several per SDG
Sample Header	20	Sample identifying, qualifying, and linking information
Results Record	30	Analyte results and qualifications
Comments Record	90	Free form comments

2.1.2 All record types given are mandatory. Type 10, representing the analytical run, contains the instrument and run IDs which act as an identifying label for the run. All 10, 20, 30, and 90 series records following that record pertain to the same analytical run. Type 20, representing the sample, contains the EPA Sample ID which acts as an identifying label for the sample. The QC code indicates whether the data is from an environmental sample, calibration, or QC sample. All 20, 30, and 90 series records following that record pertain to the same sample. Type 30, representing an individual analyte, contains an identifier to identify the analyte. All 30 series records following that record pertain to the same analyte.

3.0 PRODUCTION RUNS

3.1 Specifications

A production run represents a "group" or "batch" of samples that are processed in a continuous sequence under relatively stable conditions. Specifically:

3.1.1 Calibration - All samples in a run use the same initial calibration data. For mercury analyses, samples prepared by a certain method must be analyzed with calibration and QC standards prepared by the same method. Therefore, all samples, calibration standards, and QC standards in a run must be associated with the same Preparation Code (Type 21 record).

3.1.2 Method number - Constant throughout a run.

3.1.3 Instrument conditions - Constant throughout a run. Results obtained on different instruments cannot be combined in one run.

3.1.4 Thus, each separate group of analyses on each instrument will consist of a separate production run, and must be reported in a separate file.

3.1.5 The run numbers in a Sample Delivery Group (SDG) must be unique; that is, there shall only be one Run Number "1", only one Run Number "2", etc. in an SDG.

3.1.6 In addition, later runs within a method for an analyte shall have a higher run number than earlier ones. For example, if arsenic is quantitated by the Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) method on 01/01/1999 beginning at 12:02 and arsenic is later quantitated by the ICP-AES method on 01/01/1999 beginning at 18:06, then the run beginning at 12:02 shall have a lower run number than the run beginning at 18:06.

3.2 Example

The following is an example of the sequence of record types in a production run.

10 Contains run header information. Occurs once per run.

16 Contains additional run header information. Occurs once per run.

20 Acts as a header for the following method and instrument parameters information. Occurs at least once per run with EPA sample number equal to "MDL". Analysis year, analysis month, analysis day equal the year, month and day the Method Detection Limit (MDL) was computed. Analyte count equals the number of the Type 30 records that follow.

- 21 Contains the Preparation Code (field #5) and the Preparation Date (fields #8, 9, 10) for the MDL. Occurs at least once per run with each Type 21 record preceded by the relevant Type 20 record and immediately followed by its related Type 30 record(s).

- 30 Contains the Analyte Identifier "C" (field #2), the Analyte CAS Number (field #3), the MDL Label "U" (field #20), and the MDL (field #21). Occurs once for each analyte used in the run.

20

21

30

20 Acts as a header for the following instrument parameter information. Occurs once per run with EPA sample number equal to "LRV". Analysis year, analysis month, analysis day equal the year, month and day the linear ranges were computed. Analyte count equals the number of Type 30, 32 and 34 groups that follow.

30 Contains only the Analyte CAS Number and the Analyte Identifier. Occurs once for each analyte used in the run.

32 Contains integration time information for the preceding analyte on the Type 30 record.

34 Contains the Contract Required Quantitation Limit (CRQL) and Linear Range information for the preceding analyte on the Type 30 record. There are as many consecutive Type 34 records as there are different wavelengths or masses used for the analyte identified on preceding Type 30.

30

32

34

20 Acts as a header for the following instrument parameter information. Occurs once per run with EPA sample number equal to "BCD". Analysis year, analysis month, analysis day equal the year, month and day the background correction factors were computed. Analyte count equals the number of the Type 30 and 35 groups that follow.

30 Contains only the Analyte CAS Number and the Analyte Identifier. Occurs once for each analyte used in the run.

35 Contains the background and interelement correction information for the preceding analyte on the Type 30 record. There are as many consecutive Type 35 records as there are interelement correction factors for the analyte identified on preceding Type 30.

30

35

20 Contains header information for sample and QC data.

21 Contains additional information for analytical and instrument QC samples. Will always be preceded by a Type 20 record.

22 Contains additional information for analytical samples. Will usually follow a Type 21 record.

30 Contains the sample level concentration, true or added value and QC value for each analyte. Occurs once for

each analytical result for the EPA sample number of the previous Type 20 record.

31 Reports any instrumental data necessary to obtain the result reported on the previous Type 30 record. Will always be preceded by a Type 30 or 31 record. For Inductively Couple Plasma - Mass Spectrometry (ICP-MS), there are as many Type 31 records as there are isotopes for the analyte identified on the preceding Type 30 record.

30 Values for the next analyte being measured.

31 Values for the next analyte being measured.

30

31

Type 30-31 record sequence continues as many times as the value of the ANALYTE COUNT on the previous Type 20 record.

20 Next Sample Header record - The following applies to the next sample data.

21

22

30

31

30

31 etc.

20

21

22

30

31 etc.

4.0 RECORD SEQUENCE

4.1 Specifications

A Run Header (Type 10) record must be present as the first record in the file (run). Further occurrences of the Type 10 record in the file are not allowed.

4.1.1 A Type 16 record must immediately follow the Type 10 record. Further occurrences of the Type 16 record in the file are not allowed.

4.1.2 The first Type 20 records with EPA sample numbers MDL, LRV, and BCD are headers for the run-wide method and instrument parameters.

4.1.3 The first Type 20 record of the Type 21, 30 group is a header for the annually determined Method Detection Limits (MDLs) and must immediately follow the Type 16 record. A Type 20 record of the Type 21, 30 group must be present for each MDL reported in the run. For ICP-AES, ICP-MS, and cyanide analyses, an MDL associated with Preparation Code "NP1" must be present in each run. This MDL shall be used in the qualification of the data reported for non-prepared samples and instrument QC analyses (except the distilled Initial Calibration Verification (ICV) standard for cyanide).

4.1.4 The next Type 20 record of the Type 30, 32, 34 group is a header for the Linear Range Values (LRVs) and must immediately follow the last Type 30 record of the Type 21, 30 group that pertains to the MDL. The linear range values for all methods except the Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) methods are the analytically determined concentrations of the highest instrument calibration standards that are used in the generation of the calibration curve at the beginning of every run. The linear range values for the ICP-AES and ICP-MS methods are the quarterly determined values that are reported on Form XI-IN of the hardcopy.

4.1.5 The next Type 20 record of the Type 30, 35 group is a header for the ICP-AES Background Correction Data (BCD) and must immediately follow the last Type 34 record of the Type 30, 32, 34 group that pertains to the linear range values. This Type 20 record is not required for methods MS, AV, CV, CA, AS and C (i.e., ICP-MS, mercury, and cyanide analyses).

4.1.6 These are the only occurrences of the Type 20 records that do not relate to actual analyses in the run. Therefore, the only fields that are not blank in these occurrences of the Type 20 record are the RECORD TYPE ("20"); EPA SAMPLE NUMBER ("MDL", "LRV" and "BCD"); Analysis Year/Year Computed, Analysis Month/Month Computed, Analysis Day/Day Computed ("YYYY", "MM", "DD"); and ANALYTE COUNT.

4.1.7 A minimum of one Type 30 record must immediately follow the Type 21 record of the Type 21, 30 group with EPA sample number MDL, and the total number of Type 30 records must be equivalent to the ANALYTE COUNT on the Type 20 record.

4.1.8 A minimum of one Type 30, 32, 34 group with EPA sample number LRV must immediately follow the Type 20 record which is preceded by the last Type 30 record of the final Type 21, 30 group. The information in each Type 30, 32, 34 group must pertain to one and only one analyte. The number of Type 30, 32, 34 groups must be equivalent to the ANALYTE COUNT on the Type 20 record.

4.1.9 A minimum of one Type 30, 35 group with EPA sample number BCD must immediately follow the Type 20 record for background correction data (if required). This Type 20 is preceded by the last Type 34 record of the final Type 30, 32, 34 group. The information in each Type 30, 35 group must pertain to one and only one analyte. The number of Type 30, 35 groups must be equivalent to the ANALYTE COUNT on the Type 20 record.

4.1.10 The Type 20 record that relates to the analysis of the first instrument calibration standard must immediately follow the last Type 30, 35 group for ICP-AES, or the last Type 30, 32, 34 group for mercury and cyanide analyses. For ICP-MS, the Type 20 record for the first instrument tune standard analysis must immediately follow the last Type 30, 32, 34 group and the Type 20 record for the first instrument calibration standard must immediately follow the last 30, 31 group from the last tune standard analyzed. After the appearance of these Type 20 records in the file, further occurrences of the Type 32, 34 and 35 records in that file are not allowed.

4.1.11 Each environmental sample, calibration, or Quality Control (QC) sample is represented by a group composed of Type 20, 21, and 22 records, which hold sample level identifying information, followed by a minimum of one group composed of Type 30 and 31 records for each analyte. The Type 20 record holds a count for the number of analytes being used to determine results. The ANALYTE COUNTER must have a value equivalent to the number of Type 30 groups associated with each Type 20 record.

4.1.12 Except for the first Type 20 records (EPA sample numbers MDL, LRV, BCD) for method ICP-AES and the first two Type 20 records (EPA sample numbers MDL, LRV) for the methods for ICP-MS, mercury and cyanide analyses, all Type 20 records should occur in the order of sample analysis.

4.1.13 Type 90 comment records may be defined to occupy any position except before the Type 10 (header) record. Comments pertaining to the whole run such as ones on Cover Page must appear before the first Type 20 record. Comments pertaining to a particular sample such as ones on Forms IA-IN and IB-IN must appear after the Type 20 record for that sample, but before the first Type 30 record associated with that sample. Comments pertaining to a particular analyte must appear after the Type 30 record of that analyte, but before the Type 30 record of the following analyte.

4.1.14 The Type 92 record which contains the sample associated data that is reported at the bottom of Forms IA-IN and IB-IN must appear anywhere after the Type 22 record for that EPA Field Sample, but before the Type 20 record of the next sample.

5.0 FILE/RECORD INTEGRITY

All record types must contain the following check fields to ensure file and record integrity:

Record Position	Field Length	Field Contents	Remarks
First Field	2	Record type or identifier	"10" or as appropriate
Last Field	5	Record sequence number	00000-99999, repeated as necessary. The record sequence numbers within a run must be in ascending order and shall not repeat until 99999 has been reached.
	4	Record checksum[1]	Four hexadecimal digits. The combination of record sequence number and record checksum must be unique within each run.
	2	Must contain CR and LF	

6.0 DATES AND TIMES

Date or time-of-day information consists of successive groups of digits, each separated by delimiters. Dates are given in the order YYYY MM DD, and times as HH MM. All hours must be given as 00 to 23 using a 24 hour clock and must be local time. All days shall be given as 01 to 31. All months shall be given as 01 to 12 (e.g., 01 is January, 02 is February).

7.0 MULTIPLE VOLUME DATA

There is no requirement under this format that all the data from an entire Sample Delivery Group (SDG) fit onto a single diskette. However, each single production run must fit onto a single diskette if possible. If that is not possible, then it is necessary that all files start with a Type 10 record, and that the multiple Type 10 records for each file of the same production run be identical. Information for a single sample may not be split between files.

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[1]The checksum is the sum of the ASCII representation of the data on the record up to the Record Sequence Number (not including the Record Sequence Number), plus the checksum of the previous record. The sum is taken modulo 65536 (2^{16}) and is represented as four hexadecimal digits (i.e., the remainder of the sum divided by 65536 represented as four hexadecimal digits).

8.0 DELIVERABLE

8.1 Requirements

The file shall be submitted on IBM-compatible, 3.5 inch, high density 1.44 MB diskettes. The diskettes shall be formatted and recorded using DOS/Windows Operating Systems. The diskettes shall contain all information relevant to one and only one Sample Delivery Group (SDG). An alternative means of electronic transmission may be utilized if approved in advance by USEPA.

8.1.1 USEPA Agency Standard data from an entire SDG may not fit onto a single diskette. If a single production run is being split onto multiple diskettes, then all files shall start with a Type 10 record, and the multiple Type 10 records for each file of the same production run shall be identical. Do not split the data from a single sample onto multiple diskettes.

8.1.2 Information on the diskette **must correspond** to information submitted in the hardcopy raw data package and on the hardcopy raw data package forms. Unused records shall not be included on the diskettes. If the information submitted in the hardcopy data package forms is changed, the information in the electronic file (e.g., diskette) shall be changed accordingly, and a complete electronic deliverable containing all the information for the SDG shall be resubmitted along with the hardcopy at no additional cost to USEPA.

8.1.3 Each diskette shall be identified with an external label containing (in this order) the following information:

Disk Density
File Name(s)
Laboratory Name (optional)
Laboratory Code
Contract Number
Case Number/SDG
NRAS Number (where applicable)
Initial Submission or Resubmission (as applicable) and Date

8.1.4 The format for File Name shall be XXXXXX.I01 to XXXXXX.I99, where XXXXXX is the SDG identifier, I designates inorganics, and 01 through 99 is the file number.

8.1.5 Dimensions of the label must be in the range of 2-1/2" to 2-3/4" long by 2" to 2-1/8" wide for a 3-1/2" diskette.

9.0 RECORD LISTING

The following section provides information for the usage of each of the record types. Where specified, labels indicate the nature of the value(s) that follow on that record. If the value(s) will not be reported, the label shall be omitted. Listed below is every record type required to report data from a single Sample Delivery Group (SDG).

9.1 Production Run First Header Record (Type 10)

Use: Each production run will start with a Record Type 10.

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"10"
1	Delimiter	|
4	ANALYSIS START YEAR	YYYY
1	Delimiter	|
2	ANALYSIS START MONTH	MM
1	Delimiter	|
2	ANALYSIS START DAY	DD
1	Delimiter	|
2	ANALYSIS START HOUR	HH
1	Delimiter	|
2	ANALYSIS START MINUTE	MM
1	Delimiter	|
5	METHOD TYPE	CHARACTER[2]
1	Delimiter	|
8	METHOD NUMBER	"ILM05.3" (SOW)
1	Delimiter	|
3	MANAGER'S INITIALS	CHARACTER
1	Delimiter	|
6	LAB CODE	CHARACTER
4	Delimiter	||||
11	CONTRACT NUMBER	CHARACTER
1	Delimiter	|
10	INSTRUMENT ID	CHARACTER
2	Delimiter	||
25	LABORATORY NAME	CHARACTER
1	Delimiter	|
2	RUN NUMBER	NUMERIC[3]
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

---

[2]Analysis Method Types are:
"P" for ICP-AES
"MS" for ICP-MS
"CV" for Manual Cold Vapor AA
"AV" for Automated Cold Vapor AA
"AS" for Semi-Automated Spectrophotometric
"C" for Manual Spectrophotometric

[3]Run number values are 01 through 99. Each production run will be assigned a unique Run Number. Run Numbers are to be assigned sequentially beginning with 01 and will equal the number of production runs.

9.2 Production Run Second Header Record (Type 16)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"16"
1	Delimiter	|
4	ANALYSIS END YEAR	YYYY
1	Delimiter	|
2	ANALYSIS END MONTH	MM
1	Delimiter	|
2	ANALYSIS END DAY	DD
1	Delimiter	|
2	ANALYSIS END HOUR	HH
1	Delimiter	|
2	ANALYSIS END MINUTE	MM
1	Delimiter	|
1	AUTO-SAMPLER USED	"Y" or "N"[4]
1	Delimiter	|
1	INTERELEMENT CORRECTIONS APPLIED	"Y" or "N"[5]
1	Delimiter	|
1	BACKGROUND CORRECTIONS APPLIED	"Y" or "N"[5]
1	Delimiter	|
1	RAW DATA GENERATED	"Y" or "N" or "B"[6]
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

[4]Enter "Y" if an auto-sampler is used with equal time and intervals between analysis.

[5]These are the answers to the first two questions on the Cover Page of the hardcopy deliverable. "Y" equals "YES", and "N" equals "NO".

[6]This is the answer to the third question on the Cover Page of the hardcopy deliverable. "Y" equals "YES", "B" equals BLANK, and "N" equals "NO".

9.3 Mandatory Sample Header Data Record (Type 20)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD	"20"
1	Delimiter	|
2	REGION	NUMERIC
1	Delimiter	|
12	EPA SAMPLE NUMBER	CHARACTER[7]
1	Delimiter	|
5	MATRIX	CHARACTER[8]
1	Delimiter	|
3	QC CODE	CHARACTER
1	Delimiter	|
3	SAMPLE QUALIFIER	CHARACTER
1	Delimiter	|
5	CASE NUMBER	CHARACTER
1	Delimiter	|
6	SDG NUMBER	CHARACTER
1	Delimiter	|
4	ANALYSIS YEAR/YEAR COMPUTED	YYYY
1	Delimiter	|
2	ANALYSIS MONTH/MONTH COMPUTED	MM
1	Delimiter	|
2	ANALYSIS DAY/DAY COMPUTED	DD
1	Delimiter	|
2	ANALYSIS HOUR	HH
1	Delimiter	|
2	ANALYSIS MINUTE	MM
2	Delimiter	||
2	SAMPLE WT/VOL UNITS	"G"/"ML"[9]
1	Delimiter	|
5	SAMPLE WT/VOL	NUMERIC[10]
1	Delimiter	|
3	ANALYTE COUNT	NUMERIC
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

[7]EPA Sample Number as it appears on Form XIII-IN of the hardcopy deliverable except for the first Type 20 records. The first Type 20 record must have an EPA sample number of "MDL"; after all Type 20 records with an EPA sample number of "MDL", the next Type 20 record must have an EPA sample number of "LRV"; for ICP-AES, the Type 20 record following the "LRV" must have an EPA sample number of "BCD".

[8]For matrix, "1" equals "WATER" and "F" equals "SOIL". A matrix identifier ("1" or "F") is required for all EPA sample numbers except "BCD".

[9]"G" equals grams and "ML" equals milliliters.

[10]This is the size of the sample at the beginning of the digestion procedure.

9.3.1 SAMPLE QC CODES LISTING FOR TYPE 20

NOTE: These QC codes appear in the QC code field on the Type 20 record (R20F5). They are used to indicate the type of data that is being reported.

QCC	Name	Definition
LRB	LABORATORY (REAGENT) BLANK	The Preparation Blank (see Exhibit G).
LCB	LABORATORY CALIBRATION BLANK	The Continuing Calibration Blank (CCB) (see Exhibit G).
LIB	LABORATORY INITIAL BLANK	The Initial Calibration Blank (ICB) (see Exhibit G).
LCM	LABORATORY CONTROL SOLUTION	The Laboratory Control Sample (LCS) (see Exhibit G).
LD2	LABORATORY DUPLICATE SECOND MEMBER	This is the second aliquot and is identified as "D" on Form VI-IN of the hardcopy.
LVM	LABORATORY CALIBRATION VERIFICATION SOLUTION	These values are identified as "Initial Calibration Verification" (ICV) on Form IIA-IN of hardcopy.
LVC	LABORATORY CONTINUING CALIBRATION VERIFICATION	These values are identified as "Continuing Calibration Verification" (CCV) on Form IIA-IN of hardcopy.
LVD	LABORATORY DISTILLED VERIFICATION SOLUTION	These values are the "distilled ICV" results for cyanide. Refer to Exhibit D, Section 12.7.1 for cyanide.
LSF	LABORATORY SPIKED SAMPLE - FINAL VALUES	These are the "Spiked Sample Result (SSR)" values of Form VA-IN of hardcopy.
LDO	LABORATORY DILUTED SAMPLE BACKGROUND (ORIGINAL) VALUES	These values are the "Initial Sample Result (I)" values on Form VIII-IN of hardcopy.
LDF	LABORATORY DILUTED SAMPLE - FINAL VALUES	These are the "Serial Dilution Result(S)" values Form VIII-IN of hardcopy.

PDO	POST-DIGESTION SPIKE BACKGROUND (ORIGINAL) VALUES	This value is identified as "Sample Result" (SR) on Form VB-IN of hardcopy.
PDF	POST-DIGESTION SPIKE BACKGROUND (FINAL) VALUES	This value is identified as "Spiked Sample Result" (SSR) on Form VB-IN of hardcopy.
LPC	CRQL CHECK STANDARD	Laboratory Performance Check Solution for analysis methods P, MS, CV, AV, AS, and C (EPA sample number is CRI). These results are reported on Form IIB-IN of hardcopy.
LSA	LABORATORY INTERFERENCE CHECK SOLUTION A	The results of this solution analysis (EPA sample number is ICSA) are reported on Forms IVA and IVB-IN of hardcopy.
LSB	LABORATORY INTERFERENCE CHECK SOLUTION AB	The results of this solution analysis (EPA sample number is ICSAB) are reported on Forms IVA and IVB-IN of hardcopy.
LTS	LABORATORY TUNE SAMPLE	The results of these solution analyses are reported on Form XIV-IN of hardcopy.
FRB	FIELD BLANK	This is any sample that is submitted from the field and is identified as a blank. This includes trip blanks, rinsates, equipment blanks, etc.
FRM	PERFORMANCE EVALUATION (PE) SAMPLE	This is a sample of known composition provided by USEPA for Contractor analysis and is used to evaluate Contractor performance.
FLD	FIELD SAMPLE	This is the sample that is identified by a unique EPA sample number on the Traffic Report/Chain of Custody Record.
ZZQ	NON-SDG SAMPLE	This is any sample that is analyzed and is not part of the SDG (EPA sample number is ZZZZZZ).
STB	CALIBRATION STANDARD	This is the instrument calibration Blank Standard (EPA sample number is S0).

STC	CALIBRATION STANDARD	This is the instrument calibration CRQL Standard (EPA sample number is Sx where x is the CRQL value of the analyte).
STD	CALIBRATION STANDARD	This is the instrument calibration standard other than the Blank Standard or the CRQL Standard (EPA sample number is S).
STM	MIDRANGE STANDARD	This is the distilled cyanide Mid-range Standard (EPA sample number is MIDRANGE). Refer to Exhibit D, Section 10.2.1.1, for cyanide.
STR	RESLOPE SAMPLE	This is the resloping that is permitted for mercury analysis (EPA sample number is RESLOPE). Refer to Exhibit D, Section 9.1.5, for mercury.
STL	BASELINE SAMPLE	This is the baseline correction that is permitted for mercury analysis (EPA sample number is BASELINE). Refer to Exhibit D, Section 9.1.5, for mercury.
MDQ	METHOD DETECTION LIMIT	These are the annually determined analyte detection limits that are reported on Form IX-IN of hardcopy. (EPA sample number is MDL).
LRQ	LINEAR RANGE VALUE	These are the quarterly determined values for ICP-AES and ICP-MS methods that are reported on Form XI-IN of hardcopy. For all other methods, these are the analytically determined concentrations of the highest instrument calibration standards that are used in the generation of the calibration curve at the beginning of every run. (EPA sample number is LRV).
BCQ	BACKGROUND CORRECTION	These are the ICP-AES annually determined interelement correction factors that are reported on Forms XA and XB-IN of hardcopy. (EPA sample number is BCD).

NOTE: All field samples that are reported on the Traffic Report/Chain of Custody Record shall contain the QC code "FLD" in Record Type 20

Field Number 5 (R20F5) except when "FLD" is superseded by "FRB" (Field Blank Sample), "FRM" (PE Sample).

For Matrix Spike and Duplicate sample analysis (Forms VA-IN and VI-IN of hardcopy), the "Sample" result shall contain the QC code "FLD" in R20F5, the "Spiked Sample Result" shall contain the QC Code "LSF" in R20F5, and the "Duplicate" result shall contain the QC code "LD2" in R20F5.

9.4 Sample Header Record (Type 21)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"21"
2	Delimiter	||
3	LEVEL	"LOW"/"MED"
2	Delimiter	||
3	PREPARATION CODE	CHARACTER[11]
1	Delimiter	|
6	NRAS NUMBER	CHARACTER
1	Delimiter	|
14	LAB SAMPLE ID	CHARACTER
1	Delimiter	|
4	PREPARATION YEAR	YYYY
1	Delimiter	|
2	PREPARATION MONTH	MM
1	Delimiter	|
2	PREPARATION DAY	DD
2	Delimiter	||
4	YEAR RECEIVED	YYYY
1	Delimiter	|
2	MONTH RECEIVED	MM

[11]Preparation Codes: A Preparation Code is required for all EPA sample numbers except "LRV", "BCD", and "TUNE".
"HW1" - Hotplate/Block digestion for ICP-AES analysis of water samples.
"HW2" - Hotplate/Block digestion for ICP-MS analysis of water samples.
"HW3" - Hotplate/Block digestion for ICP-MS analysis of water samples.
"MW1" - Microwave digestion for ICP-AES analysis of water samples.
"MW2" - Microwave digestion for ICP-AES analysis of water samples.
"HS1" - Hotplate/Block digestion for ICP-AES analysis of soil samples.
"HS2" - Hotplate/Block digestion for ICP-AES analysis of soil samples.
"MS1" - Microwave digestion for ICP-AES analysis of soil samples.
"CW1" - Preparation for the Manual Cold Vapor AA analysis of water samples.
"CS1" - Preparation for the Manual Cold Vapor AA analysis of soil samples.
"CW2" - Preparation for the Automated Cold Vapor analysis of water samples.
"DW1" - Distillation for the manual and semi-automated spectrophotometric analysis of water samples.
"DW2" - Midi-distillation for the semi-automated spectrophotometric analysis of water samples.
"DS1" - Distillation for the manual and semi-automated spectrophotometric analysis of soil samples.
"DS2" - Midi-distillation for the semi-automated spectrophotometric analysis of soil samples.
"NP1" - No preparation.

Sample Header Record (Type 21) (Con't)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
1	Delimiter	|
2	DAY RECEIVED	DD
1	Delimiter	|
9	SOLUTION SOURCE	CHARACTER[12]
1	Delimiter	|
8	INJECTION/ALIQUOT VOLUME	NUMERIC[13]
1	Delimiter	|
2	PREPARATION START HOUR	HH[14]
1	Delimiter	|
2	PREPARATION START MINUTE	MM[14]
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

[12]This is the source of the solutions that are reported on Inorganic Forms IIA-IN, IIB-IN, IV-IN, and VII-IN of the hardcopy (ICV, CCV, CRI, ICS, and LCS), and the source of the instrument calibration standards.

[13]This is the portion of the sample that is injected into the instrument excitation system for the purpose of measuring the absorbence, emission, or concentration of an analyte.

[14]This is the time at which the preparation is started. It is used to differentiate between different batches on the same day.

9.5 Associated Injection and Counter Record (Type 22)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"22"
8	Delimiter	||||||||
5	VOLUME ADJUSTMENT FACTOR	NUMERIC[15]
2	Delimiter	||
8	FINAL VOLUME	NUMERIC[16]
1	Delimiter	|
8	DILUTION FACTOR	NUMERIC
3	Delimiter	|||
5	PERCENT SOLIDS	NUMERIC
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

[15]This field is used to report any additional volume adjustments in the preparation method. As an example, the factor of 1.25 that results from the chloride interference volume adjustment in Preparation Method/Code HW2.

[16]This is the final volume that is currently reported on Form XII-IN of the hardcopy.

9.6 Results Data Record (Type 30)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"30"
1	Delimiter	|
1	ANALYTE IDENTIFIER	"C"[17]
1	Delimiter	|
9	ANALYTE CAS NUMBER	CHARACTER[18]
2	Delimiter	||
5	CONCENTRATION UNITS	"UG/L"/"MG/KG"
1	Delimiter	|
3	CONCENTRATION QUALIFIER	CHARACTER[19]
1	Delimiter	|
15	CONCENTRATION	NUMERIC[20,21]
1	Delimiter	|
1	VALUE DESCRIPTOR	"T"/"F"[22]
1	Delimiter	|
10	AMOUNT ADDED OR TRUE VALUE	NUMERIC
1	Delimiter	|
1	QC VALUE DESCRIPTOR, P	"P"[23]
1	Delimiter	|
10	QC VALUE	NUMERIC
1	Delimiter	|||
1	QC VALUE DESCRIPTOR, L	"L"[23]
1	Delimiter	|
10	QC VALUE	NUMERIC
1	Delimiter	|
1	MATRIX SPIKE QC LIMIT QUALIFIER	"N"[24]
1	Delimiter	|
10	QC LOWER LIMIT	NUMERIC[25]
1	Delimiter	|
10	QC UPPER LIMIT	NUMERIC[25]
1	Delimiter	|
1	QC LIMIT QUALIFIER	"*"/"E"[26]
1	Delimiter	|
1	MDL LABEL	"U"
1	Delimiter	|
10	MDL	NUMERIC[27]
2	Delimiter	||
15	RAW DATA AVERAGE	NUMERIC[28]
1	Delimiter	||
10	RAW DATA %RSD	NUMERIC
1	Delimiter	||
5	RECORD SEQUENCE NO.	NUMERIC
4	CHECKSUM	CHARACTER

FORMAT OF THE RESULTS DATA RECORD (TYPE 30) FOOTNOTES

[17]"C" (CAS Registry Number) is used for all metals and cyanide.

[18]The CAS Numbers for metals and cyanide are in Exhibit B, Form IA-IN, and Table 1 - Inorganic Target Analyte List and Contract Required Quantitation Limits (CRQLs), in Exhibit C. NOTE: The CAS Numbers for the ICS non-target interferents are as follows: carbon (7440-44-0); chlorine (7782-50-5); molybdenum (7439-98-7); phosphorus (7723-14-0); sulfur (7704-34-9), and titanium (7440-32-6).

[19]"BDL" means below detection limit.

"NSQ" means there is not sufficient quantity to prepare sample according specification in Exhibit D; therefore, a smaller sample size is used.

"NAR" means no analysis result required.

"LTC" means less than the CRQL but greater than or equal to the MDL.

"FQC" means failed Quality Control (QC) criteria.

"GTL" means greater than the linear range. The result is reported from a re-analysis at an appropriate dilution.

"RIN" means that the analysis result was not used to report data in the SDG. The result is reported from a later re-analysis of the same sample aliquot.

"REX" means that the analysis result was not used to report data in the SDG. The result is reported from a later re-analysis of a repreparation of the same sample.

Note that, except for "NAR", none of these codes relieves the Contractor from reporting a valid result. They only explain why or if the result is qualified. Also note that ICP-MS internal standard results are not to be qualified.

[20]EPA Field Samples reported on Traffic Report/Chain of Custody Record (QC codes FLD, FRB, FRM) shall have their analytes' results reported to four decimal places.

[21]Follow the instructions for the reporting of data in Exhibit B in reporting results for samples with QC codes. For example, the LD2 QC code sample results shall be reported to four decimal places because the duplicate results on Form VI-IN have to be reported to four decimal places. Refer to Section 9.3.1 for QC codes and definitions.

[22]"T" stands for an analyte's true value in a solution. This includes the concentration of all Instrument Calibration Standards for ALL methods of analysis. "F" stands for an added concentration to a sample such as a pre- or post-digestion spike.

[23]"P" equals Percent Recovery (%R), Percent Difference (%D), Relative Percent Difference (RPD), Percent Relative Standard Deviation (%RSD), Percent Relative Intensity (%RI), or correlation coefficient. "L" equals control limit for duplicates. The matrix spike sample %R shall be entered on the Type 30 record of the EPA sample number with the "S" suffix (QC code=LSF). The post digest spike sample %R shall be entered on the Type 30 record of the EPA sample number with the "A" suffix (QC code=PDF). The RPD and the control limit for duplicates shall be entered on the Type 30 record of the EPA sample number with the "D" suffix (QC code=LD2). The ICP serial dilutions %D shall be entered on the Type 30 record of the EPA sample number with the "L" suffix (QC code=LDF). The average %RSD for ICP-MS tune analyses shall be entered on the Type 30 record of the last EPA sample number "TUNE" (QC code=LTS) in each run. The %RI for ICP-MS internal standards shall be entered on the Type 30 record of all EPA samples numbers (except "TUNE", "ZZZZZZ", "MDL", and "LRV").

The correlation coefficient for the calibration for mercury and cyanide analyses shall be reported on the Type 30 record of the EPA sample number associated with the final standard analyzed in the calibration curve (immediately preceding the ICV).

[24]"N" is the qualifier that is used on Form VA-IN of the hardcopy to indicate that the matrix or pre-digestion spike sample recovery for an analyte is not within the specified control limits. The "N" qualifier shall be entered on the Type 30 record of the EPA sample number with the "S" suffix (QC code=LSF).

[25]These are the control limits for the ICV/CCV percent recovery (%R) on Form IIA-IN, the CRI %R on Form IIB-IN, the ICSA/ICSAB %R on Forms IVA and IVB-IN, the matrix spike %R on Form VA-IN, and the LCSW %R and the LCSS upper and lower limits on Form VII-IN. The QC upper and lower limits for the Spike Sample Recovery shall be entered on the Type 30 record of the EPA sample number with the "S" suffix (QC code=LSF).

[26]"*" is the qualifier that is used on Form VI-IN of the hardcopy to indicate that the duplicate sample analysis for an analyte is out of control, and "E" is the qualifier that is used on Form VIII-IN of the hardcopy to indicate that the ICP serial dilution analysis results are estimated because of the existence of significant physical or chemical interferences. The "*" qualifier should be entered on the Type 30 record of the EPA sample number with the "D" suffix (QC code=LD2) The "E" qualifier shall be entered on the Type 30 record of the EPA sample number with the "L" suffix (QC code=LDF).

[27]The MDL shall be reported to 2 significant figures for values less than 10 and to 3 significant figures for values greater than or equal to 10. MDLs shall be reported in UG/L for water samples, ICV, ICB, CCV, CCB, CRI, ICSA, ICSAB and MIDRANGE (for cyanide), and any other samples with concentration results reported in "UG/L". MDLs shall be reported in MG/KG for soil samples.

[28]The average value of the replicate injections or exposures are reported in this field. The average values for mercury and cyanide analyses are also reported in this field. In addition, the raw data average value shall always be reported in units of UG/L to a minimum of four decimal places, regardless of the units the instrument readings are reported in, on record Type 31. The raw data average value shall not be corrected for dilutions or volume adjustments.

For Instrument Calibration Standards analyses and Instrument Tune Standards analyses, the raw data average is not required to be reported.

9.7 Instrumental Data Readout (Type 31)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"31"
1	Delimiter	|
1	TYPE OF DATA	"W"/"M"[29]
1	Delimiter	|
1	TYPE OF VALUE	CHARACTER[30]
2	Delimiter	||
8	ANALYTE WAVELENGTH/MASS	NUMERIC (TO 2 DECIMAL PLACES)
1	Delimiter	|
15	FIRST INSTRUMENT VALUE	NUMERIC[31]
2	Delimiter	||
15	SECOND INSTRUMENT VALUE	NUMERIC[31]
2	Delimiter	||
15	THIRD INSTRUMENT VALUE	NUMERIC[31]
2	Delimiter	||
15	FOURTH INSTRUMENT VALUE	NUMERIC[31]
2	Delimiter	||
15	FIFTH INSTRUMENT VALUE	NUMERIC[31]
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

[29]"W" equals wavelength, "M" equals mass.

[30]"C" equals concentration in µg/L, "B" equals absorbance, "I" equals intensity (counts per second or equivalent).

[31]Used to report data for method analyses that require replicate injections or exposures. If a single instrument measurement is used, then enter it in the first instrument value field, and leave the other four fields empty. If two instrument measurements are used, then enter them in the first and second instrument value fields in the order of their analyses, and leave the other three fields empty, etc. In addition, the instrument values shall be reported to a minimum of four decimal places.

9.8 Auxiliary Data Record (Type 32)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"32"
10	Delimiter	||||||||||
2	INTEGRATION TIME CODE	"IT"
1	Delimiter	|
10	INTEGRATION TIME	IN SECONDS
4	Delimiter	||||
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

9.9 QC Limit Record (Type 34)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"34"[32]
4	Delimiter	||||
8	ANALYTE WAVELENGTH OR MASS	NUMERIC (TO 2 DECIMAL PLACES)
1	Delimiter	|
10	CRQL	NUMERIC
1	Delimiter	|
10	LINEAR RANGE VALUE	NUMERIC
6	Delimiter	||||||
5	RECORD SEQUENCE NO.	NUMERIC
4	CHECKSUM	CHARACTER

[32]There must be as many consecutive Type 34 records as there are wavelengths or masses used for the analyte identified in the preceding Type 30 record.

9.10 Correction Data Record (Type 35)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"35"
1	Delimiter	|
3	TYPE OF CORRECTION	"ICP"
1	Delimiter	|||||
9	CAS NUMBER OF INTERFERING ANALYTE	CHARACTER
1	Delimiter	|
8	ANALYTE WAVELENGTH	NUMERIC (TO 2 DECIMAL PLACES)
1	Delimiter	|
10	CORRECTION FACTOR	NUMERIC
1	Delimiter	|
5	RECORD SEQUENCE NO.	NUMERIC
4	CHECKSUM	CHARACTER

9.11 Comment Record (Type 90)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"90"
1	Delimiter	|
67	ANY COMMENT	CHARACTER
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

9.12 Sample Associated Data Record (Type 92)

MAXIMUM LENGTH	CONTENTS	FORMAT/CONTENTS
2	RECORD TYPE	"92"
1	Delimiter	|
9	COLOR BEFORE	CHARACTER
1	Delimiter	|
9	COLOR AFTER	CHARACTER
1	Delimiter	|
6	CLARITY BEFORE	CHARACTER
1	Delimiter	|
6	CLARITY AFTER	CHARACTER
1	Delimiter	|
6	TEXTURE	CHARACTER
1	Delimiter	|
3	ARTIFACTS	"YES"/BLANK
1	Delimiter	|
5	RECORD SEQUENCE NUMBER	NUMERIC
4	CHECKSUM	CHARACTER

APPENDIX A -- FORMAT OF RECORDS FOR SPECIFIC USES

DISCLAIMER

The USEPA does not warrant or guarantee the completeness and/or accuracy of the representative examples of record type uses provided in this appendix. This appendix serves as an example for the usage of record types and in no way redefines or supersedes the specifications or requirements stated in Exhibits A through H of ILM05.3.

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Appendix A -- Format of Records for Specific Uses

Table of Contents

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1.0 ICP

1.1 ICP-AES

1.1.1 Start of an ICP-AES Run with Record Types 10 and 16 and the First Type 20 Records

```
10|1999|09|17|09|06|P|ILM05.3|ABC|TESLAB||||68-D2-0039|P2||TEST LABSINC.|2|000001879
16|1999|09|17|12|03|Y|Y|Y|N|000012114

20|1|MDL|1|MDQ||||1999|07|15||||||04|000044B9D
21||||NP1||||||||||||||000053CD5
30|C|7440-22-4||UG/L|||||||||||||||U|3.1||||||000065996
30|C|7429-90-5||UG/L|||||||||||||||U|21.8||||||0000767D1
30|C|7440-39-3||UG/L|||||||||||||||U|11.5||||||0000875CB
30|C|7440-41-7||UG/L|||||||||||||||U|1.1||||||0000983C5

20|1|MDL|1|MDQ||||1999|07|15||||||04|0000104B9D
21||||HW1|||1999|07|15|||||||08|00|0000113CD5
30|C|7440-22-4||UG/L|||||||||||||||U|3.4||||||0000125996
30|C|7429-90-5||UG/L|||||||||||||||U|22.8||||||00001367D1
30|C|7440-39-3||UG/L|||||||||||||||U|12.5||||||00001475CB
30|C|7440-41-7||UG/L|||||||||||||||U|2.1||||||00001583C5

20|1|MDL|F|MDQ||||1999|07|16||||||04|000164B9D
21||||HS1|||1999|07|15|||||||08|00|00017A212
30|C|7440-22-4||MG/KG|||||||||||||||U|0.82||||||00018C248
30|C|7429-90-5||MG/KG|||||||||||||||U|4.8||||||00019B321
30|C|7440-39-3||MG/KG|||||||||||||||U|3.1||||||00020CE75
30|C|7440-41-7||MG/KG|||||||||||||||U|0.42||||||00021A21B

20|1|LRV|1|LRQ||||1999|07|15||||||04|0002356C2
30|C|7440-22-4|||||||||||||||||||||||||0002463D1
32||||||||||IT|5.00||||000256CDA
34||||328.00|5|40000||||||000267591
30|C|7429-90-5|||||||||||||||||||||||||0002782AD
32||||||||||IT|5.00||||000288BB6
34||||308.20|200|1000000||||||0002994FB
30|C|7440-39-3|||||||||||||||||||||||||00030A211
32||||||||||IT|5.00||||00031AB1A
34||||493.40|20|100000||||||00032B436
30|C|7440-41-7|||||||||||||||||||||||||00033C149
32||||||||||IT|5.00||||00034CA52
34||||313.00|2|25000||||||00035D2DA

20|1|BCD||BCQ||||1999|07|01||||||04|0007894FB
30|C|7440-22-4|||||||||||||||||||||||||00079A20A
35|ICP|||||7439-89-6|259.90|-0.0002500|00080AC9B
35|ICP|||||7439-96-5|257.60|0.0002200|00081B6F4
30|C|7429-90-5|||||||||||||||||||||||||00082C410
35|ICP|||||7439-96-5|257.60|0.0004900|00083CE72
35|ICP|||||7440-62-2|292.40|-0.0419200|00084D8EF
30|C|7440-39-3|||||||||||||||||||||||||00085E605
35|ICP|||||7439-96-5|257.60|0.0000600|00086F060
30|C|7440-41-7|||||||||||||||||||||||||00087FD73
35|ICP|||||7440-50-8|324.70|0.0046200|0008914D1
35|ICP|||||7439-96-5|257.60|0.0015400|000901F30
```

1.1.2 ICP-AES Instrument Calibration Standards, S0 and S

```
20|1|S0|1|STB||20596|MAX123|1999|09|17|09|06||||04|00128D199
21||||NP1||STDB|1999|09|17|||||TESLAB||||00129DD31
22||||||||||||1.0||||00130E598
```

```
30|C|7440-22-4|||||T|0.0|||||||||||U|3.1||||||00131F8F5
31|W|I||328.00|0.0304||0.0374||0.0400|||||001320305
30|C|7429-90-5|||||T|0.0|||||||||||U|21.8||||||001331697
31|W|I||308.20|0.0104||0.0136||0.0120|||||001342137
30|C|7440-39-3|||||T|0.0|||||||||||U|11.5||||||00135348D
31|W|I||493.40|-0.0002||0.0002||0.0000|||||001363EA4
30|C|7440-41-7|||||T|0.0|||||||||||U|1.1||||||0013751FA
31|W|I||313.00|0.0006||0.0002||0.0004|||||001385C04

20|1|S|1|STD||20596|MAX123|1999|09|17|09|11||||04|00206314E
21||||NP1||STD1|1999|09|17|||||TESLAB||||002073CD5
22||||||||||||1.0||||00208453C
30|C|7440-22-4|||||T|5000|||||||||||U|3.1||||||002139157
31|W|I||328.00|1.9540||1.9610||1.9660|||||002149B6E
30|C|7429-90-5|||||T|1000|||||||||||U|21.8||||||00215ADE2
31|W|I||308.20|0.8384||0.8378||0.8440|||||00216B7EC
30|C|7440-39-3|||||T|5000|||||||||||U|11.5||||||00219E77D
31|W|I||493.40|1.9460||1.9510||1.9684|||||00220F18F
30|C|7440-41-7|||||T|5000|||||||||||U|1.1||||||002210410
31|W|I||313.00|0.9924||0.9910||1.0010|||||002220E25
```

1.1.3 Duplicates, Spike Sample Recovery, and Serial Dilutions Performed on the Same Field Sample (QC Codes FLD, LDO, LD2, LSF, LDF)

```
20|1|MAX123|F|FLD||20596|MAX123|1999|09|17|11|09||G|1.05|08|01568C5FD
21||LOW||HS1||S308233-01|1999|09|14||1999|08|24|||08|30|01569D451
22||||||||||200|1.0|||91.5|01570DE17
90|STONES|01571E154
92|GREY|GREY|||MEDIUM|YES|01572EA43
30|C|7440-22-4||MG/KG|BDL|2.0817||||||||||||U|0.82||1.1567||||01573FD12
31|W|C||328.00|4.2000||0.5500||-1.2800|||||0157409A5
30|C|7429-90-5||MG/KG||6227.0101||||||||||||U|4.8||29913.0000||||015751DCD
31|W|C||308.20|29992.0000||29654.0000||30093.0000|||||015762CA0
30|C|7440-39-3||MG/KG|LTC|21.9349||||||||||||U|3.1||105.3700||||01577400C
31|W|C||493.40|107.2400||101.6400||107.2300|||||015784DA6
30|C|7440-41-7||MG/KG|BDL|1.0409||||||||||||U|0.42||1.4900||||01579606A
31|W|C||313.00|1.4900||1.4900||1.4900|||||015806CD9

20|1|MAX123|F|LDO||20596|MAX123|1999|09|17|11|09||G|1.05|08|01650C630
21||LOW||HS1||S308233-01|1999|09|14||1999|08|24|||08|30|01651D484
22||||||||||200|1.0|||91.5|01652DE4A
30|C|7440-22-4||UG/L|BDL|10.00||||||||||||U|3.9||1.1567||||01655FC98
31|W|C||328.00|4.2000||0.5500||-1.2800|||||01656092B
30|C|7429-90-5||UG/L||29913.00||||||||||||U|23.1||29913.0000||||016571C09
31|W|C||308.20|29992.0000||29654.0000||30093.0000|||||016582ADC
30|C|7440-39-3||UG/L|LTC|105.37||||||||||||U|14.9||105.3700||||016593DCE
31|W|C||493.40|107.2400||101.6400||107.2300|||||016604B68
30|C|7440-41-7||UG/L|BDL|5.00||||||||||||U|2.0||1.4900||||01579606A
31|W|C||313.00|1.4900||1.4900||1.4900|||||015806CD9

20|1|MAX123D|F|LD2||20596|MAX123|1999|09|17|11|11||G|1.04|08|016913BCF
21||LOW||HS1||S308233-02|1999|09|14||1999|08|24|||08|30|016924A23
22||||||||||200|1.0|||90.9|0169353EC
30|C|7440-22-4||MG/KG|BDL|2.1017||||||||||||U|0.82||0.9600||||0169466BE
31|W|C||328.00|1.6400||1.6300||-0.3900|||||016957356
30|C|7429-90-5||MG/KG||6622.7406|||P|6.2|||||||||U|4.8||31511.0000||||016968784
31|W|C||308.20|31993.0000||31313.0000||31227.0000|||||016979641
30|C|7440-39-3||MG/KG|LTC|25.1387|||P|13.6|||||||||U|3.1||119.6100||||01698AAC5
31|W|C||493.40|121.4600||118.9300||118.4400|||||01699B86C
30|C|7440-41-7||MG/KG|BDL|1.0509||||||||||||U|0.42||1.5000||||01700CC13
31|W|C||313.00|1.5000||1.5000||1.5000|||||01701D86A
```

```
20|1|MAX123S|F|LSF||20596|MAX123|1999|09|17|11|14||G|1.01|08|01730BE3C
21||LOW||HS1||S308233-03|1999|09|14||1999|08|24|||08|30|01731CC90
22||||||||||200|1.0|||91.5|01732D656
30|C|7440-22-4||MG/KG||10.7212|F|10.82|P|99||||||75|125||U|0.82||49.5400||||01733EBC7
31|W|C||328.00|48.8400||49.2000||50.5800|||||01734F8DC
30|C|7429-90-5||MG/KG|NAR|6859.9253|||||||||||||U|4.8||31698.0000||||017350E27
31|W|C||308.20|31578.0000||31766.0000||31750.0000|||||017361CF1
30|C|7440-39-3||MG/KG||326.3539|F|432.83|P|70|||||N|75|125||U|3.1||1508.0000||||017373339
31|W|C||493.40|1524.0000||1504.4000||1495.6000|||||017384171
30|C|7440-41-7||MG/KG||10.4290|F|10.82|P|96||||||75|125||U|0.42||48.1900||||0173956E4
31|W|C||313.00|48.1900||48.2000||48.1800|||||0174063EB

20|1|MAX123L|F|LDF||20596|MAX123|1999|09|17|11|17||||08|017696573
21||LOW||||S308233-04|||||1999|08|24|||||017707255
22||||||||||||5.0|||91.5|017717B8D
30|C|7440-22-4||UG/L|BDL|50.00|||||||||||||U|3.9||0.6100||||017728DDF
31|W|C||328.00|1.4500||-0.3800||0.7600|||||017739A7B
30|C|7429-90-5||UG/L||25575.50|||P|15||||||||E|U|23.1||5115.1000||||01774AE69
31|W|C||308.20|5038.6000||5126.4000||5180.3000|||||01775BCAC
30|C|7440-39-3||UG/L|LTC|111.30|||P|6|||||||||U|14.9||22.2600||||01776D0AA
31|W|C||493.40|22.2600||22.7700||21.7500|||||01777DDB9
30|C|7440-41-7||UG/L|BDL|25.00|||||||||||||U|2.0||0.3000||||0173956E4
31|W|C||313.00|0.1900||0.2000||0.51|||||0174063EB
```

1.2 ICP-MS

1.2.1 Start of an ICP-MS Run with Record Types 10 and 16 and the First Type 20 Records

```
10|1999|09|17|09|06|MS|ILM05.3|ABC|TESLAB||||68-D2-0039|P2||TEST LABSINC.|2|000001879
16|1999|09|17|12|03|Y|Y|Y|N|000012114

20|1|MDL|1|MDQ||||1999|07|15||||||04|000044B9D
21||||NP1|||||||||||||||00005DD31
30|C|7440-22-4||UG/L|||||||||||||||U|0.40||||||000065996
30|C|7429-90-5||UG/L|||||||||||||||U|12.8||||||0000767D1
30|C|7440-39-3||UG/L|||||||||||||||U|3.0||||||0000875CB
30|C|7440-41-7||UG/L|||||||||||||||U|0.44||||||0000983C5

20|1|MDL|1|MDQ||||1999|07|15||||||04|000044B9D
21||||HW2|||1999|07|15|||||||09|00|00005DD31
30|C|7440-22-4||UG/L|||||||||||||||U|0.41||||||000065996
30|C|7429-90-5||UG/L|||||||||||||||U|13.8||||||0000767D1
30|C|7440-39-3||UG/L|||||||||||||||U|4.0||||||0000875CB
30|C|7440-41-7||UG/L|||||||||||||||U|0.43||||||0000983C5

20|1|LRV|1|LRQ||||1999|07|15||||||04|0002356C2
30|C|7440-22-4|||||||||||||||||||||||||0002463D1
32||||||||||IT|5.00||||000256CDA
34||||107.00|5|40000||||||000267591
30|C|7429-90-5|||||||||||||||||||||||||0002782AD
32||||||||||IT|5.00||||000288BB6
34||||27.00|200|1000000||||||0002994FB
30|C|7440-39-3|||||||||||||||||||||||||00030A211
32||||||||||IT|5.00||||00031AB1A
34||||137.00|20|100000||||||00032B436
30|C|7440-41-7|||||||||||||||||||||||||00033C149
32||||||||||IT|5.00||||00034CA52
34||||111.00|2|25000||||||00035D2DA
```

1.2.2 ICP-MS Instrument Tune and Calibration Standards, S0 and S

```
20|3|TUNEA1|1|LTS||26791|MCSB00|1999|02|06|20|00||||5|000917DD7
```

```
  21||||||TUNE1||||||||TESLAB||||000917DD8
  22||||||||||||1.0||||000917DD9
  30|C|7440-41-7|||||T|100|||||||||||||||||000917DE0
  31|M|I||9.01|100000||100000||100000|||||000917DE1
  30|C|7439-95-4|||||T|100|||||||||||||||||000914DE2
  31|M|I||23.99|79000||79000||79000|||||000917DE3
  31|M|I||24.99|10000||10000||10000|||||000917DE4
  31|M|I||25.98|11000||11000||11000|||||000917DE5
  30|C|7440-48-4|||||T|100|||||||||||||||||000917DE6
  31|M|I||58.93|100000||100000||100000|||||000917DE7
  30|C|7440-74-6|||||T|100|||||||||||||||||000917DE8
  31|M|I||112.90|4000||4000||4000|||||000917DE9
  31|M|I||114.90|96000||96000||96000|||||000917DF0
  30|C|7439-92-1|||||T|100|||||||||||||||||000917DF1
  31|M|I||205.97|24000||24000||24000|||||000917DF2
  31|M|I||206.98|22000||22000||22000|||||000917DF3
  31|M|I||207.98|52000||52000||52000|||||000917DF4

  20|3|TUNEA2|1|LTS||26791|MCSB00|1999|02|06|20|10||||5|000917DD7
  21||||||TUNE2||||||||TESLAB||||000917DD8
  22||||||||||||1.0||||000917DD9
  30|C|7440-41-7|||||T|100|||||||||||||100000||||000917DE0
  31|M|I||9.01|100000||100000||100000|||||000917DE1
  30|C|7439-95-4|||||T|100|||||||||||||||||000914DE2
  31|M|I||23.99|79000||79000||79000|||||000917DE3
  31|M|I||24.99|10000||10000||10000|||||000917DE4
  31|M|I||25.98|11000||11000||11000|||||000917DE5
  30|C|7440-48-4|||||T|100|||||||||||||100000||||000917DE6
  31|M|I||58.93|100000||100000||100000|||||000917DE7
  30|C|7440-74-6|||||T|100|||||||||||||||||000917DE8
  31|M|I||112.90|4000||4000||4000|||||000917DE9
  31|M|I||114.90|96000||96000||96000|||||000917DF0
  30|C|7439-92-1|||||T|100|||||||||||||||||000917DF1
  31|M|I||205.97|24000||24000||24000|||||000917DF2
  31|M|I||206.98|22000||22000||22000|||||000917DF3
  31|M|I||207.98|52000||52000||52000|||||000917DF4

  20|3|TUNEA3|1|LTS||26791|MCSB00|1999|02|06|20|20||||5|000917DD7
  21||||||TUNE3||||||||TESLAB||||000917DD8
  22||||||||||||1.0||||000917DD9
  30|C|7440-41-7|||||T|100|||||||||||||||||000917DE0
  31|M|I||9.01|100000||100000||100000|||||000917DE1
  30|C|7439-95-4|||||T|100|||||||||||||||||000914DE2
  31|M|I||23.99|79000||79000||79000|||||000917DE3
  31|M|I||24.99|10000||10000||10000|||||000917DE4
  31|M|I||25.98|11000||11000||11000|||||000917DE5
  30|C|7440-48-4|||||T|100|||||||||||||||||000917DE6
  31|M|I||58.93|100000||100000||100000|||||000917DE7
  30|C|7440-74-6|||||T|100|||||||||||||||||000917DE8
  31|M|I||112.90|4000||4000||4000|||||000917DE9
  31|M|I||114.90|96000||96000||96000|||||000917DF0
  30|C|7439-92-1|||||T|100|||||||||||||||||000917DF1
  31|M|I||205.97|24000||24000||24000|||||000917DF2
  31|M|I||206.98|22000||22000||22000|||||000917DF3
  31|M|I||207.98|52000||52000||52000|||||000917DF4

  20|3|TUNEA4|1|LTS||26791|MCSB00|1999|02|06|20|30||||5|000917DD7
  21||||||TUNE4||||||||TESLAB||||000917DD8
  22||||||||||||1.0||||000917DD9
  30|C|7440-41-7|||||T|100|||||||||||||||||000917DE0
  31|M|I||9.01|100000||100000||100000|||||000917DE1
  30|C|7439-95-4|||||T|100|||||||||||||||||000914DE2
```

```
31|M|I||23.99|79000||79000||79000|||||000917DE3
31|M|I||24.99|10000||10000||10000|||||000917DE4
31|M|I||25.98|11000||11000||11000|||||000917DE5
30|C|7440-48-4|||||T|100|||||||||||||||||||000917DE6
31|M|I||58.93|100000||100000||100000|||||000917DE7
30|C|7440-74-6|||||T|100|||||||||||||||||||000917DE8
31|M|I||112.90|4000||4000||4000|||||000917DE9
31|M|I||114.90|96000||96000||96000|||||000917DF0
30|C|7439-92-1|||||T|100|||||||||||||||||||000917DF1
31|M|I||205.97|24000||24000||24000|||||000917DF2
31|M|I||206.98|22000||22000||22000|||||000917DF3
31|M|I||207.98|52000||52000||52000|||||000917DF4

20|3|TUNEA5|1|LTS||26791|MCSB00|1999|02|06|20|40||||5|000917DD7
21||||||TUNE5|||||||TESLAB||||000917DD8
22||||||||||||1.0||||000917DD9
30|C|7440-41-7|||||T|100|P|0.0|||||||||||||||000917DE0
31|M|I||9.01|100000||100000||100000|||||000917DE1
30|C|7439-95-4|||||T|100|P|0.0|||||||||||||||000914DE2
31|M|I||23.99|79000||79000||79000|||||000917DE3
31|M|I||24.99|10000||10000||10000|||||000917DE4
31|M|I||25.98|11000||11000||11000|||||000917DE5
30|C|7440-48-4|||||T|100|P|0.0|||||||||||||||000917DE6
31|M|I||58.93|100000||100000||100000|||||000917DE7
30|C|7440-74-6|||||T|100|P|0.0|||||||||||||||000917DE8
31|M|I||112.90|4000||4000||4000|||||000917DE9
31|M|I||114.90|96000||96000||96000|||||000917DF0
30|C|7439-92-1|||||T|100|P|0.0|||||||||||||||000917DF1
31|M|I||205.97|24000||24000||24000|||||000917DF2
31|M|I||206.98|22000||22000||22000|||||000917DF3
31|M|I||207.98|52000||52000||52000|||||000917DF4

20|1|S0|1|STB||20596|MAX123|1999|09|17|09|06||||04|00128D199
21||||NP1||STDB|1999|09|17|||||TESLAB||||00129DD31
22||||||||||||1.0||||00130E598
30|C|7440-22-4|||||T|0.0||||||||||||U|0.40||||||00131F8F5
31|M|I||107.00|0.0304||0.0374||0.0400|||||001320305
30|C|7429-90-5|||||T|0.0||||||||||||U|12.8||||||001331697
31|M|I||27.00|0.0104||0.0136||0.0120|||||001342137
30|C|7440-39-3|||||T|0.0||||||||||||U|3.0||||||00135348D
31|M|I||137.00|-0.0002||0.0002||0.0000|||||001363EA4
30|C|7440-41-7|||||T|0.0||||||||||||U|0.44||||||0013751FA
31|M|I||111.00|0.0006||0.0002||0.0004|||||001385C04

20|1|S|1|STD||20596|MAX123|1999|09|17|09|11||||04|00206314E
21||||NP1||STD1|1999|09|17|||||TESLAB||||002073CD5
22||||||||||||1.0||||00208453C
30|C|7440-22-4|||||T|5000||||||||||||U|0.40||||||002139157
31|M|I||107.00|1.9540||1.9610||1.9660|||||002149B6E
30|C|7429-90-5|||||T|1000||||||||||||U|12.8||||||00215ADE2
31|M|I||27.00|0.8384||0.8378||0.8440|||||00216B7EC
30|C|7440-39-3|||||T|5000||||||||||||U|3.0||||||00219E77D
31|M|I||136.00|1.9460||1.9510||1.9684|||||00220F18F
30|C|7440-41-7|||||T|5000||||||||||||U|0.44||||||002210410
31|M|I||111.00|0.9924||0.9910||1.0010|||||002220E25
```

1.2.3 Field Samples

```
20|1|MAX123|1|FLD||20596|MAX123|1999|09|17|09|06||ML|100|04|00128D199
21||||HW2||S308233-01|1999|09|17||1999|09|16|TESLAB||09|30|00129DD31
22||||||||1.25||50|1.0|||0.0|00130E598
30|C|7440-22-4||UG/L|LTC|0.6625||||||||||||U|0.41||0.5300||||00131F8F5
```

```
31|M|I||107.00|0.5300||0.5300||0.5300|||||001320305
30|C|7429-90-5||UG/L||56.3750|||||||||||||U|13.8||45.1000||||001331697
31|M|I||27.00|45.1000||45.1000||45.1000|||||001342137
30|C|7440-39-3||UG/L||11.0000|||||||||||||U|4.0||8.8000||||00135348D
31|M|I||137.00|8.8000||8.8000||8.8000|||||001363EA4
30|C|7440-41-7||UG/L|BDL|1.000|||||||||||||U|0.43||0.3210||||0013751FA
31|M|I||111.00|0.3210||0.3210||0.3210|||||001385C04

20|1|MAX124|1|FLD||20596|MAX123|1999|09|17|09|06||ML|20|04|00128D199
21||||NP1||S308234-01|1999|09|17||1999|09|16|TESLAB||09|30|00129DD31
22||||||||||20|1.0|||0.0|00130E598
30|C|7440-22-4||UG/L|LTC|0.5300|||||||||||||U|0.40||0.5300||||00131F8F5
31|M|I||107.00|0.5300||0.5300||0.5300|||||001320305
30|C|7429-90-5||UG/L||45.1000|||||||||||||U|12.8||45.1000||||001331697
31|M|I||27.00|45.1000||45.1000||45.1000|||||001342137
30|C|7440-39-3||UG/L|LTC|8.8000|||||||||||||U|3.0||8.8000||||00135348D
31|M|I||137.00|8.8000||8.8000||8.8000|||||001363EA4
30|C|7440-41-7||UG/L|BDL|1.000|||||||||||||U|0.44||0.3210||||0013751FA
31|M|I||111.00|0.3210||0.3210||0.3210|||||001385C04
```

2.0 MERCURY

2.1 Start of a Mercury Run for Water Samples with Record Types 10 and 16 and the First Type 20 Records

```
10|1999|09|09|08|44|CV|ILM05.3|ABC|TESLAB||||68-D2-0039|M3||TEST LABS INC.|6|0000018F7
16|1999|09|09|14|34|N||||000012099

20|1|MDL|1|MDQ||||1999|07|15||||||1|000044AEB
21||||CW1|||1999|07|15|||||||||000053CD5
30|C|7439-97-6||UG/L|||||||||||||||U|0.042||||||0000658F4

20|1|LRV|1|LRQ||||1999|09|09||||||1|0000666A6
30|C|7439-97-6|||||||||||||||||||||||||0000773CB
32||||||||||||||000087D02
34||||253.70|0.2|5||||||00009852D
```

2.1.1 Start of a Mercury Run for Soil Samples with Record Types 10 and 16 and the First Type 20 Records

```
10|1999|09|09|08|44|CV|ILM05.3|ABC|TESLAB||||68-D2-0039|M3||TEST LABS INC.|6|0000018F7
16|1999|09|09|14|34|N||||000012099

20|1|MDL|F|MDQ||||1999|07|16||||||1|000074AEB
21||||CS1|||1999|07|16|||||||09|00|000083CD5
30|C|7439-97-6||MG/KG|||||||||||||||U|0.0092||||||0000958F4

20|1|LRV|1|LRQ||||1999|09|09||||||1|0001066A6
30|C|7439-97-6|||||||||||||||||||||||||0001173CB
32||||||||||||||000127D02
34||||253.70|0.2|5||||||00013852D
```

2.2 Mercury Instrument Calibration Standards: Blank (S0) and Four Other Standards

```
20|1|S0|1|STB||20596|MAX123|1999|09|09|08|44||||1|00010936F
21||||CS1||0PPB|1999|09|09|||||TESLAB||07|00|000119F0C
22||||||||||||1.0||||00012A773
30|C|7439-97-6|||||T|0.0||||||||||U|0.018||0.0122||||00013BAD9
31|W|C||253.70|0.0122|||||||||00014C4EC

20|1|S0.2|1|STC||20596|MAX123|1999|09|09|08|48||||1|00015D392
21||||CS1||0.2PPB|1999|09|09|||||TESLAB||07|00|00016DF8F
22||||||||||||1.0||||00017E7F6
```

```
30|C|7439-97-6|||||T|0.2||||||||||U|0.018||0.0896||||00018FB5E
31|W|C||253.70|0.0896|||||||||000190571

20|1|S1.0|1|STD||20596|MAX123|1999|09|09|08|53||||1|000201412
21||||CS1||1.0PPB|1999|09|09|||||TESLAB||07|00|00021200E
22||||||||||1.0||||000222875
30|C|7439-97-6|||||T|1.0||||||||||U|0.018||1.0128||||000233BDC
31|W|C||253.70|1.0128|||||||||0002445EF

20|1|S2.0|1|STD||20596|MAX123|1999|09|09|08|57||||1|000255495
21||||CS1||2.0PPB|1999|09|09|||||TESLAB||07|00|000266092
22||||||||||1.0||||0002768F9
30|C|7439-97-6|||||T|2.0||||||||||U|0.018||2.0055||||000287C61
31|W|C||253.70|2.0055|||||||||000298674

20|1|S5.0|1|STD||20596|MAX123|1999|09|09|09|01||||1|000309513
21||||CS1||5.0PPB|1999|09|09|||||TESLAB||07|00|00031A113
22||||||||||1.0||||00032A97A
30|C|7439-97-6|||||T|5.0|P|0.9997|||||||||U|0.018||4.9952||||00033BCE5
31|W|C||253.70|4.9952|||||||||00034C6F8
```

2.3 Spike Sample Recovery and Duplicates Performed on Different Samples (QC Codes FLD, LSF, FLD, LD2)

```
20|1|MAX123|F|FLD||20596|MAX123|1999|09|09|13|20||G|0.20|1|002106798
21||LOW||CS1||S308233-01|1999|09|09||1999|08|24|||07|00|0021175EF
22||||||||||100|1.0|||91.5|002127FB4
30|C|7439-97-6||MG/KG|BDL|0.1093||||||||||||U|0.0092||0.0049||||002159EC0
31|W|C||253.70|0.0049|||||||||00216A8E3

20|1|MAX123S|F|LSF||20596|MAX123|1999|09|09|13|25||G|0.20|1|00229534B
21||LOW||CS1||S308233-03|1999|09|09||1999|08|24|||07|00|0023061A2
22||||||||||100|1.0|||91.5|002316B67
30|C|7439-97-6||MG/KG||0.5664|F|0.55|P|103||||||75|125||U|0.0092||1.0366||||00232807A
31|W|C||253.70|1.0366|||||||||002338A9D

20|1|MAX126|F|FLD||20596|MAX123|1999|09|09|13|30||G|0.20|1|00217B9F5
21||LOW||CS1||S308233-06|1999|09|09||1999|08|24|||07|00|00218C84C
22||||||||||100|1.0|||85.6|00219D211
30|C|7439-97-6||MG/KG||1.5053||||||||||||U|0.0092||2.5771||||00222F11D
31|W|C||253.70|2.5771|||||||||00223FB40

20|1|MAX126D|F|LD2||20596|MAX123|1999|09|09|13|35||G|0.20|1|002240C9D
21||LOW||CS1||S308233-07|1999|09|09||1999|08|24|||07|00|002251AF4
22||||||||||100|1.0|||85.1|0022624BC
30|C|7439-97-6||MG/KG|BDL|0.1175|||P|200|||L|0.0383||||*|U|0.0092||0.0028||||002273795
31|W|C||253.70|0.0028|||||||||0022841B9
```

2.4 Duplicates and Spike Sample Recovery Performed on the Same Sample (QC Codes FLD, LD2, LSF)

```
20|1|MAX126|F|FLD||20596|MAX123|1999|09|09|16|10||G|0.20|1|002106798
21||LOW||CS1||S308233-06|1999|09|09||1999|08|24|||07|00|0021175EF
22||||||||||100|1.0|||91.5|002127FB4
30|C|7439-97-6||MG/KG||0.6429||||||||||||U|0.0092||1.1765||||002159EC0
31|W|C||253.70|1.1765|||||||||00216A8E3

20|1|MAX126D|F|LD2||20596|MAX123|1999|09|09|16|15||G|0.20|1|002240C9D
21||LOW||CS1||S308233-07|1999|09|09||1999|08|24|||07|00|002251AF4
22||||||||||100|1.0|||90.9|0022624BC
30|C|7439-97-6||MG/KG||0.2342|||P|94|||L|0.0364||||*|U|0.0092||0.4286||||002273795
31|W|C||253.70|0.4286|||||||||0022841B9
```

```
20|1|MAX126S|F|LSF||20596|MAX123|1999|09|09|16|20||G|0.20|1|00229534B
21||LOW||CS1||S308233-08|1999|09|09||1999|08|24|||07|00|0023061A2
22||||||||||100|1.0|||91.5|002316B67
30|C|7439-97-6||MG/KG||0.9710|F|0.55|P|60|||||N|75|125||U|0.0092||1.7769||||00232807A
31|W|C||253.70|1.7769|||||||||002338A9D
```

2.5 Initial Calibration Verification (ICV) with LVM QC Code

```
20|1|ICV1A|1|LVM||20596|MAX123|1999|09|09|09|06||||1|00035D687
21||||CS1||ICV-5|1999|09|09|||07|00|ICF(0791)||07|00|00036E25E
22||||||||||2.0||||00037EAC6
30|C|7439-97-6||UG/L||4.91|T|4.9|P|100||||||80.0|120.0||U|0.018||2.4559||||00038FFD0
31|W|C||253.70|2.4559|||||||||0003909FC
```

2.6 Laboratory Control Sample (Solid) with LCM QC Code

```
20|1|LCSSC3|F|LCM||20596|MAX123|1999|09|09|12|24||G|0.20|1|001256DBA
21||||CS1||LCSHG|1999|09|09|||||QAL-0287||07|00|001267B1B
22||||||||||100|1.0||||001278443
30|C|7439-97-6||MG/KG||4.6|T|4.2|P|110||||||2.8|6.0||U|0.0092||9.2000||||00128996D
31|W|C||253.70|2.7719|||||||||00129A39A
```

3.0 CYANIDE

3.1 Start of a Cyanide Run with Record Types 10 and 16 and the First Type 20 Records

```
10|1999|09|01|14|09|AS|ILM05.3|ABC|TESLAB||||68-D2-0039|C1||TEST LABS INC.|7|00000189C
16|1999|09|01|15|03|Y||||000012033

20|1|MDL|1|MDQ||||1999|07|15||||||1|000044A74
21||||NP1|||1999|07|15|||||||10|30|000053CD5
30|C|57-12-5||UG/L|||||||||||||||U|1.7||||||0000656DC

20|1|MDL|1|MDQ||||1999|07|15||||||1|000044A74
21||||DW1|||1999|07|15|||||||10|30|000053CD5
30|C|57-12-5||UG/L|||||||||||||||U|1.8||||||0000656DC

20|1|MDL|F|MDQ||||1999|07|16||||||1|000044A74
21||||DS2|||1999|07|16|||||||07|45|000053CD5
30|C|57-12-5||MG/KG|||||||||||||||U|0.092||||||0000656DC

20|1|LRV|1|LRQ||||1999|09|01||||||1|000066486
30|C|57-12-5|||||||||||||||||||||||||000076FDA
32||||||||||IT|45.00||||000087917
34||||620.00|10|400||||||000098169
```

3.2 Cyanide Instrument Calibration Standards: Blank (S0) and Five Other Standards

```
20|1|S0|1|STB||20596|MAX123|1999|09|01|14|09||||1|000108FA1
21||||NP1||0PPB||||||||TESLAB||||000119B3E
22||||||||||||1.0||||00012A3A5
30|C|57-12-5|||||T|0.0||||||||||U|1.7||0.3543||||00013B48B
31|W|C||620.00|0.3543|||||||||00014BD34

20|1|S10|1|STC||20596|MAX123|1999|09|01|14|10||||1|00015CB95
21||||NP1||10PPB||||||||TESLAB||||00016D763
22||||||||||||1.0||||00017DFCA
30|C|57-12-5|||||T|10.0||||||||||U|1.7||11.1700||||00018F0D2
31|W|C||620.00|11.1700|||||||||00019F97B

20|1|S40|1|STD||20596|MAX123|1999|09|01|14|11||||1|0002007E0
21||||NP1||40PPB||||||||TESLAB||||0002113B1
22||||||||||||1.0||||000221C18
```

```
30|C|57-12-5|||||T|40.0|||||||||||U|1.7||38.4000||||000232D23
31|W|C||620.00|38.4000|||||||||0002435CC

20|1|S100|1|STD||20596|MAX123|1999|09|01|14|12||||1|00025445F
21||||NP1||100PPB|||||||||TESLAB||||00026505D
22|||||||||||1.0||||0002758C4
30|C|57-12-5|||||T|100.0|||||||||||U|1.7||99.7400||||000232D23
31|W|C||620.00|99.7400|||||||||0002972A5

20|1|S200|1|STD||20596|MAX123|1999|09|01|14|12||||1|000308139
21||||NP1||200PPB|||||||||TESLAB||||000318D38
22|||||||||||1.0||||00032959F
30|C|57-12-5|||||T|200.0|||||||||||U|1.7||201.3000||||00033A6D8
31|W|C||620.00|201.3000|||||||||00034AF81

20|1|S400|1|STD||20596|MAX123|1999|09|01|14|13||||1|00035BE18
21||||NP1||400 PPB|||||||||TESLAB||||00036CA19
22|||||||||||1.0||||00037D280
30|C|57-12-5|||||T|400.0|P|1.0000|||||||||U|1.7||399.5000||||00038E3BB
31|W|C||620.00|399.5000|||||||||00039EC64
```

3.3 Preparation Blank (Soil) with LRB QC Code

```
20|1|PBSD1|F|LRB||20596|MAX123|1999|09|01|14|23||G|1.00|1|000928FA0
21||||DS2||PB|1999|08|30|||||||08|30|000939A40
22||||||||||50|1.0||||00094A30C
30|C|57-12-5||MG/KG|BDL|1.0000|||||||||||||U|0.092||-0.0030||||00095B433
31|W|C||620.00|-0.0030|||||||||00096BE6F
```

3.4 Laboratory Control Sample (Soil) with LCM QC Code

```
20|1|LCSSD1|F|LCM||20596|MAX123|1999|09|01|14|24||G|1.00|1|00097CF4D
21||||DS2||LCSCN|1999|08|30|||||QAL-0689||08|30|00098DCB0
22||||||||||50|1.0||||00099E57C
30|C|57-12-5||MG/KG||5.0|T|5.6|P|89||||||4.3|6.9||U|0.092||100.0933||||00100F89B
31|W|C||620.00|100.0933|||||||||001010315
```

3.5 Continuing Calibration Verification (CCV) with LVC QC Code

```
20|1|CCV11|1|LVC||20596|MAX123|1999|09|01|14|30||||1|0015045A3
21||||NP1||200 PPB|||||||||TESLAB||||0015151A2
22|||||||||||1.0||||001525A09
30|C|57-12-5||UG/L||188.48|T|200.0|P|94||||||85.0|115.0||U|1.7||188.4772||||001536E87
31|W|C||620.00|188.4772|||||||||001547916
```

3.6 Spike Sample Recovery and Post Distillation Spike Sample Recovery Performed on the Same Sample (QC Codes FLD, PDO, LSF, PDF)

```
20|1|MAX123|F|FLD||20596|MAX123|1999|09|01|14|35||G|1.06|1|001955D8E
21||LOW||DS2||S308233-01|1999|08|30||1999|08|24|||08|30|001966BDF
22||||||||||50|1.0|||71.0|001977578
30|C|57-12-5||MG/KG|LTC|0.2952|||||||||||||U|0.092||4.4441||||002009309
31|W|C||620.00|4.4441|||||||||002019D4B

20|1|MAX123|F|PDO||20596|MAX123|1999|09|01|14|35||G|1.06|1|00202AE62
21||LOW||DS2||S308233-01|1999|08|30||1999|08|24|||08|30|00203BCB3
22||||||||||50|1.0|||71.0|00204C64C
30|C|57-12-5||UG/L|LTC|4.44|||||||||||||U|1.4||4.4441||||00207E3DD
31|W|C||620.00|4.4441|||||||||00208EE1F

20|1|MAX123S|F|LSF||20596|MAX123|1999|09|01|14|36||G|1.02|1|00209FF7A
21||LOW||DS2||S308233-02|1999|08|30||1999|08|24|||08|30|002100DCB
22||||||||||50|1.0|||71.0|002111767
```

```
30|C|57-12-5||MG/KG||4.6341|F|6.90|P|63|||||N|75|125||U|0.092||67.1210||||0021228D6
31|W|C||620.00|67.1210|||||||||002133324

20|1|MAX123A|F|PDF||20596|MAX123|1999|09|01|14|37||G|1.06|1|0021444AD
21||LOW||||S308233-03|1999|08|30||1999|08|24|||||0021552FE
22||||||||||50|1.0|||71.0|002165C98
30|C|57-12-5||UG/L||21.23|F|20.0|P|84|||||||||U|1.4||21.2279||||0021770C0
31|W|C||620.00|21.2279|||||||||002187B4E
```

APPENDIX B - Modified Analysis

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Appendix B - Modified Analysis

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MODIFIED ANALYSIS

The Contractor may be requested by USEPA to perform modified analyses. These modifications will be within the scope of this SOW and may include, but are not limited to, analysis of additional analytes and/or lower quantitation limits. These requests will be made by the USEPA Regional CLP Project Officer (CLP PO), USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB) Inorganic Program Manager (PM), and USEPA Contracting Officer (CO) in writing, prior to sample scheduling. If the Contractor voluntarily elects to perform these modified analyses, these analyses will be performed with no increase in per sample price. All contract requirements specified in the SOW/Specifications will remain in effect unless the USEPA CO provides written approval for the modification(s) and a waiver for associated defects. The USEPA CO approval must be obtained prior to sample scheduling.

GRAPHITE FURNACE ATOMIC ABSORPTION METHOD

1.0 SCOPE AND APPLICATION

This method is a graphite furnace atomic absorption spectroscopy procedure that is used to analyze water, sediment, sludge, and soil samples taken from hazardous waste sites. The following metals: arsenic, lead, selenium, and thallium that are contained in the Target Analyte List (TAL) in Exhibit C may be quantitated by the Graphite Furnace Atomic Absorption (GFAA) method.

2.0 SUMMARY OF METHOD

Water and soil samples are treated with acids and heat to solubilize the metals present. These digestates are then analyzed for trace metals by the Graphite Furnace Atomic Absorption (GFAA) spectroscopic technique. In this technique, a tube of graphite is located in the sample compartment of the Atomic Absorption (AA) spectrophotometer, with the light passing through it. A small volume of sample solution is quantitatively placed into the tube, normally through a sample injection hole located in the center of the tube wall. The tube is heated through a programmed temperature sequence until finally the analyte present in the sample is dissociated into atoms and atomic absorption occurs.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

Several types of interference effects may contribute to inaccuracies in the determination of trace elements in water and soil/sediments. Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 milligrams per Liter (mg/L). In addition, total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects.

Interferences from the Graphite Furnace Atomic Absorption (GFAA) technique can be divided into two broad categories, spectral and nonspectral interferences. Spectral interferences are those resulting from light absorption by molecules or by atoms other than those of the analyte element; that is, spectral interference exists if the atomic absorption profile of an element overlaps the emission line of another. Nonspectral interferences are those which affect the production or availability of analyte atoms which create the measured atomic absorption.

4.1 Spectral Interferences

4.1.1 Emission Interference - this interference arises when the intense light emitted by the hot graphite tube reaches the instrument's light detector, the Photomultiplier Tube (PMT). This problem is manifested by increased signal variability (noise) which degrades analytical performance. In severe circumstances, emission interference may temporarily blind the PMT, resulting in erratic, meaningless readings at atomization.

4.1.2 Background Absorption - this is the most severe spectral interference encountered with graphite furnace analyses. Background absorption is a nonspecific attenuation of light at the analyte wavelength caused by matrix components in the sample. Unlike atomic absorption, background absorption is broad band, sometimes covering tens or even hundreds of nanometers. This broad band absorption normally is due to molecular absorption or light scattering caused by undissociated sample matrix components in the light path at atomization. Since background absorption is broad band, the chance of overlap with a desired analyte wavelength is significant.

4.1.3 Emission interference is controlled by primarily by spectrophotometer optical design. Techniques for controlling and reducing background absorption include matrix modification (sample treatment) and optical background correction. Through matrix modification, a reagent or "matrix modifier" is added to the sample or standard. The matrix modifier is selected to generate either an increased matrix volatility or decreased analyte volatility. One type of background correction, Zeeman, can correct for higher and more spectrally complicated background absorption and provide more precise and accurate analytical results. Zeeman background correction uses the principle that the electronic energy levels of an atom placed in a strong magnetic field are changed thereby changing the atomic spectra; the spectral nature of background absorption, on the other hand is unaffected by a magnetic field.

4.2 Nonspectral Interferences

In order for atomic absorption to occur, free atoms of the analyte element must be present in the spectrophotometer light path. Nonspectral interferences result when diverse components in the sample matrix inhibit the formation of free analyte atoms. An often used approach to compensate for nonspectral interferences is known as the "Method of Standard Additions".

5.0 SAFETY

See Section 1.14 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Glassware/Labware

6.1.1 250 milliliter (mL) beaker or other appropriate vessel

6.1.2 Watch glasses

6.1.3 Funnels

6.1.4 Graduated cylinders

6.1.5 Various volumetric flasks (Type A)

6.1.6 Thermometer that covers a range of 0-200°C

6.1.7 Whatman No. 42 filter paper or equivalent

6.1.8 Hot plate, block digester, or other heating source capable of maintaining 92-95°C

6.1.9 Balances - Analytical Balance, 300 gram (g) capacity, and minimum ±0.01 g.

6.2 Atomic Absorption Spectrophotometer - with graphite furnace atomizer and background correction. Hollow Cathode Lamp (HCL) and/or Electrodeless Discharge Lamp (EDL).

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. (Redistilled acids are acceptable.)

7.1.1 Reagent water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-77). Use this preparation for all reagents, standards, and dilutions of solutions.

7.1.2 Nitric acid - Concentrated (specific gravity 1.41).

7.1.3 Nitric acid, 5% (v/v) - Add 50 milliliters (mL) conc. HNO_3 to 500 mL reagent water; dilute to 1 Liter (L).

7.1.4 Hydrochloric acid - Concentrated (specific gravity 1.19).

7.1.5 Hydrogen peroxide (30%)

7.1.6 Matrix Modifiers

7.1.6.1 Ammonium Phosphate solution (40%): Dissolve 40 grams (g) of ammonium phosphate, $(NH_4)_2PO_4$ (analytical reagent grade) in reagent water and dilute to 100 mL.

7.1.6.2 Calcium Nitrate solution: Dissolve 11.8 g of calcium nitrate, $Ca(NO_3)_2 \bullet 4H_2O$ (analytical reagent grade) in reagent water and dilute to 100 mL. 1 mL = 20 mg Ca.

7.1.6.3 Lanthanum Nitrate solution: Dissolve 58.64 g of American Chemical Society (ACS) reagent grade 2. La_2O_3 in 100 mL conc. HNO_3 and dilute to 1000 mL with reagent water. 1 mL = 50 mg La.

7.1.6.4 Nickel Nitrate solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \bullet 6H_2O$ in reagent water and make up to 100 mL.

7.1.6.5 Nickel Nitrate solution, 1%: Dilute 20 mL of the 5% nickel nitrate to 100 mL with reagent water.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 8.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.2 Stock Standard Solutions

7.2.2.1 Stock standard solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 hour at 105°C unless otherwise specified.

(CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow.

7.2.2.2 Arsenic solution, stock [1 mL = 1 mg As (1000 mg/1)] - Dissolve 1.320 g of As_2O_3 in 100 mL of reagent water containing 0.4 g NaOH. Acidify the solution with 20 mL conc. HNO_3 and dilute to 1 L.

7.2.2.3 Lead solution, stock [1 mL = 1 mg Pb (1000 mg/L)] - Dissolve 1.599 g of $Pb(NO_3)_2$ in reagent water. When solution is complete, acidify with 10 mL of conc. HNO_3 and dilute to 1 L with reagent water.

7.2.2.4 Selenium solution, stock [1 mL = 1 mg Se (1000 mg/L)] - Dissolve 0.3453 g of H_2SeO_3 (actual assay 94.6%) in reagent water and make up to 200 mL.

7.2.2.5 Thallium solution stock [1 mL = 1 mg Tl (1000 mg/L)] - Dissolve 1.303 g of $TlNO_3$ in reagent water. Add 10 mL of conc. nitric acid and dilute to 1 L with reagent water.

7.2.3 Working Standards

7.2.3.1 Secondary Dilution Standards

Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions". The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

7.2.3.2 Calibration Blank

Prepared by diluting 1 mL of (1+1) HNO_3 and 2 mL 30% H_2O_2 to 100 mL with reagent water.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All samples must be collected in glass or polyethylene containers. Water/aqueous samples must be preserved with nitric acid to pH less than 2 immediately after collection. All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until digestion.

8.1.1 Dissolved Metals

For the determination of dissolved metals, the sample must be filtered through a 0.45 micrometer (µm) pore diameter membrane filter at the time of collection or as soon as possible. Use a portion of the sample to rinse the filter flask, discard this portion, and collect the required volume of filtrate. Preserve the filtrate with nitric acid to pH less than 2 immediately after filtration.

8.2 Procedure for Sample Storage

The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days the samples may be disposed of in a manner that complies with all applicable regulations.

8.3 Procedure for Sample Digestate Storage

Sample digestates must be stored until 365 days after delivery of a complete, reconciled data package to USEPA.

8.4 Contract Required Holding Time

The maximum holding time for metals is 180 days from Validated Time of Sample Receipt (VTSR).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. The Method Detection Limit (MDL), precision, and interference effects must be investigated and established for each individual analyte line on that particular instrument. All measurements must be within the instrument calibrated range. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 Graphite Furnace Atomic Absorption (GFAA) Instrument Calibration Procedure

9.2.1 Instruments shall be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time shall be included in the raw data.

9.2.2 Calibration standards shall be prepared fresh daily or each time an analysis is to be made and discarded after use. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. One atomic absorption calibration standard shall be at the CRQL. The calibration standards shall be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following sample preparation.

9.2.3 Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. Date and time of preparation and analysis shall be given in the raw data.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact Sample Management Office (SMO) to inform them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample and analyze one or more of the phases, separately. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do any of the following:

- Separate the phases and analyze the phase(s) that is(are) amenable to analysis. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Water/Aqueous Sample Preparation

10.1.3.1 Shake sample and transfer 50-100 mL of well-mixed sample to a 250 mL heating vessel, add 1 milliliter (mL) of (1+1) HNO_3 and 2 mL of 30% H_2O_2 to the sample. Cover with watch glass or similar cover and heat on a hot plate, block digester, or equivalent heating source which is adjustable and capable of maintaining a temperature of 92-95°C for 2 hours or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material.

NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

Adjust sample volume to 50-100 mL with reagent water. The sample is now ready for analysis. Concentrations so determined shall be reported as "total". If volumes less than 100 mL are used, all other reagents shall be reduced appropriately (e.g., if 50 mL is

used, reduce reagent volumes by one-half). The final volume of the digestate must equal the initial volume of the sample aliquot.

10.1.4 Soil/Sediment Sample Preparation

10.1.4.1 A representative 1.0 gram (g) (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Nitric acid is employed as the final reflux acid for the Graphite Furnace Atomic Absorption (GFAA) analysis of As, Pb, Se, and Tl. A separate sample shall be dried for a percent solids determination.

10.1.4.2 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 to 1.5 g portion of sample and transfer to a beaker.

10.1.4.3 Add 10 mL of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 92-95°C on hot plate or block digestor, and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, as appropriate, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the heating vessel.

10.1.4.4 After the second reflux step has been completed and the sample has cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return the heating vessel to the heat source for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the heat vessel.

Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

10.1.4.5 If the sample is being prepared for the GFAA analysis of As, Pb, Se, and Tl, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 mL, add 10 mL of reagent water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with reagent water.

NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

Dilute the digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. For analysis, withdraw aliquots of appropriate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

10.2 Sample Analysis

10.2.1 Set up instrument with proper operating parameters established in Section 9.1.

10.2.2 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using calibration standard solutions.

10.2.3 Instrument Parameters - Suggested Conditions

10.2.3.1 Arsenic

10.2.3.1.1 Wavelength: 193.7 nm

10.2.3.1.2 Operating parameters should be set as specified by the particular instrument manufacturer.

10.2.3.1.3 The use of background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferents (i.e., Al, Fe). If conditions occur where significant interference is suspected, the laboratory must switch to an alternate wavelength or take other appropriate actions to compensate for the interference effects.

10.2.3.1.4 The use of the Electrodeless Discharge Lamps (EDLs) for the light source is recommended.

10.2.3.2 Lead

10.2.3.2.1 Wavelength: 283.3 nm

10.2.3.2.2 Operating parameters should be set as specified by the particular instrument manufacturer.

10.2.3.2.3 The use of background correction is required.

10.2.3.2.4 Greater sensitivity can be achieved using the 217.0 nm line, but the optimum concentration range is reduced. The use of an EDL at this lower wavelength has been found to be advantageous. Also a lower atomization temperature (2400°C) may be preferred.

10.2.3.2.5 To suppress sulfate interference (up to 1500 ppm), lanthanum is added as the nitrate to both samples and calibration standards.

10.2.3.2.6 Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately prior to use, and once cleaned, should not be open to the atmosphere except when necessary.

10.2.3.3 Selenium

10.2.3.3.1 Wavelength: 196.0 nm

10.2.3.3.2 Operating parameters should be set as specified by the particular instrument manufacturer.

10.2.3.3.3 Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/L, both samples and standards should be prepared to contain 1% nickel.

10.2.3.3.4 The use of the EDL for the light source is recommended.

10.2.3.4 Thallium

10.2.3.4.1 Wavelength: 276.8 nm

10.2.3.4.2 Operating parameters should be set as specified by the particular instrument manufacturer.

10.2.3.4.3 The use of background correction is required.

10.2.3.4.4 Nitrogen may also be used as the purge gas.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Water/Aqueous Sample Calculation

The concentrations determined in the digestate are to be reported in units of microgram per Liter (µg/L):

EQ. 1 Aqueous Sample Concentration

$$\text{Concentration} = C \times \frac{V_f}{V_i}$$

WHERE,
C = Instrument value in µg/L
V_f = Final digestion volume
V_i = Initial digestion volume

11.2 Soil Sample Calculation

The concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample, in units of milligram per kilogram (mg/kg):

EQ. 2 Soil Sample Concentration

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S}$$

WHERE,
C = Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample
S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6).

11.3 Corrections For Sample Dilutions

If dilutions were performed, the appropriate factor shall be applied to the sample values as follows:

EQ. 3 Correction for Dilution

$$C\ (\mu g/L) = C_i \times DF$$

WHERE, C = Concentration of analyte in sample

C_i = Instrument value concentration

DF = Dilution Factor

12.0 QUALITY CONTROL

For specific Quality Control (QC) requirements, the Contractor shall follow the instructions provided by the USEPA Region requesting the analysis.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 1.15 in Exhibit D - Introduction to Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 1.16 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 206.2. March 1983.

16.2 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 239.2. March 1983.

16.3 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 270.2. March 1983.

16.4 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 279.2. March 1983.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Not applicable.

USEPA CONTRACT LABORATORY PROGRAM

STATEMENT OF WORK

FOR

INORGANIC ANALYSIS

Multi-Media, Multi-Concentration

ILM05.3
March 2004

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STATEMENT OF WORK

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EXHIBIT A

SUMMARY OF REQUIREMENTS

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Exhibit A - Summary of Requirements

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1.0 PURPOSE

The purpose of the multi-media, multi-concentration inorganic analytical service is to provide analytical data for use by the U.S. Environmental Protection Agency (USEPA) in support of the investigation and clean-up activities under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986 (SARA). Other USEPA Program Offices that have similar analytical data needs also use this service.

2.0 DESCRIPTION OF SERVICE

The inorganic analytical service provides a contractual framework for laboratories. This framework applies USEPA Contract Laboratory Program (CLP) analytical methods for the isolation, detection, and quantitative measurement of 23 metals (including mercury) and cyanide in water/aqueous and/or soil/sediment samples. The analytical service contract provides specific contractual requirements by which USEPA will evaluate the data.

3.0 DATA USES

This analytical service contract provides data which USEPA uses for a variety of purposes, such as: determining the nature and extent of contamination at a hazardous waste site, assessing priorities for response based on risks to human health and the environment, determining appropriate cleanup actions, and determining when remedial actions are complete. The data may be used in all stages in the investigation of hazardous waste sites, including: site inspections, Hazard Ranking System (HRS) scoring, remedial investigation/feasibility studies, remedial design, treatability studies, and removal actions.

The data may also be used in litigation against Potentially Responsible Parties in the enforcement of Superfund legislation. As a result, the Contractor must be aware of the importance of maintaining the integrity of the data generated under this contract, since it is used to make major decisions regarding public health and environmental welfare. The Contractor may be required to appear and testify to the accuracy and/or validity of the data generated.

4.0 SUMMARY OF REQUIREMENTS

4.1 Introduction to the Inorganic Statement of Work

The Statement of Work (SOW) is comprised of eight exhibits and two appendices. Exhibit A provides an overview of the SOW and its general requirements. Exhibit B contains a description of the reporting and deliverables requirements, in addition to the data reporting forms and instructions. Exhibit C specifies the Inorganic Target Analyte List (TAL) for this SOW with the Contract Required Quantitation Limits (CRQLs) for the sample matrices. Exhibit D details the required analytical procedures to be used with this SOW and resulting contracts. Exhibit E provides descriptions of required Quality Assurance/Quality Control (QA/QC), Standard Operating Procedures (SOPs), QA/QC performance, and the reporting of data. Exhibit F contains chain-of-custody and sample documentation requirements. To ensure proper understanding of the terms utilized in this SOW, a glossary can be found in Exhibit G. When a term is used in the text without explanation, the glossary meaning shall be applicable. Specifications for reporting data in computer-readable format appear in Exhibit H. Appendix A provides examples of the data format requirements specified in Exhibit H. Appendix B contains a description of the requirements for performing

modified analyses, as well as the analytical procedure for Graphite Furnace Atomic Absorption (GFAA).

4.2 Overview of Major Task Areas

For each sample, the Contractor shall perform the tasks described in each section. Specific requirements for each task are detailed in the exhibits referenced in the following sections.

4.2.1 Task I: Sample Receiving, Storage, and Disposal

4.2.1.1 Chain-of-Custody

The Contractor shall receive and maintain samples under proper chain-of-custody. All associated document control and inventory procedures shall be developed and followed. Documentation described herein shall be required to show that all procedures are strictly followed. This documentation shall be reported as the Complete Sample Delivery Group (SDG) File (CSF) (see Exhibit B). The Contractor shall establish and use appropriate procedures to safeguard confidential information received from USEPA.

4.2.1.2 Sample Scheduling/Shipments

Sample shipments to the Contractor's facility will be scheduled and coordinated by the Contract Laboratory Program (CLP) Sample Management Office (SMO). USEPA may request analyses that include all or a subset of the Inorganic Target Analytes listed in Exhibit C. The Contractor shall communicate with SMO personnel by telephone as necessary throughout the process of sample scheduling, shipment, analysis, and data reporting, to ensure that samples are properly processed.

4.2.1.2.1 Samples will be shipped routinely to the Contractor through an overnight delivery service. However, as necessary, the Contractor shall be responsible for any handling or processing of the receipt of sample shipments. This includes the pick-up of samples at the nearest servicing airport, bus station, or other carrier within the Contractor's geographical area. The Contractor shall be available to receive and process sample shipments at any time the delivery service is operating, including Saturdays, to ensure that short sample analysis time requirements can be met.

4.2.1.2.2 If there are problems with the samples (e.g., mixed media, containers broken or leaking) or sample documentation and paperwork (e.g., Traffic Reports/Chain of Custody Records not with shipment, sample and Traffic Report/Chain of Custody Record do not correspond), the Contractor shall immediately contact SMO for resolution. The Contractor shall immediately notify SMO and the USEPA Regional CLP Project Officer (CLP PO) regarding any problems and laboratory conditions that affect the timeliness of analyses and data reporting. In particular, the Contractor shall immediately notify SMO personnel and the USEPA Regional CLP PO in advance regarding sample data that will be delivered late and shall specify the estimated delivery date.

4.2.1.2.3 To monitor the temperature of the sample shipping cooler more effectively, each USEPA Regional Office may include a sample shipping cooler temperature blank with each cooler shipped. The temperature blank will be clearly labeled: USEPA COOLER

TEMPERATURE INDICATOR. The Contractor shall record the presence or absence of the cooler temperature indicator bottle on Form DC-1, Item 8 - Cooler Temperature Indicator Bottle (see Exhibit B).

4.2.1.2.3.1 When the USEPA Regional Office supplies a cooler temperature indicator bottle in the sample shipping cooler, the Contractor shall use the USEPA supplied cooler temperature indicator bottle to determine the cooler temperature. The temperature of the cooler shall be measured at the time of sample receipt by the Contractor.

4.2.1.2.3.2 The temperature of the sample shipping cooler shall be measured and recorded immediately upon opening the cooler.

4.2.1.2.3.3 To determine the temperature of the cooler: the Contractor shall locate the cooler temperature indicator bottle in the sample shipping cooler, remove the cap, and insert a calibrated thermometer into the cooler temperature indicator bottle. Prior to recording the temperature, the Contractor shall allow a minimum of 3 minutes, but not greater than 5 minutes, for the thermometer to equilibrate with the liquid in the bottle. At a minimum, the calibrated thermometer (±1°C) shall have a measurable range of 0-50°C. Other devices which can measure temperature may be used if they can be calibrated to ±1°C and have a range of 0-50°C. If a temperature indicator bottle is not present in the cooler, an alternative means of determining cooler temperature shall be used. Under no circumstances shall a thermometer or any other device be inserted into a sample bottle for the purpose of determining cooler temperature. The Contractor shall contact SMO and inform them that a temperature indicator bottle was not present in the cooler. The Contractor shall document the alternative technique used to determine cooler temperature in the SDG Narrative.

4.2.1.2.3.4 If the temperature of the sample shipping cooler's temperature indicator exceeds 10°C, the Contractor shall contact SMO and inform them of the temperature deviation. SMO will contact the Region from which the samples were shipped for instruction on how to proceed. The Region will either require that no sample analysis(es) be performed or that the Contractor proceed with the analysis(es). SMO will in turn notify the Contractor of the Region's decision. The Contractor shall document the Region's decision and the EPA sample numbers of all samples for which temperatures exceeded 10°C in the SDG Narrative.

4.2.1.2.3.5 The Contractor shall record the temperature of the cooler on Form DC-1, under Item 9 - Cooler Temperature, and in the SDG Narrative (see Exhibit B).

4.2.1.2.4 The Contractor is required to retain unused sample volume, used sample containers, and empty sample bottle containers for a period of 60 days after data submission. From time of receipt until analysis, the Contractor shall maintain <u>all</u> water/aqueous (preserved and unpreserved) and/or soil/sediment samples at 4°C (±2°C) (see Exhibit B).

4.2.1.2.5 The Contractor shall be required to routinely return sample shipping containers (e.g., coolers) to the appropriate sampling

office within 14 calendar days following shipment receipt (see contract, Section G titled, "Government Furnished Samples").

4.2.1.2.6 Sample analyses will be scheduled by groups of samples, each defined as a Case and identified by a unique EPA Case number assigned by SMO. A Case signifies a group of samples collected at one site or geographical area over a finite time period, and will include one or more field samples with associated blanks. Samples may be shipped to the Contractor in a single shipment or multiple shipments over a period of time, depending on the size of the Case.

4.2.1.2.6.1 A Case consists of one or more SDGs. An SDG is defined by the following, whichever is most frequent:

- Each Case of field samples received, or
- Each 20 field samples [excluding Performance Evaluation (PE) samples] within a Case, or
- Each 7 calendar day period (3 calendar day period for 7 day turnaround) during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).
- In addition, all samples and/or sample fractions assigned to an SDG must have been scheduled under the same contractual turnaround time. Preliminary Results have **no impact** on defining the SDG.

4.2.1.2.6.2 Samples may be assigned to SDGs by matrix (i.e., all soils in one SDG, all waters in another), at the discretion of the laboratory. However, PE samples received within a Case shall be assigned to an SDG containing field samples for that Case. Such assignment shall be made at the time the samples are received, and shall <u>not</u> be made retroactively.

4.2.1.2.6.3 Each sample received by the Contractor will be labeled with an EPA sample number, and accompanied by a Traffic Report/Chain of Custody Record bearing the sample number and descriptive information regarding the sample. EPA sample numbers are six digits in length. If the Contractor receives a sample number of any other length, the Contractor shall contact SMO immediately. The Contractor shall complete and sign the Traffic Report/Chain of Custody Record, recording the date of sample receipt and sample condition on receipt for each sample container. <u>The Contractor shall also follow the instructions given on the Traffic Report/Chain of Custody Record in choosing the Quality Control (QC) samples when such information is provided</u>. If no QC sample is designated on the Traffic Report/Chain of Custody Record, the Contractor shall select a sample and notify SMO for Regional acceptance. SMO shall contact the Region for confirmation immediately after notification.

4.2.1.2.6.4 The Contractor shall submit signed copies of Traffic Reports/Chain of Custody Records for all samples in a SDG to SMO within **three working days** following receipt of the last sample in the SDG. Faxed copies of Traffic Reports/Chain of Custody Records do not meet this requirement. Traffic Reports/Chain of Custody Records shall be submitted in SDG

sets (i.e., all Traffic Reports/Chain of Custody Records for a SDG shall be clipped together) with an SDG Cover Sheet containing information regarding the SDG, as specified in Exhibit B.

4.2.1.2.6.5 EPA Case numbers, SDG numbers, and EPA sample numbers shall be used by the Contractor in identifying samples received under this contract both verbally and in reports/ correspondence.

4.2.1.3 Modified Analysis

The Contractor may be requested by USEPA to perform modified analyses. These modifications will be within the scope of this SOW and may include, but are not limited to, analysis of additional analytes and/or lower quantitation limits. These requests will be made by the USEPA Regional CLP PO, USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch Inorganic Program Manager (ASB PM), and Contracting Officer (CO) in writing, prior to sample scheduling. If the Contractor voluntarily elects to perform these modified analyses, these analyses will be performed with no increase in per sample price. All contract requirements specified in the SOW/Specifications will remain in effect unless the USEPA CO provides written approval for the modification(s) and a waiver for associated defects. The USEPA CO approval must be obtained prior to sample scheduling.

4.2.2 Task II: Sample Preparation and Analysis

4.2.2.1 Overview

The Contractor is advised that the samples received under this contract are usually from known or suspected hazardous waste sites and may contain high (greater than 15%) levels of organic and inorganic materials of a potentially hazardous nature and of unknown structure and concentration, and should be handled throughout the analysis with appropriate caution. It is the Contractor's responsibility to take all necessary measures to ensure laboratory safety.

4.2.2.2 The Contractor shall prepare and analyze samples as described in Exhibit D. Sample preparation methods shall remain consistent for all samples analyzed within a Case. Prior to sample analysis, the Contractor shall review the Traffic Report/Chain of Custody Record for any special sample analysis instructions. Anomalies that occur during sample analysis shall be reported to SMO and the USEPA Regional CLP PO immediately.

The Contractor shall collectively review all analytical results associated with a sample. This includes undiluted, diluted, serial dilution, and interference results. The Contractor shall report any significant anomalies between these results in the SDG Narrative indicating possible matrix interferences.

4.2.2.3 Quality Assurance/Quality Control Procedures

4.2.2.3.1 The Contractor shall strictly adhere to all specific QA/QC procedures prescribed in Exhibits D and E. Records documenting the use of the protocol shall be maintained in accordance with the document control procedures prescribed in Exhibit F, and shall be reported in accordance with Exhibits B and H.

4.2.2.3.2 The Contractor shall maintain a Quality Assurance Management Plan (QAP) with the objective of providing sound analytical chemical measurements. This program shall incorporate the QC procedures, any necessary corrective action, and all documentation required during data collection as well as the quality assessment measures performed by management to ensure acceptable data production.

4.2.2.3.3 Additional QC shall be conducted in the form of the analysis of laboratory PE samples submitted to the laboratory by USEPA. Unacceptable results of all such QC or laboratory PE samples may be used as the basis for an equitable adjustment to reflect the reduced value of the data to USEPA or rejection of the data for specific analyte(s) within an SDG or the entire SDG. Also, unacceptable results may be used as the basis for contract action. "Compliant performance" is defined as that which yields correct analyte identification and concentration values as determined by USEPA, as well as meeting the contract requirements for analysis (Exhibit D); QA/QC (Exhibit E); data reporting and other deliverables (Exhibits B and H); and sample custody, sample documentation, and SOP documentation (Exhibit F).

4.2.3 Task III: Sample Reporting

4.2.3.1 USEPA has provided to the Contractor formats for the reporting of data (Exhibits B and H). The Contractor shall be responsible for completing and submitting analysis data sheets, computer-readable data on diskette (or via an alternate means of electronic transmission approved in advance by USEPA) in a format specified in this SOW and within the time specified in Exhibit B, Section 1.1.

4.2.3.2 Use of formats other than those designated by USEPA (see Exhibits B and H) will be deemed as noncompliant. Such data are unacceptable. Resubmission in the specified format at no additional cost to the Government shall be required.

4.2.3.3 Computer generated forms may be submitted in the hardcopy Sample Data Package(s) provided that the forms are in **exact USEPA format**. This means that the order of data elements is the same as on each USEPA required form, including form numbers and titles, page numbers, and header information.

4.2.3.4 The data reported by the Contractor on the hardcopy data forms and the associated computer-readable data submitted by the Contractor on diskette (or via an alternate means of electronic transmission, if approved in advance by USEPA) shall contain identical information. If discrepancies are found during Government inspection, the Contractor shall be required to resubmit either the hardcopy forms or the computer-readable data, or both sets of data, at no additional cost to USEPA.

EXHIBIT B

REPORTING AND DELIVERABLES REQUIREMENTS

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Exhibit B - REPORTING AND DELIVERABLES REQUIREMENTS

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1.0 CONTRACT REPORTS/DELIVERABLES DISTRIBUTION

1.1 Report Deliverable Schedule

The following table reiterates the contract reporting and deliverables requirements and specifies the distribution that is required for each deliverable. The turnaround times for Items B through E are 7, 14, or 21 days.

NOTE: Specific recipient names and addresses are subject to change during the term of the contract. The USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB) Inorganic Program Manager (ASB PM) will notify the Contractor in writing of such changes when they occur.

TABLE 1

Item		No. of Copies[A]	Delivery Schedule	Distribution			
				SMO	Region	CLP PO[D]	QATS
A.	Sample Traffic Reports/Chain of Custody Records	1	3 working days after receipt of last sample in Sample Delivery Group (SDG).[1]	X			
B.[2]	Sample Data Package	1	XX[C] days after Validated Time of Sample Receipt (VTSR)[1] of last sample in SDG.	X			
C.[2]	Data in Computer-Readable Format	1	XX[C] days after VTSR of last sample in SDG.	X	X		
D.[2]	Results of Intercomparison Study/PE Sample Analysis Study	1	XX[C] days after VTSR of last sample in SDG.	X			X
E.[2,3]	Complete SDG File (CSF)[B]	1	XX[C] days after VTSR of last sample in SDG.		X		
F.[4]	Preliminary Results	1	Within 72 hours after receipt of each sample at laboratory, if requested.	X	X		
G.[5,6]	Quarterly Verification of ICP-AES/ICP-MS Linear Ranges and ICP-AES Interelement Correction Factors	1	Quarterly: 15th day of January, April, July, and October.	X		X	X
	Annual Verification of Method Detection Limits (MDLs)	1	Annually: 15th day of January.	X		X	X

TABLE 1 (Con't)

Item		No. of Copies[A]	Delivery Schedule	Distribution			
				SMO	Region	CLP PO[D]	QATS
H.[6,7]	Standard Operating Procedures (SOPs)	1	Revise within 30 days after contract award and receipt of USEPA comments. Submit within 7 days of receipt of written request to recipients as directed. (See Exhibit E, Section 6) Submit within 14 days of amended SOP(s) as directed in Exhibit E, Section 6.4.	As Directed Amended SOPs distributed to CLP PO and QATS			
I.[6,7]	Quality Assurance Management Plan (QAP)	1	Revise within 30 days after contract award and receipt of USEPA comments. Submit within 7 days of receipt of written request to recipients as directed. (See Exhibit E, Section 5) Submit within 14 days of amended QAP as directed in Exhibit E, Section 5.3.	As Directed Amended QAP distributed to CLP PO and QATS			
J.	Electronic Instrument Data	Lot	Retain for 3 years after data submission. Submit within 7 days after receipt of written request by the USEPA Regional CLP PO. (See Exhibit E, Section 13)	As Directed			

Footnotes:

[A]The number of copies specified is the number of copies required to be delivered to each recipient.

[B]Contractor-concurrent delivery to USEPA's designated recipient [e.g., Quality Assurance Technical Support (QATS)] may be required upon request by the USEPA OSRTI ASB Inorganic Program Manager (ASB PM). Retain for 365 days after data submission, and submit as directed within 7 days after receipt of written request by the USEPA ASB PM.

[C]The number of days associated with these elements will be provided in the associated laboratory contract document and will also be provided at the time of sample scheduling by the Sample Management Office (SMO) Contractor.

[D]The CLP PO is the USEPA Regional Contract Laboratory Program (CLP) Project Officer (CLP PO) designated on the contract.

[1]Validated Time of Sample Receipt (VTSR) is the date of sample receipt at the Contractor's facility, as recorded on the shipper's delivery receipt and sample Traffic Report/Chain of Custody Record. Sample Delivery Group (SDG) is a group of samples within a Case, received over a period of 7 days or less with the same laboratory turnaround and not exceeding 20 samples [excluding Performance Evaluation (PE) samples]. Data for all samples in the SDG are due concurrently. The date of delivery of the SDG or any samples within the SDG is the date that the last sample in the SDG is received. See Exhibit A for further description.

[2]**DELIVERABLES ARE TO BE REPORTED TOTAL AND COMPLETE.** Concurrent delivery is required. Delivery shall be made such that all designated recipients receive the item on the same calendar day. This includes resubmission of both the hardcopy and electronic deliverable. The date of delivery of the SDG, or any sample within the SDG, is the date all samples have been delivered. **If the deliverables are due on a Saturday, Sunday, or Federal holiday, then they shall be delivered on the next business day. Deliverables received after this time will be considered late.**

[3]Complete SDG File (CSF) will contain the original Sample Data Package plus all of the original documents described in Exhibit B, Section 2.6.

[4]If required at the time of sample scheduling, the Contractor shall provide Preliminary Results, consisting of all Form Is (see Exhibit B, Section 2.9). Facsimile or electronic transmittal is required as requested by the Region. Electronic transmittals shall be transmitted as WordPerfect, MS Word, PDF, or other USEPA-approved formats. The Contractor will be notified of the format, fax numbers, or email address(es) at the time of sample scheduling. Sample Traffic Reports/Chain of Custody Records and SDG Cover Sheets shall be submitted with the Preliminary Results. The Contractor shall document all communication in a telephone log.

Preliminary Results Delivery Schedule:

If a sample requiring Preliminary Results arrives before 5 p.m., the Preliminary Results are due within the required turnaround time. If a sample requiring Preliminary Results is received after 5 p.m., the Preliminary Results are due within the required turnaround time beginning at 8 a.m. the following day.

[5]Also required in each Sample Data Package.

[6]See Exhibit E for description. Time is cited in calendar days.

Footnotes (Con't):

[7]The Contractor shall deliver both hardcopy and electronic (i.e., diskette) copies of the Standard Operating Procedures (SOPs) and Quality Assurance Management Plan (QAP).

1.2 Distribution

The following addresses correspond to the "Distribution" column in Exhibit B, Section 1.1, Table 1.

SMO: USEPA Contract Laboratory Program (CLP)
Sample Management Office (SMO)[1]
15000 Conference Center Drive
Chantilly, VA 20151-3808

Region: USEPA REGIONS: SMO will provide the Contractor with the list of addressees for data delivery for the 10 USEPA Regions. SMO will provide the Contractor with updated Regional address/name lists as necessary throughout the period of the contract and identify other client recipients on a case-by-case basis.

USEPA Regional CLP Project Officer (CLP PO):

SMO will provide the Contractor with the list of addresses for the USEPA Regional CLP POs. SMO will provide the Contractor with updated name/address lists as necessary throughout the period of the contract.

QATS: USEPA Contract Laboratory Program (CLP)
Quality Assurance Technical Support (QATS) Laboratory[2]
2700 Chandler Avenue, Building C
Las Vegas, NV 89120
Attn: Data Audit Staff

In addition, the mailing and delivery addresses for the USEPA ASB Inorganic Program Manager (ASB PM) are:

Mailing Address: USEPA OSRTI Analytical Services Branch
Ariel Rios Building (5204G)
1200 Pennsylvania Avenue, N.W.
Washington, DC 20460
Attn: CLP Inorganic Program Manager

Fed-Ex/Overnight Delivery: USEPA OSRTI Analytical Services Branch
1235 Jefferson Davis Highway
Crystal Gateway I, 12th Floor
Arlington, VA 22202
Attn: CLP Inorganic Program Manager

[1]The SMO is a Contractor-operated facility operating under the SMO contract awarded and administered by USEPA.

[2]The QATS laboratory is a Contractor-operated facility operating under the QATS contract awarded and administered by USEPA.

2.0 REPORTING REQUIREMENTS AND ORDER OF DATA DELIVERABLES

2.1 Introduction

The Contractor shall provide reports and other deliverables as specified in Exhibit B, Section 1.1. The required content and form of each deliverable is described in this exhibit. All reports and documentation **shall be:**

- Legible;
- Clearly labeled and completed in accordance with instructions in this exhibit;
- Arranged in the order specified in this section;
- Paginated sequentially according to instructions in this exhibit; and
- Double-sided.

NOTE: Complete Sample Delivery Group (SDG) Files (CSFs) need not be double-sided. (The CSF is composed of original documents.) However, Sample Data Packages delivered to the USEPA Contract Laboratory Program (CLP) Sample Management Office (SMO) and the Region, [and USEPA designated recipients, e.g., Quality Assurance Technical Support (QATS), upon written request] must be double-sided.

2.1.1 The Contractor shall use EPA Case numbers, SDG numbers, and EPA sample numbers to identify samples received under this contract, both verbally and in reports and correspondence. The contract number shall be specified in all correspondence.

2.1.2 Section 4 of this exhibit contains the required Data Reporting Forms in Agency-specified format. Section 3 of this Exhibit contains instructions to the Contractor for properly completing all data reporting forms to provide USEPA with all required data. Data elements and field descriptors for reporting data in computer-readable format are contained in Exhibit H.

2.2 Resubmission of Data

If submitted documentation does not conform to the above criteria, the Contractor is required to resubmit such documentation with deficiency(ies) corrected within 4 business days, at no additional cost to USEPA.

2.2.1 Whenever the Contractor is required to submit or resubmit data as a result of an on-site laboratory evaluation, through the USEPA Regional CLP Project Officer (CLP PO) action, or through a Regional data reviewer's request, the data shall be clearly marked as "Additional Data" and shall be sent to both contractual data recipients (SMO and Region) and to USEPA's designated recipient (e.g., QATS) when a written request for the Sample Data Package has been made. A cover letter shall be included which describes what data is being delivered, to which USEPA Case(s) the data pertains, and **who requested the data**.

2.2.2 Whenever the Contractor is required to submit or resubmit data as a result of Contract Compliance Screening (CCS) review by SMO, the data shall be sent to the two contractual data recipients (SMO and Region) and to USEPA's designated recipient (e.g., QATS) when a written request for the Sample Data Package has been made. In all instances, the Contractor shall include a color-coded cover sheet (Laboratory

Response to Results of Contract Compliance Screening) provided by SMO. Electronic deliverables shall be submitted or resubmitted to SMO and the Region. Revised DC-1 and DC-2 forms shall be resubmitted to SMO and the Region.

2.3 Quality Assurance (QA) Management Plan and Standard Operating Procedures (SOPs)

The Contractor shall adhere to the requirements in Exhibits E and F.

2.4 Sample Traffic Reports/Chain of Custody Records

Each sample received by the Contractor will be labeled with an EPA sample number and will be accompanied by a Sample Traffic Report/Chain of Custody Record bearing the sample number and descriptive information regarding the sample. The current CLP Traffic Report is the "Inorganic Traffic Report & Chain of Custody Record". The CLP Traffic Report/Chain of Custody Record is one form divided into two sections: the Traffic Report section which consists of everything above the Chain of Custody Record section, and the bottom section which is the Chain of Custody Record. The Contractor shall complete the CLP Traffic Report/Chain of Custody Record (marked "Lab Copy for Return to SMO"), recording the date of sample receipt, verifying the number of samples, and signing the CLP Traffic Report/Chain of Custody Record.

Upon receipt, the Contractor shall sign for receipt of samples. The laboratory signature box is located at the bottom of the CLP Traffic Report/Chain of Custody Record in the Chain of Custody Record section. The laboratory sample custodian or designated recipient opening and verifying the contents of the cooler shall then verify receipt of all samples identified within the CLP Traffic Report section and sign and date the signature box located in the upper half of the CLP Traffic Report/Chain of Custody Record. If a non-CLP Traffic Report/Chain of Custody Record is submitted with the samples, for example a Regional Traffic Report/Chain of Custody Record, then the Contractor shall (1) sign and date receipt of the samples to maintain the chain-of-custody and (2) the sample custodian or designated recipient shall sign and date the Traffic Report/Chain of Custody Record to verify sample information.

The Contractor shall also enter the Sample Delivery Group (SDG) number, Case number, and the laboratory contract number on the CLP Traffic Report/Chain of Custody Record, in the appropriate boxes. The EPA sample number of the first sample received in the SDG is the SDG number. When several samples are received together in the first SDG shipment, the SDG number shall be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG. Under no circumstances should any SDG number be replicated within a Case. If necessary, select an alternative sample number for the SDG number. The SDG number is also reported on all data reporting forms (see Exhibit B, Section 3 - Form Instructions). If the laboratory is requested to transfer samples to another facility, the Contractor shall date and enter the name of the facility to where the samples will be transferred on the CLP Traffic Report/Chain of Custody Record.

2.4.1 The Contractor shall submit Traffic Reports/Chain of Custody Records in SDG sets (i.e., Traffic Reports/Chain of Custody Records for all samples in an SDG shall be clipped together), with an SDG Cover Sheet attached. The SDG Cover Sheet shall contain the following items:

- Laboratory name;
- Contract number;
- Sample analysis price (full sample price from the contract);
- Case number; and
- List of EPA sample numbers of all samples in the SDG, identifying the **first** and **last** samples received, and their Laboratory Receipt Dates (LRDs).

NOTE: When more than one sample is received in the first or last SDG shipment, the "first" sample received would be the sample with the lowest sample number (considering both alpha and numeric designations); the "last" sample received would be the sample with the highest sample number (considering both alpha and numeric designations).

2.4.2 EPA field sample numbers are six digits in length and continuous (without spaces or hyphens). If the Contractor receives sample numbers of any other length, the Contractor shall contact SMO immediately. The original Sample Traffic Report/Chain of Custody Record page marked "Lab Copy for Return to SMO", with laboratory receipt information and signed with original Contractor signature, shall be submitted for each sample in the SDG.

2.4.3 If samples are received at the laboratory with multi-sample Traffic Reports/Chain of Custody Records, all the samples on one multi-sample Traffic Report/Chain of Custody Record may not necessarily be in the same SDG. In this instance, the Contractor shall make the appropriate number of photocopies of the Traffic Report/Chain of Custody Record, and submit one copy with each SDG Cover Sheet.

2.5 Sample Data Package

The Sample Data Package shall include data for analysis of all samples in one SDG, including field and analytical samples, blanks, spikes, duplicates, and Laboratory Control Samples (LCSs). The Sample Data Package shall be complete before submission, and shall be consecutively paginated (starting with page number one and ending with the number of all pages in the package). The Sample Data Package shall include the following:

2.5.1 Cover Documentation

2.5.1.1 Cover Page for the inorganic analyses Data Package shall include: laboratory name; laboratory code; contract number; Case number; SDG number; Non-Routine Analytical Service (NRAS) number (if appropriate); EPA sample numbers in alphanumeric order showing EPA sample numbers cross-referenced with laboratory Sample ID numbers; and completion of the questions on use of background and interelement corrections for the samples.

2.5.1.1.1 The Cover Page shall contain the following statement, <u>verbatim</u>: **"I certify that this Sample Data Package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy Sample Data Package and in the computer-readable data submitted on diskette (or via an alternate means of electronic transmission, if approved in advance by USEPA) has been authorized by the Laboratory Manager or the Manager's designee, as verified by**

the following signature." This statement shall be directly followed by the signature of the Laboratory Manager or designee with typed lines containing the signer's name and title, and the date of signature.

2.5.1.2 SDG Narrative. This document shall be clearly labeled "SDG Narrative" and shall contain: laboratory name, Case number, SDG number, contract number, and detailed documentation of any Quality Control (QC), sample, shipment, and/or analytical problems encountered in processing the samples reported in the Sample Data Package. The Contractor shall include any technical and administrative problems encountered and the resolution or corrective actions taken. This includes documenting the alternative technique used to determine cooler temperature if a temperature indicator bottle is not present in the cooler. The Contractor shall also provide, in the SDG Narrative, sufficient information, including equations or curves (at least one equation or curve per method), to allow the recalculation of sample results from raw instrument output. The Contractor shall also include a discussion of any flexibility Statement of Work (SOW) modification. This includes attaching a copy of the USEPA approved modification form to the SDG Narrative. Additionally the Contractor shall also identify and explain any differences which exist between the Form Is and supporting documentation provided in the data package and those previously provided as Preliminary Results.

2.5.1.3 Sample Log-In Sheet [Form DC-1]

2.5.1.4 Full Inorganics Complete SDG File (CSF) Inventory Sheet [Form DC-2]

2.5.1.5 Sample Traffic Reports/Chain of Custody Records

2.5.2 Sample Data

Sample data shall be submitted with the inorganic analysis data reporting forms for all samples in the SDG. Data should be arranged in increasing alphanumeric EPA sample number order, followed by the QC analyses data, quarterly and annual verification of method and instrument parameters forms, raw data, and copies of the digestion and distillation logs.

2.5.2.1 Inorganic Analysis Data Sheet [Form IA-IN and Form IB-IN]. Tabulated analytical results of the requested analytes shall be included. The validation and release of these results is authorized by a specific signed statement on the Cover Page. In the event that the laboratory cannot verify all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample(s) in the SDG Narrative.

2.5.2.1.1 Appropriate concentration units shall be specified and entered on Forms IA-IN and IB-IN. The quantitative values shall be reported in units of micrograms per Liter (UG/L) for water samples and milligrams per kilogram (MG/KG) for solid samples. (No other units are acceptable.) Results for solid samples shall be reported on a dry weight basis. Analytical results shall be reported to two significant figures if the result value is less than 10 and to three significant figures if the value is greater than or equal to 10. Results for percent solids shall be reported to one decimal place. The preceding discussion concerning significant numbers applies to Forms IA-

IN, IB-IN, and IX-IN only. For other forms, follow the instructions specific to those forms as discussed in this exhibit.

2.5.2.2 Quality Control (QC) Data

2.5.2.2.1 The QC summary for inorganic analysis shall contain the forms listed below.

NOTE: If more than one form is necessary, duplicate forms must be arranged in chronological order.

2.5.2.2.1.1 Initial and Continuing Calibration Verification [Form IIA-IN]

2.5.2.2.1.2 CRQL Check Standard [Form IIB-IN]

2.5.2.2.1.3 Blanks [Form III-IN]

2.5.2.2.1.4 ICP-AES Interference Check Sample [Form IVA-IN]

2.5.2.2.1.5 ICP-MS Interference Check Sample [Form IVB-IN]

2.5.2.2.1.6 Matrix Spike Sample Recovery [Form VA-IN]

2.5.2.2.1.7 Post-Digestion Spike Sample Recovery [Form VB-IN]

2.5.2.2.1.8 Duplicates [Form VI-IN]

2.5.2.2.1.9 Laboratory Control Sample [Form VII-IN]

2.5.2.2.1.10 ICP-AES and ICP-MS Serial Dilutions [Form VIII-IN]

2.5.2.2.1.11 Method Detection Limits (Annually) [Form IX-IN]

2.5.2.2.1.12 ICP-AES Interelement Correction Factors (Quarterly) [Form XA-IN]

2.5.2.2.1.13 ICP-AES Interelement Correction Factors (Quarterly) [Form XB-IN]

2.5.2.2.1.14 ICP-AES and ICP-MS Linear Ranges (Quarterly) [Form XI-IN]

2.5.2.2.1.15 Preparation Log [Form XII-IN]

2.5.2.2.1.16 Analysis Run Log [Form XIII-IN]

2.5.2.2.1.17 ICP-MS Tune [Form XIV-IN]

2.5.2.2.1.18 ICP-MS Internal Standards Relative Intensity Summary [Form XV-IN]

2.5.2.3 Raw Data

For each reported value, the Contractor shall include in the Sample Data Package all raw data used to obtain that value. This applies to all required QA/QC measurements, instrument standardization, as well as all sample analysis results. This statement does not apply to the quarterly and annual verification of method and instrument parameters submitted as a part of each Sample Data Package. When analysis of the ICP-AES or ICP-MS target analytes listed in Exhibit C of this SOW (or any subset or additional analytes) is requested, the raw data shall include, for

all samples, not only the results for the requested analyte(s), but also those for all the interferents (Exhibit D/ICP-AES, Table 1, or Exhibit D/ICP-MS, Section 7.2.4.4.1, as appropriate). The raw data shall also contain the results of any other analyte(s) which have been determined to interfere with the requested analytes(s).

2.5.2.3.1 Raw data shall contain all instrument readouts and data pertinent to the reconstruction of the analysis and results (e.g., Batch Sheets) used for the sample results. Each exposure or instrumental reading shall be provided, including those readouts that may fall below the Method Detection Limit (MDL). Raw data shall not be corrected for dilutions or volume adjustments. All Atomic Absorption (AA), Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES), and Inductively Coupled Plasma - Mass Spectrometer (ICP-MS) instruments shall provide a legible hardcopy of the direct real-time instrument readout (i.e., strip charts, printer tapes, etc.) or a printout of the unedited instrument data output file. A photocopy of the instrument's direct sequential readout shall be included. A hardcopy of the instrument's direct readout shall be included for cyanide if the instrumentation has the capability.

2.5.2.3.2 The order of raw data in the Sample Data Package for inorganic analyses shall be: ICP-AES, Graphite Furnace Atomic Absorption (GFAA), ICP-MS, Mercury, and Cyanide. All raw data shall include concentration units for ICP, and absorbances or concentration units for Mercury and Cyanide.

2.5.2.3.3 Corrections to the laboratory data reporting forms and raw data shall be made by drawing single lines through the errors and entering the correct information. Information shall not be obliterated or rendered unreadable. Corrections and additions to information shall be signed (or initialed) and dated.

2.5.2.3.4 Raw data shall be labeled with EPA sample numbers and appropriate codes, shown in Exhibit B, Table 2 - Codes for Labeling Data, following, to unequivocally identify:

- Calibration standards, including source and preparation date. Standard preparation logbooks can be submitted if they contain this information;
- Initial and Continuing Calibration Blanks (ICBs/CCBs) and Preparation Blanks (PBs);
- Initial and Continuing Calibration Verification (ICV/CCV) standards, Interference Check Samples (ICSs), serial dilution samples, Contract Required Quantitation Limit (CRQL) Check Standard (CRI), LCS, and post digestion spike;
- Diluted and undiluted samples (by EPA sample number) and all weights, dilutions, and volumes used to obtain the reported values (if the volumes, weights, and dilutions are consistent for all samples in a given SDG, a general statement outlining these parameters is sufficient);
- Duplicates;
- Spikes (indicating standard solutions used, final spike concentrations, and volumes involved). If spike information (source, concentration, volume) is consistent

for a given SDG, a general statement outlining these parameters is sufficient;

- Instrument used, any instrument adjustments, data corrections or other apparent anomalies on the measurement record, including all data voided or data not used to obtain reported values and a brief written explanation; and

- Time and date of each analysis. Instrument run logs can also be submitted if they contain time and date of analysis. If the instrument does not automatically provide times of analysis, these shall be manually entered on all raw data (e.g., ICV/CCV, blanks, and the CRQL Check Standard).

Table 2
Codes for Labeling Data[1,2]

Sample	XXXXXX
Sample Not Part of the SDG	ZZZZZZ
Duplicate	XXXXXXD
Matrix Spike	XXXXXXS
Serial Dilution	XXXXXXL
Analytical Spike/Post Digestion/Distillation Spike	XXXXXXA
Instrument Calibration Standards:	
ICP	S or S0 for blank standard
Atomic Absorption and Cyanide	S0, S10,...etc.
Initial Calibration Verification	ICV
Initial Calibration Blank	ICB
Continuing Calibration Verification	CCV
Continuing Calibration Blank	CCB
Interference Check Samples:	
Solution A	ICSA
Solution AB	ICSAB
CRQL Check Standard	CRI
Laboratory Control Samples:	
Aqueous (Water)	LCSW
Solid (Soil/Sediment)	LCSS
Preparation Blank (Water)	PBW
Preparation Blank (Soil)	PBS
Linear Range Analysis Standard	LRS
Baseline Correction	BASELINE
Reslope	RESLOPE
Cyanide Mid-Range Standard	MIDRANGE
ICP-MS Tune Check	TUNE

[1]The numeric suffix that follows the "S" suffix for the standards indicates the true value of the concentration of the standard in ug/L.

[2]ICP-AES and ICP-MS calibration standards usually consist of several analytes at different concentrations. Therefore, no numeric suffix can follow the ICP calibration standards unless all the analytes in the standard are prepared at the same concentrations. For instance, the blank for ICP shall be formatted "S0".

2.5.2.4 Digestion and Distillation Logs. The following logs shall be submitted as appropriate for each preparation procedure: digestion logs for ICP-AES, ICP-MS, mercury preparations, and cyanide. These logs shall include: (1) date; (2) sample weights and volumes, with initial sample weight/volume and final volume clearly indicated; (3) sufficient information to unequivocally identify which QC samples (i.e., LCS, PB) correspond to each batch digested; (4) comments describing any significant sample changes or reactions which occur during preparation shall be entered in the log and noted in the SDG Narrative; (5) indication of pH less than 2 or greater than 12, as applicable; and (6) identification of the sample preparer(s) [signature(s)].

2.6 Complete SDG File (CSF)

As specified in the Delivery Schedule, one CSF (including the original Sample Data Package) shall be delivered to the Region concurrently with the delivery of a copy of the Sample Data Package to SMO. Delivery to USEPA's designated recipient (e.g., QATS) is only required upon written request.

2.6.1 The CSF shall contain all original documents where possible. No photocopies of original documents shall be placed in the CSF unless the original data was initially written in a bound notebook, maintained by the Contractor, or the originals were previously submitted to USEPA with another Case/SDG in accordance with the requirements described in Exhibit F. The CSF shall contain all original documents and be numbered according to the specifications in Exhibit B, Sections 3 and 4, and Form DC-2.

2.6.2 The CSF shall consist of the following original documents in addition to the documents in the Sample Data Package.

NOTE: All Case-related documentation may be used or admitted as evidence in subsequent legal proceedings. Any other Case-specific documents generated after the CSF is sent to USEPA, as well as copies that are altered in any fashion, are also deliverables to USEPA. Send the original to the Region and a copy to SMO. Send to USEPA's designated recipient (e.g., QATS) only upon written request.

2.6.2.1 Original Sample Data Package

2.6.2.2 A completed and signed Full Inorganics Complete SDG File (CSF) Inventory Sheet [Form DC-2]

2.6.2.3 All original shipping documents, including, but not limited to, the following documents:

- USEPA Sample Traffic Reports/Chain of Custody Records
- Airbills (if an airbill is not received, include a hardcopy receipt requested from the shipping company or a printout of the shipping company's electronic tracking information); and
- Sample Tags (if present) sealed in plastic bags.

2.6.2.4 All original receiving documents, including, but not limited to, the following documents:

- Form DC-1;
- Other receiving forms or copies of receiving logbooks; and
- SDG Cover Sheet.

2.6.2.5 All original laboratory records of sample transfer, preparation, and analysis, including, but not limited to, the following documents:

- Original preparation and analysis forms or copies of preparation and analysis logbook pages; and
- Internal sample and sample digestate and distillate transfer Chain of Custody Records.

2.6.2.6 All other original SDG-specific documents in the possession of the laboratory, including, but not limited to, the following documents:

- Telephone contact logs;
- Copies of personal logbook pages;
- All handwritten SDG-specific notes; and
- Any other SDG-specific documents not covered by the above.

2.6.3 If the Contractor does submit SDG-specific documents to USEPA after submission of the CSF, the documents shall be numbered as an addendum to the CSF and a revised Form DC-2 shall be submitted; or the documents shall be numbered as a new CSF and a new Form DC-2 shall be submitted to the Region only.

2.6.4 The Contractor shall retain a legible electronic (PDF) or hard copy of the CSF for 365 days after submission of the reconciled data package. After this time, the Contractor may dispose of the package.

2.7 Data in Computer-Readable Format

The Contractor shall provide a computer-readable copy for all samples in the SDG, as specified in Exhibit H, and delivered as specified in Exhibit B, Section 1.1. Computer-readable data deliverables shall be submitted on DOS formatted 3.5-inch high density 1.44 MB diskette(s) (or via an alternate means of electronic transmission, if approved in advance by USEPA).

2.7.1 When submitted, diskette(s) shall be packaged and shipped in such a manner that the diskette(s) cannot be bent or folded and will not be exposed to extreme heat/cold or any type of electromagnetic radiation. The diskette(s) shall be included in the same shipment as the hardcopy data, and, at a minimum, be enclosed in a diskette mailer.

2.7.2 The data shall be recorded in the file format and adhere to the file, record, and field specifications listed in Exhibit H, "Data Dictionary and Format for Data Deliverables in Computer-Readable Format".

2.8 Results of the Intercomparison and Performance Evaluation (PE) Sample Analyses

Tabulation of analytical results for intercomparison/PE sample analyses includes all requirements specified in Exhibit B, Sections 2.5 and 2.7.

2.9 Preliminary Results

The Form Is data results (including all appropriate qualifiers and flags) shall be submitted for all samples in one SDG of a Case. Sample analysis shall follow all requirements stipulated in Exhibit D. The Contractor shall clearly identify the Preliminary Results by labeling each Form I as "Preliminary Results" under the form title (e.g., under Inorganic Analysis Data Sheet). The Contractor shall also include a disclaimer in the "Comments" field on all Form Is stating that the "Data results contained on this Form I are for scanning purposes only, and may not have been validated for CLP criteria." Sample Traffic Reports/Chain of Custody Records and SDG Cover Sheets shall be submitted with the Preliminary Results.

2.9.1 The Contractor shall submit the Cover Page following the specifications in Exhibit B, Sections 2.5.1 and 3.4.1. The Cover Page shall be clearly labeled to indicate that the data being reported are Preliminary Results. The Cover Page shall contain the following statement, verbatim: **"I certify that these Preliminary Results are in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package has been authorized by the Laboratory Manager or the Manager's designee, as verified by the following signature."** This statement shall be directly followed by the signature of the Laboratory Manager or designee with typed lines containing the signer's name and title, and the date of signature.

2.10 Quarterly Verification of Linear Ranges and Interelement Correction Factors and Annual Verification of MDLs

The Contractor shall perform and report quarterly verification of instrument linear range and annual verification of MDLs by the methods specified in Exhibit D for each instrument used under this contract. The Contractor shall also perform and report quarterly ICP-AES interelement correction factors (including method of determination), wavelengths used, and integration times. Forms reporting results for quarterly and annual verification of method and instrument parameters for the current quarter and year shall be submitted in each Sample Data Package, using Inorganic Forms IX, XA, XB, and XI. Submission of the quarterly and annual verification of method and instrument parameters shall include the raw data used to determine the values reported.

2.11 Electronic Instrument Data

The Contractor shall adhere to the requirements in Exhibit E.

2.12 Corrective Action Procedures

If the Contractor fails to adhere to the requirements detailed in this SOW, the Contractor will be in noncompliance with the contract and may be subjected to sanctions as described in the contract.

3.0 FORM INSTRUCTIONS

3.1 Introduction

This section contains specific instructions for the completion of all required Inorganic Data Reporting Forms.

3.2 General Information

Values shall be reported on the hardcopy forms according to the respective form instructions in this section. Each form submitted shall be filled out completely for all analytes before proceeding to the next form of the same type. Do not submit multiple forms if the information on those forms can be submitted on one form.

3.2.1 The data reporting forms discussed in Exhibit B, Section 3.4, and presented in Exhibit B, Section 4.0, have been designed in conjunction with the computer-readable data formats specified in Exhibit H, "Data Dictionary and Format for Data Deliverables in Computer-Readable Format". The specific length of each variable for computer-readable data transmission purposes is given in Exhibit H. Information entered on these forms shall **not** exceed the size of the field given on the form, including such laboratory-generated items as "Lab Name" and "Lab Sample ID".

NOTE: On the hardcopy forms, the space provided for entries is greater in some instances than the length prescribed for the variable as written to the electronic deliverable (see Exhibit H). Greater space is provided on the hardcopy forms for the sake of visual clarity.

3.2.2 All characters which appear on the data reporting forms presented in the contract shall be reproduced by the Contractor when submitting data, and the format of the forms submitted shall be identical to that shown in the contract. No information may be added, deleted, or moved from its specified position without prior written approval of the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) or the USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB) Inorganic Program Manager (ASB PM). The names of various fields and analytes (i.e., "Lab Code", "Aluminum") shall appear as they do on the forms in the contract, including the options specified in the form (i.e., "Matrix (soil/water):" shall appear, not just "Matrix").

3.2.3 Alphabetic entries made onto the forms by the Contractor shall be in ALL UPPERCASE letters (i.e., "LOW", not "Low" or "low"). If an entry does not fill the entire blank space provided on the form, null characters shall be used to remove the remaining underscores that comprise the blank line (see Exhibit H for additional instructions). However, do **not** remove the underscores or vertical bar characters that delineate "boxes" on the forms.

3.3 Header Information

Six pieces of information are common to the header sections of each data reporting form. These are: Laboratory Name, Contract, Laboratory Code, Case number, Non-Routine Analytical Services (NRAS) number, and Sample Delivery Group (SDG) number. Except as noted for NRAS number, this information shall be entered on every form and shall match on all forms.

3.3.1 Laboratory Name. The "Lab Name" shall be the name chosen by the Contractor to identify the laboratory. It may not exceed 25 characters.

3.3.2 Contract. The "Contract" is the number of the USEPA contract under which the analyses were performed.

3.3.3 Laboratory Code. The "Lab Code" is an alphabetic abbreviation of up to six characters, assigned by USEPA, to identify the laboratory and aid in data processing. This laboratory code will be assigned by USEPA at the time a contract is awarded. The laboratory code shall not be modified by the Contractor, except at the direction of USEPA. If a change of name or ownership occurs at the laboratory, the laboratory code will remain the same until the Contractor is directed by USEPA to use another laboratory code.

3.3.4 Case Number. The "Case No." is the SMO-assigned Case number (to five characters) associated with the sample, and reported on the Traffic Report/Chain of Custody Record.

3.3.5 NRAS Number. The "NRAS No." is the USEPA assigned number for analyses performed under Non-Routine Analytical Services (NRAS). If samples are to be analyzed under NRAS only, and reported on these forms, then enter the NRAS number and leave the Case number blank. If samples are analyzed according to the Routine Analytical Services (RAS) protocol and have additional NRAS requirements, list both the Case number and NRAS number on all forms. If the analyses have no NRAS requirements, leave the "NRAS No." field blank.

3.3.6 SDG Number. The "SDG No." is the Sample Delivery Group (SDG) number. The SDG number is the EPA sample number of the first sample received in the SDG, except when this would cause duplication. When several samples are received together in the first SDG shipment, the SDG number shall be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG. If fractions of the same field samples are scheduled under different turnaround times, thus creating separate SDGs containing the same sample numbers, a different sample number shall be utilized in the assignment of the SDG number for each SDG. If a situation arises where there are an insufficient number of samples for assignment of SDG numbers, the contractor shall contact SMO for the assignment of a SDG number.

3.3.7 Sample Number. The "EPA Sample No." appears either in the header information of the form or as the left column of a table summarizing data from a number of samples. When an EPA sample number is entered in the triple-spaced box in the upper right-hand corner of a form, it shall be centered on the middle line of the three lines that form the box.

3.3.7.1 **All** samples, matrix spikes, post digestion/distillation spikes, duplicates, and serial dilutions shall be identified with an EPA sample number. For samples, an EPA sample number is the unique identifying number given in the Traffic Report/Chain of Custody Record that accompanied that sample. In order to facilitate data assessment, the sample suffixes listed in Exhibit B, Table 2 - Codes for Labeling Data, must be used.

3.3.8 Other Common Fields. Other pieces of information are common to many of the data reporting forms. These include Matrix and Level.

- For "Matrix", enter "SOIL" for soil/sediment samples and "WATER" for water samples.

  NOTE: The matrix must be spelled out. Abbreviations such as "S" or "W" shall **not** be used.

- For "Level", enter the determination of concentration level. Enter as "LOW" or "MED", **not** "L" or "M".

3.3.9 Rounding Rule. For rounding off numbers to the appropriate level of precision, observe the following common rules. If the figure following those to be retained is greater than or equal to 5, the absolute value of the result is to be rounded up; otherwise the absolute value of the result is rounded down. For example, -0.4365 rounds to -0.437 and -2.3564 rounds to -2.356. Also see "Rounding Rules" in Exhibit G.

3.3.9.1 Before evaluating a number for being in control or out of control of a certain limit [other than the Contract Required Quantitation Limit (CRQL)], the number evaluated shall be rounded using the above rounding rules to the significance reported for that limit. For example, the control limit for an Initial Calibration Verification is plus or minus 10% of the true value. Then a calculated percent recovery of 110.46 shall be reported on Form IIA-IN as 110, which is within the control limits of 90-110. On the other hand, a calculated percent recovery of 110.50 shall be reported on Form IIA-IN as 111, which is not within the 90-110 percent control limits.

NOTE: All results shall be transcribed to Inorganic Forms IIA-IN through XV-IN from the raw data to the specified number of decimal places that are described in Exhibits B and H. The raw data result is to be rounded only when the number of figures in the raw data result exceeds the maximum number of figures specified for that result entry for that form. If there are not enough figures in the raw data result to enter in the specified space for that result, then zeros shall be used for decimal places to the specified number of reporting decimals for that result for a specific form. The following examples are provided:

Raw Data Result	Specified Format	Correct Entry on Form
95.99653	5.4 (to four decimal places)	95.9965
95.99653	5.3 (to three decimal places)	95.997
95.99653	5.2 (to two decimal places)	96.00
95.996	5.4 (to four decimal places)	95.9960
95.9	5.4 (to four decimal places)	95.9000

3.4 Inorganic Forms

3.4.1 Cover Page - [COVER PAGE]

3.4.1.1 Purpose. This form is used to list all samples analyzed within an SDG and provide certain analytical information and general comments. It is also the document that is signed by the Laboratory Manager to authorize and release all data and deliverables associated with the SDG.

3.4.1.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.1.2.1 For samples analyzed using this Statement of Work (SOW), enter "ILM05.3" for the SOW Number.

3.4.1.2.2 Enter an EPA sample number including spikes and duplicates (to seven spaces) of every sample analyzed within the SDG. Spikes shall contain an "S" suffix and duplicates a "D" suffix. These sample numbers shall be listed on the form in ascending alphanumeric order. Thus, if MAB123 is the lowest (considering both alpha and numeric characters) EPA sample number within the SDG, it would be entered in the first EPA sample number field. Samples would be listed below it, in ascending sequence - MAB124, MAB125, MAC111, MA1111, MA1111D, etc.

3.4.1.2.3 A maximum of 20 field sample numbers (excluding PE samples) can be entered on this form. Submit additional Cover Pages, as appropriate, if the total number of samples, duplicates, and spikes in the SDG is greater than 22.

3.4.1.2.4 A Laboratory Sample ID (to ten spaces) may be entered for each EPA sample number. If a Laboratory Sample ID is entered, it shall be entered identically (for each EPA sample number) on all associated data.

3.4.1.2.5 Enter "YES" or "NO" in answer to each of the two questions concerning Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) corrections. Each question shall be explicitly answered with a "YES" or a "NO". The third question shall be answered with a "YES" or "NO" if the answer to the second question is "YES". It shall be left blank if the answer to the second question is "NO".

3.4.1.2.6 Under "Comments", enter any statements relevant to the analyses performed under the SDG as a whole.

3.4.1.2.7 Each Cover Page shall be signed and dated, in original, by the Laboratory Manager or the Manager's designee to authorize the release and verify the contents of all data and deliverables associated with an SDG.

3.4.2 Inorganic Analysis Data Sheet [Forms IA-IN and IB-IN]

3.4.2.1 Purpose. These forms are used to tabulate and report sample analysis results for inorganic target analytes (see Exhibit C).

3.4.2.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.2.2.1 "Date Received" is the date (formatted MM/DD/YYYY) of sample receipt at the laboratory, as recorded on the Traffic Report/Chain of Custody Record [i.e., the Validated Time of Sample Receipt (VTSR)].

3.4.2.2.2 "% Solids" is the percent of solids on a weight-by-weight basis in the sample which is determined by drying the sample as specified in Exhibit D - Introduction to Analytical Methods, Section 1.6. Report percent solids to one decimal place (i.e.,

5.3%). If the percent solids is not required because the sample is fully aqueous, or is less than 1% solid, then enter "0.0".

3.4.2.2.3 Enter the appropriate concentration units (UG/L for water or MG/KG dry weight for soil). Entering "MG/KG" means "mg/kg dry weight" on this form.

3.4.2.2.4 Under the column labeled "Concentration", enter for each analyte, the value of the result [if the concentration is greater than or equal to the Method Detection Limit (MDL)] corrected for any dilutions; or, enter the CRQL for the analyte, adjusted if necessary and corrected for any dilutions, if the concentration is less than the MDL. The concentration result shall be reported to two significant figures if the result is less than 10 or three significant figures if the value is greater than or equal to 10.

3.4.2.2.5 Under the columns labeled "C", "Q", and "M", enter result qualifiers as identified below. If additional qualifiers are used, their explicit definitions shall be included on the Cover Page in the "Comments" section.

Forms IA-IN and IB-IN include fields for three types of result qualifiers. These qualifiers shall be completed as follows:

3.4.2.2.5.1 C (Concentration) Qualifier. Enter "J" if the reported value was obtained from a reading that was less than the CRQL but greater than or equal to the MDL. If the reading was less than the MDL, a "U" shall be entered.

The MDL obtained for a given preparation method, analysis method, and instrument shall be used for qualification of the results for samples associated with that preparation method, analysis method, and instrument. Serial dilution and post-digestion spike results shall be qualified using the MDL and CRQL values utilized for the corresponding field sample.

All three values (i.e., the instrument reading, CRQL, and MDL) shall be converted to the same units prior to determining the appropriate C (Concentration) Qualifier.

NOTE: The water CRQL (in ug/L) and the MDL obtained from direct analysis (Preparation Method "NP1") for a given analysis method and instrument shall be used to qualify the results of instrument QC standards that are not taken through a preparation procedure (e.g., ICB, CCB, and CRI for ICP-AES].

3.4.2.2.5.2 Q Qualifier. Specified entries and their meanings are as follows:

E: The reported value is estimated due to the presence of interference. An explanatory note shall be included under "Comments" on the Cover Page (if the problem applies to all samples), or on the specific Form IA-IN or Form IB-IN (if it is an isolated problem).

N: Spiked sample recovery not within control limits.

*: Duplicate analysis not within control limits.

D: The reported value is from a dilution.

3.4.2.2.5.3 M (Analysis Method) Qualifier. Specified entries and their meanings are as follows:

P: ICP-AES
MS: ICP-MS
CV: Manual Cold Vapor Atomic Absorption (AA)
AV: Automated Cold Vapor AA
AS: Semi-Automated Spectrophotometric
C: Manual Spectrophotometric
" ": Where no data have been entered
NR: If the analyte is not required to be analyzed

3.4.2.2.6 A brief physical description of the sample, both before and after digestion, shall be reported in the fields for color (before and after), clarity (before and after), texture, and artifacts. For water samples, report color and clarity. For soil samples, report color, texture, and artifacts. The following descriptive terms are recommended:

- Color - red, blue, yellow, green, orange, violet, white, colorless, brown, grey, and black;
- Clarity - clear, cloudy, and opaque; and
- Texture - fine (powdery), medium (sand), and coarse (large crystals or rocks).

If artifacts are present, enter "YES" in the artifacts field and describe the artifacts in the "Comments" field. If artifacts are not present, leave this field blank. Note any significant changes that occur during sample preparation (i.e., emulsion formation) in the "Comments" field. Enter any sample-specific comments concerning the analyte results in the "Comments" field. Also document raw instrument results that are less than minus two times the CRQL (-2xCRQL) in the "Comments" field and in the Sample Delivery Group (SDG) Narrative.

3.4.2.2.7 If more than two additional analytes were requested, submit Form IB-IN as appropriate.

3.4.3 Initial (ICV) and Continuing Calibration Verification (CCV) [Form IIA-IN]

3.4.3.1 Purpose. This form is used to report analyte recoveries from calibration verification solutions.

3.4.3.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.3.2.1 Enter the ICV Source (12 characters maximum) and the CCV Source (12 characters maximum). Enter sufficient information in the available 12 spaces to identify the manufacturer and the solution used.

Use additional Form(s) IIA-IN if more calibration verification sources were used.

3.4.3.2.2 Under "Initial Calibration Verification True", enter the value [in micrograms per Liter (ug/L), to one decimal place] of the concentration of each analyte in the ICV Solution.

3.4.3.2.3 Under "Initial Calibration Verification Found", enter the most recent value (in ug/L, to two decimal places), of the concentration of each analyte measured in the ICV Solution.

3.4.3.2.4 Under "Initial Calibration Verification %R", enter the value (to the nearest whole number) of the percent recovery computed according to the following equation:

EQ. 1 ICV Percent Recovery

$$\%R = \frac{\text{Found(I CV)}}{\text{True(ICV)}} x100$$

WHERE, "True(ICV)" is the true concentration of the analyte in the ICV Solution and "Found(ICV)" is the found concentration of the analyte in the ICV Solution.

The values used in EQ. 1 for "True(ICV)" and "Found(ICV)" shall be exactly those reported on this form.

3.4.3.2.5 Under "Continuing Calibration Verification True", enter the value (in ug/L, to one decimal place) of the concentration of each analyte in the CCV Solution.

3.4.3.2.6 Under "Continuing Calibration Verification Found", enter the value (in ug/L, to two decimal places) of the concentration of each analyte measured in the CCV Solution.

NOTE: The form contains two "Continuing Calibration Verification Found" columns. The column to the left shall contain values for the first CCV, and the column to the right shall contain values for the second CCV.

3.4.3.2.7 If more than one Form IIA-IN is required to report multiple CCVs, then the column to the left on the second form shall contain values for the third CCV, the column to the right shall contain values for the fourth CCV, and so on.

3.4.3.2.8 Under "Continuing Calibration Verification %R", enter the value (to the nearest whole number) of the percent recovery computed according to the following equation:

EQ. 2 CCV Percent Recovery

$$\%R = \frac{\text{Found(CCV)}}{\text{True(CCV)}} x100$$

WHERE, "True(CCV)" is the true concentration of each analyte, and "Found(CCV)" is the found concentration of the analyte in the CCV Solution.

The values used in EQ. 2 for "True(CCV)" and "Found(CCV)" shall be exactly those reported on this form.

NOTE: The form contains two "Continuing Calibration Verification %R" columns. Entries to these columns shall follow the sequence detailed above for entries to the "Continuing Calibration Verification Found" columns.

3.4.3.2.9 Under "M", enter the method used or "NR", as explained in Exhibit B, Section 3.4.2.2.5.3.

3.4.3.2.10 If more than one wavelength/mass is used to analyze an analyte, submit additional Form(s) IIA-IN as appropriate.

3.4.3.2.11 The order of reporting ICVs and CCVs for each analyte shall follow the chronological order in which the standards were run. Start with the first Form IIA-IN and move from the left to the right, continuing to the following Form IIA-INs as appropriate. For instance, the first ICV for all analytes shall be reported on the first Form IIA-IN. In a run where three CCVs were analyzed, the first CCV shall be reported in the left CCV column on the first Form IIA-IN and the second CCV shall be reported in the right column of the same form. The third CCV shall be reported in the left CCV column of the second Form IIA-IN. On the second Form IIA-IN, the ICV column and the right CCV column shall be left empty in this example. In the previous example, if a second run for an analyte was needed, the ICV of that run shall be reported on a third Form IIA-IN and the CCVs follow in the same fashion as explained before. In the case where two wavelengths are used for an analyte, all ICV and CCV results of one wavelength from all runs shall be reported before proceeding to report the results of the second wavelength used.

3.4.4 CRQL Check Standard [Form IIB-IN]

3.4.4.1 Purpose. This form is used to report analyte recoveries from analyses of the CRQL Check Standards (CRIs).

3.4.4.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.4.2.1 Enter the CRQL Check Standard Source (12 characters maximum) as explained in Exhibit B, Section 3.4.3.2.1.

3.4.4.2.2 Under "CRQL Check Standard True", enter the value (in ug/L, to one decimal place) of the concentration of each analyte in the CRQL Check Standard that was analyzed for analytical samples associated with the SDG.

3.4.4.2.3 Under "CRQL Check Standard Initial Found", enter the result (in ug/L, to two decimal places) measured in the CRQL Check Standard analyzed at the beginning of the run. For each analyte, enter the value of the result (if the concentration is greater than or equal to the MDL); or enter the CRQL of the analyte if the concentration is less than the MDL. If applicable, enter the concentration qualifier "J" or "U" after the concentration (e.g., 1.96J for Lead), as specified in Exhibit B, Section 3.4.2.2.5.1.

3.4.4.2.4 Under "CRQL Check Standard Initial %R", enter the value (to the nearest whole number) of the percent recovery computed according to the following equation:

EQ. 3 CRQL Check Standard Initial Percent Recovery

$$\%R = \frac{\text{CRQL Check Standard Initial Found}}{\text{CRQL Check Standard True}} x100$$

3.4.4.2.5 Under "CRQL Check Standard Final Found", enter the results (in ug/L, to two decimal places) measured in the CRQL Check Standard(s) analyzed after the beginning of the run. For each analyte, enter the value of the result (if the concentration is greater than or equal to the MDL); or enter the CRQL of the analyte if the concentration is less than the MDL. If applicable, enter the concentration qualifier "J" or "U" after the concentration (e.g., 1.96J for Lead), as specified in Exhibit B, Section 3.4.2.2.5.1.

3.4.4.2.6 Under "CRQL Check Standard Final %R", enter the value (to the nearest whole number) of the percent recovery computed according to the following equation:

EQ. 4 CRQL Check Standard Final Percent Recovery

$$\%R = \frac{\text{CRQL Check Standard Final Found}}{\text{CRQL Check Standard True}} x100$$

3.4.4.2.7 All percent recovery values reported in EQs. 3 and 4 shall be calculated using the exact true and found values reported on this form. A value of zero shall be used in calculations if the analyte value is less than the MDL.

NOTE: For every initial solution reported there must be a final one. However, the opposite is <u>not</u> true. If a CRQL Check Standard was required to be analyzed in the middle of a run, it shall be reported in the "Final Found" section of this form.

3.4.4.2.8 If more CRI analyses were required or analyses were performed using more than one wavelength per analyte, submit additional Form(s) IIB-IN as appropriate.

3.4.4.2.9 The order of reporting CRIs for each analyte shall follow the chronological order in which the standards were run starting with the first Form IIB-IN and continuing to the following Forms IIB-IN as appropriate. When multiple wavelengths are used for one analyte, all the results of one wavelength shall be reported before proceeding to the next wavelength.

3.4.5 Blanks [Form III-IN]

3.4.5.1 Purpose. This form is used to report analyte concentrations found in the Initial Calibration Blank (ICB), Continuing Calibration Blanks (CCB), and the Preparation Blank (PB).

3.4.5.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.5.2.1 Enter "SOIL" or "WATER" as appropriate as the matrix of the PB. No abbreviations or other matrix descriptors may be used.

3.4.5.2.2 According to the matrix specified for the PB, enter the PB concentration units as "UG/L" for water or "MG/KG" for soil.

3.4.5.2.3 Under "Initial Calibration Blank", enter the concentration (in ug/L, to three decimal places) of each analyte in the most recent ICB, as described in Exhibit B, Section 3.4.5.2.8, below.

3.4.5.2.4 For each calibration blank associated with a given method and instrument, enter "J" under the "C" qualifier field on Form III-IN if the absolute value of the analyte concentration is less than the CRQL for water but greater than or equal to the MDL that was obtained from direct analysis (Preparation Method "NP1") using that method and instrument.

For prepared calibration blanks (e.g., mercury), the CRQL for water and the MDL for the preparation method, analysis, and instrument shall be used.

Enter "U" if the absolute value of the analyte in the blank is less than the MDL obtained from direct analysis or the preparation method.

3.4.5.2.5 Under "Continuing Calibration Blank 1", enter the concentration (in ug/L, to three decimal places) of each analyte detected in the first required CCB analyzed after the ICB, as described in Exhibit B, Section 3.4.5.2.8, below. Enter any appropriate qualifier, as explained for the "Initial Calibration Blank", to the "C" qualifier column immediately following the "Continuing Calibration Blank 1" column.

3.4.5.2.6 If up to three CCBs were analyzed, complete the columns labeled "2" and "3" in accordance with the instructions for the "Continuing Calibration Blank 1" column. If more than three CCBs were analyzed, then complete additional Form(s) III-IN as appropriate.

3.4.5.2.7 Under "Preparation Blank", enter the concentration in ug/L (to three decimal places) for a water blank, or mg/kg (to three decimal places) for a soil blank, of each analyte in the PB, as described in Exhibit B, Section 3.4.5.2.8, below. Evaluate the absolute value of the analyte concentration to determine the appropriate concentration qualifier, as explained in Exhibit B, Section 3.4.2.2.5.1, and enter the qualifier in the "C" column immediately following the "Preparation Blank" column.

3.4.5.2.8 For all blanks, enter the concentration (positive or negative) for each analyte, if the absolute value of the concentration is greater than or equal to the appropriate MDL. Enter the CRQL value for the analyte, if the absolute value of the concentration is less than the appropriate MDL.

For example, arsenic has a MDL of 3 ug/L for Preparation Method "NP1" [CRQL for arsenic is 10 ug/L (water)]. Therefore, a CCB instrument reading of -4.2485 ug/L will be reported as -4.249J; a CCB instrument reading of -2.4356 ug/L will be reported as 10.000U; a CCB instrument reading of 4.3586 ug/L will be reported as 4.359J; and a CCB instrument reading of 2.1584 ug/L will be reported as 10.000U.

3.4.5.2.9 Under "M", enter the method used, as explained in Exhibit B, Section 3.4.2.2.5.3.

3.4.5.2.10 If more than one wavelength/mass is used to analyze an analyte, submit additional Form(s) III-IN as appropriate.

3.4.5.2.11 The order of reporting ICBs and CCBs for each analyte shall follow the chronological order in which the blanks were run starting with the first Form III-IN and moving from left to right and continuing to additional Forms III-IN. When multiple wavelengths are used for the analysis of one analyte, all the results of one wavelength shall be reported before proceeding to the next wavelength.

3.4.6 ICP-AES and ICP-MS Interference Check Sample (ICS) [Forms IVA-IN and IVB-IN]

3.4.6.1 Purpose. These forms are used to report ICS results for each ICP-AES or ICP-MS instrument used in SDG analyses.

3.4.6.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions. The instructions for Forms IVA-IN and IVB-IN are identical except where specified.

3.4.6.2.1 For "ICP Instrument ID", enter an identifier that uniquely identifies a specific instrument within the Contractor laboratory. No two ICP instruments within a laboratory may have the same ICP Instrument ID.

3.4.6.2.2 Enter "ICS Source" (12 characters maximum) as explained in Exhibit B, Section 3.4.3.2.1. For USEPA solutions, include in the source name a number identifying it (e.g., EPA-LV87).

3.4.6.2.3 Under "True Sol. A", enter the true concentration (in ug/L, to two significant figures if the value is less than 10 and three significant figures if the value is greater than or equal to 10) of each analyte present in Solution A. Enter "0" for each analyte with no specified true value in Solution A.

3.4.6.2.4 Under "True Sol. AB", enter the true concentration (in ug/L, to two significant figures if the value is less than 10 and three significant figures if the value is greater than or equal to 10) of each analyte present in Solution AB. Enter "0" for each analyte with no specified true value in Solution AB.

3.4.6.2.5 Under "Initial Found Sol. A" on Form IVA-IN (ICP-AES), and "Found Sol. A" on Form IVB-IN (ICP-MS), enter the concentration (positive, negative, or zero, in ug/L, to two significant figures if the value is less than 10 and three significant figures if the value is greater than or equal to 10). Enter the concentration of each analyte and interferent for ICP-AES and of each analyte for ICP-MS in the initial analysis of Solution A as required in Exhibit D.

3.4.6.2.6 Under "Initial Found Sol. A %R" on Form IVA-IN (ICP-AES), and "Found Sol. A %R" on Form IVB-IN (ICP-MS), enter the value (to the nearest whole number) of the percent recovery computed for true Solution A greater than zero according to the following equation:

EQ. 5 Initial Found Sol. A Percent Recovery

$$\%R = \frac{\text{Initial Found Solution A}}{\text{True Found Solution A}} x100$$

Leave the field blank if "True Solution A" equals zero.

3.4.6.2.7 Under "Initial Found Sol. AB" on Form IVA-IN (ICP-AES), and "Found Sol. AB" on Form IVB-IN (ICP-MS), enter the concentration (positive, negative, or zero, in ug/L, to two significant figures if the value is less than 10 and three significant figures if the value is greater than or equal to 10) of each analyte and interferent for ICP-AES and of each analyte for ICP-MS in the initial analysis of Solution AB as required in Exhibit D.

3.4.6.2.8 Under "Initial Found Sol. AB %R" on Form IVA-IN (ICP-AES), and "Found Sol. AB %R" on Form IVB-IN (ICP-MS), enter the value (to the nearest whole number) of the percent recovery computed for True Solution AB greater than zero according to the following equation:

EQ. 6 Initial Found Sol. AB Percent Recovery

$$\%R = \frac{\text{Initial Found Solution A}}{\text{True Solution A}} x100$$

Leave the field blank if "True Solution AB" equals zero.

3.4.6.2.9 Under "Final Found Sol. A", enter the concentration (positive, negative, or zero, in ug/L, to two significant figures if the value is less than 10 and three significant figures if the value is greater than or equal to 10) of each analyte and interferent for ICP-AES in the final analysis of Solution A as required in Exhibit D. ICP-MS analysis (Form IVB-IN) does not require a final analysis.

3.4.6.2.10 Under "Final Found Sol. A %R" enter the value (to the nearest whole number) of the percent recovery computed for true Solution A greater than zero according to the following equation:

EQ. 7 Final Found Sol. A Percent Recovery

$$\%R = \frac{\text{Final Found Solution A}}{\text{True Solution A}} x100$$

Leave the field blank if "True Solution A" equals zero.

3.4.6.2.11 Under "Final Found Sol. AB", enter the concentration (positive, negative, or zero, in ug/L, to two significant figures if the value is less than 10 and three significant figures if the value is greater than or equal to 10) of each analyte and interferent for ICP-AES in the final analysis of Solution AB as required in Exhibit D. ICP-MS analysis (Form IVB-IN) does not require a final analysis.

3.4.6.2.12 For all found values of Solutions A and AB, enter the concentration (positive, negative, or zero) of each analyte and interferent at each wavelength used for analysis by ICP.

3.4.6.2.13 Under "Final Found Sol. AB %R", enter the value (to the nearest whole number) of the percent recovery computed for true Solution AB greater than zero according to the following equation:

EQ. 8 Final Found Sol. AB Percent Recovery

$$\%R = \frac{\text{Final Found Solution AB}}{\text{True Solution AB}} x100$$

Leave the field empty if "True Solution AB" equals zero.

All percent recovery values reported shall be calculated using the exact true and found values reported on this form.

NOTE: For ICP-AES (Form IVA-IN), for every initial solution reported there must be a final solution reported. However, the opposite is not true. If an ICS was required to be analyzed in the middle of a run, it shall be reported in the "Final Found" section of this form.

3.4.6.2.14 If more ICS analyses were required, submit additional Form(s) IVA-IN and/or IVB-IN as appropriate.

3.4.6.2.15 The order of reporting ICSs for each analyte shall follow the chronological order in which the standards were run, starting with the first Form IVA-IN and/or IVB-IN and continuing to the following Forms IV-IN as appropriate. When multiple wavelengths/masses are used for one analyte, all the results of one wavelength/mass shall be reported before proceeding to the next wavelength/mass.

3.4.7 Matrix Spike Sample Recovery [Form VA-IN]

3.4.7.1 Purpose. This form is used to report results for the pre-digest spike.

3.4.7.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.7.2.1 Indicate the appropriate matrix, level, and concentration units (ug/L for water and mg/kg dry weight for soil) as explained in Exhibit B, Sections 2.5.2.1.1 and 3.3.8.

3.4.7.2.2 For "% Solids for Sample", enter the percent solids (see Exhibit B, Section 3.4.2.2.2) for the original sample of EPA sample number reported on the form. Note that this number must equal the one reported on Form IA-IN for that sample.

3.4.7.2.3 In the "EPA Sample No." box, enter an EPA sample number (7 places maximum) of the sample from which the spike results on this form were obtained. The number shall be centered in the box.

3.4.7.2.4 Under "Control Limit %R", enter "75-125" if the sample result is less than or equal to four times the spike added value. If

the sample result is greater than four times the Spike Added (SA) value, leave this field empty.

3.4.7.2.5 Under "Spiked Sample Result (SSR)", enter the measured value (to four decimal places), in appropriate units, for each relevant analyte in the matrix spike sample. Enter the value of the result (if the concentration is greater than or equal to the MDL) corrected for any dilutions; or enter the CRQL for the analyte, adjusted if necessary and corrected for any dilutions if the concentration is less than the MDL. Enter any appropriate concentration qualifier, as explained in Exhibit B, Section 3.4.2.2.5.1, to the "C" qualifier column immediately following the "Spiked Sample Result (SSR)" column.

3.4.7.2.6 Under "Sample Result (SR)", enter the measured value (to four decimal places) for each required analyte in the sample (reported in "EPA Sample No." box) on which the matrix spike was performed. Enter the value of the result (if the concentration is greater than or equal to the MDL) corrected for any dilutions; or enter the CRQL for the analyte, adjusted if necessary and corrected for any dilutions, if the concentration is less than the MDL. Enter any appropriate concentration qualifier, as explained in Exhibit B, Section 3.4.2.2.5.1, to the "C" qualifier column immediately following the "Sample Result (SR)" column.

3.4.7.2.7 Under "Spike Added (SA)", enter the value (to two decimal places) for the concentration of each analyte added to the sample. The same concentration units shall be used for "SSR", "SR", and "SA". If the "Spike Added" concentration is specified in the contract, the value added and reported shall be the specific concentration in appropriate units, corrected for spiked sample weight and percent solids (soils) or spiked sample volume (waters).

3.4.7.2.8 Under "%R", enter the value (to the nearest whole number) of the percent recovery for all spiked analytes computed according to the following equation:

EQ. 9 Spike Percent Recovery

$$\%R = \frac{SSR - SR}{SA} x100$$

Percent recovery shall be reported, whether it is negative, positive or zero.

The values for "SSR", "SR", and "SA" must be exactly those reported on this form. A value of zero shall be used in calculations for "SSR" or "SR" if the analyte value is less than the MDL.

3.4.7.2.9 Under "Q", enter "N" if the Spike Recovery (%R) is out of the control limits (75-125) and the Sample Result (SR) is less than or equal to four times the SA.

3.4.7.2.10 Under "M", enter the method used (as explained in Exhibit B, Section 3.4.2.2.5.3) or enter "NR" if the analyte is not required in the spike.

3.4.7.2.11 If different samples were used for spike sample analysis of different analytes, additional Form(s) VA-IN shall be submitted for each sample as appropriate.

3.4.8 Post-Digestion Spike Sample Recovery [Form VB-IN]

3.4.8.1 Purpose. This form is used to report results for the post-digest spike recovery which is based upon the addition of a known quantity of analyte to an aliquot of the digested sample.

3.4.8.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.8.2.1 In the "EPA Sample No." box, enter an EPA sample number (seven characters maximum) of the sample from which the spike results on this form were obtained. The number shall be centered in the box.

3.4.8.2.2 The "Control Limit %R" and "Q" fields shall be left blank until limits are established by USEPA. At that time, the Contractor will be informed how to complete these fields.

3.4.8.2.3 Under "Spiked Sample Result (SSR)", enter the measured value (in ug/L, to two decimal places) for each analyte in the post-digest spike sample. Enter the value of the result (if the concentration is greater than or equal to the MDL); or enter the CRQL for the analyte if the concentration is less than the MDL. Enter any appropriate concentration qualifier, as explained in Exhibit B, Section 3.4.2.2.5.1, to the "C" qualifier column immediately following the "Spiked Sample Result (SSR)" column.

3.4.8.2.4 Under "Sample Result (SR)", enter the measured value (in ug/L, to two decimal places) for the concentration of each analyte in the sample (reported in "EPA Sample No." box) on which the spike was performed. Enter the value of the result (if the concentration is greater than or equal to the MDL); or enter the CRQL for the analyte if the concentration is less than the MDL. Enter any appropriate concentration qualifier, as explained in Exhibit B, Section 3.4.2.2.5.1, to the "C" qualifier column immediately following the "Sample Result (SR)" column.

3.4.8.2.5 Under "Spike Added (SA)", enter the value (in ug/L, to one decimal place) for each analyte added to the sample. If the SA concentration is specified in the contract, the value added and reported shall be that specific concentration in appropriate units.

3.4.8.2.6 Under "%R", enter the value (to the nearest whole number) of the percent recovery for all spiked analytes computed according to EQ. 9 in Exhibit B, Section 3.4.7.2.8. Percent recovery shall be reported, whether it is negative, positive, or zero. The values for "SSR", "SR", and "SA" must be exactly those reported on this form. A value of zero shall be substituted for "SSR" or "SR" if the analyte value is less than the MDL.

3.4.8.2.7 Under "M", enter the method used as explained in Exhibit B, Section 3.4.2.2.5.3, or enter "NR" if the spike was not required.

3.4.8.2.8 If different samples were used for spike sample analysis of different analytes, additional Form(s) VB-IN shall be submitted.

3.4.9 Duplicates [Form VI-IN]

3.4.9.1 Purpose. The duplicates form is used to report results of duplicate analyses. Duplicate analyses are required for percent solids values and all analyte results.

3.4.9.2 Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.9.2.1 Indicate the appropriate matrix, level, and concentration units (ug/L for water and mg/kg dry weight for soil) as explained in Exhibit B, Sections 2.5.2.1.1 and 3.3.8.

3.4.9.2.2 For "% Solids for Sample", enter the percent solids (as explained in Exhibit B, Section 3.4.2.2.2) for the original sample of the EPA sample number reported on the form. Note that this number must equal the one reported on Form IA-IN for that sample.

3.4.9.2.3 For "% Solids for Duplicate", enter the percent solids (as explained in Exhibit B, Section 3.4.2.2.2) for the duplicate sample of the EPA sample number reported on the form.

3.4.9.2.4 In the "EPA Sample No." box, enter EPA sample number (seven characters maximum) of the sample from which the duplicate sample results on this form were obtained. The number shall be centered in the box.

3.4.9.2.5 Under "Control Limit", enter the CRQL (in appropriate units, ug/L for water or mg/kg dry weight basis corrected for the original sample weight and percent solids) for the analyte if either the sample or duplicate value was less than 5 times the CRQL. If the sample and duplicate values were greater than or equal to 5 times the CRQL, or if the sample and duplicate values were less than the CRQL, leave the field empty.

3.4.9.2.6 Under "Sample (S)", enter the original measured value (to four decimal places) for the concentration of each analyte in the sample (reported in "EPA Sample No." box) on which a duplicate analysis was performed. Concentration units are those specified on the form. Enter the value of the result (if the concentration is greater than or equal to the MDL) corrected for any dilutions; or enter the CRQL for the analyte, adjusted if necessary and corrected for any dilutions, if the concentration is less than the MDL. Enter any appropriate concentration qualifier, as explained in Exhibit B, Section 3.4.2.2.5.1, to the "C" qualifier column immediately following the "Sample (S)" column.

3.4.9.2.7 Under "Duplicate (D)", enter the measured value (to four decimal places) for each analyte in the duplicate sample. Concentration units are those specified on the form. Enter the value of the result (if the concentration is greater than or equal to the MDL) corrected for any dilutions; or enter the CRQL for the analyte, adjusted if necessary and corrected for any dilutions, if the concentration is less than the MDL. Enter any appropriate concentration qualifier, as explained in

Exhibit B, Section 3.4.2.2.5.1, to the "C" qualifier column immediately following the "Duplicate (D)" column.

3.4.9.2.8 For solid samples, the concentration of the original sample shall be computed using the weight and percent solids of the original sample. The concentration of the duplicate sample shall be computed using the weight of the duplicate sample, but the percent solids of the original sample.

3.4.9.2.9 Under "RPD", enter the absolute value (to the nearest whole number) of the Relative Percent Difference (RPD) for all analytes detected above the MDL in either the sample or the duplicate, computed according to the following equation:

EQ. 10 Duplicate Sample Relative Percent Difference

$$RPD = \frac{|S - D|}{(S + D)/2} x100$$

The values for "S" and "D" shall be exactly those reported on this form. A value of zero shall be substituted for "S" or "D" if the analyte concentration is less than the MDL in either one. If the analyte concentration is less than the MDL in both "S" and "D", leave the "RPD" field empty.

3.4.9.2.10 Under "Q", enter "*" if the duplicate analysis for the analyte is out of control. If both sample and duplicate values are greater than or equal to 5 times the CRQL, then the RPD must be less than or equal to 20% to be in control. If either the sample or duplicate value is less than 5 times the CRQL, then the absolute difference between the sample and duplicate values shall be less than the CRQL to be in control.

3.4.9.2.11 If both values are below the CRQL, then no control limit is applicable.

3.4.9.2.12 Under "M", enter method used as explained in Exhibit B, Section 3.4.2.2.5.3.

3.4.10 Laboratory Control Sample [Form VII-IN]

3.4.10.1 Purpose. This form is used to report results for the solid and aqueous LCSs.

3.4.10.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.10.2.1 For the Solid LCS Source (12 characters maximum), enter the appropriate EPA sample number if EPA provided standard was used. Substitute an appropriate number provided by EPA for LCS solutions prepared in the future. If other sources were used, identify the source. For the aqueous LCS Source, enter the source name (12 characters maximum) as explained in Exhibit B, Section 3.4.3.2.1.

3.4.10.2.2 Under "Aqueous True", enter the value (in ug/L, to one decimal place) of the concentration of each analyte in the Aqueous LCS Standard Source.

3.4.10.2.3 Under "Aqueous Found", enter the measured concentration (in ug/L, to two decimal places) of each analyte found in the Aqueous LCS solution.

3.4.10.2.4 Under "Aqueous %R", enter the value of the percent recovery (to the nearest whole number) computed according to the following equation:

EQ. 11 Aqueous LCS Percent Recovery

$$\%R = \frac{\text{Solid LCS Found}}{\text{Solid LCS True}} x100$$

3.4.10.2.5 Under "Solid True", enter the value (in mg/kg, to one decimal place) of the concentration of each analyte in the solid LCS Source.

3.4.10.2.6 Under "Solid Found", enter the measured value (in mg/kg, to one decimal place) of each analyte found in the solid LCS solution. Enter the value of the result (if the concentration is greater than or equal to the MDL) corrected for any dilutions; or enter the CRQL for the analyte, adjusted if necessary and corrected for any dilutions, if the concentration is less than the MDL.

3.4.10.2.7 Under "C", enter "J" or "U" or leave empty, to describe the found value of the solid LCS as explained in Exhibit B, Section 3.4.2.2.5.1.

3.4.10.2.8 Under "Limits", enter the lower limit (in mg/kg, to one decimal place) in the left column, and the upper limit (in mg/kg, to one decimal place) in the right column, for each analyte in the solid LCS solution.

3.4.10.2.9 Under "Solid %R", enter the value of the percent recovery (to the nearest whole number) computed according to the following equation:

EQ. 12 Solid LCS Percent Recovery

$$\%R = \frac{\text{Solid LCS Found}}{\text{Solid LCS True}} x100$$

3.4.10.2.10 The values for true and found aqueous and solid LCSs used in EQs. 11 and 12 shall be exactly those reported on this form. If the analyte concentration is less than the MDL, a value of zero shall be substituted for the aqueous and solid LCS found.

3.4.10.2.11 Submit additional Form(s) VII-IN as appropriate if more than one aqueous LCS or solid LCS was required.

3.4.11 ICP-AES and ICP-MS Serial Dilutions [Form VIII-IN]

3.4.11.1 Purpose. This form is used to report results for ICP-AES and ICP-MS serial dilutions.

3.4.11.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.11.2.1 In the "EPA Sample No." box, enter EPA sample number (7 places maximum) of the sample for which serial dilution analysis results on this form were obtained. The number shall be centered in the box.

3.4.11.2.2 Under "Initial Sample Result (I)", enter the instrument measured value (in ug/L to two decimal places) for each ICP analyte. This value shall not be corrected for any dilution. Enter the instrument measured value (if the concentration is greater than or equal to the MDL); or enter the CRQL if the concentration is less than the MDL. Enter any appropriate concentration qualifier, as explained in Exhibit B, Section 3.4.2.2.5.1, to the "C" qualifier column immediately following the "Initial Sample Result (I)" column.

NOTE: The initial sample concentration for an analyte does not have to equal the value for that analyte reported on Form IA-IN for that sample. It is the value of the analyte's instrument measured value (uncorrected for dilution) that is within the linear range of the instrument.

3.4.11.2.3 Under "Serial Dilution Result (S)", enter the instrument measured value corrected for a five-fold dilution (in ug/L to two decimal places) for each ICP analyte in the diluted sample. Enter the corrected instrument measured value (if the concentration is greater than or equal to the MDL); or enter the CRQL if the concentration is less than the MDL. Enter any appropriate concentration qualifier, as explained in Exhibit B, Section 3.4.2.2.5.1, to the "C" qualifier column immediately following the "Serial Dilution Result (S)" column.

NOTE: The "Serial Dilution Result (S)" is obtained by multiplying by five the instrument measured value (in ug/L) of the serially diluted sample. The "C" qualifier for the serial dilution shall be established based on the serial dilution result before correcting it for the five-fold dilution regardless of the value reported on Form VIII-IN.

For example, if the instrument readout value for the "Initial Sample Result (I)" for silver in a two-fold diluted sample MAX123 is 1164.36 ug/L, and the instrument readout value for the "Serial Dilution Result (S)" for silver in a ten-fold diluted sample MAX123 (MAX123L) is 241.67 ug/L, then the concentration reported for silver in the "Initial Sample Result (I)" column will be 1164.36 ug/L (not 2 times the instrument readout value which equals 2328.72 ug/L), and the concentration reported for silver in the "Serial Dilution Result (S)" column will be five times the instrument readout value which equals 1208.35 ug/L (not 10 times the instrument readout value which equals 2416.70 ug/L).

3.4.11.2.4 Under "% Difference", enter the absolute value (to the nearest whole number) of the percent difference in concentration of required analytes, between the original sample and the diluted sample (adjusted for dilution) according to the following formula:

EQ. 13 Serial Dilution Percent Difference

$$\%\text{Difference} = \frac{|I - S|}{I} x100$$

The values for "I" and "S" used to calculate percent difference in EQ. 13 shall be exactly those reported on this form. A value of zero shall be substituted for "S" if the analyte concentration is less than the MDL. If the analyte concentration in (I) is less than the MDL concentration, leave the "% Difference" field empty.

3.4.11.2.5 Under "Q", enter "E" if the percent difference is greater than 10% and the original sample concentration (reported on Form IA-IN) is greater than 50 times the MDL reported on Form IX-IN.

3.4.11.2.6 Under "M", enter the method of analysis for each analyte as explained in Exhibit B, Section 3.4.2.2.5.3.

3.4.12 Method Detection Limits (Annually) [Form IX-IN]

3.4.12.1 Purpose. This form documents the Method Detection Limits (MDLs) for each preparation method and instrument that the Contractor used to obtain data for the SDG. Only the methods, instruments, and wavelengths used to generate data for the SDG shall be included. The Contractor shall also report MDLs, obtained from direct analysis, for each instrument used to obtain data for the SDG. The MDLs obtained from direct analysis shall be used in the qualification of data associated with samples and instrument QC standards that are not taken through a preparation procedure. Although the MDLs are determined annually, a copy of the annual MDLs shall be included with each Sample Data Package on Forms IX-IN.

3.4.12.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.12.2.1 Enter the Analysis Method qualifier as specified in Exhibit B, Section 3.4.2.2.5.3, in the "Instrument Type" field.

3.4.12.2.2 Enter the Instrument ID in the "Instrument ID" field (12 characters maximum). These instrument IDs are used to uniquely identify each instrument that the laboratory used to perform the analysis.

3.4.12.2.3 Enter the date (formatted MM/DD/YYYY) on which the MDL analysis was performed in the "Date" field.

3.4.12.2.4 For "Preparation Method", enter the method of preparation (three characters maximum) for which the MDLs listed on Form IX-IN were established. Use appropriate sample preparation codes as specified below:

HW1: Hotplate/Block digestion for ICP-AES analysis of water samples.
HW2: Hotplate/Block digestion for ICP-MS analysis of water samples.
HW3: Hotplate/Block digestion for ICP-MS analysis of water samples.
MW1: Microwave digestion for ICP-AES analysis of water samples.
MW2: Microwave digestion for ICP-AES analysis of water samples.
HS1: Hotplate/Block digestion for ICP-AES analysis of soil samples.
HS2: Hotplate/Block digestion for ICP-AES analysis of soil samples.
MS1: Microwave digestion for ICP-AES analysis of soil samples.
CW1: Preparation for the Manual Cold Vapor AA analysis of water samples.
CS1: Preparation for the Manual Cold Vapor AA analysis of soil samples.
CW2: Preparation for the Automated Cold Vapor AA analysis of water samples.
DW1: Distillation for the manual and semi-automated spectrophotometric analysis of water samples.
DW2: Midi-distillation for the semi-automated spectrophotometric analysis of water samples.
DS1: Distillation for the manual and semi-automated spectrophotometric analysis of soil samples.
DS2: Midi-distillation for the semi-automated spectrophotometric analysis of soil samples.
NP1: No preparation.

3.4.12.2.5 Enter the concentration units (UG/L for water or MG/KG wet weight for soil) for the results reported on Form IX-IN in the "Concentration Units" field. Enter "UG/L" for MDL results obtained from direct analysis (Preparation Method "NP1").

3.4.12.2.6 Under "Wavelength/Mass", enter the wavelength in nanometers (nm) to two decimal places or the mass in atomic mass units (amu) to two decimal places for each analyte for which an MDL has been established and is listed in the MDL column. If more than one wavelength or mass is used for an analyte, use additional Form(s) IX-IN as appropriate to report the MDL.

3.4.12.2.7 Contract Required Quantitation Limits (in ug/L for water and mg/kg for soil) as established in Exhibit C, shall be reported in the column headed "CRQL". The CRQL shall be reported in ug/L on Form(s) IX-IN associated with Preparation Method "NP1".

3.4.12.2.8 Under "MDL", enter the MDL (in ug/L for water and direct analysis, or mg/kg for soil, to two significant figures for values less than 10, and three significant figures for values greater than or equal to 10) as determined by the Contractor for each analyte analyzed by the instrument for which the ID is listed on this form. When calculating MDL values, always round up to the appropriate significant figure (e.g., 14.81 rounds to 14.9 and 146.6 rounds to 147). This deviation from the rounding rule is necessary to prevent the reporting of detected values for results that fall in the noise region of the calibration curve.

NOTE: Zeros used to set the decimal point in a number less than one are not significant but all trailing zeros are significant.

For example, a calculated MDL value of 0.074 ug/L will be reported as 0.074 and a calculated MDL value of 0.1 or 0.08 will be reported as 0.10 and 0.080, respectively.

3.4.12.2.9 Use additional Form(s) IX-IN if more preparation methods, instruments and wavelengths or masses are used. Note that the date on this form shall not exceed the analysis dates in the Sample Data Package or precede them by more than twelve months.

3.4.12.2.10 Use the "Comments" section to indicate alternative wavelengths and the conditions under which they are used.

3.4.13 ICP-AES Interelement Correction Factors (Quarterly) [Form XA-IN]

3.4.13.1 Purpose. This form documents for each ICP-AES instrument the interelement correction factors applied by the Contractor to obtain data for the SDG. Although the correction factors are determined quarterly, a copy of the results of the quarterly interelement correction factors shall be included with each Sample Data Package on Form XA-IN and Form XB-IN as appropriate.

3.4.13.2 Instructions. Complete the header information according to instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.13.2.1 Enter the ICP-AES Instrument ID (12 characters maximum), which is a unique number designated by the Contractor to identify each ICP-AES instrument used to produce data in the Sample Data Package. If more than one ICP-AES instrument is used, submit additional Form(s) XA-IN as appropriate.

3.4.13.2.2 Report the date (formatted as MM/DD/YYYY) on which these correction factors were determined for use. This date shall not exceed the ICP-AES analysis dates in the Sample Data Package or precede them by more than three calendar months.

3.4.13.2.3 Under "Wavelength", list the wavelength in nm (to two decimal places) used for each ICP-AES analyte. If more than one wavelength is used, submit additional Form(s) XA-IN or Form(s) XB-IN as appropriate.

3.4.13.2.4 Under "Al", "Ca", "Fe", and "Mg", enter the correction factor (negative, positive or zero, to seven decimal places, 10 characters maximum) for each ICP-AES analyte. Correction factors for one other analyte shall be reported using the empty column and listing the analyte's chemical symbol in the blank two-space header field provided for that column.

3.4.13.2.5 If corrections are not applied for an analyte, a zero shall be entered for that analyte to indicate that the corrections were determined to be zero. Correction factors for more than one additional analyte shall be reported using Form XB-IN.

NOTE: Correction factors for Al, Ca, Fe, and Mg are all required and are to be listed first (as they appear on Form XA-IN).

3.4.14 ICP-AES Interelement Correction Factors (Quarterly) [Form XB-IN]

3.4.14.1 Purpose. This form is used if correction factors for analytes other than Al, Ca, Fe, Mg, and one more analyte of the Contractor's choice were applied to the analytes analyzed by ICP-AES.

3.4.14.2 Instructions. Complete this form following the instructions for Form XA-IN (see Exhibit B, Section 3.4.13) by listing the chemical symbol for additional analytes in the heading of the empty columns in the two-space fields provided.

3.4.14.2.1 Columns of correction factors for additional analytes shall be entered left to right starting on Form XA-IN and proceeding to Form XB-IN, according to the alphabetical order of their chemical symbols.

3.4.15 ICP-AES and ICP-MS Linear Ranges (Quarterly) [Form XI-IN]

3.4.15.1 Purpose. This form documents the quarterly linear range analysis for each ICP instrument that the Contractor used to obtain data for the SDG.

3.4.15.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.15.2.1 Enter the ICP Instrument ID (12 characters maximum), which is a unique number designated by the Contractor to identify each ICP instrument used to produce data for the SDG. If more than one ICP instrument is used, submit additional Form(s) XI-IN as appropriate.

3.4.15.2.2 Report the date (formatted as MM/DD/YYYY) on which these linear ranges were analyzed. This date shall not exceed the dates of analysis by ICP in the Sample Data Package and shall not precede the analysis dates by more than three calendar months.

3.4.15.2.3 Under "Integ. Time (Sec.)", enter the integration time (in seconds to two decimal places) used for each measurement taken from the ICP instrument.

3.4.15.2.4 Under "Concentration", enter the concentration (in ug/L) that is the upper limit of the ICP instrument linear range as determined in Exhibit D. Any measurement above it is out of the linear range, and thus, is an estimated value and shall be diluted into the linear range.

3.4.15.2.5 Under "M", enter the method of analysis for each analyte as explained in Exhibit B, Section 3.4.2.2.5.3.

3.4.15.2.6 If more instruments or analyte wavelengths/masses are used, submit additional Form(s) XI-IN as appropriate.

3.4.16 Preparation Log [Form XII-IN]

3.4.16.1 Purpose. This form is used to report the preparation run log.

3.4.16.1.1 All field samples and all Quality Control (QC) preparations (including duplicates, matrix spikes, LCSs, PBs, and re-preparations) associated with the SDG shall be reported on Form XII-IN. In addition, for mercury analyses, all prepared

calibration standards and QC standards (e.g., ICV, CCV, ICB, CCB, CRI) shall also be reported on Form XII-IN. For cyanide analyses, the distilled ICV and the mid-range standard shall also be reported on Form XII-IN.

3.4.16.1.2 Submit one Form XII-IN per batch, per method, if no more than thirty-two preparations, including QC preparations, were performed. If more than 32 preparations per batch, per method, were performed, then submit additional copies of Form XII-IN as appropriate. Submit a separate Form XII-IN for each batch.

3.4.16.1.3 The order in which the Preparation Logs are submitted is very important. Form XII-IN shall be organized by method, by batch. Later batches within a method shall follow earlier ones. Each batch shall start on a separate Form XII-IN.

3.4.16.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.16.2.1 For “Preparation Method”, enter the method of preparation (three characters maximum) for which the preparations listed on Form XII-IN were made, as specified in Exhibit B, Section 3.4.12.2.4.

3.4.16.2.2 Under “EPA Sample No.”, enter EPA sample number of each sample in the SDG, and of all other preparations such as duplicates, matrix spikes, LCSs, PBs, and re-preparations (all formatted according to Exhibit B, Table 2). All EPA sample numbers shall be listed in ascending alphanumeric order, continuing to the next Form XII-IN if applicable.

3.4.16.2.3 Under “Preparation Date”, enter the date (formatted MM/DD/YYYY) on which each sample was prepared for analysis by the method indicated in the header section of the form.

NOTE: The date never changes on a single Form XII-IN because the form shall be submitted per batch.

3.4.16.2.4 Under “Weight”, enter the wet weight (in grams, to two decimal places) of each soil sample prepared for analysis by the method indicated in the header section of the form. If the sample matrix is water, then leave the field empty.

3.4.16.2.5 Under “Volume”, enter the final volume (in mL, to the nearest whole number) of the preparation for each sample prepared for analysis by the method indicated in the header section of the form. This field shall have a value for each sample listed.

3.4.17 Analysis Run Log [Form XIII-IN]

3.4.17.1 Purpose. This form is used to report the sample analysis run log.

3.4.17.1.1 A run is defined as the totality of analyses performed by an instrument throughout the sequence initiated by, and including, the first SOW-required calibration standard or tune standard, and terminated by, and including, the CCV and CCB following the last SOW-required analytical sample.

3.4.17.1.2 All field samples and all QC analyses (including tunes, calibration standards, ICVs, CCVs, ICBs, CCBs, CRIs, ICSs, LRSs, LCSs, PBs, duplicates, serial dilutions, matrix spikes,

and post-digestion/distillation spikes) associated with the SDG shall be reported on Form XIII-IN. The run shall be continuous and inclusive of all analyses performed on the particular instrument during the run.

3.4.17.1.3 Submit one Form XIII-IN per run if no more than thirty-two (32) analyses, including instrument calibration, were analyzed in the run. If more than thirty-two analyses were performed in the run, submit additional Form(s) XIII-IN as appropriate.

3.4.17.1.4 The order in which the Analysis Run Logs are submitted is very important. Form XIII-IN shall be organized by method, and by run. Later runs within a method shall follow earlier ones. Each analytical run shall start on a separate Form XIII-IN. Therefore, instrument calibration or tune shall be the first entry on the form for each new run. In addition, the run is considered to have ended if it is interrupted for any reason, including termination for failing QC parameters.

3.4.17.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.17.2.1 For "Instrument ID", enter the Instrument ID (12 characters maximum) which shall be an identifier designated by the Contractor to uniquely identify each instrument used to produce data which are required to be reported in the SDG deliverable. If more than one instrument is used, submit additional Form(s) XIII-IN as appropriate. The Instrument ID shall exactly match that reported on Forms IVA, IVB, IX, XA, XB, XI, XIV, and XV.

3.4.17.2.2 For "Analysis Method", enter the method code (two characters maximum) according to the specifications in Exhibit B, Section 3.4.2.2.5.3.

3.4.17.2.3 For "Start Date", enter the date (formatted MM/DD/YYYY) on which the analysis run was started.

3.4.17.2.4 For "End Date", enter the date (formatted MM/DD/YYYY) on which the analysis run was ended.

3.4.17.2.5 Under "EPA Sample No.", enter EPA sample number of each analysis, including all QC operations applicable to the SDG (formatted according to Exhibit B, Table 2). All EPA sample numbers shall be listed in increasing chronological (date and time) order of analysis, continuing to the next Form XIII-IN for the instrument run, if applicable. The analysis date and time of other analyses not associated with the SDG, but analyzed by the instrument in the reported analytical run, shall be reported. Those analyses shall be identified with EPA sample number of "ZZZZZZ".

3.4.17.2.6 Under "D/F", enter the dilution factor (to two significant figures) by which the final digestate or distillate needed to be diluted for each analysis to be performed. The dilution factor does not include the dilution inherent in the preparation as specified by the preparation procedures in Exhibit D.

3.4.17.2.7 The dilution factor is required for all entries on Form XIII-IN.

NOTE: For a particular sample a dilution factor of "1.0" shall be entered if the digestate or distillate was analyzed without adding any further volume of dilutant or any other solutions to the "Volume" or an aliquot of the "Volume" listed on Form XII-IN for that sample.

3.4.17.2.8 For USEPA supplied solutions such as ICVs, ICSs, and LCSs, a dilution factor shall be entered if the supplied solution had to be diluted to a dilution different from that specified by the instructions provided with the solution. The dilution factor reported in such a case shall be that which would make the reported true values on the appropriate form for the solution equal those that were supplied with the solution by USEPA. For instance, ICV-2(0887) has a true value of 104.0 ug/L at a 20-fold dilution. If the solution is prepared at a 40-fold dilution, a dilution factor of "2.0" shall be entered on Form XIII-IN and the uncorrected instrument reading is compared to a true value of 52 ug/L. In this example, Form IIA-IN will have a true value of 104.0 regardless of the dilution used. The found value for the ICV shall be corrected for the dilution listed on Form XIII-IN using the following formula:

EQ. 14 ICV/CCV Correction for Dilution

Found value on Form II = Instrument readout (ug/L) x D/F

3.4.17.2.9 Under "Time", enter the time (in military format - HHMM) at which each analysis was performed.

3.4.17.2.10 Under "Analytes", enter "X" in the column of the designated analyte to indicate that the analyte value was used from the reported analysis to report data in the SDG. Leave the column empty for each analyte if the analysis was not used to report the particular analyte.

3.4.17.2.11 Entering "X" appropriately is very important. The "X" is used to link the samples with their related QC. It also links the dilution factor with the appropriate result reported on Inorganic Forms I-VIII. For each analyte result reported on any of the Forms I-VIII, there shall be one, and only one, properly identified entry on Form XIII-IN for which an "X" is entered in the column for that analyte.

3.4.17.2.12 If, on Form XIII-IN, an "X" is entered in the column for an analyte for a field sample associated with a dilution factor greater than 1.0, flag the data for that analyte with a "D" on the appropriate Form IA-IN or Form IB-IN.

3.4.18 ICP-MS Tune [Form XIV-IN]

3.4.18.1 Purpose. This form is used to report the tuning results for each ICP-MS instrument used in SDG analyses.

3.4.18.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.18.2.1 For "ICP-MS Instrument ID", enter an identifier that uniquely identifies a specific instrument within the Contractor

laboratory. No two ICP-MS instruments within a laboratory may have the same ICP-MS Instrument ID.

3.4.18.2.2 Report the date (formatted as MM/DD/YYYY) on which the ICP-MS tune was performed. This date shall not exceed the dates of analysis by ICP-MS in the Sample Data Package.

3.4.18.2.3 For "Avg. Measured Mass (amu)", enter the average mass calculated from the five or more tune analyses (in atomic mass units, to two decimals places) measured for each isotope.

3.4.18.2.4 For "Avg. Peak Width at Peak Height (amu)" enter the average peak width calculated from the analysis (in atomic mass units, to two decimal places) at the percent of peak height recommended by the instrument manufacturer for each isotope.

3.4.18.2.5 For "%RSD", enter the percent Relative Standard Deviation of the absolute signals (intensities) for each isotope calculated from the five or more tune analyses.

3.4.19 ICP-MS Internal Standards Relative Intensity Summary [Form XV-IN]

3.4.19.1 Purpose. This form is used to report the relative internal standard intensity levels during a run for ICP-MS. The relative intensity of each of the internal standards in all analyses performed by ICP-MS must be reported on the form. If more than one ICP-MS instrument or run is used, submit additional Form(s) XV-IN as appropriate. All runs for the lowest alphanumeric instrument must be reported in ascending order before proceeding to the runs for the next highest instrument.

3.4.19.2 Instructions. Complete the header information according to the instructions in Exhibit B, Section 3.3. Complete the remainder of the form using the following instructions.

3.4.19.2.1 For "ICP-MS Instrument ID", enter an identifier that uniquely identifies a specific instrument within the Contractor laboratory. No two ICP-MS instruments within a laboratory may have the same ICP-MS Instrument ID.

3.4.19.2.2 For "Start Date", enter the date (formatted MM/DD/YYYY) on which the analysis run was started.

3.4.19.2.3 For "End Date", enter the date (formatted MM/DD/YYYY) on which the analysis run was ended.

3.4.19.2.4 Under "EPA Sample No.", enter EPA sample number of each analysis, including all QC operations applicable to the SDG. All EPA sample numbers must be listed in increasing chronological (date and time) order of analysis, continuing to the next Form XV for the instrument run, if applicable. The order must agree with the order reported on Form XIII-IN for that run. The analysis date and time of other analyses not associated with the SDG, but analyzed by the instrument in the reported analytical run, must be reported. Those analyses must be identified with EPA sample number of "ZZZZZZ." Samples identified as "ZZZZZZ" need not have intensities reported for internal standards.

3.4.19.2.5 Under "Time", enter the time (in military format - HHMM) at which each analysis was performed.

3.4.19.2.6 Under "Internal Standards %RI for:", enter the chemical symbol and elemental expression number of the internal standard in the "Element" header field provided to indicate the internal standard and elemental expression for which the Relative Intensity (RI) of the internal standards will be calculated in that column.

3.4.19.2.6.1 In the "Element" column, enter the internal standard relative intensity (to the nearest whole number) of the internal standard for each sample analysis listed on the form (excluding "ZZZZZZ"). The internal standard relative intensity (%RI) is calculated using the following formula:

EQ. 15 Internal Standard Percent Relative Intensity

$$\%RI = \frac{I_n}{I_o} x100$$

WHERE, "I_o" is the intensity of the internal standard in the blank calibration standard and "I_n" is the intensity of the internal standard in the EPA sample number in the same units.

3.4.19.2.7 Under the "Q" column to the right of each "Element" column, enter an "R" if the %RI for a field sample, PE, duplicate, or spike is less than 60 or greater than 125; otherwise leave the field blank.

3.4.19.2.8 Columns of internal standard RI must be entered left to right starting with the internal standards of the lower mass on the first Form XV-IN and proceeding to the following Form XV-IN as appropriate. All Forms XV-IN for the lowest numeric instrument must be reported in ascending order by the run number before proceeding to the next Form XV.

3.4.19.3 All field samples and all QC samples (including calibration standards, ICVs, CCVs, ICBs, CCBs, CRIs, ICSs, LCS, PB, serial dilutions, duplicates, PE samples, and spikes) associated with the SDG must be reported on Form XV-IN. The run must be continuous and inclusive of all analyses performed on the particular instrument during the run.

3.4.19.4 Submit one Form XV-IN per run if no more than 32 analyses, including instrument calibration, were analyzed in the run. If more than 32 analyses were performed in the run, submit additional Form(s) XV-IN as appropriate. Each new run must be started on the first line of Form XV-IN.

3.5 Sample Log-In Sheet [Form DC-1]

3.5.1 Purpose. This form is used to document the receipt and inspection of samples and containers. At least one original Form DC-1 is required for each sample shipping container (e.g., cooler). If the samples in a single sample shipping container must be assigned to more than one SDG, the original Form DC-1 shall be placed with the deliverables for the SDG of the lowest alpha-numeric number and a copy of Form DC-1 shall be placed with the deliverables for the other SDG(s). The copies should be identified as "copy(ies)", and the location of the original should be noted on the copies.

3.5.2 Instructions

3.5.2.1 Sign and date the airbill. (If an airbill is not received, include a hardcopy receipt requested from the shipping company or a printout of the shipping company's electronic tracking information).

3.5.2.2 Examine the shipping container and record the presence/absence of custody seals and their condition (i.e., intact, broken) in Item 1.

3.5.2.3 Record the custody seal numbers in Item 2.

3.5.2.4 Open the container, remove the enclosed sample documentation, and record the presence/absence of USEPA forms (i.e., Traffic Reports/Chain of Custody Records, packing lists) and airbills or airbill stickers in Items 3 and 4. Specify if there is an airbill present or an airbill sticker in Item 4. Record the airbill or sticker number in Item 5.

3.5.2.5 Remove the samples from the shipping container(s), examine the samples and the sample tags (if present), and record the condition of the sample bottles (i.e., intact, broken, leaking) and presence or absence of sample tags in Items 6 and 7.

3.5.2.6 Record the presence or absence of a cooler temperature indicator bottle in Item 8.

3.5.2.7 Record the cooler temperature in Item 9.

3.5.2.8 Review the sample shipping documents and compare the information recorded on all the documents and samples and mark the appropriate answer in Item 10.

3.5.2.9 The log-in date should be recorded at the top of Form DC-1; record the date and time of cooler receipt at the laboratory in Items 11 and 12.

3.5.2.10 If there are no problems observed during receipt, sign and date (include the time) Form DC-1 and Traffic Report/Chain of Custody Record, and write the sample numbers in the "EPA Sample No." column.

3.5.2.11 Record the pH for all aqueous samples received.

3.5.2.12 Record the appropriate sample tags and assigned laboratory numbers, if applicable.

3.5.2.13 Any comments should be made in the "Remarks" column.

3.5.2.14 Record the fraction designation (if appropriate) and the specific area designation (e.g., refrigerator number) in the "Sample Transfer" block located in the bottom left corner of Form DC-1. Sign and date the sample transfer block.

3.5.2.15 For Items 1, 3, 4, 6, 7, 8 and 10, circle the appropriate response. Responses can be underlined if this form is completed by automated equipment. Unused columns and spaces shall be crossed out, initialed, and dated.

3.5.2.16 If there are problems observed during receipt (including samples that have not been preserved to the proper pH) or an answer marked

with an asterisk (e.g., "absent*") was circled, contact SMO and document the contact as well as resolution of the problem on a CLP Communication Log. Following resolution, sign and date the forms as specified in the preceding paragraph and note, where appropriate, the resolution of the problem.

3.6 Full Inorganics Complete SDG File (CSF) Inventory Sheet [Form DC-2]

3.6.1 Purpose. The CSF Inventory Sheet is used to record both the inventory of Complete SDG File (CSF) documents and the number of documents in the original Sample Data Package which is sent to the USEPA Region.

3.6.2 Instructions

3.6.2.1 Organize all EPA-CSF documents as described in Exhibit B, Sections 2 and 3. Assemble the documents in Exhibit B, Section 2 in the order specified on Form DC-2, and stamp each page with the consecutive number. Inventory the CSF by reviewing the document numbers and recording page number ranges in the columns provided on Form DC-2. The Contractor shall verify and record in the "Comments" section on Form DC-2 all intentional gaps in the page numbering sequence (for example, "page numbers not used, XXXX-XXXX, XXXX-XXXX"). If there are no documents for a specific document type, enter an "NA" in the empty space.

3.6.2.2 Certain laboratory-specific documents related to the CSF may not fit into a clearly defined category. The laboratory should review Form DC-2 to determine if it is most appropriate to place them under Categories 33, 34, 35, or 36. Category 36 should be used if there is no appropriate previous category. These types of documents should be described or listed in the blanks under each appropriate category.

3.6.2.3 If it is necessary to insert new or inadvertently omitted documents, the Contractor shall follow these steps:

- Number all documents to be inserted with the next sequential numbers and file the inserts in their logical positions within the CSF (e.g., file document 1000 between documents 6 and 7).

- Identify where the inserts are filed in the CSF by recording the document numbers and their locations under the "Other Records" section of Form DC-2 (e.g., document 1000 is filed between 6 and 7).

4.0 DATA REPORTING FORMS

The data reporting forms are shown on the following pages.

EXHIBIT B

INORGANIC FORMS

COVER PAGE

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

SOW No.: _____

EPA Sample No.	Lab Sample ID

		ICP-AES	ICP-MS
Were ICP-AES and ICP-MS interelement corrections applied?	(Yes/No)	_____	_____
Were ICP-AES and ICP-MS background corrections applied?	(Yes/No)	_____	_____
If yes, were raw data generated before application of background corrections?	(Yes/No)	_____	_____

Comments:

_____

_____

I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package and in the computer-readable data submitted on diskette (or via an alternate means of electronic transmission, if approved in advance by USEPA) has been authorized by the Laboratory Manager or the Manager's designee, as verified by the following signature.

Signature: _____ Name: _____

Date: _____ Title: _____

1A-IN
INORGANIC ANALYSIS DATA SHEET

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

Matrix: (soil/water) _____ Lab Sample ID: _____

Level: (low/med) _____ Date Received: _____

% Solids: _____

Concentration Units (**ug/L** or **mg/kg** dry weight): _____

CAS No.	Analyte	Concentration	C	Q	M
7429-90-5	Aluminum				
7440-36-0	Antimony				
7440-38-2	Arsenic				
7440-39-3	Barium				
7440-41-7	Beryllium				
7440-43-9	Cadmium				
7440-70-2	Calcium				
7440-47-3	Chromium				
7440-48-4	Cobalt				
7440-50-8	Copper				
7439-89-6	Iron				
7439-92-1	Lead				
7439-95-4	Magnesium				
7439-96-5	Manganese				
7439-97-6	Mercury				
7440-02-0	Nickel				
7440-09-7	Potassium				
7782-49-2	Selenium				
7440-22-4	Silver				
7440-23-5	Sodium				
7440-28-0	Thallium				
7440-62-2	Vanadium				
7440-66-6	Zinc				
57-12-5	Cyanide				

Color Before: _____ Clarity Before: _____ Texture: _____

Color After: _____ Clarity After: _____ Artifacts: _____

Comments:

_____
_____
_____
_____

1B-IN
INORGANIC ANALYSIS DATA SHEET

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

Matrix: (soil/water) _____ Lab Sample ID: _____

Level: (low/med) _____ Date Received: _____

% Solids: _____

Concentration Units (**ug/L** or **mg/kg** dry weight): _____

CAS No.	Analyte	Concentration	C	Q	M

Color Before: _____ Clarity Before: _____ Texture: _____

Color After: _____ Clarity After: _____ Artifacts: _____

Comments:

_____

_____

_____

_____

2A-IN
INITIAL AND CONTINUING CALIBRATION VERIFICATION

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

Initial Calibration Verification Source: _____

Continuing Calibration Verification Source: _____

Concentration Units: ug/L

	Initial Calibration Verification			Continuing Calibration Verification					M
Analyte	True	Found	%R(1)	True	Found	%R(1)	Found	%R(1)	
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

(1) Control Limits: Mercury 80-120; Other Metals 90-110; Cyanide 85-115

2B-IN
CRQL CHECK STANDARD

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

CRQL Check Standard Source: _____

Concentration Units: ug/L

Analyte	CRQL Check Standard				
	Initial			Final	
	True	Found*	%R(1)	Found*	%R(1)
Aluminum					
Antimony					
Arsenic					
Barium					
Beryllium					
Cadmium					
Calcium					
Chromium					
Cobalt					
Copper					
Iron					
Lead					
Magnesium					
Manganese					
Mercury					
Nickel					
Potassium					
Selenium					
Silver					
Sodium					
Thallium					
Vanadium					
Zinc					
Cyanide					

(1) Control Limits: 70-130 with the following exceptions:
ICP-AES - Antimony, Lead, and Thallium: 50-150.
ICP-MS - Cobalt, Manganese, and Zinc: 50-150.

* If applicable, enter the concentration qualifier “J” or ”U” after the concentration in these columns (e.g., 0.20U for Mercury).

3-IN
BLANKS

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

Preparation Blank Matrix (soil/water): _____

Preparation Blank Concentration Units (ug/L or mg/kg): _____

Analyte	Initial Calibration Blank (ug/L)	C	Continuing Calibration Blank (ug/L) 1	C	2	C	3	C	Preparation Blank	C	M
Aluminum											
Antimony											
Arsenic											
Barium											
Beryllium											
Cadmium											
Calcium											
Chromium											
Cobalt											
Copper											
Iron											
Lead											
Magnesium											
Manganese											
Mercury											
Nickel											
Potassium											
Selenium											
Silver											
Sodium											
Thallium											
Vanadium											
Zinc											
Cyanide											

4A-IN
ICP-AES INTERFERENCE CHECK SAMPLE

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

ICP-AES Instrument ID: _____ ICS Source: _____

Concentration Units: ug/L

Analyte	True		Initial Found				Final Found			
	Sol. A	Sol. AB	Sol. A	%R	Sol. AB	%R	Sol. A	%R	Sol. AB	%R
Aluminum										
Antimony										
Arsenic										
Barium										
Beryllium										
Cadmium										
Calcium										
Chromium										
Cobalt										
Copper										
Iron										
Lead										
Magnesium										
Manganese										
Nickel										
Potassium										
Selenium										
Silver										
Sodium										
Thallium										
Vanadium										
Zinc										

4B-IN
ICP-MS INTERFERENCE CHECK SAMPLE

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

ICP-MS Instrument ID: _____ ICS Source: _____

Concentration Units: ug/L

Analyte	True		Found			
	Sol. A	Sol. AB	Sol. A	%R	Sol. AB	%R
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Carbon						
Chloride						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Molybdenum						
Nickel						
Phosphorus						
Potassium						
Selenium						
Silver						
Sodium						
Sulfur						
Thallium						
Titanium						
Vanadium						
Zinc						

5A-IN
MATRIX SPIKE SAMPLE RECOVERY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

Matrix: (soil/water) _____ Level: (low/med) _____

% Solids for Sample: _____

Concentration Units (ug/L or mg/kg dry weight): _____

Analyte	Control Limit %R	Spiked Sample Result (SSR)	C	Sample Result (SR)	C	Spike Added (SA)	%R	Q	M
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

Comments:

_____
_____
_____
_____

5B-IN
POST-DIGESTION SPIKE SAMPLE RECOVERY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

Matrix: (soil/water) _____ Level: (low/med) _____

Concentration Units: ug/L

Analyte	Control Limit %R	Spiked Sample Result (SSR)	C	Sample Result (SR)	C	Spike Added (SA)	%R	Q	M
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

Comments:

_____
_____
_____
_____

6-IN
DUPLICATES

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

Matrix: (soil/water) _____ Level: (low/med) _____

% Solids for Sample: _____ % Solids for Duplicate: _____

Concentration Units (ug/L or mg/kg dry weight): _____

Analyte	Control Limit	Sample (S)	C	Duplicate (D)	C	RPD	Q	M
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Potassium								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								
Cyanide								

7-IN
LABORATORY CONTROL SAMPLE

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

Solid LCS Source: _____

Aqueous LCS Source: _____

	Aqueous (ug/L)			Solid (mg/kg)					
Analyte	True	Found	%R	True	Found	C	Limits		%R
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

8-IN
ICP-AES and ICP-MS SERIAL DILUTIONS

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

Matrix: (soil/water) _____ Level: (low/med) _____

Concentration Units: ug/L

Analyte	Initial Sample Result (I)	C	Serial Dilution Result (S)	C	% Difference	Q	M
Aluminum							
Antimony							
Arsenic							
Barium							
Beryllium							
Cadmium							
Calcium							
Chromium							
Cobalt							
Copper							
Iron							
Lead							
Magnesium							
Manganese							
Nickel							
Potassium							
Selenium							
Silver							
Sodium							
Thallium							
Vanadium							
Zinc							

9-IN
METHOD DETECTION LIMITS (ANNUALLY)

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

Instrument Type: _____ Instrument ID: _____ Date: _____

Preparation Method: _____

Concentration Units (ug/L or mg/kg): _____

Analyte	Wavelength /Mass	CRQL	MDL
Aluminum			
Antimony			
Arsenic			
Barium			
Beryllium			
Cadmium			
Calcium			
Chromium			
Cobalt			
Copper			
Iron			
Lead			
Magnesium			
Manganese			
Mercury			
Nickel			
Potassium			
Selenium			
Silver			
Sodium			
Thallium			
Vanadium			
Zinc			
Cyanide			

Comments:

10A-IN
ICP-AES INTERELEMENT CORRECTION FACTORS (QUARTERLY)

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

ICP-AES Instrument ID: _____ Date: _____

Analyte	Wave-length (nm)	Interelement Correction Factors for: Al	Ca	Fe	Mg	___
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						

Comments:

10B-IN
ICP-AES INTERELEMENT CORRECTION FACTORS (QUARTERLY)

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

ICP-AES Instrument ID: _____ Date: _____

Analyte	Wave-length (nm)	Interelement Correction Factors for: ____	____	____	____	____
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						

Comments:

_____
_____
_____
_____

11-IN
ICP-AES and ICP-MS LINEAR RANGES (QUARTERLY)

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

ICP Instrument ID: _____ Date: _____

Analyte	Integ. Time (Sec.)	Concentration (ug/L)	M
Aluminum			
Antimony			
Arsenic			
Barium			
Beryllium			
Cadmium			
Calcium			
Chromium			
Cobalt			
Copper			
Iron			
Lead			
Magnesium			
Manganese			
Nickel			
Potassium			
Selenium			
Silver			
Sodium			
Thallium			
Vanadium			
Zinc			

Comments:

_____

_____

_____

_____

USEPA - CLP

12-IN
PREPARATION LOG

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

Preparation Method: _____

EPA Sample No.	Preparation Date	Weight (gram)	Volume (mL)

USEPA - CLP

13-IN
ANALYSIS RUN LOG

Lab Name: ______________________ Contract: ______________________

Lab Code: __________ Case No.: __________ NRAS No.: ____________ SDG No.: ____________

Instrument ID: ______________ Analysis Method: __________________

Start Date: ________________ End Date: ________________

EPA Sample No.	D/F	Time	Analytes																									
			AL	SB	AS	BA	BE	CD	CA	CR	CO	CU	FE	PB	MG	MN	HG	NI	K	SE	AG	NA	TL	V	ZN	CN		

14-IN
ICP-MS Tune

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

ICP-MS Instrument ID: _____ Date: _____

Element - Mass	Avg. Measured Mass (amu)	Avg. Peak Width at Peak Height (amu)	%RSD
Be - 9			
Mg - 24			
Mg - 25			
Mg - 26			
Co - 59			
In - 113			
In - 115			
Pb - 206			
Pb - 207			
Pb - 208			

Comments:

_____

_____

_____

_____

15-IN
ICP-MS Internal Standards Relative Intensity Summary

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ NRAS No.: _____ SDG No.: _____

ICP-MS Instrument ID: _____ Start Date: _____ End Date: _____

EPA Sample No.	Time	Internal Standards %RI For:									
		Element	Q	Element	Q	Element	Q	Element	Q	Element	Q

SAMPLE LOG-IN SHEET

Lab Name					Page __ of __
Received By (Print Name)					Log-in Date
Received By (Signature)					
Case Number		Sample Delivery Group No.			NRAS Number

Remarks:		EPA Sample #	Aqueous Sample pH	Corresponding		Remarks: Condition of Sample Shipment, etc.
				Sample Tag #	Assigned Lab #	
1. Custody Seal(s)	Present/Absent* Intact/Broken					
2. Custody Seal Nos.	_____ _____					
3. Traffic Reports/Chain of Custody Records or Packing Lists	Present/Absent*					
4. Airbill	Airbill/Sticker Present/Absent*					
5. Airbill No.	_____ _____					
6. Sample Tags	Present/Absent*					
Sample Tag Numbers	Listed/Not Listed on Traffic Report/Chain of Custody Record					
7. Sample Condition	Intact/Broken*/ Leaking					
8. Cooler Temperature Indicator Bottle	Present/Absent*					
9. Cooler Temperature	_____					
10. Does information on Traffic Reports/Chain of Custody Records and sample tags agree?	Yes/No*					
11. Date Received at Lab	_____					
12. Time Received	_____					
Sample Transfer						
Fraction	Fraction					
Area #	Area #					
By	By					
On	On					

* Contact SMO and attach record of resolution

Reviewed By		Logbook No.
Date		Logbook Page No.

FULL INORGANICS COMPLETE SDG FILE (CSF) INVENTORY SHEET

LABORATORY NAME _____

CITY/STATE _____

CASE NO. _____ SDG NO. _____

SDG NOs. TO FOLLOW _____ _____ _____

NRAS NO. _____

CONTRACT NO. _____

SOW NO. _____

All documents delivered in the Complete SDG File must be original documents where possible. (Reference - Exhibit B Section 2.6)

		PAGE NOs.		CHECK	
		FROM	TO	LAB	REGION
1.	Cover Page				
2.	SDG Narrative				
3.	Sample Log-In Sheet (DC-1)				
4.	Inventory Sheet (DC-2))				
5.	Traffic Report/Chain of Custody Record(s)				
	Inorganic Analysis				
6.	Data Sheet (Form I-IN)				
7.	Initial & Continuing Calibration Verification (Form IIA-IN)				
8.	CRQL Standard (Form IIB-IN)				
9.	Blanks (Form III-IN)				
10.	ICP-AES Interference Check Sample (Form IVA-IN)				
11.	ICP-MS Interference Check Sample (Form IVB-IN)				
12.	Matrix Spike Sample Recovery (Form VA-IN)				
13.	Post-Digestion Spike Sample Recovery (Form VB-IN)				
14.	Duplicates (Form VI-IN)				
15.	Laboratory Control Sample (Form VII-IN)				
16.	ICP-AES and ICP-MS Serial Dilutions (Form VIII-IN)				
17.	Method Detection Limits (Annually) (Form IX-IN)				
18.	ICP-AES Interelement Correction Factors (Quarterly) (Form XA-IN)				
19.	ICP-AES Interelement Correction Factors (Quarterly) (Form XB-IN)				
20.	ICP-AES and ICP-MS Linear Ranges (Quarterly) (Form XI-IN)				
21.	Preparation Log (Form XII-IN)				

	PAGE NOs. FROM	TO	CHECK LAB	REGION
22. Analysis Run Log (Form XIII-IN)	____	____	____	____
23. ICP-MS Tune (Form XIV-IN)	____	____	____	____
24. ICP-MS Internal Standards Relative Intensity Summary (Form XV-IN)	____	____	____	____
25. ICP-AES Raw Data	____	____	____	____
26. GFAA Raw Data (If Applicable)	____	____	____	____
27. ICP-MS Raw Data	____	____	____	____
28. Mercury Raw Data	____	____	____	____
29. Cyanide Raw Data	____	____	____	____
30. Preparation Logs Raw Data	____	____	____	____
31. Percent Solids Determination Log	____	____	____	____
32. USEPA Shipping/Receiving Documents				
Airbill (No. of Shipments ____)	____	____	____	____
Sample Tags			____	____
Sample Log-In Sheet (Lab)	____	____	____	____
33. Misc. Shipping/Receiving Records (list all individual records)				
Telephone Logs	____	____	____	____
_____	____	____	____	____
_____	____	____	____	____
34. Internal Lab Sample Transfer Records & Tracking Sheets (describe or list)				
_____	____	____	____	____
_____	____	____	____	____
35. Internal Original Sample Prep & Analysis Records (describe or list)				
Prep Records _____	____	____	____	____
Analysis Records _____	____	____	____	____
Description _____	____	____	____	____
36. Other Records (describe or list)				
Telephone Communications Log	____	____	____	____
_____	____	____	____	____
_____	____	____	____	____

37. Comments:_____

_____

_____

_____

Completed by:

(CLP Lab) _____ _____ _____

(Signature) (Print Name & Title) (Date)

Audited by:

(USEPA) _____ _____ _____

(Signature) (Print Name & Title) (Date)

EXHIBIT C

INORGANIC TARGET ANALYTE LIST
WITH CONTRACT REQUIRED
QUANTITATION LIMITS

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EXHIBIT C - INORGANIC TARGET ANALYTE LIST WITH CONTRACT REQUIRED QUANTITATION LIMITS

Table of Contents

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1.0 INORGANIC TARGET ANALYTE LIST AND CONTRACT REQUIRED QUANTITATION LIMITS (CRQLs)

Analyte	CAS Number	ICP-AES CRQL for Water[1,2,3,4] (µg/L)	ICP-AES CRQL for Soil[1,2,3,4,5] (mg/kg)	ICP-MS CRQL for Water[1,2,4] (µg/L)
Aluminum	7429-90-5	200	20	--
Antimony	7440-36-0	60	6	2
Arsenic	7440-38-2	10	1	1
Barium	7440-39-3	200	20	10
Beryllium	7440-41-7	5	0.5	1
Cadmium	7440-43-9	5	0.5	1
Calcium	7440-70-2	5000	500	--
Chromium	7440-47-3	10	1	2
Cobalt	7440-48-4	50	5	1
Copper	7440-50-8	25	2.5	2
Iron	7439-89-6	100	10	--
Lead	7439-92-1	10	1	1
Magnesium	7439-95-4	5000	500	--
Manganese	7439-96-5	15	1.5	1
Mercury	7439-97-6	0.2	0.1	--
Nickel	7440-02-0	40	4	1
Potassium	7440-09-7	5000	500	--
Selenium	7782-49-2	35	3.5	5
Silver	7440-22-4	10	1	1
Sodium	7440-23-5	5000	500	--
Thallium	7440-28-0	25	2.5	1
Vanadium	7440-62-2	50	5	1
Zinc	7440-66-6	60	6	2
Cyanide	57-12-5	10	2.5	--

[1]The CRQLs are the minimum levels of quantitation acceptable under the contract Statement of Work (SOW).

[2]Subject to the restrictions specified in Exhibit D, any analytical method specified in ILM05.3 Exhibit D may be utilized as long as the documented Method Detection Limits (MDLs) are less than one-half the CRQLs.

[3]Mercury is analyzed by cold vapor atomic absorption. Cyanide is analyzed by colorimetry/spectrophotometry.

[4]Changes to the Inorganic Target Analyte List (TAL) (e.g., adding an additional analyte) or CRQLs may be requested under the modified analysis clause in the contract.

[5]The CRQLs for soil are based on 100% solids and on the exact weights and volumes specified in Exhibit D. Samples with less than 100% solids may have CRQLs greater than those listed in the table above.

ILM05.3 to ILM05.4
Summary of Changes

The ILM05.3 SOW document has been revised to ILM05.4 as identified in the Exhibit section(s) (and any other applicable sections within the ILM05.3 SOW) shown below. All changes identified in this document should be adhered to in conjunction with the ILM05.3 SOW as stipulated below.

Exhibit Section(s)	Revisions
Global	All references to “ILM05.3” are changed to “ILM05.4”.
Exhibit A: Section 4.2.3.1	The reporting requirement has been modified as follows: The Contractor shall be responsible for completing and submitting analysis data sheets and computer-readable data on diskette or compact disc (CD) (or via an alternate means of electronic transmission approved in advance by USEPA) in a format specified in this SOW and within the time specified in Exhibit B, Section 1.1.
Exhibit B: Section 2.7	The Data in Computer-Readable Format has been modified as follows: The Contractor shall provide a computer-readable copy for all samples in the SDG, as specified in Exhibit H and delivered as specified in Exhibit B, Section 1.1. Computer-readable data deliverables shall be submitted on DOS/Windows formatted 3.5-inch high-density 1.44 MB diskette(s), compact disc (CD), or via an alternate means of electronic transmission, if approved in advance by USEPA.
Exhibit B: Section 2.7.1	Add the following to the end of the section: The CD shall be packaged and shipped in such a manner that the CD cannot be bent or folded and will not be exposed to extreme heat/cold. The CD shall be included in the same shipment as the hardcopy data, and, at a minimum, be enclosed in a CD mailer.
Exhibit C: Section 1.0	The ICP-MS CRQL in water (µg/L) for vanadium has been modified from 1 to 5.
Exhibit D: Introduction: Section 1.6.2	The temperature range for the oven has been modified to 105˚C (± 5˚C).

Exhibit Section(s)	Revisions
Exhibit D: ICP-AES: Section 10.1.3.2.11	This section is modified as follows: Sample Filtration – The digested samples are shaken well to mix in any condensate within the digestion vessel before being opened. If necessary, the digestates are then filtered into 50 mL glass volumetric flasks through Whatman No. 41 (or equivalent) filter paper and diluted to 50 mL (if necessary). In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The samples are now ready for analysis. The sample results must be corrected by a factor of 1.11 in order to report final concentration values based on an initial volume of 45 mL. Concentrations so determined shall be reported as "Total".
Exhibit D: ICP-AES: Section 10.1.3.3.4	This section is modified as follows: Sample Filtration - The digested samples are shaken well to mix in any condensate within the digestion vessel before being opened. If necessary, the digestates are then filtered through Whatman No. 41 (or equivalent) filter paper and diluted to 55 mL (if necessary). In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The samples are now ready for analysis. The sample results must be corrected by a factor of 1.1 in order to report final concentration values based on an initial volume of 50 mL. Concentrations so determined shall be reported as "Total".
Exhibit D: ICP-AES: Section 10.1.4.3.13	This section is modified as follows: Sample Filtration – Shake the sample well to mix in any condensate within the digestion vessel before being opened. Filter the digestate into a 50 mL glass volumetric flask through Whatman No. 42 (or equivalent) filter paper. Rinse the sample digestion vessel, cap, connecting tube, and (if venting occurred) the overflow vessel into the 50 mL flask. Dilute to 50 mL. In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The samples are now ready for analysis. Concentrations so determined shall be reported as "Total".
Exhibit D: ICP-MS: Section 10.2.5	This section is modified as follows: All masses which might affect data quality must be monitored during the analytical run. At a minimum, the masses listed in Table 2 – Recommended Isotopes and Masses for Selected Elements, should be monitored. The masses must be monitored in the same scan that is used for the collection of the data. This information should be used to correct the data for identified interferences. Based on the instrument manufacturer's recommended procedures, the laboratory is not required to monitor every mass listed for each element. The laboratory may monitor additional masses not listed in Table 2.

Exhibit Section(s)	Revisions
Exhibit D: ICP-MS: Section 17 Table 2	The table is modified as follows: Table 2. Recommended Isotopes and Masses for Selected Elements

Element of Interest	Analyte Masses - Choose One, or More – **Calibrated**	Masses to be Monitored
Antimony	121	
Arsenic	75	77, 82 (Isobaric Equation Required)
Barium	135, 137	
Beryllium	9	
Cadmium	111	106, 108 (Isobaric Equation Required)
Chromium	52	
Cobalt	59	
Copper	63, 65	
Lead	206, 207, 208	
Manganese	55	
Nickel	60	
Selenium	78, 82	
Silver	107, 109	
Thallium	203, 205	
Vanadium	51	52, 53 (Isobaric Equation Required)
Zinc	66	
Potential Interferent		
Aluminum		27
Calcium (CaO on 60Ni)		44 (No Isobaric Equation Required)
Magnesium		24, 25, 26
Iron		54, 56, 57
Titanium (TiO on 63Cu)		47 (No Isobaric Equation Required)
Krypton (Kr on 82Se)		83 (No Isobaric Equation Required)
Tin (Sn on 115In)		118 (Isobaric Equation Required)

Exhibit Section(s)	Revisions
Exhibit D: ICP-MS: Section 17 Table 2	The NOTE is modified as follows: NOTE: Where possible, alternative isotopes are indicated. For laboratories using instruments that employ either collision cells or reaction cells to remove certain isobaric interferences, the use of stable compounds of a target analyte(s) with masses free from interference for quantitation is permitted. One example of this would be the quantitation of arsenic as the oxide at mass 91.
Exhibit D: Mercury: Section 10.1.3.1.1	The section is modified as follows: Transfer aliquots of the working mercury solution to a series of 300 mL BOD bottles, disposable polymer vials, or other suitable digestion vessels. Add sufficient reagent water to each vessel to make a total volume of 50-100 mL.
Exhibit D: Mercury: Section 10.1.3.2.1.1	The section is modified as follows: Transfer 50-100 mL, or an aliquot diluted to 50-100 mL, containing not more than 1 µg of mercury to a 300 mL BOD bottle, disposable polymer vial, or other suitable digestion vessel, and continue as described in Section 10.1.3.1.2.
Exhibit D: Mercury: Section 10.1.4.1.1	The section is modified as follows: Transfer aliquots of the working mercury solutions (see Section 7.2.1.3) to a series of 300 mL BOD bottles, disposable polymer vials, or other suitable digestion vessels. Add sufficient reagent water to each vessel to make a total volume of 10 mL.
Exhibit D: Mercury: Section 10.1.4.2.1.1	The section is modified as follows: Weigh a representative 0.20 g (±0.01 g) portion of wet sample and place in the bottom of a BOD bottle, disposable polymer vial, or other suitable digestion vessel. Add enough reagent water to each sample to make a total volume of 10 mL. Continue as described in Section 10.1.4.1.2.
Exhibit D: Cyanide: Section 7.1.4.1	The following language is added to the section: The phosphate buffer described in USEPA Method MCAWW 335.2 may be substituted for the acetate buffer.
Exhibit D: Cyanide: Section 7.1.5.2	The following language is added to the section: The phosphate buffer described in USEPA Method MCAWW 335.3 may be substituted for the acetate buffer.

Exhibit Section(s)	Revisions
Exhibit D: Cyanide: Section 9.5.2	The section is modified as follows: Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses, and other related operations that may affect the CCV measured result may not be applied to the CCV to greater extent than the extent applied to the associated analytical samples.
Exhibit D: Cyanide: Section 10.3.1.1	The section is modified as follows: Allow all standards and samples to come to ambient room temperature prior to analysis. Withdraw 50 mL or less of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25N sodium hydroxide solution (see Section 7.1.3.1). Add 1.0 mL of acetate buffer or 15 mL of phosphate buffer and mix. The dilution factor must be reported on Form XIII-IN.
Exhibit E: Section 8.3.3	A new section is added as follows: Logbooks shall be kept for all dilutions of standards and reagents. All subsequent dilutions from the primary standard and the calculations for determining their concentrations shall be recorded and verified by a second person. All solution standards shall be refrigerated, if required, when not in use. All solution standards shall be clearly labeled as to the identity of the analyte or analytes, the standard ID number of the solution, concentration, date prepared, solvent, expiration date of the solution, special storage requirements (if any), and initials of the preparer.
Exhibit H: Section 8.1	The section is modified as follows: The file shall be submitted on 3.5 inch, high density 1.44 MB diskettes or on compact discs (CD). The diskettes or CDs shall be formatted and recorded using DOS/Windows Operating Systems. The diskettes or CDs shall contain information relevant to one and only one Sample Delivery Group (SDG). An alternate means of electronic transmission may be utilized, if approved in advance by USEPA.
Exhibit H: Section 8.1.2	References to diskette are modified to refer to diskette or CD.
Exhibit H: Section 8.1.3	References to diskette are modified to refer to diskette or CD.

United States Environmental Protection Agency
Office of Superfund Remediation and Technology Innovation (5202P)

EPA 540-R-07-02
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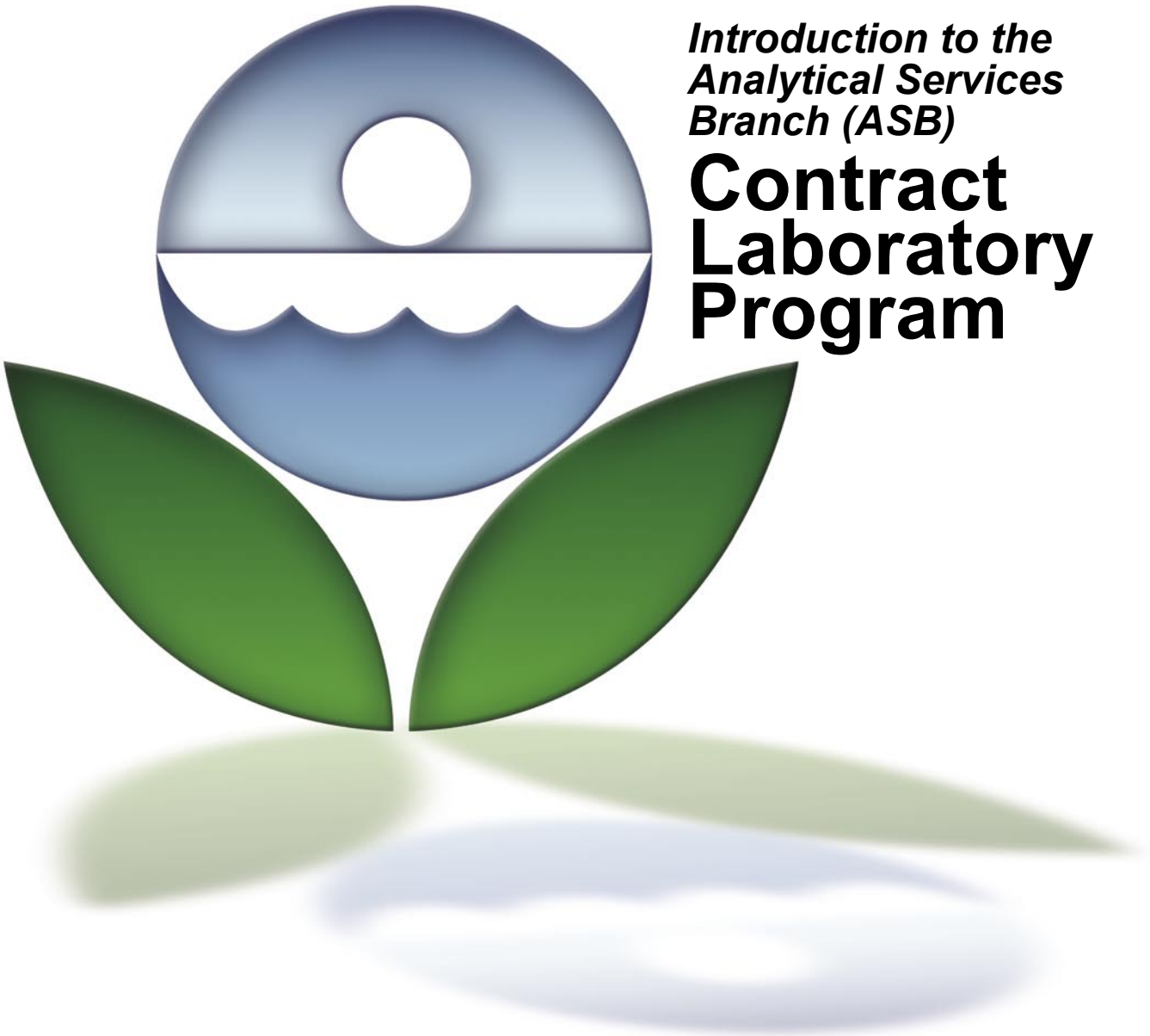


Introduction to the Analytical Services Branch (ASB)

Contract Laboratory Program

Disclaimer: This final version of the document replaces any prior versions of the document in their entirety.

Introduction

This document is designed primarily to educate the United States Environmental Protection Agency's (USEPA's) Superfund staff and managers [e.g., Remedial Project Managers (RPMs), On-Scene Coordinators (OSCs), Site Assessment Managers, and Risk Assessors] about how to obtain laboratory analytical services for Superfund and Brownfields sites. The Contract Laboratory Program (CLP) is administered by the Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB), Regional CLP Project Officers (CLP POs), and Regional Sample Control Center (RSCC) Coordinators. Other programs or agencies can participate in the CLP. Please refer to the CLP Participants section of Chapter 1, or contact the Sample Management Office (SMO) Project Officer for additional information.

CLP analytical data is used to demonstrate the nature and extent of contamination at hazardous waste sites, assess priorities for response based on risks to human health and the environment, establish appropriate cleanup actions, and determine when remedial actions are complete. Each CLP sample is properly documented to ensure timely, accurate, and complete analysis for all parameters requested, and to support the use of sample data in potential enforcement actions against Potentially Responsible Parties (PRPs). Data collected and analyzed under the CLP is not available to PRPs since the CLP is Federally funded and use by PRPs would cause a conflict of interest.

Key Information

Text in blue and underlined indicates an external link to information outside of this document.

The images below are located throughout the document to draw attention to important information and each are labeled accordingly:

Information

Note

Additional copies of this document may be downloaded from the CLP Web site at:

http://www.epa.gov/superfund/programs/clp/guidance.htm

Table of Contents

Chapter 1

Welcome to the Contract Laboratory Program (CLP)

Background

Welcome to the CLP. The CLP is a national network of United States Environmental Protection Agency (USEPA) personnel, commercial laboratories, and support contractors whose fundamental mission is to provide customers [e.g., USEPA Regions, United States Army Corp of Engineers (USACE), and other Federal, State, or Tribal Agencies] with analytical data of known and documented quality. Initiated in 1980, the CLP supports environmental data users in identifying contaminants and determining the level of contamination at Superfund hazardous waste sites prior to, during, and after site cleanup.

Data of Known and Documented Quality:

Analytical data that adheres to EPA Order 5360.1 A2, calls for environmental programs and decisions to be supported by data of the type and quality needed and expected for their intended use. The type and quality of data needed to support CLP data users has been defined as analytical data of known and documented quality.

Download EPA Order 5360.1 A2 at
http://www.epa.gov/quality/qs-docs/5360-1.pdf

The CLP, Superfund's preferred data quality solution for Routine Analytical Services (RAS) is available to local, State, Federal, and Tribal agencies (see the Program Providers section of Chapter 1).

Potentially Responsible Parties (PRPs) cannot access the CLP.

Benefits of the CLP

Customer satisfaction is a key factor in the design and application of all CLP services. The CLP seeks to provide its customers with timely, high-quality, high-volume, low-cost services and solutions. CLP customers receive the following benefits:

Analytical Services

- The CLP provides its customers with a full spectrum of services ranging from environmental sample analyses and electronic data review, to computerized invoicing and detailed site analytical costs.
- The CLP provides a variety of analytical services for the most commonly requested organic and inorganic analytes. The CLP target compound and analyte lists were originally derived from the USEPA Priority Pollutant list, but have been subsequently modified based on advances in analytical methods, evaluation of method performance data, and the needs of the Superfund program. The CLP has also developed several Quick Reference Fact Sheets that summarize the current analytical services provided for the Inorganic, Organic, and Organic Low Concentration programs.

Quality Assurance (QA)

- The CLP provides a comprehensive QA program through use of Performance Evaluation (PE) samples, preparation of quarterly performance reports, use of fraud detection mechanisms, performance-based scheduling, and continuous inspection of laboratory data for contractual compliance.

The CLP provides customers with total QA.

- To simplify the laboratory's Quality Assurance Project Plan (QAPP) development process, the CLP predefines elements such as: analytical methods; preventive laboratory equipment maintenance

and calibration; sample shipment chain-of-custody procedures and forms; analytical precision and accuracy (including quantitation limits for organics and inorganics); laboratory Quality Control (QC) requirements; data management; and documentation for laboratory analysis.

- CLP data is compliant with EPA Order 5360.1 A2 quality requirements for data to withstand independent review and confirmation.

Enhanced Automated Services

- The CLP captures all data produced for CLP customers and maintains this historical data for the client's future use in enforcement, litigation, and Cost Recovery activities.

Automated services streamline sample scheduling and analytical data assessment.

- The CLP offers Automated Data Processing (ADP) support such as automated data assessment and rapid electronic transfer of analytical data into users' databases.
- The CLP provides automated sample scheduling, and in certain instances, can accommodate same day scheduling.

Support Services

- The CLP provides support services that allow managers to focus on site assessment activities without distraction from laboratory and data management issues.

For more information on CCS, see the Data Assessment Tool (DAT) section of Chapter 2.

- CLP systems collect and disseminate financial information to USEPA management for budgetary and litigation activities (see Enforcement and Cost Recovery Support section of Chapter 2).
- The ASB staff has the technical expertise to resolve any questions about sample scheduling and funding and to assist USEPA Regions in evaluating data quality and usability.

Cost Savings

- USEPA Headquarters assumes the CLP costs for Regional clients in Superfund lead projects.

USEPA Headquarters assumes the costs for Regional clients.

- The CLP offers centralized, high-volume purchasing of analytical services, eliminating the duplication of effort for procurement, sample tracking, invoice processing, and analytical results compilation.
- The CLP offers competitive, low market per sample pricing for all projects and analytical services.

Method Flexibility

- Customers can request a variety of data turnaround options and detection limits.
- Customers can request new and/or additional methods for analysis to meet changing requirements and technological advances.

CLP services are becoming more flexible and responsive.

CLP Successes

The CLP has several successful products, programs, and activities that have helped to provide customers with analytical technical support services to achieve and maintain data of known and documented quality. These products, programs, and activities have vastly improved analytical response times and expanded the productivity of cleanup activities.

The CLP provides high-tech solutions to meet the customer's needs.

Development of the Data Assessment Tool (DAT)

The Analytical Services Branch (ASB) recognized the need for an analytical tool that would facilitate the rapid transfer and storage of electronic analytical data and would streamline the data validation process. To meet this challenge, the CLP developed DAT, a software-driven process designed to produce enhanced CLP deliverables and more usable reports.

For more information on the Data Assessment Tools, see the Data Assessment Tool (DAT) section of Chapter 2.

DAT allows Regional data users to electronically receive data that has already been assessed by this tool. DAT rapidly transfers electronic analytical data into any client database, forgoing the need for manual data entry by the Regions. Regional data validation has typically required manual data entry of post-review data.

Overall, DAT has dramatically improved data turnaround times, making it possible to transmit electronic data to the data validators and the ultimate customers [e.g., Regional Project Managers (RPMs), site assessors, and On-Scene Coordinators (OSCs)]. ASB can now provide data assessment reports to CLP customers within 24 - 48 hours of receipt of data.

Accommodation of Sample Volume with Fast Turnaround Times

During Fiscal Year 2006, a total of 86,124 samples were analyzed under the CLP. Approximately 16% of these samples were analyzed within a 7-day turnaround time, 25% were analyzed within a 14-day turnaround time, and 59% were analyzed within a 21-day turnaround time. The CLP can also provide Preliminary Results within 48 - 72 hours, depending on the type of analysis.

The CLP can accommodate a large volume of samples from multiple sites within a short time span. Turnaround times are available to meet the needs of the customer.

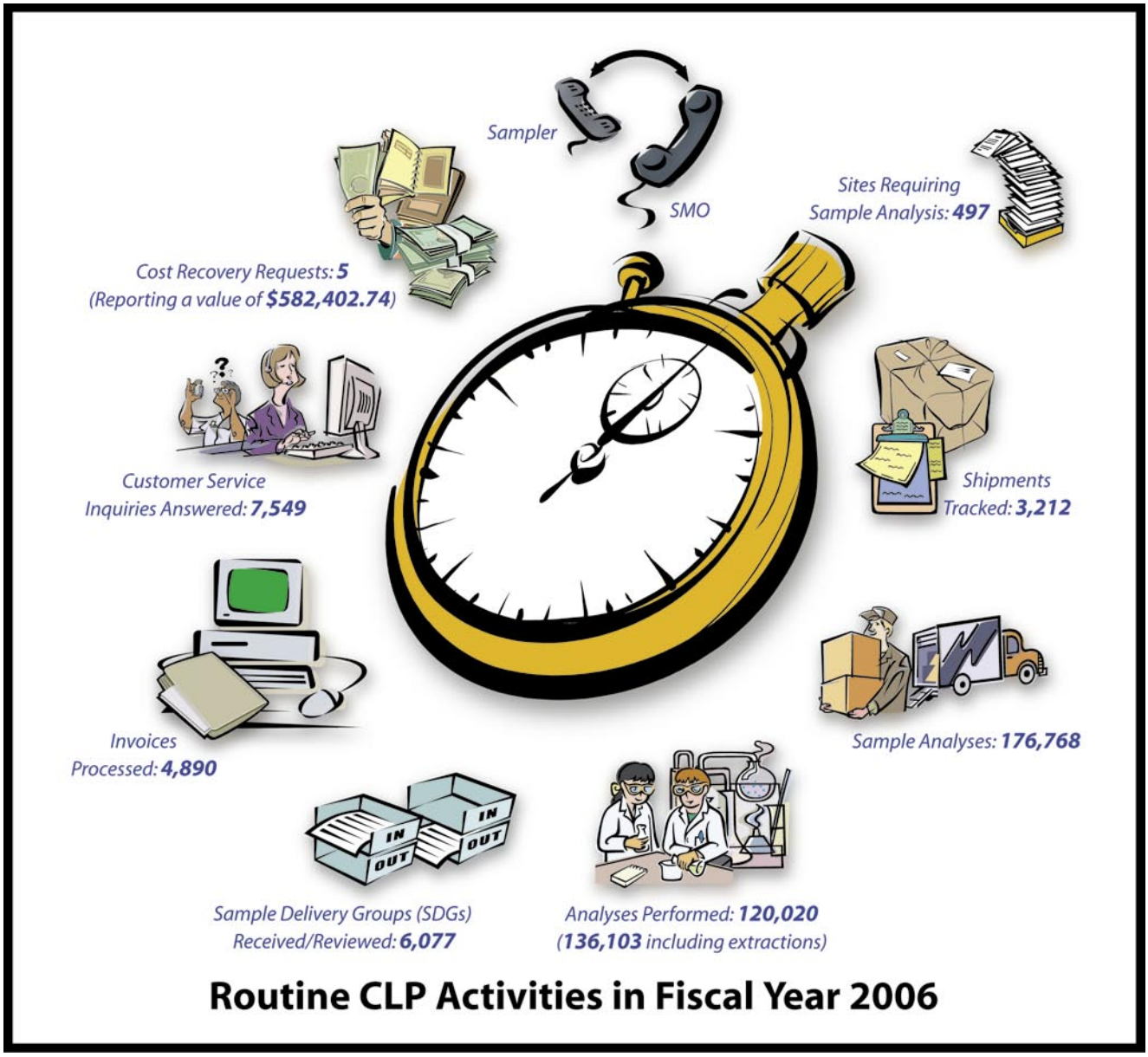
Provision of Brownfields Program

USEPA's Brownfields Program supports efforts to identify and assess potentially contaminated sites across the United States and conduct appropriate cleanup and/or release activities.

***"Brownfields"* are abandoned, idle, or under-used industrial and commercial facilities where expansion or redevelopment is complicated by real or perceived environmental contamination.**

The objective of this program is to quickly make these sites safe for reuse by addressing real or perceived risks. In Fiscal Year 2006, the CLP laboratories completed 51 separate projects involving the analysis of more than 1,311 field samples for 20 Brownfields sites.

The CLP provides Brownfields customers with certain advantages, such as comprehensive QC procedures, data turnaround options, and low market prices for high quality that may not be available through other analytical programs.



The CLP successfully supports its customers in its routine activities as well. Please see the figure above for data on routine CLP activities during Fiscal Year 2006.

Products and Services

CLP customers can combine analytical parameters and turnaround times to satisfy changing needs.

Data Analysis

The CLP provides analytical data that is used to help define the nature and extent of contamination at Superfund sites. This allows customers to:

- Assess priorities for response based on the risk to human health and the environment;
- Determine appropriate cleanup; and
- Determine when Remedial Actions (RAs) are complete.

CLP data is used in all stages of hazardous waste site investigation, including: site inspections; Hazard Ranking System (HRS) scoring; Remedial Investigation (RI) and Feasibility Study (FS); Remedial Design (RD); treatability; RA; operations and maintenance (O&M); and enforcement and litigation activities. The CLP requires that any data produced within the program be of known and documented quality.

Available Analytical Services

Currently, the CLP offers two Routine Analytical Services (RASs):

- Analysis of organic compounds in soils/sediment and water; and
- Analysis of inorganic compounds (including mercury) and cyanide in soils/sediment and water.

These types of analytical services ensure the CLP is able to meet the changing needs of its clients.

Upcoming Analytical Services and Products

The CLP is currently developing an updated inorganic analysis method, ILM06.X. Among other changes, ILM06.X will include a method for analyzing soils via Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and the addition of wipes and air filter matrices for total metals analyses.

Staged Electronic Data Deliverable (SEDD)

SEDD is an inter-agency effort to create a generic format for electronic delivery of analytical data for environmental programs. SEDD allows laboratories to meet current and future requirements for multiple programs without a complete overhaul of the laboratory EDD-producing system. For additional information about the advantages of using SEDD, please refer to the SEDD Web site.

Expert Technical and Administrative Support

The CLP's staff is comprised of experts in the fields of environmental chemistry, QA, contract management, and ADP support. The CLP has numerous resources within USEPA Regions, USEPA's own laboratories, and CLP contractors. These resources enable the CLP to address and overcome technical or operational issues for the CLP customer.

Currently Available Services:

- **Analysis of Inorganic Compounds (including Mercury) and Cyanide in Soil/Sediment and Water (ILM05.4).**

  Complete *Inorganic* Data Deliveries are available in 7, 14, and 21 days with Preliminary Results available within 72 hours.

- **Analysis of Organic Compounds including trace volatile, low/medium volatile, semivolatile, pesticide, and Aroclor target compounds in Water, and Soil/Sediment environmental samples (SOM01.1).**

  Complete *Organic* Data Deliveries are available in 7, 14, and 21 days with Preliminary Results available in 48 hours for volatiles and 72 hours for pesticides/Aroclors.

CLP Participants

Program Users

CLP customers currently include 10 USEPA Regions, State and Tribal governments, the United States Army Corps of Engineers (USACE), the United States Bureau of Reclamation (USBR), the United States Geological Survey (USGS), and various United States Territories. The CLP is available to any governmental party (except a PRP) who needs fast, reliable, environmental data of known and documented quality at reasonable prices.

The CLP is available to Federal, State, Territorial, and Tribal agencies [see Chapter 2 How to Access the Contract Laboratory Program (CLP)].

Program Providers

The CLP is operated by a team of government offices, support contractors, and environmental laboratories. The following offices comprise the CLP:

USEPA provides oversight of all program management and QA activities.

- ASB provides government oversight of all CLP activities to ensure that clients receive data of known and documented quality.
- USEPA Regional CLP Project Officers (CLP POs) and Regional Sample Control Center (RSCC) Coordinators provide program support and oversight activities on a day-to-day basis.
- The Sample Management Office (SMO) contractor provides program management (e.g., scheduling, contract compliance tools, and invoice tracking) under the direction of ASB.
- The Quality Assurance Technical Support (QATS) contractor provides QA/QC of CLP data [e.g., PE samples, and data tape audits] under the direction of ASB.
- CLP-contracted laboratories conduct sample analysis and provide data of known and documented quality.

CLP on the Internet

CLP customers can use the Internet to access information and reference documents such as:

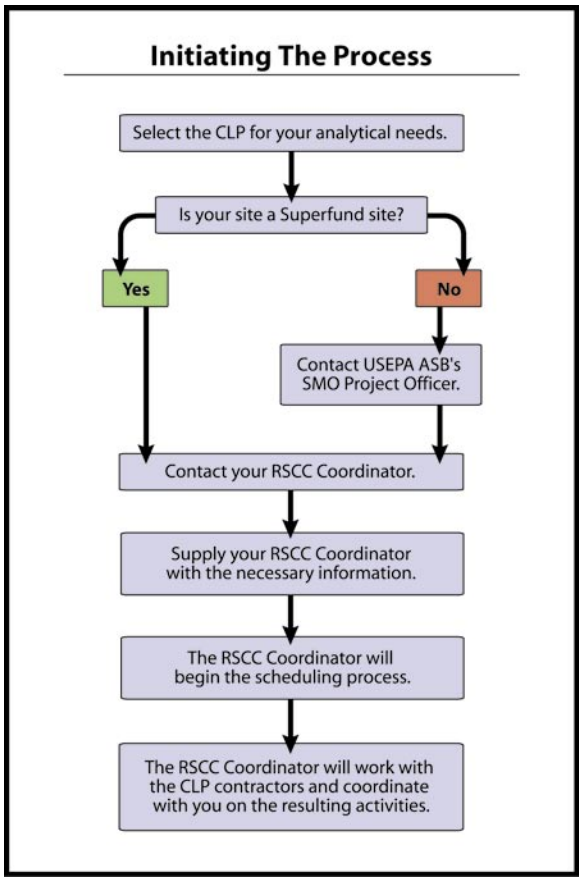
Information and a variety of guidance and method documents are available on the CLP Web site.

- Analytical Methods;
- Quick Reference Fact Sheets for the organic, inorganic, and organic low concentration analytical methods;
- Guidance Documents including National Functional Guidelines (NFGs) for data assessment and CLP Guidance for Field Samplers; and
- CLP & ASB Contacts.

Chapter 2
How to Access the Contract Laboratory Program (CLP)

CLP Services and Activities

This chapter provides guidance for initiating and using CLP services. It also provides information on several CLP-related software products available to CLP customers. The CLP offers numerous advantages to its CLP and non-CLP site customers (see the Benefits of the CLP section of Chapter 1) that may not be available in other programs. You can begin using CLP services by contacting the Analytical Services Branch (ASB).



Initiating CLP Analytical Services

The first step in accessing CLP services is determining if the CLP is the right program for your purposes. You must also determine if the site you wish to sample from is a Superfund site. If the site is part of Superfund, follow the steps listed below. If the site is not a Superfund site, proceed to Requesting CLP Analytical Services for a Non-Superfund Site in this chapter.

Requesting Routine CLP Analytical Services for a Superfund Site

Once you have decided to use the CLP, the next step is requesting analytical services. Current and new CLP customers may request Routine Analytical Services (RAS) through a USEPA Regional Sample Control Center (RSCC) Coordinator. The RSCC Coordinator schedules all CLP analysis requests through the Sample Management Office (SMO). SMO and the RSCC Coordinator work together during sampling events to ensure that all samples arrive at the laboratories as scheduled, and to resolve any issues that may arise during sample analysis. Each RSCC Coordinator is responsible for maintaining a working knowledge of current CLP Statements of Work (SOWs) to assist the customer in choosing the proper analytical method.

You must supply the RSCC Coordinator with the following information:

Each Region may have different steps for initiating analytical services. This document contains only a general description.

- Site name;
- Site location;
- Operable unit of the site where you want the sampling to take place (the operable unit is a specific portion of a whole site);
- Type(s) of analysis you require and any specific analytical requirements;
- Purpose of your sampling event [e.g., Site Assessment (SA), Remedial Design (RD), Remedial Action (RA)];
- Period of time during which the sampling will take place;

- Site identification numbers (e.g., CERCLIS ID, Site Spill ID);
- Data turnaround time(s) required for your project;
- Fax number for submission of Preliminary Results, if required; and
- Site-specific Quality Assurance Project Plan (QAPP).

The CLP requires "lead time" in order to secure laboratory space for sampling projects. You must contact your RSCC Coordinator to request RAS so that they will have ample time to contact SMO and set up scheduling by 3:00 PM Eastern Time Monday–Friday prior to the week of a sampling event.

There may be additional information required for your particular Region.

Requesting CLP Analytical Services for a Non-Superfund Site

The CLP also provides analytical and support activities to non-Superfund analyses customers through the transfer of funds from a non-Superfund program [e.g., Resource Conservation and Recovery Act (RCRA), Office of Water (OW), Brownfields]. Please contact the SMO Project Officer at ASB for additional information or to request CLP services for your non-Superfund site.

Non-Superfund Support

If you wish to utilize CLP services for non-Superfund activities, please contact the SMO Project Officer (PO) at ASB. ASB will facilitate the funds transfer process and direct the sample analysis request to the appropriate USEPA Regional office.

Determining the Appropriate SOW

The next step in accessing analytical services through the CLP is deciding which analytical service(s) best meets your needs. The CLP currently offers two SOWs for CLP inorganic and organic.

Both of the SOWs provide the technical and contractual conditions for laboratories to apply USEPA/CLP analytical methods for the isolation, detection, and quantitative measurement of the most common environmental pollutants. Contact the specified ASB Program Manager for further information.

The Inorganic SOW (ILM05.4)

The Inorganic SOW sets the requirements for the analysis of 23 metals (including mercury) and cyanide in water and soil/sediment samples. Inorganic analysis is conducted using ICP-MS, Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Atomic Absorption (AA), and colorimetric methods. Data is delivered in 7, 14, or 21 days. The customer may specify any of the three turnaround times when requesting CLP inorganic analytical services. Preliminary Results are available within 72 hours for all turnaround times. Requests can be made for all, some, or individual Metal analyses.

For a complete list of the inorganic target analytes and more information about the inorganic analytical service, including the upcoming ILM06.X, see the Multi-Media, Multi-Concentration, Inorganic Analytical Service for Superfund Fact Sheet.

The Organic SOW (SOM01.1)

The Organic SOW sets the requirements for the analysis of 52 volatile, 67 semivolatile, and 21 pesticide, and 9 Aroclor target compounds in water and soil/sediment samples. Organic compounds are analyzed using Gas Chromatography coupled with Mass Spectrometry (GC/MS) or with Electron Capture Detection (GC/ECD). Data delivery is available in 7, 14, or 21 days, any of which may be specified when requesting CLP organic analytical services. Preliminary Results are available within 48 hours for volatiles and 72 hours for semivolatiles, pesticides, and Aroclors for all turnaround times after receipt of each sample at the laboratory.

For a complete list of the organic volatile, semivolatile, pesticide, and Aroclor target compounds and more information about the organic analytical service, see the Multi-Media, Multi-Concentration, Organic Analytical (SOM01.1) Fact Sheet.

CLP Software Tools and Products

The CLP's commitment to quality does not end with data. In an effort to bring faster and more efficient services to our customers, the CLP has developed a number of software solutions that streamline data review and Quality Control (QC), Contract Compliance Screening (CCS), and administrative tasks, while promoting the sharing of analytical information.

Data Assessment Tool (DAT)

DAT is a software-driven process designed to produce enhanced CLP deliverables and more usable reports in a standard format. DAT incorporates CCS and data evaluation based on National Functional Guideline (NFG) to provide USEPA customers with PC-compatible reports and electronic files that can be transferred into client databases and programs for end-users, and to provide a complete CLP data assessment package. The electronic reports reduce the need for manual data entry and duplicate entry of information. All CLP customers receive data that has been processed through CLP data assessment tools within 24 - 48 hours after the laboratory data is received. The resultant spreadsheets are electronically delivered directly via email to the Region that requested the data.

DAT integrates CLP data review software and processes.

DAT does not include determination of data usability, qualification of data based on professional judgment, evaluation of data based on its intended use, or compliance with a site's Quality Assurance Project Plan (QAPP) or Sampling and Analysis Plan (SAP).

Field Operations Records Management System (FORMS) II Lite™

FORMS II Lite is designed to assist samplers with generating sample documentation and tracking samples during a sampling event. FORMS II Lite automates the creation and printing of labels and Traffic Report/Chain of Custody Records, thereby improving field time management and decreasing documentation errors. FORMS II Lite captures critical collection information in an electronic format early in the field sampling process.

FORMS II Lite automates routine tasks for the sampler and streamlines data collection.

FORMS II Lite enables field personnel to easily document, track, and transmit field sample information. In addition, by electronically capturing this information early in the tracking and reporting process, field sampling data is readily accessible for transmittal to RSCC Coordinators and other data users.

During Fiscal Year 2006, 64 sampling organizations used the FORMS II Lite software for sampling efforts with the 10 USEPA Regions for the CLP. The organizations include 20 States/territories and Tribes and the United States Army Corps of Engineers (USACE), United States Bureau of Reclamation, and United States Fish and Wildlife. In Fiscal Year 2006, FORMS II Lite was used to process 1,031 CLP Cases comprised of 5,516 shipments that contained a total of 69,947 samples.

Web-based Invoicing System (WIS)

WIS enables authorized CLP laboratories to electronically generate and submit invoices via the Internet. WIS provides access to a CLP database containing analytical data that the laboratory has previously submitted. Laboratories can access this submitted information and create an invoice based on the original analytical results.

Sample Delivery Group (SDG) Tracking System (STS)

The laboratory can use STS to track the status of analytical data from the delivery date to the invoice payment date. The laboratory uses their assigned Lab Code, name, and Password (as assigned by SMO) to access STS.

WIS automates laboratory submission of invoices.

Enforcement and Cost Recovery Support

The CLP has established detailed procedures and documentation to ensure that the sample data is tracked from the time of sample collection to introduction as evidence in legal proceedings. The CLP also provides documentation for program analytical costs to support Superfund Cost Recovery efforts. Cost Recovery is designed to assist CLP customers in recouping the CLP analytical and cleanup costs they have spent on a hazardous waste site.

Requesting Enforcement Support

Litigation procedures often necessitate the use of CLP data generated from the analysis of samples collected. The CLP offers a variety of services to support enforcement activities that include:

- Arranging for the delivery of all laboratory and evidence documentation relating to specific sample analyses;
- Augmenting customer resources for analytical data review; and
- Assisting in arranging for expert testimony by laboratory or CLP personnel.

The CLP provides litigation support and assists customers in recouping analytical and site cleanup costs.

Customer requests for enforcement support are initially coordinated through the SMO Project Officer at ASB. ASB will review the request and determine the appropriate CLP response, including the provision of USEPA Regional or contractor resources needed to respond to the request.

Requesting Cost Recovery Support

The CLP's Cost Recovery support normally consists of financial and analytical documentation. The following forms of documentation are available to support Cost Recovery requests:

- Reports that detail all CLP analytical and management costs associated with a site;
- Lists of CLP projects associated with a site;
- Sample analysis results; and
- Lists of each invoice associated with a particular site.

Non-standard ad-hoc reports also may be prepared if necessary. If necessary, the Cost Recovery personnel will coordinate efforts with the other USEPA offices or contractor resources in order to produce or acquire Cost Recovery documentation.

Appendix A
List of Acronyms

AA	Atomic Absorption
ADP	Automated Data Processing
ASB	Analytical Services Branch
ASF	Agency Standard Format
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CERCLIS	Comprehensive Environmental Response, Compensation, and Liability Information System
CCS	Contract Compliance Screening
CLP	Contract Laboratory Program
CLP PO	Contract Laboratory Program Project Officer
DART	Data Assessment Rapid Transmittal
DAT	Data Assessment Tool
FORMS II Lite	Field Operations Records Management System II Lite
GC/ECD	Gas Chromatography/Electron Capture Detection
GC/MS	Gas Chromatography/Mass Spectrometry
HRGC	High Resolution Gas Chromatography
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
NFG	National Functional Guidelines
NPL	National Priorities List
O&M	Operations & Maintenance
OSC	On-Scene Coordinator
OW	Office of Water
OSRTI	Office of Superfund Remediation and Technology Innovation
PE	Performance Evaluation
PO	Project Officer
PRP	Potentially Responsible Party
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QATS	Quality Assurance Technical Support
QC	Quality Control
RA	Remedial Action
RAS	Routine Analytical Service
RCRA	Resource Conservation and Recovery Act
RD	Remedial Design
RI	Remedial Investigation
RPM	Remedial Project Manager
RSCC	Regional Sample Control Center (USEPA Region)
SA	Site Assessment
SAP	Sampling and Analysis Plan
SDG	Sample Delivery Group
SEDD	Staged Electronic Data Deliverable
SMO	Sample Management Office
SOW	Statement of Work
STS	SDG Tracking System
USACE	United States Army Corps of Engineers
USBR	United States Bureau of Reclamation
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WebCCS	Web Contract Compliance Screening
WIS	Web-based Invoicing System

Appendix B
Glossary

Analyte: The element, ion, or parameter an analysis seeks to determine; the element of interest.

Analytical Services Branch (ASB): The USEPA center that directs the national Contract Laboratory Program (CLP).

Atomic Absorption (AA): A procedure for inorganic analysis based on the absorption of radiation by mercury vapor (Cold Vapor), flame, or graphite furnace.

Brownfields: Abandoned, idle, or under-used industrial and commercial facilities where expansion or redevelopment is complicated by real or perceived environmental contamination.

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA): First authorized by Congress in December 1980, and amended in 1986, CERCLA provided broad Federal authority to respond directly to the release or possible release or hazardous substances that may endanger human health or the environment. CERCLA also established a Trust Fund to provide for cleanup when no responsible party could be identified; hence, CERCLA is commonly referred to as "Superfund".

Contract Compliance Screening (CCS): The screening of electronic and hardcopy data deliverables for completeness and compliance with the contract. This screening is done under USEPA direction by the Sample Management Office (SMO) contractor.

Contract Laboratory Program (CLP): Supports the USEPA's Superfund effort by providing a range of chemical analytical services to produce environmental data of known and documented quality. This program is directed by the USEPA Analytical Services Branch (ASB).

Contract Required Quantitation Limit (CRQL): Minimum level of quantitation acceptable under the contract Statement of Work (SOW).

Cost Recovery: A legal process by which Potentially Responsible Parties (PRPs) that contributed to contamination at a Superfund site can be required to reimburse the Trust Fund for money spent during any aspect of cleanup actions by the Federal government.

Cost Recovery Request: A request issued by an Authorized Cost Recovery Requestor for detailed cost and sample documentation associated with a Superfund site.

Cyanide (Total): Cyanide ion and complex cyanide converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

Data Assessment Rapid Transmittal (DART): DART is an active notification system providing up-to-the-minute transmittal of the Contract Compliance Screening (CCS) and Computer Aided Data Review and Evaluation (CADRE) evaluation report data to Contract Laboratory Program (CLP) customers.

Data Assessment Tool (DAT): A software driven process that incorporates CCS, CADRE, and DART designed to produce enhanced CLP deliverables and more usable reports in a standard format.

Data Turnaround Time: The maximum length of time allowed for laboratories to submit analytical data to USEPA in order to avoid financial penalties (i.e., disincentives). Data turnaround time begins at the validated time of sample receipt (VTSR) at the laboratory.

Data Validation: Data validation is based on Region-defined criteria and limits, professional judgement of the data validator, and (if available) the Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP).

Feasibility Study (FS): A description and analysis of potential cleanup alternatives for a site such as one on the National Priorities List (NPL). The FS usually recommends selection of a cost-effective alternative. It usually starts as soon as the Remedial Investigation (RI) is underway. Together, they are commonly referred to as the "RI/FS".

Gas Chromatography (GC): The method used to separate analytes on a stationary phase within a chromatographic column. GC is frequently used with other instruments for analyzing organic compounds:

- *Mass Spectrometry: In volatile and semivolatile analysis, the compounds are detected by a Mass Spectrometer (MS).*
- *Electron Capture: In pesticide and Aroclor analysis, the compounds are detected by an Electron Capture Detector (ECD).*

Hazard Ranking System (HRS): A numerically-based screening system that uses information from initial, limited investigations to assess the relative potential of sites to pose a threat to human health or the environment. The HRS is the principal mechanism USEPA uses to place uncontrolled waste sites on the National Priorities List (NPL).

Hazardous Waste Site: A site contaminated with substances that can pose a substantial or potential hazard to human health or the environment.

Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES): A technique for the simultaneous or sequential multi-element determination of elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Characteristic atomic line emission spectra are produced by excitation of the sample in a radio frequency ICP.

Inductively Coupled Plasma - Mass Spectrometry (ICP-MS): A technique for the multi-element determination of elements in solution. The basis of the technique is the detection of atomic ions produced by an ICP and sorted by mass/charge ratio.

National Functional Guidelines (NFG): A document designed to offer guidance on inorganic, organic, and organic low concentration Contract Laboratory Program (CLP) analytical data evaluation and review.

National Priorities List (NPL): A list of sites for hazardous waste cleanup under the Superfund program.

Office of Solid Waste and Emergency Response (OSWER): The USEPA office that provides policy, guidance, and direction for the USEPA's OSWER programs, including Superfund.

Performance Evaluation (PE) Sample: A sample of known composition provided by USEPA for contractor analysis. Used by USEPA to evaluate contractor performance.

Pesticides: A pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. Pests can be insects, mice, and other animals, unwanted plants (weeds), fungi, or microorganisms like bacteria and viruses. Though often misunderstood to refer only to *insecticides*, the term pesticide also applies to herbicides, fungicides, and various other substances used to control pests. Under United States law, a pesticide is also any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant.

Quality Assurance (QA): An integrated system of management activities involving planning, implementation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality needed and expected by the customer.

Quality Control (QC): The overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality.

Quality Assurance Technical Support (QATS) Laboratory: A contractor-operated facility that provides Quality Assurance (QA) services operated under the QATS contract, awarded and administered by USEPA.

Remedial Action (RA): The construction or clean-up phase of a Superfund site cleanup.

Remedial Design: A phase of Remedial Action (RA) that follows the Remedial Investigation/Feasibility Study (RI/FS) and includes development of engineering drawings and specifications for a site cleanup.

Remedial Investigation (RI): An in-depth study designed to gather data needed to determine the nature and extent of contamination at a Superfund site, establish site cleanup criteria, identify preliminary alternatives for Remedial Action (RA), and support technical and cost analyses of alternatives. The RI is usually performed with the Feasibility Study (FS). Together they are usually referred to as the "RI/FS".

Remedial Project Manager (RPM): The USEPA or State official responsible for overseeing on-site studies and remediation activities.

Remedial Response: Long-term action that stops or substantially reduces a release or threat of a release of hazardous substances that is serious but not an immediate threat to public health.

Remediation: Cleanup or other methods used to remove or contain a toxic spill or hazardous materials from a Superfund site.

Routine Analytical Service (RAS): The standard inorganic, organic, and organic low concentration high volume, multi-component analyses available through the Contract Laboratory Program (CLP).

Regional Sample Control Center (RSCC) Coordinator: The RSCC Coordinator coordinates Regional sampling efforts.

Sample: A single, discrete portion of material to be analyzed, which is contained in single or multiple containers and identified by a unique sample number.

Sample Management Office (SMO): A contractor-operated facility that is awarded and administered by the USEPA. SMO provides management, operations, and administrative support to the Contract Laboratory Program (CLP).

Statement of Work (SOW): A document which specifies how laboratories analyze samples under a particular Contract Laboratory Program (CLP) analytical program.

Superfund: The program operated under the legislative authority of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Superfund Amendments and Reauthorization Act (SARA) that fund and carry out USEPA removal and remedial activities at hazardous waste sites. These activities include establishing the National Priorities List (NPL), investigating sites for inclusion on the list, determining their priority, and conducting and/or supervising cleanup and other remedial actions.

Superfund Amendments and Reauthorization Act (SARA): The 1986 amendment to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

Appendix C
List of Web References

Analysis of Metals (including Mercury) and Cyanide in Soil/Sediment and Water	http://www.epa.gov/superfund/programs/clp/inorg.htm
Analysis of Organic Compounds in Soil/ Sediment and Water	http://www.epa.gov/superfund/programs/clp/organic.htm
Analysis of Organic Compounds (to include trace volatile, low/medium volatile, semivolatile, pesticide, and Aroclor target compounds) in Water, and Soil/Sediment environmental samples	http://www.epa.gov/superfund/programs/clp/som1.htm
Analytical Methods	http://www.epa.gov/superfund/programs/clp/methods.htm
Brownfields Program	http://www.epa.gov/swerosps/bf/
CLP Web site	http://www.epa.gov/superfund/programs/clp/
CLP & ASB Contacts	http://www.epa.gov/superfund/programs/clp/contacts.htm
DAT	http://www.epa.gov/superfund/programs/clp/dat.htm
EPA Order 5360.1 A2	http://www.epa.gov/quality/qs-docs/5360-1.pdf
FORMS II Lite	http://www.epa.gov/superfund/programs/clp/f2lite.htm
Guidance Documents	http://www.epa.gov/superfund/programs/clp/guidance.htm
Introduction to the ASB CLP	http://www.epa.gov/superfund/programs/clp/guidance.htm
Low Concentration Organic Analytical Service for Superfund (Water matrix) Fact Sheet	http://www.epa.gov/superfund/programs/clp/facts.htm#lowcon
Multi-Media, Multi-Concentration, Organic Analytical Service for Superfund Fact Sheet	http://www.epa.gov/superfund/programs/clp/facts.htm#organic
Multi-Media, Multi-Concentration Inorganic Analytical Service for Superfund Fact Sheet	http://www.epa.gov/superfund/programs/clp/facts.htm#inorganic
Per Sample Pricing	http://www.epa.gov/superfund/programs/clp/prices.htm
Quick Reference Fact Sheets	http://www.epa.gov/superfund/programs/clp/facts.htm
RSCC Coordinator Contacts	http://www.epa.gov/superfund/programs/clp/rscclist.htm
SEDD	http://www.epa.gov/superfund/programs/clp/sedd.htm
STS	http://epasmoweb.dyncorp.com/sts/index.html
Target Compounds and Analyte List	http://www.epa.gov/superfund/programs/clp/target.htm
WIS	http://www.epa.gov/superfund/programs/clp/wis.htm

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) may be used to determine trace elements in solution. With the exception of groundwater samples, all aqueous and solid matrices need acid digestion prior to analysis. Groundwater samples that were prefiltered and acidified will not need acid digestion. Samples which are not digested need either an internal standard or should be matrix-matched with the standards. If either option is used, instrument software should be programmed to correct for intensity differences of the internal standard between samples and standards. Refer to Chapter Three, "Inorganic Analytes," for a listing of digestion procedures that may be appropriate. The following analytes have been determined by this method:

Element	Symbol	CAS Number	Element	Symbol	CAS Number
Aluminum	Al	7429-90-5	Mercury	Hg	7439-97-6
Antimony	Sb	7440-36-0	Molybdenum	Mo	7439-98-7
Arsenic	As	7440-38-2	Nickel	Ni	7440-02-0
Barium	Ba	7440-39-3	Phosphorus	P	7723-14-0
Beryllium	Be	7440-41-7	Potassium	K	7440-09-7
Boron	B	7440-42-8	Selenium	Se	7782-49-2
Cadmium	Cd	7440-43-9	Silica	SiO_2	7631-86-9
Calcium	Ca	7440-70-2	Silver	Ag	7440-22-4
Chromium	Cr	7440-47-3	Sodium	Na	7440-23-5
Cobalt	Co	7440-48-4	Strotium	Sr	7440-24-6
Copper	Cu	7440-50-8	Thallium	TI	7440-28-0
Iron	Fe	7439-89-6	Tin	Sn	7440-31-5
Lead	Pb	7439-92-1	Titanium	Ti	7440-32-6
Lithium	Li	7439-93-2	Vanadium	V	7440-62-2

Element	Symbol	CAS Number	Element	Symbol	CAS Number
Magnesium	Mg	7439-95-4	Zinc	Zn	7440-66-6
Manganese	Mn	7439-96-5			

CAS Number: Chemical Abstract Service Registry Number.

1.2 Table 1 lists all of the elements for which this method was validated. The sensitivity and the optimum and linear ranges for each element will vary with the wavelength, spectrometer, matrix, and operating conditions. Table 1 lists the recommended analytical wavelengths and estimated instrumental detection limits (IDLs) for the elements in clean aqueous matrices with insignificant background interferences. Other elements and matrices may be analyzed by this method if appropriate performance at the concentrations of interest (see Sec. 9.0) is demonstrated.

1.3 Analysts should clearly understand the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

1.4 Prior to employing this method, analysts are advised to consult the each preparative method that may be employed in the overall analysis (e.g., a 3000 series method) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, spectroscopists appropriately experienced and trained in the correction of spectral, chemical, and physical interferences described in this method. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using the appropriate sample preparation methods (see Chapter Three). When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis (refer to Sec. 1.1).

2.2 This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices.

2.3 Background correction is required for trace element determination. Background emission must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used should be as free as possible from spectral interference and should reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences identified in Sec. 4.0 should also be recognized and appropriate corrections made; tests for their presence are described in Secs. 9.6 and 9.7. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware. Also refer to the preparative methods to be used for discussions on interferences.

4.2 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.2.1 Compensation for background emission and stray light can usually be conducted by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

4.2.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must

be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single-element solutions are sufficient. However, for analytes such as iron that may be found in the sample at high concentration, a more appropriate test would be to use a concentration near the upper limit of the analytical range (refer to Chapter Three).

4.2.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by equations that correct for interelement contributions. Instruments that use equations for interelement correction require that the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive or positively biased determinations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Table 2. For multivariate calibration methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

4.2.4 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e., false positive analyte concentrations) arising from 100 mg/L of the interference element. For example, if As is to be determined at 193.696 nm in a sample containing approximately 10 mg/L of Al, according to Table 2, 100 mg/L of Al will yield a false positive signal for an As level equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al will result in a false positive signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. These data are provided for guidance purposes only. The interference effects must be evaluated for each individual instrument, since the intensities will vary.

4.2.5 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should continuously note that some samples may contain uncommon elements that could contribute spectral interferences.

4.2.6 The interference effects must be evaluated for each individual instrument, whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences (Table 2) as well as any other suspected

interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

4.2.7 Users of sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

4.2.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range, in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

4.2.9 When interelement corrections are applied, their accuracy should be verified daily, by analyzing spectral interference check solutions. The correction factors or multivariate correction matrices tested on a daily basis must be within the 20% criteria for five consecutive days. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change occurs, such as one in the torch, nebulizer, injector, or plasma conditions. Standard solutions should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

4.2.10 When interelement corrections are <u>not</u> used, verification of absence of interferences is required.

4.2.10.1 One method to verify the absence of interferences is to use a computer software routine for comparing the determinative data to established limits for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration (i.e., greater than the analyte instrument detection limit), or a false negative analyte concentration (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

4.2.10.2 Another way to verify the absence of interferences is to analyze an interference check solution which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is $20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

4.3 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, by using an internal standard, or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, by using a tip washer, by using a high solids nebulizer, or by diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance. This may be accomplished with the use of mass flow controllers. The test described in Sec. 9.9 will help determine if a physical interference is present.

4.4 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element. The analyst is encouraged to review the information in all of Sec. 4.0 to deal with the majority of interferences likely to be encountered when using this method.

4.4.1 The method of standard additions (MSA) can be useful when certain interferences are encountered. Refer to Method 7000 for a more detailed discussion of the MSA.

4.4.2 An alternative to using the method of standard additions is to use the internal standard technique, which involves adding one or more elements that are both not found in the samples and verified to not cause an interelement spectral interference to the samples, standards, and blanks. Yttrium or scandium are often used. The concentration should be sufficient for optimum precision, but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences, especially in high solids matrices.

4.5 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. Note the length of time necessary for reducing analyte signals to "equal to" or "less than" the lower limit of quantitation. Until the required rinse time is established, the rinse period should be at least 60 sec between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon the project-specific DQOs.

4.6 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative

values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of a measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

4.7 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

4.8 The calibration blank (Sec. 7.5.1) may restrict the sensitivity of the quantitation limit or degrade the precision and accuracy of the analysis. Consult Chapter Three for recommended precautions and procedures necessary in reducing the magnitude and variability of the calibration blank.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Concentrated nitric and hydrochloric acids are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a hood and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents. Hydrofluoric acid is a very toxic acid and penetrates the skin and tissues deeply if not treated immediately. Injury occurs in two stages; first, by hydration that induces tissue necrosis and then by penetration of fluoride ions deep into the tissue and by reaction with calcium. Boric acid and other complexing reagents and appropriate treatment agents should be administered immediately. Consult appropriate safety literature and have the appropriate treatment materials readily available prior to working with this acid. See Method 3052 for specific suggestions for handling hydrofluoric acid from a safety and an instrument standpoint.

5.3 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

5.4 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled argon plasma emission spectrometer

6.1.1 Computer-controlled emission spectrometer with background correction.

6.1.2 Radio-frequency generator compliant with FCC regulations.

6.1.3 Optional mass flow controller for argon nebulizer gas supply.

6.1.4 Optional peristaltic pump.

6.1.5 Optional autosampler.

6.1.6 Argon gas supply -- high purity.

6.2 Volumetric flasks of suitable precision and accuracy.

6.3 Volumetric pipets of suitable precision and accuracy.

7.0 REAGENTS AND STANDARDS

7.1 Reagent- or trace metals-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question, analyze for contamination. If the concentration of the contamination is less than the lower limit of quantitation, then the reagent is acceptable.

7.1.1 Hydrochloric acid (conc), HCl.

7.1.2 Hydrochloric acid HCl (1:1) -- Add 500 mL concentrated HCl to 400 mL water and dilute to 1 L in an appropriately- sized beaker.

7.1.3 Nitric acid (conc), HNO_3.

7.1.4 Nitric acid, HNO_3 (1:1) -- Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 L in an appropriately-sized beaker.

7.2 Reagent water -- All references to water in the method refer to reagent water, unless otherwise specified. Reagent water must be free of interferences.

7.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99% pure or greater). With several exceptions specifically noted, all salts must be dried for 1 hr at 105 EC.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the element fraction and the weight of the metal salt added.

NOTE: This section does not apply when analyzing samples prepared by Method 3040.

NOTE: The weight of the analyte is expressed to four significant figures for consistency with the weights below because rounding to two decimal places can contribute up to 4% error for some of the compounds.

For metals:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

For metal salts:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

7.3.1 Aluminum solution, stock, 1 mL = 1000 µg of Al

Dissolve 1.000 g of aluminum metal, accurately weighed to at least four significant figures, in an acid mixture of 4.0 mL of HCl (1:1) and 1.0 mL of concentrated $HN0_3$ in a beaker. Warm beaker slowly to dissolve the metal. When dissolution is complete, transfer solution quantitatively to a 1000-mL volumetric flask, add an additional 10.0 mL of HCl (1:1) and dilute to volume with reagent water.

7.3.2 Antimony solution, stock, 1 mL = 1000 µg of Sb

Dissolve 2.6673 g of $K(SbO)C_4H_4O_6$ (element fraction Sb = 0.3749), accurately weighed to at least four significant figures, in reagent water, add 10 mL of HCl (1:1), and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.3 Arsenic solution, stock, 1 mL = 1000 µg of As

Dissolve 1.3203 g of As_2O_3 (element fraction As = 0.7574), accurately weighed to at least four significant figures, in 100 mL of reagent water containing 0.4 g of NaOH. Acidify the solution with 2 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.4 Barium solution, stock, 1 mL = 1000 µg of Ba

Dissolve 1.5163 g of $BaCl_2$ (element fraction Ba = 0.6595), dried at 250 EC for 2 hr, accurately weighed to at least four significant figures, in 10 mL of reagent water with 1 mL of HCl (1:1). Add 10.0 mL of HCl (1:1) and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.5 Beryllium solution, stock, 1 mL = 1000 µg of Be

Do not dry. Dissolve 19.6463 g of $BeSO_4 4H_2O$ (element fraction Be = 0.0509), accurately weighed to at least four significant figures, in reagent water, add 10.0 mL of concentrated HNO_3, and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.6 Boron solution, stock, 1 mL = 1000 µg of B

Do not dry. Dissolve 5.716 g of anhydrous H_3BO_3 (B fraction = 0.1749), accurately weighed to at least four significant figures, in reagent water and dilute in a 1-L

volumetric flask with reagent water. Transfer immediately after mixing in a clean polytetrafluoroethylene (PTFE) bottle to minimize any leaching of boron from the glass container. The use of a non-glass volumetric flask is recommended to avoid boron contamination from glassware.

7.3.7 Cadmium solution, stock, 1 mL = 1000 µg of Cd

Dissolve 1.1423 g of CdO (element fraction Cd = 0.8754), accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Heat to increase the rate of dissolution. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.8 Calcium solution, stock, 1 mL = 1000 µg of Ca

Suspend 2.4969 g of $CaCO_3$ (element Ca fraction = 0.4005), dried at 180 EC for 1 hr before weighing, accurately weighed to at least four significant figures, in reagent water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.9 Chromium solution, stock, 1 mL = 1000 µg of Cr

Dissolve 1.9231 g of CrO_3 (element fraction Cr = 0.5200), accurately weighed to at least four significant figures, in reagent water. When dissolution is complete, acidify with 10 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.10 Cobalt solution, stock, 1 mL = 1000 µg of Co

Dissolve 1.000 g of cobalt metal, accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL of HCl (1:1) and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.11 Copper solution, stock, 1 mL = 1000 µg of Cu

Dissolve 1.2564 g of CuO (element fraction Cu = 0.7989), accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.12 Iron solution, stock, 1 mL = 1000 µg of Fe

Dissolve 1.4298 g of Fe_2O_3 (element fraction Fe = 0.6994), accurately weighed to at least four significant figures, in a warm mixture of 20 mL HCl (1:1) and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.13 Lead solution, stock, 1 mL = 1000 µg of Pb

Dissolve 1.5985 g of $Pb(NO_3)_2$ (element fraction Pb = 0.6256), accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.14 Lithium solution, stock, 1 mL = 1000 µg of Li

Dissolve 5.3248 g of lithium carbonate (element fraction Li = 0.1878), accurately weighed to at least four significant figures, in a minimum amount of HCl (1:1) and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.15 Magnesium solution, stock, 1 mL = 1000 µg of Mg

Dissolve 1.6584 g of MgO (element fraction Mg = 0.6030), accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL of (1:1) concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.16 Manganese solution, stock, 1 mL = 1000 µg of Mn

Dissolve 1.00 g of manganese metal, accurately weighed to at least four significant figures, in acid mixture (10 mL of concentrated HCl and 1 mL of concentrated HNO_3) and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.17 Mercury solution, stock, 1 mL = 1000 µg of Hg

WARNING: Do not dry, **mercury is a highly toxic element**.

Dissolve 1.354 g of $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL of concentrated HNO_3 and dilute to volume in 1000-mL volumetric flask with reagent water.

7.3.18 Molybdenum solution, stock, 1 mL = 1000 µg of Mo

Dissolve 1.7325 g of $(NH_4)_6Mo_7O_{24}·4H_2O$ (element fraction Mo = 0.5772), accurately weighed to at least four significant figures, in reagent water and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.19 Nickel solution, stock, 1 mL = 1000 µg of Ni

Dissolve 1.000 g of nickel metal, accurately weighed to at least four significant figures, in 10.0 mL of hot concentrated HNO_3, cool, and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.20 Phosphate solution, stock, 1 mL = 1000 µg of P

Dissolve 4.3937 g of anhydrous KH_2PO_4 (element fraction P = 0.2276), accurately weighed to at least four significant figures, in water. Dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.21 Potassium solution, stock, 1 mL = 1000 µg of K

Dissolve 1.9069 g of KCl (element fraction K = 0.5244) dried at 110 EC, accurately weighed to at least four significant figures, in reagent water, and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.22 Selenium solution, stock, 1 mL = 1000 µg of Se

Do not dry. Dissolve 1.6332 g of H_2SeO_3 (element fraction Se = 0.6123), accurately weighed to at least four significant figures, in reagent water and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.23 Silica solution, stock, 1 mL = 1000 µg SiO_2

Do not dry. Dissolve 2.964 g of NH_4SiF_6, accurately weighed to at least four significant figures, in 200 mL (1:20) HCl with heating at 85 EC to dissolve the solid. Let solution cool and dilute to volume in a 1000-mL volumetric flask with reagent water. Store in a PTFE container and protect from light.

7.3.24 Silver solution, stock, 1 mL = 1000 µg of Ag

Dissolve 1.5748 g of $AgNO_3$ (element fraction Ag = 0.6350), accurately weighed to at least four significant figures, in water and 10 mL of concentrated HNO_3. Dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.25 Sodium solution, stock, 1 mL = 1000 µg of Na

Dissolve 2.5419 g of NaCl (element fraction Na = 0.3934), accurately weighed to at least four significant figures, in reagent water. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.26 Strontium solution, stock, 1 mL = 1000 µg of Sr

Dissolve 2.4154 g of strontium nitrate ($Sr(NO_3)_2$) (element fraction Sr = 0.4140), accurately weighed to at least four significant figures, in a 1000-mL flask containing 10 mL of concentrated HCl and 700 mL of reagent water. Dilute to volume with reagent water.

7.3.27 Thallium solution, stock, 1 mL = 1000 µg of Tl

Dissolve 1.3034 g of $TlNO_3$ (element fraction Tl = 0.7672), accurately weighed to at least four significant figures, in reagent water. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.28 Tin solution, stock, 1 mL = 1000 µg of Sn

Dissolve 1.000 g of Sn shot, accurately weighed to at least 4 significant figures, in 200 mL of HCl (1:1) with heating to dissolve the metal. Let solution cool and dilute with HCl (1:1) in a 1000-mL volumetric flask.

7.3.29 Vanadium solution, stock, 1 mL = 1000 µg of V

Dissolve 2.2957 g of NH_4VO_3 (element fraction V = 0.4356), accurately weighed to at least four significant figures, in a minimum amount of concentrated HNO_3. Heat to dissolve the metal. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.30 Zinc solution, stock, 1 mL = 1000 µg of Zn

Dissolve 1.2447 g of ZnO (element fraction Zn = 0.8034), accurately weighed to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.31 Yttrium solution, stock, 1 mL = 1000 µg of Y

Dissolve 4.3081 g of $Y(NO_3)_3$0$6H_2$0 (element fraction Y = 0.2321), accurately weighed to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.4 Mixed calibration standard solutions

Prepare mixed calibration standard solutions (see Table 3) by combining appropriate volumes of the stock solutions above in volumetric flasks. Add the appropriate types and volumes of acids so that the standards are matrix-matched with the sample digestates. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. For all intermediate and working standards, especially low level standards (i.e., <1 ppm), stability must be demonstrated prior to use. Freshly-mixed standards should be prepared, as needed, with the realization that concentration can change with age. (Refer to Sec. 10.3.1 for guidance on determining the viability of standards.) Some typical calibration standard combinations are listed in Table 3.

NOTE: If the addition of silver to the recommended acid combination initially results in a precipitate, then add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver is stable under these conditions in a water matrix for 30 days, if protected from the light. Higher concentrations of silver require additional HCl.

7.5 Blanks

Two types of blanks are required for the analysis of samples prepared by any method other than Method 3040. The calibration blank is used in establishing the analytical curve and the method blank is used to identify possible contamination resulting from either the reagents (acids) or the equipment used during sample processing including filtration.

7.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial (ICB) and continuing calibration blank (CCB) determinations.

7.5.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis (refer to Sec. 9.5).

7.6 The initial calibration verification (ICV) standard is prepared by the analyst (or a purchased second source reference material) by combining compatible elements from a

standard source different from that of the calibration standard, and at concentration near the midpoint of the calibration curve (see Sec. 10.3.3 for use). This standard may also be purchased.

7.7 The continuing calibration verification (CCV) standard should be prepared in the same acid matrix using the same standards used for calibration, at a concentration near the mid-point of the calibration curve (see Sec. 10.3.4 for use).

7.8 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to Chapter Three, "Inorganic Analytes."

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to the 3000 series method to be used (e.g., Method 3005, 3010, 3015, 3031, 3040, 3050, 3051, or 3052) for appropriate QC procedures to ensure the proper operation of the various sample preparation techniques.

9.3 Instrument detection limits (IDLs) are useful means to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limit of quantitation, nor should they be used in establishing this limit. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation, however, it should be understood that the lower limit of quantitation needs to be verified according to the guidance in Sec. 10.0.

IDLs in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least every three months or at a project-specific designated frequency and kept with the instrument log book.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation (a 3000 series method) and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.5 Dilute and reanalyze samples that exceed the linear dynamic range or use an alternate, less sensitive calibration for which quality control data are already established.

9.6 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process. A method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method, and then carried through the appropriate steps of the analytical process. These steps may include, but are not limited to, prefiltering, digestion, dilution, filtering, and analysis. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank would be considered acceptable.

In the absence of project-specific DQOs, if the blank is less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples after the last acceptable method blank should be reprepared and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level or other DQOs, then the sample data may be used despite the contamination of the method blank.

9.7 Laboratory control sample (LCS)

For each batch of samples processed, at least one LCS must be carried throughout the entire sample preparation and analytical process. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory derived limit developed through the use of historical analyses. In the absence of project-specific or historical data generated criteria, this limit should be set at ± 20% of the spiked value. Acceptance limits derived from historical data should be no wider that ± 20%. If the laboratory control sample is not acceptable, then the laboratory control sample should be re-run once and, if still unacceptable, all samples after the last acceptable laboratory control sample should be reprepared and reanalyzed.

Concurrent analyses of standard reference materials (SRMs) containing known amounts of analytes in the media of interest are recommended and may be used as an LCS. For solid SRMs, 80 -120% accuracy may not be achievable and the manufacturer's established acceptance criterion should be used for soil SRMs.

9.8 Matrix spike, unspiked duplicate, or matrix spike duplicate (MS/Dup or MS/MSD)

Documenting the effect of the matrix, for a given preparation batch consisting of similar sample characteristics, should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch or as noted in the project-specific planning documents. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

For each batch of samples processed, at least one MS/Dup or MS/MSD sample set should be carried throughout the entire sample preparation and analytical process as described in Chapter One. MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/Dup or MS/MSD is used to document the bias and precision of a method in a given sample matrix.

Refer to Chapter One for definitions of bias and precision, and for the proper data reduction protocols. MS/MSD samples should be spiked at the same level, and with the same spiking material, as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory-derived limit developed through the use of historical analyses per matrix type analyzed. In the absence of project-specific or historical data generated criteria, these limits should be set at ± 25% of the spiked value for accuracy and 20 relative percent difference (RPD) for precision. Acceptance limits derived from historical data should be no wider that ± 25% for accuracy and 20% for precision. Refer to Chapter One for additional guidance. If the bias and precision indicators are outside the laboratory control limits, if the percent recovery is less than 75% or greater than 125%, or if the relative percent difference is greater than 20%, then the interference test discussed in Sec. 9.9 should be conducted.

9.8.1 The relative percent difference between spiked matrix duplicate or unspiked duplicate determinations is to be calculated as follows:

$$RPD = \frac{*D_1 - D_2*}{\left(\frac{*D_1 + D_2*}{2}\right)} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (spiked or unspiked duplicate).

9.8.2 The spiked sample or spiked duplicate sample recovery should be within ± 25% of the actual value, or within the documented historical acceptance limits for each matrix.

9.9 If less than acceptable accuracy and precision data are generated, additional quality control tests (Secs. 9.9.1 and 9.9.2) are recommended prior to reporting concentration data for the elements in this method. At a minimum, these tests should be performed with each batch of samples prepared/analyzed with corresponding unacceptable data quality results. These tests will then serve to ensure that neither positive nor negative interferences are affecting the measurement of any of the elements or distorting the accuracy of the reported values. If matrix effects are confirmed, the laboratory should consult with the data user when feasible for possible corrective actions which may include the use of alternative or modified test procedures so that the analysis is not impacted by the same interference.

9.9.1 Post digestion spike addition

If the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. Otherwise, another sample from the same preparation should be used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 80% to 120% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. If this spike fails, then the dilution test (Sec. 9.9.2) should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed.

9.9.2 Dilution test

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, then a chemical or physical interference effect should be suspected.

CAUTION: If spectral overlap is suspected, then the use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

9.10 Ultra-trace analysis requires the use of clean chemistry preparation and analysis techniques. Several suggestions for minimizing analytical blank contamination are provided in Chapter Three.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Set up the instrument with proper operating parameters established as detailed below. The instrument should be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration). For operating conditions, the analyst should follow the instructions provided by the instrument manufacturer.

10.1.1 Before using this procedure to analyze samples, data should be available documenting the initial demonstration of performance. The required data should document the location of the background points being used for correction; the determination of the linear dynamic ranges; a demonstration of the desired method sensitivity and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. These data should be generated using the same instrument, operating conditions, and calibration routine to be used for sample analysis. These data should be kept on file and be available for review by the data user or auditor.

10.1.2 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference corrections need to be established for each individual target analyte on each particular instrument. All measurements (both target analytes and constituents which interfere with the target analytes) need to be within the instrument linear range where the correction equations are valid.

10.1.3 The lower limits of quantitation should be established for all wavelengths utilized for each type of matrix analyzed and for each preparation method used and for each instrument. These limits are considered the lowest reliable laboratory reporting concentrations and should be established from the lower limit of quantitation check sample and then confirmed using either the lowest calibration point or from a low-level calibration check standard.

10.1.3.1 Lower limit of quantitation check sample

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. Ideally, this check sample and the low-level calibration verification standard will be prepared at the same concentrations with the only difference being the LLQC sample is carried through the entire preparation and analytical procedure. Lower limits of quantitation are verified when all analytes in the LLQC sample are detected within ± 30% of their true value. This check should be used to both establish and confirm the lowest quantitation limit.

10.1.3.2 The lower limits of quantitation determination using reagent water represents a best case situation and does not represent possible matrix effects of real-world samples. For the application of lower limits of quantitation on a project-specific basis with established data quality objectives, low-level matrix-specific spike studies may provide data users with a more reliable indication of the actual method sensitivity and minimum detection capabilities.

10.1.4 Specific recommended wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions are not provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality for the specific project and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a given task.

For radial viewed plasma, operating conditions for aqueous solutions usually vary from:

- 1100 to 1200 watts forward power,
- 14 to 18 mm viewing height,
- 15 to 19 L/min argon coolant flow,
- 0.6 to 1.5 L/min argon nebulizer flow,
- 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 sec per wavelength peak for sequential instruments and a rinse time of 10 sec per replicate with a 1 sec per replicate read time for simultaneous instruments.

For an axial viewed plasma, the conditions will usually vary from:

- 1100 to 1500 watts forward power,
- 15 to 19 L/min argon coolant flow,
- 0.6 to 1.5 L/min argon nebulizer flow,
- 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 sec per wavelength peak for sequential instruments and a rinse time of 10 sec per replicate with a 1 sec per replicate read time for simultaneous instruments.

One recommended way to achieve repeatable interference correction factors is to adjust the argon aerosol flow to reproduce the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively. This can be performed before daily calibration and after the instrument warm-up period.

10.1.5 Plasma optimization

The plasma operating conditions need to be optimized prior to use of the instrument. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure. This routine is not required on a daily basis, it is only required when first setting up a new instrument, or following a change in operating conditions. The following procedure is recommended, or follow the manufacturer's recommendations.

10.1.5.1 Ignite the radial plasma and select an appropriate incident radio frequency (RF) power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. While aspirating a 1000 µg/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

10.1.5.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of a calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate. Set the peristaltic pump to deliver that rate in a steady even flow.

10.1.5.3 Profile the instrument to align it optically as it will be used during analysis. The following procedure is written for vertical optimization in the radial mode, but it also can be used for horizontal optimization.

Aspirate a solution containing 10 µg/L of several selected elements. As, Se, Tl, and Pb are the least sensitive of the elements and most in need of optimization. However, other elements may be used, based on the judgement of the analyst or project-specific protocols. (V, Cr, Cu, Li and Mn also have been used with success.) Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the load coil. (This region of the plasma is referred to as the analytical zone.) Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the

best net intensity ratios for the elements analyzed or the highest intensity ratio for the least sensitive element. For optimization in the axial mode, follow the instrument manufacturer's instructions.

10.1.5.4 The instrument operating conditions finally selected as being optimum should provide the most appropriate instrument responses that correlate to the desired target analyte sensitivity while meeting the minimum quality control criteria noted in this method or as specified in the project-specific planning documents.

10.1.5.5 If the instrument operating conditions, such as incident power or nebulizer gas flow rate, are changed, or if a new torch injector tube with a different orifice internal diameter is installed, then the plasma and viewing height should be re-optimized.

10.1.5.6 After completing the initial optimization of operating conditions, and before analyzing samples, the laboratory should establish and initially verify an interelement spectral interference correction routine to be used during sample analysis with interference check standards that closely match the anticipated properties of the expected sample matrices, i.e., for saltwater type matrices the interference check standard should contain components that match the salinities of the proposed sample matrix. A general description of spectral interferences and the analytical requirements for background correction, in particular, are discussed in Sec. 4.2.

10.1.5.7 Before daily calibration, and after the instrument warmup period, the nebulizer gas flow rate should be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines, the nebulizer gas flow rate should be the same (< 2% change) from day to day.

10.2 For operation with organic solvents, the use of the auxiliary argon inlet is recommended, as is the use of solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power, to obtain stable operation and precise measurements.

10.3 All analyses require that a calibration curve be prepared to cover the appropriate concentration range based on the intended application and prior to establishing the linear dynamic range. Usually, this means the preparation of a calibration blank and mixed calibration standard solutions (Sec. 7.4), the highest of which would not exceed the anticipated linear dynamic range of the instrument. Check the instrument calibration by analyzing appropriate QC samples as follows.

10.3.1 Individual or mixed calibration standards should be prepared from known primary stock standards every six months to one year as needed based on the concentration stability as confirmed from the ICV analyses. The analysis of the ICV, which is prepared from a source independent of the calibration standards, is necessary to verify the instrument performance once the system has been calibrated for the desired target analytes. It is recommended that the ICV solution be obtained commercially as a certified traceable reference material such that an expiration date can be assigned. Alternately, the ICV solution can be prepared from an independent source on an as needed basis depending on the ability to meet the calibration verification criteria. If the ICV analysis is outside of the acceptance criteria, at a minimum the calibration standards must be

prepared fresh and the instrument recalibrated prior to beginning sample analyses. Consideration should also be given to preparing fresh ICV standards if the new calibration cannot be verified using the existing ICV standard.

NOTE: This method describes the use of both a low-level and mid-level ICV standard analysis. For purposes of verifying the initial calibration, only the mid-level ICV needs to be prepared from a source other than the calibration standards.

10.3.1.1 The calibration standards should be prepared using the same type of acid or combination of acids and at similar concentrations as will result in the samples following processing.

10.3.1.2 The response of the calibration blank should be less than the response of the typical laboratory lower limit of quantitation for each desired target analyte. Additionally, if the calibration blank response or continuing calibration blank verification is used to calculate a theoretical concentration, this value should be less than the level of acceptable blank contamination as specified in the approved quality assurance project planning documents. If this is not the case, the reason for the out-of-control condition must be found and corrected, and the sample analyses should not proceed or the previous ten samples should be reanalyzed.

10.3.2 For the initial and daily instrument operation, calibrate the system according to the instrument manufacturer's guidelines using the mixed calibration standards as noted in Sec. 7.4. The calibration curve should be prepared daily with a minimum of a calibration blank and a single standard at the appropriate concentration to effectively outline the desired quantitation range. The resulting curve should then be verified with mid-level and low-level initial calibration verification standards as outlined in Sec. 10.3.3.

Alternatively, the calibration curve can be prepared daily with a minimum of a calibration blank and three non-zero standards that effectively bracket the desired sample concentration range. If low-level as compared to mid- or high-level sample concentrations are expected, the calibration standards should be prepared at the appropriate concentrations in order to demonstrate the instrument linearity within the anticipated sample concentration range. For all multi-point calibration scenarios, the lowest non-zero standard concentration should be considered the lower limit of quantitation.

NOTE: Regardless of whether the instrument is calibrated using only a minimum number of standards or with a multi-point curve, the upper limit of the quantitation range may exceed the highest concentration calibration point and can be defined as the "linear dynamic" range, while the lower limit can be identified as the "lower limit of quantitation limit" (LLQL) and will be either the concentration of the lowest calibration standard (for multi-point curves) or the concentration of the low level ICV/CCV check standard. Results reported outside these limits would not be recommended unless they are qualified as estimated. See Sec. 10.4 for recommendations on how to determine the linear dynamic range. The guidance in this section and Sec. 10.3.3 provide options for defining the lower limit of quantitation.

10.3.2.1 To be considered acceptable, the calibration curve should have a correlation coefficient greater than or equal to 0.998. When using a multi-point calibration curve approach, every effort should be made to attain an acceptable correlation coefficient based on a linear response for each desired

target analyte. If the recommended linear response cannot be attained using a minimum of three non-zero calibration standards, consideration should be given to adding more standards, particularly at the lower concentrations, in order to better define the linear range and the lower limit of quantitation. Conversely, the extreme upper and lower calibration points may be removed from the multi-point curve as long as three non-zero points remain such that the linear range is narrowed and the non-linear upper and/or lower portions are removed. As with the single point calibration option, the multi-point calibration should be verified with both a mid- and low-level ICV standard analysis using the same 90 - 110% and 70 - 130% acceptance criteria, respectively.

10.3.2.2 Many instrument software packages allow multi-point calibration curves to be "forced" through zero. It is acceptable to use this feature, provided that the resulting calibration meets the acceptance criteria, and can be verified by acceptable QC results. Forcing a regression through zero should NOT be used as a rationale for reporting results below the calibration range defined by the lowest standard in the calibration curve.

10.3.3 After initial calibration, the calibration curve should be verified by use of an initial calibration verification (ICV) standard analysis. At a minimum, the ICV standard should be prepared from an independent (second source) material at or near the mid-range of the calibration curve. The acceptance criteria for this mid-range ICV standard should be ±10% of its true value. Additionally, a low-level initial calibration verification (LLICV) standard should be prepared, using the same source as the calibration standards, at a concentration expected to be the lower limit of quantitation. The suggested acceptance criteria for the LLICV is ± 30% of its true value. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results should be qualified and would be considered estimated values. Once the calibration acceptance criteria is met, either the lowest calibration standard or the LLICV concentration can be used to demonstrate the lower limit of quantitation and sample results should not be quantitated below this lowest standard. In some cases depending on the stated project data quality objectives, it may be appropriate to report these results as estimated, however, they should be qualified by noting the results are below the lower limit of quantitation. Therefore, the laboratory's quantitation limit cannot be reported lower than either the LLICV standard used for the single point calibration option or the low calibration and/or verification standard used during initial multi-point calibration. If the calibration curve cannot be verified within these specified limits for the mid-range ICV and LLICV analyses, the cause needs to be determined and the instrument recalibrated before samples are analyzed. The analysis data for the initial calibration verification analyses should be kept on file with the sample analysis data.

10.3.4 Both the single and multi-point calibration curves should be verified at the end of each analysis batch and after every 10 samples by use of a continuing calibration verification (CCV) standard and a continuing calibration blank (CCB). The CCV should be made from the same material as the initial calibration standards at or near the mid-range concentration. For the curve to be considered valid, the acceptance criteria for the CCV standard should be ±10% of its true value and the CCB should contain target analytes less than the established lower limit of quantitation for any desired target analyte. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable CCV/CCB must be reanalyzed. The analysis data for the CCV/CCB should be kept on file with the sample analysis data.

The low-level continuing calibration verification (LLCCV) standard should also be analyzed at the end of each analysis batch. A more frequent LLCCV analysis, i.e., every 10 samples, may be necessary if low-level sample concentrations are anticipated and the system stability at low end of the calibration is questionable. In addition, the analysis of a LLCCV on a more frequent basis will minimize the number of samples for re-analysis should the LLCCV fail if only run at the end of the analysis batch. The LLCCV standard should be made from the same source as the initial calibration standards at the established lower limit of quantitation as reported by the laboratory. The acceptance criteria for the LLCCV standard should be ± 30% of its true value. If the calibration cannot be verified within these specified limits, the analysis of samples containing the affected analytes at similar concentrations cannot continue until the cause is determined and the LLCCV standard successfully analyzed. The instrument may need to be recalibrated or the lower limit of quantitation adjusted to a concentration that will ensure a compliant LLCCV analysis. The analysis data for the LLCCV standard should be kept on file with the sample analysis data.

10.4 The linear dynamic range is established when the system is first setup, or whenever significant instrument components have been replaced or repaired, and on an as needed basis only after the system has been successfully calibrated using either the single or multi-point standard calibration approach.

The upper limit of the linear dynamic range needs to be established for each wavelength utilized by determining the signal responses from a minimum of three, preferably five, different concentration standards across the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. A standard at the upper limit should be prepared, analyzed and quantitated against the normal calibration curve. The calculated value should be within 10% (±10%) of the true value. New upper range limits should be determined whenever there is a significant change in instrument response. At a minimum, the range should be checked every six months. The analyst should be aware that if an analyte that is present above its upper range limit is used to apply an interelement correction, the correction may not be valid and those analytes where the interelement correction has been applied may be inaccurately reported.

NOTE: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self-absorption effects. These curves may be used if the instrument allows it; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.998 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and/or recalculated on a daily basis using the same calibration verification QC checks as a linear calibration curve. Since these curves are much more sensitive to changes in operating conditions than the linear lines, they should be checked whenever there have been moderate equipment changes. Under these calibration conditions, quantitation is not acceptable above or below the calibration standards. Additionally, a non-linear curve should be further verified by calculating the actual recovery of each calibration standard used in the curve. The acceptance criteria for the calibration standard recovery should be ±10% of its true value for all standards except the lowest concentration. A recovery of ± 30% of its true value should be achieved for the lowest concentration standard.

10.5 The analyst should (1) verify that the instrument configuration and operating conditions satisfy the project-specific analytical requirements and (2) maintain quality control data that demonstrate and confirm the instrument performance for the reported analytical results.

11.0 PROCEDURE

11.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater and other aqueous samples designated for a dissolved metal determination which have been prefiltered and acidified will not need acid digestion. However, all associated QC samples (i.e., method blank, LCS and MS/MSD) must undergo the same filtration and acidification procedures. Samples which are not digested must either use an internal standard or be matrix-matched with the standards. Solubilization and digestion procedures are presented in Chapter Three, "Inorganic Analytes."

11.2 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Sec. 7.4. Flush the system with the calibration blank (Sec. 7.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve should be prepared as detailed in Sec. 10.3.2.

11.3 Regardless of whether the initial calibration is performed using a single high standard and the calibration blank or the multi-point option, the laboratory should analyze an LLCCV (Sec. 10.3.4). For all analytes and determinations, the laboratory must analyze an ICV and LLICV (Sec. 10.3.3) immediately following daily calibration. It is recommended that a CCV LLCCV, and CCB (Sec. 10.3.4) be analyzed after every ten samples and at the end of the analysis batch.

11.4 Rinse the system with the calibration blank solution (Sec. 7.5.1) before the analysis of each sample. The rinse time will be one minute. Each laboratory may establish a reduction in this rinse time through a suitable demonstration. Analyze the samples and record the results.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The quantitative values must be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values. All results should be reported with up to three significant figures.

12.2 If appropriate, or required, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Digest Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample

$$S = \frac{\%\ \text{Solids}}{100}$$

Calculations must include appropriate interference corrections (see Sec. 4.2 for examples), internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

12.3 Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 In an EPA round-robin study, seven laboratories applied the ICP technique to acid-digested water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations. These data are provided for guidance purposes only.

13.3 Performance data for aqueous solutions and solid samples from a multilaboratory study are provided in Tables 5 and 6. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste*

Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St. NW, Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. C. L. Jones, *et al*., "An Interlaboratory Study of Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010 and Digestion Method 3050," EPA-600/4-87-032, U.S. Environmental Protection Agency, Las Vegas, NV, 1987.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables referenced by this method. A flow diagram of the procedure follows the tables.

TABLE 1

RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength[a] (nm)	Estimated IDL[b] (µg/L)
Aluminum	308.215	30
Antimony	206.833	21
Arsenic	193.696	35
Barium	455.403	0.87
Beryllium	313.042	0.18
Boron	249.678 x2	3.8
Cadmium	226.502	2.3
Calcium	317.933	6.7
Chromium	267.716	4.7
Cobalt	228.616	4.7
Copper	324.754	3.6
Iron	259.940	4.1
Lead	220.353	28
Lithium	670.784	2.8
Magnesium	279.079	20
Manganese	257.610	0.93
Mercury	194.227 x2	17
Molybdenum	202.030	5.3
Nickel	231.604 x2	10
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	50
Silica (SiO_2)	251.611	17
Silver	328.068	4.7
Sodium	588.995	19
Strontium	407.771	0.28
Thallium	190.864	27
Tin	189.980 x2	17
Titanium	334.941	5.0
Vanadium	292.402	5.0
Zinc	213.856 x2	1.2

TABLE 1
(continued)

[a] The wavelengths listed (where x2 indicates second order) are recommended because of their sensitivity. Other wavelengths may be substituted (e.g., in the case of an interference) if they provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

[b] The estimated instrumental detection limits shown are provided for illustrative purposes only. Each laboratory must determine IDLs and MDLs, as necessary, for their specific application of the method. These IDLs represent radial plasma data and axial plasma IDLs may be lower.

[c] Highly dependent on operating conditions and plasma position.

TABLE 2

POTENTIAL INTERFERENCES AND ANALYTE CONCENTRATION EQUIVALENTS (mg/L) ARISING FROM INTERFERENCE AT THE 100-mg/L LEVEL

Analyte	Wavelenth (nm)	Interferant[a,b]									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al at 1000 mg/L	Cu at 200 mg/L	Mn at 200 mg/L
Ca at 1000 mg/L	Fe at 1000 mg/L	Ti at 200 mg/L
Cr at 200 mg/L	Mg at 1000 mg/L	V at 200 mg/L

[b] The data shown above as analyte concentration equivalents are not the actual observed concentrations. To obtain those data, add the listed concentration to the interferant figure.

[c] Interferences will be affected by background choice and other interferences may be present.

TABLE 3

MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As and Mo
IV	Al, Ca, Cr, K, Na, Ni, Li, and Sr
V	Ag[a], Mg, Sb, and Tl
VI	P

[a] See the note in Sec. 7.4.

TABLE 4

EXAMPLE ICP PRECISION AND ACCURACY DATA[a]

Element	Sample No. 1				Sample No. 2				Sample No. 3			
	True Conc. (µg/L)	Mean Conc. (µg/L)	RSD[b] (%)	Accuracy[d] (%)	True Conc. (µg/L)	Mean Conc. (µg/L)	RSD[b] (%)	Accuracy[d] (%)	True Conc. (µg/L)	Mean Conc. (µg/L)	RSD[b] (%)	Accuracy[d] (%)
Be	750	733	6.2	98	20	20	9.8	100	180	176	5.2	98
Mn	350	345	2.7	99	15	15	6.7	100	100	99	3.3	99
V	750	749	1.8	100	70	69	2.9	99	170	169	1.1	99
As	200	208	7.5	104	22	19	23	86	60	63	17	105
Cr	150	149	3.8	99	10	10	18	100	50	50	3.3	100
Cu	250	235	5.1	94	11	11	40	100	70	67	7.9	96
Fe	600	594	3.0	99	20	19	15	95	180	178	6.0	99
Al	700	696	5.6	99	60	62	33	103	160	161	13	101
Cd	50	48	12	96	2.5	2.9	16	116	14	13	16	93
Co	700	512	10	73	20	20	4.1	100	120	108	21	90
Ni	250	245	5.8	98	30	28	11	93	60	55	14	92
Pb	250	236	16	94	24	30	32	125	80	80	14	100
Zn	200	201	5.6	100	16	19	45	119	80	82	9.4	102
Se[c]	40	32	21.9	80	6	8.5	42	142	10	8.5	8.3	85

These data are provided for guidance purposes only.

[a] Not all elements were analyzed by all laboratories.

[b] RSD = relative standard deviation.

[c] Results for Se are from two laboratories.

[d] Accuracy is expressed as the mean concentration divided by the true concentration times 100.

TABLE 5

EXAMPLE ICP-AES PRECISION AND ACCURACY FOR AQUEOUS SOLUTIONS

Element	Mean Conc. (mg/L)	n	RSD (%)	Accuracy (%)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102
Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Mo	3.70	8	6.9	100
Ni	3.70	7	5.7	100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Ag	3.69	6	9.1	100
Na	14.0	8	4.2	95
Tl	15.1	7	8.5	102
V	3.51	8	6.6	95
Zn	3.57	8	8.3	96

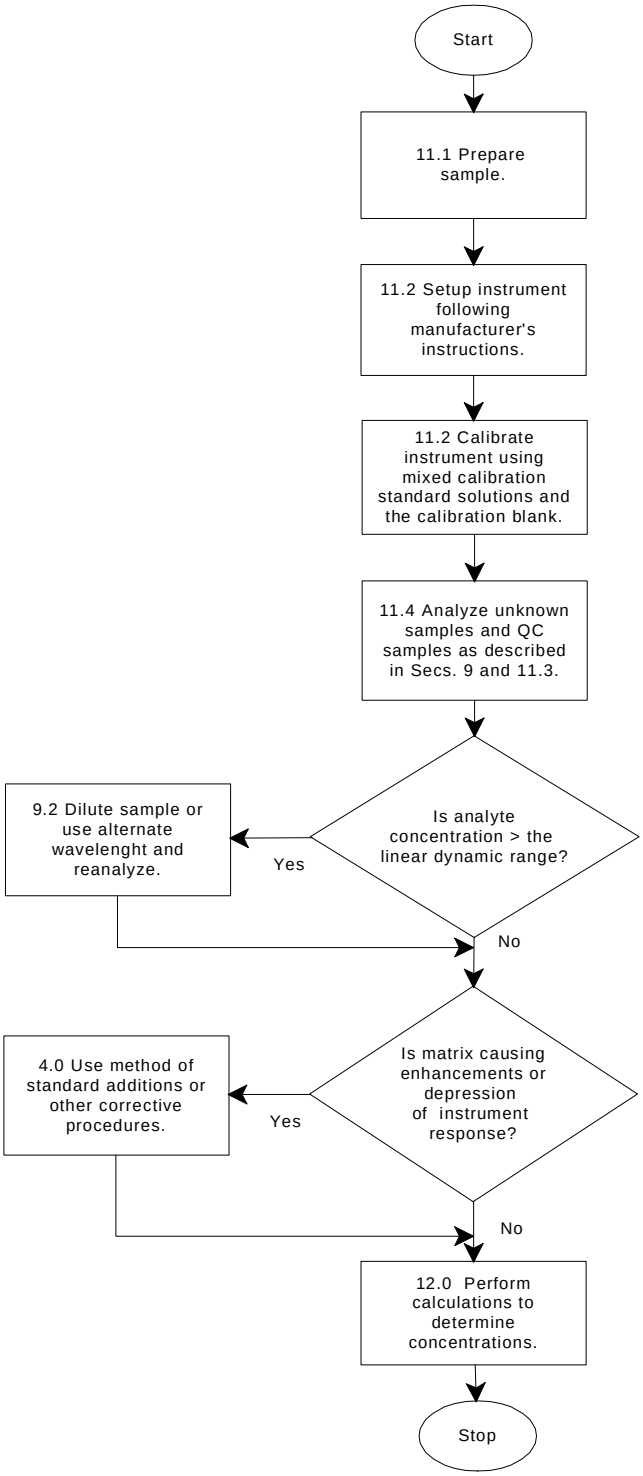
These performance values are independent of sample preparation because the labs analyzed portions of the same solutions and are provided for illustrative purposes only.
n= Number of measurements.
Accuracy is expressed as a percentage of the nominal value for each analyte in acidified, multi-element solutions.
These data are provided for guidance purposes only.

TABLE 6

EXAMPLE ICP-AES PRECISION AND BIAS FOR SOLID WASTE DIGESTS

	Spiked Coal Fly Ash (NIST-SRM 1633a)				Spiked Electroplating Sludge			
Element	Mean Conc. (mg/L)	n	RSD (%)	Bias (% AA)	Mean Conc. (mg/L)	n	RSD (%)	Bias (% AA)
Al	330	8	16	104	127	8	13	110
Sb	3.4	6	73	96	5.3	7	24	120
As	21	8	83	270	5.2	7	8.6	87
Ba	133	8	8.7	101	1.6	8	20	58
Be	4.0	8	57	460	0.9	7	9.9	110
Cd	0.97	6	5.7	101	2.9	7	9.9	90
Ca	87	6	5.6	208	954	7	7.0	97
Cr	2.1	7	36	106	154	7	7.8	93
Co	1.2	6	21	94	1.0	7	11	85
Cu	1.9	6	9.7	118	156	8	7.8	97
Fe	602	8	8.8	102	603	7	5.6	98
Pb	4.6	7	22	94	25	7	5.6	98
Mg	15	8	15	110	35	8	20	84
Mn	1.8	7	14	104	5.9	7	9.6	95
Mo	891	8	19	105	1.4	7	36	110
Ni	1.6	6	8.1	91	9.5	7	9.6	90
K	46	8	4.2	98	51	8	5.8	82
Se	6.4	5	16	73	8.7	7	13	101
Ag	1.4	3	17	140	0.75	7	19	270
Na	20	8	49	130	1380	8	9.8	95
Tl	6.7	4	22	260	5.0	7	20	180
V	1010	5	7.5	100	1.2	6	11	80
Zn	2.2	6	7.6	93	266	7	2.5	101

These performance values are independent of sample preparation because the labs analyzed portions of the same digests and are provided for illustrative purposes only.
n = Number of measurements.
Bias for the ICP-AES data is expressed as a percentage of atomic absorption spectroscopy (AA) data for the same digests.
These data are provided for guidance purposes only.


Start
11.1 Prepare sample.
11.2 Setup instrument following manufacturer's instructions.
11.2 Calibrate instrument using mixed calibration standard solutions and the calibration blank.
11.4 Analyze unknown samples and QC samples as described in Secs. 9 and 11.3.
Is analyte concentration > the linear dynamic range?
Yes
9.2 Dilute sample or use alternate wavelenght and reanalyze.
No
Is matrix causing enhancements or depression of instrument response?
Yes
4.0 Use method of standard additions or other corrective procedures.
No
12.0 Perform calculations to determine concentrations.
Stop

MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4; or

2. 0.25% Iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method will refer to reagent water unless otherwise specified.

5.2 Sulfuric acid (H_2SO_4), concentrated: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

5.4 Nitric acid (HNO_3), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N H_2SO_4. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of reagent water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated HNO_3 and adjust the volume to 100.0 mL (1 mL = 1 mg Hg). Stock solutions may also be purchased.

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at

0.15% nitric acid. This acid should be added to the flask, as needed, before addition of the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with HNO_3. The suggested maximum holding times for mercury is 28 days.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Transfer 100 mL, or an aliquot diluted to 100 mL, containing <1.0 g of mercury, to a 300-mL BOD bottle or equivalent. Add 5 mL of H_2SO_4 and 2.5 mL of concentrated HNO_3, mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 mL of stannous sulfate, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles. Add enough reagent water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 to each bottle. Add 15 mL of $KMnO_4$ solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 mL of the stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass

valve, remove the stopper and frit from the BOD bottle, and continue the aeration. Because of instrument variation refer to the manufacturers recommended operating conditions when using this method.

7.4 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.5 Calculate metal concentrations (1) by the method of standard additions, or (2) from a calibration curve. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

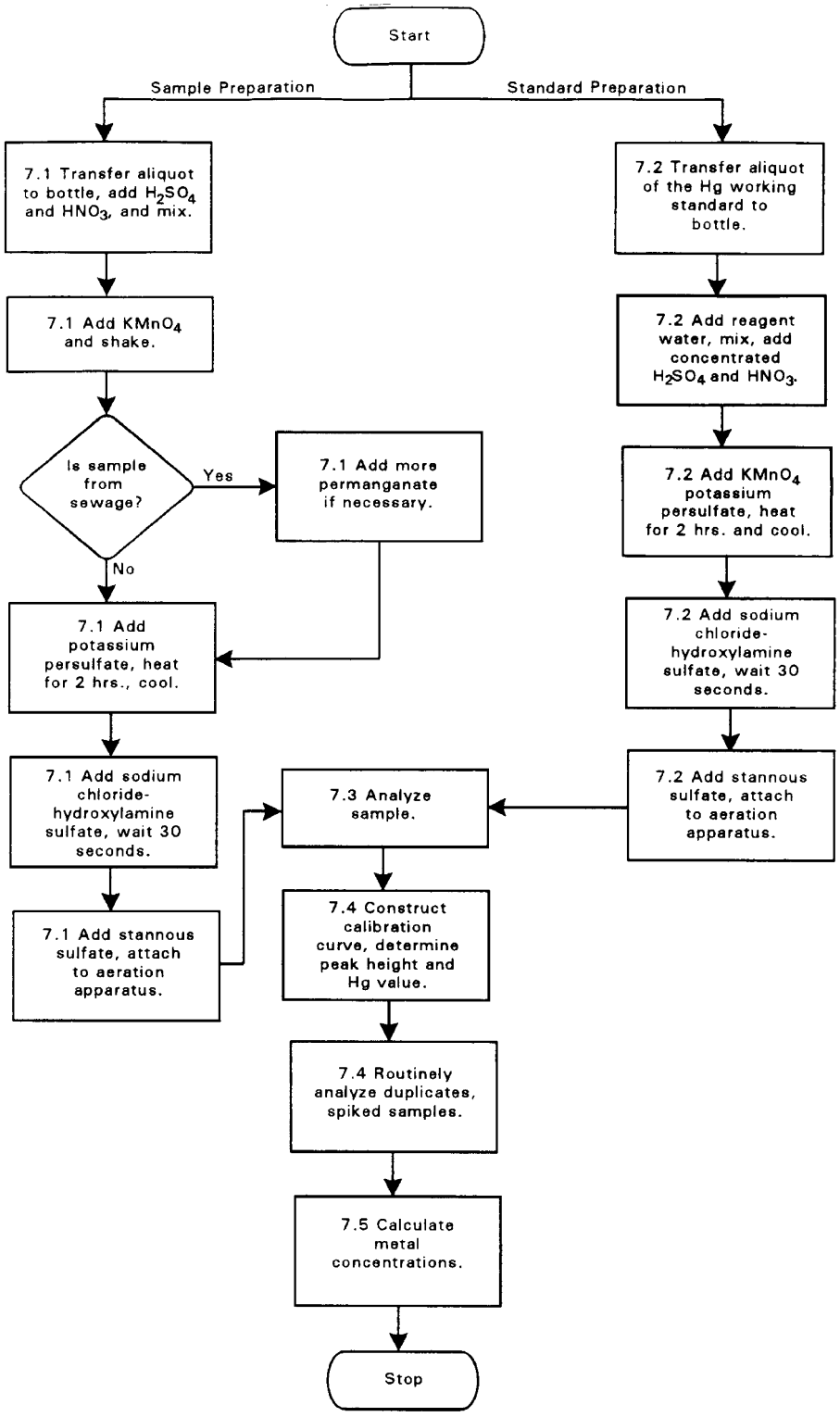
8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.1.


Start
Sample Preparation
Standard Preparation
7.1 Transfer aliquot to bottle, add H_2SO_4 and HNO_3, and mix.
7.1 Add $KMnO_4$ and shake.
Is sample from sewage?
Yes
No
7.1 Add more permanganate if necessary.
7.1 Add potassium persulfate, heat for 2 hrs., cool.
7.1 Add sodium chloride-hydroxylamine sulfate, wait 30 seconds.
7.1 Add stannous sulfate, attach to aeration apparatus.
7.2 Transfer aliquot of the Hg working standard to bottle.
7.2 Add reagent water, mix, add concentrated H_2SO_4 and HNO_3.
7.2 Add $KMnO_4$ potassium persulfate, heat for 2 hrs. and cool.
7.2 Add sodium chloride-hydroxylamine sulfate, wait 30 seconds.
7.2 Add stannous sulfate, attach to aeration apparatus.
7.3 Analyze sample.
7.4 Construct calibration curve, determine peak height and Hg value.
7.4 Routinely analyze duplicates, spiked samples.
7.5 Calculate metal concentrations.
Stop

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is a cold-vapor atomic absorption procedure for measuring the following RCRA analyte in soils, sediments, bottom deposits, and sludge-type materials:

Analyte	CAS Number*
Mercury, total (organic and inorganic)	7439-97-6

* Chemical Abstracts Service Registry Number

1.2 All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

1.3 Prior to employing this method, analysts are advised to consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.4 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 This method uses cold-vapor atomic absorption and is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical instrument detection limit (IDL) for this method is 0.0002 mg/L.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware. Also refer to Method 7000 for a discussion of interferences.

4.2 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

4.3 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

4.4 Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 254 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Alternatively, the sample may be allowed to stand for at least an hour under a hood (without active purging) to remove the chlorine.

4.5 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents may be used to determine if this type of interference is present.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of concentrated mercury reagents. Concentrated mercury reagents should only be handled by analysts knowledgeable of their risks and of safe handling procedures.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Atomic absorption spectrophotometer or equivalent -- Any atomic absorption unit equipped with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

6.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

6.3 Recording device -- Any multirange variable-speed recorder compatible equipped with the UV detection system or any other compatible data collection device.

6.4 Absorption cell -- Standard spectrophotometer cells 10 cm long equipped with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in diameter x 1/16 in thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in x 2-in cards. One inch diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

6.5 Air pump -- Any peristaltic pump capable of delivering air at 1 L/min may be used. A Masterflex pump equipped with electronic speed control has been found to be satisfactory.

6.6 Flowmeter -- Capable of measuring an air flow of 1 L/min.

6.7 Aeration tubing -- A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

6.8 Drying tube -- 6-in x 3/4-in diameter tube containing 20 g of magnesium perchlorate or a small reading lamp, equipped with a 60-W bulb, which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10 °C above ambient.

6.9 The cold-vapor generator is assembled as shown in Figure 1 of Ref. 1 or according to the instrument manufacturer's instructions. The apparatus shown in Figure 1 of Ref. 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass was included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or
2. Iodine 0.25% in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby-Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

6.10 Heating source -- Adjustable and capable of maintaining a temperature of 95 ± 3 °C. (e.g., hot plate, block digestor, microwave, etc.)

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water -- Reagent water should be interference free. All references to water in this method refer to reagent water unless otherwise specified.

7.3 Aqua regia -- Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.4 Sulfuric acid, 0.5 N -- Dilute 14.0 mL of concentrated sulfuric acid to 1 L.

7.5 Stannous sulfate -- Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride (in water) can be substituted for the acidic stannous sulfate solution.

NOTE: If line clogging occurs when using an automated system, use a less concentrated stannous chloride solution.

7.6 Sodium chloride-hydroxylamine sulfate solution -- Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. Hydroxylamine

hydrochloride may be used in place of hydroxylamine sulfate. In this case, dissolve 12 g of hydroxylamine hydrochloride in reagent water and dilute to 100 mL.

7.7 Potassium permanganate, mercury-free, 5% solution (w/v) -- Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

7.8 Mercury stock solution -- Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg). Alternatively, a mercury stock solution may be purchased from a reputable source with a concentration of 1.0 mg Hg/mL. Verify the quality of the standard by checking it against a second source standard (see second paragraph of Sec. 9.4).

7.9 Mercury working standard -- Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Three, "Inorganic Analytes."

8.2 All sample containers must be prewashed with detergents, acids, and reagent water. Glass, plastic, and polytetraflouroethylene (PTFE) containers are suitable in most cases. Polymers are not suitable for samples containing metallic mercury.

8.3 Metallic mercury, some inorganic mercury compounds, and many organic mercury compounds are volatile and unstable. It is advantageous to analyze the samples as soon as possible to determine the total mercury in the sample but in no case exceed the 28-day limit as defined in Chapter Three of this manual. Non-aqueous samples must be analyzed as soon as possible. If solid samples are not analyzed immediately, refrigeration is necessary.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency by following the sample preparation and analytical procedures described in this method and generating data of acceptable accuracy and precision for the target analyte (Mercury) in a clean matrix. The laboratory must also

repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.3 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process. A method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method and then carried through the appropriate steps of the analytical process. These steps may include but are not limited to digestion, dilution, filtering, and analysis. If the method blank does not contain the target analyte at a level that interferes with the project-specific data quality objectives then the method blank would be considered acceptable. In the absence of project-specific data quality objectives, if the blank is less than the lower level of quantitation or less than 10% of the lowest sample concentration for the analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once and if still unacceptable then all samples after the last acceptable method blank must be reprepped and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated.

9.4 For each batch of samples processed, at least one laboratory control sample must be carried throughout the entire sample preparation and analytical process. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or, when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the spiked value. After the determination of historical data, ± 20% should still be the limit of maximum deviation to express acceptability. If the laboratory control sample cannot be considered acceptable, the laboratory control sample should be re-run once and if still unacceptable then all samples after the last acceptable laboratory control sample must be reprepped and reanalyzed. Refer to Chapter One for more information.

If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring satisfactorily a LCS or mid-range standard or reference standard after every 10 samples. This sample value should be within 20% of the true value, or the previous 10 samples must be reanalyzed.

9.5 Matrix spike/matrix spike duplicates (MS/MSDs) -- MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/MSD is used to document the bias and precision of a method in a given sample matrix. Based on the analyst's discretion, a separate spike sample and a separate duplicate sample may be analyzed in lieu of the MS/MSD. For each batch of sample processed, at least one MS/MSD sample must be carried throughout the entire sample preparation and analytical process. MS/MSD samples should be spiked at the same level as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the spiked value for precision and $\leq$ 20 relative percent difference (RPD). After the determination of historical data, 20% should still be the limit of maximum deviation for both percent recovery and relative percent difference to express acceptability.

9.6 The method of standard additions can be used to verify linearity or if matrix interference is suspected. Refer to Method 7000 for standard addition procedures.

9.7 Refer to Method 7000 for additional QA and QC information that may be applicable.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Standard preparation -- Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 µg of mercury, to a series of 300-mL BOD bottles or equivalent. Add enough reagent water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min at 95 ± 3 °C. Allow the sample to cool; add 50 mL of reagent water and 15 mL of $KMnO_4$ solution to each bottle and heat again at 95 ± 3 °C for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Sec. 11.3.

10.2 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart or other recording device and read the mercury value from the standard curve.

11.0 PROCEDURE

11.1 Sample preparation

Weigh a 0.5 - 0.6 g-aliquot of a well homogenized sample and place in the bottom of a BOD bottle or other appropriate analysis vessel. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min at 95 ± 3 °C. Cool; then add 50 mL of reagent water and 15 mL of potassium permanganate solution to each sample and let stand at least 15 min. Add additional portions of permanganate solution, if needed, until the purple color persists for at least 15 min (see Sec. 4.4). Ensure that equal amounts of permanganate are added to standards and blanks. Mix thoroughly, then heat for 30 min at 95 ± 3 °C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

CAUTION: Do this addition under a hood, because Cl_2 could evolve. Add 55 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under Sec. 11.3.

See Sec. 10.1 for directions regarding standard preparation.

11.2 Alternate digestion procedure

An alternate digestion procedure employing an autoclave may also be used. In this procedure, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.5 - 0.6 g of sample. Add 5 mL of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121 ± 3 °C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under Sec. 11.3. Refer to the caution statement in Sec. 11.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

11.3 Analysis

At this point, allow the sample to stand quietly without manual agitation. Allow the circulating pump, which was previously adjusted to a rate of 1 L/min, to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the absorbance reading levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration. Because of instrument variation refer to the manufacturer's recommended operating conditions when using this method.

11.4 See Sec. 10.2 for directions regarding calibration curve construction.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Results need to be reported in units commensurate with their intended use and all dilutions need to be taken into account when computing final results.

12.2 Calculate metal concentrations (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes. These data are provided for guidance purposes only.

13.2 The data shown in Table 1 were obtained from records of State and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. U.S. EPA, "Method 245.5," Methods for Chemical Analysis of Water and Wastes, Pub. EPA-600/4-82-055, December 1982. .

2. A. Gaskill, "Compilation and Evaluation of RCRA Method Performance Data," Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following page contains the table referenced by this method.

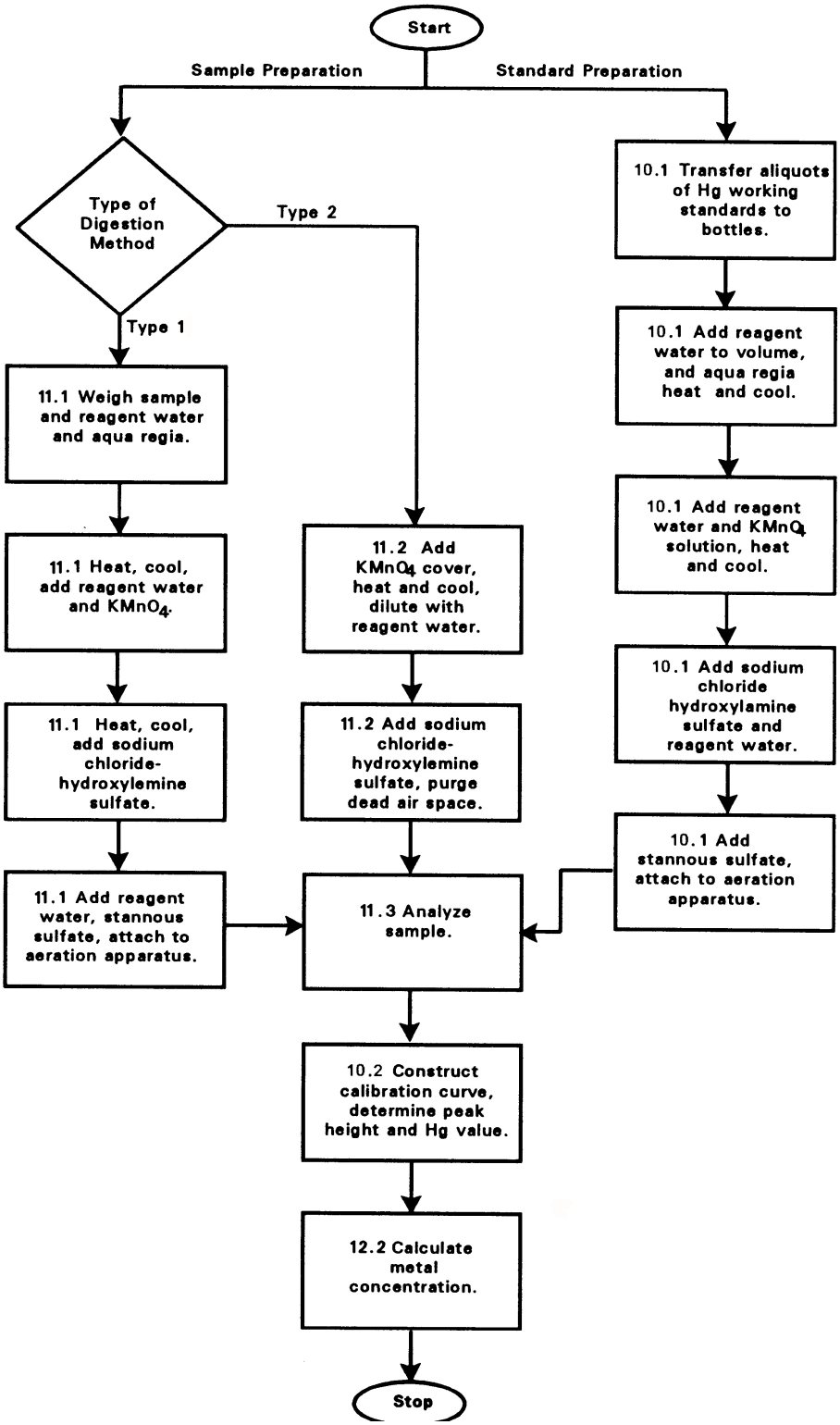
TABLE 1

EXAMPLE METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 µg/g
Wastewater treatment sludge	Not known	0.4, 0.28 µg/g

Data taken from Ref. 2.

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)



ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be methods which contain general information on how to perform an analytical procedure or technique, which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method may be used to determine the concentrations of various organochlorine pesticides in extracts from solid and liquid matrices, using fused-silica, open-tubular, capillary columns with electron capture detectors (ECD) or electrolytic conductivity detectors (ELCD). The following RCRA compounds have been determined by this method using either a single- or dual-column analysis system:

Compound	CAS Registry No.[a]
Aldrin	309-00-2
α-BHC	319-84-6
β-BHC	319-85-7
γ-BHC (Lindane)	58-89-9
δ-BHC	319-86-8
cis-Chlordane	5103-71-9
trans-Chlordane	5103-74-2
Chlordane -- not otherwise specified (n.o.s.)	57-74-9
Chlorobenzilate	510-15-6
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Diallate	2303-16-4
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4

Compound	CAS Registry No.[a]
Endrin ketone	53494-70-5
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorocyclopentadiene	77-47-4
Isodrin	465-73-6
Methoxychlor	72-43-5
Toxaphene	8001-35-2

[a]Chemical Abstract Service Registry Number

1.2 This method no longer includes PCBs as Aroclors in the list of target analytes. The analysis of PCBs should be undertaken using Method 8082, which includes specific cleanup and quantitation procedures designed for PCB analysis. This change was made to obtain PCB data of better quality and to eliminate the complications inherent in a combined organochlorine pesticide and PCB method. Therefore, if the presence of PCBs is suspected, use Method 8082 for PCB analyses, and this method (Method 8081) for organochlorine pesticide analyses. If there is no information on the likely presence of PCBs, either employ a PCB-specific screening procedure such as an immunoassay (e.g., Method 4020), or split the sample extract *prior to* any cleanup steps, and process part of the extract for organochlorine pesticide analysis and the other portion for PCB analysis using Method 8082.

1.3 The analyst must select columns, detectors and calibration procedures most appropriate for the specific analytes of interest in a study. Matrix-specific performance data must be established and the stability of the analytical system and instrument calibration must be established for each analytical matrix (e.g., hexane solutions from sample extractions, diluted oil samples, etc.). Example chromatograms and GC conditions are provided as guidance.

1.4 Although performance data are presented for many of the target analytes, it is unlikely that all of them could be determined in a single analysis. The chemical and chromatographic behaviors of many of these chemicals can result in coelution of some target analytes. Several cleanup/fractionation schemes are provided in this method and in Method 3600.

1.5 Several multi-component mixtures (i.e., chlordane and toxaphene) are listed as target analytes. When samples contain more than one multi-component analyte, a higher level of analyst expertise is necessary to attain acceptable levels of qualitative and quantitative analysis. The same is true of multi-component analytes that have been subjected to environmental degradation or degradation by treatment technologies. These result in "weathered" multi-component mixtures that may have significant differences in peak patterns to those of standards.

1.6 Compound identification based on single-column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS (e.g., Method 8270) is also recommended as a confirmation technique, if sensitivity permits (also see Sec. 11.7 of this method). GC/AED may also be used as a confirmation technique, if sensitivity permits (see Method 8085).

1.7 This method includes a dual-column option that describes a hardware configuration in which two GC columns are connected to a single injection port and to two separate detectors. The option allows one injection to be used for dual-column simultaneous analysis.

1.8 The following compounds may also be determined using this method. They have been grouped separately from the compounds in Sec. 1.1 because they have not been as extensively validated by EPA. If these compounds are to be determined using this procedure, the analyst is advised that additional efforts may be necessary in order to optimize the instrument operating conditions and to demonstrate acceptable method performance.

Compound	CAS Registry No.
Alachlor	15972-60-8
Captafol	2425-06-1
Carbophenothion	786-19-6
Chloroneb	2675-77-6
Chloropropylate	5836-10-2
Chlorothalonil	1897-45-6
Dacthal (DCPA)	1861-32-1
Dichlone	117-80-6
Dichloran	99-30-9
Dicofol	115-32-2
Etridiazole	2593-15-9
Halowax-1000	58718-66-4
Halowax-1001	58718-67-5
Halowax-1013	12616-35-2
Halowax-1014	12616-36-3
Halowax-1051	2234-13-1
Halowax-1099	39450-05-0
Mirex	2385-85-5
Nitrofen	1836-75-5
trans-Nonachlor	39765-80-5
Pentachloronitrobenzene (PCNB)	82-68-8
Permethrin (*cis* + *trans*)	52645-53-1
Perthane	72-56-0
Propachlor	1918-16-7
Strobane	8001-50-1
Trifluralin	1582-09-8

1.9 Kepone extracted from samples or in standards exposed to water or methanol may produce peaks with broad tails that elute later than the standard by up to 1 min. This shift is presumably the result of the formation of a hemi-acetal from the ketone functionality and may seriously affect the ability to identify this compound on the basis of its retention time. As a result, this method is not recommended for determining Kepone. Method 8270 may be more appropriate for the analysis of Kepone.

1.10 Extracts suitable for analysis by this method may also be analyzed for organophosphorus pesticides (Method 8141). Some extracts may also be suitable for triazine herbicide analysis, if low recoveries (normally samples taken for triazine analysis must be preserved) are not a problem.

1.11 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.12 Use of this method is restricted to use by, or under the supervision of, personnel appropriately experienced and trained in the use of gas chromatographs (GCs) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of liquid or solid sample is extracted using the appropriate matrix-specific sample extraction technique.

2.1.1 Aqueous samples may be extracted at neutral pH with methylene chloride using either Method 3510 (separatory funnel), Method 3520 (continuous liquid-liquid extractor), Method 3535 (solid-phase extraction), or other appropriate technique.

2.1.2 Solid samples may be extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Method 3540 (Soxhlet), Method 3541 (automated Soxhlet), Method 3545 (pressurized fluid extraction), Method 3546 (microwave extraction), Method 3550 (ultrasonic extraction), Method 3562 (supercritical fluid extraction), or other appropriate technique or solvents.

2.2 A variety of cleanup steps may be applied to the extract, depending on the nature of the matrix interferences and the target analytes. Suggested cleanups include alumina (Method 3610), Florisil (Method 3620), silica gel (Method 3630), gel permeation chromatography (Method 3640), and sulfur (Method 3660).

2.3 After cleanup, the extract is analyzed by injecting a measured aliquot into a gas chromatograph equipped with either a narrow-bore or wide-bore fused-silica capillary column, and either an electron capture detector (GC/ECD) or an electrolytic conductivity detector (GC/ELCD).

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to the chapter text for general guidance on the cleaning of glassware. Also refer to Methods 3500, 3600, and 8000 for a discussion of interferences.

4.2 Interferences co-extracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into three broad categories, as follows.

4.2.1 Contaminated solvents, reagents, or sample processing hardware.

4.2.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

4.2.3 Compounds extracted from the sample matrix to which the detector will respond.

4.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.

4.3.1 Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations.

4.3.2 Exhaustive cleanup of solvents, reagents and glassware may be necessary to eliminate background phthalate ester contamination.

4.3.3 These materials may be removed prior to analysis using Method 3640 (Gel Permeation Cleanup) or Method 3630 (Silica Gel Cleanup).

4.4 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Glassware must be scrupulously cleaned.

Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware and dry it in an oven at 130 °C for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment. (Other appropriate glassware cleaning procedures may be employed.)

4.5 The presence of sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur contamination should be expected with sediment samples. Method 3660 is suggested for removal of sulfur. Since the recovery of endrin aldehyde is drastically reduced when using the TBA procedure in Method 3660, this compound must be determined prior to sulfur cleanup when it is an analyte of interest and the TBA procedure is to be used for cleanup. Endrin aldehyde is not affected by the copper powder, so endrin aldehyde can be determined after the removal of sulfur using the copper powder technique in Method 3660. However, as indicated in Method 3660, the use of copper powder may adversely affect the recoveries of other potential analytes of interest, including some organochlorine compounds and many organophosphorous compounds.

4.6 Waxes, lipids, and other high molecular weight materials can be removed by gel permeation chromatography (GPC) cleanup (Method 3640).

4.7 Other halogenated pesticides or industrial chemicals may interfere with the analysis of pesticides. Certain coeluting organophosphorus pesticides may be eliminated using Method 3640 (GPC -- pesticide option). Coeluting chlorophenols may be eliminated by using Method 3630 (silica gel), Method 3620 (Florisil), or Method 3610 (alumina). Polychlorinated biphenyls (PCBs) also may interfere with the analysis of the organochlorine pesticides. The problem may be most severe for the analysis of multicomponent analytes such as chlordane, toxaphene, and Strobane. If PCBs are known or expected to occur in samples, the analyst should consult Methods 3620 and 3630 for techniques that may be used to separate the pesticides from the PCBs.

4.8 Coelution among the many target analytes in this method can cause interference problems. The following target analytes may coelute on the GC columns listed, when using the single-column analysis scheme:

DB 608	Trifluralin/diallate isomers
	PCNB/dichlone/Isodrin
DB 1701	Captafol/mirex
	Methoxychlor/endosulfan sulfate

4.9 The following compounds may coelute using the dual-column analysis scheme. In general, the DB-5 column resolves fewer compounds than the DB-1701.

DB-5	Permethrin/heptachlor epoxide
	Endosulfan I/*cis*-chlordane
	Perthane/endrin
	Endosulfan II/chloropropylate/chlorobenzilate
	4,4'-DDT/endosulfan sulfate
	Methoxychlor/dicofol
DB-1701	Chlorothalonil/β-BHC
	δ-BHC/DCPA/permethrin
	cis-Chlordane/*trans*-nonachlor

Nitrofen, dichlone, carbophenothion, and dichloran exhibit extensive peak tailing on both columns. Simazine and atrazine give poor responses on the ECD detector. Triazine

compounds should be analyzed using Method 8141 (nitrogen-phosphorus detector, or NPD, option).

5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Gas chromatograph (GC) -- An analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all necessary accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and recorder/integrator or data system. Electrolytic conductivity detectors (ELCD) may also be employed if appropriate for project needs. If the dual-column option is employed, the gas chromatograph must be equipped with two detectors.

6.2 GC columns

This method describes procedures for both single-column and dual-column analyses. The single-column approach involves one analysis to determine that a compound is present, followed by a second analysis to confirm the identity of the compound (Sec. 11.7 describes how GC/MS confirmation techniques may be employed). The single-column approach may employ either narrow-bore ($\leq$0.32-mm ID) columns or wide-bore (0.53-mm ID) columns. The dual-column approach generally employs a single injection that is split between two columns that are mounted in a single gas chromatograph. The dual-column approach generally employs wide-bore (0.53-mm ID) columns, but columns of other diameters may be employed if the analyst can demonstrate and document acceptable performance for the intended application. A third alternative is to employ dual columns mounted in a single GC, but with each column connected to a separate injector and a separate detector.

The columns listed in this section were the columns used in developing the method. The listing of these columns in this method is not intended to exclude the use of other columns that are available or that may be developed. Laboratories may use these columns or other columns provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

6.2.1 Narrow-bore columns for single-column analysis (use both columns to confirm compound identifications unless another confirmation technique such as GC/MS is

employed). Narrow-bore columns should be installed in split/splitless (Grob-type) injectors.

6.2.1.1 30-m x 0.25-mm or 0.32-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1-µm film thickness.

6.2.1.2 30-m x 0.25-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent), 2.5 µm coating thickness, 1-µm film thickness.

6.2.2 Wide-bore columns for single-column analysis (use two of the three columns listed to confirm compound identifications unless another confirmation technique such as GC/MS is employed). Wide-bore columns should be installed in 1/4-inch injectors, with deactivated liners designed specifically for use with these columns.

6.2.2.1 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5-µm or 0.83-µm film thickness.

6.2.2.2 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), 1.0-µm film thickness.

6.2.2.3 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 95 percent dimethyl - 5 percent diphenyl polysiloxane (DB-5, SPB-5, RTx-5, or equivalent), 1.5-µm film thickness.

6.2.3 Wide-bore columns for dual-column analysis -- The two pairs of recommended columns are listed below.

6.2.3.1 Column pair 1

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5-µm film thickness.

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), 1.0-µm film thickness.

Column pair 1 is mounted in a press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog No. 705-0733) or a Y-shaped fused-silica connector (Restek, Catalog No. 20405), or equivalent.

NOTE: When connecting columns to a press-fit Y-shaped connector, a better seal may be achieved by first soaking the ends of the capillary columns in alcohol for about 10 sec to soften the polyimide coating.

6.2.3.2 Column pair 2

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 0.83-µm film thickness.

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), 1.0-µm film thickness.

Column pair 2 is mounted in an 8-inch deactivated glass injection tee (Supelco, Catalog No. 2-3665M, or equivalent).

6.3 Column rinsing kit -- Bonded-phase column rinse kit (J&W Scientific, Catalog No. 430-3000), or equivalent.

6.4 Volumetric flasks, 10-mL and 25-mL, for preparation of standards.

6.5 Analytical balance, capable of weighing to 0.0100 g.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade or pesticide-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at $\leq$6 °C in polytetrafluoroethylene (PTFE)-sealed containers, in the dark. When a lot of standards is prepared, aliquots of that lot should be stored in individual small vials. All stock standard solutions must be replaced after one year, or sooner if routine QC (see Sec. 9.0) indicates a problem. All other standard solutions must be replaced after six months, or sooner if routine QC (see Sec. 9.0) indicates a problem.

7.2 Solvents used in the extraction and cleanup procedures (see appropriate 3500 and 3600 series methods) include *n*-hexane, diethyl ether, methylene chloride, acetone, ethyl acetate, and isooctane (2,2,4-trimethylpentane) and the solvents must be exchanged to *n*-hexane or isooctane prior to analysis. Therefore, the use of *n*-hexane and isooctane will be required in this procedure. All solvents should be pesticide grade in quality or equivalent, and each lot of solvent should be determined to be free of phthalates.

7.3 The following solvents may be necessary for the preparation of standards. All solvent lots must be pesticide grade in quality or equivalent and should be determined to be free of phthalates.

7.3.1 Acetone, $(CH_3)_2CO$

7.3.2 Toluene, $C_6H_5CH_3$

7.4 Organic-free reagent water -- All references to water in this method refer to organic-free reagent water as defined in Chapter One.

7.5 Standard solutions

The following sections describe the preparation of stock, intermediate, and working standards for the compounds of interest. This discussion is provided as an example, and other

approaches and concentrations of the target compounds may be used, as appropriate for the intended application. See Method 8000 for additional information on the preparation of calibration standards.

7.6 Stock standard solutions (1000 mg/L) -- May be prepared from pure standard materials or can be purchased as certified solutions.

7.6.1 Prepare stock standard solutions by accurately weighing 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

7.6.2 β-BHC, dieldrin, and some other standards may not be adequately soluble in isooctane. A small amount of acetone or toluene should be used to dissolve these compounds during the preparation of the stock standard solutions.

7.7 Composite stock standard -- May be prepared from individual stock solutions.

7.7.1 For composite stock standards containing less than 25 components, take exactly 1 mL of each individual stock solution at a concentration of 1000 mg/L, add solvent, and mix the solutions in a 25-mL volumetric flask. For example, for a composite containing 20 individual standards, the resulting concentration of each component in the mixture, after the volume is adjusted to 25 mL, will be 1 mg/25 mL. This composite solution can be further diluted to obtain the desired concentrations.

7.7.2 For composite stock standards containing more than 25 components, use volumetric flasks of the appropriate volume (e.g., 50-mL, 100-mL), and follow the procedure described above.

7.8 Calibration standards -- Should be prepared at a minimum of five different concentrations by dilution of the composite stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector. See Method 8000 for additional information on the preparation of calibration standards.

7.8.1 Although all single component analytes can be resolved on a new 35 percent phenyl methyl silicone column (e.g., DB-608), two calibration mixtures should be prepared for the single component analytes of this method. This procedure is established to minimize potential resolution and quantitation problems on confirmation columns or on older 35 percent phenyl methyl silicone (e.g. DB-608) columns and to allow determination of endrin and DDT breakdown for instrument quality control (Sec. 9.0).

7.8.2 Separate calibration standards are necessary for each multi-component target analyte (e.g., toxaphene and chlordane). Analysts should evaluate the specific toxaphene standard carefully. Some toxaphene components, particularly the more heavily chlorinated components, are subject to dechlorination reactions. As a result, standards from different vendors may exhibit marked differences which could lead to possible false negative results or to large differences in quantitative results.

7.9 Internal standard (optional)

7.9.1 Pentachloronitrobenzene is suggested as an internal standard for the single-column analysis, when it is not considered to be a target analyte. 1-Bromo-2-nitrobenzene may also be used. Prepare a solution of 5000 mg/L (5000 ng/µL) of pentachloronitrobenzene or 1-bromo-2-nitrobenzene. Spike 10 µL of this solution into each 1 mL of sample extract.

7.9.2 1-Bromo-2-nitrobenzene is suggested as an internal standard for the dual-column analysis. Prepare a solution of 5000 mg/L (5000 ng/µL) of 1-bromo-2-nitrobenzene. Spike 10 µL of this solution into each 1 mL of sample extract.

7.10 Surrogate standards

The performance of the method should be monitored using surrogate compounds. Surrogate standards are added to all samples, method blanks, matrix spikes, and calibration standards. The following compounds are recommended as possible surrogates. Other surrogates may be used, provided that the analyst can demonstrate and document performance appropriate for the data quality needs of the particular application.

7.10.1 Decachlorobiphenyl and tetrachloro-*m*-xylene have been found to be a useful pair of surrogates for both the single-column and dual-column configurations. Method 3500 describes the procedures for preparing these surrogates.

7.10.2 4-Chloro-3-nitrobenzotrifluoride may also be useful as a surrogate if the chromatographic conditions of the dual-column configuration cannot be adjusted to preclude coelution of a target analyte with either of the surrogates in Sec. 7.9.1. However, this compound elutes early in the chromatographic run and may be subject to other interference problems. A recommended concentration for this surrogate is 500 ng/µL. Use a spiking volume of 100 µL for a 1-L aqueous sample. (Other surrogate concentrations may be used, as appropriate for the intended application.)

7.10.3 Store surrogate spiking solutions at $\leq$6 °C in PTFE-sealed containers in the dark.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes."

8.2 Extracts must be stored under refrigeration in the dark and should be analyzed within 40 days of extraction.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions

for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for specific determinative method QC procedures. Refer to Method 3500 for QC procedures to ensure the proper operation of the various sample preparation techniques. If an extract cleanup procedure is performed, refer to Method 3600 for the appropriate QC procedures. Any more specific quality control procedures provided in this method will supersede those noted in Methods 8000, 3500, or 3600.

9.3 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000 and include evaluation of retention time windows, calibration verification, and chromatographic analysis of samples.

9.3.1 Include a calibration standard after each group of 20 samples (it is *recommended* that a calibration standard be included after every 10 samples to minimize the number of repeat injections) in the analysis sequence as a calibration check. Thus, injections of method blank extracts, matrix spike samples, and other non-standards are counted in the total. Solvent blanks, injected as a check on cross-contamination, need not be counted in the total. The response factors for the calibration verification standard should be within ±20% of the initial calibration (see Sec. 11.5.2). When this calibration verification standard falls out of this acceptance window, the laboratory should stop analyses and take corrective action.

9.3.2 Whenever quantitation is accomplished using an internal standard, internal standards must be evaluated for acceptance. The measured area of the internal standard must be no more than 50 percent different from the average area calculated during initial calibration. When the internal standard peak area is outside the limit, all samples that fall outside the QC criteria must be reanalyzed. The retention times of the internal standards must also be evaluated. A retention time shift of >30 sec necessitates reanalysis of the affected sample.

9.3.3 DDT and endrin are easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated with high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a standard containing only 4,4'-DDT and endrin. Presence of 4,4'-DDE, 4,4'-DDD, endrin ketone or endrin indicates breakdown. If degradation of either DDT or endrin exceeds 15%, take corrective action before proceeding with calibration. Unless otherwise specified in an approved project plan, this test should be performed even when DDT and endrin are not target analytes for a given project, as a test of the inertness of the analytical system.

9.3.3.1 Calculate percent breakdown as follows:

$$\%\ \text{breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD + DDE)}}{\text{sum of all peak areas (DDT + DDE + DDD)}} \times 100$$

$$\% \text{ breakdown of endrin} = \frac{\text{sum of degradation peak areas (aldehyde + ketone)}}{\text{sum of all peak areas (endrin + aldehyde + ketone)}} \times 100$$

9.3.3.2 The breakdown of DDT and endrin should be measured before samples are analyzed and at the beginning of each 12-hr shift. Injector maintenance and recalibration should be completed (see Sec. 11.9.2) if the breakdown is greater than 15% for either compound.

9.3.4 Whenever silica gel (Method 3630) or Florisil® (Method 3620) cleanups are used, the analyst must demonstrate that the fractionation scheme is reproducible. Batch to batch variation in the composition of the silica gel or Florisil® or overloading the column may cause a change in the distribution patterns of the organochlorine pesticides. When compounds are found in two fractions, add the concentrations found in the fractions, and correct for any additional dilution.

9.4 Initial demonstration of proficiency

9.4.1 Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish a demonstration of proficiency.

9.4.2 It is suggested that the QC reference sample concentrate (as discussed in Methods 8000 and 3500) contain each analyte of interest at 10 mg/L in the concentrate. A 1-mL spike of this concentrate into 1 L of reagent water will yield a sample concentration of 10 µg/L. If this method is to be used for analysis of chlordane or toxaphene only, the QC reference sample concentrate should contain the most representative multi-component mixture at a suggested concentration of 50 mg/L in acetone. See Method 8000 for additional information on how to accomplish this demonstration. Other concentrations may be used, as appropriate for the intended application.

9.4.3 Calculate the average recovery and the standard deviation of the recoveries of the analytes in each of the four QC reference samples. Refer to Method 8000 for procedures for evaluating method performance.

9.5 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the laboratory should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if

reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

9.6 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy. method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample when surrogates are used. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.6.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use a matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.6.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.6.3 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance found in Method 8000.

9.7 Surrogate recoveries

If surrogates are used, the laboratory should evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000 for information on evaluating surrogate data and developing and updating surrogate limits. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in an approved project plan.

9.8 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10.0 CALIBRATION AND STANDARDIZATION

See Sec 11.0 for information on calibration and standardization.

11.0 PROCEDURE

11.1 Sample extraction

Refer to Chapter Two and Method 3500 for guidance in choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride using a separatory funnel (Method 3510), a continuous liquid-liquid extractor (Method 3520), solid-phase extraction (Method 3535), or other appropriate technique. Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using one of the Soxhlet extraction methods (Method 3540 or 3541), pressurized fluid extraction (Method 3545), microwave extraction (Method 3546), ultrasonic extraction (Method 3550), or other appropriate technique. Solid samples may also be extracted using supercritical fluid extraction (Method 3562).

NOTE: Hexane-acetone (1:1) may be more effective than methylene chloride-acetone (1:1) as an extraction solvent for organochlorine pesticides in some environmental and waste matrices. Relative to the methylene chloride-acetone mixture, the use of hexane-acetone generally reduces the amount of interferences that are extracted and improves the signal-to-noise ratio.

The choice of extraction solvent will depend on the analytes of interest. No single solvent or extraction procedure is universally applicable to all analyte groups and sample matrices. The analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest, for any solvent system employed, *including* those specifically listed in this method. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Each new sample type must be spiked with the compounds of interest to determine the percent recovery. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

11.2 Extract cleanup

Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. General guidance for sample extract cleanup is provided in this section and in Method 3600.

11.2.1 If a sample is of biological origin, or contains high molecular weight materials, the use of Method 3640 (GPC -- pesticide option) is recommended. Frequently, one of the adsorption chromatographic cleanups (alumina, silica gel, or Florisil®) may also be necessary following the GPC cleanup.

11.2.2 Method 3610 (alumina) may be used to remove phthalate esters.

11.2.3 Method 3620 (Florisil®) may be used to separate organochlorine pesticides from aliphatic compounds, aromatics, and nitrogen-containing compounds.

11.2.4 Method 3630 (silica gel) may be used to separate single component organochlorine pesticides from some interferants.

11.2.5 Sulfur, which may be present in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur should be removed by the technique described in Method 3660.

11.3 GC conditions

This method allows the analyst to choose between a single-column or a dual-column configuration in the injector port. The columns listed in this section were the columns used to develop the method performance data. The listing of these columns in this method is not intended to exclude the use of other columns that are available or that may be developed. Wide-bore or narrow-bore columns may be used with either option. Laboratories may use these or other capillary columns or columns of other dimensions, provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

11.3.1 Single-column analysis

This capillary GC/ECD method allows the analyst the option of using 0.25 or 0.32-mm ID capillary columns (narrow-bore) or 0.53-mm ID capillary columns (wide-bore). Performance data are provided for both options. Figures 1 - 6 provide example chromatograms.

11.3.1.1 Narrow-bore columns generally provide greater chromatographic resolution than wide-bore columns, although narrow-bore columns have a lower sample capacity. As a result, narrow-bore columns may be more suitable for relatively clean samples or for extracts that have been prepared with one or more of the clean-up options referenced in the method. Wide-bore columns (0.53-mm ID) may be more suitable for more complex environmental and waste matrices. However, the choice of the appropriate column diameter is left to professional judgement of the analyst.

11.3.1.2 Table 1 lists example retention times for the target analytes using wide-bore capillary columns. Table 2 lists example retention times for the target analytes using narrow-bore capillary columns. The retention times listed in these tables are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

11.3.1.3 Table 3 lists suggested GC operating conditions for the single-column method of analysis.

11.3.2 Dual-column analysis

The dual-column/dual-detector approach recommends the use of two 30-m x 0.53-mm ID fused-silica open-tubular columns of different polarities, thus of different selectivities toward the target analytes. The columns are connected to an injection tee and separate electron capture detectors or to both separate injectors and separate detectors. However, the choice of the appropriate column dimensions is left to the professional judgement of the analyst.

11.3.2.1 Example retention times for the organochlorine analytes on dual-columns are provided in Table 5. The retention times listed in the table are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method. The

suggested GC operating conditions for the compounds in Table 5 are given in Table 6.

11.3.2.2 Multi-component mixtures of toxaphene and Strobane were analyzed separately (Figures 4 and 5) using the operating conditions in Table 6.

11.3.2.3 Figure 6 is an example chromatogram for a mixture of organochlorine pesticides. The retention times of the individual components detected in these mixtures are given in Table 5, and are provided as examples.

11.3.2.4 Suggested operating conditions for a more heavily loaded DB-5/DB-1701 pair are given in Table 7. This column pair was used for the detection of multi-component organochlorine compounds.

11.3.2.5 Suggested operating conditions for a DB-5/DB-1701 column pair having thinner films, a different type of splitter, and a slower temperature programming rate are provided in Table 6. These conditions gave better peak shapes for nitrofen and dicofol. Table 5 lists the retention times for the compounds on this column pair.

11.4 Calibration

11.4.1 Prepare calibration standards using the procedures in Sec. 7.0. Refer to Method 8000 and Sec. 9.3 of this method for proper calibration techniques for both initial calibration and calibration verification. The procedure for either internal or external calibration may be used. In most cases, external standard calibration is used with this method because of the sensitivity of the electron capture detector and the probability of the internal standard being affected by interferences. Because several of the pesticides may coelute on any single column (see Sec. 4.8), analysts should use two calibration mixtures. The specific mixture should be selected to minimize the problem of peak overlap.

NOTE: Because of the sensitivity of the electron capture detector, always clean the injection port and column prior to performing the initial calibration.

11.4.1.1 Unless otherwise necessary for a specific project, the analysis of the multi-component analytes employs a single-point calibration. A single calibration standard near the mid-point of the expected calibration range of each multi-component analyte is included with the initial calibration of the single component analytes for pattern recognition, so that the analyst is familiar with the patterns and retention times on each column. The calibration standard may be at a lower concentration than the mid-point of the expected range, if appropriate for the project.

11.4.1.2 For calibration verification (each 12-hr shift), all target analytes specified in the project plan must be injected.

11.4.2 Establish the GC operating conditions appropriate for the configuration (single-column or dual column, see Sec. 11.3) using as guidance and as appropriate the operating condition information found in Tables 3, 4, 6, or 7. Optimize the instrumental conditions for resolution of the target analytes and sensitivity. An initial oven temperature of $\leq$ 140 - 150 °C may be necessary to resolve the four BHC isomers. A final temperature of between 240 °C and 270 °C may be necessary to elute decachlorobiphenyl. The use of injector pressure programming will improve the chromatography of late eluting peaks.

NOTE: Once established, the same operating conditions must be used for both calibrations and sample analyses.

11.4.3 A 2-µL injection volume of each calibration standard is recommended. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest.

11.4.4 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day or more. Therefore, the GC column should be primed (or deactivated) by injecting a pesticide standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning the initial calibration or calibration verification.

CAUTION: Several analytes, including aldrin, may be observed in the injection just following this system priming because of carry-over. Always run an acceptable blank prior to running any standards or samples.

11.4.5 Calibration factors

When external standard calibration is employed, calculate the calibration factor for each analyte at each concentration, the mean calibration factor, and the relative standard deviation (RSD) of the calibration factors, using the formulae below. If internal standard calibration is employed, refer to Method 8000 for the calculation of response factors.

11.4.5.1 Calculate the calibration factor for each analyte at each concentration as:

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

11.4.5.2 Calculate the mean calibration factor for each analyte as:

$$\text{mean CF} = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

where n is the number of standards analyzed.

11.4.5.3 Calculate the standard deviation (SD) and the RSD of the calibration factors for each analyte as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{CF}} \times 100$$

If the RSD for each analyte is $\leq$ 20%, then the response of the instrument is considered linear and the mean calibration factor may be used to quantitate sample results. If the RSD is greater than 20%, the analyst should consult Method 8000 for other calibration options, which may include either a linear calibration not through the origin or a non-linear calibration model (e.g., a polynomial equation).

11.4.6 Retention time windows

Absolute retention times are generally used for compound identification. When absolute retention times are used, retention time windows are crucial to the identification of target compounds, and should be established by one of the approaches described in Method 8000. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis. Analysts should consult Method 8000 for the details of establishing retention time windows. Other approaches to compound identification may be employed, provided that the analyst can demonstrate and document that the approaches are appropriate for the intended application.

11.4.6.1 Before establishing the retention time windows, make sure that the gas chromatographic system is operating within optimum conditions.

11.4.6.2 The widths of the retention time windows are defined as described in Method 8000. However, the experience of the analyst should weigh heavily during the interpretation of the chromatograms.

11.5 Gas chromatographic analysis of sample extracts

11.5.1 The same GC operating conditions used for the initial calibration must be employed for the analysis of samples.

11.5.2 Verify calibration at least once each 12-hr shift by injecting calibration verification standards prior to conducting any sample analyses. Analysts should alternate the use of high and low concentration mixtures of single-component analytes and multi-component analytes for calibration verification. A calibration standard must also be injected at intervals of not less than once every twenty samples (after every 10 samples is recommended to minimize the number of samples requiring re-injection when QC limits are exceeded) and at the end of the analysis sequence. See Sec. 9.3 for additional guidance on the frequency of the standard injections.

11.5.2.1 The calibration factor for each analyte should not exceed a ±20 percent difference from the mean calibration factor calculated for the initial calibration. If a calibration approach other than the RSD method has been employed for the initial calibration (e.g., a linear model not through the origin, a non-linear calibration model, etc.), consult Method 8000 for the specific details of calibration verification.

11.5.2.2 If the calibration does not meet the ±20% limit on the basis of each compound, check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ±20%, then a new initial calibration must be prepared. The effects of a failing calibration verification standard on sample results are discussed in Sec. 11.5.7.

11.5.3 Compare the retention time of each analyte in the calibration standard with the absolute retention time windows established in Sec. 11.4.6. Each analyte in each subsequent standard run during the 12-hr period must fall within its respective retention time window. If not, the gas chromatographic system must either be adjusted so that a second analysis of the standard does result in all analytes falling within their retention time windows, or a new initial calibration must be performed and new retention time windows established. As noted in Sec. 11.4.6, other approaches to compound identification may be employed, provided that the analyst can demonstrate and document that the approaches are appropriate for the intended application.

11.5.4 Inject a measured aliquot of the concentrated sample extract. A 2-µL aliquot is suggested, however, the same injection volume should be used for both the calibration standards and the sample extracts, unless the analyst can demonstrate acceptable performance using different volumes or conditions. Record the volume injected and the resulting peak size in area units.

11.5.5 Confirmation

Tentative identification of an analyte (either single-component or multi-component) occurs when a peak from a sample extract falls within the daily retention time window. Confirmation is necessary when the sample composition is not well characterized. Confirmatory techniques such as gas chromatography with a dissimilar column or a mass spectrometer should be used. See Method 8000 for information on confirmation of tentative identifications. See Sec. 11.7 of this method for information on the use of GC/MS as a confirmation technique.

When results are confirmed using a second GC column of dissimilar stationary phase, the analyst should check the agreement between the quantitative results on both columns once the identification has been confirmed. See Method 8000 for a discussion of such a comparison and appropriate data reporting approaches.

11.5.6 When using the external calibration procedure (Method 8000), determine the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes, as follows. The appropriate selection of a baseline from which the peak area or height can be determined is necessary for proper quantitation.

11.5.6.1 For aqueous samples:

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(V_t)(D)}{(\overline{CF})(V_i)(V_s)}$$

where:

A_x = Area (or height) of the peak for the analyte in the sample.

V_t = Total volume of the concentrated extract (µL).

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

$\overline{CF}$ = Mean calibration factor from the initial calibration (area/ng).

V_i = Volume of the extract injected (µL). The injection volume for samples and calibration standards should be the same, unless the analyst can demonstrate acceptable performance using different volumes or conditions.

V_s = Volume of the aqueous sample extracted in mL. If units of liters are used for this term, multiply the results by 1000.

Using the units given here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.

11.5.6.2 For non-aqueous samples:

$$\text{Concentration } (\mu g/kg) = \frac{(A_x)(V_t)(D)}{(\overline{CF})(V_i)(W_s)}$$

where A_x, V_t, D, $\overline{CF}$, and V_i are the same as for aqueous samples, and

W_s = Weight of sample extracted (g). The wet weight or dry weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

Using the units given here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.

11.5.6.3 See Method 8000 for the equation used for internal standard quantitation.

11.5.6.4 If the responses exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended

over peak area integration when overlapping peaks cause errors in area integration.

11.5.6.5 If partially overlapping or coeluting peaks are found, change GC columns or try GC/MS quantitation (see Sec. 9.0 of this method and see Method 8270).

11.5.7 Each sample analysis employing external standard calibration must be bracketed with an acceptable initial calibration, calibration verification standards (each 12-hr analytical shift), or calibration standards interspersed within the samples. The results from these bracketing standards must meet the calibration verification criteria in Sec. 11.5.2.

Although analysis of a single mid-concentration standard (standard mixture or multi-component analyte) will satisfy the minimum requirements, analysts are urged to use different calibration verification standards during organochlorine pesticide analyses. Also, multi-level standards (mixtures or multi-component analytes) are highly recommended to ensure that the detector response remains stable for all the analytes over the calibration range.

When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be evaluated to prevent misquantitations and possible false negative results, and reinjection of the sample extracts may be necessary. More frequent analyses of standards will minimize the number of sample extracts that would have to be reinjected if the QC limits are violated for the standard analysis.

However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >20%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, as the verification standard has demonstrated that the analyte would have been detected were it present. In contrast, if an analyte above the QC limits was detected in a sample extract, then reinjection is necessary to ensure accurate quantitation. If an analyte was not detected in the sample and the standard response is more than 20% below the initial calibration response, then reinjection is necessary to ensure that the detector response has not deteriorated to the point that the analyte would not have been detected even though it was present (i.e., a false negative result).

11.5.8 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. It is recommended that standards be analyzed after every 10 samples (required after every 20 samples and at the end of a set) to minimize the number of samples that must be re-injected when the standards fail the QC limits. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

11.5.9 The use of internal standard calibration techniques does not require that all sample results be bracketed with calibration verification standards. However, when internal standard calibration is used, the retention times of the internal standards and the area responses of the internal standards should be checked for each analysis. Retention time shifts of >30 sec from the retention time of the most recent calibration standard and/or changes in internal standard areas of more than -50 to +100% are cause for concern and must be investigated.

11.5.10 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. Consult with the source of the sample to determine whether further concentration of the sample is warranted.

11.5.11 Use the calibration standards analyzed during the sequence to evaluate retention time stability. Each subsequent injection of a standard during the 12-hr analytical shift (i.e., those standards injected every 20 samples, or more frequently) must be checked against the retention time windows. If any of these subsequent standards fall outside their absolute retention time windows, the GC system is out of control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

11.5.12 The identification of mixtures (i.e., chlordane and toxaphene) is not based on a single peak, but rather on the characteristic peaks that comprise the "fingerprint" of the mixture, using both the retention times and shapes of the indicator peaks. Quantitation is based on the areas of the characteristic peaks as compared to the areas of the corresponding peaks at the same retention times in the calibration standard, using either internal or external calibration procedures. See Method 8000 for information on confirmation of tentative identifications. See Sec. 11.7 of this procedure for information on the use of GC/MS as a confirmation technique.

11.5.13 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines), cleanup of the extract or replacement of the capillary column or detector is warranted. Rerun the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to Method 3600 for the procedures to be followed in sample cleanup.

11.6 Quantitation of multi-component analytes -- Multi-component analytes present problems in measurement. Suggestions are offered in the following sections for handling toxaphene, Strobane, chlordane, BHC, and DDT.

11.6.1 Toxaphene and Strobane -- Toxaphene is manufactured by the chlorination of camphenes, whereas Strobane results from the chlorination of a mixture of camphenes and pinenes. Quantitation of toxaphene or Strobane is difficult, but reasonable accuracy can be obtained. To calculate toxaphene from GC/ECD results:

11.6.1.1. Adjust the sample size so that the major toxaphene peaks are 10 - 70% of full-scale deflection (FSD).

11.6.1.2 Inject a toxaphene standard that is estimated to be within ±10 ng of the sample amount.

11.6.1.3 Quantitate toxaphene using the total area of the toxaphene pattern or using 4 to 6 major peaks.

11.6.1.3.1 While toxaphene contains a large number of compounds that will produce well resolved peaks in a GC/ECD chromatogram, it also contains many other components that are not chromatographically resolved. This unresolved complex mixture results in the "hump" in the chromatogram that is characteristic of this mixture. Although the resolved peaks are important for the identification of the mixture, the area of the unresolved complex mixture contributes a significant portion of the area of the total response.

11.6.1.3.2 To measure total area, construct the baseline of toxaphene in the sample chromatogram between the retention times of the first and last eluting toxaphene components in the standard. In order to use the total area approach, the pattern in the sample chromatogram must be compared to that of the standard to ensure that all of the major components in the standard are present in the sample. Otherwise, the sample concentration may be significantly underestimated.

11.6.1.3.3 Toxaphene may also be quantitated on the basis of 4 to 6 major peaks. A collaborative study of a series of toxaphene residues evaluated several approaches to quantitation of this compound, including the use of the total area of the peaks in the toxaphene chromatogram and the use of a subset of 4 to 6 peaks. That study indicated that the use of 4 to 6 peaks provides results that agree well with the total peak area approach and may avoid difficulties when interferences with toxaphene peaks are present in the early portion of the chromatogram from compounds such as DDT. Whichever approach is employed should be documented and available to the data user, if necessary.

11.6.1.3.4 When toxaphene is determined using the 4 to 6 peaks approach, the analyst must take care to evaluate the relative areas of the peaks chosen in the sample and standard chromatograms. It is highly unlikely that the peaks will match exactly, but the analyst should not employ peaks from the sample chromatogram whose relative sizes or areas appear to be disproportionally larger or smaller in the sample compared to the standard.

11.6.1.3.5 The heights or areas of the 4 to 6 peaks that are selected should be summed together and used to determine the toxaphene concentration. Alternatively, use each peak in the standard to calculate a calibration factor for that peak, using the total mass of toxaphene in the standard. These calibration factors are then used to calculate the concentration of each corresponding peak in the sample chromatogram and the 4 to 6 resulting concentrations are averaged to provide the final result for the sample.

11.6.2 Chlordane -- Technical chlordane is a mixture of at least 11 major components and 30 or more minor components that have been used to prepare specific pesticide formulations. The nomenclature of the various forms of chlordane has been the subject of some confusion in both Agency methods and the open literature for some time. The CAS number for technical chlordane is properly given as 12789-03-6. The two most prevalent major components of technical chlordane are *cis*-chlordane, CAS number 5103-71-9 and *trans*-chlordane, CAS number 5103-74-2. The structure represented by *trans*-chlordane has on occasion been mistakenly referred to by the name *gamma*-chlordane, and a separate CAS number of 5566-34-7 has been assigned by CAS to that designation. For the purposes of the RCRA program, the name *gamma*-chlordane is not generally used, and when reporting technical chlordane it is important to distinguish the difference between the *trans* and *gamma* isomers.

The exact percentages of *cis*-chlordane and *trans*-chlordane in the technical material are not completely defined, and are not consistent from batch to batch. Moreover, changes may occur when the technical material is used to prepare specific pesticide formulations. The approach used for evaluating and reporting chlordane results

will often depend on the end use of the results and the analyst's skill in interpreting this multicomponent pesticide residue. The following sections discuss three specific options: reporting technical chlordane (CAS number 12789-03-6), reporting chlordane (not otherwise specified, or n.o.s., CAS number 57-74-9), and reporting the individual chlordane components that can be identified under their individual CAS numbers.

11.6.2.1 When the GC pattern of the residue resembles that of technical chlordane, the analyst may quantitate chlordane residues by comparing the total area of the chlordane chromatogram using three to five major peaks or the total area. If the heptachlor epoxide peak is relatively small, include it as part of the total chlordane area for calculation of the residue. If heptachlor and/or heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected chlordane area.

NOTE: Octachloro epoxide, a metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.

To measure the total area of the chlordane chromatogram, inject an amount of a technical chlordane standard which will produce a chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms. Construct the baseline of technical chlordane in the standard chromatogram between the retention times of the first and last eluting chlordane components. Use this area and the mass of technical chlordane in the standard to calculate a calibration factor. Construct a similar baseline in the sample chromatogram, measure the area, and use the calibration factor to calculate the concentration in the sample.

11.6.2.2 The GC pattern of a chlordane residue in a sample may differ considerably from that of the technical chlordane standard. In such instances, it may not be practical to relate a sample chromatogram back to the pesticide active ingredient technical chlordane. Therefore, depending on the objectives of the analysis, the analyst may choose to report the sum of all the identifiable chlordane components as "chlordane (n.o.s.)" under the CAS number 57-74-9.

11.6.2.3 The third option is to quantitate the peaks of *cis*-chlordane, *trans*-chlordane, and heptachlor separately against the appropriate reference materials, and report these individual components under their respective CAS numbers.

11.6.2.4 To measure the total area of the chlordane chromatogram, inject an amount of a technical chlordane standard which will produce a chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms.

11.6.3 Hexachlorocyclohexane -- Hexachlorocyclohexane is also known as BHC, from the former name, benzene hexachloride. Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor. It consists of a mixture of six chemically distinct isomers and one or more heptachlorocyclohexanes and octachlorocyclohexanes. Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. Quantitate each isomer (α, β, γ, and δ) separately against a standard of the respective pure isomer.

11.6.4 DDT -- Technical DDT consists primarily of a mixture of 4,4'-DDT (approximately 75%) and 2,4'-DDT (approximately 25%). As DDT weathers, 4,4'-DDE,

2,4'-DDE, 4,4'-DDD, and 2,4'-DDD are formed. Since the 4,4'-isomers of DDT, DDE, and DDD predominate in the environment, and these are the isomers normally regulated by EPA, sample extracts should be quantitated against standards of the respective pure isomers of 4,4'-DDT, 4,4'-DDE, and 4,4'-DDD.

11.7 GC/MS confirmation

GC/MS confirmation may be used in conjunction with either single-column or dual-column analysis if the concentration is sufficient for detection by GC/MS.

11.7.1 Full-scan GC/MS will normally require a concentration of approximately 10 ng/µL in the final extract for each single-component compound. Ion trap or selected ion monitoring will normally require a concentration of approximately 1 ng/µL.

11.7.2 The GC/MS must be calibrated for the specific target pesticides when it is used for quantitative analysis. If GC/MS is used only for confirmation of the identification of the target analytes, then the analyst must demonstrate that those pesticides identified by GC/ECD can be confirmed by GC/MS. This demonstration may be accomplished by analyzing a single-point standard containing the analytes of interest at or below the concentrations reported in the GC/ECD analysis.

11.7.3 GC/MS is not recommended for confirmation when concentrations are below 1 ng/µL in the extract, unless a more sensitive mass spectrometer is employed.

11.7.4 GC/MS confirmation should be accomplished by analyzing the same extract that is used for GC/ECD analysis and the extract of the associated method blank.

11.7.5 If a base/neutral/acid extraction of an aqueous sample was performed for an analysis of semivolatile organics (e.g., Method 8270), then that extract and the associated blank may be used for GC/MS confirmation if the surrogates and internal standards do not interfere and if it is demonstrated that the analyte is stable during acid/base partitioning. However, if the compounds are *not* detected in the base/neutral/acid extract, then GC/MS analysis of the pesticide extract should be performed.

11.8 GC/AED confirmation by Method 8085 may be used in conjunction with either single-column or dual-column analysis if the concentration is sufficient for detection by GC/AED.

11.9 Chromatographic system maintenance as corrective action

When system performance does not meet the established QC requirements, corrective action is required, and may include one or more of the activities described below.

11.9.1 Splitter connections

For dual-columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few centimeters (up to 30 cm) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

11.9.2 GC injector ports

The injector ports can be of critical concern, especially in the analysis of DDT and endrin. Injectors that are contaminated, chemically active, or too hot can cause the degradation ("breakdown") of the analytes. Endrin and DDT break down to endrin aldehyde, endrin ketone, DDD, or DDE. When such breakdown is observed, clean and deactivate the injector port, break off at least 30 cm of the column and remount it. Check the injector temperature and lower it to 205 °C, if necessary. Endrin and DDT breakdown is less of a problem when ambient on-column injectors are used.

11.9.3 Metal injector body

Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

11.9.3.1 Place a beaker beneath the injector port inside the oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene, catching the rinsate in the beaker.

11.9.3.2 Prepare a solution of a deactivating agent (Sylon-CT or equivalent), following the manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, rinse the injector body with toluene, methanol, acetone, then hexane. Reassemble the injector and replace the columns.

11.9.4 Column rinsing

Rinse the column with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone. Methylene chloride is a good final rinse and in some cases may be the only solvent necessary. Fill the column with methylene chloride and allow it to stand flooded overnight to allow materials within the stationary phase to migrate into the solvent. Afterwards, flush the column with fresh methylene chloride, drain the column, and dry it at room temperature with a stream of ultrapure nitrogen.

12.0 DATA ANALYSIS AND CALCULATIONS

See Secs. 11.4 through 11.6 and Method 8000 for information on data analysis and calculations.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. <u>These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.</u>

13.2 The chromatographic separations in this method were tested in a single laboratory by using clean hexane and liquid and solid waste extracts that were spiked with the test compounds at three concentrations. Single-operator precision, overall precision, and method accuracy were found to be related to the concentration of the compound and the type of matrix.

13.3 The levels of accuracy and precision that can be achieved with this method depend on the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used.

13.4 Tables 8 and 9 contain precision (as % RSD) and accuracy (as % recovery) data generated for sewage sludge and dichloroethane stillbottoms. Table 10 contains recovery data for a clay soil, taken from Reference 10. The spiking concentration for the clay soil was 500 µg/kg. The spiking solution was mixed into the soil and then immediately transferred to the extraction device and immersed in the extraction solvent. The spiked sample was then extracted by Method 3541 (Automated Soxhlet). The data represent a single determination. Analysis was by capillary column gas chromatography/electron capture detector. These data are provided for guidance purposes only.

13.5 Table 11 contains single-laboratory precision and accuracy data for solid-phase extraction of TCLP buffer solutions spiked at two levels and extracted using Method 3535. These data are provided for guidance purposes only.

13.6 Table 12 contains multiple-laboratory data for solid-phase extraction of spiked TCLP soil leachates extracted using Method 3535. These data are provided for guidance purposes only.

13.7 Table 13 contains single-laboratory data on groundwater and wastewater samples extracted by solid-phase extraction, using Method 3535. These data are provided for guidance purposes only.

13.8 Tables 14 and 15 contain single-laboratory performance data using supercritical fluid extraction (Method 3562). Samples were analyzed by GC/ELCD. The method was performed using a variable restrictor and solid trapping material (octadecyl silane [ODS]). Three different soil samples were spiked at 5 and 250 µg/kg. Soil 1 (Delphi) is described as loamy sand, with 2.4% clay, 94% sand, 0.9% organic matter, 3.4% silt, and 0.1% moisture. Soil 2 (McCarthy) is described as sandy-loam, with 11% clay, 56% sand, 22% organic matter, 33% silt, and 8.7% moisture. Soil 3 (Auburn) is described as clay loam, with 32% clay, 21% sand, 5.4% organic matter, 46% silt, and 2.2% moisture. Seven replicate extractions were made of each soil at the two concentrations. These data are provided for guidance purposes only.

13.9 Tables 16 through 18 contain single-laboratory accuracy data for chlorinated pesticides extracted by pressurized fluid extraction (Method 3545) from clay, loam, and sand samples spiked by a commercial supplier at three certified concentrations (low, medium, and high). Samples of 10 to14 g were extracted with hexane:acetone (1:1), at 100 °C and 2000 psi, using a 5-min heating time and a 5-min static extraction. Extract volumes were 13 to 15 mL, and were adjusted prior to GC/EC analysis to match the linear range of the instrumentation. The data are taken from Reference 14, where the PFE results were presented as the percent of the results from an automated Soxhlet (Method 3541) extraction, which were in turn reported as a percent of the certified values. These data are provided for guidance purposes only.

13.10 Tables 19 and 20 contain single-laboratory accuracy data for chlorinated pesticides extracted from natural soils, glass-fiber, and sand matrices, using microwave extraction (Method 3546). Concentrations of each target analyte ranged from between 0.5 to 10 µg/g. Four real-world split samples contaminated with pesticides and creosotes were also used (obtained from

US EPA ERT, Edison, NJ). The latter were extracted by an independent laboratory using standard Soxhlet procedures and results compared to those obtained with this procedure. All samples were extracted using 1:1 hexane:acetone. Extracts were analyzed by Method 8081. Method blanks and five spiked replicates were included. Work was also carried out to assess the level of degradation of thermally labile pesticides and it was found that no significant degradation takes place under the procedure described herein. The data are taken from Reference 15. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC, 20036, (202) 872-4477), http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. V. Lopez-Avila, E. Baldin, J. Benedicto, J. Milanes, W. F. Beckert, "Application of Open-Tubular Columns to SW-846 GC Methods," report to the U.S. Environmental Protection Agency, Contract 68-03-3511, Mid-Pacific Environmental Laboratory, Mountain View, CA, 1990.

2. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters," Category 10, Pesticides and PCB Report for the U.S. Environmental Protection Agency, Contract 68-03-2606.

3. D. F. Goerlitz, L. M. Law, "Removal of Elemental Sulfur Interferences from Sediment Extracts for Pesticide Analysis," *Bull. Environ. Contam. Toxicol.*, 6, 9, 1971.

4. S. Jensen, L. Renberg, L. Reutergardth, "Residue Analysis of Sediment and Sewage Sludge for Organochlorines in the Presence of Elemental Sulfur," *Anal. Chem.*, 49, 316-318, 1977.

5. R. H. Wise, D. F. Bishop, R. T. Williams, B. M. Austern, B.M., "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges," U.S. Environmental Protection Agency, Cincinnati, OH.

6. H. B. Pionke, G. Chesters, D.E. Armstrong, "Extraction of Chlorinated Hydrocarbon Insecticides from Soil," *Agron. J*., 60, 289, 1968.

7. J. A. Burke, P. A. Mills, D.C. Bostwick, "Experiments with Evaporation of Solutions of Chlorinated Pesticides," *J. Assoc. Off. Anal. Chem*., 49, 999, 1966.

8. J. A. Glazer, et al., "Trace Analyses for Wastewaters," *Environ. Sci. and Technol.*, 15, 1426 , 1981.

9. P. J. Marsden, "Performance Data for SW-846 Methods 8270, 8081, and 8141," U.S. Environmental Protection Agency, EMSL-Las Vegas, EPA/600/4-90/015.

10. V. Lopez-Avila (Beckert, W., Project Officer), "Development of a Soxtec Extraction Procedure for Extracting Organic Compounds from Soils and Sediments," EPA 600/X-91/140, US Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, NV, October 1991.

11. C. Markell, "Solid-Phase Extraction of TCLP Leachates," Proceedings of the Tenth Annual Waste Testing and Quality Assurance Symposium, Arlington, VA, July, 1994.

12. D. Bennett, B. Lesnik, S. M. Lee, "Supercritical Fluid Extraction of Organochlorine Pesticide Residues from Soils," Proceedings of the Tenth Annual Waste Testing and Quality Assurance Symposium, Arlington, VA, July, 1994.

13. C. Markell, "3M Data Submission to EPA," letter to B. Lesnik, June 27, 1995.

14. B. Richter, J. Ezzell, and D. Felix, "Single Laboratory Method Validation Report -- Extraction of Organophosphorus Pesticides, Herbicides and Polychlorinated Biphenyls Using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC/NPD and GC/ECD," Dionex, Salt Lake City, UT, Document 101124, December 2, 1994.

15. K. Li, J. M. R. Bélanger, M. P. Llompart, R. D. Turpin, R. Singhvi, and J. R. J. Paré. Evaluation of rapid solid sample extraction using the microwave-assisted process (MAP™) under closed-vessel conditions. *Spectros. Int. J.* 13 (1), 1-14 (1997).

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

EXAMPLE GAS CHROMATOGRAPHIC RETENTION TIMES FOR THE ORGANOCHLORINE PESTICIDES USING WIDE-BORE CAPILLARY COLUMNS SINGLE-COLUMN METHOD OF ANALYSIS

	Retention Time (min)	
Compound	DB-608[a]	DB-1701[a]
Aldrin	11.84	12.50
α-BHC	8.14	9.46
β-BHC	9.86	13.58
δ-BHC	11.20	14.39
γ-BHC (Lindane)	9.52	10.84
cis-Chlordane	15.24	16.48
trans-Chlordane	14.63	16.20
4,4'-DDD	18.43	19.56
4,4'-DDE	16.34	16.76
4,4'-DDT	19.48	20.10
Dieldrin	16.41	17.32
Endosulfan I	15.25	15.96
Endosulfan II	18.45	19.72
Endosulfan sulfate	20.21	22.36
Endrin	17.80	18.06
Endrin aldehyde	19.72	21.18
Heptachlor	10.66	11.56
Heptachlor epoxide	13.97	15.03
Methoxychlor	22.80	22.34
Toxaphene	MR	MR

MR = Multiple response compound.
[a] See Table 4 for the GC operating conditions used for these analyses.

All data are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

TABLE 2

EXAMPLE GAS CHROMATOGRAPHIC RETENTION TIMES FOR THE ORGANOCHLORINE PESTICIDES USING NARROW-BORE CAPILLARY COLUMNS SINGLE-COLUMN METHOD OF ANALYSIS

	Retention Time (min)	
Compound	DB-608[a]	DB-5[a]
Aldrin	14.51	14.70
α-BHC	11.43	10.94
β-BHC	12.59	11.51
δ-BHC	13.69	12.20
γ-BHC (Lindane)	12.46	11.71
cis-Chlordane	NA	NA
trans-Chlordane	17.34	17.02
4,4'-DDD	21.67	20.11
4,4'-DDE	19.09	18.30
4,4'-DDT	23.13	21.84
Dieldrin	19.67	18.74
Endosulfan I	18.27	17.62
Endosulfan II	22.17	20.11
Endosulfan sulfate	24.45	21.84
Endrin	21.37	19.73
Endrin aldehyde	23.78	20.85
Heptachlor	13.41	13.59
Heptachlor epoxide	16.62	16.05
Methoxychlor	28.65	24.43
Toxaphene	MR	MR

NA = Data not available.
MR = Multiple response compound.
[a] See Table 3 for the GC operating conditions.

All data are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

TABLE 3

SUGGESTED GC OPERATING CONDITIONS FOR ORGANOCHLORINE COMPOUNDS
SINGLE-COLUMN ANALYSIS USING NARROW-BORE COLUMNS

Column 1 -- 30-m x 0.25 or 0.32-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1-µm film thickness.	
Carrier gas	Helium
Carrier gas pressure	16 psi
Injector temperature	225 °C
Detector temperature	300 °C
Initial temperature	100 °C, hold 2 min
Temperature program	100 °C to 160 °C at 15 °C/min, followed by 160 °C to 270 °C at 5 °C/min
Final temperature	270 °C

Column 2 -- 30-m x 0.25-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent), 1-µm film thickness.	
Carrier gas	Nitrogen
Carrier gas pressure	20 psi
Injector temperature	225 °C
Detector temperature	300 °C
Initial temperature	160 °C, hold 2 min
Temperature program	160 °C to 290 °C at 5 °C/min
Final temperature	290 °C, hold 1 min

TABLE 4

SUGGESTED GC OPERATING CONDITIONS FOR ORGANOCHLORINE COMPOUNDS
SINGLE-COLUMN ANALYSIS USING WIDE-BORE COLUMNS

Column 1 -- 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5-µm or 0.83-µm film thickness.

Column 2 -- 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent), 1.0-µm film thickness.

Both Column 1 and Column 2 use the same GC operating conditions.

Carrier gas	Helium
Carrier gas flow rate	5-7 mL/min
Makeup gas	argon/methane (P-5 or P-10) or nitrogen
Makeup gas flow rate	30 mL/min
Injector temperature	250 °C
Detector temperature	290 °C
Initial temperature	150 °C, hold 0.5 min
Temperature program	150 °C to 270 °C at 5 °C/min
Final temperature	270 °C, hold 10 min

Column 3 -- 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5-µm film thickness.

Carrier gas	Helium
Carrier gas flow rate	6 mL/min
Makeup gas	argon/methane (P-5 or P-10) or nitrogen
Makeup gas flow rate	30 mL/min
Injector temperature	205 °C
Detector temperature	290 °C
Initial temperature	140 °C, hold 2 min
Temperature program	140 °C to 240 °C at 10 °C/min, hold 5 min at 240 °C, 240 °C to 265 °C at 5 °C/min
Final temperature	265 °C, hold 18 min

TABLE 5

EXAMPLE RETENTION TIMES OF THE ORGANOCHLORINE PESTICIDES[a]
DUAL-COLUMN METHOD OF ANALYSIS

Compound	DB-5 RT (min)	DB-1701 RT (min)
DBCP	2.14	2.84
Hexachlorocyclopentadiene	4.49	4.88
Etridiazole	6.38	8.42
Chloroneb	7.46	10.60
Hexachlorobenzene	12.79	14.58
Diallate	12.35	15.07
Propachlor	9.96	15.43
Trifluralin	11.87	16.26
α-BHC	12.35	17.42
PCNB	14.47	18.20
γ-BHC	14.14	20.00
Heptachlor	18.34	21.16
Aldrin	20.37	22.78
Alachlor	18.58	24.18
Chlorothalonil	15.81	24.42
Alachlor	18.58	24.18
β-BHC	13.80	25.04
Isodrin	22.08	25.29
DCPA	21.38	26.11
δ-BHC	15.49	26.37
Heptachlor epoxide	22.83	27.31
Endosulfan-I	25.00	28.88
trans-Chlordane	24.29	29.32
cis-Chlordane	25.25	29.82
trans-Nonachlor	25.58	30.01
4,4'-DDE	26.80	30.40
Dieldrin	26.60	31.20
Perthane	28.45	32.18
Endrin	27.86	32.44
Chloropropylate	28.92	34.14
Chlorobenzilate	28.92	34.42
Nitrofen	27.86	34.42
4,4'-DDD	29.32	35.32
Endosulfan II	28.45	35.51
4,4'-DDT	31.62	36.30

TABLE 5
(continued)

Compound	DB-5 RT (min)	DB-1701 RT (min)
Endrin aldehyde	29.63	38.08
Mirex	37.15	38.79
Endosulfan sulfate	31.62	40.05
Methoxychlor	35.33	40.31
Captafol	32.65	41.42
Endrin ketone	33.79	42.26
Permethrin	41.50	45.81
Kepone	31.10	[b]
Dicofol	35.33	[b]
Dichlone	15.17	[b]
α,α´-Dibromo-*m*-xylene	9.17	11.51
2-Bromobiphenyl	8.54	12.49

[a] See Table 6 for the GC operating conditions.

[b] Not detected at 2 ng per injection.

All data are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

TABLE 6

SUGGESTED GC OPERATING CONDITIONS FOR ORGANOCHLORINE PESTICIDES
FOR DUAL-COLUMN METHOD OF ANALYSIS
LOW TEMPERATURE, THIN FILM

Column 1:	DB-1701 or equivalent 30-m x 0.53-mm ID 1.0-µm film thickness
Column 2:	DB-5 or equivalent 30-m x 0.53-mm ID 0.83-µm film thickness
Carrier gas	Helium
Carrier gas flow rate	6 mL/min
Makeup gas	Nitrogen
Makeup gas flow rate	20 mL/min
Injector temperature	250 °C
Detector temperature	320 °C
Initial temperature	140 °C, hold 2 min
Temperature program	140 °C to 270 °C at 2.8 °C/min
Final temperature	270 °C, hold 1 min

TABLE 7

SUGGESTED GC OPERATING CONDITIONS FOR ORGANOCHLORINE PESTICIDES
FOR THE DUAL-COLUMN METHOD OF ANALYSIS
HIGH TEMPERATURE, THICK FILM

Column 1:	DB-1701 or equivalent 30-m x 0.53-mm ID 1.0-µm film thickness
Column 2:	DB-5 or equivalent 30-m x 0.53-mm ID 1.5-µm film thickness
Carrier gas:	Helium
Carrier gas flow rate:	6 mL/min
Makeup gas:	Nitrogen
Makeup gas flow rate:	20 (mL/min)
Injector temperature:	250 °C
Detector temperature:	320 °C
Initial temperature:	150 °C, hold 0.5 min
Temperature program:	150 °C to 190 °C at 12 °C/min, hold 2 min190 °C to 275 °C at 4 °C/min
Final temperature	275 °C, hold 10 min

TABLE 8

EXAMPLE ANALYTE RECOVERY FROM SEWAGE SLUDGE

	Ultrasonic Extraction		Soxhlet	
Compound	% Recovery	% RSD	% Recovery	% RSD
Hexachloroethane	80	7	79	1
2-Chloronapthalene	50	56	67	8
4-Bromodiphenyl ether	118	4	nd	nd
α-BHC	88	25	265	18
γ-BHC	55	9	155	29
Heptachlor	60	13	469	294
Aldrin	92	33	875	734
β-BHC	351	71	150	260
δ-BHC	51	11	57	2
Heptachlor epoxide	54	11	70	3
Endosulfan I	52	11	70	4
trans-Chlordane	50	9	65	1
cis-Chlordane	49	8	66	0
DDE	52	11	74	1
Dieldrin	89	19	327	7
Endrin	56	10	92	15
Endosulfan II	52	10	88	11
DDT	57	10	95	17
Endrin aldehyde	45	6	42	10
DDD	57	11	99	8
Tetrachloro-*m*-xylene	71	19	82	1
Decachlorobiphenyl	26	23	28	48

nd = Not detected
Concentration spiked in the sample: 500-1000 ng/g, analyses of three replicates.
Soxhlet extraction by Method 3540 with methylene chloride.
Ultrasonic extraction by Method 3550 with methylene chloride/acetone (1:1).
Cleanup by Method 3640.
GC column: DB-608, 30-m x 0.53-mm ID.

These data are provided for guidance purposes only.

TABLE 9

EXAMPLE ANALYTE RECOVERY FROM DICHLOROETHANE STILLBOTTOMS

	Ultrasonic Extraction		Soxhlet	
Compound	% Recovery	% RSD	% Recovery	% RSD
Hexachloroethane	70	2	50	30
2-Chloronapthalene	59	3	35	35
4-Bromodiphenyl ether	159	14	128	137
α-BHC	55	7	47	25
γ-BHC	43	6	30	30
Heptachlor	48	6	55	18
Aldrin	48	5	200	258
β-BHC	51	7	75	42
δ-BHC	43	4	119	129
Heptachlor epoxide	47	6	66	34
Endosulfan I	47	4	41	18
trans-Chlordane	48	5	47	13
cis-Chlordane	45	5	37	21
DDE	45	4	70	40
Dieldrin	45	5	58	24
Endrin	50	6	41	23
Endosulfan II	49	5	46	17
DDT	49	4	40	29
Endrin aldehyde	40	4	29	20
DDD	48	5	35	21
Tetrachloro-*m*-xylene	49	2	176	211
Decachlorobiphenyl	17	29	104	93

Concentration spiked in the sample: 500-1000 ng/g, three replicates analyses.
Soxhlet extraction by Method 3540 with methylene chloride.
Ultrasonic extraction by Method 3550 with methylene chloride/acetone (1:1).
Cleanup by Method 3640.
GC column: DB-608, 30-m x 0.53-mm ID.

These data are provided for guidance purposes only.

TABLE 10

EXAMPLE SINGLE-LABORATORY ACCURACY DATA FOR THE EXTRACTION OF ORGANOCHLORINE PESTICIDES FROM SPIKED CLAY SOIL BY METHOD 3541 (AUTOMATED SOXHLET)[a]

	Percent Recovery	
Compound	DB-5	DB-1701
α-BHC	89	94
β-BHC	86	ND
Heptachlor	94	95
Aldrin	ND	92
Heptachlor epoxide	97	97
trans-Chlordane	94	95
Endosulfan I	92	92
Dieldrin	ND	113
Endrin	111	104
Endosulfan II	104	104
4,4'-DDT	ND	ND
Mirex	108	102

[a] The operating conditions for the automated Soxhlet were:

Immersion time 45 min
Extraction time 45 min
10-g sample size
Extraction solvent 1:1 acetone/hexane
No equilibration time following spiking.

ND = Not able to determine because of interference.

All compounds were spiked at 500 µg/kg.

Data are taken from Reference 10.

These data are provided for guidance purposes only.

TABLE 11

EXAMPLE SINGLE-LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION OF ORGANOCHLORINE PESTICIDES FROM TCLP BUFFERS SPIKED AT TWO LEVELS

Compound	Spike Level (µg/L)	Buffer 1 (pH = 2.886)		Buffer 2 (pH = 4.937)	
		Recovery (%)	RSD	Recovery (%)	RSD
Low Level Spike					
Toxaphene	250	86	13	77	17
Chlordane	15	88	7	95	6
γ-BHC (Lindane)	200	115	7	98	5
Heptachlor	4	95	11	77	23
Heptachlor epoxide	4	107	9	104	12
Endrin	10	89	5	100	6
Methoxychlor	5000	97	8	95	6
High Level Spike					
Toxaphene	1000	106	7	85	15
Chlordane	60	116	12	107	12
γ-BHC (Lindane)	800	109	19	112	5
Heptachlor	16	113*	18*	93	3
Heptachlor epoxide	16	82	17	91	7
Endrin	40	84	19	82	4
Methoxychlor	20,000	100	4	87	8

Results were from seven replicate spiked buffer samples, except where noted with *, which indicates that only three replicates were analyzed.

These data are provided for guidance purposes only.

TABLE 12

EXAMPLE RECOVERY DATA FROM THREE LABORATORIES FOR SOLID-PHASE EXTRACTION OF ORGANOCHLORINE PESTICIDES FROM SPIKED TCLP LEACHATES FROM SOIL SAMPLES

Compound	Spike Level (µg/L)*	Lab 1			Lab 2			Lab 3		
		%R	RSD	n	%R	RSD	n	%R	RSD	n
Buffer 1 pH = 2.886										
Toxaphene	500	75	25	7	95.4	2.4	3	86.0	4.3	3
Chlordane	30	80	15	7	57.8	12.0	3	73.8	0.9	3
γ-BHC (Lindane)	400	104	11	7	99.3	0.6	3	86.6	6.4	3
Heptachlor	8	88	13	7	70.8	20.4	3	88.0	9.1	3
Heptachlor epoxide	8	92	13	7	108.7	6.9	3	75.0	2.8	3
Endrin	20	106	12	7	110	0	3	78.3	4.6	3
Methoxychlor	10,000	107	12	7	86.7	2.2	3	84.8	8.5	3
Buffer 2 pH = 4.937										
Toxaphene	500	87	9	7	98	4.1	3	88.8	4.1	3
Chlordane	30	91	8	7	66.7	5.0	3	73.7	11.5	3
γ-BHC (Lindane)	400	74	20	7	102.7	2.2	3	89.3	3.1	3
Heptachlor	8	71	21	7	62.5	20	3	85.0	1.5	3
Heptachlor epoxide	8	118	1	3	113	0	3	81.3	2.7	3
Endrin	20	124	7	3	111.7	2.6	3	83.0	3.4	3
Methoxychlor	10,000	73	22	7	88.8	2.7	3	89.6	2.7	3

* 250-mL aliquots of leachate were spiked by Labs 2 and 3 at the levels shown. Lab 1 spiked at one-half these levels.
These data are provided for guidance purposes only.

TABLE 13
EXAMPLE SINGLE-LABORATORY ACCURACY AND PRECISION DATA FOR SOLID-PHASE EXTRACTION BY METHOD 3535[1]

	Bias (%)				Precision (%)			
Compound	Ground water (low)	Ground water (high)	Waste water (low)	Waste water (high)	Ground water (low)	Ground water (high)	Waste water (low)	Waste water (high)
Aldrin	37.3	93.5	79.3	94.0	23.7	5.5	6.7	3.4
β-BHC	89.2	107.8	79.7	82.3	6.5	2.5	1.6	4.2
δ-BHC	106.2	86.0	88.9	83.4	5.6	2.4	2.5	4.2
cis-Chlordane	75.4	112.3	78.9	89.5	12.8	2.7	4.7	2.4
trans-Chlordane	70.7	98.9	79.9	93.9	15.8	2.7	4.6	2.9
Dieldrin	83.4	96.1	81.2	93.3	7.1	2.3	3.8	3.6
Endosulfan I	79.6	99.1	79.6	87.9	10.6	2.3	4.1	3.8
Endosulfan II	94.5	101.6	82.7	93.5	5.8	2.8	4.2	4.1
Endrin	88.3	98.4	85.1	89.6	6.2	2.3	3.1	2.9
Endrin aldehyde	87.5	99.9	69.0	80.2	6.0	4.0	3.3	5.9
Heptachlor	43.1	95.4	71.8	78.6	19.2	3.9	5.0	2.8
Heptachlor epoxide	76.4	97.6	75.3	83.4	12.1	2.4	2.9	3.3
Lindane	81.3	115.2	82.1	85.3	11.1	3.2	2.4	3.1
4,4'-DDE	80.3	96.0	85.1	97.9	8.3	2.5	4.4	2.4
4,4'-DDT	86.6	105.4	105	111	4.4	2.7	4.3	4.7
4,4'-TDE (DDD)	90.5	101.1	74.9	79.6	4.8	2.4	4.6	2.9

[1]All results determined from seven replicates of each sample type. Two spiking levels were used. "Low" samples were spiked at 5-10 µg/L for each analyte, while "high" samples were spiked at 250 - 500 µg/L.
These data are provided for guidance purposes only.

TABLE 14

EXAMPLE RECOVERY (BIAS) OF ORGANOCHLORINE PESTICIDES USING SFE METHOD 3562
(Seven replicates)

Compound	Delphi[a] 250 µg/kg	Delphi[a] 5 µg/kg	McCarthy[b] 250 µg/kg	McCarthy[b] 5 µg/kg	Auburn[c] 250 µg/kg	Auburn[c] 5 µg/kg	Mean Recovery
γ-BHC	102.6	66.4	80.7	82.7	86.0	86.1	84.1
β-BHC	101.9	73.0	86.1	85.1	87.4	86.3	86.6
Heptachlor	101.3	61.6	78.0	79.1	83.3	80.4	80.6
δ-BHC	120.9	82.3	90.4	89.6	92.9	89.4	94.2
Aldrin	56.7	28.7	52.1	77.1	42.1	74.6	55.2
Heptachlor epoxide	102.3	71.9	87.1	87.4	89.6	91.1	88.2
cis-Chlordane	106.4	87.1	88.1	105.9	91.7	97.1	96.1
4,4'DDE	110.9	75.7	88.4	118.7	83.6	110.9	98.0
Dieldrin	106.9	80.4	88.1	140.8	90.6	80.1	97.8
Endrin	211.0	87.0	111.7	98.7	90.5	87.6	114.4
4,4'-DDD	93.0	80.4	85.0	88.1	83.7	90.4	86.8
Endosulfan II	105.6	89.9	92.1	88.6	87.7	92.9	92.5
4,4'-DDT	126.7	81.3	110.9	199.7	83.6	124.3	121.1
Endrin aldehyde	64.3	74.0	63.0	86.7	21.0	38.3	37.9
Matrix Mean Recovery	107.9	74.3	85.9	102.0	79.8	87.8	89.5

[a] Delphi: Loamy sand soil
[b] McCarthy: Sandy loamy-organic rich soil
[c] Auburn: Clay-loamy soil
These data are provided for guidance purposes only.

TABLE 15

EXAMPLE RELATIVE STANDARD DEVIATION (PRECISION) OF ORGANOCHLORINE PESTICIDES USING SFE METHOD 3562
(Seven replicates)

Compound	Delphi[a] 250 µg/kg	Delphi[a] 5 µg/kg	McCarthy[b] 250 µg/kg	McCarthy[b] 5 µg/kg	Auburn[c] 250 µg/kg	Auburn[c] 5 µg/kg	Mean
γ-BHC	3.9	3.3	3.3	6.5	4.0	1.6	3.7
β-BHC	6.5	3.0	3.0	4.3	4.6	2.0	3.9
Heptachlor	4.4	2.1	4.3	5.0	4.4	2.6	3.8
δ-BHC	5.3	3.1	3.3	7.1	4.1	3.5	4.4
Aldrin	2.9	5.5	2.8	4.6	1.6	1.9	3.2
Heptachlor epoxide	3.0	2.7	3.6	4.3	4.7	4.2	3.8
cis-Chlordane	3.6	5.7	4.8	13.8	4.2	2.5	5.8
4,4'DDE	5.2	15.3	4.8	4.2	7.7	3.4	6.8
Dieldrin	4.3	4.5	2.9	23.9	5.0	3.1	7.3
Endrin	7.2	6.0	4.5	6.0	4.3	10.5	6.4
4,4'-DDD	6.9	3.1	3.7	3.5	4.3	7.4	4.8
Endosulfan II	5.1	4.7	3.2	3.3	5.5	4.6	4.4
4,4'-DDT	12.5	6.2	6.6	5.9	4.9	3.4	6.6
Endrin aldehyde	3.9	7.5	4.7	11.6	1.9	26.0	9.3
Matrix Mean Recovery	5.3	5.2	4.0	7.4	4.4	5.5	5.3

[a] Delphi: Loamy sand soil
[b] McCarthy: Sandy loamy-organic rich soil
[c] Auburn: Clay-loamy soil
These data are provided for guidance purposes only.

TABLE 16

EXAMPLE SINGLE-LABORATORY ORGANOCHLORINE PESTICIDES DATA FROM THREE SOIL MATRICES SPIKED AT 5 TO 10 PPB AND EXTRACTED USING METHOD 3545 (PRESSURIZED FLUID EXTRACTION)

		PFE Recovery and Precision					
	Certified Value	Clay		Loam		Sand	
Compound	(µg/L)	% Rec.	RSD	% Rec	RSD	% Rec	RSD
Aldrin	5.2	65	10	60	6	71	11
α-BHC	5.0	52	7	50	10	60	12
β-BHC	5.0	84	6	76	5	92	11
δ-BHC	5.0	100	7	96	4	104	11
γ-BHC (Lindane)	5.0	6	6	62	8	74	12
cis-Chlordane	4.9	9	7	86	4	84	11
trans-Chlordane	4.9	9	8	82	5	86	11
4,4'-DDD	10.1	8	8	84	5	87	10
4,4'-DDE	4.9	10	7	90	5	96	12
4,4'-DDT	4.8	90	7	67	6	88	17
Dieldrin	5.0	94	8	84	4	88	11
Endosulfan I	5.0	88	8	80	5	78	11
Endosulfan II	5.0	88	7	84	4	86	10
Endosulfan sulfate	9.5	93	7	87	3	88	11
Endrin	9.8	84	9	81	5	85	11
Endrin aldehyde	5.0	86	7	76	4	64	15
Endrin ketone	9.7	100	6	90	4	94	11
Heptachlor	5.0	70	8	64	8	76	12
Heptachlor epoxide	5.0	78	8	76	5	82	11
Methoxychlor	5.0	82	7	62	6	80	17

Seven replicate extractions were performed using 14-g samples of spiked soil from a commercial supplier. Hexane:acetone (1:1) was used as the extraction solvent, at 100 °C and 2000 psi, using a 5-min heating time and a 5-min static extraction.

Data are adapted from Reference 14.
These data are provided for guidance purposes only.

TABLE 17

EXAMPLE SINGLE-LABORATORY ORGANOCHLORINE PESTICIDES DATA FROM THREE SOIL MATRICES SPIKED AT 50 TO 100 PPB AND EXTRACTED USING METHOD 3545 (PRESSURIZED FLUID EXTRACTION)

		PFE Recovery and Precision					
		Clay		Loam		Sand	
Compound	Certified Value (µg/L)	% Rec.	RSD	% Rec	RSD	% Rec	RSD
Aldrin	51.5	77	5	77	11	72	9
α-BHC	49.5	64	6	67	11	62	9
β-BHC	49.5	79	3	81	9	77	7
δ-BHC	50.0	85	4	88	9	83	7
γ-BHC (Lindane)	49.5	74	5	77	11	73	9
cis-Chlordane	48.6	87	4	85	9	81	8
trans-Chlordane	49.1	87	3	85	9	82	8
4,4'-DDD	101.0	90	3	90	7	87	8
4,4'-DDE	49.1	95	4	93	8	90	8
4,4'-DDT	48.4	79	7	73	13	75	15
Dieldrin	49.6	94	4	88	8	85	8
Endosulfan I	49.8	85	3	82	9	80	8
Endosulfan II	49.7	94	4	91	7	88	8
Endosulfan sulfate	94.7	93	4	89	7	87	8
Endrin	98.0	86	3	83	8	81	8
Endrin aldehyde	49.5	78	4	75	7	75	8
Endrin ketone	97.2	95	4	91	8	85	8
Heptachlor	49.5	70	5	72	11	68	10
Heptachlor epoxide	49.8	89	3	84	9	80	8
Methoxychlor	49.6	79	8	74	12	74	14

Seven replicate extractions were performed using 10-g samples of spiked soil from a commercial supplier. Hexane:acetone (1:1) was used as the extraction solvent, at 100 °C and 2000 psi, using a 5-min heating time and a 5-min static extraction.

Data are adapted from Reference 14.
These data are provided for guidance purposes only.

TABLE 18

EXAMPLE SINGLE-LABORATORY ORGANOCHLORINE PESTICIDES DATA FROM THREE SOIL MATRICES SPIKED AT 250 TO 500 PPB AND EXTRACTED USING METHOD 3545 (PRESSURIZED FLUID EXTRACTION)

		PFE Recovery and Precision					
	Certified Value	Clay		Loam		Sand	
Compound	(µg/L)	% Rec.	RSD	% Rec	RSD	% Rec	RSD
Aldrin	257	66	3	71	11	60	16
α-BHC	247	54	5	59	11	51	14
β-BHC	247	67	2	72	9	63	13
δ-BHC	250	70	2	76	10	66	13
γ-BHC (Lindane)	247	64	4	69	11	60	14
cis-Chlordane	243	72	2	76	9	65	15
trans-Chlordane	245	73	2	76	9	65	15
4,4'-DDD	507	72	3	76	8	66	14
4,4'-DDE	246	83	3	87	9	75	14
4,4'-DDT	242	77	6	82	10	71	20
Dieldrin	248	78	2	81	9	70	15
Endosulfan I	249	71	2	74	9	64	15
Endosulfan II	249	82	2	84	8	72	15
Endosulfan sulfate	474	81	4	83	8	72	17
Endrin	490	70	3	72	8	63	15
Endrin aldehyde	247	71	3	74	8	64	17
Endrin ketone	486	92	3	94	8	81	16
Heptachlor	247	63	3	68	11	58	16
Heptachlor epoxide	249	70	2	75	9	64	15
Methoxychlor	248	81	7	85	9	74	19

Seven replicate extractions were performed using 10-g samples of spiked soil from a commercial supplier. Hexane:acetone (1:1) was used as the extraction solvent, at 100 °C and 2000 psi, using a 5-min heating time and a 5-min static extraction.

Data are adapted from Reference 14.
These data are provided for guidance purposes only.

TABLE 19

EXAMPLE SINGLE-LABORATORY ORGANOCHLORINE PESTICIDES DATA FROM A REAL-WORLD SOIL MATRIX SPIKED AT THE 500 PPB LEVEL AND EXTRACTED USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Recovery (%)	RSD (%)
α-BHC	96	3
β-BHC	126	8
γ-BHC	103	4
δ-BHC	115	5
Heptachlor	131	5
Aldrin	103	2
Heptachlor epoxide	126	9
Endosulfan I	122	5
DDE + Dieldrin	118	4
Endrin	155	12
Endosulfan II	116	5
DDD	95	7
Endosulfan aldehyde	103	9
Endosulfan sulfate	122	5
DDT	118	5
Methoxychlor	119	6

n = 3

DDE and dieldrin are reported as the sum of the two compounds since they were not resolved by chromatography.

Concentrations of each analyte ranged from between 0.5 to 10 µg/g.

Data are taken from Reference 15.
These data are provided for guidance purposes only.

TABLE 20

EXAMPLE SINGLE-LABORATORY COMPARISON OF
METHOD 3546 (MICROWAVE EXTRACTION) AND METHOD 3540 (SOXHLET EXTRACTION)
OF ORGANOCHLORINE PESTICIDES FROM A REAL-WORLD CONTAMINATED SOIL

	Microwave Extraction Results				
Compound	Average Concentration (µg/kg)	Standard Deviation (µg/kg)	RSD (%)	n	Soxhlet Result (µg/kg)
DDE + dieldrin	3,400	340	10	3	7,100
Endrin	22,000	2,300	11	3	22,000
*DDD	40,000	5,800	14	3	45,000
*DDT	63,000	8,400	13	3	62,000
*Methoxychlor	17,000	2,000	12	3	16,000
cis-Chlordane	730	100	13	3	750
trans-Chlordane	720	90	12	3	910

* Sample extracts were diluted 1:5 for these compounds.

Soil samples obtained from the US EPA Emergency Response Center archive bank through their contract laboratory, REAC (Edison, NJ). The single Soxhlet extraction was performed by REAC three years earlier and the long storage period is believed to account for the low DDE + dieldrin recovery in the present study.

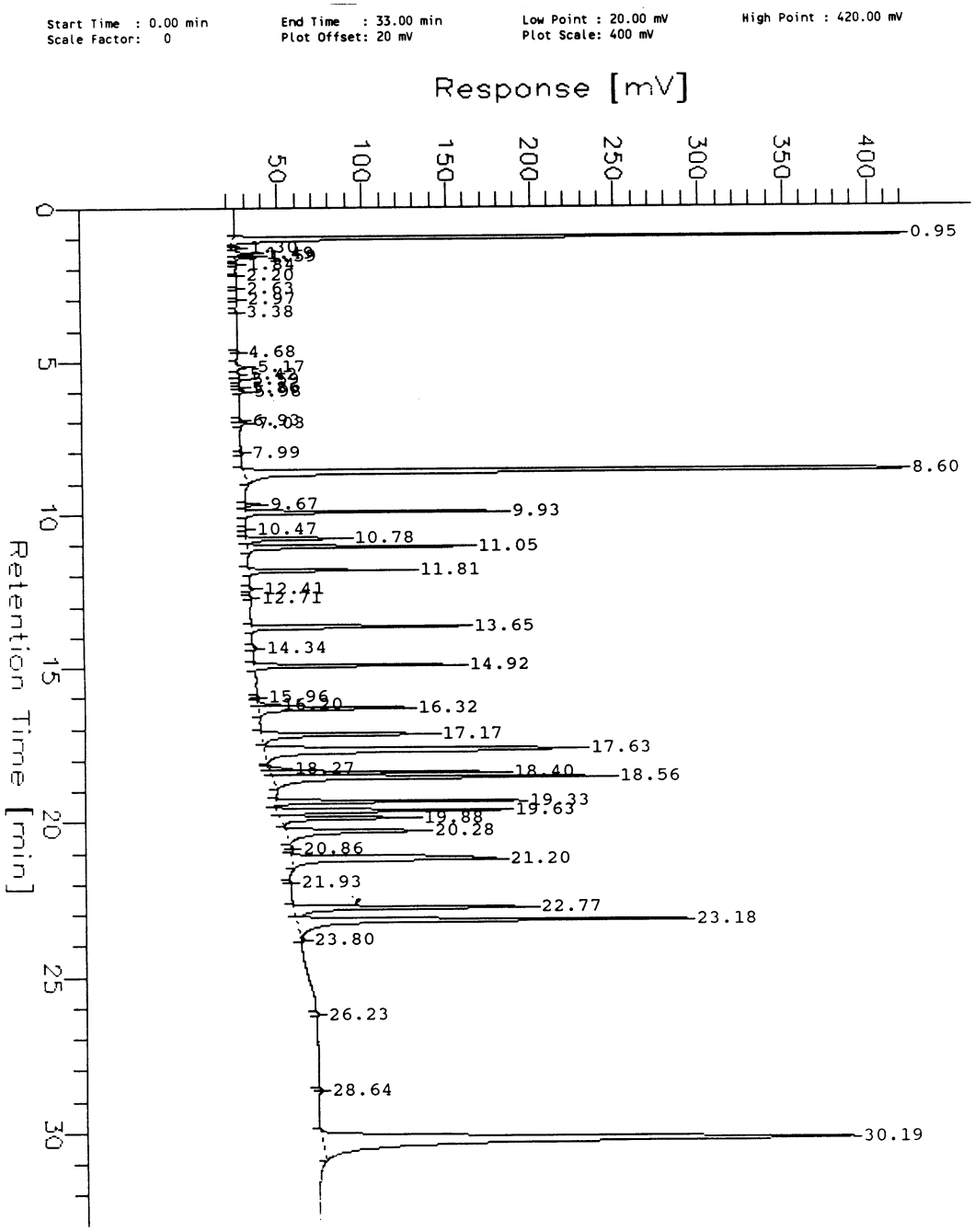
DDE and dieldrin are reported as the sum of the compounds since they were not resolved by chromatography.

Concentrations of each analyte ranged from between 0.5 to 10 µg/g.

Data are taken from Reference 15.
These data are provided for guidance purposes only.

FIGURE 1

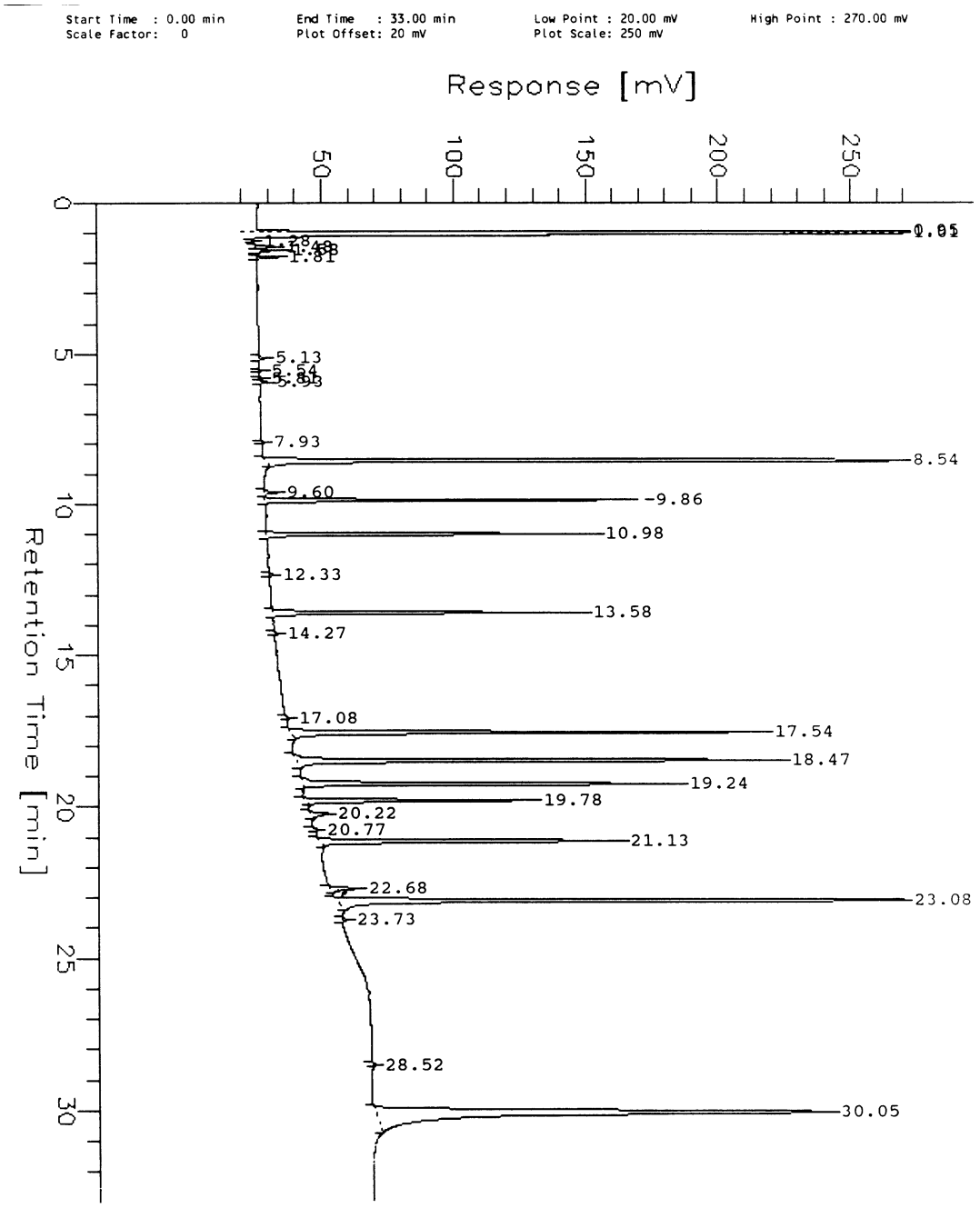
EXAMPLE GAS CHROMATOGRAM OF
THE MIXED ORGANOCHLORINE PESTICIDE STANDARD



Column: 30-m x 0.25-mm ID, DB-5
Temperature program: 100 °C (hold 2 min) to 160 °C at 15 °C/min, then at 5 °C/min to 270 °C; carrier He at 16 psi

FIGURE 2

EXAMPLE GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX A

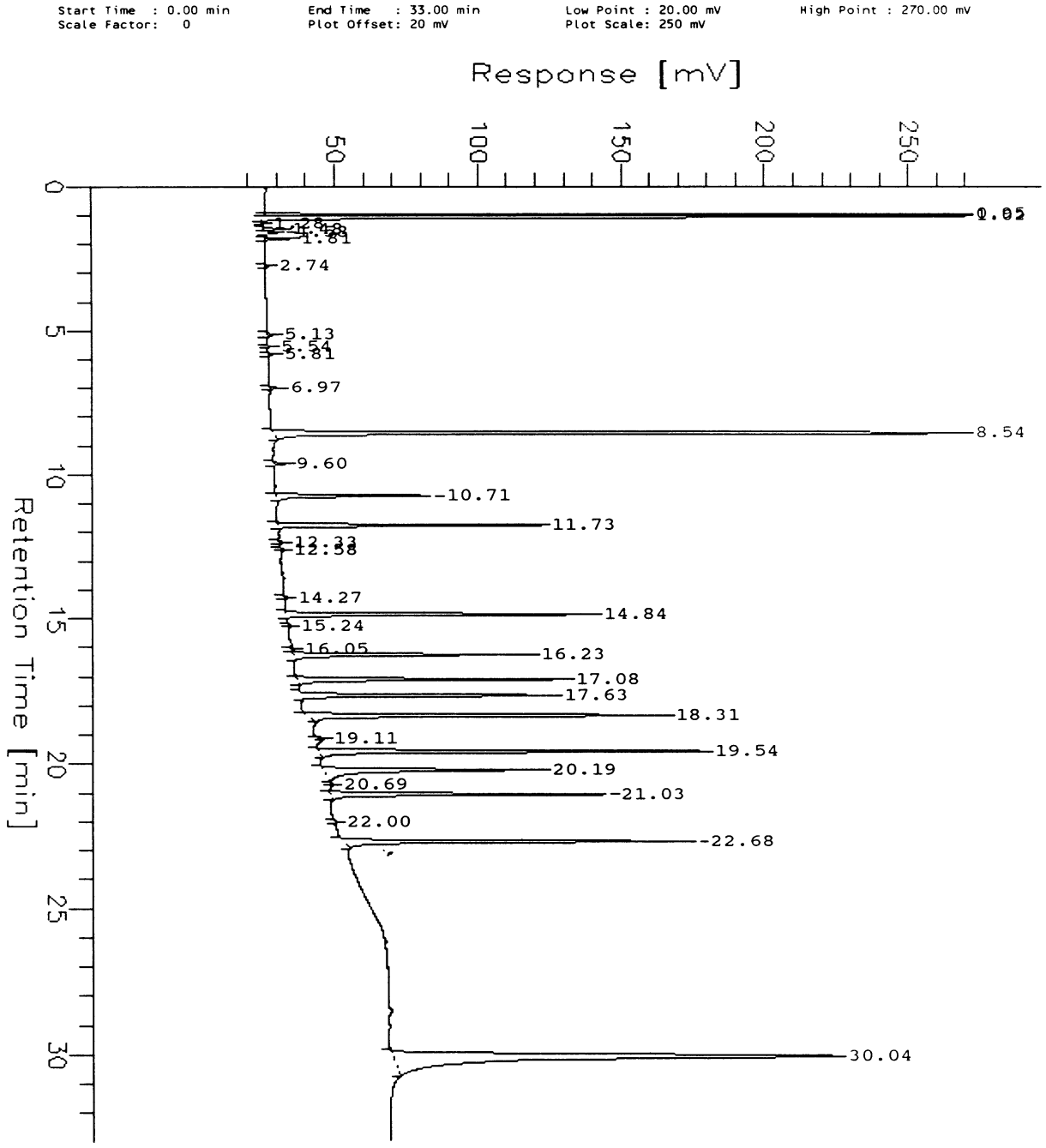


Column: 30-m x 0.25-mm ID, DB-5

Temperature program: 100 °C (hold 2 min) to 160 °C at 15 °C/min, then at 5 °C/min to 270 °C; carrier He at 16 psi.

FIGURE 3

EXAMPLE GAS CHROMATOGRAM OF INDIVIDUAL ORGANOCHLORINE PESTICIDE STANDARD MIX B

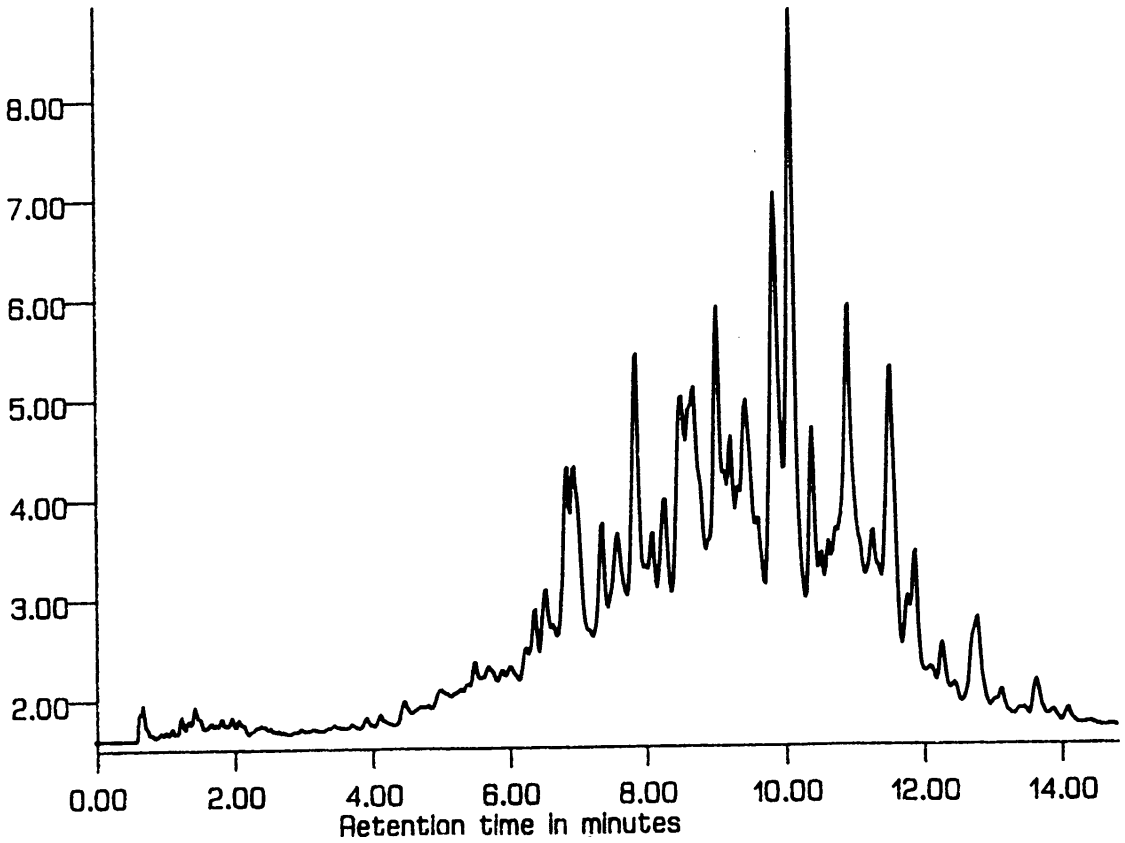


Column: 30-m x 0.25-mm ID, DB-5

Temperature program: 100 °C (hold 2 min) to 160 °C at 15 °C/min, then at 5 °C/min to 270 °C; carrier He at 16 psi.

FIGURE 4

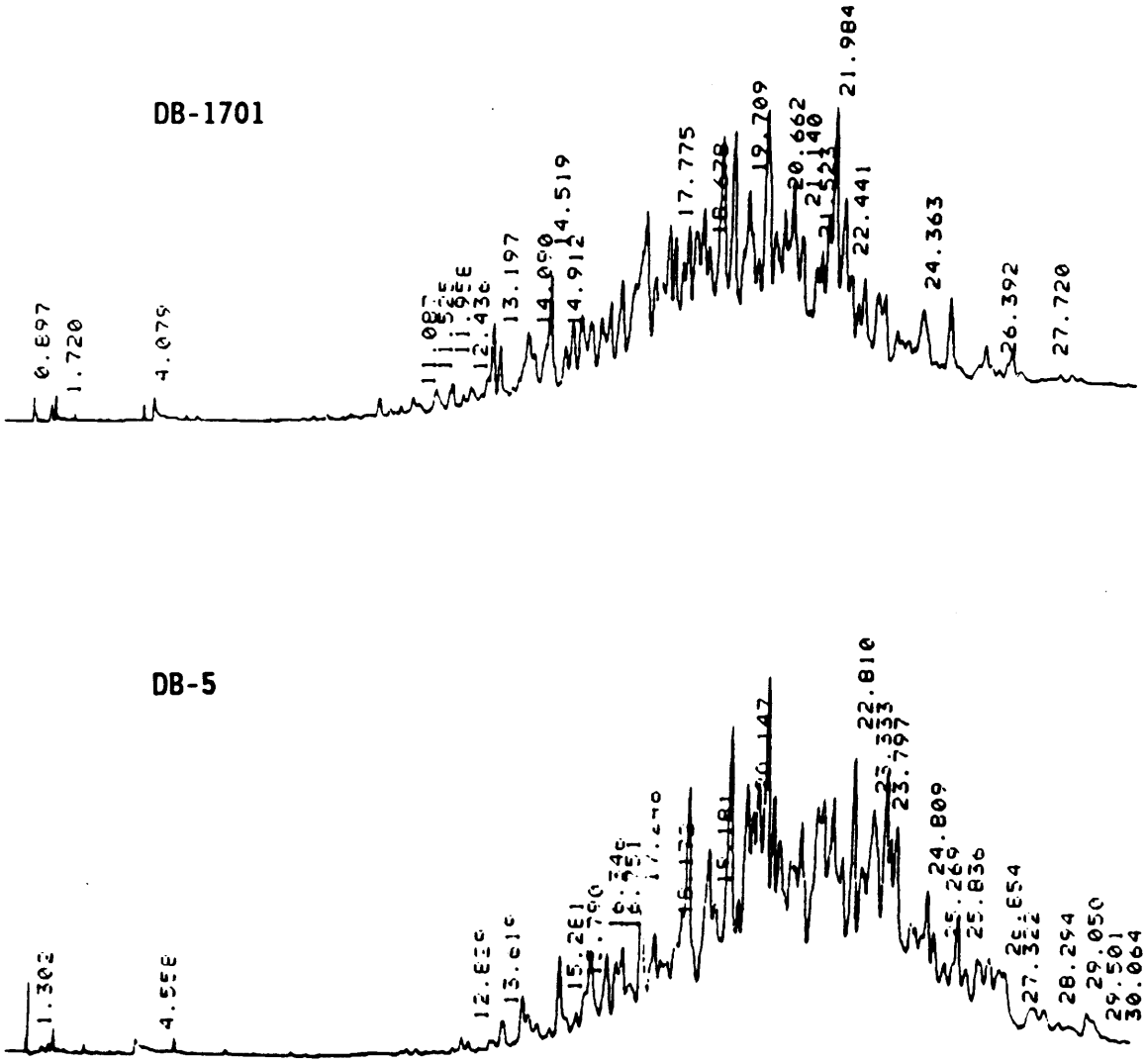
EXAMPLE GAS CHROMATOGRAM OF TOXAPHENE



Toxaphene analyzed on an SPB-608 fused-silica open-tubular column. The GC operating conditions were as follows: 30-m x 0.53-mm ID SPB-608. Temperature program: 200 °C (2 min hold) to 290 °C at 6 °C/min.

FIGURE 5

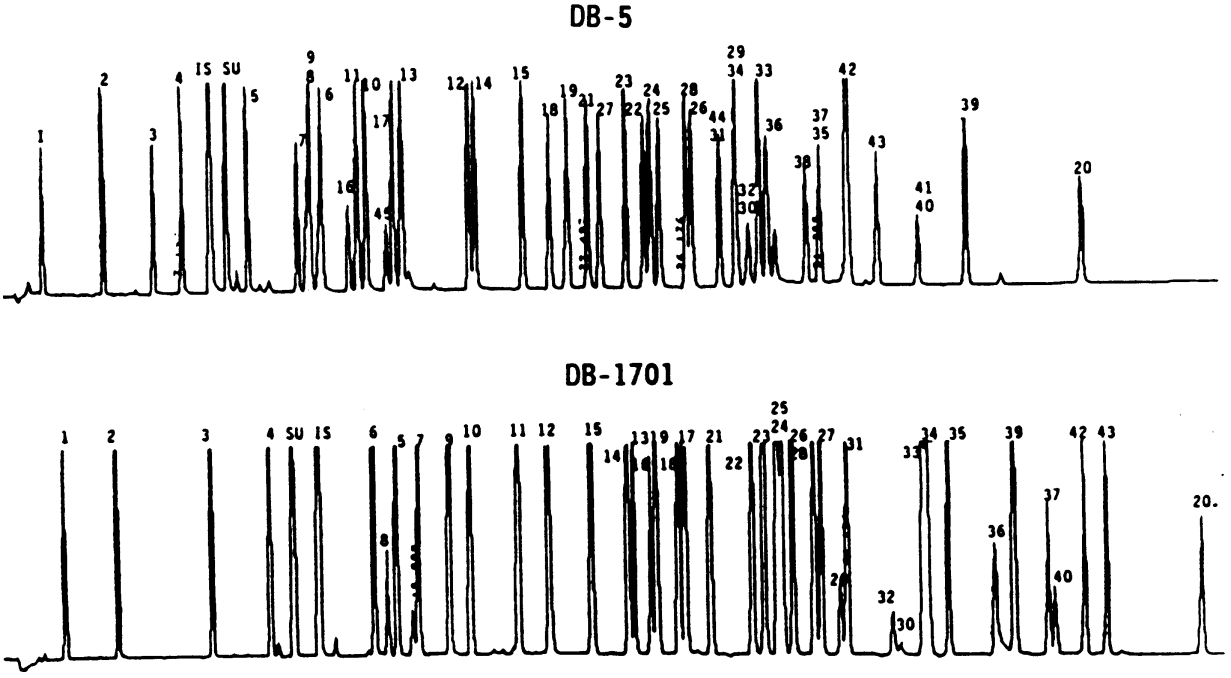
EXAMPLE GAS CHROMATOGRAM OF STROBANE



Strobane analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30-m x 0.53-mm ID DB-5 (1.5-µm film thickness) and 30-m x 0.53-mm ID DB-1701 (1.0-µm film thickness) connected to a J&W Scientific press-fit Y-shaped inlet splitter. Temperature program: 150 °C (0.5 min hold) to 190 °C (2 min hold) at 12 °C/min then to 275 °C (10 min hold) at 4 °C/min.

FIGURE 6

EXAMPLE GAS CHROMATOGRAM OF ORGANOCHLORINE PESTICIDES



Organochlorine pesticides analyzed on a DB-5/DB-1701 fused-silica open-tubular column pair. The GC operating conditions were as follows: 30-m x 0.53-mm ID DB-5 (0.83-µm film thickness) and 30-m x 0.53-mm ID DB-1701 (1.0-µm film thickness) connected to an 8-in. injection tee (Supelco Inc.). Temperature program: 140 °C (2 min hold) to 270 °C (1 min hold) at 2.8 °C/min.

METHOD 8082A

POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be followed by individuals formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method may be used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors or as individual PCB congeners in extracts from solid, tissue, and aqueous matrices, using open-tubular, capillary columns with electron capture detectors (ECD) or electrolytic conductivity detectors (ELCD). The Aroclors and PCB congeners listed below have been determined by this method, using either a single- or dual column analysis system, and this method may be appropriate for additional congeners and Aroclors (see Sec. 1.4). The method also may be applied to other matrices such as oils and wipe samples, if appropriate sample extraction procedures are employed.

Compound	CAS Registry No.[a]	IUPAC #
Aroclor 1016	12674-11-2	-
Aroclor 1221	11104-28-2	-
Aroclor 1232	11141-16-5	-
Aroclor 1242	53469-21-9	-
Aroclor 1248	12672-29-6	-
Aroclor 1254	11097-69-1	-
Aroclor 1260	11096-82-5	-
2-Chlorobiphenyl	2051-60-7	1
2,3-Dichlorobiphenyl	16605-91-7	5
2,2',5-Trichlorobiphenyl	37680-65-2	18
2,4',5-Trichlorobiphenyl	16606-02-3	31
2,2',3,5'-Tetrachlorobiphenyl	41464-39-5	44
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	52
2,3',4,4'-Tetrachlorobiphenyl	32598-10-0	66
2,2',3,4,5'-Pentachlorobiphenyl	38380-02-8	87
2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	101
2,3,3',4',6-Pentachlorobiphenyl	38380-03-9	110
2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	138
2,2',3,4,5,5'-Hexachlorobiphenyl	52712-04-6	141

Compound	CAS Registry No.[a]	IUPAC #
2,2',3,5,5',6-Hexachlorobiphenyl	52663-63-5	151
2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	153
2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6	170
2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	180
2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1	183
2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0	187
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	40186-72-9	206

[a]Chemical Abstract Service Registry No.

1.2 Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns compared to those of Aroclor standards.

1.3 The seven Aroclors listed in Sec. 1.1 are those that are commonly specified in EPA regulations. The quantitation of PCBs as Aroclors is appropriate for many regulatory compliance determinations, but is particularly difficult when the Aroclors have been weathered by long exposure in the environment. Therefore, this method provides procedures for the determination of a selected group of the 209 possible PCB congeners, as another means to measure the concentrations of weathered Aroclors. The 19 PCB congeners listed above have been tested by this method and were chosen for testing because many of them represent congeners specific to the common Aroclor formulations (see Table 6). These 19 PCB congeners do not represent the co-planar PCBs or the other PCBs of greatest toxicological significance. **The analytical procedures for these 19 congeners may be appropriate for the analysis of other congeners not specifically included in this method and may be used as a template for the development of such a procedure.** However, all 209 PCB congeners cannot be separated using the GC columns and procedures described in this method. If this procedure is expanded to encompass other congeners, then the analyst must either document the resolution of the congeners in question, or establish procedures for reporting the results of coeluting congeners that are appropriate for the intended application.

1.4 The PCB congener approach potentially affords greater quantitative accuracy when PCBs are known to be present. As a result, this method may be used to determine Aroclors, some PCB congeners, or "total PCBs," depending on regulatory requirements and project needs. The congener method is of particular value in determining weathered Aroclors. However, analysts should use caution when using the congener method when regulatory requirements are based on Aroclor concentrations. Also, this method is not appropriate as currently written for the determination of the co-planar PCB congeners at the very low (sub part per trillion) concentrations sometimes needed for risk assessment purposes.

1.5 Compound identification based on single-column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS (e.g., Method 8270) is also recommended as a confirmation technique, if sensitivity permits (also see Sec. 11.11 of this method). GC/AED may also be used as a confirmation technique, if sensitivity permits (see Method 8085).

1.6 This method includes a dual-column option that describes a hardware configuration in which two GC columns are connected to a single injection port and to two separate detectors. The option allows one injection to be used for dual-column simultaneous analysis.

1.7 The analyst must select columns, detectors and calibration procedures most appropriate for the specific analytes of interest in a study. Matrix-specific performance data must be established and the stability of the analytical system and instrument calibration must be established for each analytical matrix (e.g., hexane solutions from sample extractions, diluted oil samples, etc.). Example chromatograms and GC conditions are provided as guidance.

1.8 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.9 Use of this method is restricted to use by, or under the supervision of, personnel appropriately experienced and trained in the use of gas chromatographs (GCs) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample is extracted using the appropriate matrix-specific sample extraction technique.

2.1.1 Aqueous samples may be extracted at neutral pH with methylene chloride using either Method 3510 (separatory funnel), Method 3520 (continuous liquid-liquid extractor), Method 3535 (solid-phase extraction), or other appropriate technique or solvents.

2.1.2 Solid samples may be extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Method 3540 (Soxhlet), Method 3541 (automated Soxhlet), Method 3545 (pressurized fluid extraction), Method 3546 (microwave extraction), Method 3550 (ultrasonic extraction), Method 3562 (supercritical fluid extraction), or other appropriate technique or solvents.

2.1.3 Tissue samples may be extracted using Method 3562 (supercritical fluid extraction), or other appropriate technique. The extraction techniques for other solid matrices (see Sec. 2.1.2) may be appropriate for tissue samples.

2.2 Extracts for PCB analysis may be subjected to a sequential sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for these analytes. This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides. Therefore, this method is not applicable to the analysis of those compounds. Instead, use Method 8081.

2.3 After cleanup, the extract is analyzed by injecting a measured aliquot into a gas chromatograph equipped with either a narrow- or wide-bore fused-silica capillary column and either an electron capture detector (GC/ECD) or an electrolytic conductivity detector (GC/ELCD).

2.4 The chromatographic data may be used to determine the seven Aroclors in Sec. 1.1, selected individual PCB congeners, or total PCBs (see Secs. 11.8 and 11.9).

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware. Also refer to Methods 3500, 3600, and 8000 for a discussion of interferences.

4.2 Interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into four broad categories, as follows:

4.2.1 Contaminated solvents, reagents, or sample processing hardware.

4.2.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

4.2.3 Compounds extracted from the sample matrix to which the detector will respond, such as single-component chlorinated pesticides, including the DDT analogs (DDT, DDE, and DDD).

NOTE: A standard of the DDT analogs should be injected to determine which of the PCB or Aroclor peaks may be subject to interferences on the analytical columns used. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples.

4.2.4 Coelution of related analytes -- All 209 PCB congeners cannot be separated using the GC columns and procedures described in this method. If this procedure is expanded to encompass other congeners, then the analyst must either

document the resolution of the congeners in question or establish procedures for reporting the results of coeluting congeners that are appropriate for the intended application.

4.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determinations. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.

4.3.1 Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations.

4.3.2 Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

4.3.3 These materials can be removed prior to analysis using Method 3665 (sulfuric acid/permanganate cleanup).

4.4 Cross-contamination of clean glassware can routinely occur when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Glassware must be scrupulously cleaned.

4.4.1 Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware, and dry it in an oven at 130 °C for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.

CAUTION: Oven-drying of glassware used for PCB analysis can increase contamination because PCBs are readily volatilized in the oven and spread to other glassware. Therefore, exercise caution, and do not dry glassware from samples containing high concentrations of PCBs with glassware that may be used for trace analyses.

4.4.2 Other appropriate glassware cleaning procedures may be employed, such as using a muffle furnace at 430 °C for at least 30 min. However, analysts are advised not to place volumetric glassware in a muffle furnace, since the heat will burn off the markings on the glassware and may warp the glassware, changing its volume.

4.5 Sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur contamination should be expected with sediment samples. Sulfur can be removed through the use of Method 3660.

5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Gas chromatograph -- An analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all necessary accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and recorder/integrator or data system. Electrolytic conductivity detectors (ELCDs) may also be employed if appropriate for project needs. If the dual-column option is employed, the gas chromatograph must be equipped with two separate detectors.

6.2 GC columns

This method describes procedures for both single-column and dual-column analyses. The single-column approach involves one analysis to determine that a compound is present, followed by a second analysis to confirm the identity of the compound (Sec. 11.11 describes how GC/MS confirmation techniques may be employed). The single-column approach may employ either narrow-bore ($\leq$ 0.32-mm ID) columns or wide-bore (0.53-mm ID) columns. The dual-column approach generally employs a single injection that is split between two columns that are mounted in a single gas chromatograph. The dual-column approach generally employs wide-bore (0.53-mm ID) columns, but columns of other diameters may be employed if the analyst can demonstrate and document acceptable performance for the intended application. A third alternative is to employ dual columns mounted in a single GC, but with each column connected to a separate injector and a separate detector.

The columns listed in this section were the columns used in developing the method. The listing of these columns in this method is not intended to exclude the use of other columns that are available or that may be developed. Laboratories may use these columns or other columns provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

6.2.1 Narrow-bore columns for single-column analysis (use both columns to confirm compound identifications unless another confirmation technique such as GC/MS is employed). Narrow-bore columns should be installed in split/splitless (Grob-type) injectors.

6.2.1.1 30-m x 0.25-mm or 0.32-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1-µm film thickness.

6.2.1.2 30-m x 0.25-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent), 2.5 µm coating thickness, 1-µm film thickness.

6.2.2 Wide-bore columns for single-column analysis (use two of the three columns listed to confirm compound identifications unless another confirmation technique

such as GC/MS is employed). Wide-bore columns should be installed in 1/4-inch injectors, with deactivated liners designed specifically for use with these columns.

6.2.2.1 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5-µm or 0.83-µm film thickness.

6.2.2.2 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0-µm film thickness.

6.2.2.3 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5-µm film thickness.

6.2.3 Wide-bore columns for dual-column analysis -- The three pairs of recommended columns are listed below.

6.2.3.1 Column pair 1

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5-µm film thickness.

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0-µm film thickness.

Column pair 1 is mounted in a press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog No. 705-0733) or a Y-shaped fused-silica connector (Restek, Catalog No. 20405), or equivalent.

NOTE: When connecting columns to a press-fit Y-shaped connector, a better seal may be achieved by first soaking the ends of the capillary columns in alcohol for about 10 sec to soften the polyimide coating.

6.2.3.2 Column pair 2

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 0.83-µm film thickness.

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0-µm film thickness.

Column pair 2 is mounted in an 8-in. deactivated glass injection tee (Supelco, Catalog No. 2-3665M), or equivalent.

6.2.3.3 Column pair 3

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5-µm film thickness.

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (HP-608, DB-608, SPB-608, RTx-35, or equivalent), 0.5-µm film thickness.

Column pair 3 is mounted in separate injectors and separate detectors.

6.3 Column rinsing kit -- Bonded-phase column rinse kit (J&W Scientific, Catalog No. 430-3000), or equivalent.

6.4 Volumetric flasks -- 10-mL and 25-mL, for preparation of standards.

6.5 Analytical balance, capable of weighing to 0.0001 g.

7.0 REAGENTS AND STANDARDS.

7.1 Reagent-grade or pesticide-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at ≤ 6 °C in polytetrafluoroethylene (PTFE)-sealed containers in the dark. When a lot of standards is prepared, aliquots of that lot should be stored in individual small vials. All stock standard solutions must be replaced after one year, or sooner if routine QC (see Sec. 9.0) indicates a problem. All other standard solutions must be replaced after six months, or sooner if routine QC (see Sec. 9.0) indicates a problem.

7.2 Solvents used in the extraction and cleanup procedures (appropriate 3500 and 3600 series methods) include *n*-hexane, diethyl ether, methylene chloride, acetone, ethyl acetate, and isooctane (2,2,4-trimethylpentane) and the solvents must be exchanged to *n*-hexane or isooctane prior to analysis. Therefore, *n*-hexane and isooctane will be required in this procedure. All solvents should be pesticide grade in quality or equivalent, and each lot of solvent should be determined to be free of phthalates.

7.3 The following solvents may be necessary for the preparation of standards. All solvent lots must be pesticide grade in quality or equivalent and should be determined to be free of phthalates.

7.3.1 Acetone, $(CH_3)_2CO$

7.3.2 Toluene, $C_6H_5CH_3$

7.4 Organic-free reagent water -- All references to water in this method refer to organic-free reagent water as defined in Chapter One.

7.5 Standard solutions

The following sections describe the preparation of stock, intermediate, and working standards for the compounds of interest. This discussion is provided as an example, and other approaches and concentrations of the target compounds may be used, as appropriate for the intended application. See Method 8000 for additional information on the preparation of calibration standards.

7.6 Stock standard solutions (1000 mg/L) -- May be prepared from pure standard materials or can be purchased as certified solutions.

7.6.1 Prepare stock standard solutions by accurately weighing 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution.

7.6.2 Commercially-prepared stock standard solutions may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.7 Calibration standards for Aroclors

7.7.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing multi-point initial calibrations for each of the seven Aroclors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample.

Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector. See Method 8000 for additional information regarding the preparation of calibration standards.

7.7.2 Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards described in Sec. 7.7.1 have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors also may be used to determine the calibration factor for each Aroclor when a linear calibration model through the origin is chosen (see Sec. 11.4). Prepare a standard for each of the other Aroclors. The concentrations should generally correspond to the mid-point of the linear range of the detector, but lower concentrations may be employed at the discretion of the analyst based on project requirements.

7.7.3 Other standards (e.g., other Aroclors) and other calibration approaches (e.g., non-linear calibration for individual Aroclors) may be employed to meet project needs. When the nature of the PCB contamination is already known, use standards of those particular Aroclors. See Method 8000 for information on non-linear calibration approaches.

7.8 Calibration standards for PCB congeners

7.8.1 If results are to be determined for individual PCB congeners, then standards for the pure congeners must be prepared. The table in Sec. 1.1 lists 19 PCB congeners that have been tested by this method along with the IUPAC numbers designating these congeners. This procedure may be appropriate for other congeners as well, but the analyst must either document the resolution of the congeners in question or establish procedures for reporting the results of coeluting congeners that are appropriate for the intended application.

7.8.2 Stock standards may be prepared in a fashion similar to that described for the Aroclor standards, or may be purchased as commercially-prepared solutions. Stock standards should be used to prepare a minimum of five concentrations by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

7.9 Internal standard

7.9.1 When PCB congeners are to be determined, the use of an internal standard is highly recommended. Decachlorobiphenyl may be used as an internal standard, added to each sample extract prior to analysis, and included in each of the initial calibration standards.

7.9.2 When PCBs are to be determined as Aroclors, an internal standard is typically not used, and decachlorobiphenyl is employed as a surrogate (see Sec. 7.10).

7.9.3 When decachlorobiphenyl is an analyte of interest, as in some PCB congener analyses, see Sec. 7.10.3.

7.10 Surrogate standards

The performance of the method should be monitored using surrogate compounds. Surrogate standards are added to all samples, method blanks, matrix spikes, and calibration standards. The choice of surrogate compounds will depend on analysis mode chosen, e.g., Aroclors or congeners. The following compounds are recommended as surrogates. Other surrogates may be used, provided that the analyst can demonstrate and document performance appropriate for the data quality needs of the particular application.

7.10.1 When PCBs are to be determined as Aroclors, decachlorobiphenyl may be used as a surrogate, and is added to each sample prior to extraction. Prepare a solution of decachlorobiphenyl in acetone. The recommended spiking solution concentration is 5 mg/L. Tetrachloro-*m*-xylene also may be used as a surrogate for Aroclor analysis. If used, the recommended spiking solution concentration is 5 mg/L in acetone. (Other surrogate concentrations may be used, as appropriate for the intended application.)

7.10.2 When PCB congeners are to be determined, decachlorobiphenyl is recommended for use as an internal standard, and therefore it cannot also be used as a surrogate. Tetrachloro-*m*-xylene may be used as a surrogate for PCB congener analysis. The recommended spiking solution concentration is 5 mg/L in acetone. (Other surrogate concentrations may be used, as appropriate for the intended application.)

7.10.3 If decachlorobiphenyl is a target congener for the analysis, 2,2',4,4',5,5'-hexabromobiphenyl may be used as an internal standard or a surrogate.

7.11 DDT analog standard -- Used to determine if the commonly found DDT analogs (DDT, DDE, and DDD) elute at the same retention times as any of the target analytes (congeners or Aroclors). A single standard containing all three compounds should be sufficient. The concentration of the standard is left to the judgement of the analyst.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes."

8.2 Extracts should be stored under refrigeration in the dark and should be analyzed within 40 days of extraction.

NOTE: The holding time above is a recommendation. PCBs are very stable in a variety of matrices, and holding times under the conditions listed above may be as long as a year.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for specific determinative method QC procedures. Refer to Method 3500 for QC procedures to ensure the proper operation of the various sample preparation techniques. If an extract cleanup procedure is performed, refer to Method 3600 for the appropriate QC procedures. Any more specific QC procedures provided in this method will supersede those noted in Methods 8000, 3500, or 3600.

9.3 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

9.3.1 Include a calibration standard after each group of 20 samples (it is *recommended* that a calibration standard be included after every 10 samples to minimize the number of repeat injections) in the analysis sequence as a calibration check. Thus, injections of method blank extracts, matrix spike samples, and other non-standards are counted in the total. Solvent blanks, injected as a check on cross-contamination, need not be counted in the total. The response factors for the calibration should be within ±20 percent of the initial calibration (see Sec. 11.6.2). When this continuing calibration is out of this acceptance window, the laboratory should stop analyses and take corrective action.

9.3.2 Whenever quantitation is accomplished using an internal standard, internal standards must be evaluated for acceptance. The measured area of the internal standard must be no more than 50 percent different from the average area calculated during initial calibration. When the internal standard peak area is outside the limit, all samples that fall outside the QC criteria must be reanalyzed. The retention times of the internal standards must also be evaluated. A retention time shift of >30 sec necessitates reanalysis of the affected sample.

9.4 Initial demonstration of proficiency

9.4.1 Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish a demonstration of proficiency.

9.4.2 It is suggested that the QC reference sample concentrate (as discussed in Methods 8000 and Method 3500) contain PCBs as Aroclors at 10-50 mg/L in the concentrate for water samples, or PCBs as congeners at the same concentrations. A 1-mL volume of this concentrate spiked into 1 L of reagent water will result in a sample concentration of 10-50 µg/L. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for the QC reference sample. See Method 8000 for additional information on how to accomplish this demonstration. Other concentrations may be used, as appropriate for the intended application.

9.4.3 Calculate the average recovery and the standard deviation of the recoveries of the analytes in each of the four QC reference samples. Refer to Method 8000 for procedures for evaluating method performance.

9.5 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the laboratory should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

9.6 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample when surrogates are used. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.6.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike

duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair, spiked with the Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for spiking. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.6.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.6.3 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house acceptance criteria for evaluating method performance should be developed using the guidance found in Method 8000.

9.7 Surrogate recoveries

If surrogates are used, the laboratory should evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000 for information on evaluating surrogate data and developing and updating surrogate limits. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in an approved project plan.

9.8 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10.0 CALIBRATION AND STANDARDIZATION

See Sec. 11.0 for information on calibration and standardization.

11.0 PROCEDURE

11.1 Sample extraction

11.1.1 Refer to Chapter Two and Method 3500 for guidance in choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride using a separatory funnel (Method 3510), a continuous liquid-liquid extractor (Method 3520), solid-phase extraction (Method 3535), or other appropriate technique. Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using one of the Soxhlet extraction methods (Method 3540 or 3541), pressurized fluid extraction (Method 3545), microwave extraction (Method 3546),

ultrasonic extraction (Method 3550), supercritical fluid extraction (Method 3562), or other appropriate technique or solvents. Tissue samples are extracted using supercritical fluid extraction (Method 3562) or other appropriate technique.

NOTE: The use of hexane-acetone generally reduces the amount of interferences that are extracted and improves signal-to-noise.

The choice of extraction solvent and procedure will depend on the analytes of interest. No single solvent or extraction procedure is universally applicable to all analyte groups and sample matrices. The analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest, for any solvent system and extraction procedure employed, *including* those specifically listed in this method. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Each new sample type must be spiked with the compounds of interest to determine the percent recovery. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

11.1.2 Reference materials, field-contaminated samples, or spiked samples should be used to verify the applicability of the selected extraction technique to each new sample type. Such samples should contain or be spiked with the compounds of interest in order to determine the percent recovery and the limit of detection for that sample type (see Chapter One). When other materials are not available and spiked samples are used, they should be spiked with the analytes of interest, either specific Aroclors or PCB congeners. When the presence of specific Aroclors is not anticipated, the Aroclor 1016/1260 mixture may be an appropriate choice for spiking. See Methods 3500 and 8000 for guidance on demonstration of initial method proficiency as well as guidance on matrix spikes for routine sample analysis.

11.1.3 The extraction techniques for solids may be applicable to wipe samples and other sample matrices not addressed in Sec. 11.1.1. The analysis of oil samples may need special sample preparation procedures that are not described here. Analysts should follow the steps described in Sec. 11.1.2 to verify the applicability of the sample preparation and extraction techniques for matrices such as wipes and oils.

11.2 Extract cleanup

Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. Refer to Methods 3600, 3660 and 3665 for general guidance on extract cleanup.

11.3 GC conditions

This method allows the analyst to choose between a single-column or a dual-column configuration in the injector port. The columns listed in this section were the columns used to develop the method performance data. Listing these columns in this method is not intended to exclude the use of other columns that are available or that may be developed. Wide-bore or narrow-bore columns may be used with either option. Laboratories may use either the columns listed in this method or other capillary columns or columns of other dimensions, provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

11.3.1 Single-column analysis

This capillary GC/ECD method allows the analyst the option of using 0.25-mm or 0.32-mm ID capillary columns (narrow-bore) or 0.53-mm ID capillary columns (wide-bore). Narrow-bore columns generally provide greater chromatographic resolution than wide-bore columns, although narrow-bore columns have a lower sample capacity. As a result, narrow-bore columns may be more suitable for relatively clean samples or for extracts that have been prepared with one or more of the clean-up options referenced in the method. Wide-bore columns (0.53-mm ID) may be more suitable for more complex environmental and waste matrices. However, the choice of the appropriate column diameter is left to the professional judgement of the analyst.

11.3.2 Dual-column analysis

The dual-column/dual-detector approach recommends the use of two 30-m x 0.53-mm ID fused-silica open-tubular columns of different polarities, thus, different selectivities towards the target analytes. The columns may be connected to an injection tee and separate electron capture detectors, or to both separate injectors and separate detectors. However, the choice of the appropriate column dimensions is left to the professional judgement of the analyst.

11.3.3 GC temperature programs and flow rates

11.3.3.1 Table 1 lists suggested GC operating conditions for the analysis of PCBs as Aroclors for single-column analysis, using either narrow-bore or wide-bore capillary columns. Table 2 lists suggested GC operating conditions for the dual-column analysis. Use the conditions in these tables as guidance and establish the GC temperature program and flow rate necessary to separate the analytes of interest.

11.3.3.2 When determining PCBs as congeners, difficulties may be encountered with coelution of congener 153 and other sample components. When determining PCBs as Aroclors, chromatographic conditions should be adjusted to give adequate separation of the characteristic peaks in each Aroclor (see Sec. 11.4.6).

11.3.3.3 Tables 3 and 4 summarize example retention times of up to 73 Aroclor peaks determined during dual-column analysis using the operating conditions listed in Table 2. These retention times are provided as guidance as to what may be achieved using the GC columns, temperature programs, and flow rates described in this method. Each laboratory must determine retention times and retention time windows for their specific application of the method. Note that the peak numbers used in these tables are *not* the IUPAC congener numbers, but represent the elution order of the peaks on these GC columns.

11.3.3.4 Once established, the same operating conditions must be used for the analysis of samples and standards.

11.4 Calibration

11.4.1 Prepare calibration standards using the procedures in Sec. 7.0. Refer to Method 8000 and Sec. 9.3 for proper calibration techniques for both initial calibration and calibration verification. When PCBs are to be determined as congeners, the use of internal standard calibration is highly recommended. Therefore, the calibration standards

must contain the internal standard (see Sec. 7.9) at the same concentration as the sample extracts. When PCBs are to be determined as Aroclors, external standard calibration is generally used.

NOTE: Because of the sensitivity of the electron capture detector, always clean the injection port and column prior to performing the initial calibration.

11.4.2 When PCBs are to be quantitatively determined as congeners, an initial multi-point calibration must be performed that includes standards for all the target analytes (congeners). See Method 8000 for details on calibration options.

11.4.3 When PCBs are to be quantitatively determined as Aroclors, the initial calibration consists of two parts, described below.

11.4.3.1 As noted in Sec. 7.7.1, a standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Therefore, an initial multi-point calibration is performed using the mixture of Aroclors 1016 and 1260 described in Sec. 7.7.1. See Method 8000 for guidance on the use of linear and non-linear calibrations.

11.4.3.2 Standards of the other five Aroclors are necessary for pattern recognition. When employing the traditional model of a linear calibration through the origin, these standards are also used to determine a single-point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 mixture in Sec. 11.4.3.1 has been used to describe the detector response. The standards for these five Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five 1016/1260 standards in Sec. 11.4.3.1. For non-linear calibrations, see Sec. 11.4.3.3.

11.4.3.3 In situations where only a few Aroclors are of interest for a specific project, the analyst may employ a multi-point initial calibration of each of the Aroclors of interest (e.g., five standards of Aroclor 1232 if this Aroclor is of concern and linear calibration is employed) and not use the 1016/1260 mixture described in Sec. 11.4.3.1 or the pattern recognition standards described in 11.4.3.2. When non-linear calibration models are employed, more than five standards of each Aroclor of interest will be needed to adequately describe the detector response (see Method 8000).

11.4.4 Establish the GC operating conditions appropriate for the configuration (single-column or dual column, Sec. 11.3), using Tables 1 or 2 as guidance. Optimize the instrumental conditions for resolution of the target compounds and sensitivity. A final temperature of between 240 °C and 275 °C may be needed to elute decachlorobiphenyl. The use of injector pressure programming will improve the chromatography of late eluting peaks.

NOTE: Once established, the same operating conditions must be used for both calibrations and sample analyses.

11.4.5 A 2-µL injection of each calibration standard is recommended. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest.

11.4.6 Record the peak area (or height) for each congener or each characteristic Aroclor peak to be used for quantitation.

11.4.6.1 A minimum of 3 peaks must be chosen for each Aroclor, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found in both of these Aroclors.

11.4.6.2 Late-eluting Aroclor peaks are generally the most stable in the environment. Table 5 lists diagnostic peaks in each Aroclor, along with example retention times on two GC columns suitable for single-column analysis. Table 6 lists 13 specific PCB congeners found in Aroclor mixtures. Table 7 lists PCB congeners with example retention times on a DB-5 wide-bore GC column. Use these tables as guidance in choosing the appropriate peaks. Each laboratory must determine retention times and retention time windows for their specific application of the method.

11.4.7 When determining PCB congeners by the internal standard procedure, calculate the response factor (RF) for each congener in the calibration standards relative to the internal standard, decachlorobiphenyl, using the equation that follows.

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

11.4.8 When determining PCBs as Aroclors by the external standard technique, calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards (from either Sec. 11.4.3.1 or 11.4.3.2) using the equation below.

$$CF = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in nanograms)}}$$

Using the equation above, a calibration factor will be determined for each characteristic peak, using the total mass of the Aroclor injected. These individual calibration factors are used to quantitate sample results by applying the factor for each individual peak to the area of that peak, as described in Sec. 11.9.

For a five-point calibration, five sets of calibration factors will be generated for the Aroclor 1016/1260 mixture, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture, e.g., there will be at least 25 separate calibration factors for the mixture. The single standard for each of the other Aroclors (see Sec. 11.4.3.1) will generate at least three calibration factors, one for each selected peak.

If a non-linear calibration model is employed, as described in Method 8000, then additional standards containing each Aroclor of interest will be employed, with a corresponding increase in the total number of calibration factors.

11.4.9 The response factors or calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration, if a linear calibration model is used. This involves the calculation of the mean response or calibration factor, the standard deviation, and the relative standard deviation (RSD) for each congener or Aroclor peak.

When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the linear calibration models must be applied to the other five Aroclors for which only single standards are analyzed. If multi-point calibration is performed for individual Aroclors (see Sec. 11.4.3.3), use the calibration factors from those standards to evaluate linearity.

See Method 8000 for the specifics of the evaluation of the linearity of the calibration and guidance on performing non-linear calibrations. In general, non-linear calibrations also will consider each characteristic Aroclor peak separately.

11.5 Retention time windows

Absolute retention times are generally used for compound identification. When absolute retention times are used, retention time windows are crucial to the identification of target compounds, and should be established by one of the approaches described in Method 8000. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis. Analysts should consult Method 8000 for the details of establishing retention time windows. Other approaches to compound identification may be employed, provided that the analyst can demonstrate and document that the approaches are appropriate for the intended application. When PCBs are determined as congeners by an internal standard technique, absolute retention times may be used in conjunction with relative retention times (relative to the internal standard).

When conducting either Aroclor or congener analysis, it is important to determine that common single-component pesticides such as DDT, DDD, and DDE do not elute at the same retention times as the target congeners. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples. Therefore, in conjunction with determining the retention time windows of the congeners, the analyst should analyze a standard containing the DDT analogs. This standard need only be analyzed when the retention time

windows are determined. It is not considered part of the routine initial calibration or calibration verification steps in the method, nor are there any performance criteria associated with the analysis of this standard.

If Aroclor analysis is performed and any of the DDT analogs elute at the same retention time as an Aroclor peak that was chosen for use in quantitation (see Sec. 11.4.6), then the analyst must either adjust the GC conditions to achieve better resolution, or choose another peak that is characteristic of that Aroclor and does not correspond to a peak from a DDT analog. If PCB congener analysis is performed and any of the DDT analogs elute at the same retention time as a PCB congener of interest, then the analyst must adjust the GC conditions to achieve better resolution.

11.6 Gas chromatographic analysis of sample extracts

11.6.1 The same GC operating conditions used for the initial calibration must be employed for the analysis of samples.

11.6.2 Verify calibration at least once each 12-hr shift by injecting calibration verification standards prior to conducting any sample analyses. A calibration standard must also be injected at intervals of not less than once every twenty samples (after every 10 samples is recommended to minimize the number of samples requiring reinjection when QC limits are exceeded) and at the end of the analysis sequence. For Aroclor analyses, the calibration verification standard should be a mixture of Aroclor 1016 and Aroclor 1260. The calibration verification process does not *require* analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclors after the 1016/1260 mixture used for calibration verification throughout the analytical sequence.

11.6.2.1 The calibration factor for each analyte calculated from the calibration verification standard (CF_v) should not exceed a difference of more than ±20 percent when compared to the mean calibration factor from the initial calibration curve. If a calibration approach other than the RSD method has been employed for the initial calibration (e.g., a linear model not through the origin, a non-linear calibration model, etc.), consult Method 8000 for the specifics of calibration verification.

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

11.6.2.2 When internal standard calibration is used for PCB congeners, the response factor calculated from the calibration verification standard (RF_v) should not exceed a ±20 percent difference when compared to the mean response factor from the initial calibration. If a calibration approach other than the RSD method has been employed for the initial calibration (e.g., a linear model not through the origin, a non-linear calibration model, etc.), consult Method 8000 for the specifics of calibration verification.

$$\% \text{ Difference} = \frac{\overline{RF} - RF_v}{\overline{RF}} \times 100$$

11.6.2.3 If the calibration does not meet the ±20% limit on the basis of each compound, check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ±20%, then a new initial calibration must be prepared. See Sec. 11.6.6 for a discussion on the effects of a failing calibration verification standard on sample results.

11.6.3 Inject a measured aliquot of the concentrated sample extract. A 2-µL aliquot is suggested, however, other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest. The same injection volume should be used for both the calibration standards and the sample extracts, unless the analyst can demonstrate acceptable performance using different volumes or conditions. Record the volume injected and the resulting peak size in area units.

11.6.4 Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in Sec. 11.7.

11.6.5 Quantitative results are determined for each identified analyte (Aroclors or congeners), using the procedures described in Secs. 11.8 and 11.9 for either the internal or the external calibration procedure (Method 8000). If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area when overlapping peaks cause errors in area integration.

11.6.6 Each sample analysis employing external standard calibration must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hr analytical shift), or calibration standards interspersed within the samples. The results from these bracketing standards must meet the calibration verification criteria in Sec. 11.6.2.

Multi-level standards (mixtures or multi-component analytes) are highly recommended to ensure that detector response remains stable for all analytes over the calibration range.

When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that met the QC criteria must be evaluated to prevent misquantitations and possible false negative results, and reinjection of the sample extracts may be required. More frequent analyses of standards will minimize the number of sample extracts that would have to be reinjected if the QC limits are violated for the standard analysis.

However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >20%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, since the verification standard has demonstrated that the analyte would have been detected if it were present. In contrast, if an analyte

above the QC limits was detected in a sample extract, then reinjection is necessary to ensure accurate quantitation.

If an analyte was not detected in the sample and the standard response is more than 20% below the initial calibration response, then reinjection is necessary. The purpose of this reinjection is to ensure that the analyte could be detected, if present, despite the change in the detector response, e.g., to protect against a false negative result.

11.6.7 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. It is *recommended* that standards be analyzed after every 10 samples (*required* after every 20 samples and at the end of a set) to minimize the number of samples that must be re-injected when the standards fail the QC limits. The sequence ends when the set of samples has been injected or when qualitative or quantitative QC criteria are exceeded.

11.6.8 The use of internal standard calibration techniques does not require that all sample results be bracketed with calibration verification standards. However, when internal standard calibration is used, the retention times of the internal standards and the area responses of the internal standards should be checked for each analysis. Retention time shifts of more than 30 sec from the retention time of the most recent calibration standard and/or changes in internal standard areas of more than -50 to +100% are cause for concern and must be investigated.

11.6.9 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.

11.6.10 Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.

11.6.11 If compound identification or quantitation is precluded due to interferences (e.g., broad, rounded peaks or ill-defined baselines are present), corrective action is warranted. Cleanup of the extract or replacement of the capillary column or detector may be necessary. The analyst may begin by rerunning the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to Method 3600 for the procedures to be followed in sample cleanup.

11.7 Qualitative identification

The identification of PCBs as either Aroclors or congeners using this method with an electron capture detector is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of the target analytes. See Method 8000 for information on the establishment of retention time windows.

Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Confirmation is necessary when the sample composition is not well characterized. See Method 8000 for information on confirmation of tentative identifications. See Sec. 11.11 of this procedure for information on the use of GC/MS as a confirmation technique.

When results are confirmed using a second GC column of dissimilar stationary phase, the analyst should check the agreement between the quantitative results on both columns once the identification has been confirmed. See Method 8000 for a discussion of such a comparison and appropriate data reporting approaches.

11.7.1 When simultaneous analyses are performed from a single injection (the dual-column GC configuration described in Sec. 11.3), it is not practical to designate one column as the analytical (primary) column and the other as the confirmation column. Since the calibration standards are analyzed on both columns, both columns must meet the calibration acceptance criteria. If the retention times of the peaks on both columns fall within the retention time windows on the respective columns, then the target analyte identification has been confirmed.

11.7.2 The results of a single column/single injection analysis may be confirmed, if necessary, on a second, dissimilar, GC column. In order to be used for confirmation, retention time windows must have been established for the second GC column. In addition, the analyst must demonstrate the sensitivity of the second column analysis. This demonstration must include the analysis of a standard of the target analyte at a concentration at least as low as the concentration estimated from the primary analysis. That standard may be either the individual congeners, individual Aroclor or the Aroclor 1016/1260 mixture.

11.7.3 When samples are analyzed from a source known to contain specific Aroclors, the results from a single-column analysis may be confirmed on the basis of a clearly recognizable Aroclor pattern. This approach should not be attempted for samples from unknown or unfamiliar sources or for samples that appear to contain mixtures of Aroclors. In order to employ this approach, the analyst must document:

- The peaks that were evaluated when comparing the sample chromatogram and the Aroclor standard.
- The absence of major peaks representing any other Aroclor.
- The source-specific information indicating that Aroclors are anticipated in the sample (e.g., historical data, generator knowledge, etc.).

This information should either be provided to the data user or maintained by the laboratory.

11.7.4 See Sec. 11.11 for information on GC/MS confirmation.

11.8 Quantitation of PCBs as congeners

11.8.1 The quantitation of PCB congeners is accomplished by the comparison of the sample chromatogram to those of the PCB congener standards, using the internal standard technique (see Method 8000). Calculate the concentration of each congener.

11.8.2 Depending on project requirements, the PCB congener results may be reported as congeners, or may be summed and reported as total PCBs. The analyst should use caution when using the congener method for quantitation when regulatory requirements are based on Aroclor concentrations. See Sec. 11.9.3.

11.8.3 The analytical procedures for these 19 congeners may be appropriate for the analysis of other congeners not specifically included in this method and may be used

as a template for the development of such a procedure. However, all 209 PCB congeners cannot be separated using the GC columns and procedures described in this method. If this procedure is expanded to encompass other congeners, then the analyst must either document the resolution of the congeners in question or establish procedures for reporting the results of coeluting congeners that are appropriate for the intended application.

11.9 Quantitation of PCBs as Aroclors

The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

11.9.1 Use the individual Aroclor standards (not the 1016/1260 mixtures) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, and 1254. The patterns for Aroclors 1016 and 1260 will be evident in the mixed calibration standards.

11.9.2 Once the Aroclor pattern has been identified, compare the responses of 3 to 5 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen in Sec. 11.4.6.1. and the calibration model (linear or non-linear) established from the multi-point calibration of the 1016/1260 mixture. Non-linear calibration may result in different models for each selected peak. A concentration is determined using each of the characteristic peaks, using the individual calibration factor calculated for that peak in Sec. 11.4.8, and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor.

11.9.3 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. If the purpose of the analysis is <u>not</u> regulatory compliance monitoring on the basis of Aroclor concentrations, then it may be more appropriate to perform the analyses using the PCB congener approach described in this method. If results in terms of Aroclors <u>are</u> required, then the quantitation as Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area. When quantitation is performed in this manner, the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

11.10 Confirmation

Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Confirmation is necessary when the sample composition is not well characterized. Confirmatory techniques such as gas chromatography with a dissimilar column or a mass spectrometer should be used. See Method 8000 for information on confirmation of tentative identifications.

When results are confirmed using a second GC column of dissimilar stationary phase, the analyst should check the agreement between the quantitative results on both columns once the identification has been confirmed. See Method 8000 for a discussion of such a comparison and appropriate data reporting approaches.

When the dual-column approach is employed, the target phenols are identified and confirmed when they meet the identification criteria on both columns.

11.11 GC/MS confirmation

GC/MS confirmation may be used in conjunction with either single-or dual-column analysis if the concentration is sufficient for detection by GC/MS.

11.11.1 Full-scan quadrupole GC/MS will normally require a higher concentration of the analyte of interest than full-scan ion trap or selected ion monitoring techniques. The concentrations will be instrument-dependent, but values for full-scan quadrupole GC/MS may be as high as 10 ng/µL in the final extract, while ion trap or SIM may only be a concentration of 1 ng/µL.

11.11.2 The GC/MS must be calibrated for the target analytes when it is used for quantitative analysis. If GC/MS is used only for confirmation of the identification of the target analytes, then the analyst must demonstrate that those PCBs identified by GC/ECD can be confirmed by GC/MS. This demonstration may be accomplished by analyzing a single-point standard containing the analytes of interest at or below the concentrations reported in the GC/ECD analysis. When using SIM techniques, the ions and retention times should be characteristic of the Aroclors to be confirmed.

11.11.3 GC/MS confirmation should be accomplished by analyzing the same extract used for GC/ECD analysis and the extract of the associated blank.

11.12 GC/AED confirmation by Method 8085 may be used in conjunction with either single-column or dual-column analysis if the concentration is sufficient for detection by GC/AED.

11.13 Chromatographic system maintenance as corrective action

When system performance does not meet the established QC requirements, corrective action is required, and may include one or more of the following.

11.13.1 Splitter connections

For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few centimeters (up to 30 cm) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

11.13.2 Metal injector body

Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

11.13.2.1 Place a beaker beneath the injector port inside the oven. Using a wash bottle, rinse the entire inside of the injector port with acetone and then rinse it with toluene, catching the rinsate in the beaker.

11.13.2.2 Consult the manufacturer's instructions regarding deactivating the injector port body. Glass injection port liners may need deactivation with a silanizing solution containing dimethyldichlorosilane. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, rinse the injector body with toluene, methanol, acetone, then hexane. Reassemble the injector and replace the columns.

11.13.3 Column rinsing

Rinse the column with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone. Methylene chloride is a good final rinse and in some cases may be the only solvent necessary. Fill the column with methylene chloride and allow it to stand flooded overnight to allow materials within the stationary phase to migrate into the solvent. Afterwards, flush the column with fresh methylene chloride, drain the column, and dry it at room temperature with a stream of ultrapure nitrogen.

12.0 DATA ANALYSIS AND CALCULATIONS

See Secs. 11.6 through 11.9 for information regarding data analysis and calculations.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance goals for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 The accuracy and precision obtainable with this method depend on the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used. Table 8 provides single laboratory recovery data for Aroclors spiked into clay and soil and extracted with automated Soxhlet. Table 9 provides multiple laboratory data on the precision and accuracy for Aroclors spiked into soil and extracted by automated Soxhlet. These data are provided for guidance purposes only.

13.3 During method performance studies, the concentrations determined as Aroclors were higher than those obtained using the congener method for the limited set of congeners listed in Sec. 1.1. In certain soils, interference prevented the measurement of congener 66. Recoveries of congeners from environmental reference materials ranged from 51 - 66% of the certified Aroclor values, illustrating the potential difficulties in using congener analysis to demonstrate compliance with Aroclor-based regulatory limits. These data are provided for guidance purposes only.

13.4 Tables 10 and 11 contain laboratory performance data for several PCB congeners using supercritical fluid extraction (Method 3562) on an HP 7680 to extract solid samples, including soils, sewage sludge, and fish tissue. Seven replicate extractions were performed on each sample. The method was performed using a variable restrictor and solid trapping material (Florisil). These data are provided for guidance purposes only. Sample analysis was performed by GC/ECD. The following solid samples were used for this study:

13.4.1 Two field-contaminated certified reference materials were extracted by a single laboratory. One of the materials (EC-5) was a lake sediment from Environment Canada. The other material (EC-1) was soil from a dump site and was provided by the National Science and Engineering Research Council of Canada. The average recoveries for EC-5 are based on the certified value for that sample. The average recoveries for EC-1 are based on the certified value of the samples or a Soxhlet value, if a certified value was unavailable for a specific analyte. These data are provided for guidance purposes only.

13.4.2 Four certified reference materials were extracted by two independent laboratories. The materials included a marine sediment from NIST (SRM 1941), a fish tissue from NIST (SRM 2974), a sewage sludge from BCR European Union (CRM 392), and a soil sample from BCR European Union (CRM 481). The average recoveries were based on the certified value of the samples or a Soxhlet value, if a certified value was unavailable for a specific analyte. These data are provided for guidance purposes only.

13.4.3 A weathered sediment sample from Michigan (Saginaw Bay) was extracted by a single laboratory. Soxhlet extractions were carried out on this sample and the SFE recovery is relative to that for each congener. The average recoveries were based on the certified value of the samples. Additional data are shown in the tables for some congeners for which no certified values were available. These data are provided for guidance purposes only.

13.5 Tables 12 through 14 contain single laboratory recovery data for Aroclor 1254 using solid-phase extraction (Method 3535). Recovery data at 2, 10, and 100 µg/L are presented. Results represent three replicate solid-phase extractions of spiked wastewaters. Two different wastewaters from each wastewater type were spiked. All of the extractions were performed using 90-mm C_{18} disks. These data are provided for guidance purposes only.

13.6 Single-laboratory data were developed for PCBs extracted by pressurized fluid extraction (Method 3545) from sewage sludge, a river sediment standard reference material (SRM 1939), and a certified soil reference material (CRM911-050). Certified values were available for five PCB congeners for the sewage sludge and for four congeners in SRM 1939. The soil reference material was certified for Aroclor 1254. All pressurized fluid extractions were conducted using hexane:acetone (1:1), at 100 °C, 1300-1500 psi, and a 5-min static extraction. Extracts were analyzed by GC/ECD. The data are presented in Tables 15 through 17 and are reported in detail in Reference 13. These data are provided for guidance purposes only.

13.7 Single-laboratory accuracy data were obtained for PCBs extracted by microwave extraction (Method 3546) from three reference materials, EC-1, EC-2, and EC-3, from Environment Canada. Natural soils, glass fiber, and sand samples were also used as matrices that were spiked with PCBs. Concentrations varied between 0.2 and 10 µg/g (total PCBs). All samples were extracted using 1:1 hexane:acetone. Extracts were analyzed by GC/ECD. Method blanks, spikes and spike duplicates were included for the low concentration spikes; matrix spikes were included for all other concentrations. The data are presented in Tables 18 through 20 and are reported in detail in Reference 14. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of

environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC, 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. V. Lopez-Avila, E. Baldin, J. Benedicto, J. Milanes, W. F. Beckert, "Application of Open-Tubular Columns to SW-846 GC Methods," Final Report to the U.S. Environmental Protection Agency on Contract 68-03-3511, Mid-Pacific Environmental Laboratory, Mountain View, CA, 1990.

2. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 10 -- Pesticides and PCB Report for the U.S. Environmental Protection Agency on Contract 68-03-2606.

3. M. Ahnoff, B. Josefsson, "Cleanup Procedures for PCB Analysis on River Water Extracts," *Bull. Environ. Contam. Toxicol.*, 1975, 13, 159.

4. P. J. Marsden, "Performance Data for SW-846 Methods 8270, 8081, and 8141," U.S. Environmental Protection Agency, EMSL-Las Vegas, EPA/600/4-90/015.

5. P. J. Marsden, "Analysis of PCBs," U.S. Environmental Protection Agency, EMSL-Las Vegas, NV, EPA/600/8-90/004.

6. M. Erickson, Analytical Chemistry of PCBs, Butterworth Publishers, Ann Arbor Science Book, 1986.

7. J. Stewart, "EPA Verification Experiment for Validation of the SOXTEC® PCB Extraction Procedure," Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6138, October 1988.

8. V. Lopez-Avila, "Development of a Soxtec Extraction Procedure for Extracting Organic Compounds from Soils and Sediments," EPA 600/X-91/140, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, NV, October 1991.

9. J. H. Stewart, C. K. Bayne, R. L. Holmes, W. F. Rogers, and M. P. Maskarinec, "Evaluation of a Rapid Quantitative Organic Extraction System for Determining the Concentration of PCB in Soils," Proceedings of the U.S. EPA Symposium on Waste Testing and Quality Assurance, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, July 11-15, 1988.

10. S. F. Tsang, P. J. Marsden, and B. Lesnik, "Quantitation of Polychlorinated Biphenyls Using 19 Specific Congeners," Proceedings of the 9th Annual Waste Testing and Quality Assurance Symposium, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC, July 1993.

11. S. Bøwadt, B. Johansson, S. Wunderli, M. Zennegg, L. F. de Alencastro and D. Grandjean, "Independent Comparison of Soxhlet and Supercritical Fluid Extraction for the Determination of PCBs in an Industrial Soil," *Anal. Chem.*, 1995, 67(14) 2424-2430.

12. C. Markell, "3M Data Submission to EPA," letter to B. Lesnik, June 27, 1995.

13. B. Richter, J. Ezzell, and D. Felix "Single Laboratory Method Validation Report -- Extraction of Organophosphorus Pesticides, Herbicides and Polychlorinated Biphenyls using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC/NPD and GC/ECD," Dionex, Salt Lake City, UT, Document 101124, December 2, 1994.

14. K. Li, J. M. R. Bélanger, M. P. Llompart, R. D. Turpin, R. Singhvi, and J. R. J. Paré, "Evaluation of Rapid Solid Sample Extraction Using the Microwave-assisted Process (MAP™) under Closed-vessel Conditions," *Spectros. Int. J.* 13 (1), 1-14, 1997.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

SUGGESTED GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
SINGLE-COLUMN ANALYSIS

Narrow-bore columns

Narrow-bore Column 1 -- 30-m x 0.25 or 0.32-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1 µm film thickness.

Carrier gas (He)	16 psi
Injector temperature	225 °C
Detector temperature	300 °C
Initial temperature	100 °C, hold 2 min
Temperature program	100 °C to 160 °C at 15 °C/min, followed by 160 °C to 270 °C at 5 °C/min
Final temperature	270 °C

Narrow-bore Column 2 -- 30-m x 0.25-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent) 25 µm coating thickness, 1 µm film thickness

Carrier gas (N_2)	20 psi
Injector temperature	225 °C
Detector temperature	300 °C
Initial temperature	160 °C, hold 2 min
Temperature program	160 °C to 290 °C at 5 °C/min
Final temperature	290 °C, hold 1 min

Wide-bore columns

Wide-bore Column 1 -- 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

Wide-bore Column 2 -- 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Carrier gas (He)	5-7 mL/min
Makeup gas (argon/methane [P-5 or P-10] or N_2)	30 mL/min
Injector temperature	250 °C
Detector temperature	290 °C
Initial temperature	150 °C, hold 0.5 min
Temperature program	150 °C to 270 °C at 5 °C/min
Final temperature	270 °C, hold 10 min

TABLE 1
(continued)

SUGGESTED GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
SINGLE-COLUMN ANALYSIS

Wide-bore Columns (continued)

Wide-bore Column 3 -- 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

Carrier gas (He)	6 mL/min
Makeup gas (argon/methane [P-5 or P-10] or N_2)	30 mL/min
Injector temperature	205 °C
Detector temperature	290 °C
Initial temperature	140 °C, hold 2 min
Temperature program	140 °C to 240 °C at 10 °C/min, hold 5 min at 240 °C, 240 °C to 265 °C at 5 °C/min
Final temperature	265 °C, hold 18 min

TABLE 2

SUGGESTED GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
FOR THE DUAL-COLUMN METHOD OF ANALYSIS

Column 1 -- DB-1701 or equivalent, 30-m x 0.53-mm ID, 1.0 µm film thickness.

Column 2 -- DB-5 or equivalent, 30-m x 0.53-mm ID, 1.5 µm film thickness.

Carrier gas (He) flow rate	6 mL/min
Makeup gas (N_2) flow rate	20 mL/min
Temperature program	0.5 min hold 150 °C to 190 °C, at 12 °C/min, 2 min hold 190 °C to 275 °C, at 4 °C/min, 10 min hold
Injector temperature	250 °C
Detector temperature	320 °C
Injection volume	2 µL
Solvent	Hexane
Type of injector	Flash vaporization
Detector type	Dual ECD
Range	10
Attenuation	64 (DB-1701)/64 (DB-5)
Type of splitter	J&W Scientific press-fit Y-shaped inlet splitter

TABLE 3
(continued)

TABLE 3

EXAMPLE RETENTION TIMES OF AROCLORS
ON THE DB-5 COLUMN[a], DUAL-COLUMN ANALYSIS

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
1		5.85	5.85				
2		7.63	7.64	7.57			
3	8.41	8.43	8.43	8.37			
4	8.77	8.77	8.78	8.73			
5	8.98	8.99	9.00	8.94	8.95		
6	9.71			9.66			
7	10.49	10.50	10.50	10.44	10.45		
8	10.58	10.59	10.59	10.53			
9	10.90		10.91	10.86	10.85		
10	11.23	11.24	11.24	11.18	11.18		
11	11.88		11.90	11.84	11.85		
12	11.99		12.00	11.95			
13	12.27	12.29	12.29	12.24	12.24		
14	12.66	12.68	12.69	12.64	12.64		
15	12.98	12.99	13.00	12.95	12.95		
16	13.18		13.19	13.14	13.15		
17	13.61		13.63	13.58	13.58	13.59	13.59
18	13.80		13.82	13.77	13.77	13.78	
19	13.96		13.97	13.93	13.93	13.90	
20	14.48		14.50	14.46	14.45	14.46	
21	14.63		14.64	14.60	14.60		
22	14.99		15.02	14.98	14.97	14.98	
23	15.35		15.36	15.32	15.31	15.32	
24	16.01			15.96			
25			16.14	16.08	16.08	16.10	
26	16.27		16.29	16.26	16.24	16.25	16.26
27						16.53	
28			17.04		16.99	16.96	16.97
29			17.22	17.19	17.19	17.19	17.21
30			17.46	17.43	17.43	17.44	
31					17.69	17.69	
32				17.92	17.91	17.91	
33				18.16	18.14	18.14	
34			18.41	18.37	18.36	18.36	18.37
35			18.58	18.56	18.55	18.55	
36							18.68
37			18.83	18.80	18.78	18.78	18.79
38			19.33	19.30	19.29	19.29	19.29

TABLE 3
(continued)

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
39						19.48	19.48
40						19.81	19.80
41			20.03	19.97	19.92	19.92	
42						20.28	20.28
43					20.46	20.45	
44						20.57	20.57
45				20.85	20.83	20.83	20.83
46			21.18	21.14	21.12	20.98	
47					21.36	21.38	21.38
48						21.78	21.78
49				22.08	22.05	22.04	22.03
50						22.38	22.37
51						22.74	22.73
52						22.96	22.95
53						23.23	23.23
54							23.42
55						23.75	23.73
56						23.99	23.97
57							24.16
58						24.27	
59							24.45
60						24.61	24.62
61						24.93	24.91
62							25.44
63						26.22	26.19
64							26.52
65							26.75
66							27.41
67							28.07
68							28.35
69							29.00

[a] GC operating conditions are given in Table 2. All retention times in minutes and are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

[b] The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 4

EXAMPLE RETENTION TIMES OF AROCLORS
ON THE DB-1701 COLUMN[a], DUAL-COLUMN ANALYSIS

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
1		4.45	4.45				
2		5.38					
3		5.78					
4		5.86	5.86				
5	6.33	6.34	6.34	6.28			
6	6.78	6.78	6.79	6.72			
7	6.96	6.96	6.96	6.90	6.91		
8	7.64			7.59			
9	8.23	8.23	8.23	8.15	8.16		
10	8.62	8.63	8.63	8.57			
11	8.88		8.89	8.83	8.83		
12	9.05	9.06	9.06	8.99	8.99		
13	9.46		9.47	9.40	9.41		
14	9.77	9.79	9.78	9.71	9.71		
15	10.27	10.29	10.29	10.21	10.21		
16	10.64	10.65	10.66	10.59	10.59		
17				10.96	10.95	10.95	
18	11.01		11.02	11.02	11.03		
19	11.09		11.10				
20	11.98		11.99	11.94	11.93	11.93	
21	12.39		12.39	12.33	12.33	12.33	
22			12.77	12.71	12.69		
23	12.92			12.94	12.93		
24	12.99		13.00	13.09	13.09	13.10	
25	13.14		13.16				
26						13.24	
27	13.49		13.49	13.44	13.44		
28	13.58		13.61	13.54	13.54	13.51	13.52
29				13.67		13.68	
30			14.08	14.03	14.03	14.03	14.02
31			14.30	14.26	14.24	14.24	14.25
32					14.39	14.36	
33			14.49	14.46	14.46		
34						14.56	14.56
35					15.10	15.10	
36			15.38	15.33	15.32	15.32	
37			15.65	15.62	15.62	15.61	16.61
38			15.78	15.74	15.74	15.74	15.79
39			16.13	16.10	16.10	16.08	
40							16.19
41						16.34	16.34

TABLE 4
(continued)

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
42						16.44	16.45
43						16.55	
44			16.77	16.73	16.74	16.77	16.77
45			17.13	17.09	17.07	17.07	17.08
46						17.29	17.31
47				17.46	17.44	17.43	17.43
48				17.69	17.69	17.68	17.68
49					18.19	18.17	18.18
50				18.48	18.49	18.42	18.40
51						18.59	
52						18.86	18.86
53				19.13	19.13	19.10	19.09
54						19.42	19.43
55						19.55	19.59
56						20.20	20.21
57						20.34	
58							20.43
59					20.57	20.55	
60						20.62	20.66
61						20.88	20.87
62							21.03
63						21.53	21.53
64						21.83	21.81
65						23.31	23.27
66							23.85
67							24.11
68							24.46
69							24.59
70							24.87
71							25.85
72							27.05
73							27.72

[a] GC operating conditions are given in Table 2. All retention times are in minutes and are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

[b] The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 5

EXAMPLE RETENTION TIMES OF PEAKS DIAGNOSTIC OF PCBs
ON A 0.53-mm ID COLUMNS DURING SINGLE-COLUMN ANALYSIS

Peak No.[a]	RT on DB-608[b]	RT on DB-1701[b]	Aroclor[c]
I	4.90	4.66	1221
II	7.15	6.96	1221, 1232, 1248
III	7.89	7.65	1061, 1221, 1232, 1242
IV	9.38	9.00	1016, 1232, 1242, 1248
V	10.69	10.54	1016, 1232, 1242
VI	14.24	14.12	1248, 1254
VII	14.81	14.77	1254
VIII	16.71	16.38	1254
IX	19.27	18.95	1254, 1260
X	21.22	21.23	1260
XI	22.89	22.46	1260

[a]Peaks are sequentially numbered in elution order and are not isomer numbers

[b]Temperature program: T_i = 150 °C, hold 30 sec; 5 °C/min to 275 °C.

[c]Underline indicates the largest peak in the pattern for that Aroclor

All retention times are in minutes and are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

TABLE 6

SPECIFIC PCB CONGENERS THAT ARE MAJOR COMPONENTS IN COMMON AROCLORS

		Aroclor						
Congener	IUPAC Number	1016	1221	1232	1242	1248	1254	1260
Biphenyl	--		X					
2-CB	1	X	X	X	X			
2,3-DCB	5	X	X	X	X	X		
3,4-DCB	12	X		X	X	X		
2,4,4'-TCB	28*	X		X	X	X	X	
2,2',3,5'-TCB	44			X	X	X	X	X
2,3',4,4'-TCB	66*					X	X	X
2,3,3',4',6-PCB	110						X	
2,3',4,4',5-PCB	118*						X	X
2,2',4,4',5,5'-HCB	153							X
2,2',3,4,4',5'-HCB	138							X
2,2',3,4,4',5,5'-HpCB	180							X
2,2',3,3',4,4',5-HpCB	170							X

*Apparent co-elution of: 28 with 31 (2,4',5-trichlorobiphenyl)
66 with 95 (2,2',3,5',6-pentachlorobiphenyl)
118 with 149 (2,2',3,4',5',6-hexachlorobiphenyl)

This table is not intended to illustrate all of the congeners that may be present in a given Aroclor, but rather to illustrate the major congener components.

TABLE 7
EXAMPLE RETENTION TIMES OF PCB CONGENERS ON THE DB-5 WIDE-BORE COLUMN

IUPAC Number	Retention Time (min)
1	6.52
5	10.07
18	11.62
31	13.43
52	14.75
44	15.51
66	17.20
101	18.08
87	19.11
110	19.45
151	19.87
153	21.30
138	21.79
141	22.34
187	22.89
183	23.09
180	24.87
170	25.93
206	30.70
209 (internal standard)	32.63

All data are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

TABLE 8

EXAMPLE SINGLE-LABORATORY RECOVERY DATA FOR THE EXTRACTION OF PCBs FROM CLAY AND SOIL BY AUTOMATED SOXHLET (METHOD 3541)[a]

Matrix	Aroclor	Spike Level (ppm)	Trial	Percent Recovery[b]
Clay	1254	5	1	87
			2	93
			3	94
			4	99
			5	79
			6	28
Clay	1254	50	1	65
			2	72
			3	97
			4	80
			5	50
			6	59
Clay	1260	5	1	87
			2	75
			3	61
			4	94
			5	97
			6	113
Clay	1260	50	1	74
			2	70
			3	92
			4	89
			5	90
			6	67

TABLE 8
(continued)

Matrix	Aroclor	Spike Level (ppm)	Trial	Percent Recovery[b]
Soil	1254	5	1	70
			2	89
			3	92
			4	83
			5	63
Soil	1254	50	1	84
			2	78
			3	92
			4	67
			5	82
			6	62
Soil	1260	5	1	84
			2	83
			3	82
			4	96
			5	94
			6	94
			7	98
Soil	1260	50	1	77
			2	69
			3	93
			4	82
			5	83
			6	76

[a]The operating conditions for the automated Soxhlet
Immersion time: 60 min
Reflux time: 60 min

[b]Multiple results from two different extractors

Data are taken from Reference 9
These data are provided for guidance purposes only.

TABLE 9

EXAMPLE MULTIPLE-LABORATORY PRECISION AND ACCURACY DATA
FOR THE EXTRACTION OF PCBs FROM SPIKED SOIL
BY AUTOMATED SOXHLET (METHOD 3541)

		Percent Recovery at Aroclor 1254 Spike Concentration (µg/kg)			Percent Recovery at Aroclor 1260 Spike Concentration (µg/kg)			Mean Recovery
		5	50	500	5	50	500	All Levels
Lab 1	n	3	3		3	3		12
	Mean	101.2	74.0		83.9	78.5		84.4
	S. D.	34.9	41.8		7.4	7.4		26.0
Lab 2	n		6	6		6	6	24
	Mean		56.5	66.9		70.1	74.5	67.0
	S. D.		7.0	15.4		14.5	10.3	13.3
Lab 3	n	3	3		3	3		12
	Mean	72.8	63.3		70.6	57.2		66.0
	S. D.	10.8	8.3		2.5	5.6		9.1
Lab 4	n	6	6		6	6		24
	Mean	112.6	144.3		100.3	84.8		110.5
	S. D.	18.2	30.4		13.3	3.8		28.5
Lab 5	n		3	3		3	3	12
	Mean		97.1	80.1		79.5	77.0	83.5
	S. D.		8.7	5.1		3.1	9.4	10.3
Lab 6	n	2	3		3	4		12
	Mean	140.9	127.7		138.7	105.9		125.4
	S. D.	4.3	15.5		15.5	7.9		18.4
Lab 7	n	3	3		3	3		12
	Mean	100.1	123.4		82.1	94.1		99.9
	S. D.	17.9	14.6		7.9	5.2		19.0
Lab 8	n	3	3		3	3		12
	Mean	65.0	38.3		92.8	51.9		62.0
	S. D.	16.0	21.9		36.5	12.8		29.1
All Labs	n	20	30	9	21	31	9	120
	Mean	98.8	92.5	71.3	95.5	78.6	75.3	87.6
	S. D.	28.7	42.9	14.1	25.3	18.0	9.5	29.7

Data are taken from Reference 7
These data are provided for guidance purposes only.

TABLE 10

EXAMPLE PERCENT RECOVERY (BIAS) OF PCBs IN VARIOUS SOILS
USING SUPERCRITICAL FLUID EXTRACTION (METHOD 3562)

PCB No.[a]	EC-1 Dump Site Soil Low #1	SRM 1941 Marine Sediment Low #2	EC-5 Lake Sediment Low #3	CRM 481[b] European Soil High #1	Saginaw Bay Sediment High #2	CRM 392 Sewage Sludge High #3	SRM 2974 Fish Tissue Mussel Low #4	Congener Mean
28	148.4	63.3	147.7	67.3	114.7	89.2	101.7	104.6
52	88.5	106.6	115.8	84.5	111.1	96.2	131.4	104.9
101	93.3	91.2	100.2	84.5	111.5	93.9	133.2	101.1
149	92.6	105.1	101.5	73.2	111.2		69.4	92.2
118	89.9	66.1	108.9	82.1	110.8	73.5	82.7	87.7
153	90.8	65.1	95.1	82.8	118.6	97.3	107.5	94.0
105[b]	89.1	72.6	96.6	83.4	111.8		79.4	88.8
138	90.1	57.4	97.9	76.9	126.9		73.1	87.1
128	90.8	69.9	101.2	65.9	87.6		62.5	79.7
156[b]	90.6	88.9	94.3	85.2	101.1		59.3	86.6
180	92.4	142.4	93.3	82.2	109.2	100.5	65.7	98.0
170	91.3	101.1	95.2	80.5			33.0	81.8
Matrix Mean	95.7	85.8	104.0	79.0	108.7	91.8	83.2	92.2

[a] Congeners which are either certified or have had Soxhlet confirmation.
[b] Congener 105 was not resolved from congener 132 and congener 156 was not resolved from congener 171 by the GC method used for samples EC-1 and EC-5.

TABLE 11

PRECISION (AS %RSD) OF PCBs EXTRACTED USING SUPERCRITICAL FLUID EXTRACTION (METHOD 3562)

PCB No.[a]	EC-1 Dump Site Soil Low #1	SRM 1941 Marine Sediment Low #2	EC-5 Lake Sediment Low #3	CRM 481 European Soil High #1	Saginaw Bay Sediment High #2	CRM 392 Sewage Sludge High #3	SRM 2974 Fish Tissue Mussel Low #4	Congener Mean
28	11.5	1.5	3.8	5.6	2.4	1.9	2.7	4.2
52	9.1	3.3	3.9	5.4	2.2	2.9	3.1	4.3
101	9.1	2.9	2.8	4.9	1.4	5.2	2.9	4.2
149	7.1	0.7	3.8	3.9	3.4		2.2	3.0
118	9.8	1.9	4.5	5.4	2.0	3.3	2.4	4.2
153	8.4	1.5	3.0	4.3	4.3	9.5	3.0	4.9
105[b]	6.6	3.7	2.7	4.3	2.7		2.5	3.2
138	9.2	1.8	3.1	4.7	2.3		2.9	3.4
128	6.0	5.3	3.3	4.9	2.8		3.3	3.7
156[b]	8.3	0.0	5.1	4.5	1.9		3.8	3.4
180	8.0	1.3	3.6	4.3	3.1	9.6	2.7	4.7
170	5.7	2.3	3.6	3.9	2.3		4.0	3.1
Matrix Mean	8.2	2.2	3.6	4.7	2.6	2.7	3.0	3.8

[a] Congeners which are either certified or have had Soxhlet confirmation.

[b] Congener 105 was not resolved from congener 132 and congener 156 was not resolved from congener 171 by the GC method used for samples EC-1 and EC-5.

These data are provided for guidance purposes only.

TABLE 12

EXAMPLE SINGLE-LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF AROCLOR 1254 FROM WASTEWATER MATRICES SPIKED AT 2 µg/L

Wastewater Type	Mean Conc. (µg/L)	Percent Recovery	Std. Dev. (µg/L)	RSD (%)
Chemical Industry	2.4	120	0.41	17.2
Chemical Industry	0.6	28	0.03	5.4
Paper Industry	3.0	150	0.56	18.5
Paper Industry	2.3	115	0.08	3.7
Pharmaceutical Industry	1.5	76	0.03	1.7
Pharmaceutical Industry	1.0	51	0.03	2.9
Refuse	0.5	27	0.04	6.7
Refuse	0.6	31	0.10	16.0
POTW	1.9	96	0.15	7.8
POTW	2.1	105	0.04	1.8

Results represent three replicate solid-phase extractions of spiked wastewaters. Two different wastewaters from each wastewater type were spiked. All extractions were performed using 90-mm C_{18} extraction disks.
These data are provided for guidance purposes only.

TABLE 13

EXAMPLE SINGLE-LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF AROCLOR 1254 FROM WASTEWATER MATRICES SPIKED AT 10 µg/L

Wastewater Type	Mean Conc. (µg/L)	Percent Recovery	Std. Dev. (µg/L)	RSD (%)
Chemical Industry	8.8	88	1.07	12.2
Chemical Industry	8.1	81	0.06	0.7
Paper Industry	8.9	89	0.71	7.9
Paper Industry	10.1	101	0.15	1.4
Pharmaceutical Industry	9.2	92	0.24	2.6
Pharmaceutical Industry	8.4	84	0.17	2.0
Refuse	8.8	88	0.49	5.6
Refuse	8.0	80	1.44	18.0
POTW	9.5	82	0.17	2.1
POTW	8.2	82	0.17	2.1

Results represent three replicate solid-phase extractions of spiked wastewaters. Two different wastewaters from each wastewater type were spiked. All extractions were performed using 90-mm C_{18} extraction disks.
These data are provided for guidance purposes only.

TABLE 14

EXAMPLE SINGLE-LABORATORY RECOVERY DATA
FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF AROCLOR 1254
FROM WASTEWATER MATRICES SPIKED AT 100 µg/L

Wastewater Type	Mean Conc. (µg/L)	Percent Recovery	Std. Dev. (µg/L)	RSD (%)
Chemical Industry	81.7	82	1.46	1.8
Chemical Industry	89.7	90	0.66	0.7
Paper Industry	73.7	74	3.94	5.3
Paper Industry	95.3	95	1.89	2.0
Pharmaceutical Industry	86.4	86	1.95	2.3
Pharmaceutical Industry	79.2	79	3.92	4.9
Refuse	85.7	86	1.59	1.9
Refuse	71.5	72	1.61	2.2
POTW	87.8	88	1.76	2.0
POTW	80.6	81	0.40	0.5

Results represent three replicate solid-phase extractions of spiked wastewaters. Two different wastewaters from each wastewater type were spiked. All extractions were performed using 90-mm C_{18} extraction disks.
These data are provided for guidance purposes only.

TABLE 15

EXAMPLE SINGLE-LABORATORY PCB CONGENER DATA
FROM A SEWAGE SLUDGE SAMPLE EXTRACTED BY
PRESSURIZED FLUID EXTRACTION (METHOD 3545)

PCB No.	Mean Recovery (%)	%RSD	Certified Value (µg/kg)
52	114	4.7	163
101	143	7.4	161
138	110	3.9	193
153	110	5.8	198
180	160	7.5	207

Percent recoveries are the mean of six replicate extractions.

Data are taken from Reference 13.
These data are provided for guidance purposes only.

TABLE 16

EXAMPLE SINGLE-LABORATORY PCB CONGENER DATA
FROM A RIVER SEDIMENT REFERENCE MATERIAL
EXTRACTED BY PRESSURIZED FLUID EXTRACTION (METHOD 3545)

PCB No.	Mean Recovery (%)	%RSD	Certified Value (µg/kg)
101	89	3.7	780
138	122	2.3	570
153	62	4.1	370
180	112	5.9	180

Percent recoveries are the mean of six replicate extractions.
The river sediment reference material was SRM 1939.

Data are taken from Reference 13.
These data are provided for guidance purposes only.

TABLE 17

EXAMPLE SINGLE-LABORATORY AROCLOR 1254 DATA
FROM A SOIL REFERENCE MATERIAL
EXTRACTED BY PRESSURIZED FLUID EXTRACTION (METHOD 3545)

Replicate Extraction	Aroclor 1254 Concentration (µg/kg)
1	1290
2	1370
3	1280
4	1370
Mean	1330
%RSD	3.5%
Certified value	1340
Mean recovery (%)	99%

Data are taken from Reference 13.
These data are provided for guidance purposes only.

TABLE 18

EXAMPLE SINGLE-LABORATORY PCB HOMOLOGUE DATA BY MICROWAVE EXTRACTION (METHOD 3546) FROM A CERTIFIED GREAT LAKE SEDIMENT MATERIAL (EC-2)

	Microwave Extraction			Soxhlet Extraction		
PCB homologue	µg/kg	Peaks[a]	% RSD	µg/kg	Peaks[a]	% RSD
Trichlorobiphenyl	130	4	21.8	100	4	14.6
Tetrachlorobiphenyl	400	10	13.2	390	20	10.2
Pentachlorobiphenyl	310	9	1.9	300	9	8.7
Hexachlorobiphenyl	120	3	0.0	110	3	9.1

[a] Number of PCB peaks detected
Cl_3 to Cl_{10} homologues analyzed
n=3
Data are taken from Reference 14. These data are provided for guidance purposes only.

TABLE 19

EXAMPLE SINGLE-LABORATORY PCB HOMOLOGUE DATA BY MICROWAVE EXTRACTION (METHOD 3546) FROM A CERTIFIED HARBOR SEDIMENT MATERIAL (SRM-1944)

	Microwave Extraction			Soxhlet Extraction		
PCB homologue	µg/kg	Peaks[a]	% RSD	µg/kg	Peaks[a]	% RSD
Trichlorobiphenyl	450	8	10.1	360	6	5.8
Tetrachlorobiphenyl	580	12	3.9	580	11	6.0
Pentachlorobiphenyl	330	9	6.1	330	9	7.9
Hexachlorobiphenyl	260	3	12.4	240	3	5.1
Heptachlorobiphenyl	60	2	43.8	80	2	27.3

[a] Number of PCB peaks detected
Cl_3 to Cl_{10} homologues analyzed
n=3
Data are taken from Reference 14. These data are provided for guidance purposes only.

TABLE 20

EXAMPLE SINGLE-LABORATORY PCB DATA BY MICROWAVE EXTRACTION (METHOD 3546) FROM CERTIFIED GREAT LAKE SEDIMENT MATERIALS

Sediment	Total Aroclor Concentration (µg/kg)	Standard Deviation (µg/kg)	RSD (%)	n	Certified Value (µg/kg)
EC-1	1850	0.07	3.78	3	2000 ± 54
EC-2	1430	0.09	6.60	4	1160 ± 70
EC-3	670	0.02	3.12	3	660 ± 54

Sample size = 2 g extracted into a final volume of 4 mL

EC-2 and EC-3 certified values were only provisional values at the time the work was conducted. The data presented herein were part of the validation data package used to confirm the certified values.

Data are taken from Reference 14.
These data are provided for guidance purposes only.

FIGURE 1. Example GC/ECD chromatogram of the Aroclor 1016/1260 mixture analyzed on a Rtx-5/HP-608 column pair connected to separate injectors. The top trace is the Rtx-5 column (30-m x 0.53-mm ID, 1.5-µm film thickness) and the bottom trace is the HP-608 column (30-m x 0.53-mm ID, 0.5-µm film thickness). Temperature program: 150 °C (1.0 min hold) to 280 °C (17 min hold) at 8 °C/min.

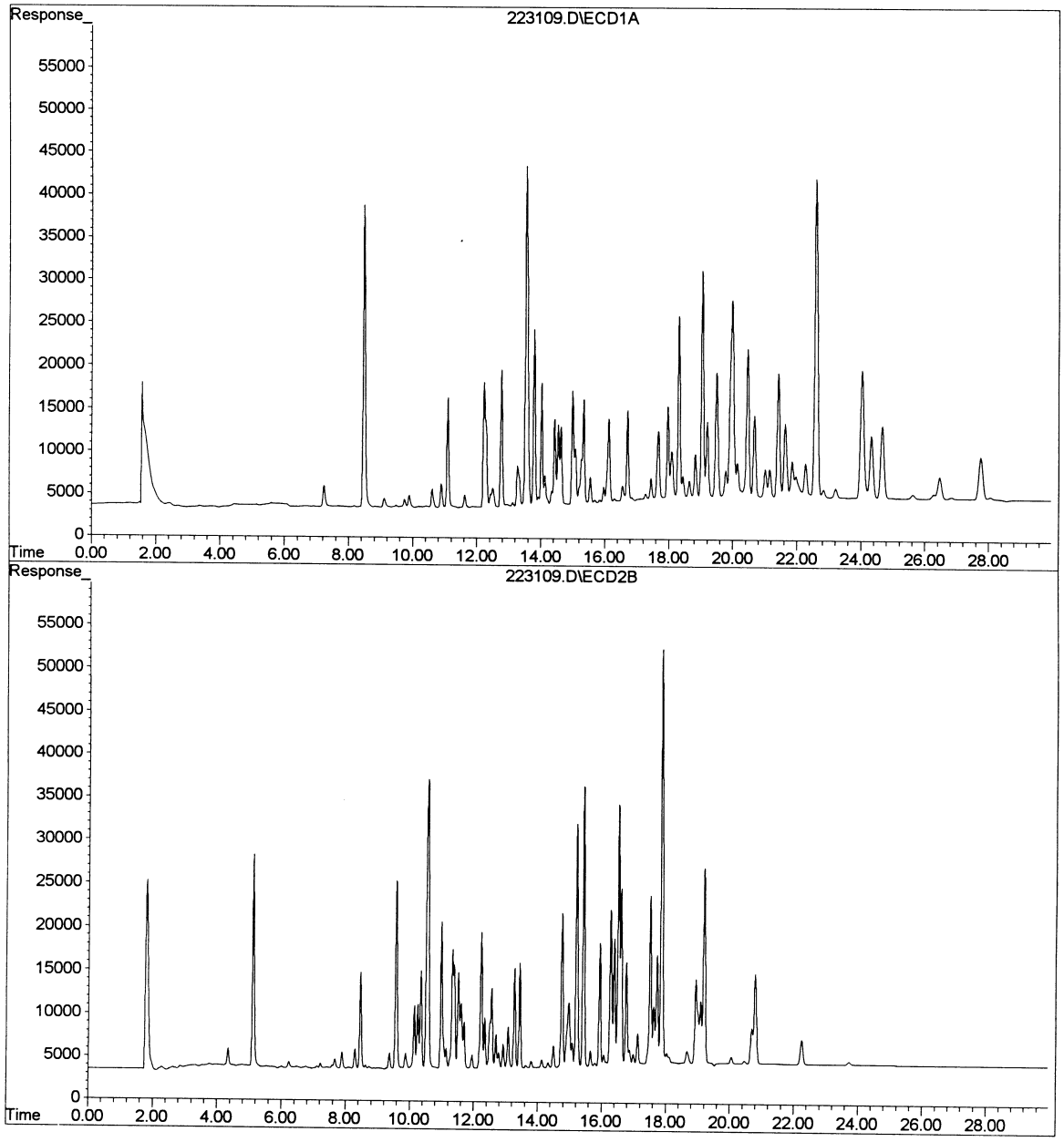


FIGURE 2. Example GC/ECD chromatogram of Aroclor 1221 analyzed on a Rtx-5/HP-608 column pair connected to separate injectors. The top trace is the Rtx-5 column (30-m x 0.53-mm ID, 1.5-µm film thickness) and the bottom trace is the HP-608 column (30-m x 0.53-mm ID, 0.5-µm film thickness). Temperature program: 150 °C (1.0 min hold) to 280 °C (17 min hold) at 8 °C/min.

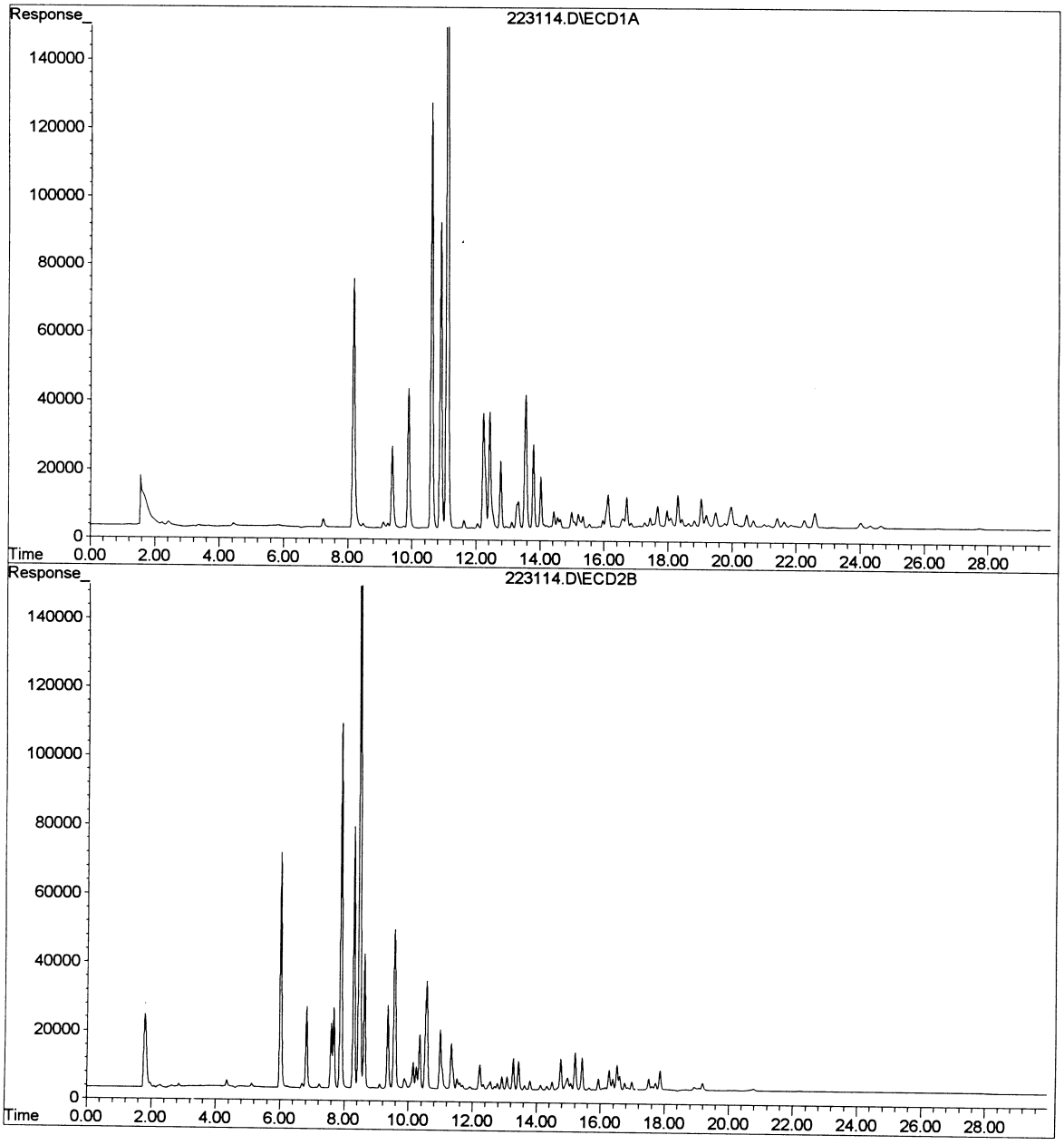


FIGURE 3. Example GC/ECD chromatogram of Aroclor 1232 analyzed on a Rtx-5/HP-608 column pair connected to separate injectors. The top trace is the Rtx-5 column (30-m x 0.53-mm ID, 1.5-µm film thickness) and the bottom trace is the HP-608 column (30-m x 0.53-mm ID, 0.5-µm film thickness). Temperature program: 150 °C (1.0 min hold) to 280 °C (17 min hold) at 8 °C/min.

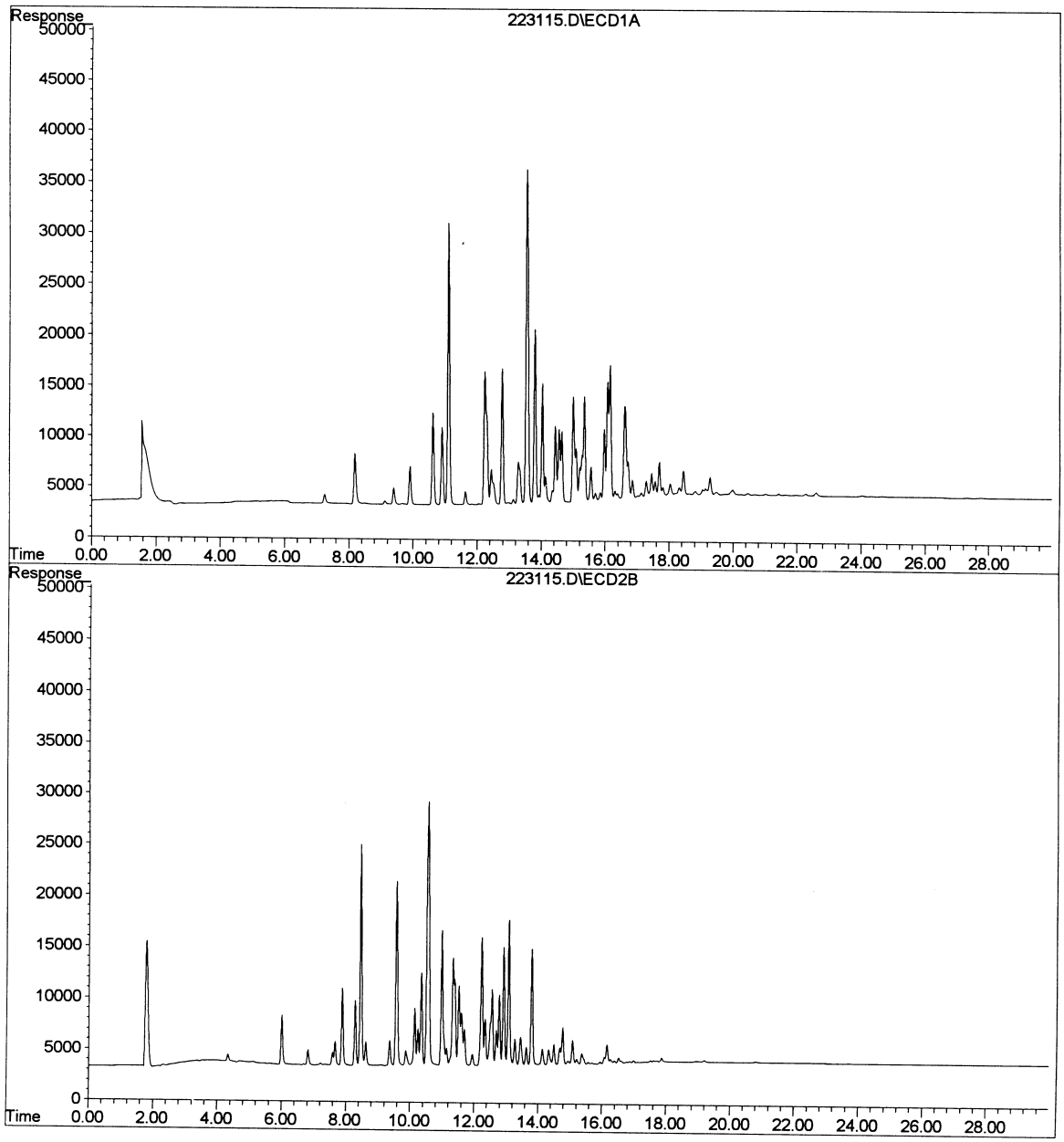


FIGURE 4. Example GC/ECD chromatogram of Aroclor 1242 analyzed on a Rtx-5/HP-608 column pair connected to separate injectors. The top trace is the Rtx-5 column (30-m x 0.53-mm ID, 1.5-µm film thickness) and the bottom trace is the HP-608 column (30-m x 0.53-mm ID, 0.5-µm film thickness). Temperature program: 150 °C (1.0 min hold) to 280 °C (17 min hold) at 8 °C/min.

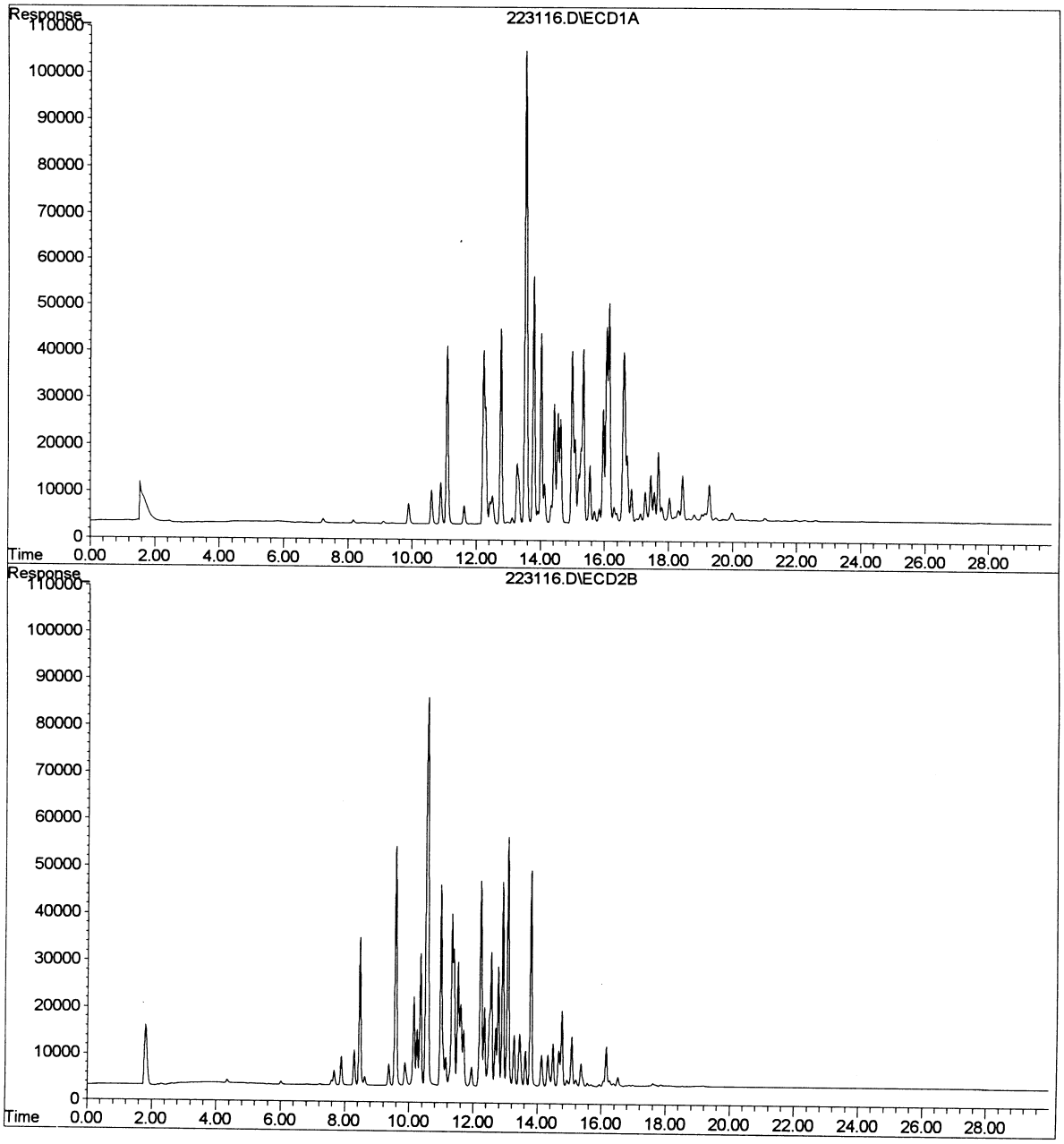


FIGURE 5. Example GC/ECD chromatogram of Aroclor 1248 analyzed on a Rtx-5/HP-608 column pair connected to separate injectors. The top trace is the Rtx-5 column (30-m x 0.53-mm ID, 1.5-µm film thickness) and the bottom trace is the HP-608 column (30-m x 0.53-mm ID, 0.5-µm film thickness). Temperature program: 150 °C (1.0 min hold) to 280 °C (17 min hold) at 8 °C/min.

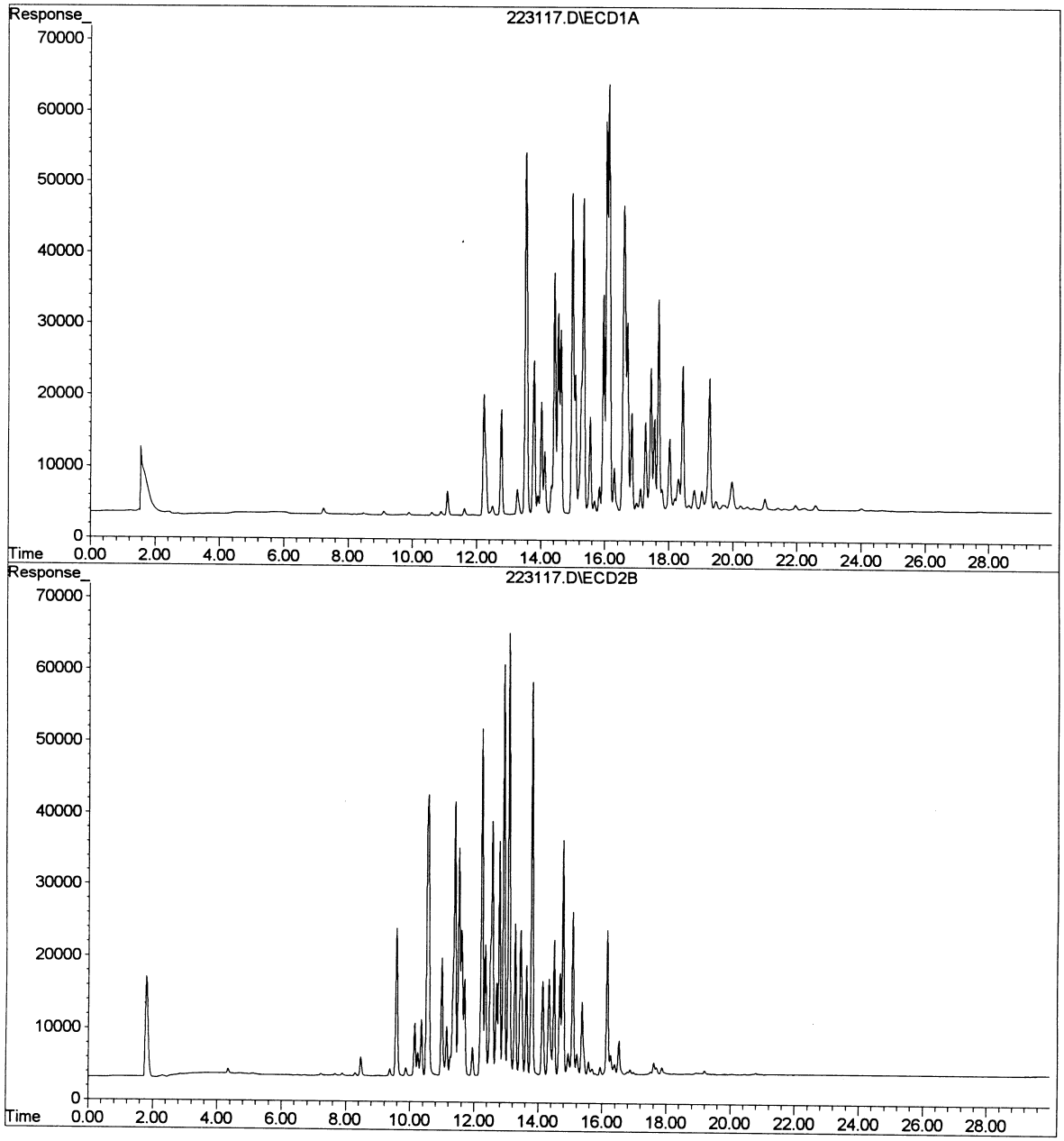
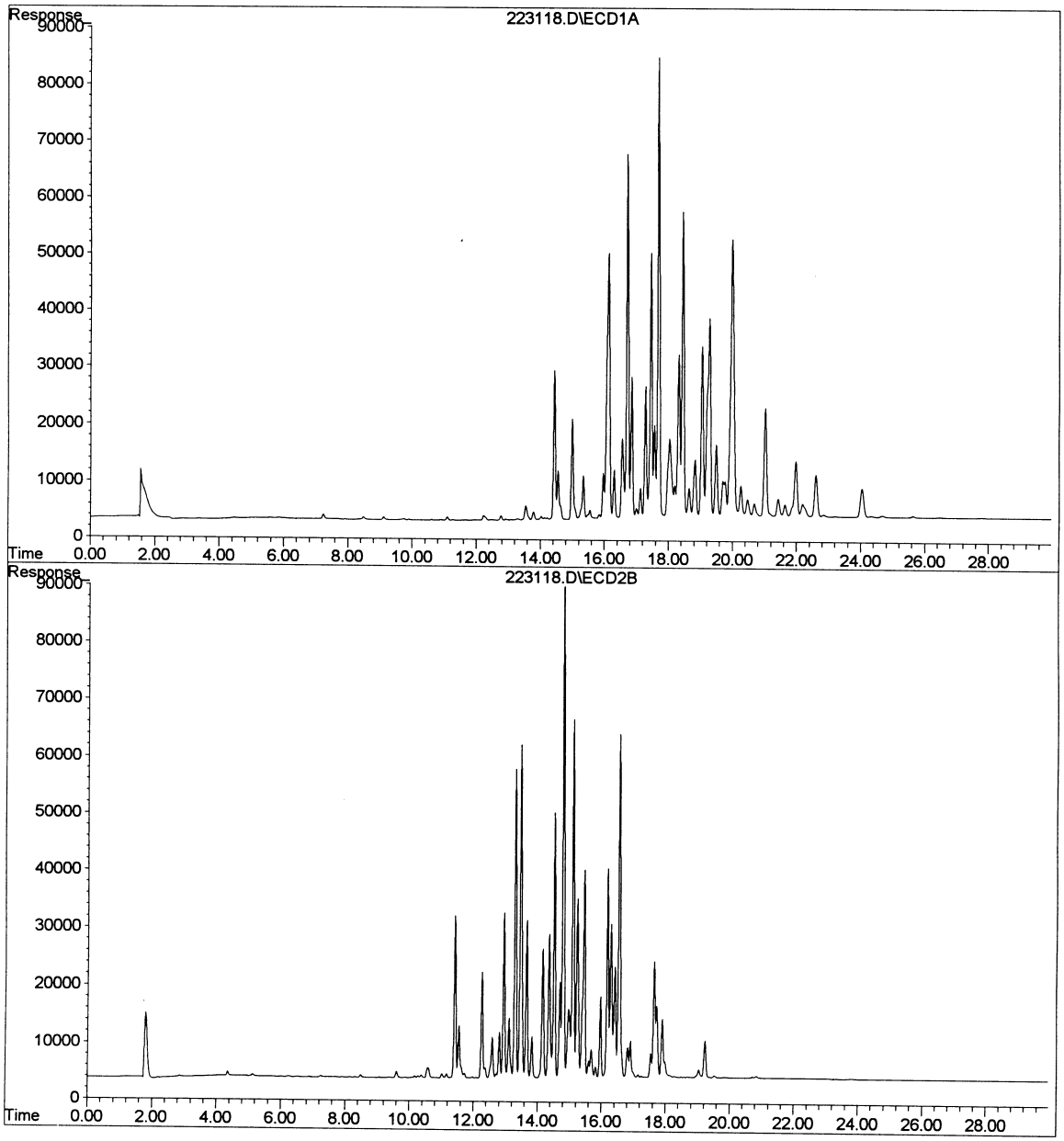


FIGURE 6. Example GC/ECD chromatogram of Aroclor 1254 analyzed on a Rtx-5/HP-608 column pair connected to separate injectors. The top trace is the Rtx-5 column (30-m x 0.53-mm ID, 1.5-µm film thickness) and the bottom trace is the HP-608 column (30-m x 0.53-mm ID, 0.5-µm film thickness). Temperature program: 150 °C (1.0 min hold) to 280 °C (17 min hold) at 8 °C/min.



METHOD 8151A

CHLORINATED HERBICIDES BY GC USING METHYLATION OR PENTAFLUOROBENZYLATION DERIVATIZATION

1.0 SCOPE AND APPLICATION

1.1 Method 8151 is a capillary gas chromatographic (GC) method for determining certain chlorinated acid herbicides and related compounds in aqueous, soil and waste matrices. Specifically, Method 8151 may be used to determine the following compounds:

Compound	CAS No.[a]
2,4-D	94-75-7
2,4-DB	94-82-6
2,4,5-TP (Silvex)	93-72-1
2,4,5-T	93-76-5
Dalapon	75-99-0
Dicamba	1918-00-9
Dichloroprop	120-36-5
Dinoseb	88-85-7
MCPA	94-74-6
MCPP	93-65-2
4-Nitrophenol	100-02-1
Pentachlorophenol	87-86-5

[a] Chemical Abstract Service Registry Number

1.2 Because these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), Method 8151 describes a hydrolysis step that can be used to convert herbicide esters into the acid form prior to analysis. Herbicide esters generally have a half-life of less than one week in soil.

1.3 When Method 8151 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. Sec. 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.4 The estimated detection limits for each of the compounds in aqueous and soil matrices are listed in Table 1. The detection limits for a specific waste sample may differ from those listed, depending upon the nature of the interferences and the sample matrix.

1.5 The following compounds may also be determined using this method:

Compound	CAS No.[a]
Acifluorfen	50594-66-6
Bentazon	25057-89-0
Chloramben	133-90-4
DCPA diacid[b]	2136-79-0
3,5-Dichlorobenzoic acid	51-36-5
5-Hydroxydicamba	7600-50-2
Picloram	1918-02-1

[a] Chemical Abstract Service Registry Number
[b] DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.7 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (explosive, carcinogenic).

2.0 SUMMARY OF METHOD

2.1 Method 8151 provides extraction, derivatization, and gas chromatographic conditions for the analysis of chlorinated acid herbicides in water, soil, and waste samples. An option for the hydrolysis of esters is also described.

2.2 Water samples are extracted with diethyl ether and then esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents.

2.3 Soil and waste samples are extracted and esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents.

2.4 If herbicide esters are to be determined using this method, hydrolysis conditions for the esters in water and soil extracts are described.

2.5 The sensitivity of Method 8151 depends on the level of interferences in addition to instrumental limitations. Table 1 lists the GC/ECD and GC/MS detection limits that can be obtained in aqueous and soil matrices in the absence of interferences. Detection limits for a typical waste sample should be higher.

3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

3.2.1 Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by rinsing it with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water, then with organic-free reagent water. Glassware should be solvent-rinsed with acetone and pesticide-quality hexane. After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store glassware inverted or capped with aluminum foil. Immediately prior to use, glassware should be rinsed with the next solvent to be used.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

3.4 Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure. The determination using pentafluorobenzylation is more sensitive, and more prone to interferences from the presence of organic acids or phenols than by methylation.

3.5 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis. However, hydrolysis may result in the loss of dinoseb and the formation of aldol condensation products if any residual acetone remains from the extraction of solids.

3.6 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed and then rinsed to constant pH with organic-free reagent water. Sodium sulfate must be acidified.

3.7 Sample extracts should be dry prior to methylation or else poor recoveries will be obtained.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - Analytical system complete with gas chromatograph suitable for Grob-type injection using capillary columns, and all required accessories including detector, capillary analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.2 GC columns

The analyst may chose either narrow-bore or wide-bore GC columns. Narrow-bore column 1a is useful for GC/MS confirmation of these analytes. When using an electron capture detector, analyses two columns are necessary to provide confirmation of identifications.

Although not specifically evaluated under the chromatographic conditions described in this procedure, the analyst may opt to configure the GC for simultaneous dual-column operation using commercially-available Y-adapters to connect both columns to a single injector port and employing a separate electron capture detector for each column.

4.2.1 Narrow-bore columns

4.1.2.1 Primary column 1 - 30 m x 0.25 mm, 5% phenyl/95% methyl silicone (DB-5, J&W Scientific, or equivalent), 0.25 µm film thickness.

4.1.2.2 Primary column 1a (GC/MS) - 30 m x 0.32 mm, 5% phenyl/95% methyl silicone, (DB-5, J&W Scientific, or equivalent), 1 µm film thickness.

4.1.2.3 Column 2 - 30 m x 0.25 mm, 35% phenyl methylpolysiloxane (DB-608, J&W Scientific or equivalent), a 0.25 µm film thickness.

4.1.2.4 Confirmation column - 30 m x 0.25 mm, 14% cyanopropyl phenyl silicone, (DB-1701, J&W Scientific, or equivalent), 0.25 µm film thickness.

4.2.2 Wide-bore columns

4.2.2.1 Primary Column - 30 m x 0.53 mm DB-608 (J&W Scientific or equivalent) with 0.83 µm film thickness.

4.2.2.2 Confirmation Column - 30 m x 0.53 mm, 14% cyanopropyl phenyl silicone, (DB-1701, J&W Scientific, or equivalent), 1.0 µm film thickness.

4.3 Electron capture detector (ECD).

4.4 Kuderna-Danish (K-D) apparatus.

4.4.1 Concentrator tube - 10-mL graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.4.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.4.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

NOTE: The following glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required

by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.4.6 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.5 Diazomethane generator - Refer to Sec. 7.5 to determine which method of diazomethane generation should be used for a particular generation.

4.5.1 Diazald kit - Recommended for the generation of diazomethane (Aldrich Chemical Co., Catalog No. 210,025-0, or equivalent).

4.5.2 As an alternative, assemble from two 20 mm x 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Figure 1. The procedure for use of this type of generator is given in Sec. 7.5.

4.6 Beaker - 400-mL, thick-walled.

4.7 Funnel - 75 mm diameter.

4.8 Separatory funnel - 500-mL, with polytetrafluoroethylene (PTFE) stopcock.

4.9 Centrifuge bottle - 500-mL, Pyrex® 1260 or equivalent.

4.10 Erlenmeyer flasks - 250-mL and 500-mL, with a ground-glass joint at the neck.

4.11 Pipet - Pasteur, glass, disposable (140 mm x 5 mm ID).

4.12 Vials - 10-mL, glass, with PTFE-lined screw-caps.

4.13 Volumetric flasks, Class A - 10-mL to 1000-mL.

4.14 Filter paper - 15 cm diameter (Whatman No. 1 or equivalent).

4.15 Glass wool - Pyrex®, acid washed.

4.16 Boiling chips - Solvent-extracted with methylene chloride, approximately 10/40 mesh (silicon carbide or equivalent).

4.17 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.18 Balance - Analytical, capable of accurately weighing to 0.0001 g.

4.19 Centrifuge.

4.20 Ultrasonic extraction system - A horn-type device equipped with a titanium tip, or a device that will give equivalent performance, should be used. The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturer's instructions for preparing the disrupter for extraction of samples. Use a 3/4" horn for most samples.

4.21 Sonabox - Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

4.22 pH paper - wide range

4.23 Silica gel cleanup column (Bond Elut™ - Analytichem, Harbor City, CA or equivalent).

4.24 Microsyringe - 10-µL.

4.25 Wrist shaker - Burrell Model 75 or equivalent.

4.26 Drying column - 400 mm x 20 mm ID Pyrex® chromatographic column with Pyrex® glass wool at bottom and a PTFE stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex® glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free water, as defined in Chapter One.

5.3 Sodium hydroxide solution (0.1 N), NaOH - Dissolve 4 g of NaOH in organic-free reagent water and dilute to 1.0 L.

5.4 Potassium hydroxide solution (37% aqueous solution (w/v)), KOH - Dissolve 37 g of potassium hydroxide pellets in organic-free reagent water and dilute to 100 mL.

5.5 Phosphate buffer (0.1 M), pH = 2.5 - Dissolve 12 g sodium phosphate (NaH_2PO_4) in organic-free reagent water and dilute to 1.0 L. Add phosphoric acid to adjust the pH to 2.5.

5.6 N-methyl-N-nitroso-p-toluenesulfonamide (Diazald) - High purity (Aldrich Chemical Co., or equivalent).

5.7 Silicic acid, H_2SiO_5 - 100-mesh powder, store at 130°C.

5.8 Potassium carbonate, K_2CO_3.

5.9 2,3,4,5,6-Pentafluorobenzyl bromide (PFBBr), $C_6F_5CH_2Br$ - Pesticide quality or equivalent.

5.10 Sodium sulfate (granular, acidified, anhydrous), Na_2SO_4 - Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate. Acidify by slurrying 100 g sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether under vacuum. Mix 1 g of the resulting solid with 5 mL of organic-free reagent water and measure the pH of the mixture. It must be below a pH of 4. Store the remaining solid at 130°C.

5.11 Solvents - All solvents should be pesticide quality or equivalent.

5.11.1 Methylene chloride, CH_2Cl_2.

5.11.2 Acetone, CH_3COCH_3.

5.11.3 Methanol, CH_3OH.

5.11.4 Toluene, $C_6H_5CH_3$.

5.11.5 Diethyl Ether, $C_2H_50C_2H_5$. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips.

NOTE: Diethyl ether used for this procedure should be stabilized with BHT, not with ethanol, as when ethanol-stabilized ether is used, the methylation reaction may not proceed efficiently, leading to low recoveries of target analytes.

5.11.6 Isooctane, $(CH_3)_3CH_2CH(CH_3)_2$.

5.11.7 Hexane, C_6H_{14}.

5.11.8 Carbitol (diethylene glycol monoethyl ether), $C_2H_5OCH_2CH_2OCH_2CH_2O$ - optional, for producing alcohol-free diazomethane.

5.12 Stock standard solutions (1000 mg/L) - May be prepared from pure standard materials or purchased as certified solutions.

5.12.1 Prepare stock standard solutions by accurately weighing about 0.010 g of pure acid. Dissolve the material in pesticide quality acetone and dilute to volume in a 10-mL volumetric flask. Stocks prepared from pure methyl esters are dissolved in 10% acetone/isooctane (v/v). Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

5.12.2 Transfer the stock standard solutions to vials with PTFE-lined screw-caps. Store at 4°C, protected from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially immediately prior to preparing calibration standards from them.

5.12.3 Stock standard solutions of the derivatized acids must be replaced after 1 year, or sooner, if comparison with check standards indicates a problem. Stock standard solutions of the free acids degrade more quickly and should be replaced after two months, or sooner if comparison with check standards indicates a problem.

5.13 Internal Standard Spiking Solution (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences.

5.13.1 The compound 4,4'-dibromooctafluorobiphenyl (DBOB) has been shown to be an effective internal standard, but other compounds, such as 1,4-dichlorobenzene, may be used if there is a DBOB interference.

5.13.2 Prepare an internal standard spiking solution by accurately weighing approximately 0.0025 g of pure DBOB. Dissolve the DBOB in acetone and dilute to volume in a 10 mL volumetric flask. Transfer the internal standard spiking solution to a vial with a PTFE-lined screw-cap, and store at room temperature. Addition of 10 µL of the internal standard spiking solution to 10 mL of sample extract results in a final internal standard concentration of 0.25 µg/L. The solution should be replaced if there is a change in internal standard response greater than 20 percent of the original response recorded.

5.14 Calibration standards - Prepare a minimum of five different concentrations for each parameter of interest, through dilution of the stock standards with diethyl ether or hexane. One of the standards should be at a concentration near, but above, the method detection limit. The remaining standards should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.14.1 Derivatize each calibration standard prepared from free acids in a 10-mL K-D concentrator tube, according to the procedures beginning at Sec. 7.5.

5.14.2 Add a known, constant, amount of one or more internal standards to each derivatized calibration standard, and dilute to volume with the solvent indicated in the derivative option used.

5.15 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and determinative step, and the effectiveness of the method in dealing with each sample matrix, by spiking each sample, standard, and blank with one or two herbicide surrogates (e.g., herbicides that are not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates in gas chromatographic analysis due to coelution problems.

5.15.1 The recommended surrogate is 2,4-Dichlorophenylacetic acid (DCAA).

5.15.2 Prepare a surrogate spiking solution by accurately weighing approximately 0.001 g of pure DCAA. Dissolve the DCAA in acetone, and dilute to volume in a 10-mL volumetric flask. Transfer the surrogate spiking solution to a vial with a PTFE-lined screw-cap, and store at room temperature. Addition of 50 µL of the surrogate spiking solution to 1 L of sample, prior to extraction, results in a final concentration in the extract of 0.5 mg/L.

5.16 pH Adjustment Solutions

5.16.1 Sodium hydroxide, NaOH, 6 N.

5.16.2 Sulfuric acid, H_2SO_4, 12 N.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1. One-Liter samples should be collected.

6.2 Extracts must be stored under refrigeration (4°C) and protected from light.

7.0 PROCEDURE

7.1 Extraction and hydrolysis of high concentration waste samples

7.1.1 Follow Method 3580, Waste Dilution, with the following exceptions:

7.1.1.1 Use diethyl ether as the dilution solvent.

7.1.1.2 Use acidified anhydrous sodium sulfate and acidified glass wool.

7.1.1.3 Spike the sample with surrogate(s) according to Sec. 5.15.

7.1.2 If the sample is to be analyzed for both herbicide esters and acids, then the sample extract must be hydrolyzed. In this case, transfer 1.0 mL (a smaller volume or a dilution may be required if herbicide concentrations are large) to a 250-mL Erlenmeyer flask with a ground-glass joint at the neck. Proceed to Sec. 7.2.3. If the analysis is for acid herbicides only, proceed to Sec. 7.5 for derivatization by diazomethane (if PFB derivatization is selected, reduce the volume of diethyl ether to 0.1 -0.5 mL as per Sec. 7.2 and then dilute to 4 mL with acetone).

7.2 Extraction and hydrolysis of soil, sediment, and other solid samples

Two extraction procedures are applicable to solid samples: ultrasonic extraction and shaker extraction. The same hydrolysis procedures (Sec. 7.2.3) apply to both types of extracts.

7.2.1 Ultrasonic extraction

7.2.1.1 Add 30 g (dry weight) of the well-mixed solid sample to a 400-mL thick-wall beaker. Adjust the pH to 2 with concentrated hydrochloric acid or acidify solids in the beaker with 85 mL of 0.1 M phosphate buffer (pH = 2.5) and thoroughly mix the contents with a glass stirring rod. Spike the sample with surrogate(s) (Sec. 5.15).

7.2.1.2 The ultrasonic extraction of solids must be optimized for each type of sample. In order for the ultrasonic extractor to efficiently extract solid samples, the sample must be free flowing when the solvent is added. Acidified anhydrous sodium sulfate should be added to clay type soils (normally 1:1), or any other solid that is not a free flowing sandy mixture, until a free flowing mixture is obtained.

7.2.1.3 Add 100 mL of methylene chloride/acetone (1:1 v/v) to the beaker. Perform ultrasonic extraction for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Allow the solids to settle. Transfer the organic layer into a 500-mL centrifuge bottle.

7.2.1.4 Ultrasonically extract the sample twice more using 100 mL of methylene chloride and the same ultrasonic conditions.

7.2.1.5 Combine the three organic extracts from the sample in the centrifuge bottle and centrifuge 10 minutes to settle the fine particles. Filter the combined extract through filter paper (Whatman #1, or equivalent) containing 7-10 g of acidified sodium sulfate into a 500-mL 24/40 Erlenmeyer flask. Add 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours. See NOTE in Sec. 7.3.6 that emphasizes the need for a dry extract prior to esterification.

7.2.1.6 Quantitatively transfer the contents of the flask to a 500-mL K-D flask with a 10-mL concentrator tube attached. Add boiling chips and attach the macro Snyder column. Evaporate the extract on the water bath to a volume of approximately 5 mL. Remove the flasks from the water bath and allow them to cool.

7.2.1.7 If hydrolysis or additional cleanup is not required and the sample is dry, proceed to Sec. 7.4.4. Otherwise, proceed to Sec. 7.2.3 for hydrolysis or Sec. 7.2.4 for cleanup.

7.2.2 Shaker extraction

7.2.2.1 Add 50 g (dry weight) of the well mixed, moist solid sample to a 500-mL wide-mouth Erlenmeyer flask. Adjust the pH to 2 with concentrated HCl and monitor the pH for 15 minutes with occasional stirring. If necessary, add additional HCl until the pH remains at 2. Spike the sample with surrogate(s) (Sec. 5.15).

7.2.2.2 Add 20 mL of acetone to the flask and mix the contents with the wrist shaker for 20 minutes. Add 80 mL diethyl ether to the same flask and shake again for 20 minutes. Decant the extract and measure the volume of solvent recovered.

7.2.2.3 Extract the sample twice more using 20 mL of acetone followed by 80 mL of diethyl ether. After addition of each solvent, the mixture should be shaken with the wrist shaker for 10 minutes and the acetone-ether extract decanted.

7.2.2.4 After the third extraction, the volume of extract recovered should be at least 75% of the volume of added solvent. If this is not the case, additional extractions may be necessary. Combine the extracts in a 2-L separatory funnel containing 250 mL of reagent water. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified sodium sulfate equal to the weight of the sample may be added, if necessary.

7.2.2.5 Check the pH of the extract. If it is not at or below pH 2, add more concentrated HCl until stabilized at the desired pH. Gently mix the contents of the separatory funnel for 1 minute and allow the layers to separate. Collect the aqueous phase in a clean beaker and the extract phase (top layer) in a 500-mL ground glass-

stoppered Erlenmeyer flask. Place the aqueous phase back into the separatory funnel and re-extract using 25 mL of diethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in a 500-mL K-D flask.

7.2.2.6 If hydrolysis or additional cleanup is not required and the sample is dry, proceed to Sec. 7.4.4. Otherwise , proceed to Sec. 7.2.3 for hydrolysis or Sec. 7.2.4 for extract cleanup.

7.2.3 Hydrolysis of soil, sediment, or other solid sample extracts

Use this step only if herbicide esters in addition to herbicide acids are to be determined.

7.2.3.1 Add 5 mL of 37% aqueous potassium hydroxide and 30 mL of water to the extract. Add additional boiling chips to the K-D flask. Reflux the mixture on a water bath at 60 - 65°C until the hydrolysis step is completed (usually 1 - 2 hours). Remove the flasks from the water bath and cool to room temperature.

CAUTION: The presence of residual acetone will result in the formation of aldol condensation products which will cause GC interference.

7.2.3.2 Transfer the hydrolyzed aqueous solution to a 500-mL separatory funnel and extract the solution three times with 100-mL portions of methylene chloride. Discard the methylene chloride phase. At this point, the basic (aqueous) solution contains the herbicide salts.

7.2.3.3 Adjust the pH of the solution to <2 with cold (4°C) sulfuric acid (1:3) and extract once with 40 mL of diethyl ether and twice with 20-mL portions of ether. Combine the extracts and pour them through a pre-rinsed drying column containing 7 to 10 cm of acidified anhydrous sodium sulfate. Collect the dried extracts in a 500-mL Erlenmeyer flask (with a 24/40 joint) containing 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours. See NOTE in Sec. 7.3.6 that emphasizes the need for a dry extract prior to esterification. Quantitatively transfer the contents of the flask to a 500-mL Kuderna-Danish flask with a 10-mL concentrator tube attached when the extract is known to be dry.

7.2.3.4 Proceed to Sec. 7.4 for extract concentration. If additional cleanup is required, proceed to Sec. 7.2.4.

7.2.4 Cleanup of non-hydrolyzed herbicides

Use this step if additional cleanup of the non-hydrolyzed herbicides is required.

7.2.4.1 Partition the herbicides by extracting the methylene chloride from 7.2.1.7 (or diethyl ether from 7.2.3.4) three times with 15-mL portions of aqueous base prepared by carefully mixing 30 mL of reagent water into 15 mL of 37% aqueous potassium hydroxide. Discard the methylene chloride or ether phase. At this point the basic (aqueous) solution contains the herbicide salts.

7.2.4.2 Adjust the pH of the solution to <2 with cold (4°C) sulfuric acid (1:3) and extract once with 40 mL of diethyl ether and twice with 20-mL portions of ether. Combine the extracts and pour them through a pre-rinsed drying column containing 7-10 cm of

acidified anhydrous sodium sulfate. Collect the dried extracts in a 500-mL Erlenmeyer flask (with a 24/40 joint) containing 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours. See NOTE in Sec. 7.3.6 that emphasizes the need for a dry extract prior to esterification. Quantitatively transfer the contents of the flask to a 500-mL Kuderna-Danish flask with a 10-mL concentrator tube attached when the extract is known to be dry.

7.2.4.3 Proceed to Sec. 7.4 for extract concentration.

7.3 Preparation of aqueous samples

7.3.1 Using a graduated cylinder, transfer a 1-L sample aliquot to a 2-L separatory funnel. Spike the sample with surrogate compound(s) according to Sec. 5.15.

7.3.2 Add 250 g of NaCl to the sample, seal, and shake to dissolve the salt.

7.3.3 Use this step only if herbicide esters, in addition to herbicide acids, are to be determined

7.3.3.1 Add 17 mL of 6 N NaOH to the sample, seal, and shake. Check the pH of the sample with pH paper. If the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 6 N NaOH. Let the sample sit at room temperature until the hydrolysis step is completed (usually 1 - 2 hours), shaking the separatory funnel and contents periodically.

7.3.3.2 Add 60 mL of methylene chloride to the sample bottle and rinse both the bottle and the graduated cylinder. Transfer the methylene chloride to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between the layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase.

7.3.3.3 Add a second 60-mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, discarding the methylene chloride layer. Perform a third extraction in the same manner.

7.3.4 Add 17 mL of cold (4°C) 12 N sulfuric acid to the sample (or hydrolyzed sample), seal, and shake to mix. Check the pH of the sample with pH paper. If the sample does not have a pH less than or equal to 2, adjust the pH by adding more acid.

7.3.5 Add 120 mL diethyl ether to the sample, seal, and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum techniques to complete the phase separation depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Remove the aqueous phase to a 2-L Erlenmeyer flask and collect the ether phase in a 500-mL Erlenmeyer

flask containing approximately 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the extract and drying agent.

7.3.6 Return the aqueous phase to the separatory funnel, add 60 mL of diethyl ether to the sample, and repeat the extraction procedure a second time, combining the extracts in the 500-mL Erlenmeyer flask. Perform a third extraction with 60 mL diethyl ether in the same manner. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

NOTE: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all of the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held in contact with the sodium sulfate overnight.

7.3.7 Pour the dried extract through a funnel plugged with acid washed glass wool, and collect the extract in the K-D concentrator. Use a glass rod to crush any caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and funnel with 20 to 30 mL of diethyl ether to complete the quantitative transfer. Proceed to Sec. 7.4 for extract concentration.

7.4 Extract concentration

7.4.1 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top of the column. Attach the solvent vapor recovery glassware (condenser and collection device) (Sec. 4.4.6) to the Snyder column of the K-D apparatus following manufacturer's instructions. Place the K-D apparatus on a hot water bath (15 - 20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 - 20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.4.2 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of diethyl ether. The extract may be further concentrated by using either the micro Snyder column technique (Sec. 7.4.3) or nitrogen blowdown technique (Sec. 7.4.4).

7.4.3 Micro Snyder column technique

7.4.3.1 Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding about 0.5 mL of diethyl ether to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower

joints with about 0.2 mL of diethyl ether and add to the concentrator tube. Proceed to Sec. 7.4.5.

7.4.4 Nitrogen blowdown

7.4.4.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.4.4.2 The internal wall of the tube must be rinsed down several times with diethyl ether during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry. Proceed to Sec. 7.4.5.

7.4.5 Dilute the extract with 1 mL of isooctane and 0.5 mL of methanol. Dilute to a final volume of 4 mL with diethyl ether. The sample is now ready for methylation with diazomethane. If PFB derivation is being performed, dilute to 4 mL with acetone.

7.5 Esterification - For diazomethane derivatization proceed with Sec. 7.5.1. For PFB derivatization proceed with Sec. 7.5.2.

7.5.1 Diazomethane derivatization - Two methods may be used for the generation of diazomethane: the bubbler method (see Figure 1), Sec. 7.5.1.1, and the Diazald kit method, Sec. 7.5.1.2.

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

The bubbler method is suggested when small batches of samples (10 - 15) require esterification. The bubbler method works well with samples that have low concentrations of herbicides (e.g., aqueous samples) and is safer to use than the Diazald kit procedure. The Diazald kit method is good for large quantities of samples needing esterification. The Diazald kit method is more effective than the bubbler method for soils or samples that may contain high concentrations of herbicides (e.g., samples such as soils that may result in yellow extracts following hydrolysis may be difficult to handle by the bubbler method).

The diazomethane derivatization procedures described below will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use.

The following precautions should be taken:

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90°C - EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, and glass stirrers - EXPLOSION may result.

- Store away from alkali metals - EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.5.1.1 Bubbler method - Assemble the diazomethane bubbler (see Figure 1).

7.5.1.1.1 Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% KOH, and 0.1 - 0.2 g of Diazald to the second test tube. Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 minutes or until the yellow color of diazomethane persists. The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1 - 0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 minutes of total esterification.

7.5.1.1.2 Remove the concentrator tube and seal it with a Neoprene or PTFE stopper. Store at room temperature in a hood for 20 minutes.

7.5.1.1.3 Destroy any unreacted diazomethane by adding 0.1 - 0.2 g of silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube or transfer 1 mL of sample to a GC vial, and store refrigerated if further processing will not be performed immediately. Analyze by gas chromatography.

7.5.1.1.4 Extracts should be stored at 4°C away from light. Preservation study results indicate that most analytes are stable for 28 days; however, it is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur.

7.5.1.2 Diazald kit method - Instructions for preparing diazomethane are provided with the generator kit.

7.5.1.2.1 Add 2 mL of diazomethane solution and let the sample stand for 10 minutes with occasional swirling. The yellow color of diazomethane should be evident and should persist for this period.

7.5.1.2.2 Rinse the inside wall of the ampule with 700 µL of diethyl ether. Reduce the sample volume to approximately 2 mL to remove excess diazomethane by allowing the solvent to evaporate spontaneously at room temperature. Alternatively, 10 mg of silicic acid can be added to destroy the excess diazomethane.

7.5.1.2.3 Dilute the sample to 10.0 mL with hexane. Analyze by gas chromatography. It is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur.

7.5.2 PFB derivatization

7.5.2.1 Add 30 µL of 10% K_2CO_3 and 200 µL of 3% PFBBr in acetone. Close the tube with a glass stopper and mix on a vortex mixer. Heat the tube at 60°C for 3 hours.

7.5.2.2 Evaporate the solution to 0.5 mL with a gentle stream of nitrogen. Add 2 mL of hexane and repeat evaporation just to dryness at ambient temperature.

7.5.2.3 Redissolve the residue in 2 mL of toluene:hexane (1:6) for column cleanup.

7.5.2.4 Top a silica column (Bond Elut™ or equivalent) with 0.5 cm of anhydrous sodium sulfate. Prewet the column with 5 mL hexane and let the solvent drain to the top of the adsorbent. Quantitatively transfer the reaction residue to the column with several rinsings of the toluene:hexane solution (total 2 - 3 mL).

7.5.2.5 Elute the column with sufficient toluene:hexane to collect 8 mL of eluent. Discard this fraction, which contains excess reagent.

7.5.2.6 Elute the column with toluene:hexane (9:1) to collect 8 mL of eluent containing PFB derivatives in a 10-mL volumetric flask. Dilute to 10 mL with hexane. Analyze by GC/ECD.

7.6 Gas chromatographic conditions (recommended)

7.6.1 Narrow-bore columns

Temperature program:	60°C to 300°C, at 4°C/min
Helium carrier flow:	30 cm/sec
Injection volume:	2 µL, splitless, 45 sec delay
Injector temperature:	250°C
Detector temperature:	320°C

7.6.2 Wide-bore columns

Temperature program:	0.5 minute at 150°C, 150°C to 270°C, at 5°C/min
Helium carrier flow:	7 mL/min
Injection volume:	1 µL
Injector temperature:	250°C
Detector temperature:	320°C

7.7 Calibration

The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures. Use Table 1 for guidance on selecting the lowest point on the calibration curve.

7.8 Gas chromatographic analysis of samples

7.8.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to injection.

7.8.2 Follow Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.8.3 An example of a chromatogram for a methylated chlorophenoxy herbicide is shown in Figure 2. Tables 2 and 3 present retention times for the target analytes after esterification, using the diazomethane derivatization procedure and the PFBBr derivatization procedure, respectively.

7.8.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.8.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.8.6 If calibration standards have been analyzed in the same manner as the samples (e.g., have undergone hydrolysis and esterification), then the calculation of concentration given in Method 8000 should be used. However, if calibration is performed using standards made from methyl ester compounds (compounds not esterified by application of this method), then the calculation of concentration must include a correction for the molecular weight of the methyl ester versus the acid herbicide.

7.8.7 If peak detection and identification are prevented due to interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from reagents.

7.9 GC/MS confirmation

7.9.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Refer to Method 8270 for the appropriate GC/MS operating conditions and analysis procedures.

7.9.2 When available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

7.9.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate GC columns or additional cleanup.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Method 3500. Each laboratory should maintain a

formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the

laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 In single laboratory studies using organic-free reagent water and clay/still bottom samples, the mean recoveries presented in Tables 4 and 5 were obtained for diazomethane derivatization. The standard deviations of the percent recoveries of these measurements are also in Tables 4 and 5.

9.2 Table 6 presents relative recoveries of the target analytes obtained using the PFBBr derivatization procedure with spiked water samples.

10.0 REFERENCES

1. Goerlitz, D.G., Lamar, W.L., "Determination of Phenoxy Acid Herbicides in Water by Electron Capture and Microcoulometric Gas Chromatography", U.S. Geol. Survey Water Supply Paper 1967, 1817-C.

2. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis: Some Practical Aspects", J. Assoc. Off. Anal. Chem. (JAOAC), 1965, 48, 1037.

3. "Extraction and Cleanup Procedures for the Determination of Phenoxy Acid Herbicides in Sediment", U.S. Environmental Protection Agency, EPA Toxicant and Analysis Center, Bay St. Louis, MS, 1972.

4. Shore, F.L., Amick, E.N., Pan, S.T., "Single Laboratory Validation of EPA Method 8151 for the Analysis of Chlorinated Herbicides in Hazardous Waste", U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, 1985; EPA-60014-85-060.

5. Method 515.1, "Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector", Revision 4.0, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH.

6. Gurka, D.F, Shore, F.L., Pan, S.T., "Single Laboratory Validation of EPA Method 8150 for Determination of Chlorinated Herbicides in Hazardous Waste", JAOAC, 69, 970, 1986.

TABLE 1

ESTIMATED METHOD DETECTION LIMITS FOR
DIAZOMETHANE DERIVATIZATION

Compound	Aqueous Samples GC/ECD Estimated Detection Limit[a] (µg/L)	Soil Samples GC/ECD Estimated Detection Limit[b] (µg/kg)	Soil Samples GC/MS Estimated Identification Limit[c] (ng)
Acifluorfen	0.096	-	-
Bentazon	0.2	-	-
Chloramben	0.093	4.0	1.7
2,4-D	0.2	0.11	1.25
Dalapon	1.3	0.12	0.5
2,4-DB	0.8	-	-
DCPA diacid[e]	0.02	-	-
Dicamba	0.081	-	-
3,5-Dichlorobenzoic acid	0.061	0.38	0.65
Dichloroprop	0.26	-	-
Dinoseb	0.19	-	-
5-Hydroxydicamba	0.04	-	-
MCPP	0.09[d]	66	0.43
MCPA	0.056[d]	43	0.3
4-Nitrophenol	0.13	0.34	0.44
Pentachlorophenol	0.076	0.16	1.3
Picloram	0.14	-	-
2,4,5-T	0.08	-	-
2,4,5-TP	0.075	0.28	4.5

[a] EDL = estimated detection limit; defined as either the MDL, or a concentration of analyte in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

[b] Detection limits determined from standard solutions corrected back to 50-g samples, extracted and concentrated to 10 mL, with 5 µL injected. Chromatography using narrow-bore capillary column, 0.25 µm film, 5% phenyl/95% methyl silicone.

[c] The minimum amount of analyte to give a Finnigan INCOS FIT value of 800 as the methyl derivative vs. the spectrum obtained from 50 ng of the respective free acid herbicide.

[d] From Method 1658, "The Determination of Phenoxy-Acid Herbicides in Municipal and Industrial Wastewater", Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, EPA-821-R-93-010-A, the USEPA Office of Water, Engineering and Analysis Division. MDLs were obtained with an electrolytic conductivity detector.

[e] DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 2

RETENTION TIMES (MINUTES) OF METHYL DERIVATIVES OF CHLORINATED HERBICIDES

Analyte	Narrow Bore Columns		Wide-bore Columns	
	Primary[a] Column	Confirmation[a] Column	Primary[b] Column	Confirmation[b] Column
Dalapon	3.4	4.7	-	-
3,5-Dichlorobenzoic acid	18.6	17.7	-	-
4-Nitrophenol	18.6	20.5	-	-
DCAA (surrogate)	22.0	14.9	-	-
Dicamba	22.1	22.6	4.39	4.39
Dichloroprop	25.0	25.6	5.15	5.46
2,4-D	25.5	27.0	5.85	6.05
DBOB (internal std.)	27.5	27.6	-	-
Pentachlorophenol	28.3	27.0	-	-
Chloramben	29.7	32.8	-	-
2,4,5-TP	29.7	29.5	6.97	7.37
5-Hydroxydicamba	30.0	30.7	-	-
2,4,5-T	30.5	30.9	7.92	8.20
2,4-DB	32.2	32.2	8.74	9.02
Dinoseb	32.4	34.1	-	-
Bentazon	33.3	34.6	-	-
Picloram	34.4	37.5	-	-
DCPA diacid[c]	35.8	37.8	-	-
Acifluorfen	41.5	42.8	-	-
MCPP	-	-	4.24	4.55
MCPA	-	-	4.74	4.94

[a] Primary Column: 5% phenyl/95% methyl silicone
Confirmation Column: 14% cyanopropyl phenyl silicone
Temperature program: 60°C to 300°C, at 4°C/min
Helium carrier flow: 30 cm/sec
Injection volume: 2 µL, splitless, 45 sec delay
Injector temperature: 250°C
Detector temperature: 320°C

[b] Primary Column: DB-608
Confirmatory Column: 14% cyanopropyl phenyl silicone
Temperature program: 0.5 minute at 150°C, 150°C to 270°C, at 5°C/min
Helium carrier flow: 7 mL/min
Injection volume: 1 µL

[c] DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 3

RETENTION TIMES (MINUTES) OF PFB DERIVATIVES OF CHLORINATED HERBICIDES

	Gas Chromatographic Column		
Compound	Thin-film DB-5[a]	SP-2250[b]	Thick-film DB-5[c]
Dalapon	10.41	12.94	13.54
MCPP	18.22	22.30	22.98
Dicamba	18.73	23.57	23.94
MCPA	18.88	23.95	24.18
Dichloroprop	19.10	24.10	24.70
2,4-D	19.84	26.33	26.20
Silvex	21.00	27.90	29.02
2,4,5-T	22.03	31.45	31.36
Dinoseb	22.11	28.93	31.57
2,4-DB	23.85	35.61	35.97

[a] DB-5 capillary column, 0.25 µm film thickness, 0.25 mm ID x 30 m long. Column programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 17 minutes.

[b] SP-2550 capillary column, 0.25 µm film thickness, 0.25 mm ID x 30 m long. Column programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 10 minutes.

[c] DB-5 capillary column, 1.0 µm film thickness, 0.32 mm ID x 30 m long. Column programmed: 70°C for 1 minute, program 10°C/min. to 240°C, hold for 10 minutes.

TABLE 4

ACCURACY AND PRECISION FOR DIAZOMETHANE DERIVATIZATION
ORGANIC-FREE REAGENT WATER MATRIX

Compound	Spike Concentration (µg/L)	Mean[a] Percent Recovery	Standard Deviation of Percent Recovery
Acifluorfen	0.2	121	15.7
Bentazon	1	120	16.8
Chloramben	0.4	111	14.4
2,4-D	1	131	27.5
Dalapon	10	100	20.0
2,4-DB	4	87	13.1
DCPA diacid[b]	0.2	74	9.7
Dicamba	0.4	135	32.4
3,5-Dichlorobenzoic acid	0.6	102	16.3
Dichloroprop	2	107	20.3
Dinoseb	0.4	42	14.3
5-Hydroxydicamba	0.2	103	16.5
4-Nitrophenol	1	131	23.6
Pentachlorophenol	0.04	130	31.2
Picloram	0.6	91	15.5
2,4,5-TP	0.4	117	16.4
2,4,5-T	0.2	134	30.8

[a] Mean percent recovery calculated from 7-8 determinations of spiked organic-free reagent water.

[b] DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 5

ACCURACY AND PRECISION FOR DIAZOMETHANE DERIVATIZATION
CLAY MATRIX

Compound	Mean Percent Recovery[a]	Linear Concentration Range[b] (ng/g)	Percent Relative Standard Deviation[c] (n=20)
Dicamba	95.7	0.52 - 104	7.5
MCPP	98.3	620 - 61,800	3.4
MCPA	96.9	620 - 61,200	5.3
Dichloroprop	97.3	1.5 - 3,000	5.0
2,4-D	84.3	1.2 - 2,440	5.3
2,4,5-TP	94.5	0.42 - 828	5.7
2,4,5-T	83.1	0.42 - 828	7.3
2,4-DB	90.7	4.0 - 8,060	7.6
Dinoseb	93.7	0.82 - 1,620	8.7

[a] Mean percent recovery calculated from 10 determinations of spiked clay and clay/still bottom samples over the linear concentration range.

[b] Linear concentration range was determined using standard solutions and corrected to 50 g solid samples.

[c] Percent relative standard deviation was calculated using standard solutions, 10 samples high in the linear concentration range, and 10 samples low in the range.

TABLE 6

RELATIVE RECOVERIES OF PFB DERIVATIVES OF HERBICIDES[a]

Compound	Standard Concentration mg/L	Percent Recoveries 1	2	3	4	5	6	7	8	Mean
MCPP	5.1	95.6	88.8	97.1	100	95.5	97.2	98.1	98.2	96.3
Dicamba	3.9	91.4	99.2	100	92.7	84.0	93.0	91.1	90.1	92.7
MCPA	10.1	89.6	79.7	87.0	100	89.5	84.9	92.3	98.6	90.2
Dichloroprop	6.0	88.4	80.3	89.5	100	85.2	87.9	84.5	90.5	88.3
2,4-D	9.8	55.6	90.3	100	65.9	58.3	61.6	60.8	67.6	70.0
Silvex	10.4	95.3	85.8	91.5	100	91.3	95.0	91.1	96.0	93.3
2,4,5-T	12.8	78.6	65.6	69.2	100	81.6	90.1	84.3	98.5	83.5
2,4-DB	20.1	99.8	96.3	100	88.4	97.1	92.4	91.6	91.6	95.0
Mean		86.8	85.7	91.8	93.4	85.3	89.0	87.1	91.4	

[a]Percent recovery determinations made using eight spiked water samples.

FIGURE 1
DIAZOMETHANE GENERATOR

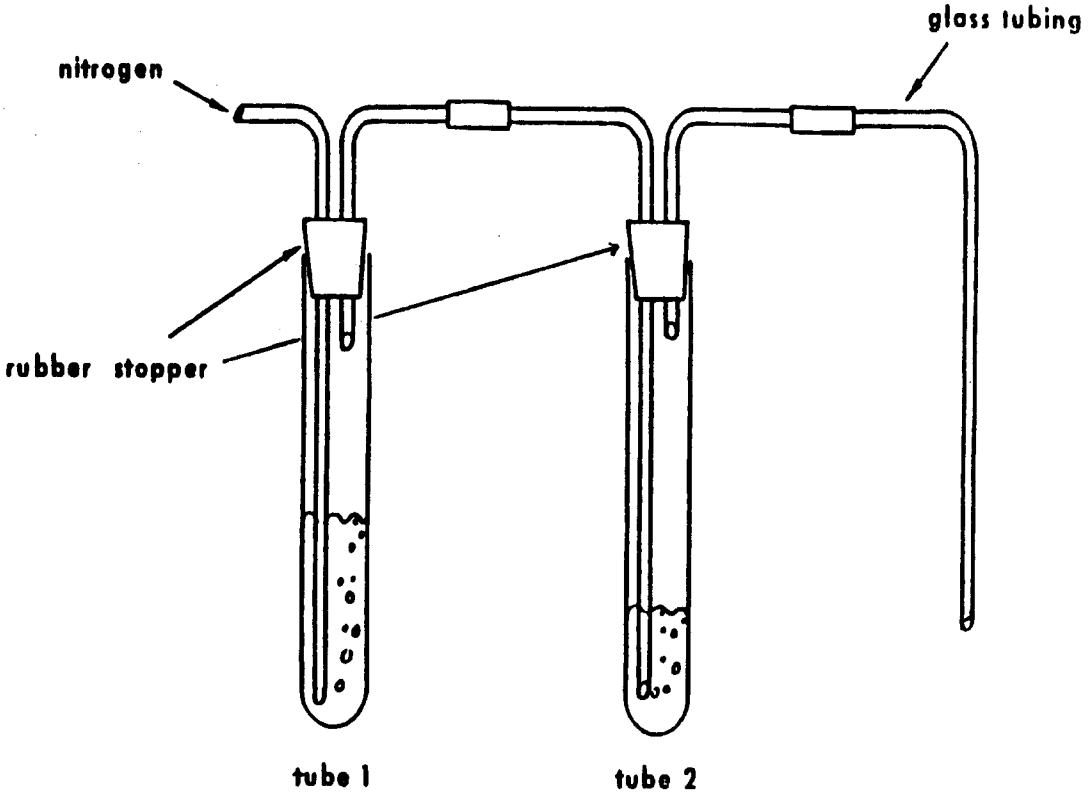
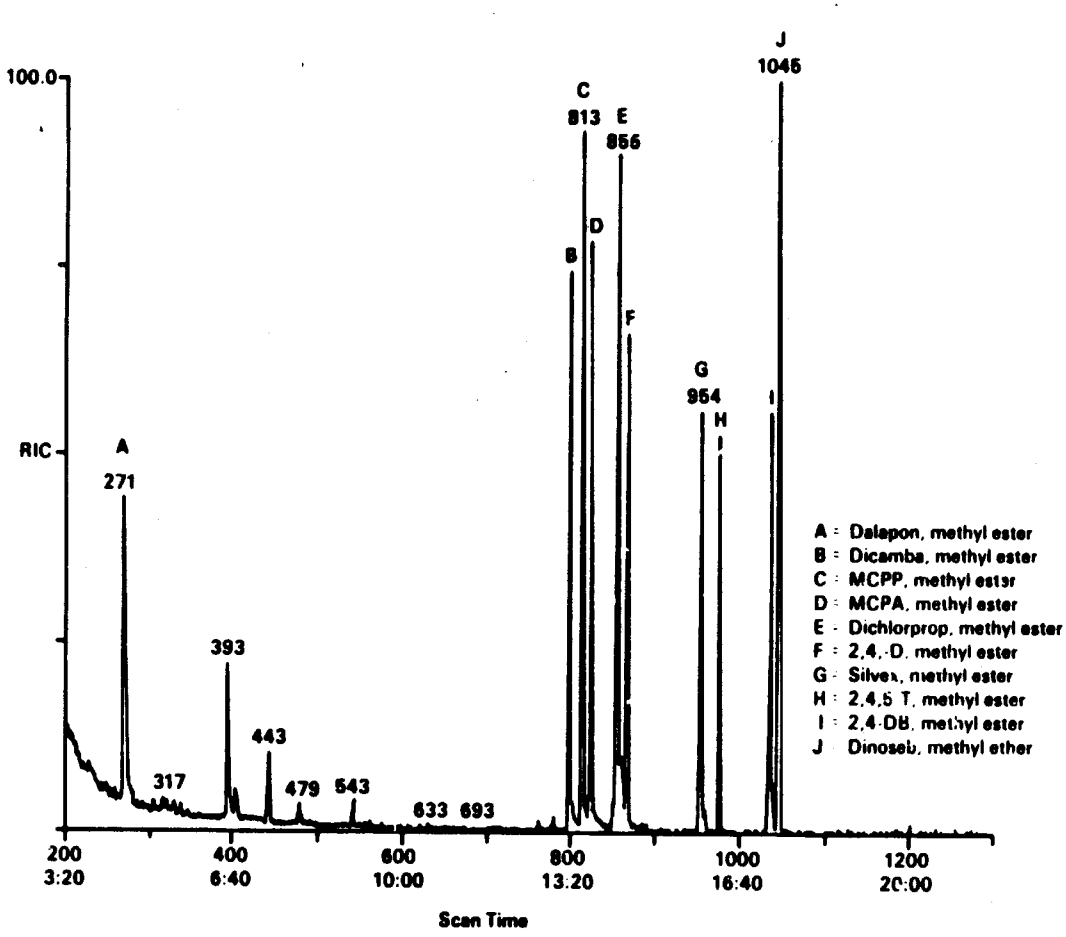
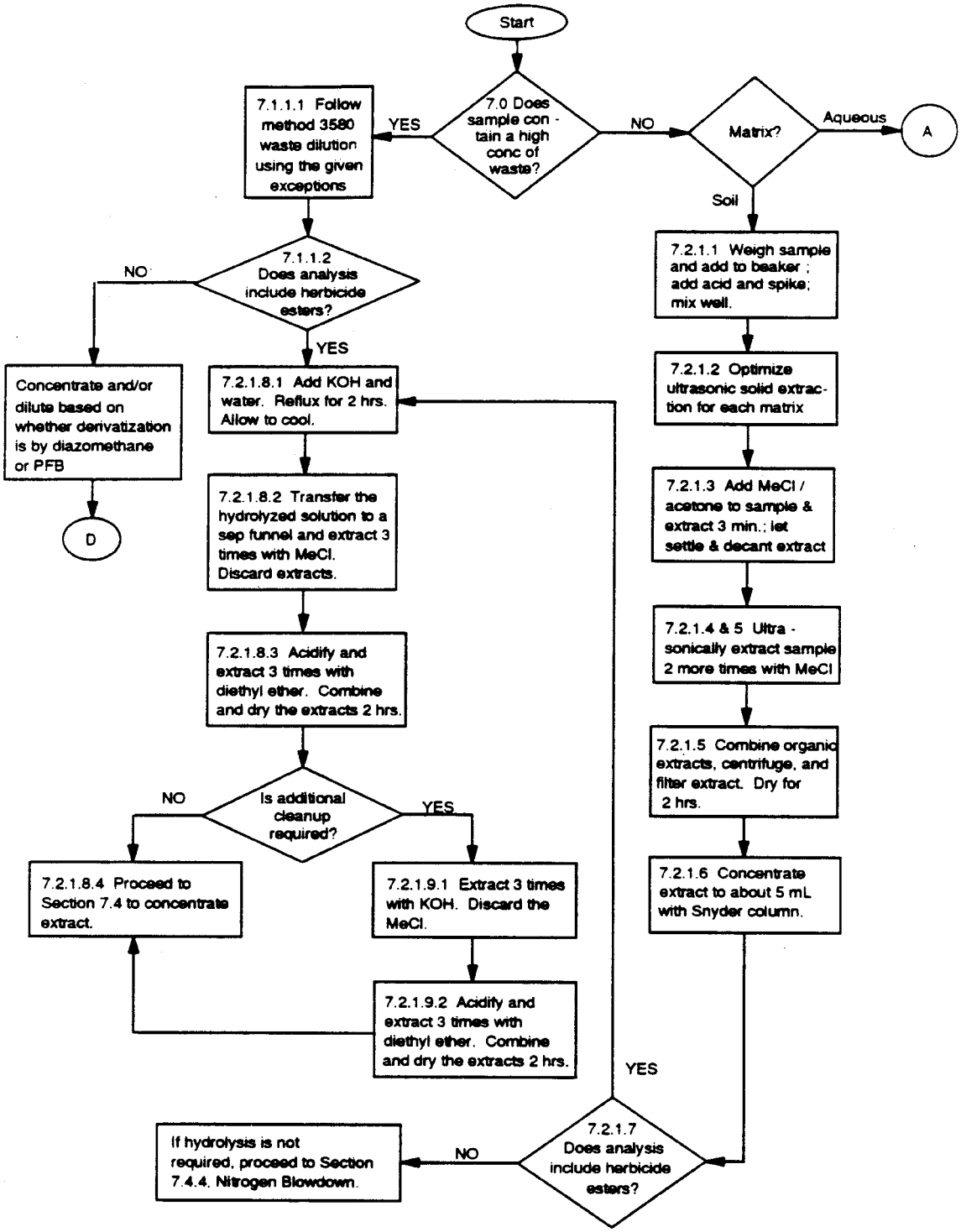


FIGURE 2
CHROMATOGRAM OF METHYL ESTERS OF CHLOROPHENOXYACIDS

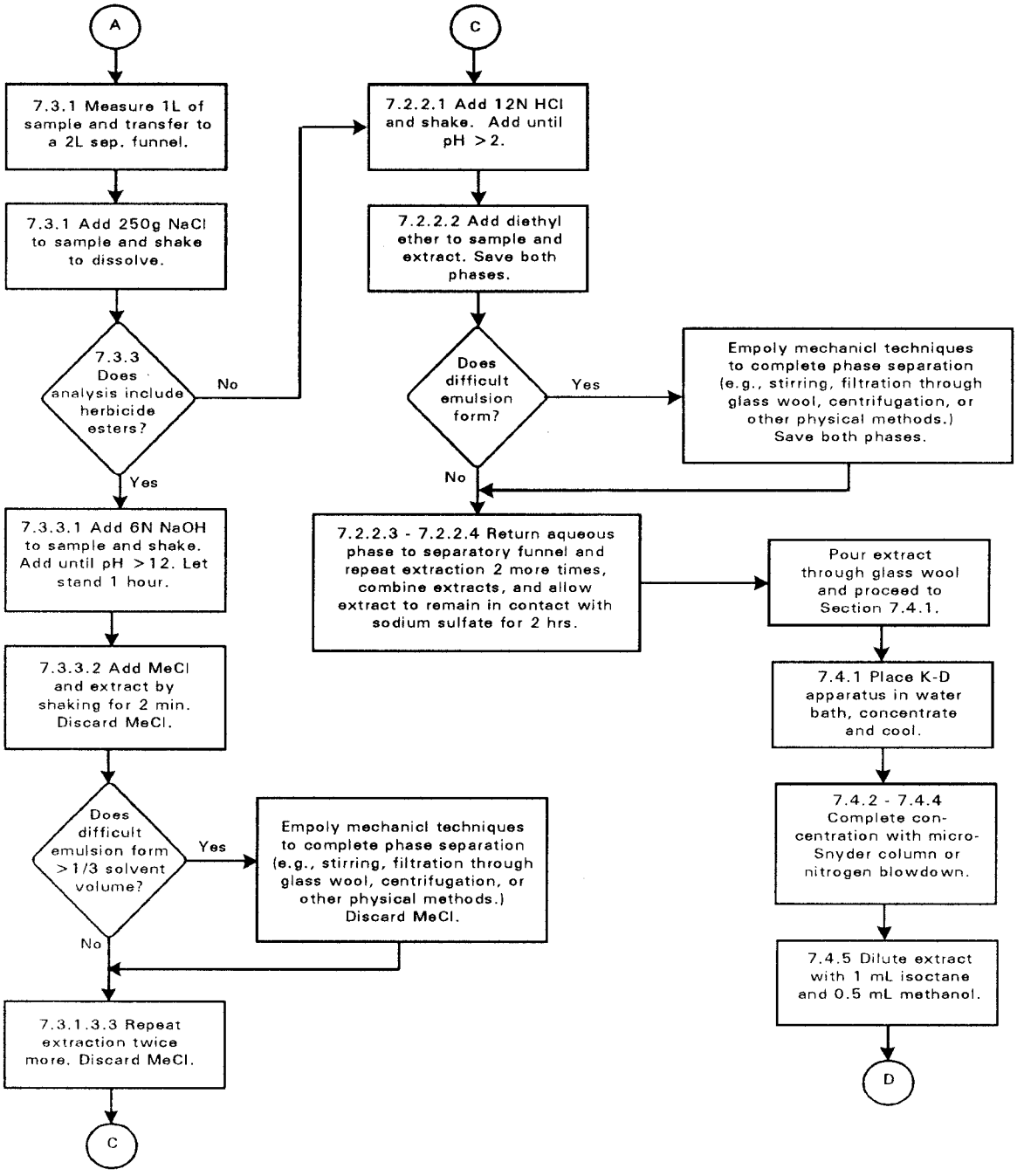


CHLORINATED HERBICIDES BY GC USING METHYLATION OR PENTAFLUOROBENZYLATION DERIVATIZATION

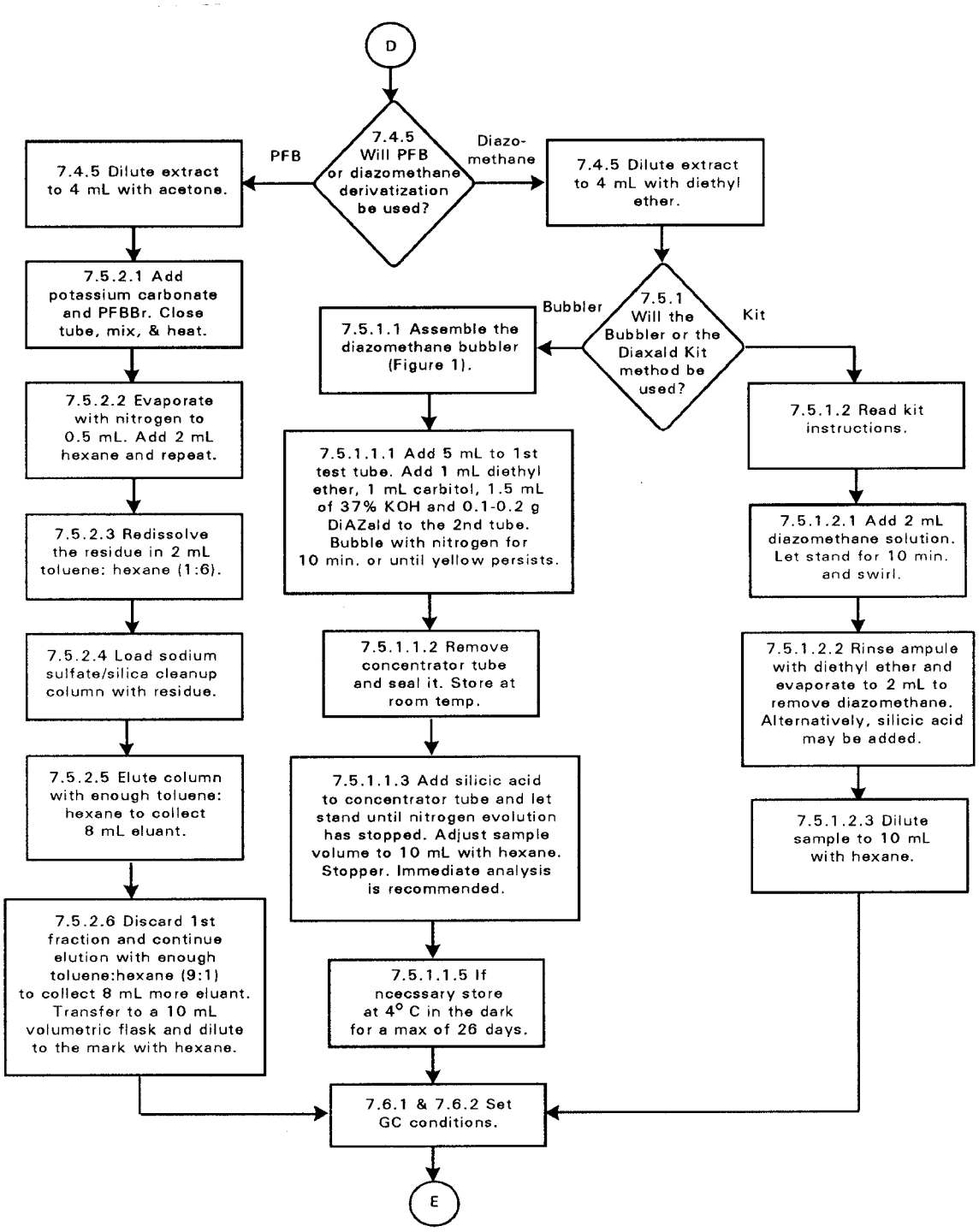
Extraction/Hydrolysis of Waste and Soil Samples



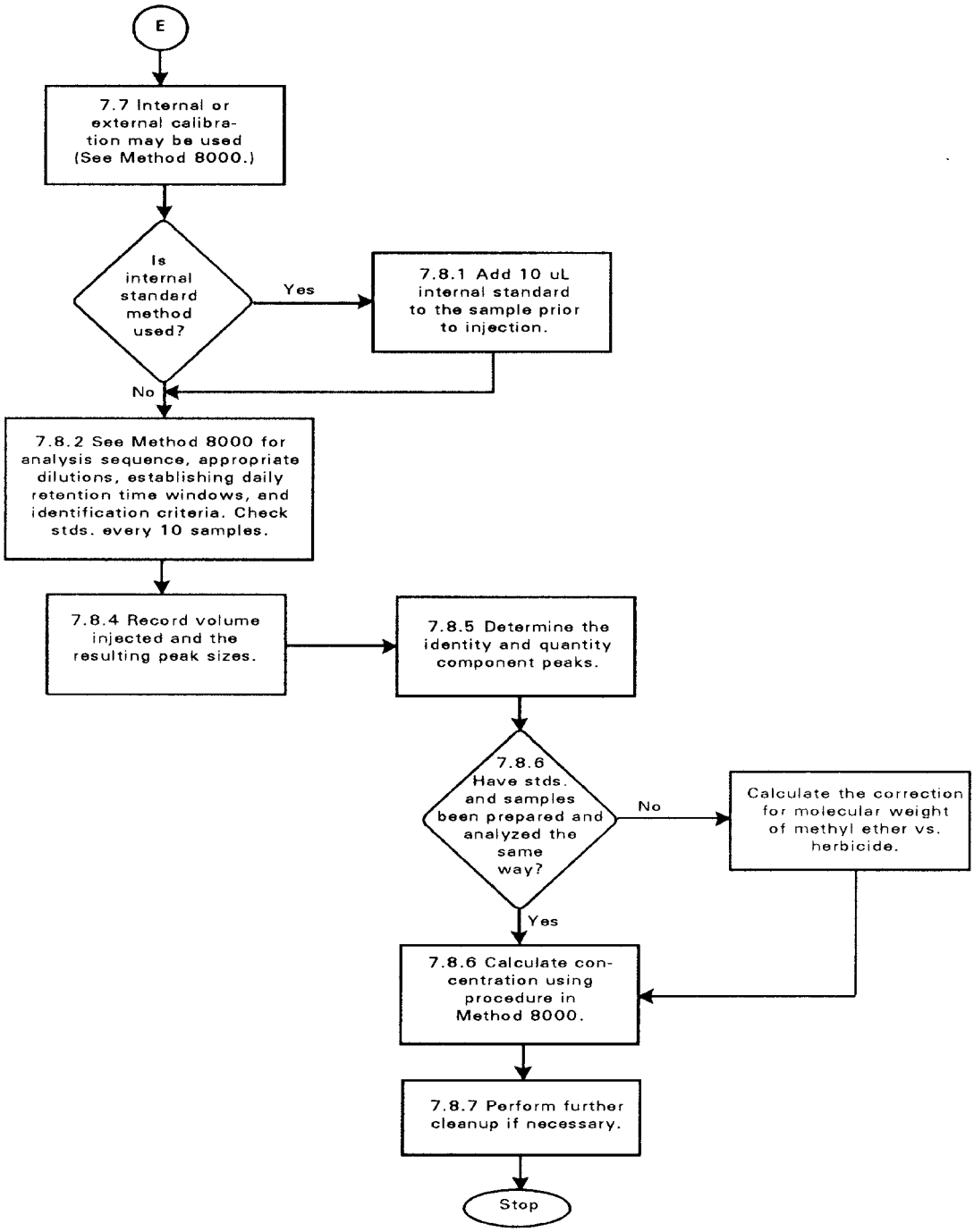
Extraction/Hydrolysis of Aqueous Samples and Extract Concentration



Extract Derivatization



Analysis by Gas Chromatography



METHOD 8260B
VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/
MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

		Appropriate Preparation Technique[a]					
Compound	CAS No.[b]	5030/ 5035	5031	5032	5021	5041	Direct Inject.
Acetone	67-64-1	pp	c	c	nd	c	c
Acetonitrile	75-05-8	pp	c	nd	nd	nd	c
Acrolein (Propenal)	107-02-8	pp	c	c	nd	nd	c
Acrylonitrile	107-13-1	pp	c	c	nd	c	c
Allyl alcohol	107-18-6	ht	c	nd	nd	nd	c
Allyl chloride	107-05-1	c	nd	nd	nd	nd	c
Benzene	71-43-2	c	nd	c	c	c	c
Benzyl chloride	100-44-7	c	nd	nd	nd	nd	c
Bis(2-chloroethyl)sulfide	505-60-2	pp	nd	nd	nd	nd	c
Bromoacetone	598-31-2	pp	nd	nd	nd	nd	c
Bromochloromethane	74-97-5	c	nd	c	c	c	c
Bromodichloromethane	75-27-4	c	nd	c	c	c	c
4-Bromofluorobenzene (surr)	460-00-4	c	nd	c	c	c	c
Bromoform	75-25-2	c	nd	c	c	c	c
Bromomethane	74-83-9	c	nd	c	c	c	c
n-Butanol	71-36-3	ht	c	nd	nd	nd	c
2-Butanone (MEK)	78-93-3	pp	c	c	nd	nd	c
t-Butyl alcohol	75-65-0	pp	c	nd	nd	nd	c
Carbon disulfide	75-15-0	pp	nd	c	nd	c	c
Carbon tetrachloride	56-23-5	c	nd	c	c	c	c
Chloral hydrate	302-17-0	pp	nd	nd	nd	nd	c
Chlorobenzene	108-90-7	c	nd	c	c	c	c
Chlorobenzene-d_5 (IS)		c	nd	c	c	c	c
Chlorodibromomethane	124-48-1	c	nd	c	nd	c	c
Chloroethane	75-00-3	c	nd	c	c	c	c
2-Chloroethanol	107-07-3	pp	nd	nd	nd	nd	c
2-Chloroethyl vinyl ether	110-75-8	c	nd	c	nd	nd	c
Chloroform	67-66-3	c	nd	c	c	c	c
Chloromethane	74-87-3	c	nd	c	c	c	c
Chloroprene	126-99-8	c	nd	nd	nd	nd	c
3-Chloropropionitrile	542-76-7	l	nd	nd	nd	nd	pc

(continued)

Compound	CAS No.[b]	Appropriate Preparation Technique[a] 5030/ 5035	5031	5032	5021	5041	Direct Inject.
Crotonaldehyde	4170-30-3	pp	c	nd	nd	nd	c
1,2-Dibromo-3-chloropropane	96-12-8	pp	nd	nd	c	nd	c
1,2-Dibromoethane	106-93-4	c	nd	nd	c	nd	c
Dibromomethane	74-95-3	c	nd	c	c	c	c
1,2-Dichlorobenzene	95-50-1	c	nd	nd	c	nd	c
1,3-Dichlorobenzene	541-73-1	c	nd	nd	c	nd	c
1,4-Dichlorobenzene	106-46-7	c	nd	nd	c	nd	c
1,4-Dichlorobenzene-d_4 (IS)		c	nd	nd	c	nd	c
cis-1,4-Dichloro-2-butene	1476-11-5	c	nd	c	nd	nd	c
trans-1,4-Dichloro-2-butene	110-57-6	pp	nd	c	nd	nd	c
Dichlorodifluoromethane	75-71-8	c	nd	c	c	nd	c
1,1-Dichloroethane	75-34-3	c	nd	c	c	c	c
1,2-Dichloroethane	107-06-2	c	nd	c	c	c	c
1,2-Dichloroethane-d_4 (surr)		c	nd	c	c	c	c
1,1-Dichloroethene	75-35-4	c	nd	c	c	c	c
trans-1,2-Dichloroethene	156-60-5	c	nd	c	c	c	c
1,2-Dichloropropane	78-87-5	c	nd	c	c	c	c
1,3-Dichloro-2-propanol	96-23-1	pp	nd	nd	nd	nd	c
cis-1,3-Dichloropropene	10061-01-5	c	nd	c	nd	c	c
trans-1,3-Dichloropropene	10061-02-6	c	nd	c	nd	c	c
1,2,3,4-Diepoxybutane	1464-53-5	c	nd	nd	nd	nd	c
Diethyl ether	60-29-7	c	nd	nd	nd	nd	c
1,4-Difluorobenzene (IS)	540-36-3	nd	nd	nd	nd	c	nd
1,4-Dioxane	123-91-1	pp	c	c	nd	nd	c
Epichlorohydrin	106-89-8	l	nd	nd	nd	nd	c
Ethanol	64-17-5	l	c	c	nd	nd	c
Ethyl acetate	141-78-6	l	c	nd	nd	nd	c
Ethylbenzene	100-41-4	c	nd	c	c	c	c
Ethylene oxide	75-21-8	pp	c	nd	nd	nd	c
Ethyl methacrylate	97-63-2	c	nd	c	nd	nd	c
Fluorobenzene (IS)	462-06-6	c	nd	nd	nd	nd	nd
Hexachlorobutadiene	87-68-3	c	nd	nd	c	nd	c
Hexachloroethane	67-72-1	l	nd	nd	nd	nd	c
2-Hexanone	591-78-6	pp	nd	c	nd	nd	c
2-Hydroxypropionitrile	78-97-7	l	nd	nd	nd	nd	pc
Iodomethane	74-88-4	c	nd	c	nd	c	c
Isobutyl alcohol	78-83-1	pp	c	nd	nd	nd	c
Isopropylbenzene	98-82-8	c	nd	nd	c	nd	c
Malononitrile	109-77-3	pp	nd	nd	nd	nd	c
Methacrylonitrile	126-98-7	pp	l	nd	nd	nd	c
Methanol	67-56-1	l	c	nd	nd	nd	c
Methylene chloride	75-09-2	c	nd	c	c	c	c
Methyl methacrylate	80-62-6	c	nd	nd	nd	nd	c
4-Methyl-2-pentanone (MIBK)	108-10-1	pp	c	c	nd	nd	c
Naphthalene	91-20-3	c	nd	nd	c	nd	c

(continued)

Compound	CAS No.[b]	Appropriate Preparation Technique[a] 5030/ 5035	5031	5032	5021	5041	Direct Inject.
Nitrobenzene	98-95-3	c	nd	nd	nd	nd	c
2-Nitropropane	79-46-9	c	nd	nd	nd	nd	c
N-Nitroso-di-n-butylamine	924-16-3	pp	c	nd	nd	nd	c
Paraldehyde	123-63-7	pp	c	nd	nd	nd	c
Pentachloroethane	76-01-7	l	nd	nd	nd	nd	c
2-Pentanone	107-87-9	pp	c	nd	nd	nd	c
2-Picoline	109-06-8	pp	c	nd	nd	nd	c
1-Propanol	71-23-8	pp	c	nd	nd	nd	c
2-Propanol	67-63-0	pp	c	nd	nd	nd	c
Propargyl alcohol	107-19-7	pp	l	nd	nd	nd	c
β-Propiolactone	57-57-8	pp	nd	nd	nd	nd	c
Propionitrile (ethyl cyanide)	107-12-0	ht	c	nd	nd	nd	pc
n-Propylamine	107-10-8	c	nd	nd	nd	nd	c
Pyridine	110-86-1	l	c	nd	nd	nd	c
Styrene	100-42-5	c	nd	c	c	c	c
1,1,1,2-Tetrachloroethane	630-20-6	c	nd	nd	c	c	c
1,1,2,2-Tetrachloroethane	79-34-5	c	nd	c	c	c	c
Tetrachloroethene	127-18-4	c	nd	c	c	c	c
Toluene	108-88-3	c	nd	c	c	c	c
Toluene-d_8 (surr)	2037-26-5	c	nd	c	c	c	c
o-Toluidine	95-53-4	pp	c	nd	nd	nd	c
1,2,4-Trichlorobenzene	120-82-1	c	nd	nd	c	nd	c
1,1,1-Trichloroethane	71-55-6	c	nd	c	c	c	c
1,1,2-Trichloroethane	79-00-5	c	nd	c	c	c	c
Trichloroethene	79-01-6	c	nd	c	c	c	c
Trichlorofluoromethane	75-69-4	c	nd	c	c	c	c
1,2,3-Trichloropropane	96-18-4	c	nd	c	c	c	c
Vinyl acetate	108-05-4	c	nd	c	nd	nd	c
Vinyl chloride	75-01-4	c	nd	c	c	c	c
o-Xylene	95-47-6	c	nd	c	c	c	c
m-Xylene	108-38-3	c	nd	c	c	c	c
p-Xylene	106-42-3	c	nd	c	c	c	c

[a] See Sec. 1.2 for other appropriate sample preparation techniques
[b] Chemical Abstract Service Registry Number

c = Adequate response by this technique
ht = Method analyte only when purged at 80°C
nd = Not determined
l = Inappropriate technique for this analyte
pc = Poor chromatographic behavior
pp = Poor purging efficiency resulting in high Estimated Quantitation Limits
surr = Surrogate
IS = Internal Standard

1.2 There are various techniques by which these compounds may be introduced into the GC/MS system. The more common techniques are listed in the table above. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035 (solid and waste oil samples), is the most commonly used technique for volatile organic analytes. However, other techniques are also appropriate and necessary for some analytes. These include direct injection following dilution with hexadecane (Method 3585) for waste oil samples; automated static headspace by Method 5021 for solid samples; direct injection of an aqueous sample (concentration permitting) or injection of a sample concentrated by azeotropic distillation (Method 5031); and closed system vacuum distillation (Method 5032) for aqueous, solid, oil and tissue samples. For air samples, Method 5041 provides methodology for desorbing volatile organics from trapping media (Methods 0010, 0030, and 0031). In addition, direct analysis utilizing a sample loop is used for sub-sampling from Tedlar® bags (Method 0040). Method 5000 provides more general information on the selection of the appropriate introduction method.

1.3 Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200°C. Volatile, water soluble compounds can be included in this analytical technique by the use of azeotropic distillation or closed-system vacuum distillation. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for analytes and retention times that have been evaluated on a purge-and-trap GC/MS system. Also, the method detection limits for 25-mL sample volumes are presented. The following compounds are also amenable to analysis by Method 8260:

Bromobenzene
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Chloroacetonitrile
1-Chlorobutane
1-Chlorohexane
2-Chlorotoluene
4-Chlorotoluene
Dibromofluoromethane
cis-1,2-Dichloroethene
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
p-Isopropyltoluene
Methyl acrylate
Methyl-t-butyl ether
Pentafluorobenzene
n-Propylbenzene
1,2,3-Trichlorobenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene

1.4 The estimated quantitation limit (EQL) of Method 8260 for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrapole instrumentation and the purge-and-trap technique, limits should be approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 3). Somewhat lower limits may be achieved using an ion trap mass spectrometer or other instrumentation of improved design. No matter which instrument is used, EQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by other methods (see Sec. 1.2). The analytes are introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a narrow-bore capillary for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

2.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.3 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted. If reporting values without correcting for the blank results in what the laboratory feels is a false positive result for a sample, the laboratory should fully explained this in text accompanying the uncorrected data.

3.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

3.3 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the entire purge-and-trap device may require dismantling and cleaning. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique (Method 5021) or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.4 Many analytes exhibit low purging efficiencies from a 25-mL sample. This often results in significant amounts of these analytes remaining in the sample purge vessel after analysis. After removal of the sample aliquot that was purged, and rinsing the purge vessel three times with organic-free water, the empty vessel should be subjected to a heated purge cycle prior to the analysis of another sample in the same purge vessel. This will reduce sample-to-sample carryover.

3.5 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean, since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

3.6 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling, handling, and storage protocols can serve as a check on such contamination.

3.7 Use of sensitive mass spectrometers to achieve lower detection level will increase the potential to detect laboratory contaminants as interferences.

3.8 Direct injection - Some contamination may be eliminated by baking out the column between analyses. Changing the injector liner will reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination. The use of direct injection will result in the need for more frequent instrument maintenance.

3.9 If hexadecane is added to waste samples or petroleum samples that are analyzed, some chromatographic peaks will elute after the target analytes. The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are volatilized.

4.0 APPARATUS AND MATERIALS

4.1 Purge-and-trap device for aqueous samples - Described in Method 5030.

4.2 Purge-and-trap device for solid samples - Described in Method 5035.

4.3 Automated static headspace device for solid samples - Described in Method 5021.

4.4 Azeotropic distillation apparatus for aqueous and solid samples - Described in Method 5031.

4.5 Vacuum distillation apparatus for aqueous, solid and tissue samples - Described in Method 5032.

4.6 Desorption device for air trapping media for air samples - Described in Method 5041.

4.7 Air sampling loop for sampling from Tedlar® bags for air samples - Described in Method 0040.

4.8 Injection port liners (HP Catalog #18740-80200, or equivalent) - modified for direct injection analysis by placing a 1-cm plug of glass wool approximately 50-60 mm down the length of the injection port towards the oven (see illustration below). A 0.53-mm ID column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

4.9 Gas chromatography/mass spectrometer/data system

4.9.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases.

4.9.1.1 The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation.

4.9.1.2 For some column configurations, the column oven must be cooled to less than 30°C, therefore, a subambient oven controller may be necessary.

4.9.1.3 The capillary column is either directly coupled to the source or interfaced through a jet separator, depending on the size of the capillary and the requirements of the GC/MS system.

4.9.1.4 Capillary pre-column interface - This device is the interface between the sample introduction device and the capillary gas chromatograph, and is necessary when using cryogenic cooling. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused-silica capillary pre-column. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.9.1.5 During the cryofocussing step, the temperature of the fused-silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

4.9.2 Gas chromatographic columns

4.9.2.1 Column 1 - 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco), 1.5-µm film thickness, or equivalent.

4.9.2.2 Column 2 - 30 - 75 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific), Rt_x-502.2 (RESTEK), or VOCOL (Supelco), 3-µm film thickness, or equivalent.

4.9.2.3 Column 3 - 30 m x 0.25 - 0.32 mm ID capillary column coated with 95% dimethyl - 5% diphenyl polysiloxane (DB-5, Rt_x-5, SPB-5, or equivalent), 1-µm film thickness.

4.9.2.4 Column 4 - 60 m x 0.32 mm ID capillary column coated with DB-624 (J&W Scientific), 1.8-µm film thickness, or equivalent.

4.9.3 Mass spectrometer - Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-Bromofluorobenzene (BFB) which meets all of the criteria in Table 4 when 5-50 ng of the GC/MS tuning standard (BFB) are injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. Because ion-molecule reactions with water and methanol in an ion trap mass spectrometer may produce interferences that coelute with chloromethane and chloroethane, the base peak for both of these analytes will be at m/z 49. This ion should be used as the quantitation ion in this case. The mass spectrometer must be capable of producing a mass spectrum for BFB which meets all of the criteria in Table 3 when 5 or 50 ng are introduced.

4.9.4 GC/MS interface - Two alternatives may be used to interface the GC to the mass spectrometer.

4.9.4.1 Direct coupling, by inserting the column into the mass spectrometer, is generally used for 0.25 - 0.32 mm ID columns.

4.9.4.2 A jet separator, including an all-glass transfer line and glass enrichment device or split interface, is used with a 0.53 mm column.

4.9.4.3 Any enrichment device or transfer line may be used, if all of the performance specifications described in Sec. 8.0 (including acceptable calibration at 50 ng or less) can be achieved. GC/MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.9.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.10 Microsyringes - 10-, 25-, 100-, 250-, 500-, and 1,000-µL.

4.11 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.12 Syringes - 5-, 10-, or 25-mL, gas-tight with shutoff valve.

4.13 Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.

4.14 Glass scintillation vials - 20-mL, with PTFE-lined screw-caps or glass culture tubes with PTFE-lined screw-caps.

4.15 Vials - 2-mL, for GC autosampler.

4.16 Disposable pipets - Pasteur.

4.17 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

4.18 Spatula - Stainless steel.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.4 Reagent Hexadecane - Reagent hexadecane is defined as hexadecane in which interference is not observed at the method detection limit of compounds of interest. Hexadecane quality is demonstrated through the analysis of a solvent blank injected directly into the GC/MS. The results of such a blank analysis must demonstrate that all interfering volatiles have been removed from the hexadecane.

5.5 Polyethylene glycol, $H(OCH_2CH_2)_nOH$ - Free of interferences at the detection limit of the target analytes.

5.6 Hydrochloric acid (1:1 v/v), HCl - Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

5.7 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to

5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store, with minimal headspace and protected from light, at -10°C or less or as recommended by the standard manufacturer. Standards should be returned to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

5.7.5 Frequency of Standard Preparation

5.7.5.1 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

5.7.5.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

5.7.6 Preparation of Calibration Standards From a Gas Mixture

An optional calibration procedure involves using a certified gaseous mixture daily, utilizing a commercially-available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichloro-difluoromethane and trichlorofluoromethane in nitrogen. Mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.7.6.1 Before removing the cylinder shipping cap, be sure the valve is completely closed (turn clockwise). The contents are under pressure and should be used in a well-ventilated area.

5.7.6.2 Wrap the pipe thread end of the Luer fitting with PTFE tape. Remove the shipping cap from the cylinder and replace it with the Luer fitting.

5.7.6.3 Transfer half the working standard containing other analytes, internal standards, and surrogates to the purge apparatus.

5.7.6.4 Purge the Luer fitting and stem on the gas cylinder prior to sample removal using the following sequence:

a) Connect either the 100-µL or 500-µL Luer syringe to the inlet fitting of the cylinder.

b) Make sure the on/off valve on the syringe is in the open position.

c) Slowly open the valve on the cylinder and withdraw a full syringe volume.

d) Be sure to close the valve on the cylinder before you withdraw the syringe from the Luer fitting.

e) Expel the gas from the syringe into a well-ventilated area.

f) Repeat steps a through e one more time to fully purge the fitting.

5.7.6.5 Once the fitting and stem have been purged, quickly withdraw the volume of gas you require using steps 5.6.6.1.4(a) through (d). Be sure to close the valve on the cylinder and syringe before you withdraw the syringe from the Luer fitting.

5.7.6.6 Open the syringe on/off valve for 5 seconds to reduce the syringe pressure to atmospheric pressure. The pressure in the cylinder is ~30 psi.

5.7.6.7 The gas mixture should be quickly transferred into the reagent water through the female Luer fitting located above the purging vessel.

NOTE: Make sure the arrow on the 4-way valve is pointing toward the female Luer fitting when transferring the sample from the syringe. Be sure to switch the 4-way valve back to the closed position before removing the syringe from the Luer fitting.

5.7.6.8 Transfer the remaining half of the working standard into the purging vessel. This procedure insures that the total volume of gas mix is flushed into the purging vessel, with none remaining in the valve or lines.

5.7.6.9 The concentration of each compound in the cylinder is typically 0.0025 µg/µL.

5.7.6.10 The following are the recommended gas volumes spiked into 5 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
40 µL	20 µg/L
100 µL	50 µg/L
200 µL	100 µg/L
300 µL	150 µg/L
400 µL	200 µg/L

5.7.6.11 The following are the recommended gas volumes spiked into 25 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
10 µL	1 µg/L
20 µL	2 µg/L
50 µL	5 µg/L
100 µL	10 µg/L
250 µL	25 µg/L

5.8 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace. Replace after one week. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Sec. 5.7.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

5.9 Surrogate standards - The recommended surrogates are toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described above, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 µg/10 mL, in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute surrogate solutions may be required.

5.10 Internal standards - The recommended internal standards are fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Secs. 5.7 and 5.8. It is recommended that the secondary dilution standard be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute internal standard solutions may be required. Area counts of the internal standard peaks should be between 50-200% of the areas of the target analytes in the mid-point calibration analysis.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/µL of BFB in methanol should be prepared. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then a more dilute BFB standard solution may be required.

5.12 Calibration standards -There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.12.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

5.12.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 7.4 for guidance on calibration verification.

5.12.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.12.4 The calibration standards must also contain the internal standards chosen for the analysis.

5.13 Matrix spiking and laboratory control sample (LCS) standards - Matrix spiking standards should be prepared from volatile organic compounds which are representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The matrix spiking solution should contain compounds that are expected to be found in the types of samples to be analyzed.

5.13.1 Some permits may require the spiking of specific compounds of interest, especially if polar compounds are a concern, since the spiking compounds listed above would not be representative of such compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.13.2 The spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

5.13.3 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C or less, in amber bottles with PTFE-lined screw-caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Various alternative methods are provided for sample introduction. All internal standards, surrogates, and matrix spiking compounds (when applicable) must be added to the samples before introduction into the GC/MS system. Consult the sample introduction method for the procedures by which to add such standards.

7.1.1 Direct injection - This includes: injection of an aqueous sample containing a very high concentration of analytes; injection of aqueous concentrates from Method 5031 (azeotropic distillation); and injection of a waste oil diluted 1:1 with hexadecane (Method 3585). Direct injection of aqueous samples (non-concentrated) has very limited applications. It is only used for the determination of volatiles at the toxicity characteristic (TC) regulatory limits or at concentrations in excess of 10,000 µg/L. It may also be used in conjunction with the test for ignitability in aqueous samples (along with Methods 1010 and 1020), to determine if alcohol is present at greater than 24%.

7.1.2 Purge-and-trap - This includes purge-and-trap for aqueous samples (Method 5030) and purge-and-trap for solid samples (Method 5035). Method 5035 also provides techniques for extraction of high concentration solid and oily waste samples by methanol (and other water-miscible solvents) with subsequent purge-and-trap from an aqueous matrix using Method 5030.

7.1.2.1 Traditionally, the purge-and-trap of aqueous samples is performed at ambient temperature, while purging of soil/solid samples is performed at 40°C, to improve purging efficiency.

7.1.2.2 Aqueous and soil/solid samples may also be purged at temperatures above those being recommended as long as all calibration standards, samples, and QC samples are purged at the same temperature, appropriate trapping material is used to handle the excess water, and the laboratory demonstrates acceptable method performance for the project. Purging of aqueous samples at elevated temperatures (e.g., 40°C) may improve the purging performance of many of the water soluble compounds which have poor purging efficiencies at ambient temperatures.

7.1.3 Vacuum distillation - this technique may be used for the introduction of volatile organics from aqueous, solid, or tissue samples (Method 5032) into the GC/MS system.

7.1.4 Automated static headspace - this technique may be used for the introduction of volatile organics from solid samples (Method 5021) into the GC/MS system.

7.1.5 Cartridge desorption - this technique may be for the introduction of volatile organics from sorbent cartridges (Method 5041) used in the sampling of air. The sorbent cartridges are from the volatile organics sampling train (VOST) or SMVOC (Method 0031).

7.2 Recommended chromatographic conditions

7.2.1 General conditions

Injector temperature:	200 - 225°C
Transfer line temperature:	250 - 300°C

7.2.2 Column 1 and Column 2 with cryogenic cooling (example chromatograms are presented in Figures 1 and 2)

Carrier gas (He) flow rate:	15 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 70°C, then 15°C/min to 145°C
Final temperature:	145°C, hold until all expected compounds have eluted.

7.2.5 Direct injection - Column 2

Carrier gas (He) flow rate:	4 mL/min
Column:	J&W DB-624, 70m x 0.53 mm
Initial temperature:	40°C, hold for 3 minutes
Temperature program:	8°C/min
Final temperature:	260°C, hold until all expected compounds have eluted.
Column Bake out:	75 minutes
Injector temperature:	200-225°C
Transfer line temperature:	250-300°C

7.2.6 Direct split interface - Column 4

Carrier gas (He) flow rate:	1.5 mL/min
Initial temperature:	35°C, hold for 2 minutes
Temperature program:	4°C/min to 50°C 10°C/min to 220°C
Final temperature:	220°C, hold until all expected compounds have eluted
Split ratio:	100:1
Injector temperature:	125°C

7.3 Initial calibration

Establish the GC/MS operating conditions, using the following as guidance:

Mass range:	35 - 260 amu
Scan time:	0.6 - 2 sec/scan
Source temperature:	According to manufacturer's specifications
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 5-50 ng injection or purging of 4-bromofluorobenzene (2-µL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, the following approach has been shown to be useful: The mass spectrum of BFB may be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of

BFB. Do not background subtract part of the BFB peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

7.3.1.2 Use the BFB mass intensity criteria in Table 4 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g., CLP, Method 524.2, or manufacturer's instructions), provided that method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

7.3.2 Set up the sample introduction system as outlined in the method of choice (see Sec. 7.1). A different calibration curve is necessary for each method because of the differences in conditions and equipment. A set of at least five different calibration standards is necessary (see Sec. 5.12 and Method 8000). Calibration must be performed using the sample introduction technique that will be used for samples. For Method 5030, the purging efficiency for 5 mL of water is greater than for 25 mL. Therefore, develop the standard curve with whichever volume of sample that will be analyzed.

7.3.2.1 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 µL of internal standard. Then transfer the contents to the appropriate device or syringe. Some of the introduction methods may have specific guidance on the volume of calibration standard and the way the standards are transferred to the device.

7.3.2.2 The internal standards selected in Sec. 5.10 should permit most of the components of interest in a chromatogram to have retention times of 0.80 - 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion.

7.3.2.3 To prepare a calibration standard for direct injection analysis of waste oil, dilute standards in hexadecane.

7.3.3 Proceed with the analysis of the calibration standards following the procedure in the introduction method of choice. For direct injection, inject 1 - 2 µL into the GC/MS system. The injection volume will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water.

7.3.4 Tabulate the area response of the characteristic ions (see Table 5) against the concentration for each target analyte and each internal standard. Calculate response factors (RF) for each target analyte relative to one of the internal standards. The internal standard selected for the calculation of the RF for a target analyte should be the internal standard that has a retention time closest to the analyte being measured (Sec. 7.6.2).

The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate.
C_{is} = Concentration of the internal standard.

7.3.5 System performance check compounds (SPCCs) - Calculate the mean RF for each target analyte using the five RF values calculated from the initial (5-point) calibration curve. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; chlorobenzene; and 1,1,2,2-tetrachloroethane. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Example problems include:

7.3.5.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.3.5.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

7.3.5.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.3.5.4 The minimum mean response factors for the volatile SPCCs are as follows:

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

7.3.6 Calibration check compounds (CCCs)

7.3.6.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Sec. 7.0 of Method 8000.

7.3.6.2 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration, as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RF_i = RF for each of the calibration standards
$\overline{RF}$ = mean RF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5

7.3.6.3 The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000. The CCCs are:

1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene
1,2-Dichloropropane	Vinyl chloride

7.3.6.4 If an RSD of greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

7.3.7 Evaluation of retention times - The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.8 Linearity of target analytes

7.3.8.1 If the RSD of any target analyte is 15% or less, then the response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation (Sec. 7.7.2).

7.3.8.2 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 of Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

NOTE: Method 8000 specifies a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.8.3 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

NOTE: The 20% RSD criteria in Method 8000 pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject or introduce 5-50 ng of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration curve (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000 for method blank performance criteria.

7.4.4 System Performance Check Compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Sec. 7.3.5.4). This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.4.5 Calibration Check Compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Sec. 7.3.6 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater

than 20% difference or drift), for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new five-point initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. Some of the screening options available utilizing SW-846 methods are automated headspace-GC/FID (Methods 5021/8015), automated headspace-GC/PID/ELCD (Methods 5021/8021), or waste dilution-GC/PID/ELCD (Methods 3585/8021) using the same type of capillary column. When used only for screening purposes, the quality control requirements in the methods above may be reduced as appropriate. Sample screening is particularly important when Method 8260 is used to achieve low detection levels.

7.5.2 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

7.5.3 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the introduction device as outlined in the method of choice.

7.5.4 The process of taking an aliquot destroys the validity of remaining volume of an aqueous sample for future analysis. Therefore, if only one VOA vial is provided to the laboratory, the analyst should prepare two aliquots for analysis at this time, to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, one 20-mL syringe could be used to hold two 5-mL aliquots. If the second aliquot is to be taken from the syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.5.5 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If lower detection limits are required, use a 25-mL syringe, and adjust the final volume to 25.0 mL.

7.5.6 The following procedure may be used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays, until the diluted sample is in a gas-tight syringe.

7.5.6.1 Dilutions may be made in volumetric flasks (10- to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilution steps may be necessary for extremely large dilutions.

7.5.6.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask, and add slightly less than this quantity of organic-free reagent water to the flask.

7.5.6.3 Inject the appropriate volume of the original sample from the syringe into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.5.6.4 Fill a 5-mL syringe with the diluted sample, as described in Sec. 7.5.5.

7.5.7 Compositing aqueous samples prior to GC/MS analysis

7.5.7.1 Add 5 mL of each sample (up to 5 samples are allowed) to a 25-mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe. Larger volumes of a smaller number of samples may be used, provided that equal volumes of each sample are composited.

7.5.7.2 The samples must be cooled to 4°C or less during this step to minimize volatilization losses. Sample vials may be placed in a tray of ice during the processing.

7.5.7.3 Mix each vial well and draw out a 5-mL aliquot with the 25-mL syringe.

7.5.7.4 Once all the aliquots have been combined on the syringe, invert the syringe several times to mix the aliquots. Introduce the composited sample into the instrument, using the method of choice (see Sec. 7.1).

7.5.7.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used, unless a 25-mL sample is to be purged.

7.5.8 Add 10 µL of the surrogate spiking solution and 10 µL of the internal standard spiking solution to each sample either manually or by autosampler. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of aqueous sample will yield a concentration of 50 µg/L of each surrogate standard. The addition of 10 µL of the surrogate spiking solution to 5 g of a non-aqueous sample will yield a concentration of 50 µg/kg of each standard.

If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute surrogate and internal standard solutions may be required.

7.5.9 Add 10 µL of the matrix spike solution (Sec. 5.13) to a 5-mL aliquot of the sample chosen for spiking. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.5.9.1 Follow the same procedure in preparing the laboratory control sample (LCS), except the spike is added to a clean matrix. See Sec. 8.4 and Method 5000 for more guidance on the selection and preparation of the matrix spike and the LCS.

7.5.9.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking and LCS solutions may be required.

7.5.10 Analyze the sample following the procedure in the introduction method of choice.

7.5.10.1 For direct injection, inject 1 to 2 µL into the GC/MS system. The volume limitation will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water (if an aqueous sample is being analyzed).

7.5.10.2 The concentration of the internal standards, surrogates, and matrix spiking standards (if any) added to the injection aliquot must be adjusted to provide the same concentration in the 1-2 µL injection as would be introduced into the GC/MS by purging a 5-mL aliquot.

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.11 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.

7.5.11.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of an organic-free reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

7.5.11.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.5.12 The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.6 Qualitative analysis

7.6.1 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library

searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

(1) Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

7.7.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (7.3.6). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8260:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the SPCC criteria described in Sec. 7.4.4 and the CCC criteria in Sec. 7.4.5, each 12 hours.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested using purge-and-trap (Method 5030) in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 µg/L. Single laboratory accuracy and precision data are presented for the method analytes in Table 6. Calculated MDLs are presented in Table 1.

9.3 The method was tested using purge-and-trap (Method 5030) with water spiked at 0.1 to 0.5 µg/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 7. MDL values were also calculated from these data and are presented in Table 2.

9.4 Direct injection (Method 3585) has been used for the analysis of waste motor oil samples using a wide-bore column. Single laboratory precision and accuracy data are presented in Tables 10 and 11 for TCLP volatiles in oil. The performance data were developed by spiking and analyzing seven replicates each of new and used oil. The oils were spiked at the TCLP regulatory concentrations for most analytes, except for the alcohols, ketones, ethyl acetate and chlorobenzene which are spiked at 5 ppm, well below the regulatory concentrations. Prior to spiking, the new oil (an SAE 30-weight motor oil) was heated at 80°C overnight to remove volatiles. The used oil (a mixture of used oil drained from passenger automobiles) was not heated and was contaminated with 20 - 300 ppm of BTEX compounds and isobutanol. These contaminants contributed to the extremely high recoveries of the BTEX compounds in the used oil. Therefore, the data from the deuterated analogs of these analytes represent more typical recovery values.

9.5 Single laboratory accuracy and precision data were obtained for the Method 5035 analytes in three soil matrices: sand; a soil collected 10 feet below the surface of a hazardous landfill, called C-Horizon; and a surface garden soil. Sample preparation was by Method 5035. Each

sample was fortified with the analytes at a concentration of 4 µg/kg. These data are listed in Tables 17, 18, and 19. All data were calculated using fluorobenzene as the internal standard added to the soil sample prior to extraction. This causes some of the results to be greater than 100% recovery because the precision of results is sometimes as great as 28%.

9.5.1 In general, the recoveries of the analytes from the sand matrix are the highest, the C-Horizon soil results are somewhat less, and the surface garden soil recoveries are the lowest. This is due to the greater adsorptive capacity of the garden soil. This illustrates the necessity of analyzing matrix spike samples to assess the degree of matrix effects.

9.5.2 The recoveries of some of the gases, or very volatile compounds, such as vinyl chloride, trichlorofluoromethane, and 1,1-dichloroethene, are somewhat greater than 100%. This is due to the difficulty encountered in fortifying the soil with these compounds, allowing an equilibration period, then extracting them with a high degree of precision. Also, the garden soil results in Table 19 include some extraordinarily high recoveries for some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection, and to the fact that no background was subtracted.

9.6 Performance data for nonpurgeable volatiles using azeotropic distillation (Method 5031) are included in Tables 12 to 16.

9.7 Performance data for volatiles prepared using vacuum distillation (Method 5032) in soil, water, oil and fish tissue matrices are included in Tables 20 to 27.

9.8 Single laboratory accuracy and precision data were obtained for the Method 5021 analytes in two soil matrices: sand and a surface garden soil. Replicate samples were fortified with the analytes at concentrations of 10 µg/kg. These data are listed in Table 30. All data were calculated using the internal standards listed for each analyte in Table 28. The recommended internal standards were selected because they generated the best accuracy and precision data for the analyte in both types of soil.

9.8.1 If a detector other than an MS is used for analysis, consideration must be given to the choice of internal standards and surrogates. They must not coelute with any other analyte and must have similar properties to the analytes. The recoveries of the analytes are 50% or higher for each matrix studied. The recoveries of the gases or very volatile compounds are greater than 100% in some cases. Also, results include high recoveries of some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection.

9.8.2 The method detection limits using Method 5021 listed in Table 29 were calculated from results of seven replicate analyses of the sand matrix. Sand was chosen because it demonstrated the least degree of matrix effect of the soils studied. These MDLs were calculated utilizing the procedure described in Chapter One and are intended to be a general indication of the capabilities of the method.

9.9 The MDL concentrations listed in Table 31 were determined using Method 5041 in conjunction with Method 8260. They were obtained using cleaned blank VOST tubes and reagent water. Similar results have been achieved with field samples. The MDL actually achieved in a given analysis will vary depending upon instrument sensitivity and the effects of the matrix. Preliminary spiking studies indicate that under the test conditions, the MDLs for spiked compounds in extremely complex matrices may be larger by a factor of 500 - 1000.

9.10 The EQL of sample taken by Method 0040 and analyzed by Method 8260 is estimated to be in the range of 0.03 to 0.9 ppm (See Table 33). Matrix effects may cause the individual compound detection limits to be higher.

10.0 REFERENCES

1. Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water Method 524.2, U.S. Environmental Protection Agency, Office of Research Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1986.

2. Bellar, T.A., Lichtenberg, J.J, J. Amer. Water Works Assoc., 1974, 66(12), 739-744.

3. Bellar, T.A., Lichtenberg, J.J., "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds"; in Van Hall, Ed.; Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp 108-129, 1979.

4. Budde, W.L., Eichelberger, J.W., "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, April 1980; EPA-600/4-79-020.

5. Eichelberger, J.W., Harris, L.E., Budde, W.L., "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems"; Analytical Chemistry 1975, 47, 995-1000.

6. Olynyk, P., Budde, W.L., Eichelberger, J.W., "Method Detection Limit for Methods 624 and 625"; Unpublished report, October 1980.

7. Non Cryogenic Temperatures Program and Chromatogram, Private Communications; M. Stephenson and F. Allen, EPA Region IV Laboratory, Athens, GA.

8. Marsden, P.J., Helms, C.L., Colby, B.N., "Analysis of Volatiles in Waste Oil"; Report for B. Lesnik, OSW/EPA under EPA contract 68-W9-001, 6/92.

9. Methods for the Determination of Organic Compounds in Drinking Water, Supplement II Method 524.2; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, 1992.

10. Flores, P., Bellar, T., "Determination of Volatile Organic Compounds in Soils Using Equilibrium Headspace Analysis and Capillary Column Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, December, 1992.

11. Bruce, M.L., Lee, R.P., Stephens, M.W., "Concentration of Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation", Environmental Science and Technology 1992, 26, 160-163.

12. Cramer, P.H., Wilner, J., Stanley, J.S., "Final Report: Method for Polar, Water Soluble, Nonpurgeable Volatile Organics (VOCs)", For U.S. Environmental Protection Agency, Environmental Monitoring Support Laboratory, EPA Contract No. 68-C8-0041.

13. Hiatt, M.H., "Analysis of Fish and Sediment for Volatile Priority Pollutants", Analytical Chemistry 1981, 53, 1541.

14. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014A, January, 1986.

15. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry" U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November 1991.

TABLE 1

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON WIDE-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes)			MDL[d]
	Column 1[a]	Column 2[b]	Column 2'[c]	(µg/L)
Dichlorodifluoromethane	1.35	0.70	3.13	0.10
Chloromethane	1.49	0.73	3.40	0.13
Vinyl Chloride	1.56	0.79	3.93	0.17
Bromomethane	2.19	0.96	4.80	0.11
Chloroethane	2.21	1.02	--	0.10
Trichlorofluoromethane	2.42	1.19	6.20	0.08
Acrolein	3.19			
Iodomethane	3.56			
Acetonitrile	4.11			
Carbon disulfide	4.11			
Allyl chloride	4.11			
Methylene chloride	4.40	2.06	9.27	0.03
1,1-Dichloroethene	4.57	1.57	7.83	0.12
Acetone	4.57			
trans-1,2-Dichloroethene	4.57	2.36	9.90	0.06
Acrylonitrile	5.00			
1,1-Dichloroethane	6.14	2.93	10.80	0.04
Vinyl acetate	6.43			
2,2-Dichloropropane	8.10	3.80	11.87	0.35
2-Butanone	--			
cis-1,2-Dichloroethene	8.25	3.90	11.93	0.12
Propionitrile	8.51			
Chloroform	9.01	4.80	12.60	0.03
Bromochloromethane	--	4.38	12.37	0.04
Methacrylonitrile	9.19			
1,1,1-Trichloroethane	10.18	4.84	12.83	0.08
Carbon tetrachloride	11.02	5.26	13.17	0.21
1,1-Dichloropropene	--	5.29	13.10	0.10
Benzene	11.50	5.67	13.50	0.04
1,2-Dichloroethane	12.09	5.83	13.63	0.06
Trichloroethene	14.03	7.27	14.80	0.19
1,2-Dichloropropane	14.51	7.66	15.20	0.04
Bromodichloromethane	15.39	8.49	15.80	0.08
Dibromomethane	15.43	7.93	5.43	0.24
Methyl methacrylate	15.50			
1,4-Dioxane	16.17			
2-Chloroethyl vinyl ether	--			
4-Methyl-2-pentanone	17.32			
trans-1,3-Dichloropropene	17.47	--	16.70	--
Toluene	18.29	10.00	17.40	0.11
cis-1,3-Dichloropropene	19.38	--	17.90	--

TABLE 1 (cont.)

Compound	Retention Time (minutes)			MDL[d]
	Column 1[a]	Column 2[b]	Column 2"[c]	(µg/L)
1,1,2-Trichloroethane	19.59	11.05	18.30	0.10
Ethyl methacrylate	20.01			
2-Hexanone	20.30			
Tetrachloroethene	20.26	11.15	18.60	0.14
1,3-Dichloropropane	20.51	11.31	18.70	0.04
Dibromochloromethane	21.19	11.85	19.20	0.05
1,2-Dibromoethane	21.52	11.83	19.40	0.06
1-Chlorohexane	--	13.29	--	0.05
Chlorobenzene	23.17	13.01	20.67	0.04
1,1,1,2-Tetrachloroethane	23.36	13.33	20.87	0.05
Ethylbenzene	23.38	13.39	21.00	0.06
p-Xylene	23.54	13.69	21.30	0.13
m-Xylene	23.54	13.68	21.37	0.05
o-Xylene	25.16	14.52	22.27	0.11
Styrene	25.30	14.60	22.40	0.04
Bromoform	26.23	14.88	22.77	0.12
Isopropylbenzene (Cumene)	26.37	15.46	23.30	0.15
cis-1,4-Dichloro-2-butene	27.12			
1,1,2,2-Tetrachloroethane	27.29	16.35	24.07	0.04
Bromobenzene	27.46	15.86	24.00	0.03
1,2,3-Trichloropropane	27.55	16.23	24.13	0.32
n-Propylbenzene	27.58	16.41	24.33	0.04
2-Chlorotoluene	28.19	16.42	24.53	0.04
trans-1,4-Dichloro-2-butene	28.26			
1,3,5-Trimethylbenzene	28.31	16.90	24.83	0.05
4-Chlorotoluene	28.33	16.72	24.77	0.06
Pentachloroethane	29.41			
1,2,4-Trimethylbenzene	29.47	17.70	31.50	0.13
sec-Butylbenzene	30.25	18.09	26.13	0.13
tert-Butylbenzene	30.59	17.57	26.60	0.14
p-Isopropyltoluene	30.59	18.52	26.50	0.12
1,3-Dichlorobenzene	30.56	18.14	26.37	0.12
1,4-Dichlorobenzene	31.22	18.39	26.60	0.03
Benzyl chloride	32.00			
n-Butylbenzene	32.23	19.49	27.32	0.11
1,2-Dichlorobenzene	32.31	19.17	27.43	0.03
1,2-Dibromo-3-chloropropane	35.30	21.08	--	0.26
1,2,4-Trichlorobenzene	38.19	23.08	31.50	0.04
Hexachlorobutadiene	38.57	23.68	32.07	0.11
Naphthalene	39.05	23.52	32.20	0.04
1,2,3-Trichlorobenzene	40.01	24.18	32.97	0.03

TABLE 1 (cont.)

Compound	Retention Time (minutes) Column 1[a]	Column 2[b]	Column 2"[c]	MDL[d] (µg/L)
INTERNAL STANDARDS/SURROGATES				
1,4-Difluorobenzene	13.26			
Chlorobenzene-d_5	23.10			
1,4-Dichlorobenzene-d_4	31.16			
4-Bromofluorobenzene	27.83	15.71	23.63	
1,2-Dichlorobenzene-d_4	32.30	19.08	27.25	
Dichloroethane-d_4	12.08			
Dibromofluoromethane	--			
Toluene-d_8	18.27			
Pentafluorobenzene	--			
Fluorobenzene	13.00	6.27	14.06	

[a] Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 8 minutes, then program to 180°C at 4°C/min.

[b] Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°C/min.

[c] Column 2" - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10 °C/min, program to 120°C at 5°C/min, then program to 180°C at 8°C/min.

[d] MDL based on a 25-mL sample volume.

TABLE 2

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON NARROW-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes) Column 3[a]	MDL[b] (µg/L)
Dichlorodifluoromethane	0.88	0.11
Chloromethane	0.97	0.05
Vinyl chloride	1.04	0.04
Bromomethane	1.29	0.03
1,1-Dichloroethane	4.03	0.03
cis-1,2-Dichloroethene	5.07	0.06
2,2-Dichloropropane	5.31	0.08
Chloroform	5.55	0.04
Bromochloromethane	5.63	0.09
1,1,1-Trichloroethane	6.76	0.04
1,2-Dichloroethane	7.00	0.02
1,1-Dichloropropene	7.16	0.12
Carbon tetrachloride	7.41	0.02
Benzene	7.41	0.03
1,2-Dichloropropane	8.94	0.02
Trichloroethene	9.02	0.02
Dibromomethane	9.09	0.01
Bromodichloromethane	9.34	0.03
Toluene	11.51	0.08
1,1,2-Trichloroethane	11.99	0.08
1,3-Dichloropropane	12.48	0.08
Dibromochloromethane	12.80	0.07
Tetrachloroethene	13.20	0.05
1,2-Dibromoethane	13.60	0.10
Chlorobenzene	14.33	0.03
1,1,1,2-Tetrachloroethane	14.73	0.07
Ethylbenzene	14.73	0.03
p-Xylene	15.30	0.06
m-Xylene	15.30	0.03
Bromoform	15.70	0.20
o-Xylene	15.78	0.06
Styrene	15.78	0.27
1,1,2,2-Tetrachloroethane	15.78	0.20
1,2,3-Trichloropropane	16.26	0.09
Isopropylbenzene	16.42	0.10
Bromobenzene	16.42	0.11
2-Chlorotoluene	16.74	0.08
n-Propylbenzene	16.82	0.10
4-Chlorotoluene	16.82	0.06

TABLE 2 (cont.)

Compound	Retention Time (minutes) Column 3[a]	MDL[b] (µg/L)
1,3,5-Trimethylbenzene	16.99	0.06
tert-Butylbenzene	17.31	0.33
1,2,4-Trimethylbenzene	17.31	0.09
sec-Butylbenzene	17.47	0.12
1,3-Dichlorobenzene	17.47	0.05
p-Isopropyltoluene	17.63	0.26
1,4-Dichlorobenzene	17.63	0.04
1,2-Dichlorobenzene	17.79	0.05
n-Butylbenzene	17.95	0.10
1,2-Dibromo-3-chloropropane	18.03	0.50
1,2,4-Trichlorobenzene	18.84	0.20
Naphthalene	19.07	0.10
Hexachlorobutadiene	19.24	0.10
1,2,3-Trichlorobenzene	19.24	0.14

[a] Column 3 - 30 meter x 0.32 mm ID DB-5 capillary with 1 µm film thickness.

[b] MDL based on a 25-mL sample volume.

TABLE 3

ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES[a]

Estimated Quantitation Limits		
5-mL Ground Water Purge (µg/L)	25-mL Ground water Purge (µg/L)	Low Soil/Sediment[b] µg/kg
5	1	5

[a] Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following footnote for further guidance on matrix-dependent EQLs.

[b] EQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

Other Matrices	Factor[c]
Water miscible liquid waste	50
High concentration soil and sludge	125
Non-water miscible waste	500

[c] EQL = [EQL for low soil sediment (Table 3)] x [Factor].

For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA[a]

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

[a] Alternate tuning criteria may be used, (e.g. CLP, Method 524.2, or manufacturers" instructions), provided that method performance is not adversely affected.

TABLE 5

CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANIC COMPOUNDS

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	58	43
Acetonitrile	41	40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl alcohol	57	58, 39
Allyl chloride	76	41, 39, 78
Benzene	78	-
Benzyl chloride	91	126, 65, 128
Bromoacetone	136	43, 138, 93, 95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64 (49*)	66 (51*)
2-Chloroethanol	49	44, 43, 51, 80
Bis(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50 (49*)	52 (51*)
Chloroprene	53	88, 90, 51
3-Chloropropionitrile	54	49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,2-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene-d_4	152	115, 150
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	58, 43, 57
Epichlorohydrin	57	49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	43, 42
Ethyl methacrylate	69	41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malononitrile	66	39, 65, 38
Methacrylonitrile	41	67, 39, 52, 66
Methyl acrylate	55	85
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	127, 141

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Methyl methacrylate	69	41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-
Nitrobenzene	123	51, 77
2-Nitropropane	46	-
2-Picoline	93	66, 92, 78
Pentachloroethane	167	130, 132, 165, 169
Propargyl alcohol	55	39, 38, 53
β-Propiolactone	42	43, 44
Propionitrile (ethyl cyanide)	54	52, 55, 40
n-Propylamine	59	41, 39
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
Internal Standards/Surrogates:		
Benzene-d_6	84	83
Bromobenzene-d_5	82	162
Bromochloromethane-d_2	51	131
1,4-Difluorobenzene	114	
Chlorobenzene-d_5	117	
1,4-Dichlorobenzene-d_4	152	115, 150
1,1,2-Trichloroethane-d_3	100	
4-Bromofluorobenzene	95	174, 176
Chloroform-d_1	84	
Dibromofluoromethane	113	

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Internal Standards/Surrogates		
Dichloroethane-d_4	102	
Toluene-d_8	98	
Pentafluorobenzene	168	
Fluorobenzene	96	77

* Characteristic ion for an ion trap mass spectrometer (to be used when ion-molecule reactions are observed).

TABLE 6

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A WIDE-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. Range (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Benzene	0.1 - 10	31	97	6.5	5.7
Bromobenzene	0.1 - 10	30	100	5.5	5.5
Bromochloromethane	0.5 - 10	24	90	5.7	6.4
Bromodichloromethane	0.1 - 10	30	95	5.7	6.1
Bromoform	0.5 - 10	18	101	6.4	6.3
Bromomethane	0.5 - 10	18	95	7.8	8.2
n-Butylbenzene	0.5 - 10	18	100	7.6	7.6
sec-Butylbenzene	0.5 - 10	16	100	7.6	7.6
tert-Butylbenzene	0.5 - 10	18	102	7.4	7.3
Carbon tetrachloride	0.5 - 10	24	84	7.4	8.8
Chlorobenzene	0.1 - 10	31	98	5.8	5.9
Chloroethane	0.5 - 10	24	89	8.0	9.0
Chloroform	0.5 - 10	24	90	5.5	6.1
Chloromethane	0.5 - 10	23	93	8.3	8.9
2-Chlorotoluene	0.1 - 10	31	90	5.6	6.2
4-Chlorotoluene	0.1 - 10	31	99	8.2	8.3
1,2-Dibromo-3-Chloropropane	0.5 - 10	24	83	16.6	19.9
Dibromochloromethane	0.1 - 10	31	92	6.5	7.0
1,2-Dibromoethane	0.5 - 10	24	102	4.0	3.9
Dibromomethane	0.5 - 10	24	100	5.6	5.6
1,2-Dichlorobenzene	0.1 - 10	31	93	5.8	6.2
1,3-Dichlorobenzene	0.5 - 10	24	99	6.8	6.9
1,4-Dichlorobenzene	0.2 - 20	31	103	6.6	6.4
Dichlorodifluoromethane	0.5 - 10	18	90	6.9	7.7
1,1-Dichlorobenzene	0.5 - 10	24	96	5.1	5.3
1,2-Dichlorobenzene	0.1 - 10	31	95	5.1	5.4
1,1-Dichloroethene	0.1 - 10	34	94	6.3	6.7
cis-1,2-Dichloroethene	0.5 - 10	18	101	6.7	6.7
trans-1,2-Dichloroethene	0.1 - 10	30	93	5.2	5.6
1,2-Dichloropropane	0.1 - 10	30	97	5.9	6.1
1,3-Dichloropropane	0.1 - 10	31	96	5.7	6.0
2,2-Dichloropropane	0.5 - 10	12	86	14.6	16.9
1,1-Dichloropropene	0.5 - 10	18	98	8.7	8.9
Ethylbenzene	0.1 - 10	31	99	8.4	8.6
Hexachlorobutadiene	0.5 - 10	18	100	6.8	6.8
Isopropylbenzene	0.5 - 10	16	101	7.7	7.6
p-Isopropyltoluene	0.1 - 10	23	99	6.7	6.7
Methylene chloride	0.1 - 10	30	95	5.0	5.3

TABLE 6 (cont.)

Compound	Conc. Range (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Naphthalene	0.1 -100	31	104	8.6	8.2
n-Propylbenzene	0.1 - 10	31	100	5.8	5.8
Styrene	0.1 -100	39	102	7.3	7.2
1,1,1,2-Tetrachloroethane	0.5 - 10	24	90	6.1	6.8
1,1,2,2-Tetrachloroethane	0.1 - 10	30	91	5.7	6.3
Tetrachloroethene	0.5 - 10	24	89	6.0	6.8
Toluene	0.5 - 10	18	102	8.1	8.0
1,2,3-Trichlorobenzene	0.5 - 10	18	109	9.4	8.6
1,2,4-Trichlorobenzene	0.5 - 10	18	108	9.0	8.3
1,1,1-Trichloroethane	0.5 - 10	18	98	7.9	8.1
1,1,2-Trichloroethane	0.5 - 10	18	104	7.6	7.3
Trichloroethene	0.5 - 10	24	90	6.5	7.3
Trichlorofluoromethane	0.5 - 10	24	89	7.2	8.1
1,2,3-Trichloropropane	0.5 - 10	16	108	15.6	14.4
1,2,4-Trimethylbenzene	0.5 - 10	18	99	8.0	8.1
1,3,5-Trimethylbenzene	0.5 - 10	23	92	6.8	7.4
Vinyl chloride	0.5 - 10	18	98	6.5	6.7
o-Xylene	0.1 - 31	18	103	7.4	7.2
m-Xylene	0.1 - 10	31	97	6.3	6.5
p-Xylene	0.5 - 10	18	104	8.0	7.7

[a] Recoveries were calculated using internal standard method. The internal standard was fluorobenzene.

[b] Standard deviation was calculated by pooling data from three concentrations.

TABLE 7

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Benzene	0.1	7	99	6.2	6.3
Bromobenzene	0.5	7	97	7.4	7.6
Bromochloromethane	0.5	7	97	5.8	6.0
Bromodichloromethane	0.1	7	100	4.6	4.6
Bromoform	0.5	7	101	5.4	5.3
Bromomethane	0.5	7	99	7.1	7.2
n-Butylbenzene	0.5	7	94	6.0	6.4
sec-Butylbenzene	0.5	7	110	7.1	6.5
tert-Butylbenzene	0.5	7	110	2.5	2.3
Carbon tetrachloride	0.1	7	108	6.8	6.3
Chlorobenzene	0.1	7	91	5.8	6.4
Chloroethane	0.1	7	100	5.8	5.8
Chloroform	0.1	7	105	3.2	3.0
Chloromethane	0.5	7	101	4.7	4.7
2-Chlorotoluene	0.5	7	99	4.6	4.6
4-Chlorotoluene	0.5	7	96	7.0	7.3
1,2-Dibromo-3-chloropropane	0.5	7	92	10.0	10.9
Dibromochloromethane	0.1	7	99	5.6	5.7
1,2-Dibromoethane	0.5	7	97	5.6	5.8
Dibromomethane	0.5	7	93	5.6	6.0
1,2-Dichlorobenzene	0.1	7	97	3.5	3.6
1,3-Dichlorobenzene	0.1	7	101	6.0	5.9
1,4-Dichlorobenzene	0.1	7	106	6.5	6.1
Dichlorodifluoromethane	0.1	7	99	8.8	8.9
1,1-Dichloroethane	0.5	7	98	6.2	6.3
1,2-Dichloroethane	0.1	7	100	6.3	6.3
1,1-Dichloroethene	0.1	7	95	9.0	9.5
cis-1,2-Dichloroethene	0.1	7	100	3.5	3.7
trans-1,2-Dichloroethene	0.1	7	98	7.2	7.3
1,2-Dichloropropane	0.5	7	96	6.0	6.3
1,3-Dichloropropane	0.5	7	99	5.8	5.9
2,2-Dichloropropane	0.5	7	99	4.9	4.9
1,1-Dichloropropene	0.5	7	102	7.4	7.3
Ethylbenzene	0.5	7	99	5.2	5.3
Hexachlorobutadiene	0.5	7	100	6.7	6.7
Isopropylbenzene	0.5	7	102	6.4	6.3
p-Isopropyltoluene	0.5	7	113	13.0	11.5
Methylene chloride	0.5	7	97	13.0	13.4
Naphthalene	0.5	7	98	7.2	7.3

TABLE 7 (cont.)

Compound	Conc. (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
n-Propylbenzene	0.5	7	99	6.6	6.7
Styrene	0.5	7	96	19.0	19.8
1,1,1,2-Tetrachloroethane	0.5	7	100	4.7	4.7
1,1,2,2-Tetrachloroethane	0.5	7	100	12.0	12.0
Tetrachloroethene	0.1	7	96	5.0	5.2
Toluene	0.5	7	100	5.9	5.9
1,2,3-Trichlorobenzene	0.5	7	102	8.9	8.7
1,2,4-Trichlorobenzene	0.5	7	91	16.0	17.6
1,1,1-Trichloroethane	0.5	7	100	4.0	4.0
1,1,2-Trichloroethane	0.5	7	102	4.9	4.8
Trichloroethene	0.1	7	104	2.0	1.9
Trichlorofluoromethane	0.1	7	97	4.6	4.7
1,2,3-Trichloropropane	0.5	7	96	6.5	6.8
1,2,4-Trimethylbenzene	0.5	7	96	6.5	6.8
1,3,5-Trimethylbenzene	0.5	7	101	4.2	4.2
Vinyl chloride	0.1	7	104	0.2	0.2
o-Xylene	0.5	7	106	7.5	7.1
m-Xylene	0.5	7	106	4.6	4.3
p-Xylene	0.5	7	97	6.1	6.3

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

TABLE 8

SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Water	Soil/Sediment
4-Bromofluorobenzene[a]	86-115	74-121
Dibromofluoromethane[a]	86-118	80-120
Toluene-d_8[a]	88-110	81-117
Dichloroethane-d_4[a]	80-120	80-120

[a] Single laboratory data, for guidance only.

TABLE 9

QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SAMPLES

Approximate Concentration Range (µg/kg)	Volume of Extract[a]
500 - 10,000	100 µL
1,000 - 20,000	50 µL
5,000 - 100,000	10 µL
25,000 - 500,000	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of solvent is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 µL for analysis.

TABLE 10

DIRECT INJECTION ANALYSIS OF NEW OIL AT 5 PPM (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone	91	14.8	1.9	5.0
Benzene	86	21.3	0.1	0.5
n-Butanol*,**	107	27.8	0.5	5.0
iso-Butanol*,**	95	19.5	0.9	5.0
Carbon tetrachloride	86	44.7	0.0	0.5
Carbon disulfide**	53	22.3	0.0	5.0
Chlorobenzene	81	29.3	0.0	5.0
Chloroform	84	29.3	0.0	6.0
1,4-Dichlorobenzene	98	24.9	0.0	7.5
1,2-Dichloroethane	101	23.1	0.0	0.5
1,1-Dichloroethene	97	45.3	0.0	0.7
Diethyl ether	76	24.3	0.0	5.0
Ethyl acetate	113	27.4	0.0	5.0
Ethylbenzene	83	30.1	0.2	5.0
Hexachloroethane	71	30.3	0.0	3.0
Methylene chloride	98	45.3	0.0	5.0
Methyl ethyl ketone	79	24.6	0.4	5.0
MIBK	93	31.4	0.0	5.0
Nitrobenzene	89	30.3	0.0	2.0
Pyridine	31	35.9	0.0	5.0
Tetrachloroethene	82	27.1	0.0	0.7
Trichlorofluoromethane	76	27.6	0.0	5.0
1,1,2-Trichlorotrifluoroethane	69	29.2	0.0	5.0
Toluene	73	21.9	0.6	5.0
Trichloroethene	66	28.0	0.0	0.5
Vinyl chloride	63	35.2	0.0	0.2
o-Xylene	83	29.5	0.4	5.0
m/p-Xylene	84	29.5	0.6	10.0

* Alternate mass employed
** IS quantitation

Data are taken from Reference 9.

TABLE 11

SINGLE LABORATORY PERFORMANCE
DATA FOR THE DIRECT INJECTION METHOD - USED OIL (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone**	105	54	2.0	5.0
Benzene	3135	44	14	0.5
Benzene-d_6	56	44	2.9	0.5
n-Butanol**	100	71	12	5.0
iso-Butanol*,**	132	27	0	5.0
Carbon tetrachloride	143	68	0	0.5
Carbon tetrachloride-^{13}C	99	44	5.1	0.5
Carbon disulfide**	95	63	0	5.0
Chlorobenzene	148	71	0	5.0
Chlorobenzene-d_5	60	44	3.6	5.0
Chloroform	149	74	0	6.0
Chloroform-d_1	51	44	2.6	6.0
1,4-Dichlorobenzene	142	72	0	7.5
1,4-Dichlorobenzene-d_4	53	44	3.4	7.5
1,2-Dichloroethane**	191	54	0	0.5
1,1-Dichloroethene*	155	51	0	0.7
1,1-Dichloroethene-d_2	68	44	3.4	0.7
Diethyl ether**	95	66	0	5.0
Ethyl acetate*,**	126	39	0	5.0
Ethylbenzene	1298	44	54	5.0
Ethylbenzene-d_{10}	63	44	3.6	5.0
Hexachloroethane	132	72	0	3.0
Hexachloroethane-^{13}C	54	45	3.5	3.0
Methylene chloride**	86	65	0.3	5.0
Methyl ethyl ketone**	107	64	0	5.0
4-Methyl-2-pentanone (MIBK)**	100	74	0.1	5.0
Nitrobenzene	111	80	0	2.0
Nitrobenzene-d_5	65	53	4.0	2.0
Pyridine**	68	85	0	5.0
Pyridine-d_5	ND	--	0	5.0
Tetrachloroethene**	101	73	0	0.7
Trichlorofluoromethane**	91	70	0	5.0
1,1,2-Cl_3F_3ethane**	81	70	0	5.0
Toluene	2881	44	128	5.0
Toluene-d_8	63	44	3.6	5.0
Trichloroethene	152	57	0	0.5
Trichloroethene-d_1	55	44	2.8	0.5

TABLE 11 (cont.)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Vinyl chloride**	100	69	0	0.2
o-Xylene	2292	44	105	5.0
o-Xylene-d_{10}	76	44	4.2	5.0
m-/p-Xylene	2583	44	253	10.0
p-Xylene-d_{10}	67	44	3.7	10.0

* Alternate mass employed
** IS quantitation
ND = Not Detected

Data are based on seven measurements and are taken from Reference 9.

TABLE 12

METHOD DETECTION LIMITS (METHOD 5031)

Compound	MDL (µg/L) Macro[a]	Concentration Factor Macro	Micro
Acetone	31	25-500	-
Acetonitrile	57	25-500	200
Acrolein	-	-	100
Acrylonitrile	16	25-500	100
Allyl Alcohol	7	25-500	-
1-Butanol	-	-	250
Crotonaldehyde	12	25-500	-
1,4-Dioxane	12	25-500	150
Ethyl Acetate	-	-	100
Isobutyl alcohol	7	25-500	-
Methanol	38	25-500	140
Methyl Ethyl Ketone	16	25-500	-
2-Methyl-1-propanol	-	-	250
n-Nitroso-di-n-butylamine	14	25-500	-
Paraldehyde	10	25-500	-
2-Picoline	7	25-500	-
1-Propanol	-	-	240
Propionitrile	11	25-500	200
Pyridine	4	25-500	-
o-Toluidine	13	25-500	-

[a] Produced by analysis of seven aliquots of reagent water spiked at 25 ppb at the listed compounds; calculations based on internal standard technique and use of the following equation:

MDL = 3.134 x Std. Dev. of low concentration spike (ppb).

[b] When a 40-mL sample is used, and the first 100 µL of distillate are collected.

TABLE 13

TARGET COMPOUNDS, SURROGATES, AND INTERNAL STANDARDS (METHOD 5031)

Target Compound	Surrogate	Internal Standard
Acetone	d_6-Acetone	d_8-Isopropyl alcohol
Acetonitrile	d_3-Acetonitrile	d_8-Isopropyl alcohol
Acrylonitrile	d_8-Isopropyl alcohol	
Allyl alcohol	d_7-Dimethyl formamide	
Crotonaldehyde	d_8-Isopropyl alcohol	
1,4-Dioxane	d_8-1,4-Dioxane	d_7-Dimethyl formamide
Isobutyl alcohol	d_7-Dimethyl formamide	
Methanol	d_3-Methanol	d_8-Isopropyl alcohol
Methyl ethyl ketone	d_8-Isopropyl alcohol	
N-Nitroso-di-n-butylamine	d_7-Dimethyl formamide	
Paraldehyde	d_7-Dimethyl formamide	
2-Picoline	d_7-Dimethyl formamide	
Propionitrile	d_8-Isopropyl alcohol	
Pyridine	d_5-Pyridine	d_7-Dimethyl formamide
o-Toluidine	d_7-Dimethyl formamide	

TABLE 14

RECOMMENDED CONCENTRATIONS FOR CALIBRATION SOLUTIONS (METHOD 5031)

Compound	Concentration(s) (ng/µL)
Internal Standards	
d_5-benzyl alcohol	10.0
d_{14}-Diglyme	10.0
d_7-Dimethyl formamide	10.0
d_8-Isopropyl alcohol	10.0
Surrogates	
d_6-Acetone	10.0
d_3-Acetonitrile	10.0
d_8-1,4-Dioxane	10.0
d_3-Methanol	10.0
d_5-Pyridine	10.0
Target Compounds	
Acetone	1.0, 5.0, 10.0, 25.0, 100.0
Acetonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Acrylonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Allyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Crotonaldehyde	1.0, 5.0, 10.0, 25.0, 100.0
1,4-Dioxane	1.0, 5.0, 10.0, 25.0, 100.0
Isobutyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Methanol	1.0, 5.0, 10.0, 25.0, 100.0
Methyl ethyl ketone	1.0, 5.0, 10.0, 25.0, 100.0
N-Nitroso-di-n-butylamine	1.0, 5.0, 10.0, 25.0, 100.0
Paraldehyde	1.0, 5.0, 10.0, 25.0, 100.0
2-Picoline	1.0, 5.0, 10.0, 25.0, 100.0
Propionitrile	1.0, 5.0, 10.0, 25.0, 100.0
Pyridine	1.0, 5.0, 10.0, 25.0, 100.0
o-Toluidine	1.0, 5.0, 10.0, 25.0, 100.0

TABLE 15

CHARACTERISTIC IONS AND RETENTION TIMES FOR VOCs (METHOD 5031)

Compound	Quantitation Ion[a]	Secondary Ions	Retention Time (min)[b]
Internal Standards			
d_8-Isopropyl alcohol	49		1.75
d_{14}-Diglyme	66	98,64	9.07
d_7-Dimethyl formamide	50	80	9.20
Surrogates			
d_6-Acetone	46	64,42	1.03
d_3-Methanol	33	35,30	1.75
d_3-Acetonitrile	44	42	2.63
d_8-1,4-Dioxane	96	64,34	3.97
d_5-Pyridine	84	56,79	6.73
d_5-Phenol[c]	99	71	15.43
Target Compounds			
Acetone	43	58	1.05
Methanol	31	29	1.52
Methyl ethyl ketone	43	72,57	1.53
Methacrylonitrile[c]	67	41	2.38
Acrylonitrile	53	52,51	2.53
Acetonitrile	41	40,39	2.73
Methyl isobutyl ketone[c]	85	100,58	2.78
Propionitrile	54	52,55	3.13
Crotonaldehyde	41	70	3.43
1,4-Dioxane	58	88,57	4.00
Paraldehyde	45	89	4.75
Isobutyl alcohol	43	33,42	5.05
Allyl alcohol	57	39	5.63
Pyridine	79	50,52	6.70
2-Picoline	93	66	7.27
N-Nitroso-di-n-butylamine	84	116	12.82
Aniline[c]	93	66,92	13.23
o-Toluidine	106	107	13.68
Phenol[c]	94	66,65	15.43

[a] These ions were used for quantitation in selected ion monitoring.
[b] GC column: DB-Wax, 30 meter x 0.53 mm, 1 µm film thickness.
Oven program: 45°C for 4 min, increased to 220°C at 12°C/min.
[c] Compound removed from target analyte list due to poor accuracy and precision.

TABLE 16

METHOD ACCURACY AND PRECISION BY MEAN PERCENT RECOVERY AND PERCENT RELATIVE STANDARD DEVIATION[a] (METHOD 5031 - MACRODISTILLATION TECHNIQUE)
(Single Laboratory and Single Operator)

Compound	25 ppb Spike		100 ppb Spike		500 ppb Spike	
	Mean %R	%RSD	Mean %R	%RSD	Mean %R	%RSD
d_6-Acetone	66	24	69	14	65	16
d_3-Acetonitrile	89	18	80	18	70	10
d_8-1,4-Dioxane	56	34	58	11	61	18
d_3-Methanol	43	29	48	19	56	14
d_5-Pyridine	83	6.3	84	7.8	85	9.0
Acetone	67	45	63	14	60	14
Acetonitrile	44	35	52	15	56	15
Acrylonitrile	49	42	47	27	45	27
Allyl alcohol	69	13	70	9.7	73	10
Crotonaldehyde	68	22	68	13	69	13
1,4-Dioxane	63	25	55	16	54	13
Isobutyl alcohol	66	14	66	5.7	65	7.9
Methanol	50	36	46	22	49	18
Methyl ethyl ketone	55	37	56	20	52	19
N-Nitroso-di-n-butylamine	57	21	61	15	72	18
Paraldehyde	65	20	66	11	60	8.9
Picoline	81	12	81	6.8	84	8.0
Propionitrile	67	22	69	13	68	13
Pyridine	74	7.4	72	6.7	74	7.3
o-Toluidine	52	31	54	15	58	12

[a] Data from analysis of seven aliquots of reagent water spiked at each concentration, using a quadrapole mass spectrometer in the selected ion monitoring mode.

TABLE 17

RECOVERIES IN SAND SAMPLES FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	8.0	7.5	6.7	5.4	6.6	6.8	13.0	34.2
Trichlorofluoromethane	13.3	16.5	14.9	13.0	10.3	13.6	15.2	68.0
1,1-Dichloroethene	17.1	16.7	15.1	14.8	15.6	15.9	5.7	79.2
Methylene chloride	24.5	22.7	19.7	19.4	20.6	21.4	9.1	107
trans-1,2-Dichloroethene	22.7	23.6	19.4	18.3	20.1	20.8	0.7	104
1,2-Dichloroethane	18.3	18.0	16.7	15.6	15.9	16.9	6.4	84.4
cis-1,2-Dichloroethene	26.1	23.1	22.6	20.3	20.8	22.6	9.0	113
Bromochloromethane	24.5	25.4	20.9	20.1	20.1	22.2	10.2	111
Chloroform	26.5	26.0	22.1	18.9	22.1	23.1	12.2	116
1,1,1-Trichloroethane	21.5	23.0	23.9	16.7	31.2	23.4	21.2	117
Carbon tetrachloride	23.6	24.2	22.6	18.3	23.3	22.4	9.4	112
Benzene	22.4	23.9	20.4	17.4	19.2	20.7	11.2	103
Trichloroethene	21.5	20.5	19.2	14.4	19.1	18.9	12.7	94.6
1,2-Dichloropropane	24.9	26.3	23.1	19.0	23.3	23.3	10.5	117
Dibromomethane	25.4	26.4	21.6	20.4	23.6	23.5	9.6	117
Bromodichloromethane	25.7	26.7	24.1	17.9	23.0	23.5	13.1	117
Toluene	28.3	25.0	24.8	16.3	23.6	23.6	16.9	118
1,1,2-Trichloroethane	25.4	24.5	21.6	17.7	22.1	22.2	12.1	111
1,3-Dichloropropane	25.4	24.2	22.7	17.0	22.2	22.3	12.8	112
Dibromochloromethane	26.3	26.2	23.7	18.2	23.2	23.5	12.5	118
Chlorobenzene	22.9	22.5	19.8	14.6	19.4	19.9	15.0	99.3
1,1,1,2-Tetrachloroethane	22.4	27.7	25.1	19.4	22.6	23.4	12.0	117
Ethylbenzene	25.6	25.0	22.1	14.9	24.0	22.3	17.5	112
p-Xylene	22.5	22.0	19.8	13.9	20.3	19.7	15.7	98.5
o-Xylene	24.2	23.1	21.6	14.0	20.4	20.7	17.3	103
Styrene	23.9	21.5	20.9	14.3	20.5	20.2	15.7	101
Bromoform	26.8	25.6	26.0	20.1	23.5	24.4	9.9	122
iso-Propylbenzene	25.3	25.1	24.2	15.4	24.6	22.9	16.6	114
Bromobenzene	19.9	21.8	20.0	15.5	19.1	19.3	10.7	96.3
1,2,3-Trichloropropane	25.9	23.0	25.6	15.9	21.4	22.2	15.8	111
n-Propylbenzene	26.0	23.8	22.6	13.9	21.9	21.6	19.0	106
2-Chlorotoluene	23.6	23.8	21.3	13.0	21.5	20.6	19.2	103
4-Chlorotoluene	21.0	19.7	18.4	12.1	18.3	17.9	17.1	89.5
1,3,5-Trimethylbenzene	24.0	22.1	22.5	13.8	22.9	21.1	17.6	105
sec-Butylbenzene	25.9	25.3	27.8	16.1	28.6	24.7	18.1	124
1,2,4-Trimethylbenzene	30.6	39.2	22.4	18.0	22.7	26.6	28.2	133
1,3-Dichlorobenzene	20.3	20.6	18.2	13.0	17.6	17.9	15.2	89.7
p-iso-Propyltoluene	21.6	22.1	21.6	16.0	22.8	20.8	11.8	104
1,4-Dichlorobenzene	18.1	21.2	20.0	13.2	17.4	18.0	15.3	90.0
1,2-Dichlorobenzene	18.4	22.5	22.5	15.2	19.9	19.7	13.9	96.6
n-Butylbenzene	13.1	20.3	19.5	10.8	18.7	16.5	23.1	82.4
1,2,4-Trichlorobenzene	14.5	14.9	15.7	8.8	12.3	13.3	18.8	66.2
Hexachlorobutadiene	17.6	22.5	21.6	13.2	21.6	19.3	18.2	96.3
1,2,3-Trichlorobenzene	14.9	15.9	16.5	11.9	13.9	14.6	11.3	73.1

Data in Tables 17, 18, and 19 are from Reference 15.

TABLE 18
RECOVERIES IN C-HORIZON SOILS FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	33.4	31.0	30.9	29.7	28.6	30.8	5.2	154
Trichlorofluoromethane	37.7	20.8	20.0	21.8	20.5	24.1	28.2	121
1,1-Dichloroethene	21.7	33.5	39.8	30.2	32.5	31.6	18.5	158
Methylene chloride	20.9	19.4	18.7	18.3	18.4	19.1	5.1	95.7
trans-1,2-Dichloroethene	21.8	18.9	20.4	17.9	17.8	19.4	7.9	96.8
1,1-Dichloroethane	23.8	21.9	21.3	21.3	20.5	21.8	5.2	109
cis-1,2-Dichloroethene	21.6	18.8	18.5	18.2	18.2	19.0	6.7	95.2
Bromochloromethane	22.3	19.5	19.3	19.0	19.2	20.0	6.0	100
Chloroform	20.5	17.1	17.3	16.5	15.9	17.5	9.2	87.3
1,1,1-Trichloroethane	16.4	11.9	10.7	9.5	9.4	11.6	22.4	57.8
Carbon tetrachloride	13.1	11.3	13.0	11.8	11.2	12.1	6.7	60.5
Benzene	21.1	19.3	18.7	18.2	16.9	18.8	7.4	94.1
Trichloroethene	19.6	16.4	16.5	16.5	15.5	16.9	8.3	84.5
1,2-Dichloropropane	21.8	19.0	18.3	18.8	16.5	18.9	9.0	94.4
Dibromomethane	20.9	17.9	17.9	17.2	18.3	18.4	6.9	92.1
Bromodichloromethane	20.9	18.0	18.9	18.2	17.3	18.6	6.6	93.2
Toluene	22.2	17.3	18.8	17.0	15.9	18.2	12.0	91.2
1,1,2-Trichloroethane	21.0	16.5	17.2	17.2	16.5	17.7	9.6	88.4
1,3-Dichloropropane	21.4	17.3	18.7	18.6	16.7	18.5	8.8	92.6
Dibromochloromethane	20.9	18.1	19.0	18.8	16.6	18.7	7.5	93.3
Chlorobenzene	20.8	18.4	17.6	16.8	14.8	17.7	11.2	88.4
1,1,1,2-Tetrachloroethane	19.5	19.0	17.8	17.2	16.5	18.0	6.2	90.0
Ethylbenzene	21.1	18.3	18.5	16.9	15.3	18.0	10.6	90.0
p-Xylene	20.0	17.4	18.2	16.3	14.4	17.3	10.9	86.3
o-Xylene	20.7	17.2	16.8	16.2	14.8	17.1	11.4	85.7
Styrene	18.3	15.9	16.2	15.3	13.7	15.9	9.3	79.3
Bromoform	20.1	15.9	17.1	17.5	16.1	17.3	8.6	86.7
iso-Propylbenzene	21.0	18.1	19.2	18.4	15.6	18.4	9.6	92.2
Bromobenzene	20.4	16.2	17.2	16.7	15.4	17.2	10.1	85.9
1,1,2,2-Tetrachloroethane	23.3	17.9	21.2	18.8	16.8	19.6	12.1	96.0
1,2,3-Trichloropropane	18.4	14.6	15.6	16.1	15.6	16.1	8.0	80.3
n-Propylbenzene	20.4	18.9	17.9	17.0	14.3	17.7	11.6	88.4
2-Chlorotoluene	19.1	17.3	16.1	16.0	14.4	16.7	9.2	83.6
4-Chlorotoluene	19.0	15.5	16.8	15.9	13.6	16.4	10.6	81.8
1,3,5-Trimethylbenzene	20.8	18.0	17.4	16.1	14.7	17.4	11.7	86.9
sec-Butylbenzene	21.4	18.3	18.9	17.0	14.9	18.1	11.8	90.5
1,2,4-Trimethylbenzene	20.5	18.6	16.8	15.3	13.7	17.0	14.1	85.0
1,3-Dichlorobenzene	17.6	15.9	15.6	14.2	14.4	15.6	7.9	77.8
p-iso-Propyltoluene	20.5	17.0	17.1	15.6	13.4	16.7	13.9	83.6
1,4-Dichlorobenzene	18.5	13.8	14.8	16.7	14.9	15.7	10.5	78.7
1,2-Dichlorobenzene	18.4	15.0	15.4	15.3	13.5	15.5	10.5	77.6
n-Butylbenzene	19.6	15.9	15.9	14.4	18.9	16.9	11.7	84.6
1,2,4-Trichlorobenzene	15.2	17.2	17.4	13.6	12.1	15.1	13.5	75.4
Hexachlorobutadiene	18.7	16.2	15.5	13.8	16.6	16.1	10.0	80.7
Naphthalene	13.9	11.1	10.2	10.8	11.4	11.5	11.0	57.4
1,2,3-Trichlorobenzene	14.9	15.2	16.8	13.7	12.7	14.7	9.5	73.2

TABLE 19
RECOVERIES IN GARDEN SOIL FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	12.7	10.9	9.8	8.1	7.2	9.7	20.2	48.7
Trichlorofluoromethane	33.7	6.4	30.3	27.8	22.9	24.2	39.6	121
1,1-Dichloroethene	27.7	20.5	24.1	15.1	13.2	20.1	26.9	101
Methylene chloride	25.4	23.9	24.7	22.2	24.2	24.1	4.4	120
trans-1,2-Dichloroethene	2.8	3.0	3.3	2.2	2.4	2.7	15.0	13.6
1,1-Dichloroethane	24.1	26.3	27.0	20.5	21.2	23.8	11.0	119
cis-1,2-Dichloroethene	8.3	10.2	8.7	5.8	6.4	7.9	20.1	39.4
Bromochloromethane	11.1	11.8	10.2	8.8	9.0	10.2	11.2	50.9
Chloroform	16.7	16.9	17.0	13.8	15.0	15.9	7.9	79.3
1,1,1-Trichloroethane	24.6	22.8	22.1	16.2	20.9	21.3	13.4	107
Carbon tetrachloride	19.4	20.3	22.2	20.0	20.2	20.4	4.6	102
Benzene	21.4	22.0	22.4	19.6	20.4	21.2	4.9	106
Trichloroethene	12.4	16.5	14.9	9.0	9.9	12.5	22.9	62.7
1,2-Dichloropropane	19.0	18.8	19.7	16.0	17.6	18.2	7.1	91.0
Dibromomethane	7.3	8.0	6.9	5.6	6.8	6.9	11.3	34.6
Bromodichloromethane	14.9	15.9	15.9	12.8	13.9	14.7	8.3	73.3
Toluene	42.6	39.3	45.1	39.9	45.3	42.4	5.9	212
1,1,2-Trichloroethane	13.9	15.2	1.4	21.3	14.9	15.9	17.0	79.6
1,3-Dichloropropane	13.3	16.7	11.3	10.9	9.5	12.3	20.3	61.7
Dibromochloromethane	14.5	13.1	14.5	11.9	14.4	13.7	7.6	68.3
Chlorobenzene	8.4	10.0	8.3	6.9	7.8	8.3	12.1	41.3
1,1,1,2-Tetrachloroethane	16.7	16.7	15.6	15.8	15.7	16.1	3.2	80.4
Ethylbenzene	22.1	21.4	23.1	20.1	22.6	21.9	4.8	109
p-Xylene	41.4	38.4	43.8	38.3	44.0	41.2	6.1	206
o-Xylene	31.7	30.8	34.3	30.4	33.2	32.1	4.6	160
Styrene	0	0	0	0	0	0	0	0
Bromoform	8.6	8.9	9.1	7.0	7.7	8.3	9.4	41.4
iso-Propylbenzene	18.1	18.8	9.7	18.3	19.6	18.9	3.5	94.4
Bromobenzene	5.1	5.4	5.3	4.4	4.0	4.8	11.6	24.1
1,1,2,2-Tetrachloroethane	14.0	13.5	14.7	15.3	17.1	14.9	8.5	74.5
1,2,3-Trichloropropane	11.0	12.7	11.7	11.7	11.9	11.8	4.5	59.0
n-Propylbenzene	13.4	13.3	14.7	12.8	13.9	13.6	4.7	68.1
2-Chlorotoluene	8.3	9.0	11.7	8.7	7.9	9.1	14.8	45.6
4-Chlorotoluene	5.1	5.4	5.5	4.8	4.5	5.0	7.9	25.2
1,3,5-Trimethylbenzene	31.3	27.5	33.0	31.1	33.6	31.3	6.8	157
sec-Butylbenzene	13.5	13.4	16.4	13.8	15.4	14.5	8.3	72.5
1,2,4-Trimethylbenzene	38.7	32.4	40.8	34.1	40.3	37.3	9.1	186
1,3-Dichlorobenzene	3.6	3.6	3.7	3.0	3.2	3.4	8.0	17.2
p-iso-Propyltoluene	14.7	14.1	16.1	13.9	15.1	14.8	5.2	73.8
1,4-Dichlorobenzene	3.0	3.5	3.3	2.6	2.8	3.0	10.2	15.0
1,2-Dichlorobenzene	3.6	4.3	4.0	3.5	3.6	3.8	8.3	19.0
n-Butylbenzene	17.4	13.8	14.0	18.9	24.0	17.6	21.2	88.0
1,2,4-Trichlorobenzene	2.8	2.9	3.3	2.6	3.2	3.0	8.5	15.0
Hexachlorobutadiene	4.8	4.0	6.1	5.6	6.0	5.3	15.1	26.4
Naphthalene	5.5	5.1	5.5	4.7	5.6	5.3	6.2	26.5
1,2,3-Trichlorobenzene	2.2	2.3	2.4	2.2	2.3	2.3	3.5	11.4

Data in Table 19 are from Reference 15.

TABLE 20

VOLATILE ORGANIC ANALYTE RECOVERY FROM SOIL
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	Soil/H_2O[b] Recovery Mean	Soil/H_2O[b] Recovery RSD	Soil/Oil[c] Recovery Mean	Soil/Oil[c] Recovery RSD	Soil/Oil/H_2O Recovery Mean	Soil/Oil/H_2O Recovery RSD
Chloromethane	61	20	40	18	108	68
Bromomethane	58	20	47	13	74	13
Vinyl chloride	54	12	46	11	72	20
Chloroethane	46	10	41	8	52	14
Methylene chloride	60	2	65	8	76	11
Acetone	INT[e]	INT	44	8		
Carbon disulfide	47	13	53	10	47	4
1,1-Dichloroethene	48	9	47	5	58	3
1,1-Dichloroethane	61	6	58	9	61	6
trans-1,2-Trichloroethane	54	7	60	7	56	5
cis-1,2-Dichloroethene	60	4	72	6	63	8
Chloroform	104	11	93	6	114	15
1,2-Dichloroethane	177	50	117	8	151	22
2-Butanone	INT	36	38	INT		
1,1,1-Trichloroethane	124	13	72	16	134	26
Carbon tetrachloride	172	122	INT	INT		
Vinyl acetate	88	11	INT			
Bromodichloromethane	93	4	91	23	104	23
1,1,2,2-Tetrachloroethane	96	13	50	12	104	7
1,2-Dichloropropane	105	8	102	6	111	6
trans-1,3-Dichloropropene	134	10	84	16	107	8
Trichloroethene	98	9	99	10	100	5
Dibromochloromethane	119	8	125	31	142	16
1,1,2-Trichloroethane	126	10	72	16	97	4
Benzene	99	7	CONT[f]	CONT		
cis-1,3-Dichloropropene	123	12	94	13	112	9
Bromoform	131	13	58	18	102	9
2-Hexanone	155	18	164	19	173	29
4-Methyl-2-pentanone	152	20	185	20	169	18
Tetrachloroethene	90	9	123	14	128	7
Toluene	94	3	CONT	CONT		
Chlorobenzene	98	7	93	18	112	5
Ethylbenzene	114	13	CONT	CONT		
Styrene	106	8	93	18	112	5
p-Xylene	97	9	CONT	CONT		
o-Xylene	105	8	112	12	144	13

TABLE 20 (cont.)

Compound	Soil/H_2O[b] Recovery Mean	Soil/H_2O[b] Recovery RSD	Soil/Oil[c] Recovery Mean	Soil/Oil[c] Recovery RSD	Soil/Oil/H_2O Recovery Mean	Soil/Oil/H_2O Recovery RSD
Surrogates						
1,2-Dichloroethane	177	50	117	8	151	22
Toluene-d_8	96	6	79	12	82	6
Bromofluorobenzene	139	13	37	13	62	5

[a] Results are for 10 min. distillations times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision value reflects the propagated errors. Each analyte was spiked at 50 ppb. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may introduce bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Soil samples spiked with 0.2 mL water containing analytes and then 5 mL water added to make slurry.

[c] Soil sample + 1 g cod liver oil, spiked with 0.2 mL water containing analytes.

[d] Soil samples + 1 g cod liver oil, spiked as above with 5 mL of water added to make slurry.

[e] Interference by co-eluting compounds prevented accurate measurement of analyte.

[f] Contamination of sample matrix by analyte prevented assessment of efficiency.

TABLE 21

VACUUM DISTILLATION EFFICIENCIES FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

Compound	Efficiency Mean (%)	RSD (%)
Chloromethane	N/A[b]	
Bromomethane	N/A[b]	
Vinyl chloride	N/A[b]	
Chloroethane	N/A[b]	
Methylene chloride	CONT[c]	
Acetone	CONT[c]	
Carbon disulfide	79	36
1,1-Dichloroethene	122	39
1,1-Dichloroethane	126	35
trans-1,2-Trichloroethene	109	46
cis-1,2-Dichloroethene	106	22
Chloroform	111	32
1,2-Dichloroethane	117	27
2-Butanone	INT[d]	
1,1,1-Trichloroethane	106	30
Carbon tetrachloride	83	34
Vinyl acetate	INT[d]	
Bromodichloromethane	97	22
1,1,2,2-Tetrachloroethane	67	20
1,2-Dichloropropane	117	23
trans-1,3-Dichloropropene	92	22
Trichloroethene	98	31
Dibromochloromethane	71	19
1,1,2-Trichloroethane	92	20
Benzene	129	35
cis-1,3-Dichloropropene	102	24
Bromoform	58	19
2-Hexanone	INT[d]	
4-Methyl-2-pentanone	113	37
Tetrachloroethene	66	20
Toluene	CONT[c]	
Chlorobenzene	65	19
Ethylbenzene	74	19
Styrene	57	14
p-Xylene	46	13
o-Xylene	83	20

TABLE 21 (cont.)

Compound	Efficiency Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	115	27
Toluene-d_8	88	24
Bromofluorobenzene	52	15

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicate 10-g aliquots of fish spiked at 25 ppb were analyzed using GC/MS external standard quantitation. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards were replicated and results reflect 1 sigma propagated standard deviation.

[b] No analyses.

[c] Contamination of sample matrix by analyte prevented accurate assessment of analyte efficiency.

[d] Interfering by co-eluting compounds prevented accurate measurement of analyte.

TABLE 22

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

Compound	Method Detection Limit (ppb) External Standard Method	Internal Standard Method
Chloromethane	7.8	7.3
Bromomethane	9.7	9.8
Vinyl chloride	9.5	9.4
Chloroethane	9.2	10.0
Methylene chloride	CONT[b]	CONT[b]
Acetone	CONT[b]	CONT[b]
Carbon disulfide	5.4	4.9
1,1-Dichloroethene	4.0	5.7
1,1-Dichloroethane	4.0	3.5
trans-1,2-Dichloroethene	4.4	4.0
cis-1,2-Dichloroethene	4.7	4.1
Chloroform	5.6	5.0
1,2-Dichloroethane	3.3	3.2
2-Butanone	INT[c]	INT[c]
1,1,1-Trichloroethane	1.1	4.2
Carbon tetrachloride	3.2	3.5
Vinyl acetate	INT[c]	INT[c]
Bromodichloromethane	3.2	2.8
1,1,2,2-Tetrachloroethane	4.4	3.8
1,2-Dichloropropane	3.8	3.7
trans-1,3-Dichloropropene	3.4	3.0
Trichloroethene	3.1	4.0
Dibromochloromethane	3.5	3.2
1,1,2-Trichloroethane	4.4	3.3
Benzene	3.6	3.2
cis-1,3-Dichloropropene	3.5	3.0
Bromoform	4.9	4.0
2-Hexanone	7.7	8.0
4-Methyl-2-pentanone	7.5	8.0
Tetrachloroethene	4.3	4.0
Toluene	3.0	2.5
Chlorobenzene	3.3	2.8
Ethylbenzene	3.6	3.5
Styrene	3.5	3.3
p-Xylene	3.7	3.5
o-Xylene	3.3	4.7

Footnotes are on the following page.

[a] Values shown are the average MDLs for studies on three non-consecutive days, involving seven replicate analyses of 10 g of fish tissue spiked a 5 ppb. Daily MDLs were calculated as three times the standard deviation. Quantitation was performed by GC/MS Method 8260 and separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] Contamination of sample by analyte prevented determination.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 23

VOLATILE ORGANIC ANALYTES RECOVERY FOR WATER
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	5 mL H_2O[b] Recovery Mean	RSD	20 mL H_2O[c] Recovery Mean	RSD	20 mL H_2O/Oil Recovery Mean	RSD
Chloromethane	114	27	116	29	176	67
Bromomethane	131	14	121	14	113	21
Vinyl chloride	131	13	120	16	116	23
Chloroethane	110	15	99	8	96	16
Methylene chloride	87	16	105	15	77	6
Acetone	83	22	65	34	119	68
Carbon disulfide	138	17	133	23	99	47
1,1-Dichloroethene	105	11	89	4	96	18
1,1-Dichloroethane	118	10	119	11	103	25
trans-1,2-Dichloroethene	105	11	107	14	96	18
cis-1,2-Dichloroethene	106	7	99	5	104	23
Chloroform	114	6	104	8	107	21
1,2-Dichloroethane	104	6	109	8	144	19
2-Butanone	83	50	106	31	INT[c]	
1,1,1-Trichloroethane	118	9	109	9	113	23
Carbon tetrachloride	102	6	108	12	109	27
Vinyl acetate	90	16	99	7	72	36
Bromodichloromethane	104	3	110	5	99	5
1,1,2,2-Tetrachloroethane	85	17	81	7	111	43
1,2-Dichloropropane	100	6	103	2	104	7
trans-1,3-Dichloropropene	105	8	105	4	92	4
Trichloroethene	98	4	99	2	95	5
Dibromochloroethane	99	8	99	6	90	25
1,1,2-Trichloroethane	98	7	100	4	76	12
Benzene	97	4	100	5	112	10
cis-1,3-Dichloropropene	106	5	105	4	98	3
Bromoform	93	16	94	8	57	21
2-Hexanone	60	17	63	16	78	23
4-Methyl-2-pentanone	79	24	63	14	68	15
Tetrachloroethene	101	3	97	7	77	14
Toluene	100	6	97	8	85	5
Chlorobenzene	98	6	98	4	88	16
Ethylbenzene	100	3	92	8	73	13
Styrene	98	4	97	9	88	16
p-Xylene	96	4	94	8	60	12
o-Xylene	96	7	95	6	72	14

TABLE 23 (cont.)

Compound	5 mL H_2O[b] Recovery Mean	RSD	20 mL H_2O[c] Recovery Mean	RSD	20 mL H_2O/Oil Recovery Mean	RSD
Surrogates						
1,2-Dichloroethane	104	6	109	6	144	19
Toluene-d_8	104	5	102	2	76	7
Bromofluorobenzene	106	6	106	9	40	8

[a] Results are for 10 min. distillation times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision values reflect the propagated errors. Concentrations of analytes were 50 ppb for 5-mL samples and 25 ppb for 20-mL samples. Recovery data generated with comparison to analyses of standards without the water matrix.

[b] Sample contained 1 gram cod liver oil and 20 mL water. An emulsion was created by adding 0.2 mL of water saturated with lecithin.

[c] Interference by co-eluting compounds prevented accurate assessment of recovery.

TABLE 24

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES
USING VACUUM DISTILLATION (METHOD 5032) (INTERNAL STANDARD METHOD)[a]

Compound	Water[b] (µg/L)	Soil[c] (µg/kg)	Tissue[d] (µg/kg)	Oil[e] (mg/kg)
Chloromethane	3.2	8.0	7.3	N/A[f]
Bromomethane	2.8	4.9	9.8	N/A[f]
Vinyl chloride	3.5	6.0	9.4	N/A[f]
Chloroethane	5.9	6.0	10.0	N/A[f]
Methylene chloride	3.1	4.0	CONT[g]	0.05
Acetone	5.6	CONT[g]	CONT[g]	0.06
Carbon disulfide	2.5	2.0	4.9	0.18
1,1-Dichloroethene	2.9	3.2	5.7	0.18
1,1-Dichloroethane	2.2	2.0	3.5	0.14
trans-1,2-Dichloroethene	2.2	1.4	4.0	0.10
cis-1,2-Dichloroethene	2.0	2.3	4.1	0.07
Chloroform	2.4	1.8	5.0	0.07
1,2-Dichloroethane	1.7	1.5	3.2	0.06
2-Butanone	7.4	INT[h]	INT[h]	INT[h]
1,1,1-Trichloroethane	1.8	1.7	4.2	0.10
Carbon tetrachloride	1.4	1.5	3.5	0.13
Vinyl acetate	11.8	INT[h]	INT[h]	INT[h]
Bromodichloromethane	1.6	1.4	2.8	0.06
1,1,2,2-Tetrachloroethane	2.5	2.1	3.8	0.02
1,2-Dichloropropane	2.2	2.1	3.7	0.15
trans-1,3-Dichloropropene	1.5	1.7	3.0	0.05
Trichloroethene	1.6	1.7	4.0	0.04
Dibromochloromethane	1.7	1.5	3.2	0.07
1,1,2-Trichloroethane	2.1	1.7	3.3	0.05
Benzene	0.5	1.5	3.2	0.05
cis-1,3-Dichloropropene	1.4	1.7	3.0	0.04
Bromoform	1.8	1.5	4.0	0.05
2-Hexanone	4.6	3.6	8.0	INT[h]
4-Methyl-2-pentanone	3.5	4.6	8.0	INT[h]
Tetrachloroethene	1.4	1.6	4.0	0.10
Toluene	1.0	3.3	2.5	0.05
Chlorobenzene	1.4	1.4	2.8	0.06
Ethylbenzene	1.5	2.8	3.5	0.04
Styrene	1.4	1.4	3.3	0.18
p-Xylene	1.5	2.9	3.5	0.20
o-Xylene	1.7	3.4	4.7	0.07

Footnotes are found on the following page.

[a] Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Method detection limits are the average MDLs for studies on three non-consecutive days.

[b] Method detection limits are the average MDLs for studies of three non-consecutive days. Daily studies were seven replicated analyses of 5 mL aliquots of 4 ppb soil. Daily MDLs were three times the standard deviation.

[c] Daily studies were seven replicated analyses of 10 g fish tissue spiked at 5 ppb. Daily MDLs were three times the standard deviation. Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[d] Method detection limits are estimated analyzing 1 g of cod liver oil samples spiked at 250 ppm. Five replicates were analyzed using Method 8260.

[e] No analyses.

[f] Contamination of sample by analyte prevented determination.

[g] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 25

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES
(METHOD 5032) (EXTERNAL STANDARD METHOD)[a]

Compound	Water[b] (µg/L)	Soil[c] (µg/kg)	Tissue[d] (µg/kg)	Oil[e] (mg/kg)
Chloromethane	3.1	8.6[f]	7.8	N/A[g]
Bromomethane	2.5	4.9[f]	9.7	N/A[g]
Vinyl chloride	4.0	7.1[f]	9.5	N/A[g]
Chloroethane	6.1	7.5[f]	9.2	N/A[g]
Methylene chloride	3.1	3.3	CONT[h]	0.08
Acetone	33.0[f]	CONT[h]	CONT[h]	0.12
Carbon disulfide	2.5	3.2	5.4	0.19
1,1-Dichloroethene	3.4	3.8	4.0	0.19
1,1-Dichloroethane	2.3	1.7	4.0	0.13
trans-1,2-Dichloroethene	3.0	3.2	4.4	0.09
cis-1,2-Dichloroethene	2.4	2.7	4.7	0.08
Chloroform	2.7	2.6	5.6	0.06
1,2-Dichloroethane	1.6	1.7	3.3	0.06
2-Butanone	57.0[f]	INT[i]	INT[i]	INT[i]
1,1,1-Trichloroethane	1.6	2.4	1.1	0.08
Carbon tetrachloride	1.5	1.7	3.2	0.15
Vinyl acetate	23.0[f]	INT[i]	INT[i]	INT[i]
Bromodichloromethane	2.0	2.3	3.2	0.05
1,1,2,2-Tetrachloroethane	3.6	3.2	4.4	0.09
1,2-Dichloropropane	2.9	3.7	3.8	0.12
trans-1,3-Dichloropropene	2.3	2.4	3.8	0.08
Trichloroethene	2.5	3.0	3.1	0.06
Dibromochloromethane	2.1	2.9	3.5	0.04
1,1,2-Trichloroethane	2.7	2.8	4.4	0.07
Benzene	1.7	2.9	3.6	0.03
cis-1,3-Dichloropropene	2.1	2.5	3.5	0.06
Bromoform	2.3	2.5	4.9	0.10
2-Hexanone	4.6	4.6	7.7	INT[i]
4-Methyl-2-pentanone	3.8	3.9	7.5	INT[i]
Tetrachloroethene	1.8	2.6	4.3	0.12
Toluene	1.8	4.4	3.0	0.09
Chlorobenzene	2.4	2.6	3.3	0.07
Ethylbenzene	2.4	4.1	3.6	0.09
Styrene	2.0	2.5	3.5	0.16
p-Xylene	2.3	3.9	3.7	0.18
o-Xylene	2.4	4.1	3.3	0.08

[a] Method detection limits are the average MDLs for studies on three non-consecutive days. Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb. Daily MDLs were three times the standard deviation.

[b] Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb.

[c] These studies were seven replicate analyses of 5-g aliquots of soil spiked at 4 ppb.

[d] These studies were seven replicate analyses of 10-g aliquots of fish tissue spiked at 5 ppb.

[e] Method detection limits were estimated by analyzing cod liver oil samples spiked at 250 ppb. Five replicates were analyzed using Method 8260.

[f] Method detection limits were estimated by analyzing replicate 50 ppb standards five times over a single day.

[g] No analyses.

[h] Contamination of sample by analyte prevented determination.

[l] Interference by co-eluting compound prevented accurate quantitation.

TABLE 26

VOLATILE ORGANIC ANALYTE RECOVERY FROM OIL
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	Recovery Mean (%)	RSD (%)
Chloromethane	N/A[b]	
Bromomethane	N/A[b]	
Vinyl chloride	N/A[b]	
Chloroethane	N/A[b]	
Methylene chloride	62	32
Acetone	108	55
Carbon disulfide	98	46
1,1-Dichloroethene	97	24
1,1-Dichloroethane	96	22
trans-1,2-Trichloroethene	86	23
cis-1,2-Dichloroethene	99	11
Chloroform	93	14
1,2-Dichloroethane	138	31
2-Butanone	INT[c]	
1,1,1-Trichloroethane	89	14
Carbon tetrachloride	129	23
Vinyl acetate	INT[c]	
Bromodichloromethane	106	14
1,1,2,2-Tetrachloroethane	205	46
1,2-Dichloropropane	107	24
trans-1,3-Dichloropropene	98	13
Trichloroethene	102	8
Dibromochloromethane	168	21
1,1,2-Trichloroethane	95	7
Benzene	146	10
cis-1,3-Dichloropropene	98	11
Bromoform	94	18
2-Hexanone	INT[c]	
4-Methyl-2-pentanone	INT[c]	
Tetrachloroethene	117	22
Toluene	108	8
Chlorobenzene	101	12
Ethylbenzene	96	10
Styrene	120	46
p-Xylene	87	23
o-Xylene	90	10

TABLE 26 (cont.)

Compound	Recovery Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	137	30
Toluene-d_8	84	6
Bromofluorobenzene	48	2

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicates of 10-g fish aliquots spiked at 25 ppb were analyzed. Quantitation was performed with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Standards and samples were replicated and precision value reflects the propagated errors. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Not analyzed.

[c] Interference by co-evaluating compounds prevented accurate measurement of analyte.

TABLE 27

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN OIL (METHOD 5032)[a]

Compound	Method Detection Limit (ppb) External Standard Method	Internal Standard Method
Chloromethane	N/A[b]	N/A[b]
Bromomethane	N/A[b]	N/A[b]
Vinyl chloride	N/A[b]	N/A[b]
Chloroethane	N/A[b]	N/A[b]
Methylene chloride	80	50
Acetone	120	60
Carbon disulfide	190	180
1,1-Dichloroethene	190	180
1,1-Dichloroethane	130	140
trans-1,2-Dichloroethene	90	100
cis-1,2-Dichloroethene	80	70
Chloroform	60	70
1,2-Dichloroethane	60	60
2-Butanone	INT[c]	INT[c]
1,1,1-Trichloroethane	80	100
Carbon tetrachloride	150	130
Vinyl acetate	INT[c]	INT[c]
Bromodichloromethane	50	60
1,1,2,2-Tetrachloroethane	90	20
1,2-Dichloropropane	120	150
trans-1,3-Dichloropropene	80	50
Trichloroethene	60	40
Dibromochloromethane	40	70
1,1,2-Trichloroethane	70	50
Benzene	30	50
cis-1,3-Dichloropropene	60	40
Bromoform	100	50
2-Hexanone	INT[c]	INT[c]
4-Methyl-2-pentanone	INT[c]	INT[c]
Tetrachloroethene	120	100
Toluene	90	50
Chlorobenzene	70	60
Ethylbenzene	90	40
Styrene	160	180
p-Xylene	180	200
o-Xylene	80	70

[a] Method detection limits are estimated as the result of five replicated analyses of 1 g cod liver oil spiked at 25 ppb. MDLs were calculated as three times the standard deviation. Quantitation was performed using a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] No analyses.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 28

INTERNAL STANDARDS FOR ANALYTES AND SURROGATES PREPARED USING EQUILIBRIUM HEADSPACE ANALYSIS (METHOD 5021)

Chloroform-d_1	1,1,2-TCA-d_3	Bromobenzene-d_5
Dichlorodifluoromethane	1,1,1-Trichloroethane	Chlorobenzene
Chloromethane	1,1-Dichloropropene	Bromoform
Vinyl chloride	Carbon tetrachloride	Styrene
Bromomethane	Benzene	iso-Propylbenzene
Chloroethane	Dibromomethane	Bromobenzene
Trichlorofluoromethane	1,2-Dichloropropane	n-Propylbenzene
1,1-Dichloroethene	Trichloroethene	2-Chlorotoluene
Methylene chloride	Bromodichloromethane	4-Chlorotoluene
trans-1,2-Dichloroethene	cis-1,3-Dichloropropene	1,3,5-Trimethylbenzene
1,1-Dichloroethane	trans-1,3-Dichloropropene	tert-Butylbenzene
cis-1,2-Dichloroethene	1,1,2-Trichloroethane	1,2,4-Trimethylbenzene
Bromochloromethane	Toluene	sec-Butylbenzene
Chloroform	1,3-Dichloropropane	1,3-Dichlorobenzene
2,2-Dichloropropane	Dibromochloromethane	1,4-Dichlorobenzene
1,2-Dichloroethane	1,2-Dibromoethane	p-iso-Propyltoluene
	Tetrachloroethene	1,2-Dichlorobenzene
	1,1,2-Trichloroethane	n-Butylbenzene
	Ethylbenzene	1,2-Dibromo-3-chloropropane
	m-Xylene	1,2,4-Trichlorobenzene
	p-Xylene	Naphthalene
	o-Xylene	Hexachlorobutadiene
	1,1,2,2-Tetrachloroethane	1,2,3-Trichlorobenzene
	1,2,3-Trichloropropane	

TABLE 29

PRECISION AND MDL DETERMINED FOR ANALYSIS OF FORTIFIED SAND[a] (METHOD 5021)

Compound	% RSD	MDL (µg/kg)
Benzene	3.0	0.34
Bromochloromethane	3.4	0.27
Bromodichloromethane	2.4	0.21
Bromoform	3.9	0.30
Bromomethane	11.6	1.3
Carbon tetrachloride	3.6	0.32
Chlorobenzene	3.2	0.24
Chloroethane	5.6	0.51
Chloroform	3.1	0.30
Chloromethane	4.1	3.5[b]
1,2-Dibromo-3-chloropropane	5.7	0.40
1,2-Dibromoethane	3.2	0.29
Dibromomethane	2.8	0.20
1,2-Dichlorobenzene	3.3	0.27
1,3-Dichlorobenzene	3.4	0.24
1,4-Dichlorobenzene	3.7	0.30
Dichlorodifluoromethane	3.0	0.28
1,1-Dichloroethane	4.5	0.41
1,2-Dichloroethane	3.0	0.24
1,1-Dichloroethene	3.3	0.28
cis-1,2-Dichloroethene	3.2	0.27
trans-1,2-Dichloroethene	2.6	0.22
1,2-Dichloropropane	2.6	0.21
1,1-Dichloropropene	3.2	0.30
cis-1,3-Dichloropropene	3.4	0.27
Ethylbenzene	4.8	0.47
Hexachlorobutadiene	4.1	0.38
Methylene chloride	8.2	0.62[c]
Naphthalene	16.8	3.4[c]
Styrene	7.9	0.62
1,1,1,2-Tetrachloroethane	3.6	0.27
1,1,2,2-Tetrachloroethane	2.6	0.20
Tetrachloroethene	9.8	1.2[c]
Toluene	3.5	0.38
1,2,4-Trichlorobenzene	4.2	0.44
1,1,1-Trichloroethane	2.7	0.27
1,1,2-Trichloroethane	2.6	0.20
Trichloroethene	2.3	0.19

TABLE 29 (cont.)

Compound	% RSD	MDL (µg/kg)
Trichlorofluoromethane	2.7	0.31
1,2,3-Trichloropropane	1.5	0.11
Vinyl chloride	4.8	0.45
m-Xylene/p-Xylene	3.6	0.37
o-Xylene	3.6	0.33

[a] Most compounds spiked at 2 ng/g (2 µg/kg)
[b] Incorrect ionization due to methanol
[c] Compound detected in unfortified sand at >1 ng

TABLE 30

RECOVERIES IN GARDEN SOIL FORTIFIED AT 20 µg/kg (ANALYSIS BY METHOD 5021)

Compound	Recovery per Replicate (ng) Sample 1	Sample 2	Sample 3	Mean (ng)	RSD	Recovery (%)
Benzene	37.6	35.2	38.4	37.1	3.7	185[a]
Bromochloromethane	20.5	19.4	20.0	20.0	2.3	100
Bromodichloromethane	21.1	20.3	22.8	21.4	4.9	107
Bromoform	23.8	23.9	25.1	24.3	2.4	121
Bromomethane	21.4	19.5	19.7	20.2	4.2	101
Carbon tetrachloride	27.5	26.6	28.6	27.6	3.0	138
Chlorobenzene	25.6	25.4	26.4	25.8	1.7	129
Chloroethane	25.0	24.4	25.3	24.9	1.5	125
Chloroform	21.9	20.9	21.7	21.5	2.0	108
Chloromethane	21.0	19.9	21.3	20.7	2.9	104[a]
1,2-Dibromo-3-chloro-propane	20.8	20.8	21.0	20.9	0.5	104
1,2-Dibromoethane	20.1	19.5	20.6	20.1	2.2	100
Dibromomethane	22.2	21.0	22.8	22.0	3.4	110
1,2-Dichlorobenzene	18.0	17.7	17.1	17.6	2.1	88.0
1,3-Dichlorobenzene	21.2	21.0	20.1	20.8	2.3	104
1,4-Dichlorobenzene	20.1	20.9	19.9	20.3	2.1	102
Dichlorodifluoromethane	25.3	24.1	25.4	24.9	2.4	125
1,1-Dichloroethane	23.0	22.0	22.7	22.6	1.9	113
1,2-Dichloroethane	20.6	19.5	19.8	20.0	2.3	100
1,1-Dichloroethene	24.8	23.8	24.4	24.3	1.7	122
cis-1,2-Dichloroethene	21.6	20.0	21.6	21.1	3.6	105
trans-1,2-Dichloroethene	22.4	21.4	22.2	22.0	2.0	110
1,2-Dichloropropane	22.8	22.2	23.4	22.8	2.1	114
1,1-Dichloropropene	26.3	25.7	28.0	26.7	3.7	133
cis-1,3-Dichloropropene	20.3	19.5	21.1	20.3	3.2	102
Ethylbenzene	24.7	24.5	25.5	24.9	1.7	125
Hexachlorobutadiene	23.0	25.3	25.2	24.5	4.3	123
Methylene chloride	26.0	25.7	26.1	25.9	0.7	130[a]
Naphthalene	13.8	12.7	11.8	12.8	6.4	63.8[a]
Styrene	24.2	23.3	23.3	23.6	1.8	118
1,1,1,2-Tetrachloroethane	21.4	20.2	21.3	21.0	2.6	105
1,1,2,2-Tetrachloroethane	18.6	17.8	19.0	18.5	2.7	92.3
Tetrachloroethene	25.2	24.8	26.4	25.5	2.7	127
Toluene	28.6	27.9	30.9	29.1	4.4	146[a]
1,2,4-Trichlorobenzene	15.0	14.4	12.9	14.1	6.3	70.5
1,1,1-Trichloroethane	28.1	27.2	29.9	28.4	4.0	142
1,1,2-Trichloroethane	20.8	19.6	21.7	20.7	4.2	104

TABLE 30 (cont.)

Compound	Recovery per Replicate (ng) Sample 1	Sample 2	Sample 3	Mean (ng)	RSD	Recovery (%)
Trichloroethene	26.3	24.9	26.8	26.0	3.1	130
Trichlorofluoromethane	25.9	24.8	26.5	25.7	2.7	129
1,2,3-Trichloropropane	18.8	18.3	19.3	18.8	2.2	94.0
Vinyl chloride	24.8	23.2	23.9	24.0	2.7	120
m-Xylene/p-Xylene	24.3	23.9	25.3	24.5	2.4	123
o-Xylene	23.1	22.3	23.4	22.9	2.0	115

[a] Compound found in unfortified garden soil matrix at >5 ng.

TABLE 31

METHOD DETECTION LIMITS AND BOILING POINTS
FOR VOLATILE ORGANICS (ANALYSIS BY METHOD 5041)[a]

Compound	Detection Limit (ng)	Boiling Point (°C)
Chloromethane	58	-24
Bromomethane	26	4
Vinyl chloride	14	-13
Chloroethane	21	13
Methylene chloride	9	40
Acetone	35	56
Carbon disulfide	11	46
1,1-Dichloroethene	14	32
1,1-Dichloroethane	12	57
trans-1,2-Dichloroethene	11	48
Chloroform	11	62
1,2-Dichloroethane	13	83
1,1,1-Trichloroethane	8	74
Carbon tetrachloride	8	77
Bromodichloromethane	11	88
1,1,2,2-Tetrachloroethane**	23	146
1,2-Dichloropropane	12	95
trans-1,3-Dichloropropene	17	112
Trichloroethene	11	87
Dibromochloromethane	21	122
1,1,2-Trichloroethane	26	114
Benzene	26	80
cis-1,3-Dichloropropene	27	112
Bromoform**	26	150
Tetrachloroethene	11	121
Toluene	15	111
Chlorobenzene	15	132
Ethylbenzene**	21	136
Styrene**	46	145
Trichlorofluoromethane	17	24
Iodomethane	9	43
Acrylonitrile	13	78
Dibromomethane	14	97
1,2,3-Trichloropropane**	37	157
total Xylenes**	22	138-144

Footnotes are found on the following page.

* The method detection limit (MDL) is defined in Chapter One. The detection limits cited above were determined according to 40 CFR, Part 136, Appendix B, using standards spiked onto clean VOST tubes. Since clean VOST tubes were used, the values cited above represent the best that the methodology can achieve. The presence of an emissions matrix will affect the ability of the methodology to perform at its optimum level.

** Boiling Point greater than 130°C. Not appropriate for quantitative sampling by Method 0030.

TABLE 32

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (METHOD 5041)

Bromochloromethane	1,4-Difluorobenzene
Acetone	Benzene
Acrylonitrile	Bromodichloromethane
Bromomethane	Bromoform
Carbon disulfide	Carbon tetrachloride
Chloroethane	Chlorodibromomethane
Chloroform	Dibromomethane
Chloromethane	1,2-Dichloropropane
1,1-Dichloroethane	cis-1,3-Dichloropropene
1,2-Dichloroethane	trans-1,3-Dichloropropene
1,2-Dichloroethane-d_4 (surrogate)	1,1,1-Trichloroethane
1,1-Dichloroethene	1,1,2-Trichloroethane
Trichloroethene	
trans-1,2-Dichloroethene	
Iodomethane	
Methylene chloride	
Trichlorofluoromethane	
Vinyl chloride	

Chlorobenzene-d_5
4-Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylenes

TABLE 33

METHOD 0040 - COMPOUNDS DEMONSTRATED TO BE APPLICABLE TO THE METHOD

Compound	Boiling Point (°C)	Condensation Point at 20°C (%)	Estimated Detection Limit[a] (ppm)
Dichlorodifluoromethane	-30	Gas	0.20
Vinyl chloride	-19	Gas	0.11
1,3-Butadiene	-4	Gas	0.90
1,2-Dichloro-1,1,2,2-tetrafluoroethane	4	Gas	0.14
Methyl bromide	4	Gas	0.14
Trichlorofluoromethane	24	88	0.18
1,1-Dichloroethene	31	22	0.07
Methylene chloride	40	44	0.05
1,1,2-Trichloro-trifluoroethane	48	37	0.13
Chloroform	61	21	0.04
1,1,1-Trichloroethane	75	13	0.03
Carbon tetrachloride	77	11	0.03
Benzene	80	10	0.16
Trichloroethene	87	8	0.04
1,2-Dichloropropane	96	5	0.05
Toluene	111	3	0.08
Tetrachloroethene	121	2	0.03

[a] Since this value represents a direct injection (no concentration) from the Tedlar® bag, these values are directly applicable as stack detection limits.

FIGURE 1
GAS CHROMATOGRAM OF VOLATILE ORGANICS

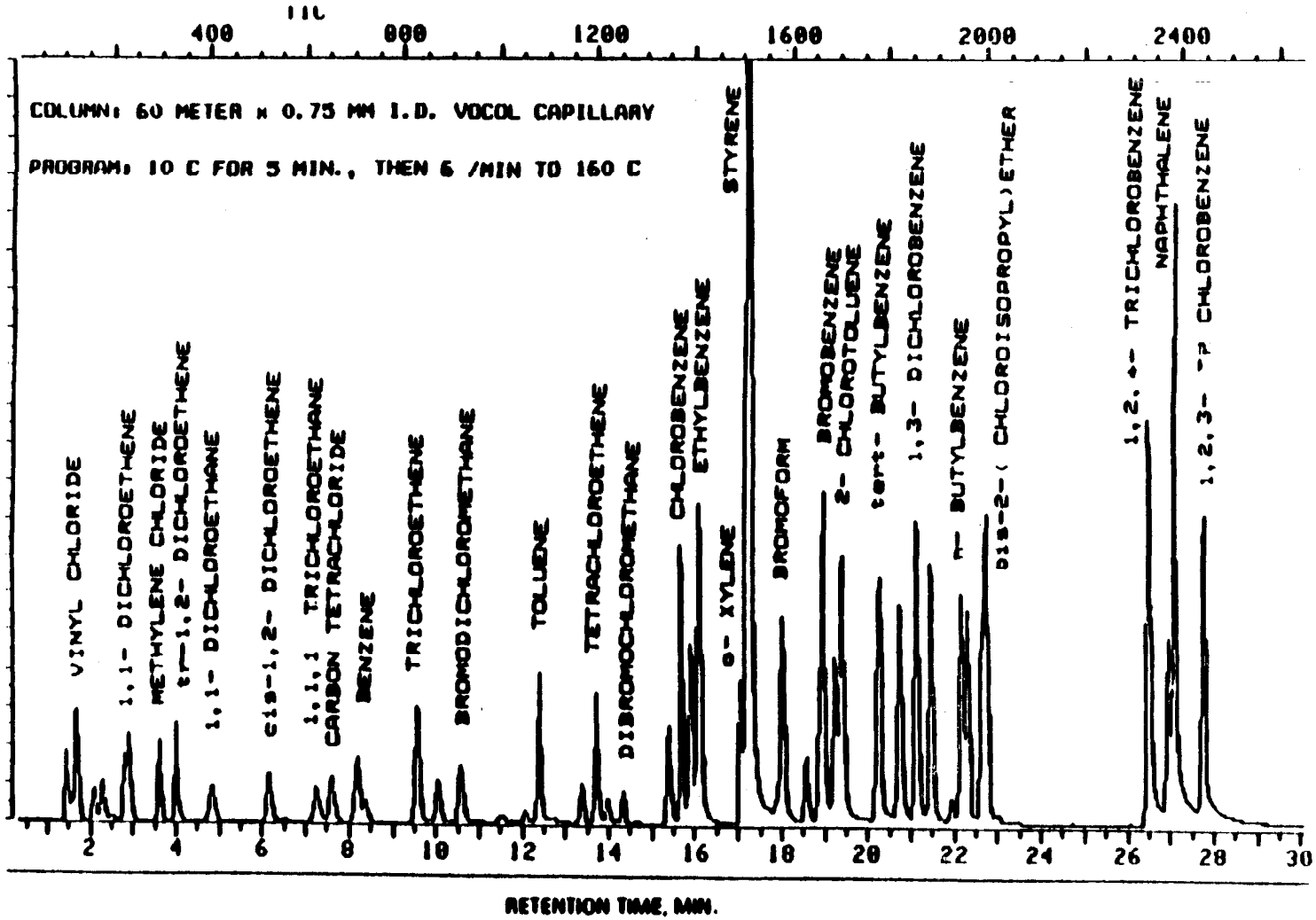


FIGURE 2
GAS CHROMATOGRAM OF VOLATILE ORGANICS

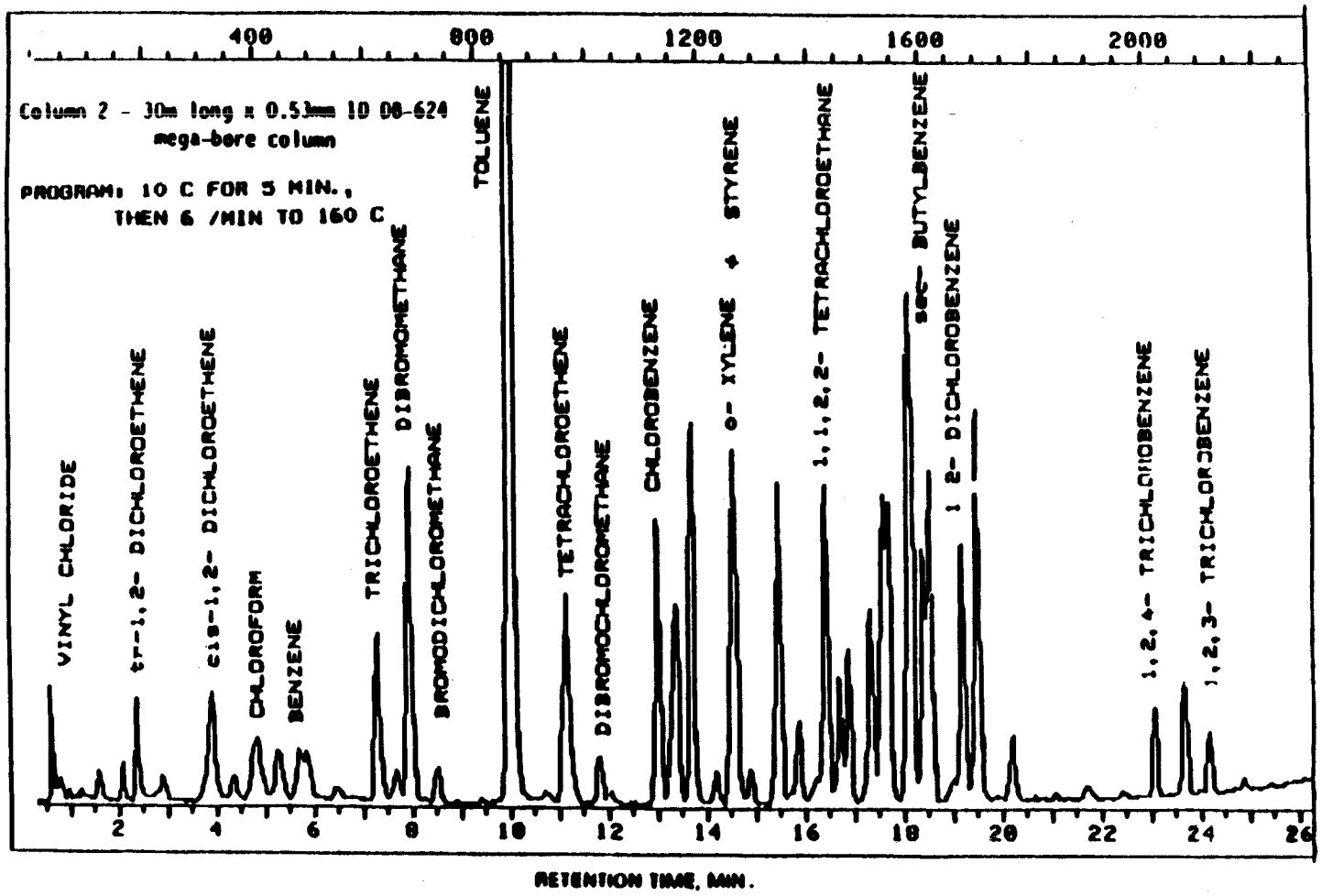


FIGURE 3
GAS CHROMATOGRAM OF VOLATILE ORGANICS

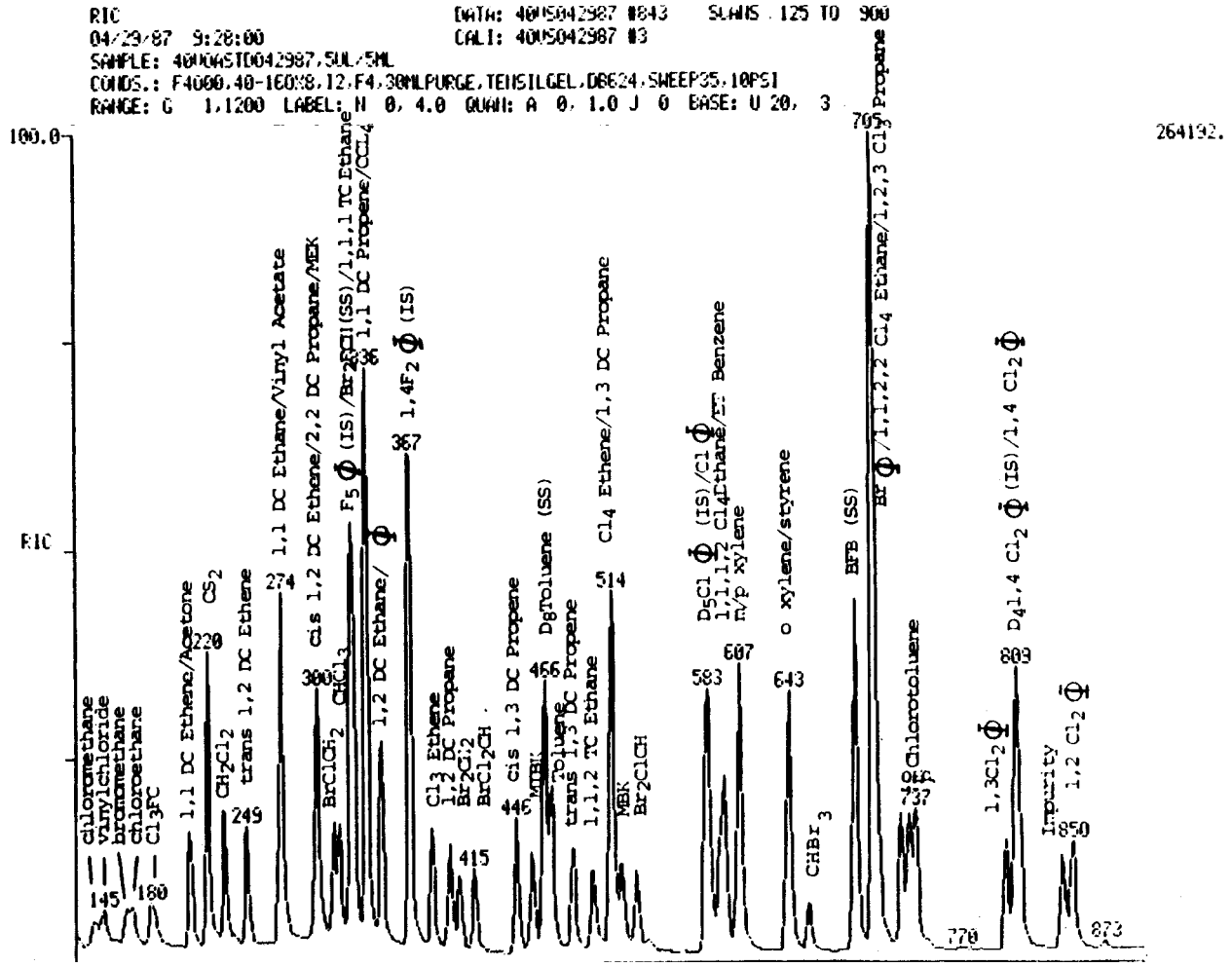
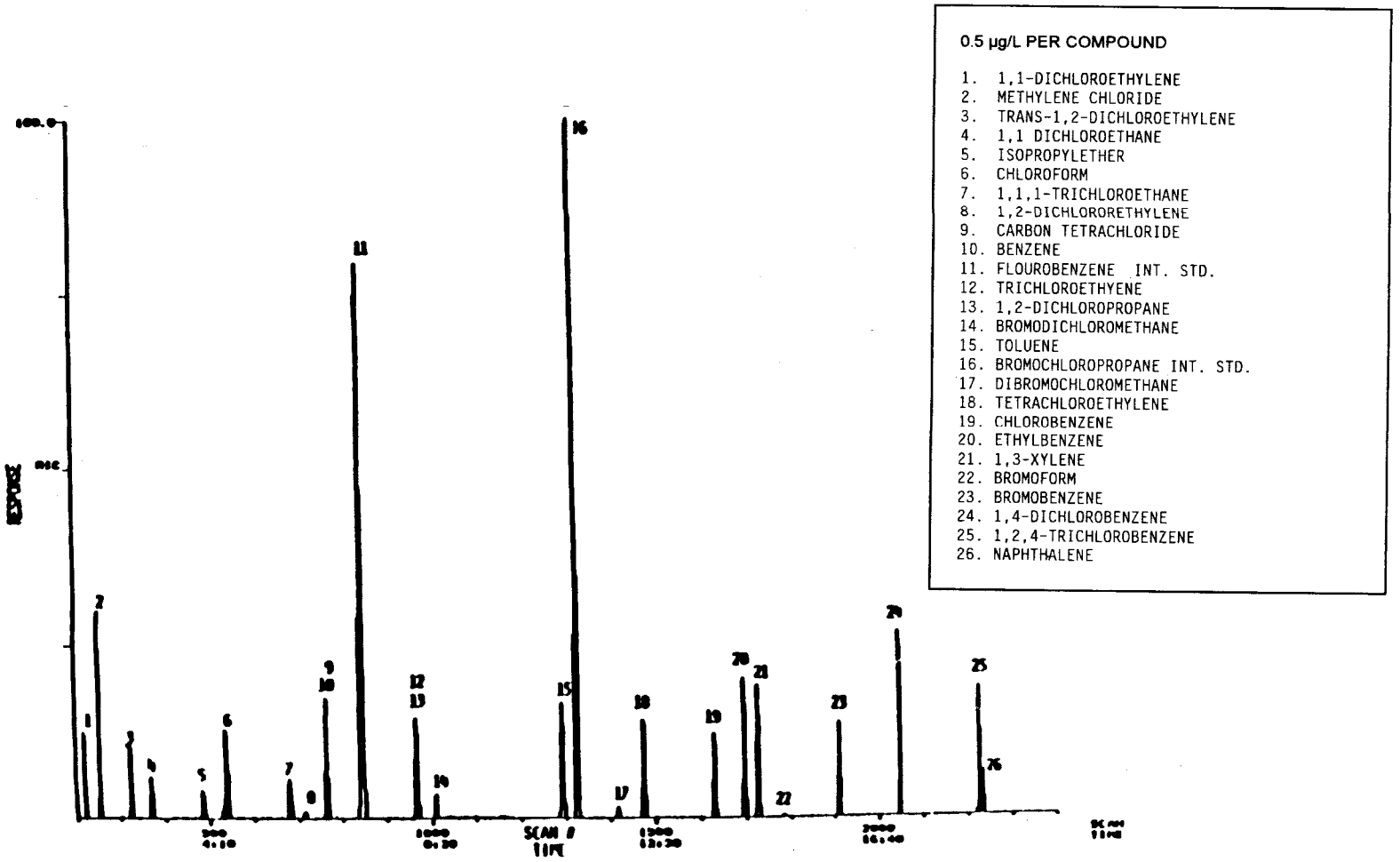
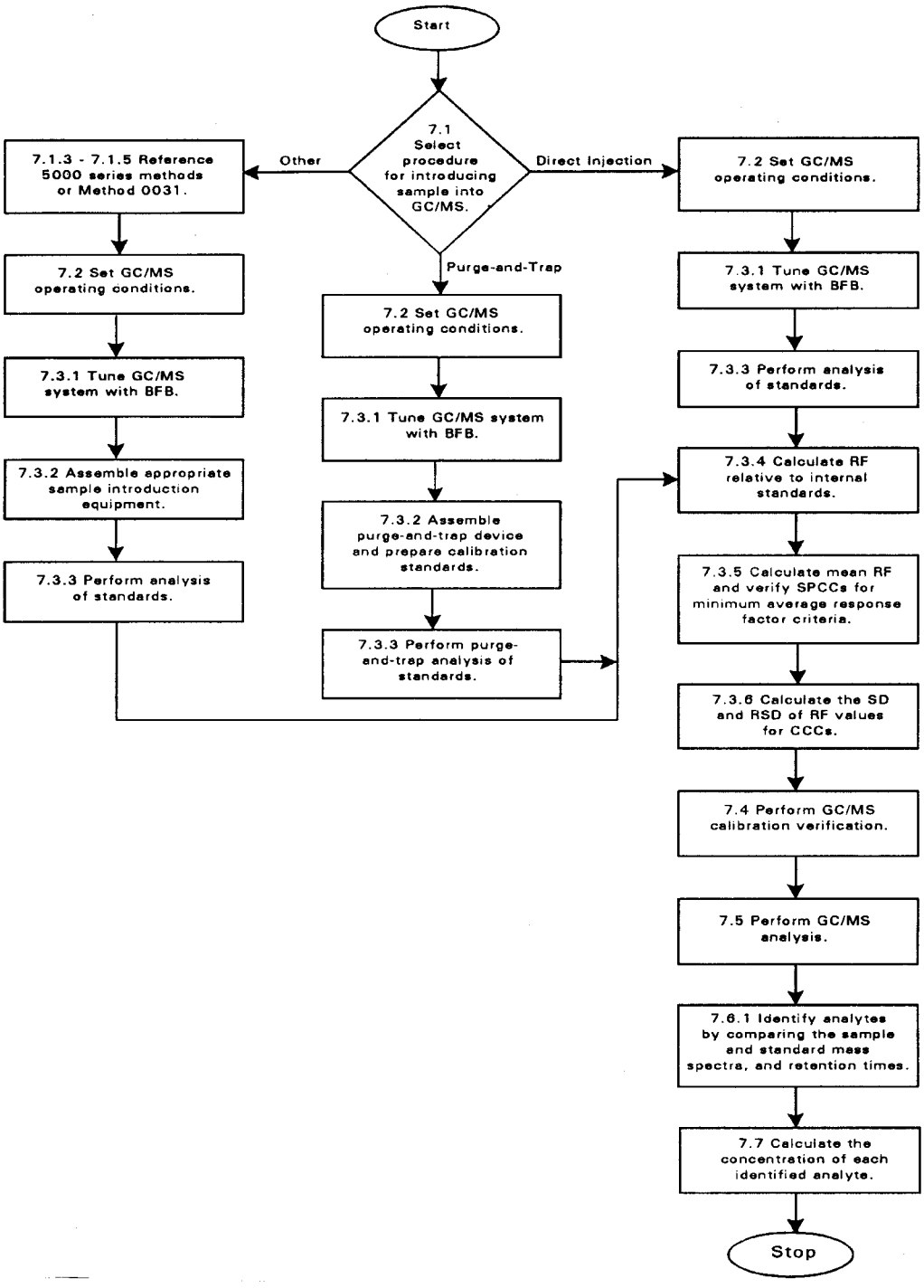


FIGURE 4
GAS CHROMATOGRAM OF TEST MIXTURE




Start
7.1 Select procedure for introducing sample into GC/MS.
Other
Purge-and-Trap
Direct Injection
7.1.3 - 7.1.5 Reference 5000 series methods or Method 0031.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble appropriate sample introduction equipment.
7.3.3 Perform analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble purge-and-trap device and prepare calibration standards.
7.3.3 Perform purge-and-trap analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.3 Perform analysis of standards.
7.3.4 Calculate RF relative to internal standards.
7.3.5 Calculate mean RF and verify SPCCs for minimum average response factor criteria.
7.3.6 Calculate the SD and RSD of RF values for CCCs.
7.4 Perform GC/MS calibration verification.
7.5 Perform GC/MS analysis.
7.6.1 Identify analytes by comparing the sample and standard mass spectra, and retention times.
7.7 Calculate the concentration of each identified analyte.
Stop

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. Direct injection of a sample may be used in limited applications. The following RCRA analytes have been determined by this method:

		Appropriate Preparation Techniques[b]				
Compounds	CAS No[a]	3510	3520	3540/ 3541	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	X
2-Acetylaminofluorene	53-96-3	X	ND	ND	ND	X
1-Acetyl-2-thiourea	591-08-2	LR	ND	ND	ND	LR
Aldrin	309-00-2	X	X	X	X	X
2-Aminoanthraquinone	117-79-3	X	ND	ND	ND	X
Aminoazobenzene	60-09-3	X	ND	ND	ND	X
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	X
3-Amino-9-ethylcarbazole	132-32-1	X	X	ND	ND	ND
Anilazine	101-05-3	X	ND	ND	ND	X
Aniline	62-53-3	X	X	ND	X	X
o-Anisidine	90-04-0	X	ND	ND	ND	X
Anthracene	120-12-7	X	X	X	X	X
Aramite	140-57-8	HS	ND	ND	ND	X
Aroclor 1016	12674-11-2	X	X	X	X	X
Aroclor 1221	11104-28-2	X	X	X	X	X
Aroclor 1232	11141-16-5	X	X	X	X	X
Aroclor 1242	53469-21-9	X	X	X	X	X
Aroclor 1248	12672-29-6	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
Aroclor 1254	11097-69-1	X	X	X	X	X
Aroclor 1260	11096-82-5	X	X	X	X	X
Azinphos-methyl	86-50-0	HS	ND	ND	ND	X
Barban	101-27-9	LR	ND	ND	ND	LR
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	X	X	X	X	X
Benzo(b)fluoranthene	205-99-2	X	X	X	X	X
Benzo(k)fluoranthene	207-08-9	X	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8	X	X	X	X	X
p-Benzoquinone	106-51-4	OE	ND	ND	ND	X
Benzyl alcohol	100-51-6	X	X	ND	X	X
α-BHC	319-84-6	X	X	X	X	X
β-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
γ-BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X
Bis(2-chloroethyl) ether	111-44-4	X	X	X	X	X
Bis(2-chloroisopropyl) ether	39638-32-9	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Bromoxynil	1689-84-5	X	ND	ND	ND	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X
Captafol	2425-06-1	HS	ND	ND	ND	X
Captan	133-06-2	HS	ND	ND	ND	X
Carbaryl	63-25-2	X	ND	ND	ND	X
Carbofuran	1563-66-2	X	ND	ND	ND	X
Carbophenothion	786-19-6	X	ND	ND	ND	X
Chlordane (NOS)	57-74-9	X	X	X	X	X
Chlorfenvinphos	470-90-6	X	ND	ND	ND	X
4-Chloroaniline	106-47-8	X	ND	ND	ND	X
Chlorobenzilate	510-15-6	X	ND	ND	ND	X
5-Chloro-2-methylaniline	95-79-4	X	ND	ND	ND	X
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
3-(Chloromethyl)pyridine hydrochloride	6959-48-4	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	X	X	X	X
2-Chlorophenol	95-57-8	X	X	X	X	X
4-Chloro-1,2-phenylenediamine	95-83-0	X	X	ND	ND	ND
4-Chloro-1,3-phenylenediamine	5131-60-2	X	X	ND	ND	ND
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
Chrysene	218-01-9	X	X	X	X	X
Coumaphos	56-72-4	X	ND	ND	ND	X
p-Cresidine	120-71-8	X	ND	ND	ND	X
Crotoxyphos	7700-17-6	X	ND	ND	ND	X
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5	X	ND	ND	ND	LR
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDE	72-55-9	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	X
Demeton-O	298-03-3	HS	ND	ND	ND	X
Demeton-S	126-75-0	X	ND	ND	ND	X
Diallate (*cis* or *trans*)	2303-16-4	X	ND	ND	ND	X
2,4-Diaminotoluene	95-80-7	DC, OE	ND	ND	ND	X
Dibenz(a,j)acridine	224-42-0	X	ND	ND	ND	X
Dibenz(a,h)anthracene	53-70-3	X	X	X	X	X
Dibenzofuran	132-64-9	X	X	ND	X	X
Dibenzo(a,e)pyrene	192-65-4	ND	ND	ND	ND	X
1,2-Dibromo-3-chloropropane	96-12-8	X	X	ND	ND	ND
Di-n-butyl phthalate	84-74-2	X	X	X	X	X
Dichlone	117-80-6	OE	ND	ND	ND	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	X
1,3-Dichlorobenzene	541-73-1	X	X	X	X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X	X
3,3'-Dichlorobenzidine	91-94-1	X	X	X	X	X
2,4-Dichlorophenol	120-83-2	X	X	X	X	X
2,6-Dichlorophenol	87-65-0	X	ND	ND	ND	X
Dichlorovos	62-73-7	X	ND	ND	ND	X
Dicrotophos	141-66-2	X	ND	ND	ND	X
Dieldrin	60-57-1	X	X	X	X	X
Diethyl phthalate	84-66-2	X	X	X	X	X
Diethylstilbestrol	56-53-1	AW, OS	ND	ND	ND	X
Diethyl sulfate	64-67-5	LR	ND	ND	ND	LR
Dimethoate	60-51-5	HE, HS	ND	ND	ND	X
3,3'-Dimethoxybenzidine	119-90-4	X	ND	ND	ND	LR
Dimethylaminoazobenzene	60-11-7	X	ND	ND	ND	X
7,12-Dimethylbenz(a)-anthracene	57-97-6	CP	ND	ND	ND	CP
3,3'-Dimethylbenzidine	119-93-7	X	ND	ND	ND	X
α,α-Dimethylphenethylamine	122-09-8	ND	ND	ND	ND	X
2,4-Dimethylphenol	105-67-9	X	X	X	X	X
Dimethyl phthalate	131-11-3	X	X	X	X	X
1,2-Dinitrobenzene	528-29-0	X	ND	ND	ND	X
1,3-Dinitrobenzene	99-65-0	X	ND	ND	ND	X
1,4-Dinitrobenzene	100-25-4	HE	ND	ND	ND	X
4,6-Dinitro-2-methylphenol	534-52-1	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
2,4-Dinitrophenol	51-28-5	X	X	X	X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X	X	X	X	X
Dinocap	39300-45-3	CP, HS	ND	ND	ND	CP
Dinoseb	88-85-7	X	ND	ND	ND	X
Diphenylamine	122-39-4	X	X	X	X	X
5,5-Diphenylhydantoin	57-41-0	X	ND	ND	ND	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Disulfoton	298-04-4	X	ND	ND	ND	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
EPN	2104-64-5	X	ND	ND	ND	X
Ethion	563-12-2	X	ND	ND	ND	X
Ethyl carbamate	51-79-6	DC	ND	ND	ND	X
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Famphur	52-85-7	X	ND	ND	ND	X
Fensulfothion	115-90-2	X	ND	ND	ND	X
Fenthion	55-38-9	X	ND	ND	ND	X
Fluchloralin	33245-39-5	X	ND	ND	ND	X
Fluoranthene	206-44-0	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl (surr)	321-60-8	X	X	X	X	X
2-Fluorophenol (surr)	367-12-4	X	X	X	X	X
Heptachlor	76-44-8	X	X	X	X	X
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Hexachlorophene	70-30-4	AW, CP	ND	ND	ND	CP
Hexachloropropene	1888-71-7	X	ND	ND	ND	X
Hexamethylphosphoramide	680-31-9	X	ND	ND	ND	X
Hydroquinone	123-31-9	ND	ND	ND	ND	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isodrin	465-73-6	X	ND	ND	ND	X
Isophorone	78-59-1	X	X	X	X	X
Isosafrole	120-58-1	DC	ND	ND	ND	X
Kepone	143-50-0	X	ND	ND	ND	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
Leptophos	21609-90-5	X	ND	ND	ND	X
Malathion	121-75-5	HS	ND	ND	ND	X
Maleic anhydride	108-31-6	HE	ND	ND	ND	X
Mestranol	72-33-3	X	ND	ND	ND	X
Methapyrilene	91-80-5	X	ND	ND	ND	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
4,4'-Methylenebis (2-chloroaniline)	101-14-4	OE, OS	ND	ND	ND	LR
4,4'-Methylenebis(*N*,*N*-dimethyl-aniline)	101-61-1	X	X	ND	ND	ND
Methyl methanesulfonate	66-27-3	X	ND	ND	ND	X
2-Methylnaphthalene	91-57-6	X	X	ND	X	X
Methyl parathion	298-00-0	X	ND	ND	ND	X
2-Methylphenol	95-48-7	X	ND	ND	ND	X
3-Methylphenol	108-39-4	X	ND	ND	ND	X
4-Methylphenol	106-44-5	X	ND	ND	ND	X
Mevinphos	7786-34-7	X	ND	ND	ND	X
Mexacarbate	315-18-4	HE, HS	ND	ND	ND	X
Mirex	2385-85-5	X	ND	ND	ND	X
Monocrotophos	6923-22-4	HE	ND	ND	ND	X
Naled	300-76-5	X	ND	ND	ND	X
Naphthalene	91-20-3	X	X	X	X	X
1,4-Naphthoquinone	130-15-4	X	ND	ND	ND	X
1-Naphthylamine	134-32-7	OS	ND	ND	ND	X
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
Nicotine	54-11-5	DC	ND	ND	ND	X
5-Nitroacenaphthene	602-87-9	X	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
3-Nitroaniline	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	X
5-Nitro-*o*-anisidine	99-59-2	X	ND	ND	ND	X
Nitrobenzene	98-95-3	X	X	X	X	X
4-Nitrobiphenyl	92-93-3	X	ND	ND	ND	X
Nitrofen	1836-75-5	X	ND	ND	ND	X
2-Nitrophenol	88-75-5	X	X	X	X	X
4-Nitrophenol	100-02-7	X	X	X	X	X
5-Nitro-o-toluidine	99-55-8	X	X	ND	ND	X
Nitroquinoline-1-oxide	56-57-5	X	ND	ND	ND	X
N-Nitrosodi-*n*-butylamine	924-16-3	X	ND	ND	ND	X
N-Nitrosodiethylamine	55-18-5	X	ND	ND	ND	X
N-Nitrosodimethylamine	62-75-9	X	X	X	X	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-*n*-propylamine	621-64-7	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b]				
		3510	3520	3540/ 3541	3550	3580
N-Nitrosomethylethylamine	10595-95-6	X	ND	ND	ND	X
N-Nitrosomorpholine	59-89-2	ND	ND	ND	ND	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
N-Nitrosopyrrolidine	930-55-2	X	ND	ND	ND	X
Octamethyl pyrophosphoramide	152-16-9	LR	ND	ND	ND	LR
4,4'-Oxydianiline	101-80-4	X	ND	ND	ND	X
Parathion	56-38-2	X	X	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenobarbital	50-06-6	X	ND	ND	ND	X
Phenol	108-95-2	DC	X	X	X	X
1,4-Phenylenediamine	106-50-3	X	ND	ND	ND	X
Phorate	298-02-2	X	ND	ND	ND	X
Phosalone	2310-17-0	HS	ND	ND	ND	X
Phosmet	732-11-6	HS	ND	ND	ND	X
Phosphamidon	13171-21-6	HE	ND	ND	ND	X
Phthalic anhydride	85-44-9	CP, HE	ND	ND	ND	CP
2-Picoline (2-Methylpyridine)	109-06-8	X	X	ND	ND	ND
Piperonyl sulfoxide	120-62-7	X	ND	ND	ND	X
Pronamide	23950-58-5	X	ND	ND	ND	X
Propylthiouracil	51-52-5	LR	ND	ND	ND	LR
Pyrene	129-00-0	X	X	X	X	X
Resorcinol	108-46-3	DC, OE	ND	ND	ND	X
Safrole	94-59-7	X	ND	ND	ND	X
Strychnine	57-24-9	AW, OS	ND	ND	ND	X
Sulfallate	95-06-7	X	ND	ND	ND	X
Terbufos	13071-79-9	X	ND	ND	ND	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
Tetrachlorvinphos	961-11-5	X	ND	ND	ND	X
Tetraethyl dithiopyrophosphate	3689-24-5	X	X	ND	ND	ND
Tetraethyl pyrophosphate	107-49-3	X	ND	ND	ND	X
Thionazine	297-97-2	X	ND	ND	ND	X
Thiophenol (Benzenethiol)	108-98-5	X	ND	ND	ND	X
Toluene diisocyanate	584-84-9	HE	ND	ND	ND	X
o-Toluidine	95-53-4	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X

Compounds	CAS No[a]	Appropriate Preparation Techniques[b] 3510	3520	3540/ 3541	3550	3580
Trifluralin	1582-09-8	X	ND	ND	ND	X
2,4,5-Trimethylaniline	137-17-7	X	ND	ND	ND	X
Trimethyl phosphate	512-56-1	HE	ND	ND	ND	X
1,3,5-Trinitrobenzene	99-35-4	X	ND	ND	ND	X
Tris(2,3-dibromopropyl) phosphate	126-72-7	X	ND	ND	ND	LR
Tri-*p*-tolyl phosphate	78-32-0	X	ND	ND	ND	X
O,*O*,*O*-Triethyl phosphorothioate	126-68-1	X	ND	ND	ND	X

[a] Chemical Abstract Service Registry Number
[b] See Sec. 1.2 for other acceptable preparation methods.

KEY TO ANALYTE LIST

AW = Adsorption to walls of glassware during extraction and storage.
CP = Nonreproducible chromatographic performance.
DC = Unfavorable distribution coefficient.
HE = Hydrolysis during extraction accelerated by acidic or basic conditions.
HS = Hydrolysis during storage potential.
LR = Low response.
ND = Not determined.
OE = Oxidation during extraction accelerated by basic conditions.
OS = Oxidation during storage potential.
X = Historically, adequate recovery can be obtained by this technique. However, actual recoveries may vary depending on the extraction efficiency, the number of constituents being analyzed concurrently, and the analytical instrumentation.

1.2 In addition to the sample preparation methods listed in the above analyte list, Method 3535 describes a solid-phase extraction procedure that may be applied to the extraction of semivolatiles from TCLP leachates (see Tables 16 and 17 of this method for performance data). Method 3542 describes sample preparation for semivolatile organic compounds in air sampled by Method 0010 (see Table 11 of this method for surrogate performance data), Method 3545 describes an automated solvent extraction device for semivolatiles in solids (see Table 12 of this method for performance data), Method 3561 describes a supercritical fluid device for the extraction of PAHs from solids (see Tables 13, 14, and 15 of this method for performance data), and Method 3546 provides an extraction procedure employing commercially available microwave equipment to extract semivolatiles while using less solvent and taking less time than procedures such as a Soxhlet extraction (see Tables 19 through 23 of this method for the applicable performance data). (The tabulated data are provided for guidance purposes only.)

1.3 This method can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride (or other suitable solvents provided that the desired performance data can be generated) and are capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic

nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated.

In most cases, this method is not appropriate for the quantitation of multicomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, etc., because of limited sensitivity for those analytes. When these analytes have been identified by another technique, Method 8270 may be appropriate for confirmation of the identification of these analytes when concentration in the extract permits. Refer to Methods 8081 and 8082 for guidance on calibration and quantitation of multicomponent analytes such as the Aroclors, Toxaphene, and Chlordane.

1.4 The following compounds may require special treatment when being determined by this method:

1.4.1 Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.

1.4.2 Under the alkaline conditions of the extraction step from aqueous matrices, α-BHC, γ-BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected to be present.

1.4.3 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

1.4.4 N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.

1.4.5 N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. For this reason, it is acceptable to report the combined result for n-nitrosodiphenylamine and diphenylamine for either of these compounds as a combined concentration.

1.4.6 1,2-Diphenylhydrazine is unstable even at room temperature and readily converts to azobenzene. Given the stability problems, it would be acceptable to calibrate for 1,2-diphenylhydrazine using azobenzene. Under these poor compound separation circumstances the results for either of these compounds should be reported as a combined concentration.

1.4.7 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4.8 Pyridine may perform poorly at the GC injection port temperatures listed in this method. Lowering the injection port temperature may reduce the amount of degradation. However, the analyst must use caution in modifying the injection port temperature, as the performance of other analytes may be adversely affected. Therefore, if pyridine is to be determined in addition to other target analytes, it may be necessary to perform separate analyses. In addition, pyridine may be lost during the evaporative concentration of the sample extract. As a result, many of the extraction methods listed above may yield low recoveries unless great care is exercised during the concentration steps. For this reason, analysts may wish to consider the use of extraction techniques such as pressurized fluid extraction (Method 3545), microwave extraction (Method 3546),

or supercritical fluid extraction, which involve smaller extract volumes, thereby reducing or eliminating the need for evaporative concentration techniques for many applications.

1.4.9 Toluene diisocyanate rapidly hydrolyzes in water (half-life of less than 30 min). Therefore, recoveries of this compound from aqueous matrices should not be expected. In addition, in solid matrices, toluene diisocyanate often reacts with alcohols and amines to produce urethane and ureas and consequently cannot usually coexist in a solution containing these materials.

1.4.10 In addition, analytes in the list provided above are flagged when there are limitations caused by sample preparation and/or chromatographic problems.

1.5 The lower limits of quantitation for this method when determining an individual compound are approximately 660 µg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for ground water samples (see Table 2). Lower limits of quantitation will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector. The lower limits of quantitation listed in Table 2 are provided for guidance and may not always be achievable.

1.6 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.7 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Method 3500) and, if necessary, sample cleanup procedures (refer to Method 3600).

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) equipped with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is

accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using an appropriate calibration curve for the intended application.

2.4 This method includes specific calibration and quality control steps that supersede the general recommendations provided in Method 8000.

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware. Also refer to Method 8000 for a discussion of interferences.

4.2 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

4.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Gas chromatograph/mass spectrometer system

6.1.1 Gas chromatograph -- An analytical system equipped with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.1.2 Column -- 30-m x 0.25-mm ID (or 0.32-mm ID) 0.25, 0.5, or 1-µm film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent). The columns listed in this section were the columns used in developing the method. The listing of these columns in this method is not intended to exclude the use of other columns that may be developed. Laboratories may use these columns or other capillary columns provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

6.1.3 Mass spectrometer

6.1.3.1 Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria as outlined in Sec. 11.3.1.

6.1.3.2 An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. The mass spectrometer must be capable of producing a mass spectrum for DFTPP which meets the criteria as outlined in Sec. 11.3.1

6.1.4 GC/MS interface -- Any GC-to-MS interface may be used that gives acceptable calibration points for each compound of interest and achieves acceptable tuning performance criteria. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.

6.1.5 Data system -- A computer system should be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer should have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software should also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

6.1.6 Guard column (optional) -- (J&W deactivated fused-silica, 0.25-mm ID x 6-m, or equivalent) between the injection port and the analytical column joined with column connectors (Agilent Catalog No. 5062-3556, or equivalent).

6.2 Syringe -- 10-µL.

6.3 Volumetric flasks, Class A -- Appropriate sizes equipped with ground-glass stoppers.

6.4 Balance -- Analytical, capable of weighing 0.0001 g.

6.5 Bottles -- Glass equipped with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 Organic-free reagent water -- All references to water in this method refer to organic-free reagent water.

7.3 Standard solutions

The following sections describe the preparation of stock, intermediate, and working standards for the compounds of interest. This discussion is provided as an example, and other approaches and concentrations of the target compounds may be used, as appropriate for the intended application. See Method 8000 for additional information on the preparation of calibration standards.

7.4 Stock standard solutions (1000 mg/L) -- Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

7.4.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.4.2 Transfer the stock standard solutions into bottles equipped with PTFE-lined screw-caps. Store, protected from light, at #6 EC or as recommended by the standard manufacturer. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.4.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

7.4.4 It is recommended that nitrosamine compounds be placed together in a separate calibration mix and not combined with other calibration mixes. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

7.4.5 Mixes with hydrochloride salts may contain hydrochloric acid, which can cause analytical difficulties. When using a premixed certified standard, consult the manufacturer's instructions for additional guidance.

7.5 Internal standard solutions -- The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} (see Table 5). Other compounds may be used as internal standards as long as the criteria in Sec. 11.3.2 are met.

7.5.1 Dissolve 0.200 g of each compound with a small volume of carbon disulfide. Transfer to a 50-mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/µL. Each 1-mL sample extract undergoing analysis should be spiked with 10 µL of the internal standard solution, resulting in a concentration of 40 ng/µL of each internal standard. Store away from any light source at #6 EC when not in use (-10 EC is recommended). When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

7.5.2 If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, a more dilute internal standard solution may be required. Area counts of the internal standard peaks should be between 50-200% of the area of the target analytes in the mid-point calibration analysis.

7.6 GC/MS tuning standard -- A methylene chloride solution containing 50 ng/µL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/µL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Alternate concentrations may be used to compensate for different injection volumes if the total amount injected is 50 ng or less. Store away from any light source at #6 EC when not in use (-10 EC is recommended). If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, a more dilute tuning solution may be necessary. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

7.7 Calibration standards -- A minimum of five calibration standards should be prepared at different concentrations. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in actual samples but should not exceed the working range of the GC/MS system. Each standard and/or series of calibration standards prepared at a given concentration should contain all the desired project-specific target analytes for which quantitation and quantitative results are to be reported by this method.

7.7.1 It is the intent of EPA that all target analytes for a particular analysis be included in the calibration standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

7.7.2 Each 1-mL aliquot of calibration standard should be spiked with 10 µL of the internal standard solution prior to analysis. All standards should be stored away from any light source at #6 EC when not in use (-10 EC is recommended), and should be freshly prepared once a year, or sooner if check standards indicate a problem. The calibration

verification standard should be prepared, as necessary, and stored at #6 EC. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

7.8 Surrogate standards -- The recommended surrogates are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for instructions on preparing the surrogate solutions.

NOTE: In the presence of samples containing residual chlorine, phenol-d_6 has been known to react to form chlorinated phenolic compounds that are not detected as the original spiked surrogate. Sample preservation precautions outlined in Chapter Four should be used when residual chlorine is known to be present in order to minimize degradation of deuterated phenols or any other susceptible target analyte.

7.8.1 Surrogate standard check -- Determine what the appropriate concentration should be for the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.

NOTE: Method 3561 (SFE Extraction of PAHs) recommends the use of bromobenzene and p-quaterphenyl to better cover the range of PAHs listed in the method.

7.8.2 If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, a more dilute surrogate solution may be necessary.

7.9 Matrix spike and laboratory control standards -- See Method 3500 for instructions on preparing the matrix spike standard. The same standard may be used as the laboratory control standard (LCS) and the spiking solution should be the same source as used for the initial calibration standards to restrict the influence of standard accuracy on the determination of recovery through preparation and analysis.

7.9.1 Matrix spike check -- Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery. It is recommended that this check be done whenever a new matrix spiking solution is prepared.

7.9.2 If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, a more dilute matrix and LCS spiking solution may be necessary.

7.9.3 Some projects may require the spiking of the specific compounds of interest, since the spiking compounds listed in Method 3500 would not be representative of the compounds of interest required for the project. When this occurs, the matrix and LCS spiking standards should be prepared in methanol, with each compound present at a concentration appropriate for the project.

7.10 Solvents -- Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents. All solvents should be pesticide quality or equivalent. Solvents may be degassed prior to use.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes."

8.2 Store the sample extracts at #6 EC, protected from light, in sealed vials (e.g., screw-cap vials or crimp-capped vials) equipped with unpierced PTFE-lined septa.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for specific determinative method QC procedures. Refer to Method 3500 or 5000 for QC procedures to ensure the proper operation of the various sample preparation techniques. If an extract cleanup procedure is performed, refer to Method 3600 for the appropriate QC procedures. Any more specific QC procedures provided in this method will supersede those noted in Methods 8000, 5000, 3500, or 3600.

9.3 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, discussions regarding the instrument QC requirements listed below can be found in the referenced sections of this method:

- The GC/MS must be tuned to meet the recommended DFTPP criteria prior to the initial calibration and for each 12-hr period during which analyses are performed. See Secs. 11.3.1 and 11.4.1 for further details.

- There must be an initial calibration of the GC/MS system as described in Sec. 11.3. In addition, the initial calibration curve should be verified immediately after performing the standard analyses using a second source standard (prepared using standards different from the calibration standards). The suggested acceptance limits for this initial calibration verification analysis are 70 - 130%. Alternative acceptance limits may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results could be used for screening purposes and would be considered estimated values.

- The GC/MS system must meet the calibration verification acceptance criteria in Sec. 11.4, each 12 hrs.

- The RRT of the sample component must fall within the RRT window of the standard component provided in Sec. 11.6.1.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish a demonstration of proficiency.

9.5 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, a method blank must be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the lab should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

9.6 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample when surrogates are used. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.6.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, laboratories may use a matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, then laboratories should use a matrix spike and matrix spike duplicate pair. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.6.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.6.3 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for

evaluating method performance should be developed using the guidance found in Method 8000.

9.7 Surrogate recoveries

If surrogates are used, the laboratory should evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000 for information on evaluating surrogate data and developing and updating surrogate limits. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in an approved project plan.

9.8 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. When any changes are made to the system (e.g., the column is changed, a septum is changed), see the guidance in Method 8000 regarding whether recalibration of the system must take place.

9.9 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10.0 CALIBRATION AND STANDARDIZATION

See Sec 11.3 for information on calibration and standardization.

11.0 PROCEDURE

11.1 Sample preparation

11.1.1 Samples are normally prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Air (particulates and sorbent resin)	3542
Water (including TCLP leachates)	3510, 3520, 3535
Soil/sediment	3540, 3541, 3545, 3546, 3550, 3560, 3561
Waste	3540, 3541, 3545, 3546, 3550, 3560, 3561, 3580

11.1.2 In very limited applications, direct injection of the sample into the GC/MS system with a 10-µL syringe may be appropriate. The quantitation limit is very high (approximately 10,000 µg/L). Therefore, it is only appropriate where concentrations in excess of 10,000 µg/L are expected.

11.2 Extract cleanup -- Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. General guidance for sample extract cleanup is provided in this section and in Method 3600.

Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Analytes of Interest	Methods
Aniline and aniline derivatives	3620
Phenols	3630, 3640, 8041[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides	3610, 3620, 3630, 3640, 3660
PCBs	3620, 3630, 3660, 3665
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620
Petroleum waste	3611, 3650
All base, neutral, and acid priority pollutants	3640

[a] Method 8041 includes a derivatization technique and a GC/ECD analysis, if interferences are encountered on GC/FID.

11.3 Initial calibration

Establish the GC/MS operating conditions, using the following recommendations as guidance.

Mass range:	35-500 amu
Scan time:	#1 sec/scan
Initial temperature:	40 EC, hold for 4 min
Temperature program:	40-320 EC at 10 EC/min
Final temperature:	320 EC, hold until 2 min after benzo[g,h,i]perylene elutes
Injector temperature:	250-300 EC
Transfer line temperature:	250-300 EC
Source temperature:	According to manufacturer's specifications
Injector:	Grob-type, splitless
Injection volume:	1-2 µL
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

Split injection is allowed if the sensitivity of the mass spectrometer is sufficient.

11.3.1 The GC/MS system must be hardware-tuned such that injecting 50 ng or less of DFTPP meets the manufacturer's specified acceptance criteria or as listed in Table 3. The tuning criteria as outlined in Table 3 were developed using quadrupole mass spectrometer instrumentation and it is recognized that other tuning criteria may be more effective depending on the type of instrumentation, e.g., Time-of-Flight, Ion Trap, etc. In

these cases it would be appropriate to follow the manufacturer's tuning instructions or some other consistent tuning criteria. However, no matter which tuning criteria is selected, the system calibration must not begin until the tuning acceptance criteria are met with the sample analyses performed under the same conditions as the calibration standards.

11.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of DFTPP from the instrument manufacturer, the following approach should be used: Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired within 20 scans of the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak or any other discrete peak that does not coelute with DFTPP.

11.3.1.2 Use the DFTPP mass intensity criteria in the manufacturer's instructions as primary tuning acceptance criteria or those in Table 3 as default tuning acceptance criteria if the primary tuning criteria are not available. Alternatively, other documented tuning criteria may be used (e.g. CLP, or Method 625), provided that method performance is not adversely affected. The analyst is always free to choose criteria that are tighter than those included in this method or to use other documented criteria provided they are used consistently throughout the initial calibration, calibration verification, and sample analyses.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

11.3.1.3 The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. (See Method 8081 for the percent breakdown calculation.) Benzidine and pentachlorophenol should be present at their normal responses, and should not exceed a tailing factor of 2 given by the following equation:

$$\text{TailingFactor} = \frac{BC}{AB}$$

Where the peak is defined as follows: AC is the width at 10% height; DE is the height of peak and B is the height at 10% of DE. This equation compares the width of the back half of the peak to the width of the front half of the peak at 10% of the height. (See Figure 1 for an example tailing factor calculation.)

11.3.1.4 If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6 to12 in. of the capillary column. The use of a guard column (Sec. 6.1.6) between the injection port and the analytical column may help prolong analytical column performance life.

11.3.2 The internal standards selected in Sec. 7.5 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion (e.g., for 1,4-dichlorobenzene-d_4, use m/z 150 for quantitation).

11.3.3 Analyze 1-2 µL of each calibration standard (containing the compounds for quantitation and the appropriate surrogates and internal standards) and tabulate the area of the primary ion against concentration for each target analyte (as indicated in Table 1). A set of at least five calibration standards is necessary (see Sec. 7.7 and Method 8000). Alternate injection volumes may be used if the applicable quality control requirements for using this method are met. The injection volume must be the same for all standards and sample extracts. Figure 2 shows a chromatogram of a calibration standard containing base/neutral and acid analytes.

11.3.4 Initial calibration calculations

Calculate response factors (RFs) for each target analyte relative to one of the internal standards (see Table 5) as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

11.3.4.1 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte using the following equations. The RSD should be less than or equal to 20% for each target analyte. It is also recommended that a minimum response factor for the most common target analytes, as noted in Table 4, be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed by this method, some compounds will fail to meet this criteria. For these occasions, it is acknowledged that the failing compounds may not be critical to the specific project and therefore they may be used as qualified data or estimated values for screening purposes. The analyst should also strive to place more emphasis on meeting the calibration criteria for those compounds that are critical project compounds, rather than meeting the criteria for those less important compounds.

$$\text{mean RF} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RF_i = RF for each of the calibration standards
RF = mean RF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5

11.3.4.2 If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure beginning with Sec. 11.3.

11.3.5 Evaluation of retention times -- The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement.

$$RRT = \frac{\text{Retention time of the analyte}}{\text{Retention time of the internal standard}}$$

11.3.6 Linearity of target analytes -- If the RSD of any target analyte is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 11.7.2).

11.3.6.1 If the RSD of any target analyte is greater than 20%, refer to Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed. The average RF should not be used for compounds that have an RSD greater than 20% unless the concentration is reported as estimated.

11.3.6.2 When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

11.3.6.3 Due to the large number of compounds that may be analyzed by this method, some compounds may fail to meet either the 20% RSD, minimum correlation coefficient criteria (0.99), or the acceptance criteria for alternative calibration procedures in Method 8000. Any calibration method described in Method 8000 may be used, but it should be used consistently. It is considered inappropriate once the calibration analyses are completed to select an alternative calibration procedure in order to pass the recommended criteria on a case-by-case basis. If compounds fail to meet these criteria, the associated concentrations may still be determined but they must be reported as estimated. In order to report non-detects, it must be demonstrated that there is adequate sensitivity to detect the failed compounds at the applicable lower quantitation limit.

11.4 GC/MS calibration verification -- Calibration verification consists of three steps that are performed at the beginning of each 12-hr analytical shift.

11.4.1 Prior to the analysis of samples or calibration standards, inject 50 ng or less of the DFTPP standard into the GC/MS system. The resultant mass spectrum for DFTPP must meet the criteria as outlined in Sec. 11.3.1 before sample analysis begins. These criteria must be demonstrated each 12-hr shift during which samples are analyzed.

11.4.2 The initial calibration function for each target analyte should be checked immediately after the first occurrence in the region of the middle of the calibration range with a standard from a source different from that used for the initial calibration. The value determined from the second source check should be within 30% of the expected concentration. An alternative recovery limit may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results could be used for screening purposes and would be considered estimated values.

11.4.3 The initial calibration (Sec. 11.3) for each compound of interest should be verified once every 12 hrs prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard (containing all the compounds for quantitation) at a concentration either near the midpoint concentration for the calibrating range of the GC/MS or near the action level for the project. The results must be compared against the most recent initial calibration curve and should meet the verification acceptance criteria provided in Secs. 11.4.5 through 11.4.7.

NOTE: The DFTPP and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

11.4.4 A method blank should be analyzed prior to sample analyses in order to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Method 8000 for information regarding method blank performance criteria.

11.4.5 Calibration verification standard criteria

11.4.5.1 Each of the most common target analytes in the calibration verification standard should meet the minimum response factors as noted in Table 4. This criteria is particularly important when the common target analytes are also critical project-required compounds. This is the same check that is applied during the initial calibration.

11.4.5.2 If the minimum response factors are not met, the system should be evaluated, and corrective action should be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

11.4.5.3 All target compounds of interest must be evaluated using a 20% criterion. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Method 8000 for guidance on calculating percent difference and drift.

11.4.5.4 If the percent difference or percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid. Due to the large numbers of compounds that may be analyzed by this method, it is expected that some compounds will fail to meet the criterion. If the criterion is not met (i.e., greater than 20% difference or drift) for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when the failed compound is present, the concentrations must be reported as estimated values.

11.4.5.5 Problems similar to those listed under initial calibration could affect the ability to pass the calibration verification standard analysis. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The calibration verification criteria must be met before sample analysis begins.

11.4.5.6 The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve, while the relative percent difference and quadratic methods of calibration do not have this potential bias. When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve (see Method 8000 for additional details). It is not necessary to re-analyze a low concentration standard, rather the data system can recalculate the concentrations as if it were an unknown sample. The recalculated concentration of the low calibration point should be within ± 30% of the standard's true concentration. Other recovery criteria may be applicable depending on the project's data quality objectives and for those situations the minimum quantitation check criteria should be outlined in a laboratory standard operating procedure, or a project-specific Quality Assurance Project Plan. Analytes which do not meet the minimum quantitation calibration re-fitting criteria should be considered "out of control" and corrective action such as redefining the lower limit of quantitation

and/or reporting those "out of control" target analytes as estimated when the concentration is at or near the lowest calibration point may be appropriate.

11.4.6 Internal standard retention time -- The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 sec from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

11.4.7 Internal standard response -- If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

11.5 GC/MS analysis of samples

11.5.1 It is highly recommended that sample extracts be screened on a GC/FID or GC/PID using the same type of capillary column used in the GC/MS system. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

11.5.2 Allow the sample extract to warm to room temperature. Just prior to analysis, add 10 µL of the internal standard solution to the 1 mL of concentrated sample extract obtained from sample preparation.

11.5.3 Inject an aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration (Sec. 11.3). The volume to be injected should include an appropriate concentration that is within the calibration range of base/neutral and acid surrogates using the surrogate solution as noted in Sec. 7.8. The injection volume must be the same volume that was used for the calibration standards.

11.5.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed. Additional internal standard solution must be added to the diluted extract to maintain the same concentration as in the calibration standards (usually 40 ng/µL, or other concentrations as appropriate, if a more sensitive GC/MS system is being used). Secondary ion quantitation should be used only when there are sample interferences with the primary ion.

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times in all samples, spikes, blanks, and standards to effectively check drifting, method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance. Internal standard responses (area counts) must be monitored in all samples, spikes, blanks for similar reasons. If the EICP area for any of the internal standards in samples, spikes and blanks changes by a factor of two (-50% to +100%) from the areas determined in the continuing calibration analyzed that day, corrective action must be taken. The samples, spikes or blanks should be reanalyzed or the data should be qualified.

11.5.4.1 When ions from a compound in the sample saturate the detector, this analysis should be followed by the analysis of an instrument blank consisting of clean solvent. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences. Contamination from one sample to the next on the instrument usually takes place in the syringe. If adequate syringe washes are employed, then carryover from high concentration samples can usually be avoided.

11.5.4.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

11.5.5 The use of selected ion monitoring (SIM) is acceptable for applications requiring quantitation limits below the normal range of electron impact mass spectrometry. However, SIM may provide a lesser degree of confidence in the compound identification, since less mass spectral information is available. Using the primary ion for quantitation and the secondary ions for confirmation set up the collection groups based on their retention times. The selected ions are nominal ions and most compounds have small mass defect, usually less than 0.2 amu, in their spectra. These mass defects should be used in the acquisition table. The dwell time may be automatically calculated by the laboratory's GC/MS software or manually calculated using the following formula. The total scan time should be less than 1,000 msec and produce at least 5 to 10 scans per chromatographic peak. The start and stop times for the SIM groups are determined from the full scan analysis using the formula below:

$$\text{Dwell Time for the Group} = \frac{\text{Scan Time (msec)}}{\text{Total Ions in the Group}}$$

Additional guidance for performing SIM analyses, in particular for PAHs and phenol target analyte compounds, can be found in the most recent CLP semivolatile organic methods statement of work (SOW). See the SIM sections from the following CLP SOW for further details: EPA CLP Organics SOW. (Reference 14)

11.6 Analyte identification

11.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. Compounds are identified when the following criteria are met.

11.6.1.1 The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the

target compound at a compound-specific retention time will be accepted as meeting this criterion.

11.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

11.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.) Use professional judgement in interpretation where interferences are observed.

11.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported (e.g., benzo(b)fluoranthene and benzo(k)fluoranthene).

11.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

11.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 30%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20 and 80%.)

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

11.7 Quantitation

11.7.1 Once a target compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

11.7.1.1 It is highly recommended to use the integration produced by the software if the integration is correct because the software should produce more consistent integrations. However, manual integrations may be necessary when the software does not produce proper integrations because baseline selection is improper; the correct peak is missed; a coelution is integrated; the peak is partially integrated; etc. The analyst is responsible for ensuring that the integration is correct whether performed by the software or done manually.

11.7.1.2 Manual integrations should not be substituted for proper maintenance of the instrument or setup of the method (e.g. retention time updates, integration parameter files, etc). The analyst should seek to minimize manual integration by properly maintaining the instrument, updating retention times, and configuring peak integration parameters.

11.7.2 If the RSD of a compound's response factor is 20% or less, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data (Sec. 11.3.4). See Method 8000 for the equations describing internal standard calibration and either linear or non-linear calibrations.

11.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 11.6.2) should be estimated. The same formula as in Sec. 11.3.4 should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

11.7.4 The resulting concentration should be reported indicating that the value is an estimate. Use the nearest internal standard free of interferences.

11.7.5 Quantitation of multicomponent compounds (e.g., Toxaphene, Aroclors, etc.) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD, for example by using Methods 8081 or 8082. However, this method (8270) may be used to confirm the identification of these compounds, when the concentrations are at least 10 ng/µL in the concentrated sample extract.

11.7.6 Quantitation of multicomponent parameters such as diesel range organics (DROs) and total petroleum hydrocarbons (TPH) using the Method 8270 recommended internal standard quantitation technique is beyond the scope of this method. Typically,

analyses for these parameters are performed using GC/FID or GC with a MS detector capability that is available with Method 8015.

11.7.7 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported (e.g., benzo(b)fluoranthene and benzo(k)fluoranthene).

12.0 DATA ANALYSIS AND CALCULATIONS

See Sec. 11.7 and Method 8000 for information on data analysis and calculations.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Single laboratory initial demonstration of capability data were generated from five replicate measurements using a modified continuous liquid-liquid extractor (Method 3520) with hydrophobic membrane. In this case only a single acid pH extraction was performed using the CLP calibration criteria and the applicable CLP target analytes. These data are presented in Table 6. Laboratories should generate their own acceptance criteria depending on the extraction and instrument conditions. (See Method 8000.)

13.3 Chromatograms from calibration standards analyzed with Day 0 and Day 7 samples were compared to detect possible deterioration of GC performance. These recoveries (using Method 3510 extraction) are presented in Table 7. These data are provided for guidance purposes only.

13.4 Method performance data using Method 3541 (automated Soxhlet extraction) are presented in Tables 8 and 9. Single laboratory accuracy and precision data were obtained for semivolatile organics in a clay soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hour prior to extraction. The spiked samples were then extracted by Method 3541 (Automated Soxhlet). Three extractions were performed and each extract was analyzed by gas chromatography/mass spectrometry following Method 8270. The low recovery of the more volatile compounds is probably due to volatilization losses during equilibration. These data as listed were taken from Reference 7 and are provided for guidance purposes only.

13.5 Surrogate precision and accuracy data are presented in Table 10 from a field dynamic spiking study based on air sampling by Method 0010. The trapping media were prepared for analysis by Method 3542 and subsequently analyzed by this method (8270). These data are provided for guidance purposes only.

13.6 Single laboratory precision and bias data using Method 3545 (pressurized fluid extraction) for semivolatile organic compounds are presented in Table 11. The samples were conditioned spiked samples prepared and certified by a commercial supplier that contained 57 semivolatile organics at three concentrations (250, 2500, and 12,500 µg/kg) on three types of soil (clay, loam and sand). Spiked samples were extracted both by the Dionex Accelerated Solvent Extraction system and by the Perstorp Environmental Soxtec™ (automated Soxhlet). The data in Table 11 represent seven replicate extractions and analyses for each individual sample and were taken from Reference 9. The average recoveries from the three matrices for all analytes and all replicates relative to the automated Soxhlet data are as follows: clay 96.8%, loam 98.7% and sand 102.1%. The average recoveries from the three concentrations also relative to the automated Soxhlet data are as follows: low - 101.2%, mid - 97.2% and high - 99.2%. These data are provided for guidance purposes only.

13.7 Single laboratory precision and bias data using Method 3561 (SFE extraction of PAHs with a variable restrictor and solid trapping material) were obtained for the method analytes by the extraction of two certified reference materials (EC-1, a lake sediment from Environment Canada and HS-3, a marine sediment from the National Science and Engineering Research Council of Canada, both naturally-contaminated with PAHs). The SFE instrument used for these extractions was a Hewlett-Packard Model 7680. Analysis was by GC/MS. Average recoveries from six replicate extractions range from 85 to 148% (overall average of 100%) based on the certified value (or a Soxhlet value if a certified value was unavailable for a specific analyte) for the lake sediment. Average recoveries from three replicate extractions range from 73 to 133% (overall average of 92%) based on the certified value for the marine sediment. The data are found in Tables 12 and 13 and were taken from Reference 10. These data are provided for guidance purposes only.

13.8 Single laboratory precision and accuracy data using Method 3561 (SFE extraction of PAHs with a fixed restrictor and liquid trapping) were obtained for twelve of the method analytes by the extraction of a certified reference material (a soil naturally contaminated with PAHs). The SFE instrument used for these extractions was a Dionex Model 703-M. Analysis was by GC/MS. Average recoveries from four replicate extractions range from 60 to 122% (overall average of 89%) based on the certified value. The instrument conditions that were utilized to extract a 3.4 g sample were as follows: Pressure -- 300 atm; time -- 60 min.; extraction fluid -- CO_2; modifier -- 10% 1:1 (v/v) methanol/methylene chloride; Oven temperature -- 80 EC; Restrictor temperature -- 120 EC; and, trapping fluid -- chloroform (methylene chloride has also been used). The data are found in Table 14 and were taken from Reference 11. These data are provided for guidance purposes only.

13.9 Tables 15 and 16 contain single-laboratory precision and accuracy data for solid-phase extraction of TCLP buffer solutions spiked at two levels and extracted using Method 3535. These data are provided for guidance purposes only.

13.10 Table 17 contains multiple-laboratory data for solid-phase extraction of spiked TCLP soil leachates extracted using Method 3535. These data are provided for guidance purposes only.

13.11 Tables 18 through 22 contain single-laboratory PAH recovery data for microwave extraction of contaminated soils and standard reference materials using Method 3546. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. J. W. Eichelberger, L. E. Harris, and W. L. Budde, W.L., "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

2. P. Olynyk, W. L. Budde, and J. W. Eichelberger, "Method Detection Limit for Methods 624 and 625," unpublished report, October 1980.

3. "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides," Final Report for EPA Contract 68-03-3102.

4. J. A. Burke, "Gas Chromatography for Pesticide Residue Analysis: Some Practical Aspects," Journal of the Association of Official Analytical Chemists (AOAC), 48, 1037, 1965.

5. S. V. Lucas, R. A. Kornfeld, "GC-MS Suitability Testing of RCRA Appendix VIII and Michigan List Analytes," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, February 20, 1987, Contract No. 68-03-3224.

6. T. M. Engel, R. A. Kornfeld, J. S. Warner, and K. D. Andrews, "Screening of Semivolatile Organic Compounds for Extractability and Aqueous Stability by SW-846, Method 3510," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, June 5, 1987, Contract 68-03-3224.

7. V. Lopez-Avila (W. Beckert, Project Officer); "Development of a Soxtec Extraction Procedure for Extraction of Organic Compounds from Soils and Sediments;" U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Las Vegas, NV, October 1991; EPA 600/X-91/140.

8. J. Bursey, R. Merrill, R. McAllister, and J. McGaughey, "Laboratory Validation of VOST and SemiVOST for Halogenated Hydrocarbons from the Clean Air Act Amendments List," Vol. 1 and 2, U.S. Environmental Protection Agency, EPA 600/R-93/123a and b, (NTIS PB 93-227163 and 93-27171), Research Triangle Park, NC, July 1993.

9. B. Richter, J. Ezzell, and D. Felix, "Single Laboratory Method Validation Report: Extraction of Target Compound List/Priority Pollutant List BNAs and Pesticides using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC/MS and GC/ECD," Document 101124, Dionex Corporation, Salt Lake City, UT, June 16, 1994.

10. H. B. Lee, T. E. Peart, R. L. Hong-You, and D. R. Gere, "Supercritical Carbon Dioxide Extraction of Polycyclic Aromatic Hydrocarbons from Sediments," J. Chromatography, A 653 83-91 (1993).

11. S. Warner, "SFE Extraction of PNAs from Solid Matrices Using the Dionex 703M SFE Extractor and a Liquid Trap," EPA Region III, Central Regional Laboratory, 839 Bestgate Road, Annapolis, MD 21401, December 12, 1994.

12. C. Markell, "3M Data Submission to EPA," letter to B. Lesnik, June 27, 1995.

13. USEPA Method 525.2, "Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry," Environmental Monitoring Systems Laboratory, Office of Research and Development, US EPA, Cincinnati, OH, Revision 2.0, March 1995.

14. USEPA, Superfund Analytical Services/Contract Laboratory Program (CLP), Multi-Media, Multi-Concentration Organics Analysis, SOM01.X, Exhibit D - Analytical Methods, "Analytical Method for the Analysis of Semivolatile Organic Compounds," November, 2003

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS IN APPROXIMATE RETENTION TIME ORDER [a]

Compound	Primary Ion	Secondary Ion(s)
2-Picoline	93	66,92
Aniline	93	66,65
Phenol	94	65,66
Bis(2-chloroethyl) ether	93	63,95
2-Chlorophenol	128	64,130
1,3-Dichlorobenzene	146	148,111
1,4-Dichlorobenzene-d_4 (IS)	152	150,115
1,4-Dichlorobenzene	146	148,111
Benzyl alcohol	108	79,77
1,2-Dichlorobenzene	146	148,111
N-Nitrosomethylethylamine	88	42,43,56
Bis(2-chloroisopropyl) ether	45	77,121
Ethyl carbamate	62	44,45,74
Thiophenol (Benzenethiol)	110	66,109,84
Methyl methanesulfonate	80	79,65,95
N-Nitrosodi-n-propylamine	70	42,101,130
Hexachloroethane	117	201,199
Maleic anhydride	54	98,53,44
Nitrobenzene	77	123,65
Isophorone	82	95,138
N-Nitrosodiethylamine	102	42,57,44,56
2-Nitrophenol	139	109,65
2,4-Dimethylphenol	122	107,121
p-Benzoquinone	108	54,82,80
Bis(2-chloroethoxy)methane	93	95,123
Benzoic acid	122	105,77
2,4-Dichlorophenol	162	164,98
Trimethyl phosphate	110	79,95,109,140
Ethyl methanesulfonate	79	109,97,45,65
1,2,4-Trichlorobenzene	180	182,145
Naphthalene-d_8 (IS)	136	68
Naphthalene	128	129,127
Hexachlorobutadiene	225	223,227
Tetraethyl pyrophosphate	99	155,127,81,109
Diethyl sulfate	139	45,59,99,111,125
4-Chloro-3-methylphenol	107	144,142
2-Methylnaphthalene	142	141
2-Methylphenol	107	108,77,79,90
Hexachloropropene	213	211,215,117,106,141
Hexachlorocyclopentadiene	237	235,272
N-Nitrosopyrrolidine	100	41,42,68,69
Acetophenone	105	71,51,120
3/4-Methylphenol[b]	107	108,77,79,90

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
2,4,6-Trichlorophenol	196	198,200
o-Toluidine	106	107,77,51,79
2-Chloronaphthalene	162	127,164
N-Nitrosopiperidine	114	42,55,56,41
1,4-Phenylenediamine	108	80,53,54,52
1-Chloronaphthalene	162	127,164
2-Nitroaniline	65	92,138
5-Chloro-2-methylaniline	106	141,140,77,89
Dimethyl phthalate	163	194,164
Acenaphthylene	152	151,153
2,6-Dinitrotoluene	165	63,89
Phthalic anhydride	104	76,50,148
o-Anisidine	108	80,123,52
3-Nitroaniline	138	108,92
Acenaphthene-d_{10} (IS)	164	162,160
Acenaphthene	154	153,152
2,4-Dinitrophenol	184	63,154
2,6-Dinitrophenol	162	164,126,98,63
4-Chloroaniline	127	129,65,92
Isosafrole	162	131,104,77,51
Dibenzofuran	168	139
2,4-Diaminotoluene	121	122,94,77,104
2,4-Dinitrotoluene	165	63,89
4-Nitrophenol	139	109,65
2-Naphthylamine	143	115,116
1,4-Naphthoquinone	158	104,102,76,50,130
p-Cresidine	122	94,137,77,93
Dichlorovos	109	185,79,145
Diethyl phthalate	149	177,150
Fluorene	166	165,167
2,4,5-Trimethylaniline	120	135,134,91,77
N-Nitrosodi-n-butylamine	84	57,41,116,158
4-Chlorophenyl phenyl ether	204	206,141
Hydroquinone	110	81,53,55
4,6-Dinitro-2-methylphenol	198	51,105
Resorcinol	110	81,82,53,69
N-Nitrosodiphenylamine	169	168,167
Safrole	162	104,77,103,135
Hexamethyl phosphoramide	135	44,179,92,42
3-(Chloromethyl)pyridine hydrochloride	92	127,129,65,39
Diphenylamine	169	168,167
1,2,4,5-Tetrachlorobenzene	216	214,179,108,143,218
1-Naphthylamine	143	115,89,63
1-Acetyl-2-thiourea	118	43,42,76
4-Bromophenyl phenyl ether	248	250,141

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
Toluene diisocyanate	174	145,173,146,132,91
2,4,5-Trichlorophenol	196	198,97,132,99
Hexachlorobenzene	284	142,249
Nicotine	84	133,161,162
Pentachlorophenol	266	264,268
5-Nitro-o-toluidine	152	77,79,106,94
Thionazine	107	96,97,143,79,68
4-Nitroaniline	138	65,108,92,80,39
Phenanthrene-d_{10} (IS)	188	94,80
Phenanthrene	178	179,176
Anthracene	178	176,179
1,4-Dinitrobenzene	168	75,50,76,92,122
Mevinphos	127	192,109,67,164
Naled	109	145,147,301,79,189
1,3-Dinitrobenzene	168	76,50,75,92,122
Diallate (cis or trans)	86	234,43,70
1,2-Dinitrobenzene	168	50,63,74
Diallate (trans or cis)	86	234,43,70
Pentachlorobenzene	250	252,108,248,215,254
5-Nitro-o-anisidine	168	79,52,138,153,77
Pentachloronitrobenzene	237	142,214,249,295,265
4-Nitroquinoline-1-oxide	174	101,128,75,116
Di-n-butyl phthalate	149	150,104
2,3,4,6-Tetrachlorophenol	232	131,230,166,234,168
Dihydrosaffrole	135	64,77
Demeton-O	88	89,60,61,115,171
Fluoranthene	202	101,203
1,3,5-Trinitrobenzene	75	74,213,120,91,63
Dicrotophos	127	67,72,109,193,237
Benzidine	184	92,185
Trifluralin	306	43,264,41,290
Bromoxynil	277	279,88,275,168
Pyrene	202	200,203
Monocrotophos	127	192,67,97,109
Phorate	75	121,97,93,260
Sulfallate	188	88,72,60,44
Demeton-S	88	60,81,89,114,115
Phenacetin	108	180,179,109,137,80
Dimethoate	87	93,125,143,229
Phenobarbital	204	117,232,146,161
Carbofuran	164	149,131,122
Octamethyl pyrophosphoramide	135	44,199,286,153,243
4-Aminobiphenyl	169	168,170,115
Dioxathion	97	125,270,153
Terbufos	231	57,97,153,103

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
α,α-Dimethylphenylamine	58	91,65,134,42
Pronamide	173	175,145,109,147
Aminoazobenzene	197	92,120,65,77
Dichlone	191	163,226,228,135,193
Dinoseb	211	163,147,117,240
Disulfoton	88	97,89,142,186
Fluchloralin	306	63,326,328,264,65
Mexacarbate	165	150,134,164,222
4,4'-Oxydianiline	200	108,171,80,65
Butyl benzyl phthalate	149	91,206
4-Nitrobiphenyl	199	152,141,169,151
Phosphamidon	127	264,72,109,138
2-Cyclohexyl-4,6-Dinitrophenol	231	185,41,193,266
Methyl parathion	109	125,263,79,93
Carbaryl	144	115,116,201
Dimethylaminoazobenzene	225	120,77,105,148,42
Propylthiouracil	170	142,114,83
Benz(a)anthracene	228	229,226
Chrysene-d_{12} (IS)	240	120,236
3,3'-Dichlorobenzidine	252	254,126
Chrysene	228	226,229
Malathion	173	125,127,93,158
Kepone	272	274,237,178,143,270
Fenthion	278	125,109,169,153
Parathion	109	97,291,139,155
Anilazine	239	241,143,178,89
Bis(2-ethylhexyl) phthalate	149	167,279
3,3'-Dimethylbenzidine	212	106,196,180
Carbophenothion	157	97,121,342,159,199
5-Nitroacenaphthene	199	152,169,141,115
Methapyrilene	97	50,191,71
Isodrin	193	66,195,263,265,147
Captan	79	149,77,119,117
Chlorfenvinphos	267	269,323,325,295
Crotoxyphos	127	105,193,166
Phosmet	160	77,93,317,76
EPN	157	169,185,141,323
Tetrachlorvinphos	329	109,331,79,333
Di-n-octyl phthalate	149	167,43
2-Aminoanthraquinone	223	167,195
Barban	222	51,87,224,257,153
Aramite	185	191,319,334,197,321
Benzo(b)fluoranthene	252	253,125
Nitrofen	283	285,202,139,253
Benzo(k)fluoranthene	252	253,125

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
Chlorobenzilate	251	139,253,111,141
Fensulfothion	293	97,308,125,292
Ethion	231	97,153,125,121
Diethylstilbestrol	268	145,107,239,121,159
Famphur	218	125,93,109,217
Tri-p-tolyl phosphate[c]	368	367,107,165,198
Benzo(a)pyrene	252	253,125
Perylene-d_{12} (IS)	264	260,265
7,12-Dimethylbenz(a)anthracene	256	241,239,120
5,5-Diphenylhydantoin	180	104,252,223,209
Captafol	79	77,80,107
Dinocap	69	41,39
Methoxychlor	227	228,152,114,274,212
2-Acetylaminofluorene	181	180,223,152
4,4'-Methylenebis(2-chloroaniline)	231	266,268,140,195
3,3'-Dimethoxybenzidine	244	201,229
3-Methylcholanthrene	268	252,253,126,134,113
Phosalone	182	184,367,121,379
Azinphos-methyl	160	132,93,104,105
Leptophos	171	377,375,77,155,379
Mirex	272	237,274,270,239,235
Tris(2,3-dibromopropyl) phosphate	201	137,119,217,219,199
Dibenz(a,j)acridine	279	280,277,250
Mestranol	277	310,174,147,242
Coumaphos	362	226,210,364,97,109
Indeno(1,2,3-cd)pyrene	276	138,277
Dibenz(a,h)anthracene	278	139,279
Benzo(g,h,i)perylene	276	138,277
1,2:4,5-Dibenzopyrene	302	151,150,300
Strychnine	334	334,335,333
Piperonyl sulfoxide	162	135,105,77
Hexachlorophene	196	198,209,211,406,408
Aldrin	66	263,220
Aroclor 1016	222	260,292
Aroclor 1221	190	224,260
Aroclor 1232	190	224,260
Aroclor 1242	222	256,292
Aroclor 1248	292	362,326
Aroclor 1254	292	362,326
Aroclor 1260	360	362,394
α-BHC	183	181,109
β-BHC	181	183,109
δ-BHC	183	181,109
γ-BHC (Lindane)	183	181,109
4,4'-DDD	235	237,165

TABLE 1
(continued)

Compound	Primary Ion	Secondary Ion(s)
4,4'-DDE	246	248,176
4,4'-DDT	235	237,165
Dieldrin	79	263,279
1,2-Diphenylhydrazine	77	105,182
Endosulfan I	195	339,341
Endosulfan II	337	339,341
Endosulfan sulfate	272	387,422
Endrin	263	82,81
Endrin aldehyde	67	345,250
Endrin ketone	317	67,319
2-Fluorobiphenyl (surr)	172	171
2-Fluorophenol (surr)	112	64
Heptachlor	100	272,274
Heptachlor epoxide	353	355,351
Nitrobenzene-d_5 (surr)	82	128,54
N-Nitrosodimethylamine	42	74,44
Phenol-d_6 (surr)	99	42,71
Terphenyl-d_{14} (surr)	244	122,212
2,4,6-Tribromophenol (surr)	330	332,141
Toxaphene	159	231,233

IS = internal standard
surr = surrogate
[a] The data presented are representative of DB-5 type analytical columns
[b] Compounds cannot be separated for quantitation
[c] Substitute for the non-specific mixture, tricresyl phosphate

TABLE 2

EXAMPLE LOWER LIMITS OF QUANTITATION FOR SEMIVOLATILE ORGANICS

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
Acenaphthene	10	660
Acenaphthylene	10	660
Acetophenone	10	ND
2-Acetylaminofluorene	20	ND
1-Acetyl-2-thiourea	1000	ND
2-Aminoanthraquinone	20	ND
Aminoazobenzene	10	ND
4-Aminobiphenyl	20	ND
Anilazine	100	ND
o-Anisidine	10	ND
Anthracene	10	660
Aramite	20	ND
Azinphos-methyl	100	ND
Barban	200	ND
Benz(a)anthracene	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzoic acid	50	3300
Benzo(g,h,i)perylene	10	660
Benzo(a)pyrene	10	660
p-Benzoquinone	10	ND
Benzyl alcohol	20	1300
Bis(2-chloroethoxy)methane	10	660
Bis(2-chloroethyl) ether	10	660
Bis(2-chloroisopropyl) ether	10	660
4-Bromophenyl phenyl ether	10	660
Bromoxynil	10	ND
Butyl benzyl phthalate	10	660
Captafol	20	ND
Captan	50	ND
Carbaryl	10	ND
Carbofuran	10	ND
Carbophenothion	10	ND
Chlorfenvinphos	20	ND
4-Chloroaniline	20	1300
Chlorobenzilate	10	ND
5-Chloro-2-methylaniline	10	ND
4-Chloro-3-methylphenol	20	1300

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
3-(Chloromethyl)pyridine hydrochloride	100	ND
2-Chloronaphthalene	10	660
2-Chlorophenol	10	660
4-Chlorophenyl phenyl ether	10	660
Chrysene	10	660
Coumaphos	40	ND
p-Cresidine	10	ND
Crotoxyphos	20	ND
2-Cyclohexyl-4,6-dinitrophenol	100	ND
Demeton-O	10	ND
Demeton-S	10	ND
Diallate (cis or trans)	10	ND
Diallate (trans or cis)	10	ND
2,4-Diaminotoluene	20	ND
Dibenz(a,j)acridine	10	ND
Dibenz(a,h)anthracene	10	660
Dibenzofuran	10	660
Dibenzo(a,e)pyrene	10	ND
Di-n-butyl phthalate	10	ND
Dichlone	NA	ND
1,2-Dichlorobenzene	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
3,3'-Dichlorobenzidine	20	1300
2,4-Dichlorophenol	10	660
2,6-Dichlorophenol	10	ND
Dichlorovos	10	ND
Dicrotophos	10	ND
Diethyl phthalate	10	660
Diethylstilbestrol	20	ND
Diethyl sulfate	100	ND
Dimethoate	20	ND
3,3'-Dimethoxybenzidine	100	ND
Dimethylaminoazobenzene	10	ND
7,12-Dimethylbenz(a)anthracene	10	ND
3,3'-Dimethylbenzidine	10	ND
2,4-Dimethylphenol	10	660
Dimethyl phthalate	10	660
1,2-Dinitrobenzene	40	ND

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
1,3-Dinitrobenzene	20	ND
1,4-Dinitrobenzene	40	ND
4,6-Dinitro-2-methylphenol	50	3300
2,4-Dinitrophenol	50	3300
2,4-Dinitrotoluene	10	660
2,6-Dinitrotoluene	10	660
Dinocap	100	ND
Dinoseb	20	ND
5,5-Diphenylhydantoin	20	ND
Di-n-octyl phthalate	10	660
Disulfoton	10	ND
EPN	10	ND
Ethion	10	ND
Ethyl carbamate	50	ND
Bis(2-ethylhexyl) phthalate	10	660
Ethyl methanesulfonate	20	ND
Famphur	20	ND
Fensulfothion	40	ND
Fenthion	10	ND
Fluchloralin	20	ND
Fluoranthene	10	660
Fluorene	10	660
Hexachlorobenzene	10	660
Hexachlorobutadiene	10	660
Hexachlorocyclopentadiene	10	660
Hexachloroethane	10	660
Hexachlorophene	50	ND
Hexachloropropene	10	ND
Hexamethylphosphoramide	20	ND
Indeno(1,2,3-cd)pyrene	10	660
Isodrin	20	ND
Isophorone	10	660
Isosafrole	10	ND
Kepone	20	ND
Leptophos	10	ND
Malathion	50	ND
Mestranol	20	ND
Methapyrilene	100	ND
Methoxychlor	10	ND

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
3-Methylcholanthrene	10	ND
Methyl methanesulfonate	10	ND
2-Methylnaphthalene	10	660
Methyl parathion	10	ND
2-Methylphenol	10	660
3-Methylphenol	10	ND
4-Methylphenol	10	660
Mevinphos	10	ND
Mexacarbate	20	ND
Mirex	10	ND
Monocrotophos	40	ND
Naled	20	ND
Naphthalene	10	660
1,4-Naphthoquinone	10	ND
1-Naphthylamine	10	ND
2-Naphthylamine	10	ND
Nicotine	20	ND
5-Nitroacenaphthene	10	ND
2-Nitroaniline	50	3300
3-Nitroaniline	50	3300
4-Nitroaniline	20	ND
5-Nitro-o-anisidine	10	ND
Nitrobenzene	10	660
4-Nitrobiphenyl	10	ND
Nitrofen	20	ND
2-Nitrophenol	10	660
4-Nitrophenol	50	3300
5-Nitro-o-toluidine	10	ND
4-Nitroquinoline-1-oxide	40	ND
N-Nitrosodi-n-butylamine	10	ND
N-Nitrosodiethylamine	20	ND
N-Nitrosodiphenylamine	10	660
N-Nitroso-di-n-propylamine	10	660
N-Nitrosopiperidine	20	ND
N-Nitrosopyrrolidine	40	ND
Octamethyl pyrophosphoramide	200	ND
4,4'-Oxydianiline	20	ND
Parathion	10	ND
Pentachlorobenzene	10	ND

TABLE 2
(continued)

Compound	Lower Limits of Quantitation[a] Ground water (µg/L)	Low Soil/Sediment[b] (µg/kg)
Pentachloronitrobenzene	20	ND
Pentachlorophenol	50	3300
Phenacetin	20	ND
Phenanthrene	10	660
Phenobarbital	10	ND
Phenol	10	660
1,4-Phenylenediamine	10	ND
Phorate	10	ND
Phosalone	100	ND
Phosmet	40	ND
Phosphamidon	100	ND
Phthalic anhydride	100	ND
2-Picoline	ND	ND
Piperonyl sulfoxide	100	ND
Pronamide	10	ND
Propylthiouracil	100	ND
Pyrene	10	660
Resorcinol	100	ND
Safrole	10	ND
Strychnine	40	ND
Sulfallate	10	ND
Terbufos	20	ND
1,2,4,5-Tetrachlorobenzene	10	ND
2,3,4,6-Tetrachlorophenol	10	ND
Tetrachlorvinphos	20	ND
Tetraethyl pyrophosphate	40	ND
Thionazine	20	ND
Thiophenol (Benzenethiol)	20	ND
o-Toluidine	10	ND
1,2,4-Trichlorobenzene	10	660
2,4,5-Trichlorophenol	10	660
2,4,6-Trichlorophenol	10	660
Trifluralin	10	ND
2,4,5-Trimethylaniline	10	ND
Trimethyl phosphate	10	ND
1,3,5-Trinitrobenzene	10	ND
Tris(2,3-dibromopropyl) phosphate	200	ND
Tri-p-tolyl phosphate(h)	10	ND

TABLE 2
(continued)

[a] Sample lower limits of quantitation are highly matrix-dependent and those listed here are provided for guidance and may not always be achievable.

[b] Lower limits of quantitation listed for soil/sediment are based on wet weight. When data are reported on a dry weight basis, the lower limits will be higher based on the % dry weight of each sample. These lower limits are based on a 30-g sample and gel permeation chromatography cleanup.

ND = Not Determined

NA = Not Applicable

Other Matrices	Factor[c]
High-concentration soil and sludges by ultrasonic extractor	7.5
Non-water miscible waste	75

[c]Lower limit of quantitation = (Lower limit of quantitation for low soil/sediment given above in Table 2) x (Factor)

TABLE 3

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a,b]

Mass	Ion Abundance Criteria
51	10-80% of Base Peak
68	< 2% of mass 69
70	< 2% of mass 69
127	10-80% of Base Peak
197	< 2% of mass 198
198	Base peak, or > 50% of Mass 442
199	5-9% of mass 198
275	10-60% of Base Peak
365	> 1% of mass 198
441	present but < 24% of mass 442
442	Base Peak, or > 50% of mass 198
443	15-24% of mass 442

[a] The majority of the data are taken from Reference 13 (Method 525.2).

[b] The criteria in this table are intended to be used as default criteria for quadrupole instrumentation if optimized manufacturer's operating conditions are not available. Alternate tuning criteria may be employed (e.g., CLP or Method 625), provided that method performance is not adversely affected. See Sec. 11.3.1

TABLE 4

RECOMMENDED MINIMUM RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION USING THE SUGGESTED IONS FROM TABLE 1

Semivolatile Compounds	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800

TABLE 4
(continued)

Semivolatile Compounds	Minimum Response Factor (RF)
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800

TABLE 4
(continued)

Semivolatile Compounds	Minimum Response Factor (RF)
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

TABLE 5

SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-	Dimethyl phthalate
Ethyl methanesulfonate	phenethylamine	2,4-Dinitrophenol
2-Fluorophenol (surr)	2,4-Dimethylphenol	2,4-Dinitrotoluene
Hexachloroethane	Hexachlorobutadiene	2,6-Dinitrotoluene
Methyl methanesulfonate	Isophorone	Fluorene
2-Methylphenol	2-Methylnaphthalene	2-Fluorobiphenyl (surr)
4-Methylphenol	Naphthalene	Hexachlorocyclopentadiene
N-Nitrosodimethylamine	Nitrobenzene	1-Naphthylamine
N-Nitroso-di-n-propylamine	Nitrobenzene-d_8 (surr)	2-Naphthylamine
Phenol	2-Nitrophenol	2-Nitroaniline
Phenol-d_6 (surr)	N-Nitrosodi-n-butylamine	3-Nitroaniline
2-Picoline	N-Nitrosopiperidine	4-Nitroaniline
	1,2,4-Trichlorobenzene	4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetrachlorobenzene
		2,3,4,6-Tetrachlorophenol
		2,4,6-Tribromophenol (surr)
		2,4,6-Trichlorophenol
		2,4,5-Trichlorophenol

(surr) = surrogate

TABLE 5
(continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
Fluoranthene	p-Dimethyl aminoazobenzene	7,12-Dimethylbenz(a) anthracene
Hexachlorobenzene	Pyrene	Di-n-octyl phthalate
N-Nitrosodiphenylamine	Terphenyl-d_{14} (surr)	Indeno(1,2,3-cd) pyrene
Pentachlorophenol		3-Methylcholanthrene
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr) = surrogate

TABLE 6

EXAMPLE SINGLE LABORATORY PERFORMANCE DATA[a]

Compound	Test conc. (µg/L)	x of 5 replicates (µg/L)	% Recovery of Avg.
Acenaphthene	50	46.7	93.4
Acenaphthylene	50	46.1	92.2
Aniline	50	8.3	16.7
Anthracene	50	48.4	96.8
Benzoic acid	50	43.7	87.4
Benz(a)anthracene	50	49.6	99.2
Benzo(b)fluoranthene	50	49.8	99.6
Benzo(k)fluoranthene	50	50.6	101
Benzo(a)pyrene	50	47.7	95.5
Benzo(g,h,i)perylene	50	52.6	105
Benzyl alcohol	50	44.4	88.8
Bis(2-chloroethyl) ether	50	44.2	88.4
Bis(2-chloroethoxy)methane	50	46.6	93.1
Bis(2-chloroisopropyl) ether	50	43.4	86.8
Bis(2-ethylhexyl) phthalate	50	50.2	100
4-Bromophenyl phenyl ether	50	48.6	97.2
Butyl benzyl phthalate	50	49.6	99.3
Carbazole	50	52.1	104
2-Chloroaniline	50	38.9	77.7
4-Chloro-3-methylphenol	50	47.3	94.6
2-Chloronaphthalene	50	45.3	90.8
2-Chlorophenol	50	43.1	86.2
4-Chlorophenyl phenyl ether	50	47.3	94.6
Chrysene	50	50.3	101
Dibenzofuran	50	47.4	94.7
Dibenz(a,h)anthracene	50	51.6	103
Di-n-butyl phthalate	50	50.5	101
1,2-Dichlorobenzene	50	35.8	71.6
1,3-Dichlorobenzene	50	33.3	66.7
1,4-Dichlorobenzene	50	34.4	68.7
3,3'-Dichlorobenzidine	50	32.0	64.0
2,4-Dichlorophenol	50	47.4	94.8
Diethyl phthalate	50	50.0	99.9
Dimethyl phthalate	50	48.5	97.0
2,4-Dimethylphenol	50	31.2	62.3
4,6-Dinitro-2-methylphenol	50	57.6	115
2,4-Dinitrophenol	50	58.7	117
2,4-Dinitrotoluene	50	51.3	103

TABLE 6
(continued)

Compound	Test conc. (µg/L)	x of 5 replicates (µg/L)	% Recovery of Avg.
2,6-Dinitrotoluene	50	50.2	100
Di-n-octyl phthalate	50	51.1	102
Fluoranthene	50	51.0	102
Fluorene	50	48.5	97.0
Hexachlorobenzene	50	49.0	97.9
Hexachlorobutadiene	50	34.7	69.5
Hexachlorocyclopentadiene	50	1.9	3.8
Hexachloroethane	50	29.9	58.8
Indeno(1,2,3-cd)pyrene	50	51.7	103
Isophorone	50	47.1	94.3
2-Methylnaphthalene	50	44.7	89.4
2-Methylphenol	50	41.7	83.4
4-Methylphenol	50	42.6	85.2
Naphthalene	50	43.4	86.8
2-Nitroaniline	50	48.4	96.7
3-Nitroaniline	50	46.8	93.6
4-Nitroaniline	50	56.1	112
Nitrobenzene	50	47.1	94.1
2-Nitrophenol	50	47.3	94.6
4-Nitrophenol	50	55.4	111
N-Nitrosodiphenylamine	50	46.7	93.4
N-Nitroso-di-propylamine	50	44.6	89.3
Pentachlorophenol	50	56.9	114
Phenanthrene	50	49.7	99.4
Phenol	50	40.9	81.8
Pyrene	50	49.2	98.4
1,2,4-Trichlorobenzene	50	39.1	78.2
2,4,5-Trichlorophenol	50	47.7	95.4
2,4,6-Trichlorophenol	50	49.2	98.4

x = Average recovery for five initial demonstration of capability measurements, in µg/L

[a] Extraction using acidic pH only with a modified continuous liquid-liquid extractor with hydrophobic membrane according to Method 3520. These values are for guidance only. Appropriate derivation of acceptance criteria for similar extraction conditions may result in much different recovery ranges. See Method 8000 for information on developing and updating acceptance criteria for method performance.

TABLE 7

EXTRACTION EFFICIENCY AND AQUEOUS STABILITY RESULTS

	Percent Recovery, Day 0		Percent Recovery, Day 7	
Compound	Mean	RSD	Mean	RSD
3-Amino-9-ethylcarbazole	80	8	73	3
4-Chloro-1,2-phenylenediamine	91	1	108	4
4-Chloro-1,3-phenylenediamine	84	3	70	3
1,2-Dibromo-3-chloropropane	97	2	98	5
Dinoseb	99	3	97	6
Parathion	100	2	103	4
4,4'-Methylenebis(N,N-dimethylaniline)	108	4	90	4
5-Nitro-o-toluidine	99	10	93	4
2-Picoline	80	4	83	4
Tetraethyl dithiopyrophosphate	92	7	70	1

Data taken from Reference 6.

TABLE 8

MEAN PERCENT RECOVERIES AND PERCENT RSD VALUES FOR SEMIVOLATILE ORGANIC FROM SPIKED CLAY SOIL AND TOPSOIL BY AUTOMATED SOXHLET EXTRACTION (METHOD 3541) WITH HEXANE-ACETONE (1:1)[a]

	Clay Soil		Topsoil	
Compound	Mean Recovery	RSD	Mean Recovery	RSD
1,3-Dichlorobenzene	0	--	0	--
1,2-Dichlorobenzene	0	--	0	--
Nitrobenzene	0	--	0	--
Benzal chloride	0	--	0	--
Benzotrichloride	0	--	0	--
4-Chloro-2-nitrotoluene	0	--	0	--
Hexachlorocyclopentadiene	4.1	15	7.8	23
2,4-Dichloronitrobenzene	35.2	7.6	21.2	15
3,4-Dichloronitrobenzene	34.9	15	20.4	11
Pentachlorobenzene	13.7	7.3	14.8	13
2,3,4,5-Tetrachloronitrobenzene	55.9	6.7	50.4	6.0
Benefin	62.6	4.8	62.7	2.9
alpha-BHC	58.2	7.3	54.8	4.8
Hexachlorobenzene	26.9	13	25.1	5.7
delta-BHC	95.8	4.6	99.2	1.3
Heptachlor	46.9	9.2	49.1	6.3
Aldrin	97.7	12	102	7.4
Isopropalin	102	4.3	105	2.3
Heptachlor epoxide	90.4	4.4	93.6	2.4
trans-Chlordane	90.1	4.5	95.0	2.3
Endosulfan I	96.3	4.4	101	2.2
Dieldrin	129	4.7	104	1.9
2,5-Dichlorophenyl-4-nitrophenyl ether	110	4.1	112	2.1
Endrin	102	4.5	106	3.7
Endosulfan II	104	4.1	105	0.4
p,p'-DDT	134	2.1	111	2.0
2,3,6-Trichlorophenyl-4'-nitrophenyl ether	110	4.8	110	2.8
2,3,4-Trichlorophenyl-4'-nitrophenyl ether	112	4.4	112	3.3
Mirex	104	5.3	108	2.2

[a] The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g; the spiking concentration was 500 ng/g, except for the surrogate compounds at 1000 ng/g, 2,5-Dichlorophenyl-4-nitrophenyl ether, 2,3,6-Trichlorophenyl-4-nitrophenyl ether, and 2,3,4-Trichlorophenyl-4-nitrophenyl ether at 1500 ng/g, Nitrobenzene at 2000 ng/g, and 1,3-Dichlorobenzene and 1,2-Dichlorobenzene at 5000 ng/g.

TABLE 9

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR THE EXTRACTION OF SEMIVOLATILE ORGANICS FROM SPIKED CLAY BY AUTOMATED SOXHLET (METHOD 3541)[a]

Compound	Mean Recovery	RSD
Phenol	47.8	5.6
Bis(2-chloroethyl)ether	25.4	13
2-Chlorophenol	42.7	4.3
Benzyl alcohol	55.9	7.2
2-Methylphenol	17.6	6.6
Bis(2-chloroisopropyl)ether	15.0	15
4-Methylphenol	23.4	6.7
N-Nitroso-di-n-propylamine	41.4	6.2
Nitrobenzene	28.2	7.7
Isophorone	56.1	4.2
2-Nitrophenol	36.0	6.5
2,4-Dimethylphenol	50.1	5.7
Benzoic acid	40.6	7.7
Bis(2-chloroethoxy)methane	44.1	3.0
2,4-Dichlorophenol	55.6	4.6
1,2,4-Trichlorobenzene	18.1	31
Naphthalene	26.2	15
4-Chloroaniline	55.7	12
4-Chloro-3-methylphenol	65.1	5.1
2-Methylnaphthalene	47.0	8.6
Hexachlorocyclopentadiene	19.3	19
2,4,6-Trichlorophenol	70.2	6.3
2,4,5-Trichlorophenol	26.8	2.9
2-Chloronaphthalene	61.2	6.0
2-Nitroaniline	73.8	6.0
Dimethyl phthalate	74.6	5.2
Acenaphthylene	71.6	5.7
3-Nitroaniline	77.6	5.3
Acenaphthene	79.2	4.0
2,4-Dinitrophenol	91.9	8.9
4-Nitrophenol	62.9	16
Dibenzofuran	82.1	5.9
2,4-Dinitrotoluene	84.2	5.4
2,6-Dinitrotoluene	68.3	5.8

Compound	Mean Recovery	RSD
Diethyl phthalate	74.9	5.4
4-Chlorophenyl-phenyl ether	67.2	3.2
Fluorene	82.1	3.4
4-Nitroaniline	79.0	7.9
4,6-Dinitro-2-methylphenol	63.4	6.8
N-Nitrosodiphenylamine	77.0	3.4
4-Bromophenyl-phenyl ether	62.4	3.0
Hexachlorobenzene	72.6	3.7
Pentachlorophenol	62.7	6.1
Phenanthrene	83.9	5.4
Anthracene	96.3	3.9
Di-n-butyl phthalate	78.3	40
Fluoranthene	87.7	6.9
Pyrene	102	0.8
Butyl benzyl phthalate	66.3	5.2
3,3'-Dichlorobenzidine	25.2	11
Benzo(a)anthracene	73.4	3.8
Bis(2-ethylhexyl) phthalate	77.2	4.8
Chrysene	76.2	4.4
Di-n-octyl phthalate	83.1	4.8
Benzo(b)fluoranthene	82.7	5.0
Benzo(k)fluoranthene	71.7	4.1
Benzo(a)pyrene	71.7	4.1
Indeno(1,2,3-cd)pyrene	72.2	4.3
Dibenz(a,h)anthracene	66.7	6.3
Benzo(g,h,i)perylene	63.9	8.0
1,2-Dichlorobenzene	0	--
1,3-Dichlorobenzene	0	--
1,4-Dichlorobenzene	0	--
Hexachloroethane	0	--
Hexachlorobutadiene	0	--

[a] Number of determinations was three. The operating conditions for the Soxtec apparatus were as follows: immersion time 45 min; extraction time 45 min; the sample size was 10 g clay soil; the spike concentration was 6 mg/kg per compound. The sample was allowed to equilibrate 1 hour after spiking.

Data taken from Reference 7.

TABLE 10

PRECISION AND BIAS VALUES FOR METHOD 3542[1]

Compound	Mean Recovery	Standard Deviation	% RSD
2-Fluorophenol	74.6	28.6	38.3
Phenol-d_5	77.8	27.7	35.6
Nitrobenzene-d_5	65.6	32.5	49.6
2-Fluorobiphenyl	75.9	30.3	39.9
2,4,6-Tribromophenol	67.0	34.0	50.7
Terphenyl-d_{14}	78.6	32.4	41.3

[1] The surrogate values shown in Table 10 represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

TABLE 11

PRESSURIZED FLUID EXTRACTION (METHOD 3545) RECOVERY VALUES
AS PERCENT OF SOXTEC™

	Clay			Loam			Sand			Mean
Compound	Low	Mid	High	Low	Mid	High	Low	Mid	High	Rec.
Phenol	93.3	78.7	135.9	73.9	82.8	124.6	108.8	130.6	89.7	102.0
Bis(2-chloroethyl) ether	102.1	85.1	109.1	96.0	88.0	103.6	122.3	119.9	90.8	101.9
2-Chlorophenol	100.8	82.6	115.0	93.8	88.9	111.1	115.0	115.3	91.9	101.6
1,3-Dichlorobenzene	127.7	129.7	110.0	*364.2	129.9	119.0	*241.3	*163.7	107.1	120.6
1,4-Dichlorobenzene	127.9	127.0	110.5	*365.9	127.8	116.4	*309.6	*164.1	105.8	119.2
1,2-Dichlorobenzene	116.8	115.8	101.3	*159.2	113.4	105.5	*189.3	134.0	100.4	112.5
2-Methylphenol	98.9	82.1	119.7	87.6	89.4	111.0	133.2	128.0	92.1	104.7
Bis(2-chloroisopropyl)ether	109.4	71.5	108.0	81.8	81.0	88.6	118.1	148.3	94.8	100.2
o-Toluidine	100.0	89.7	117.2	100.0	*152.5	120.3	100.0	*199.5	102.7	110.3
N-Nitroso-di-n-propylamine	103.0	79.1	107.7	83.9	88.1	96.2	109.9	123.3	91.4	98.1
Hexachloroethane	97.1	125.1	111.0	*245.4	117.1	128.1	*566.7	147.9	103.7	118.6
Nitrobenzene	104.8	82.4	106.6	86.8	84.6	101.7	119.7	122.1	93.3	100.2
Isophorone	100.0	86.4	98.2	87.1	87.5	109.7	135.5	118.4	92.7	101.7
2,4-Dimethylphenol	100.0	104.5	140.0	100.0	114.4	123.1	100.0	*180.6	96.3	109.8
2-Nitrophenol	80.7	80.5	107.9	91.4	86.7	103.2	122.1	107.1	87.0	96.3
Bis(chloroethoxy)methane	94.4	80.6	94.7	86.5	84.4	99.6	130.6	110.7	93.2	97.2
2,4-Dichlorophenol	88.9	87.8	111.4	85.9	87.6	103.5	123.3	107.0	92.1	98.6
1,2,4-Trichlorobenzene	98.0	97.8	98.8	123.0	93.7	94.5	137.0	99.4	95.3	104.2
Naphthalene	101.7	97.2	123.6	113.2	102.9	129.5	*174.5	114.0	89.8	106.1
4-Chloroaniline	100.0	*150.2	*162.4	100.0	125.5	*263.6	100.0	*250.8	114.9	108.1
Hexachlorobutadiene	101.1	98.7	102.2	124.1	90.3	98.0	134.9	96.1	96.8	104.7
4-Chloro-3-methylphenol	90.4	80.2	114.7	79.0	85.2	109.8	131.6	116.2	90.1	99.7
2-Methylnaphthalene	93.2	89.9	94.6	104.1	92.2	105.9	146.2	99.1	93.3	102.1
Hexachlorocyclopentadiene	100.0	100.0	0.0	100.0	100.0	6.8	100.0	100.0	*238.3	75.8
2,4,6-Trichlorophenol	94.6	90.0	112.0	84.2	91.2	103.6	101.6	95.9	89.8	95.9
2,4,5-Trichlorophenol	84.4	91.9	109.6	96.1	80.7	103.6	108.9	83.9	87.9	94.1
2-Chloronaphthalene	100.0	91.3	93.6	97.6	93.4	98.3	106.8	93.0	92.0	96.2
2-Nitroaniline	90.0	83.4	97.4	71.3	88.4	89.9	112.1	113.3	87.7	92.6
2,6-Dinitrotoluene	83.1	90.6	91.6	86.4	90.6	90.3	104.3	84.7	90.9	90.3
Acenaphthylene	104.9	95.9	100.5	99.0	97.9	108.8	118.5	97.8	92.0	101.7
3-Nitroaniline	*224.0	115.6	97.6	100.0	111.8	107.8	0.0	111.7	99.0	92.9
Acenaphthene	102.1	92.6	97.6	97.2	96.9	104.4	114.2	92.0	89.0	98.4
4-Nitrophenol	0.0	93.2	121.5	18.1	87.1	116.6	69.1	90.5	84.5	75.6
2,4-Dinitrotoluene	73.9	91.9	100.2	84.7	93.8	98.9	100.9	84.3	87.3	90.7

TABLE 11
(continued)

Compound	Clay			Loam			Sand			Mean
	Low	Mid	High	Low	Mid	High	Low	Mid	High	Rec.
Dibenzofuran	89.5	91.7	109.3	98.5	92.2	111.4	113.8	92.7	90.4	98.8
4-Chlorophenyl phenyl ether	83.0	94.5	98.7	95.7	94.3	94.2	111.4	87.7	90.3	94.4
Fluorene	85.2	94.9	89.2	102.0	95.5	93.8	121.3	85.7	90.9	95.4
4-Nitroaniline	77.8	114.8	94.5	129.6	103.6	95.4	*154.1	89.3	87.5	99.1
N-Nitrosodiphenylamine	82.6	96.7	93.8	92.9	93.4	116.4	97.5	110.9	86.7	96.8
4-Bromophenyl phenyl ether	85.6	92.9	92.8	91.1	107.6	89.4	118.0	97.5	87.1	95.8
Hexachlorobenzene	95.4	91.7	92.3	95.4	93.6	83.7	106.8	94.3	90.0	93.7
Pentachlorophenol	68.2	85.9	107.7	53.2	89.8	88.1	96.6	59.8	81.3	81.2
Phenanthrene	92.1	93.7	93.3	100.0	97.8	113.3	124.4	101.0	89.9	100.6
Anthracene	101.6	95.0	93.5	92.5	101.8	118.4	123.0	94.5	90.6	101.2
Carbazole	94.4	99.3	96.6	105.5	96.7	111.4	115.7	83.2	88.9	99.1
Fluoranthene	109.9	101.4	94.3	111.6	96.6	109.6	123.2	85.4	92.7	102.7
Pyrene	106.5	105.8	107.6	116.7	90.7	127.5	103.4	95.5	93.2	105.2
3,3'-Dichlorobenzidine	100.0	*492.3	131.4	100.0	*217.6	*167.6	100.0	*748.8	100.0	116.5
Benzo(a)anthracene	98.1	107.0	98.4	119.3	98.6	104.0	105.0	93.4	89.3	101.5
Chrysene	100.0	108.5	100.2	116.8	93.0	117.0	106.7	93.6	90.2	102.9
Benzo(b)fluoranthene	106.6	109.9	75.6	121.7	100.7	93.9	106.9	81.9	93.6	99.0
Benzo(k)fluoranthene	102.4	105.2	88.4	125.5	99.4	95.1	144.7	89.2	78.1	103.1
Benzo(a)pyrene	107.9	105.5	80.8	122.3	97.7	104.6	101.7	86.2	92.0	99.9
Indeno(1,2,3-cd)pyrene	95.1	105.7	93.8	126.0	105.2	90.4	133.6	82.6	91.9	102.7
Dibenz(a,h)anthracene	85.0	102.6	82.0	118.8	100.7	91.9	142.3	71.0	93.1	98.6
Benzo(g,h,i)perylene	98.0	0.0	81.2	0.0	33.6	78.6	128.7	83.0	94.2	66.4
Mean	95.1	94.3	101.0	95.5	96.5	104.1	113.0	100.9	92.5	

* Values greater than 150% were not used to determine the averages, but the 0% values were used.

TABLE 12

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT EC-1, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	(27.9)[b]	41.3 ± 3.6	(148)	8.7
Acenaphthylene	(0.8)	0.9 ± 0.1	(112)	11.1
Acenaphthene	(0.2)	0.2 ± 0.01	(100)	0.05
Fluorene	(15.3)	15.6 ± 1.8	(102)	11.5
Phenanthrene	15.8 ± 1.2	16.1 ± 1.8	102	11.2
Anthracene	(1.3)	1.1 ± 0.2	(88)	18.2
Fluoranthene	23.2 ± 2.0	24.1 ± 2.1	104	8.7
Pyrene	16.7 ± 2.0	17.2 ± 1.9	103	11.0
Benz(a)anthracene	8.7 ± 0.8	8.8 ± 1.0	101	11.4
Chrysene	(9.2)	7.9 ± 0.9	(86)	11.4
Benzo(b)fluoranthene	7.9 ± 0.9	8.5 ± 1.1	108	12.9
Benzo(k)fluoranthene	4.4 ± 0.5	4.1 ± 0.5	91	12.2
Benzo(a)pyrene	5.3 ± 0.7	5.1 ± 0.6	96	11.8
Indeno(1,2,3-cd)pyrene	5.7 ± 0.6	5.2 ± 0.6	91	11.5
Benzo(g,h,i)perylene	4.9 ± 0.7	4.3 ± 0.5	88	11.6
Dibenz(a,h)anthracene	(1.3)	1.1 ± 0.2	(85)	18.2

[a] Relative standard deviations for the SFE values are based on six replicate extractions.

[b] Values in parentheses were obtained from, or compared to, Soxhlet extraction results which were not certified.

Data are taken from Reference 10.

TABLE 13

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SEDIMENT HS-3, USING METHOD 3561 (SFE - SOLID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	9.0 ± 0.7	7.4 ± 0.6	82	8.1
Acenaphthylene	0.3 ± 0.1	0.4 ± 0.1	133	25.0
Acenaphthene	4.5 ± 1.5	3.3 ± 0.3	73	9.0
Fluorene	13.6 ± 3.1	10.4 ± 1.3	77	12.5
Phenanthrene	85.0 ± 20.0	86.2 ± 9.5	101	11.0
Anthracene	13.4 ± 0.5	12.1 ± 1.5	90	12.4
Fluoranthene	60.0 ± 9.0	54.0 ± 6.1	90	11.3
Pyrene	39.0 ± 9.0	32.7 ± 3.7	84	11.3
Benz(a)anthracene	14.6 ± 2.0	12.1 ± 1.3	83	10.7
Chrysene	14.1 ± 2.0	12.0 ± 1.3	85	10.8
Benzo(b)fluoranthene	7.7 ± 1.2	8.4 ± 0.9	109	10.7
Benzo(k)fluoranthene	2.8 ± 2.0	3.2 ± 0.5	114	15.6
Benzo(a)pyrene	7.4 ± 3.6	6.6 ± 0.8	89	12.1
Indeno(1,2,3-cd)pyrene	5.0 ± 2.0	4.5 ± 0.6	90	13.3
Benzo(g,h,i)perylene	5.4 ± 1.3	4.4 ± 0.6	82	13.6
Dibenz(a,h)anthracene	1.3 ± 0.5	1.1 ± 0.3	85	27.3

[a] Relative standard deviations for the SFE values are based on three replicate extractions.

Data are taken from Reference 10.

TABLE 14

SINGLE LABORATORY ACCURACY AND PRECISION FOR THE EXTRACTION OF PAHs FROM A CERTIFIED REFERENCE SOIL SRS103-100, USING METHOD 3561 (SFE - LIQUID TRAP)

Compound	Certified Value (mg/kg)	SFE Value[a] (mg/kg)	Percent of Certified Value	SFE RSD
Naphthalene	32.4 ± 8.2	29.55	91	10.5
2-Methylnaphthalene	62.1 ± 11.5	76.13	122	2.0
Acenaphthene	632 ± 105	577.28	91	2.9
Dibenzofuran	307 ± 49	302.25	98	4.1
Fluorene	492 ± 78	427.15	87	3.0
Phenanthrene	1618 ± 340	1278.03	79	3.4
Anthracene	422 ± 49	400.80	95	2.6
Fluoranthene	1280 ± 220	1019.13	80	4.5
Pyrene	1033 ± 285	911.82	88	3.1
Benz(a)anthracene	252 ± 8	225.50	89	4.8
Chrysene	297 ± 26	283.00	95	3.8
Benzo(a)pyrene	97.2 ± 17.1	58.28	60	6.5
Benzo(b)fluoranthene + Benzo(k)fluoranthene	153 ± 22	130.88	86	10.7

[a] Relative standard deviations for the SFE values are based on four replicate extractions.

Data are taken from Reference 11.

TABLE 15

SINGLE LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF BASE/NEUTRAL/ACID EXTRACTABLES FROM SPIKED TCLP BUFFERS LOW SPIKE LEVEL

Analyte	Spike Level (µg/L)	Buffer 1 (pH = 2.886)		Buffer 2 (pH = 4.937)	
		Recovery (%)	RSD	Recovery (%)	RSD
1,4-Dichlorobenzene	3,750	63	10	63	9
Hexachloroethane	1,500	55	6	77	4
Nitrobenzene	1,000	82	10	100	5
Hexachlorobutadiene	250	65	3	56	4
2,4-Dinitrotoluene	65	89	4	101	5
Hexachlorobenzene	65	98	5	95	6
o-Cresol	100,000	83	10	85	5
m-Cresol*	100,000	86	8	85	3
p-Cresol*	100,000	*	*	*	*
2,4,6-Trichlorophenol	1,000	84	12	95	12
2,4,5-Trichlorophenol	200,000	83	11	88	3
Pentachlorophenol	50,000	82	9	78	9

Results from seven replicate spiked buffer samples.

* In this study, m-cresol and p-cresol co-eluted and were quantitated as a mixture of both isomers.

Data from Reference 12.

TABLE 16

SINGLE LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF BASE/NEUTRAL/ACID EXTRACTABLES FROM SPIKED TCLP BUFFERS HIGH SPIKE LEVEL

Analyte	Spike Level (µg/L)	Buffer 1 (pH = 2.886)		Buffer 2 (pH = 4.937)	
		Recovery (%)	RSD	Recovery (%)	RSD
1,4-Dichlorobenzene	15,000	63	10	63	9
Hexachloroethane	6,000	54	7	46	7
Nitrobenzene	4,000	81	4	81	13
Hexachlorobutadiene	1,000	81	5	70	11
2,4-Dinitrotoluene	260	99	8	98	3
Hexachlorobenzene	260	89	8	91	9
o-Cresol*	400,000	92	15	90	4
m-Cresol*	400,000	95	8	82	6
p-Cresol*	400,000	82	14	84	7
2,4,6-Trichlorophenol	4,000	93	12	104	12
2,4,5-Trichlorophenol	800,000	93	14	97	23
Pentachlorophenol	200,000	84	9	73	8

Results from seven replicate spiked buffer samples.

* In this study, recoveries of these compounds were determined from triplicate spikes of the individual compounds into separate buffer solutions.

Data from Reference 12.

TABLE 17

RECOVERY DATA FROM THREE LABORATORIES FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF BASE/NEUTRAL/ACID EXTRACTABLES FROM SPIKED TCLP LEACHATES FROM SOIL SAMPLES

Buffer 1 pH = 2.886		Lab 1			Lab 2			Lab 3		
Analyte	Spike Level (µg/L)*	%R	RSD	n	%R	RSD	n	%R	RSD	n
o-Cresol	200,000	86	8	7	35.3	0.7	3	7.6	6	3
m-Cresol**	--	77	8	7	--	--	--	--	--	--
p-Cresol**	--	--	--	--	--	--	--	7.7	11	3
2,4,6-Trichlorophenol	2,000	106	6	7	96.3	3.9	3	44.8	5	3
2,4,5-Trichlorophenol	400,000	93	3	7	80.5	4.5	3	63.3	11	3
Pentachlorophenol	100,000	79	2	7	33.8	12.2	3	29.2	13	3
1,4-Dichlorobenzene	7,500	51	5	7	81.3	5.3	3	19.2	7	3
Hexachloroethane	3,000	50	5	7	66.2	2.1	3	12.6	11	3
Nitrobenzene	2,000	80	8	7	76.3	5.3	3	63.9	12	3
Hexachlorobutadiene	500	53	8	7	63.3	4.8	3	9.6	9	3
2,4-Dinitrotoluene	130	89	8	7	35.7	2.6	3	58.2	17	3
Hexachlorobenzene	130	84	21	7	92.3	1.6	3	71.7	9	3

(continued)

TABLE 17
(continued)

Buffer 2 pH = 4.937		Lab 1			Lab 2			Lab 3		
Analyte	Spike Level (µg/L)*	%R	RSD	n	%R	RSD	n	%R	RSD	n
o-Cresol	200,00	97	13	7	37.8	4.5	3	6.1	24	3
m-Cresol**	--	83	4	7	--	--	--	6.0	25	3
p-Cresol**	--	--	--	--	--	--	--	--	--	--
2,4,6-Trichlorophenol	2,000	104	4	7	91.7	8.0	3	37.7	25	3
2,4,5-Trichlorophenol	400,000	94	4	7	85.2	0.4	3	64.4	10	3
Pentachlorophenol	100,000	109	11	7	41.9	28.2	3	36.6	32	3
1,4-Dichlorobenzene	7,500	50	5	7	79.7	1.0	3	26.5	68	3
Hexachloroethane	3,000	51	3	7	64.9	2.0	3	20.3	90	3
Nitrobenzene	2,000	80	4	7	79.0	2.3	3	59.4	6	3
Hexachlorobutadiene	500	57	5	7	60	3.3	3	16.6	107	3
2,4-Dinitrotoluene	130	86	6	7	38.5	5.2	3	62.2	6	3
Hexachlorobenzene	130	86	7	7	91.3	0.9	3	75.5	5	3

* 250-mL aliquots of leachate were spiked. Lab 1 spiked at one-half these levels.

** m-Cresol and p-Cresol coelute. Lab 1 and Lab 3 reported o-Cresol and the sum of — and p-Cresol. Lab 2 reported the sum of all three isomers of Cresol.

Data from Reference 12.

TABLE 18

SINGLE-LABORATORY PAH ANALYSIS DATA FROM A REAL SOIL CONTAMINATED WITH CREOSOTE, USING METHOD 3546
(MICROWAVE EXTRACTION)

Compound	Concentration (µg/kg)	RSD (%)	REAC values (µg/kg)
Naphthalene	2,170	12.4	710,000
2-Methylnaphthalene	28,710	3.1	N/R
1-Methylnaphthalene	33,180	2.4	N/R
Biphenyl	13,440	6.0	N/R
2,6-Dimethylnaphthalene	52,990	3.8	N/R
Acenaphthylene	16,320	3.1	21,000
Acenaphthene	801,210	6.0	1,700,000
Fluorene	789,980	3.4	990,000
Phenanthrene	1,627,480	0.7	3,300,000
Anthracene	346,010	4.0	360,000
Benzo(a)anthracene	300,380	2.7	310,000
Fluoranthene	1,331,690	1.6	1,600,000
Pyrene	1,037,710	3.0	1,100,000
Chrysene	293,200	3.4	320,000
Benzo(b)fluoranthene	152,000	3.8	140,000
Benzo(k)fluoranthene	127,740	3.6	130,000
Benzo(e)pyrene	87,610	3.9	N/R
Benzo(a)pyrene	128,330	3.9	110,000
Perylene	35,260	4.3	N/R
Indeno(123-cd)pyrene	63,900	5.0	25,000
Dibenz(a,h)anthracene	17,290	6.9	N/R
Benzo(ghi)perylene	42,720	6.9	20,000

*n = 4

Soil samples obtained from US EPA Emergency Response Center archive bank through their contract laboratory REAC (Edison, NJ). The standard Soxhlet extraction procedures were performed by REAC three years earlier; this long storage period is believed to account for the low naphthalene recovery data in the present study

REAC data labeled N/R = not reported

TABLE 19

SINGLE-LABORATORY PAH RECOVERY DATA FROM HS-5 MARINE SEDIMENT MATERIALS, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Confidence Interval (µg/kg)	Recovery (%)
Naphthalene	250	180 - 320	76
Acenaphthylene	150	*	107
Acenaphthene	230	130 - 330	61
Fluorene	400	300 - 500	63
Phenanthrene	5,200	4,200 - 6,200	72
Anthracene	380	230 - 530	84
Fluoranthene	8,400	5,800 - 10,000	81
Pyrene	5,800	4,000 - 7,600	69
Benzo(a)anthracene	2,900	1,700 - 4,100	53
Chrysene	2,800	1,900 - 3,700	76
Benzo(b)fluoranthene	2,000	1,000 - 3,000	84
Benzo(k)fluoranthene	1,000	600 - 1,400	137
Benzo(a)pyrene	1,700	900 - 2,500	52
Indeno(123-cd) pyrene	1,300	600 - 2,000	63
Dibenz(a,h)anthracene	200	100 - 300	125
Benzo(ghi)perylene	1,300	1000 - 1600	64

n = 3

* values not certified

The uncertainties represent 90% confidence intervals

TABLE 20

SINGLE-LABORATORY PAH RECOVERY DATA FROM HS-4 MARINE SEDIMENT MATERIALS, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Confidence Interval (µg/kg)	Recovery (%)
Naphthalene	150	*	54
Acenaphthylene	150	*	82
Acenaphthene	150	*	63
Fluorene	150	*	81
Phenanthrene	680	600 - 760	81
Anthracene	140	70 - 210	108
Fluoranthene	1250	1,150 - 1,350	84
Pyrene	940	820 - 1,060	85
Benzo(a)anthracene	530	470 - 580	78
Chrysene	650	570 - 730	84
Benzo(b)fluoranthene	700	550 - 850	84
Benzo(k)fluoranthene	360	310 - 410	156
Benzo(a)pyrene	650	570 - 730	73
Indeno(123-cd) pyrene	510	360 - 660	88
Dibenz(a,h)anthracene	120	70 - 170	117
Benzo(ghi)perylene	580	360 - 800	91

n = 3

* values not certified

The uncertainties represent 90% confidence intervals

TABLE 21

SINGLE-LABORATORY PAH RECOVERY DATA FROM HS-3 MARINE SEDIMENT MATERIALS, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Confidence Interval (µg/kg)	Recovery (%)
Naphthalene	9,000	8300 - 9,700	61
Acenaphthylene	300	200 - 400	199
Acenaphthene	4,500	3,000 - 6,000	80
Fluorene	13,300	10,200 -16,400	58
Phenanthrene	85,000	65000 -105,000	87
Anthracene	13,400	12,900 -13,900	48
Fluoranthene	60,000	51,000-69,000	91
Pyrene	39,000	30,000-48,000	86
Benzo(a)anthracene	14,600	12,600-16,600	78
Chrysene	14,100	12,100-16,100	91
Benzo(b)fluoranthene	7,700	6,500-8,900	101
Benzo(k)fluoranthene	2,800	800-4,800	275
Benzo(a)pyrene	7,400	3,000-7,000	74
Indeno(123-cd)pyrene	5,400	4,100-6,700	100
Dibenz(a,h)anthracene	1,300	800-1,800	118
Benzo(ghi)perylene	5,000	3,000-7,000	99

n = 3

* values not certified

The uncertainties represent 90% confidence intervals

TABLE 22

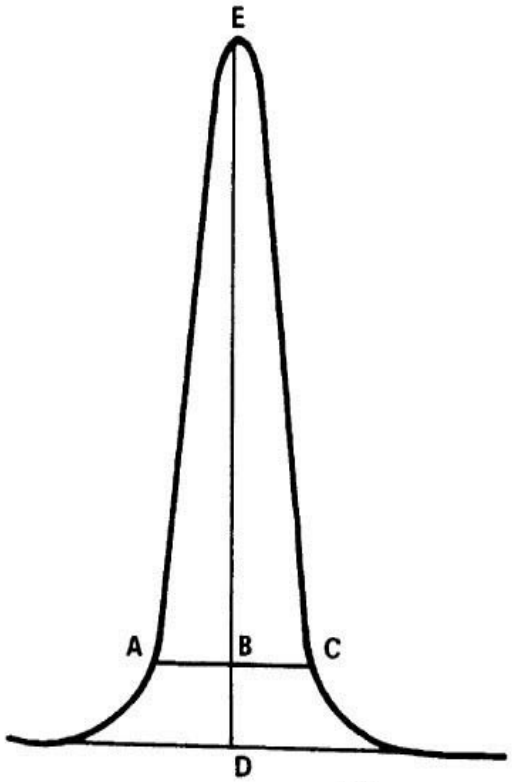
SINGLE-LABORATORY PAH RECOVERY DATA FROM SRM 1941 MARINE SEDIMENT, USING METHOD 3546 (MICROWAVE EXTRACTION)

Compound	Certified Value (µg/kg)	Recovery (%)
Naphthalene	1010	97.4
Fluorene	100	100.0
Phenanthrene	490	102.0
Fluoranthene	980	116.7
Pyrene	810	97.3
Benz(a)anthracene	430	89.8
Chrysene	380	130.3
Benzo(b)fluoranthene	740	95.8
Benzo(k)fluoranthene	360	130.2
Benz(e)pyrene	550	81.0
Benzo(a)pyrene	630	76.0
Perylene	450	72.4
Indeno(123-cd)pyrene	500	126.0
Dibenz(a,h)anthracene	110	78.7
Benz(ghi)perylene	530	85.2

n = 3

All RSDs < 10%

FIGURE 1
TAILING FACTOR CALCULATION

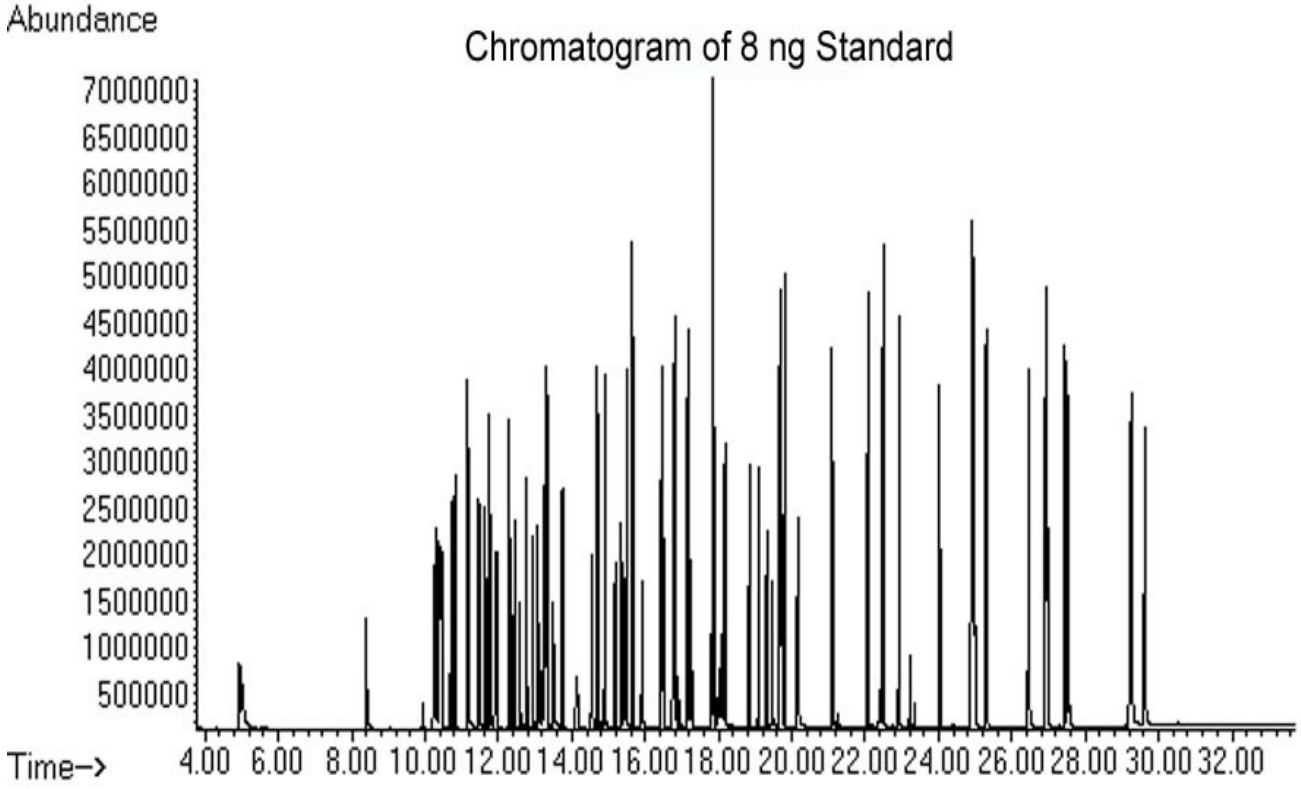


$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

FIGURE 2
GAS CHROMATOGRAM OF BASE/NEUTRAL AND ACID CALIBRATION STANDARD



METHOD 9012B

TOTAL AND AMENABLE CYANIDE (AUTOMATED COLORIMETRIC, WITH OFF-LINE DISTILLATION)

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of inorganic cyanide (CAS Registry Number 57-12-5) in wastes or leachate. This method detects inorganic cyanides that are present as either soluble salts or complexes. It is used to determine values for both total cyanide and cyanide amenable to chlorination. The "reactive" cyanide content of a waste is not determined by this method. Refer to 40 CFR 261.23 for information on the characteristic of reactivity.

2.0 SUMMARY OF METHOD

2.1 The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by automated UV colorimetry.

2.2 In the automated colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with Chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilution of the original scrubber solution to obtain colors of comparable intensity.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure. Chlorine and sulfide are interferences in this method.

3.2 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of sodium arsenite to the waste prior to preservation and storage of the sample to reduce the chlorine to chloride which does not interfere.

3.3 Sulfide interference can be removed by adding an excess of bismuth nitrate to the waste (to precipitate the sulfide) before distillation. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate.

3.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation. Nitrate and nitrite are interferences when present at levels higher than 10 mg/L and in conjunction with certain organic compounds.

3.5 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/L were not found to interfere in Method 9010.

3.6 Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in large concentrations and will make the endpoint of the titration difficult to detect. They may be extracted at pH 6-7.

4.0 APPARATUS AND MATERIALS

4.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of one liter size with inlet tube and provision for condenser. The gas scrubber may be a 270-mL Fisher-Milligan scrubber (Fisher, Part No. 07-513 or equivalent). The reflux apparatus may be a Wheaton 377160 distillation unit or equivalent.

4.2 Automated continuous-flow analytical instrument with:

4.2.1 Sampler.

4.2.2 Manifold.

4.2.3 Proportioning pump.

4.2.4 Heating bath with distillation coil.

4.2.5 Distillation head.

4.2.6 Colorimeter equipped with a 15-mm flowcell and 570 nm filter.

4.2.7 Recorder.

4.3 Hot plate stirrer/heating mantle.

4.4 pH meter.

4.5 Amber light.

4.6 Vacuum source.

4.7 Refrigerator.

4.8 5 mL microburette.

4.9 7 Class A volumetric flasks -- 100 and 250 mL.

4.10 Erlenmeyer flask -- 500 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other

grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Reagents for sample collection, preservation, and handling

5.3.1 Sodium arsenite (0.1N), $NaAsO_2$. Dissolve 3.2 g of $NaAsO_2$ in 250 mL water.

5.3.2 Ascorbic acid, $C_6H_8O_6$.

5.3.3 Sodium hydroxide solution (50%), NaOH. Commercially available.

5.3.4 Acetic acid (1.6M) CH_3COOH. Dilute one part of concentrated acetic acid with 9 parts of water.

5.3.5 2,2,4-Trimethylpentane, C_8H_{18}.

5.3.6 Hexane, C_6H_{14}.

5.3.7 Chloroform, $CHCl_3$.

5.4 Reagents for cyanides amenable to chlorination

5.4.1 Calcium hypochlorite solution (0.35M), $Ca(OCl)_2$. Combine 5 g of calcium hypochlorite and 100 mL of water. Shake before using.

5.4.2 Sodium hydroxide solution (1.25N), NaOH. Dissolve 50 g of NaOH in 1 liter of water.

5.4.3 Sodium arsenite (O.1N). See Sec. 5.3.1.

5.4.4 Potassium iodide starch paper.

5.5 Reagents for distillation

5.5.1 Sodium hydroxide (1.25N). See Sec. 5.4.2.

5.5.2 Bismuth nitrate (0.062M), $Bi(NO)_3 \cdot 5H_2O$. Dissolve 30 g of $Bi(NO)_3 \cdot 5H_2O$ in 100 mL of water. While stirring, add 250 mL of glacial acetic acid, CH_3COOH. Stir until dissolved and dilute to 1 liter with water.

5.5.3 Sulfamic acid (0.4N), H_2NSO_3H. Dissolve 40 g H_2NSO_3H in 1 liter of water.

5.5.4 Sulfuric acid (18N), H_2SO_4. Slowly and carefully add 500 mL of concentrated H_2SO_4 to 500 mL of water.

5.5.5 Magnesium chloride solution (2.5M), $MgCl_2 \cdot 6H_2O$. Dissolve 510 g of $MgCl_2 \cdot 6H_2O$ in 1 liter of water.

5.5.6 Lead acetate paper.

5.6 Reagents for automated colorimetric determination

5.6.1 Pyridine-barbituric acid reagent -- Place 15 g of barbituric acid in a 250-mL volumetric flask, add just enough reagent water to wash the sides of the flask, and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of concentrated HCl, mix, and cool to room temperature. Dilute to 250 mL with reagent water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

5.6.2 Chloramine-T solution -- Dissolve 2.0 g of white, water soluble chloramine-T in 500 mL of reagent water and refrigerate until ready to use.

5.6.3 Sodium hydroxide, 1 N -- Dissolve 40 g of NaOH in reagent water, and dilute to 1 liter.

5.6.4 All working standards should contain 2 mL of 1 N NaOH (Sec. 5.6.3) per 100 mL.

5.6.5 Dilution water and receptacle wash water (NaOH, 0.25 N) -- Dissolve 10.0 g of NaOH in 500 mL of reagent water. Dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples should be collected in plastic or glass containers. All containers must be thoroughly cleaned and rinsed.

6.2 Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with potassium iodide-starch test paper. A blue color indicates the need for treatment. Add 0.1N sodium arsenite solution a few mL at a time until a drop of sample produces no color on the indicator paper. Add an additional 5 mL of sodium arsenite solution for each liter of sample. Ascorbic acid can be used as an alternative although it is not as effective as arsenite. Add a few crystals of ascorbic acid at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

6.3 Aqueous samples must be preserved by adding 50% sodium hydroxide until the pH is greater than or equal to 12 at the time of collection.

6.4 Samples should be chilled to 4 EC.

6.5 When properly preserved, cyanide samples can be stored for up to 14 days prior to sample preparation steps.

6.6 Solid and oily wastes may be extracted prior to analysis by Method 9013 (Cyanide Extraction Procedure for Solids and Oils). It uses a dilute NaOH solution (pH = 12) as the extractant. This yields extractable cyanide.

6.7 If fatty acids, detergents, and surfactants are a problem, they may be extracted using the following procedure. Acidify the sample with acetic acid (1.6M) to pH 6.0 to 7.0.

CAUTION: This procedure can produce lethal HCN gas.

Extract with isooctane, hexane, or chloroform (preference in order named) with solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the

compounds below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with 50% NaOH solution.

7.0 PROCEDURE

7.1 Pretreatment for cyanides amenable to chlorination

7.1.1 This test must be performed under amber light. $K_3[Fe\text{-}(CN)_6]$ may decompose under UV light and hence will test positive for cyanide amenable to chlorination if exposed to fluorescent lighting or sunlight. Two identical sample aliquots are required to determine cyanides amenable to chlorination.

7.1.2 To one 500 mL sample or to a sample diluted to 500 mL, add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with 1.25N sodium hydroxide until an excess of chlorine is present as indicated by KI-starch paper turning blue. The sample will be subjected to alkaline chlorination by this step.

CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is necessary that this reaction be performed in a hood.

7.1.3 Test for excess chlorine with KI-starch paper and maintain this excess for one hour with continuous agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional calcium hypochlorite solution.

7.1.4 After one hour, add 1 mL portions of 0.1N sodium arsenite until KI-starch paper shows no residual chlorine. Add 5 mL of excess sodium arsenite to ensure the presence of excess reducing agent.

7.1.5 Test for total cyanide as described below in both the chlorinated and the unchlorinated samples. The difference of total cyanide in the chlorinated and unchlorinated samples is the cyanide amenable to chlorination.

7.1.6 If samples are known or suspected to contain sulfide, add 50 mL of 0.062M bismuth nitrate solution through the air inlet tube. Mix for three minutes. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

7.2 Distillation procedure

7.2.1 Place 500 mL of sample, or sample diluted to 500 mL in the one liter boiling flask. Pipet 50 mL of 1.25N sodium hydroxide into the gas scrubber. If the apparatus in Figure 1 is used, add water until the spiral is covered. Connect the boiling flask, condenser, gas scrubber and vacuum trap.

7.2.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enter the boiling flask through the air inlet tube.

7.2.3 If samples are known or suspected to contain nitrate or nitrite, or if bismuth nitrate was added to the sample, add 50 mL of 0.4N sulfamic acid solution through the air inlet tube. Mix for three minutes.

NOTE: Excessive use of sulfamic acid could create method bias.

7.2.4 Slowly add 50 mL of 18N sulfuric acid through the air inlet tube. Rinse the tube with water and allow the airflow to mix the flask contents for three minutes. Add 20 mL of 2.5M magnesium chloride through the air inlet and wash the inlet tube with a stream of water.

7.2.5 Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 min. After cooling the boiling flask, and closing the vacuum source, disconnect the gas scrubber.

7.2.6 Transfer the solution from the scrubber into a 250-mL volumetric flask. Rinse the scrubber into the volumetric flask. Dilute to volume with water.

7.3 Automated colorimetric determination

7.3.1 Set up the manifold in a hood or a well-ventilated area as shown in Figure 3.

7.3.2 Allow colorimeter and recorder to warm up for 30 min. Run a baseline with all reagents, feeding reagent water through the sample line.

7.3.3 Place appropriate standards in the sampler in order of increasing concentration. Complete loading of the sampler tray with unknown samples.

7.3.4 When the baseline becomes steady, begin the analysis.

7.4 Standard curve for samples without sulfide

7.4.1 Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution into 250-mL volumetric flasks. To each flask, add 50 mL of 1.25N sodium hydroxide and dilute to 250 mL with water. Prepare using the following table. The sodium hydroxide concentration will be 0.25N.

mL of Working Standard Solution (1 mL = 10 µg CN^-)	Concentration (µg CN^-/L)
0.0	Blank
1.0	40
2.0	80
5.0	200
10.0	400
15.0	600
20.0	800

7.4.2 After the standard solutions have been prepared according to the table above, pipet 50 mL of each standard solution into a 100-mL volumetric flask and proceed

to Secs. 7.3.2 and 7.3.3 to obtain absorbance values for the standard curve. The final concentrations for the standard curve will be one half of the amounts in the above table (final concentrations ranging from 20 to 400 µg/L).

7.4.3 It is recommended that at least two standards (a high and a low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ± 10% of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

7.4.4 Prepare a standard curve ranging from 20 to 400 µg/L by plotting absorbance of standard versus the cyanide concentration

7.5 Standard curve for samples with sulfide

7.5.1 It is imperative that all standards be distilled in the same manner as the samples using the method of standard additions (for example, bismuth nitrate must also be added to the standards). Standards distilled by this method will give a linear curve, at low concentrations, but as the concentration increases, the recovery decreases. It is recommended that at least five standards be distilled.

7.5.2 Prepare a series of standards similar in concentration to those mentioned in Sec. 7.4.1 and analyze as in Sec. 7.3. Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration.

7.6 Calculation -- Prepare a standard curve by plotting peak heights of standards against their concentration values. Compute concentrations of samples by comparing sample peak heights with the standard curve.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Verify the calibration curve with an independent calibration check standard. If the standards are not within 15% of the expected value, a new recalibration curve is required. Verify the calibration curve with every sample batch by analyzing a mid-range standard.

8.3 Run one matrix spike sample for every 10 samples to check the efficiency of sample distillation. A matrix spike should be prepared by adding cyanide from the working standard or intermediate standard to 500 mL of sample to ensure a concentration of approximately 40 µg/L. Both the matrix duplicate and matrix spike duplicate are brought through the entire sample preparation and analytical process.

8.4 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D2036-75, Method B, p. 505 (1976).

2. Goulden, P.D., B.K. Afghan, and P. Brooksbank, Determination of Nanogram Quantities of Simple and Complex Cyanides in Water, Anal. Chem., 44(11), pp. 1845-49 (1972).

3. Standard Methods for the Examination of Water and Wastewater, 14th ed., pp. 376 and 370, Method 413F and D (1975).

4. Technicon AutoAnalyzer II Methodology, Industrial Method No. 315-74 WCUV Digestion and Distillation, Technicon Industrial Systems, Tarrytown, New York, 10591 (1974).

FIGURE 1
APPARATUS FOR CYANIDE DISTILLATION

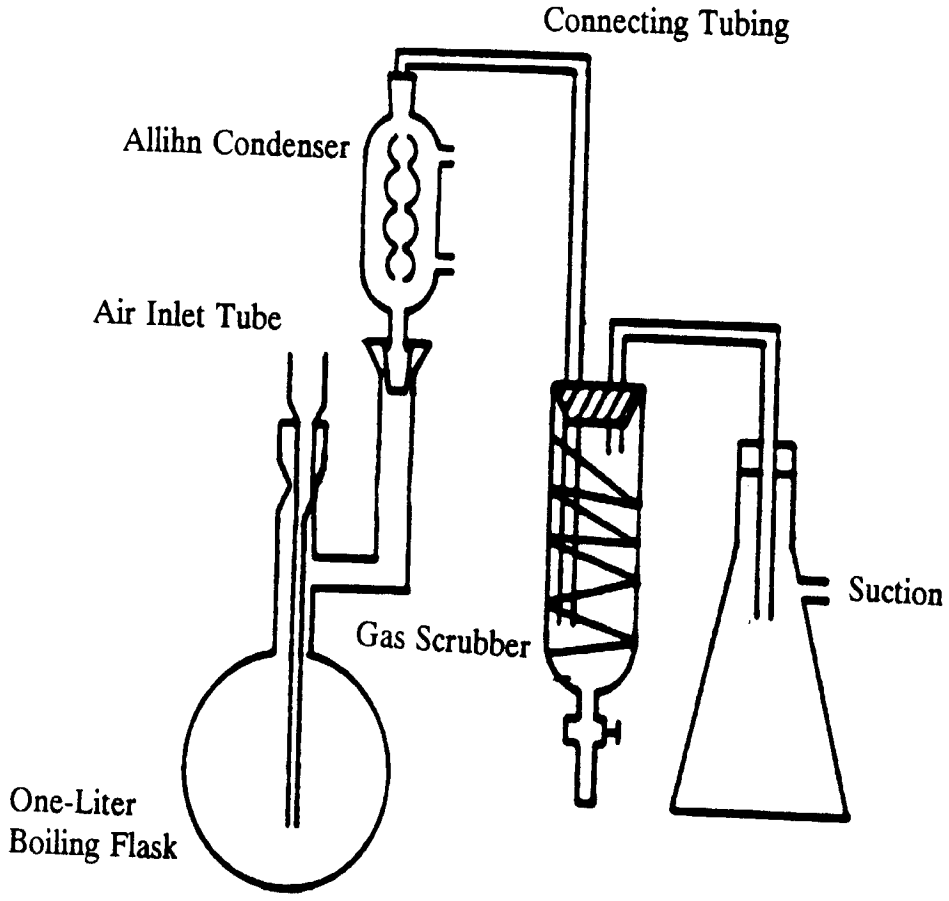


FIGURE 2
CYANIDE DISTILLATION APPARATUS

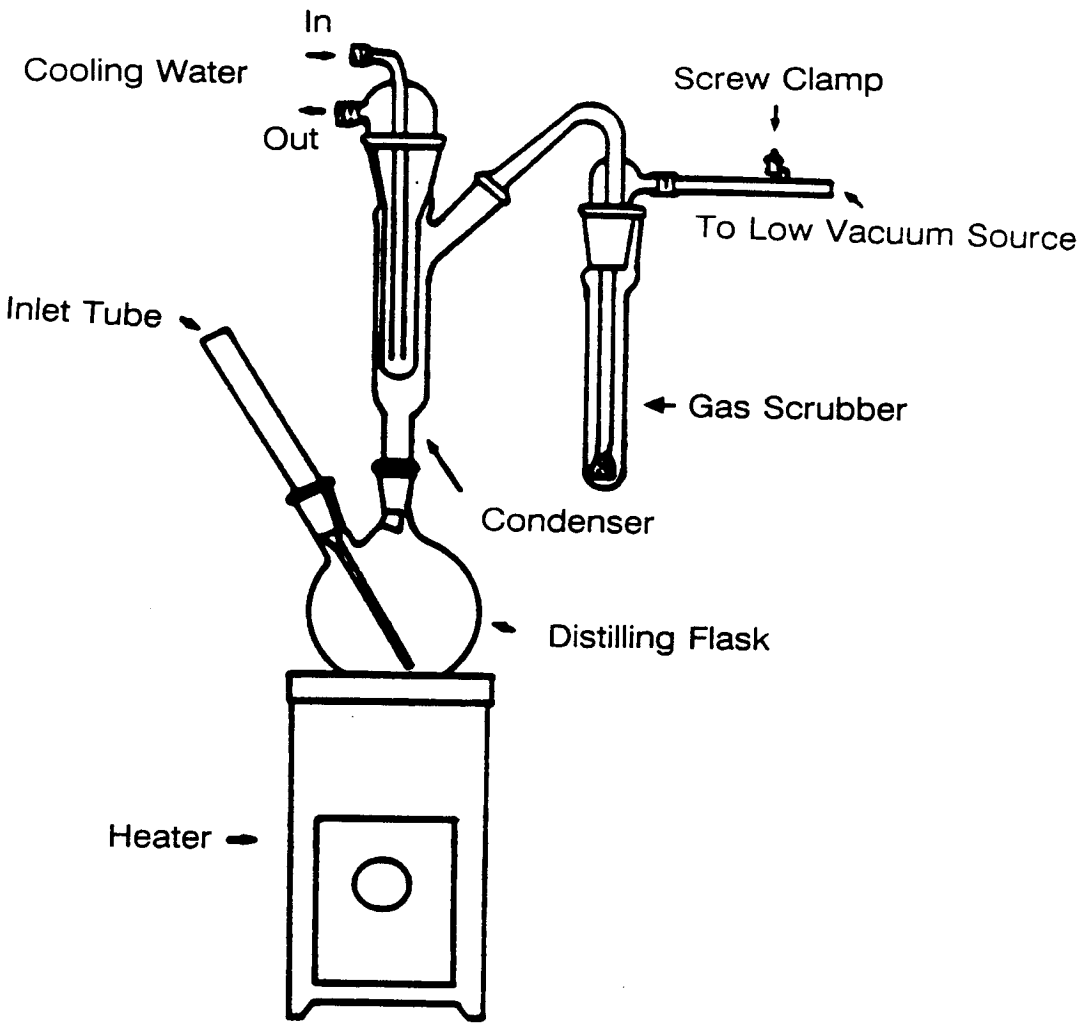
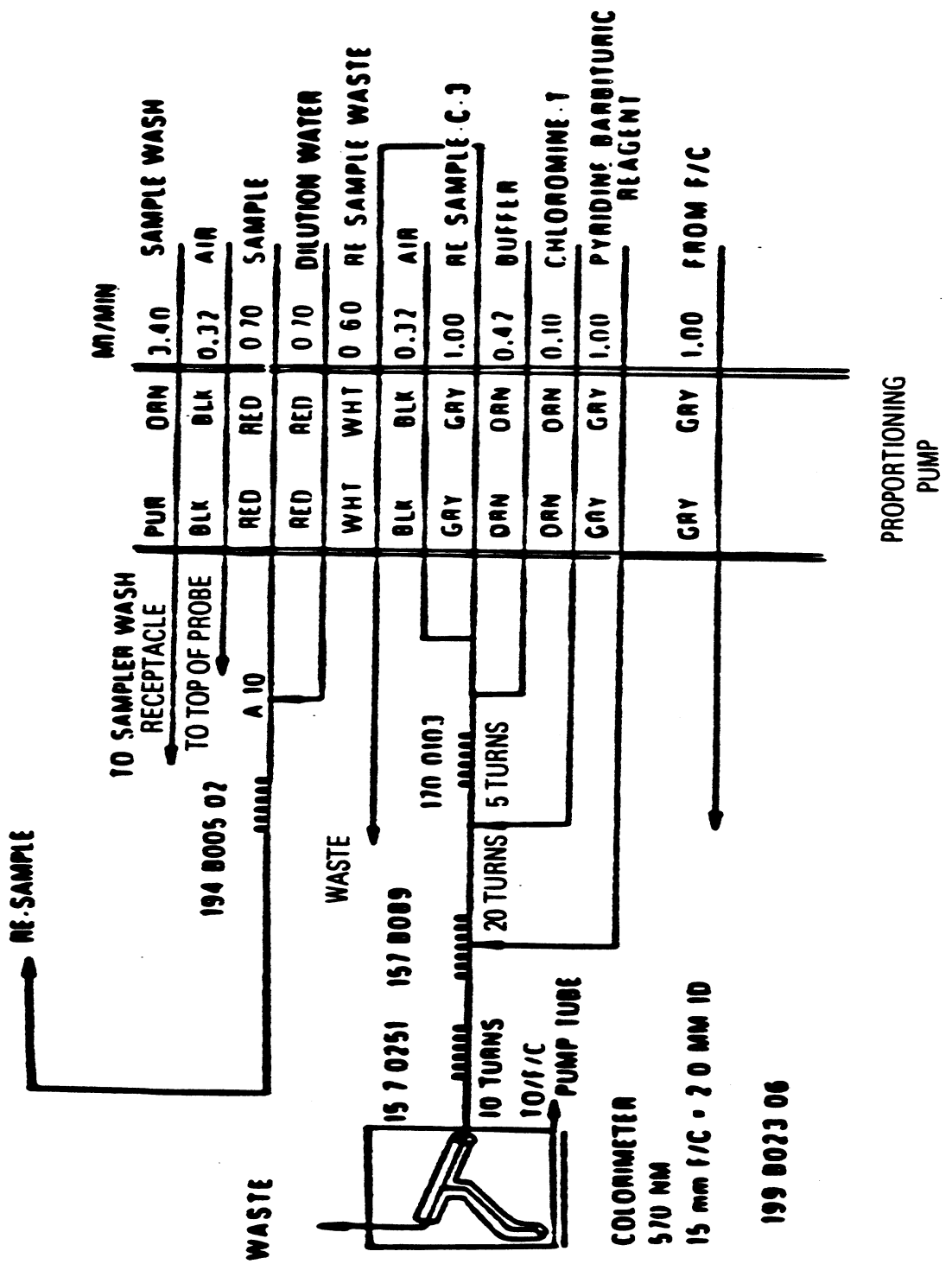
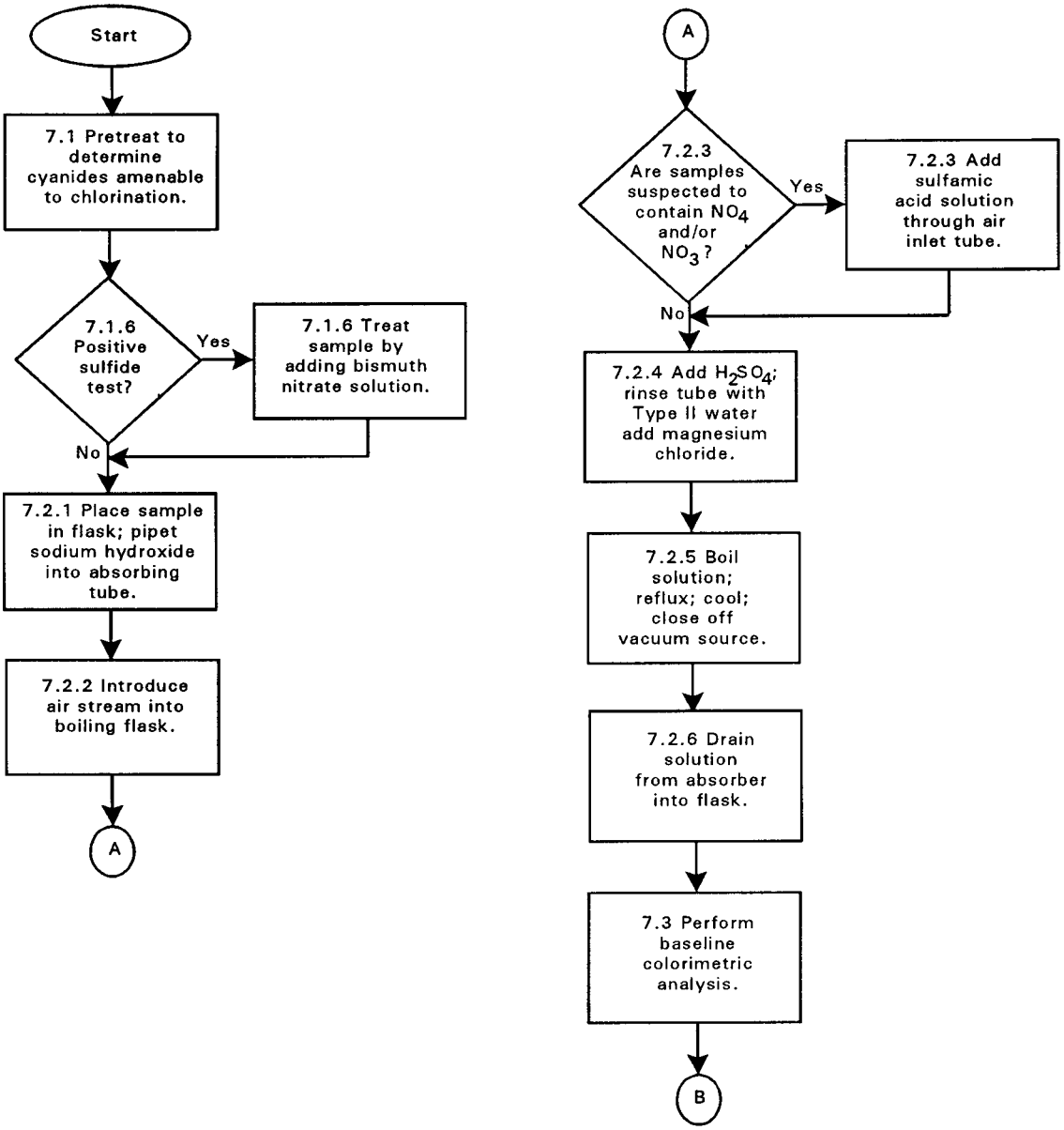
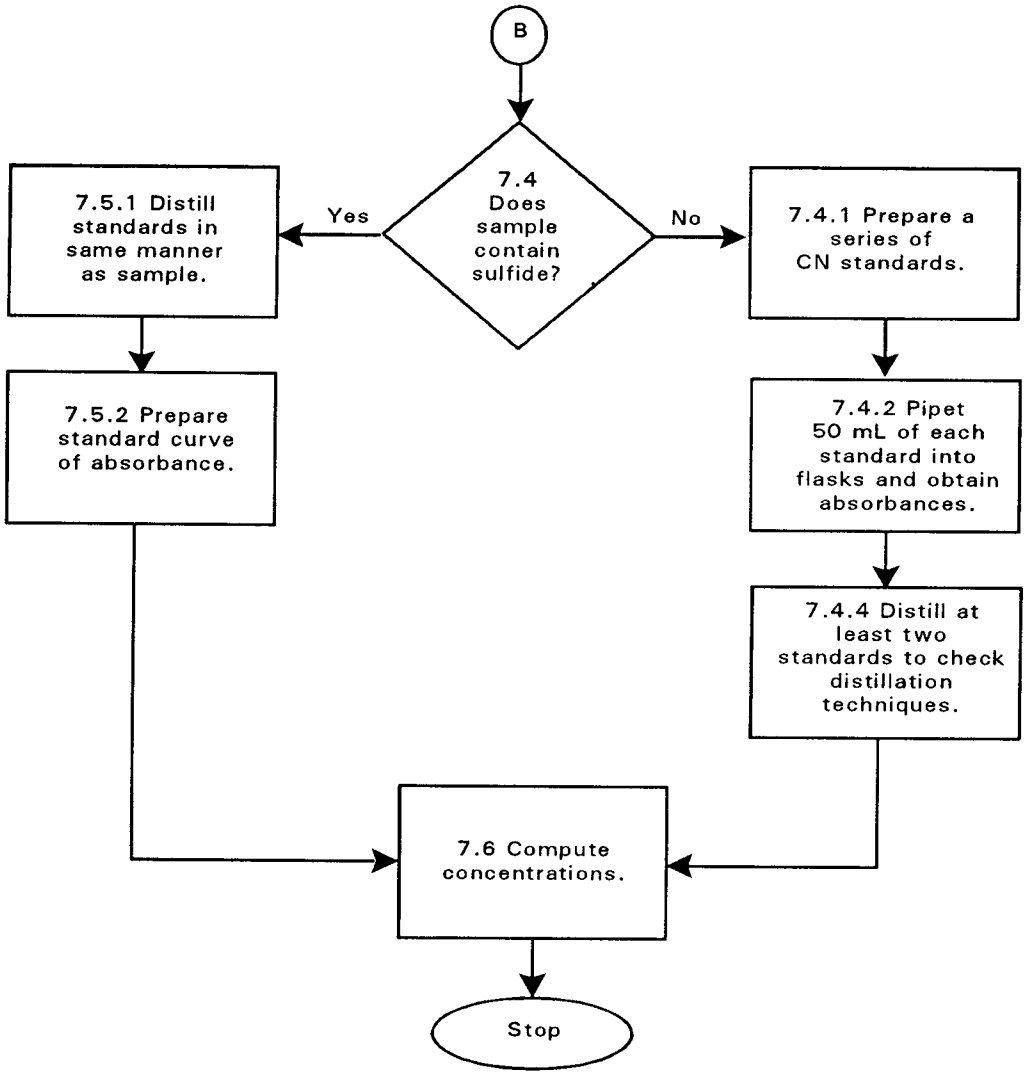


FIGURE 3
CYANIDE MANIFOLD AA11



TOTAL AND AMENABLE CYANIDE (AUTOMATED COLORIMETRIC WITH OFF-LINE DISTILLATION)

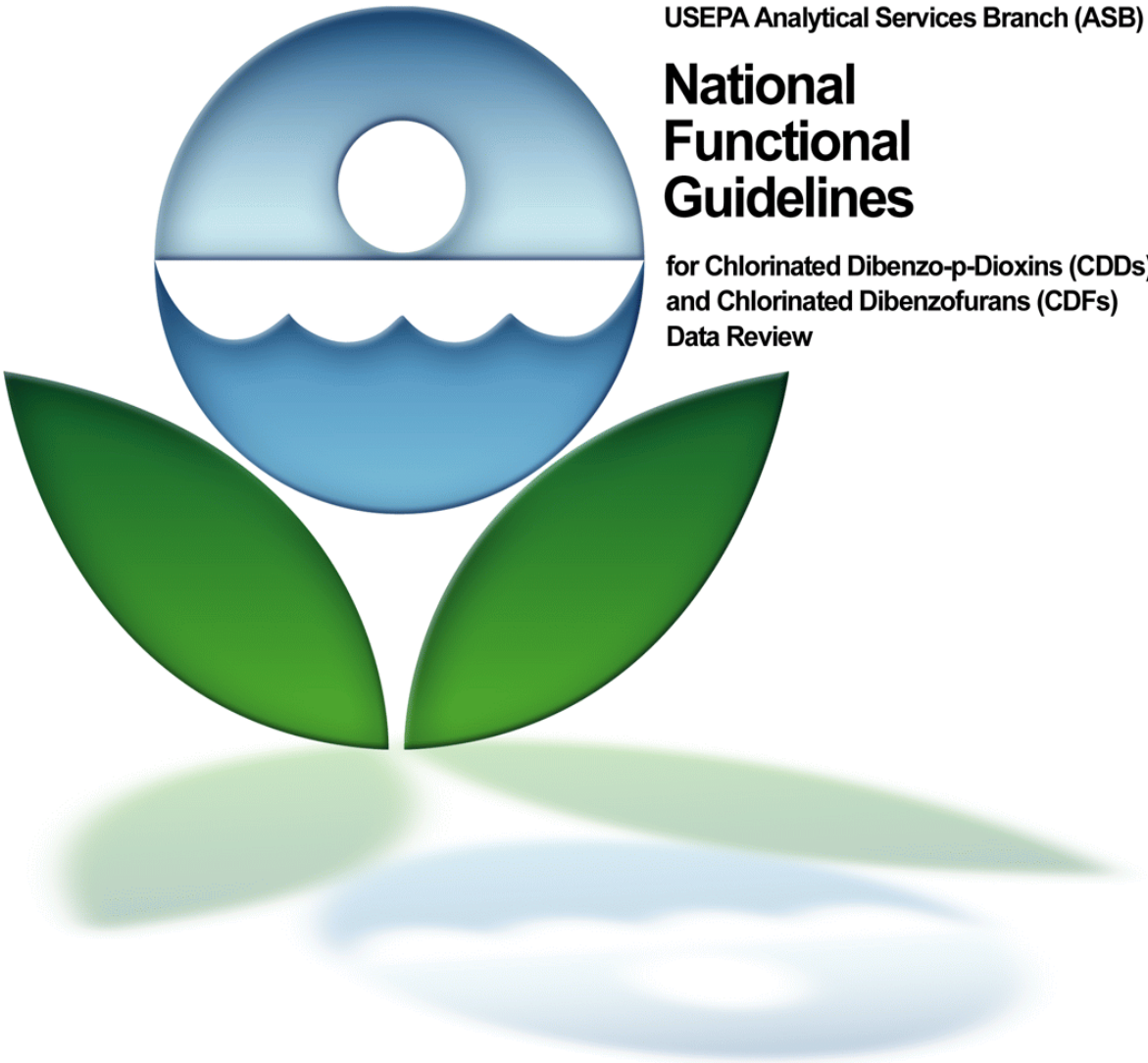



B
7.4 Does sample contain sulfide?
Yes
No
7.5.1 Distill standards in same manner as sample.
7.5.2 Prepare standard curve of absorbance.
7.4.1 Prepare a series of CN standards.
7.4.2 Pipet 50 mL of each standard into flasks and obtain absorbances.
7.4.4 Distill at least two standards to check distillation techniques.
7.6 Compute concentrations.
Stop

Office of Superfund Remediation and Technology Innovation (OSRTI)
United States Environmental Protection Agency (USEPA)
Washington, DC 20460

OSWER 9240.1-51
EPA-540-R-05-001

September 2005



USEPA Analytical Services Branch (ASB)

National Functional Guidelines

for Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Data Review

Final

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NOTICE

The policies and procedures set forth here are intended as guidance to the United States Environmental Protection Agency (hereafter referred to as USEPA) and other governmental employees. They do not constitute rule making by USEPA, and may not be relied upon to create a substantive or procedural right enforceable by any other person. The Government may take action that is at variance with the policies and procedures in this manual.

This document can be obtained from USEPA's Contract Laboratory Program (CLP) Web site at:

http://www.epa.gov/superfund/programs/clp/guidance.htm

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LIST OF TABLES

Appendix A

ACRONYMS

%D	Percent Difference
%Recovery	Percent Recovery
%RSD	Percent Relative Standard Deviation
%Solids	Percent Solids
%Valley	Percent Valley
CDD	Chlorinated Dibenzo-p-Dioxins
CDF	Chlorinated Dibenzofurans [also Polychlorinated Dibenzofuran (PCDF)]
CDWG	Chlorinated Dioxins Work Group
CLP	Contract Laboratory Program
CPS	Column Performance Solution
CRQL	Contract Required Quantitation Limits
CS	Calibration Standard
CWA	Clean Water Act
DQO	Data Quality Objective
EDL	Estimated Detection Limit
EMPC	Estimated Maximum Possible Concentration
GC	Gas Chromatography
HRGC	High Resolution Gas Chromatograph
HpCDD	Heptachlorinated Dibenzo-p-Dioxin
HpCDF	Heptachlorinated Dibenzofuran
HRMS	High Resolution Mass Spectrometer
HxCDD	Hexachlorinated Dibenzo-p-Dioxins
HxCDF	Hexachlorinated Dibenzofurans
ISC	Isomer Specificity Check
LCS	Laboratory Control Sample
Mean RR	Mean Relative Response
Mean RRF	Mean Relative Response Factor
NFG	National Functional Guidelines
OCDD	Octachlorinated Dibenzo-p-Dioxin
OCDF	Octachlorinated Dibenzofuran
PCDF	Polychlorinated Dibenzofuran
PCDPE	Polychlorinated Diphenyl Ether

PE	Performance Evaluation
PES	Performance Evaluation Sample
PeCDD	Pentachlorinated Dibenzo-p-Dioxin(s)
PeCDF	Pentachlorinated Dibenzofuran(s)
PFK	Perfluorokerosene
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QATS	Quality Assurance Technical Support
QC	Quality Control
RR	Relative Response
RRF	Relative Response Factor
RSD	Relative Standard Deviation
RT	Retention Time
RRT	Relative Retention Time
SAP	Sampling and Analysis Plan
SDG	Sample Delivery Group
SDWA	Safe Drinking Water Act
SICP	Selected Ion Current Profile
SIM	Selected Ion Monitoring
S/N	Signal-to-Noise Ratio
SOP	Standard Operating Procedure
SOW	Statement of Work
TCL	Target Compound List
TCDD	Tetrachlorinated Dibenzo-p-Dioxin(s)
TCDF	Tetrachlorinated Dibenzofuran(s)
TEF	Toxicity Equivalency Factor
TICP	Total Ion Current Profile
TO	Task Order
TOPO	Task Order Project Officer
TR/COC	Traffic Report/Chain of Custody
VTSR	Validated Time of Sample Receipt
WDM	Window Defining Mixture
USEPA	United States Environmental Protection Agency

INTRODUCTION

The *USEPA Analytical Services Branch (ASB) National Functional Guidelines for Chlorinated Dioxin and Furan Data Review* (hereafter referred to as the NFG) is designed to offer guidance on USEPA chlorinated dibenzo-p-dioxin (CDD) and chlorinated dibenzofuran (CDF) data evaluation and review. In some applications, it may be used as a Standard Operating Procedure (SOP). In other, more subjective areas, only general guidance is offered due to the complexities and uniqueness of data relative to specific samples. For example, areas where the application of specific SOPs is possible are primarily those in which definitive performance criteria are established. These criteria are concerned with specifications that are not sample dependent; they specify performance requirements that should fully be under a laboratory's control. These specific areas include blanks, calibration standards, Performance Evaluation (PE) standard materials, and instrument performance checks.

These guidelines include the requirements for the *USEPA Analytical Services Branch Statement of Work for Analysis of Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Multi-Media, Multi-Concentration (DLM02.X*) (hereafter referred to as DLM02.X SOW or DLM02.X). The DLM02.X SOW is based on USEPA Method 1613 (Revision B) and SW-846 Method 8290 (Revision 0) which use High Resolution Gas Chromatography and High Resolution Mass Spectrometry (HRGC/HRMS).

> USEPA Method 1613 (Revision B) can be obtained at:
> http://www.epa.gov/waterscience/methods/1613.pdf
>
> USEPA SW-846 Method 8290 (Revision 0) can be obtained at:
> http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8290a.pdf

The NFG is intended to assist in the technical review of analytical data generated through the DLM02.X SOW. Determining contract compliance is not the intended objective of these guidelines. The data review process provides information on analytical limitations of data, based on specific Quality Control (QC) criteria. To provide more specific usability statements, the reviewer must have a complete understanding of the intended use of the data. For this reason, it is recommended that whenever possible, the reviewer should obtain usability issues from the user prior to reviewing the data. When this is not possible, the user is encouraged to communicate any questions to the reviewer.

At times, there may be a need to use data which do not meet all contract requirements and technical criteria. Use of these data does not constitute either a new requirement standard or full acceptance of the data. Any decision to utilize data for which performance criteria have not been met is strictly to facilitate the progress of projects requiring the availability of the data. A contract laboratory submitting data which are out of specification may be required to rerun samples or resubmit data, even if the previously submitted data have been utilized due to program needs. Data which do not meet specified requirements are never fully acceptable. The only exception to this condition is in the area of the requirements for individual sample analysis; if the nature of the sample itself inhibits the attainment of specifications, appropriate allowances must be made.

Use professional judgment to determine the ultimate usability of the data.

DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the data qualifiers assigned to results in the data review process. If the data reviewer chooses to use additional qualifiers, a complete explanation of those qualifiers must accompany the data review.

Data Qualifier	Qualifier Definitions
U	The analyte was analyzed for, but was not detected at a level greater than or equal to the level of the adjusted Contract Required Quantitation Limit (CRQL) for sample and method.
J	The analyte was positively identified and the associated numerical value is the approximate concentration of the analyte in the sample [due either to the quality of the data generated because certain Quality Control (QC) criteria were not met, or the concentration of the analyte was below the adjusted CRQL].
UJ	The analyte was not detected at a level greater than or equal to the adjusted CRQL or the reported adjusted CRQL is approximate and may be inaccurate or imprecise.
R	The sample results are unusable due to the quality of the data generated because certain criteria were not met. The analyte may or may not be present in the sample.

PRELIMINARY REVIEW

The NFG is used for the review of analytical data generated through the DLM02.X SOW. To use this document effectively, the reviewer must have an understanding of the analytical method and a general overview of the Sample Delivery Group (SDG) or sample Case at hand. The exact number of samples, their assigned numbers, their matrix, and the number of laboratories involved in their analysis are essential information. Background information on the site is helpful, but often this information may be difficult to locate. If available, the field notes must be reviewed. The site manager is the best source for answers to questions, or for further direction.

Please note that individual Task Orders (TOs) may modify the DLM02.X SOW requirements, which will affect the generated data. For example, holding times, extraction procedures, compound analyses and calibration requirements, etc., may be affected by an individual TO depending on project requirements. Thus, the TO requirements must be taken into consideration, along with the requirements in the National Functional Guidelines (NFG) document, when reviewing the data.

The SDGs or Cases routinely have unique samples which require special attention by the reviewer. These samples include field blanks, field duplicates, and Performance Evaluation (PE) samples which need to be identified. The sampling records must provide:

1. The Region where the samples were taken; and

2. A complete list of samples with information on:
   a. Laboratories involved;
   b. Shipping dates;
   c. Preservatives;
   d. Sample matrix;
   e. Field blanks*;
   f. Field duplicates*;
   g. Field spikes*; and
   h. Quality Control (QC) audit samples*.

   * If applicable.

The Traffic Report/Chain of Custody (TR/COC) documentation includes sample descriptions, date(s) and time(s) of sampling, sample location, and sample matrix. The laboratory's SDG Narrative is another source of general information. Notable problems with matrices, insufficient sample volume for analysis or reanalysis, samples received in broken containers, and unusual events should be listed in the SDG Narrative.

The SDG Narrative for the sample data package must include a Laboratory Certification Statement (exactly as stated in the DLM02.X SOW), signed by the Laboratory Manager or their designee. This statement authorizes the validation and release of sample data results. In addition, the laboratory must also provide comments in the SDG Narrative describing in detail any problems encountered in processing the samples associated with the data package.

DATA REVIEW NARRATIVE

A Data Review Narrative must accompany the laboratory data forwarded to the intended data recipient (client) or user to promote communications. A copy of the Data Review Narrative must also be submitted to the Task Order Project Officer (TOPO) assigned oversight responsibility for the laboratory producing the data.

The Data Review Narrative must include comments that clearly identify the problems associated with a Case or Sample Delivery Group (SDG) and state the limitations of the data. Documentation must include the sample number, analytical method or modification, extent of the problem, and assigned qualifiers.

CHLORINATED DIOXIN AND FURAN DATA REVIEW

The data requirements to be checked are listed below:

I. Holding Times, Storage, and Preservation

II. Performance Evaluation (PE) Samples

III. Mass Calibration and Mass Spectrometer Resolution

IV. Window Defining Mixture (WDM)

V. Chromatographic Resolution

VI. Instrument Stability

VII. High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) Initial Calibration

VIII. High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) Calibration Verification

IX. Identification Criteria

X. Method Blank Analysis

XI. Laboratory Control Sample (LCS) Analysis

XII. Toxicity Equivalency Factor and Isomer Specificity

XIII. Dilution by Addition of Solvent

XIV. Dilution by Re-extraction and Reanalysis

XV. Second Column Confirmation

XVI. Estimated Detection Limit (EDL) and Estimated Maximum Possible Concentration (EMPC)

XVII. Labeled Compound Recoveries

XVIII. Regional Quality Assurance and Quality Control (QA/QC)

XIX. Overall Assessment of Data

I. Holding Times, Storage, and Preservation

A. Review Items:

Form 1DFA, 1DFB, or 1DFC (Form I-HR CDD-1, CDD-2, or CDD-3), USEPA Sample Traffic Report/Chain of Custody (TR/COC) documentation, raw data, and sample extraction sheets.

B. Objective:

Ascertain the validity of sample results based on the contractual holding time, storage, and preservation of the sample from time of collection to time of sample extraction and analysis.

C. Criteria:

Aqueous and soil samples must be stored at 4°C (± 2°C) in the dark from the time of collection until extraction. If residual chlorine is present in aqueous samples, 80 mg of sodium thiosulfate per liter of sample must be added. If the sample pH is > 9, the sample pH must be adjusted to pH 7-9 with sulfuric acid.

NOTE: Aqueous samples subject to compliance with the Clean Water Act (CWA) or Safe Drinking Water Act (SDWA) (40CFR Part 136.3) may require extraction within 7 days from the time of collection to the day of extraction.

Fish and tissue samples must be received at the laboratory at a temperature of < 4°C and must be stored at the laboratory at < -10°C until prepared. Once thawed, tissue samples must be extracted within 24 hours.

- Analysis of sample extracts must be completed within 30 days of extraction.
- Sample extracts can be stored up to one year from the date of extraction in the event that reanalysis is required.
- Holding times for oily matrices have not been established. The aqueous holding times are recommended in this case. Holding times for fish and tissue samples have not been established, however, they must be extracted within one year of collection as recommended in USEPA Method 1613 (Revision B). As always, the professional judgment of the reviewer remains the final authority in issues such as these.

D. Evaluation:

1. Technical holding times for sample extraction are established by comparing the sampling dates on the TR/COC documentation with the dates of extraction on the sample extraction sheets and on Form I-HR CDD-1, CDD-2, or CDD-3. To determine if the samples were analyzed within the holding time after extraction, compare the dates of extraction on the sample extraction sheets with the dates of analysis on Form I-HR CDD-1.

2. Verify that the TR/COC documentation indicates that the samples were received intact and iced at 4°C (± 2°C). Note in the Data Review Narrative if the samples were not iced, if there were any problems with the samples upon receipt, or if discrepancies in the sample condition could affect the data.

E. Action:

1. If holding times are exceeded, qualify all detects as estimated "J" and use professional judgment to qualify non-detects as estimated "UJ" or unusable "R". Document that holding times were exceeded (see Table 1).

2. If shipment and storage conditions are exceeded, either on the first analysis or upon reanalysis, use professional judgment to determine if the detects or non-detects are estimates and qualify with estimated "J" or "UJ", respectively.

3. If sodium thiosulfate preservative has not been added to aqueous samples, qualify all detects estimated "J" and non-detects estimated "UJ". If a residual chlorine test has been performed and found to be negative, do not qualify the data, due to lack of sodium thiosulfate preservative.

4. There is limited information concerning holding times for oily samples. Use professional judgment to evaluate the application of aqueous holding time criteria to oily samples.

5. Use professional judgment to evaluate holding times for fish and tissue samples.

6. For all sample extracts correctly stored and analyzed outside the 30-day holding time, but within the 1-year holding time, no qualification of the data is necessary.

7. For all sample extracts not correctly stored and analyzed outside the 30-day holding time but within the 1-year holding time, qualify detects estimated "J" and non-detects estimated "UJ".

8. For all sample extracts analyzed outside the 1-year holding time, qualify detects as estimated "J" and use professional judgment to qualify non-detects estimated "UJ" or unusable "R".

9. When holding times are exceeded, note in the Data Review Narrative the effect that the exceeded holding times will have on the resulting data and also note as an action item for the Task Order Project Officer (TOPO).

Table 1. Holding Times, Storage, and Preservation Evaluation Actions Data

Evaluation	Sample Type	Criteria	Action	
			Detected Associated Compounds	Non-Detected Associated Compounds
Contractual Holding Time	Aqueous	> 1 year	J	UJ or R
	Soil	> 1 year	J	UJ or R
	Fish, Tissue	> 1 year	Use professional judgment	
Storage Temperature	Aqueous	> 4°C shipment and storage	J	UJ
	Soil	> 4°C shipment and storage	J	UJ
	Fish, Tissue	> 4°C shipment and > -10°C storage	J	UJ
Preservation	Aqueous	Not added	J	UJ
Sample Extract Holding Time *	All types	> 30 days < 1 year	No qualification	
Sample Extract Holding Time **	All types	> 30 days < 1 year	J	UJ
Sample Extract Holding Time	All types	> 1 year	J	UJ or R

* If correctly stored
** If not correctly stored

II. Performance Evaluation (PE) Samples

A. Review Items:

Form 1DFA (Form I-HR CDD-1), Performance Evaluation (PE) sample score information from the Quality Assurance Technical Support (QATS) laboratory.

B. Objective:

Evaluate the laboratory's ability to achieve acceptable results through the analysis of PE samples.

C. Criteria:

1. The Region may provide the laboratory with a PE sample to be analyzed with each Sample Delivery Group (SDG). The laboratory must analyze PE samples when provided by the Region.

2. The Region may score the PE samples based on data provided by QATS.

D. Evaluation:

If PE samples are included in the SDG, verify that the PE sample results are within the action limits [99% (3σ) confidence interval] of the experimentally determined true values provided by QATS.

E. Action:

If a result is not within the action limits [99% (3σ) confidence interval] for any congener, evaluate the other Quality Control (QC) samples in the SDG [Laboratory Control Sample (LCS), calibration, labeled standard recovery, internal standard recovery, and clean-up standard recovery]. In such situations, the PE sample may not be representative of the field samples. PE samples are only one indicator of technical performance of the laboratory. In general, for PE sample analytes not within the 95% confidence intervals or action performance windows but within the 99% confidence interval, qualify associated sample detects as estimated "J" and non-detects as estimated "UJ". For data outside the 99% confidence interval, qualify the associated sample data as unusable "R" (see Table 2). Contact the Task Order Project Officer (TOPO) to determine if reanalysis of samples is required. Under certain circumstances, it may be necessary to utilize data that are not within the 99% confidence interval before reanalysis can take place. Use professional judgment to determine the usability of the data.

For Example: If hexachlorinated dibenzo-p-dioxin (HxCDD) is quantitated beyond the high-end of the action limit and all samples are non-detects for this compound, the usability of the data would not be affected.

NOTE: Qualify only those analytes that fail to meet criteria.

Table 2. PE Sample Data Evaluation Actions

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
Results are not within the 95% confidence interval but inside the 99% interval (< 3σ)	J	UJ
Results are not within the 99% confidence interval (> 3σ)	R	R

III. Mass Calibration and Mass Spectrometer Resolution

A. Review Items:

Hardcopy of Mass Spectrometer resolution demonstration.

B. Objective:

Perform mass calibration and Mass Spectrometer resolution ≥ 10,000 with perfluorokerosene (PFK) calibrant. This is a fundamental requirement for any laboratory using DLM02.X and other High Resolution Mass Spectrometry (HRMS) methods [e.g., Method 1613 (Revision B), SW-846 Method 8290 (Revision 0)]. If mass calibration and resolution tuning is not correctly performed, interferences may degrade chlorinated dibenzo-p-dioxin and chlorinated dibenzofuran (CDD/CDF) identification and quantitation. Mass calibration and resolution is the first part of the three fundamental High Resolution Gas Chromatography/HRMS (HRGC/HRMS) system performance checks. The second fundamental performance check is the Mass Spectrometer Selected Ion Monitoring (SIM) scan descriptor switching times. The third fundamental performance check is Gas Chromatograph (GC) resolution.

C. Criteria:

Laboratories are required to provide evidence of Mass Spectrometer resolution ≥ 10,000 at the beginning and end of each 12-hour analytical sequence. Documentation of Mass Spectrometer resolving power must include a hardcopy peak profile of a high-mass reference signal from PFK (e.g., m/z 380.9760) obtained during peak matching with another high-mass ion (e.g., m/z 304.9824). The selection of the low- and high-mass ions must be such that they provide the largest voltage jump in any of the five mass descriptors. The format of the peak profile representation must allow manual determination of Mass Spectrometer resolution [i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division)]. The result of the peak width measurement must appear on the hardcopy. The deviation between the exact m/z and the theoretical m/z monitored must be < 5 ppm.

D. Evaluation:

Verify that the Mass Spectrometer has been tuned to a resolution of ≥ 10,000. A demonstration of Mass Spectrometer resolving power is provided within USEPA SW-846 Method 8290 (Revision 0).

E. Action:

Mass Spectrometer resolution is critical to the success of this method of CDD/CDF analysis. In the event that Mass Spectrometer resolution is < 10,000 or is not demonstrated, qualify all associated data as unusable "R".

IV. Window Defining Mixture (WDM)

A. Review Items:

Form 5DFA (Form V-HR CDD-1).

B. Objective:

Prior to the calibration of the High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) system, establish the appropriate switching times for the Selected Ion Monitoring (SIM) descriptors (see Table A.1) and verify the chromatographic resolution. The switching times are determined by the analysis of the Window Defining Mixture (WDM) which contains the first and last eluting isomers in each homologue (see Table A.2). Chromatographic resolution is verified by analyzing one of two Isomer Specificity Check (ISC) solutions, depending on the Gas Chromatograph (GC) column used for analysis. The WDM and ISC can be combined in a single Column Performance Solution (CPS) analysis at the discretion of the analyst.

The 12-hour time period begins with the injection of the WDM or CPS.

C. Criteria:

1. To evaluate the Mass Spectrometer SIM scan descriptor switching times, the WDM must be analyzed after the perfluorokerosene (PFK) tune and before any calibration standards on each instrument and GC column used for analysis, once at the beginning of each 12-hour period during which standards or samples are analyzed and whenever adjustments or instrument maintenance activities are performed that may affect Retention Times (RTS). This commercially available, 16-component mixture contains the first and last eluting isomers in each homologue. Mixtures are available for various columns. The mixture for the DB-5 (or equivalent) column may not be appropriate for the DB-225 or other columns.

2. The ions in each of the five recommended descriptors are arranged for minimal overlap between the descriptors. The ions for the tetrachlorinated dibenzo-p-dioxin (TCDD) and tetrachlorinated dibenzofuran (TCDF) isomers are in the first descriptor, the ions for the pentachlorinated dibenzo-p-dioxin (PeCDD) and pentachlorinated dibenzofuran (PeCDF) isomers are in the second descriptor, the ions for the hexachlorinated dibenzo-p-dioxin (HxCDD) and hexachlorinated dibenzofuran (HxCDF) isomers are in the third descriptor, the ions for the heptachlorinated dibenzo-p-dioxin (HpCDD) and heptachlorinated dibenzofuran (HpCDF) isomers are in the fourth descriptor, and the ions for the octachlorinated dibenzo-p-dioxin (OCDD) and octachlorinated dibenzofuran (OCDF) isomers are in the fifth descriptor. In some cases, the tetrachlorinated and pentachlorinated dioxins and furans are combined in a single descriptor.

3. The descriptor switching times are set such that the isomers that elute from the GC during a given RT window will also be those isomers for which the ions are monitored. If homologue overlap between descriptors occur, the laboratory may use professional judgment in setting the switching times. The switching times are **not** to be set such that a change in descriptors occurs at or near the expected RT of any 2,3,7,8-substituted isomers.

4. The WDM must be analyzed at the following frequency:

   - Before initial calibration on each instrument and GC column used for analysis;
   - Each time a new initial calibration is performed, regardless of reason;
   - Each time adjustments or instrument maintenance activities are performed that may affect RTS; and
   - During each 12-hour sample analysis period prior to the calibration verification.

5. If the laboratory uses a GC column that has a different elution order than the columns specified, the laboratory must ensure that the first and last eluting isomers in each homologue are represented in the WDM used to evaluate that column. The concentrations of any additional isomers should be approximately the same as those in WDM solutions intended for use with conventional chlorinated-p-dioxin/chlorinated dibenzofuran (CDD/CDF) GC columns.

6. Analysis on a single GC column (as opposed to situations requiring second column confirmation) is acceptable if the required separation of all of the 2,3,7,8-substituted isomers is demonstrated and the resolution criteria for both the DB-5 and DB-225 (or equivalent) columns are met (see Section V).

D. Evaluation:

1. Verify that the WDM is analyzed at the required frequency.

2. Examine the WDM chromatograms to determine when descriptor switching times are turned on and off.

3. Note the RT of each first and last eluting isomer in each homologue for identification of switching times.

4. Each positive dioxin and furan result (tetra- through hepta-) must have an RT within the limits established by the WDM for the corresponding homologue. The 2,3,7,8-substituted dioxins and furans must also meet the Relative Retention Time (RRT) limits in Table A.3.

E. Action:

1. If the WDM was not analyzed at the required frequency or correct adjustments in descriptor switching times are not evident, but the calibration standards met specifications the individual 2,3,7,8-substituted target analyte, results may be usable without qualification. Qualify total homologue results as estimated "J" since one or more CDDs/CDFs may not have been detected.

2. If the chromatography for the calibration standards indicate a significant problem with descriptor switching times, qualify all associated data as unusable "R". Notify the Task Order Project Officer (TOPO) to decide if sample reanalysis is necessary.

V. Chromatographic Resolution

A. Review Items:

Form 5DFB (Form V-HR CDD-2), and the corresponding Selected Ion Current Profile (SICP) of each isomer and each of the analyses reported on Form 5DFB.

B. Objective:

Evaluate the ability of the Gas Chromatograph (GC) column to resolve the closely eluting dioxin and furan isomers. An evaluation must be made for each column used in the analysis of samples.

C. Criteria:

The resolution criteria must be evaluated using measurements made on the SICPs for the appropriate ions for each isomer. Measurements are **not** to be performed on Total Ion Current Profiles (TICPs).

1. For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of the commercially available, 4-component DB-5 Isomer Specificity Check (ISC) standard prior to both the initial and calibration verification procedures for each instrument and GC column used for analysis. Use professional judgment to combine the ISC and Window Defining Mixture (WDM) in a single Column Performance Solution (CPS) analysis.

    a. GC resolution criteria for DB-5 (or equivalent) column: The chromatographic peak separation between the 2,3,7,8-TCDD peak and the 1,2,3,8-TCDD peak shall be resolved with a valley of ≤ 25% using the following equation:

$$\text{Valley} = \frac{x}{y} \times 100$$

Where,

x = The measurement from the baseline to the deepest part of the valley between 2,3,7,8-TCDD and 1,2,3,8-TCDD

y = The peak height of 2,3,7,8-TCDD

    b. For the DB-5 (or equivalent) column, the 12-hour sample analysis period begins by analyzing the WDM or CPS solution. The identical HRGC/HRMS conditions used for the analysis of the WDM, ISC, and CPS solutions must also be used for the analysis of the initial calibration and calibration verification solutions. Evaluate the chromatographic resolution using the Quality Control (QC) criteria listed above.

2. Evaluate the chromatographic resolution for analyses on a DB-225 (or equivalent) GC column, then analyze the calibration standards. To evaluate the chromatographic resolution, use a commercially available, 3-component DB-225 ISC containing the tetrachlorinated dibenzofuran (TCDF) isomers that elute most closely with 2,3,7,8-TCDF on the GC column (1,2,3,9-TCDF and 2,3,4,7-TCDF).

   a. GC resolution criteria for DB-225 (or equivalent) column: The chromatographic peak separation between the 2,3,7,8-TCDF peak and the 2,3,4,7-TCDF peak must be resolved with a valley of ≤ 25% using the following equation:

$$\text{Valley} = \frac{x}{y} \times 100$$

   Where,

   x = The measurement from the baseline to the deepest part of the valley between 2,3,7,8-TCDF and 2,3,4,7-TCDF

   y = The peak height of 2,3,7,8-TCDF

   b. Further analysis may not proceed until the GC resolution criteria have been met.

3. If the laboratory uses a GC column other than the columns specified here, the laboratory must ensure that the isomers eluting closest to 2,3,7,8-TCDD on that column are used to evaluate GC column resolution. The chromatographic peak separation between 2,3,7,8-TCDD and the peaks representing all other tetrachlorinated dibenzo-p-dioxin (TCDD) isomers shall be resolved with a valley of ≤ 25%.

4. Analysis on a single GC column (as opposed to situations requiring second column confirmation) is acceptable if the required separation of all of the 2,3,7,8-substituted isomers is demonstrated and the resolution criteria for both the DB-5 and DB-225 (or equivalent) columns are met, as stated above.

D. Evaluation:

Verify from the SICPs that the ≤ 25% valley criteria are met. Examples of GC resolution can be found in USEPA Method 1613 (Revision B) and SW-846 Method 8290 (Revision 0).

E. Action:

If the GC resolution does not meet the specifications, qualify all detects and non-detects for 2,3,7,8-TCDD and/or 2,3,7,8-TCDF, whichever failed, as estimated "J" (see Table 3) and notify the Task Order Project Officer (TOPO) to decide on sample reanalysis.

Table 3. System Performance Checks

Criteria	Action
Mass Spectrometer resolution of ≥ 10,000 is not demonstrated	R
WDM fails, or WDM adjustments are not made, or WDM is not reported	J
WDM fails, and WDM adjustments are not made, and Calibration standards indicate a problem in detecting 2,3,7,8-substituted congeners because of gross errors in the scan descriptor times	R
CPS fails or is not reported	J

VI. Instrument Stability

A. Review Items:

Raw data for the midpoint (CS3) standard at the beginning of the 12-hour sample analysis period.

B. Objective:

Demonstrate that the High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) system has retained adequate stability, the CS3 standard is analyzed at the beginning and end of each 12-hour period or analytical sequence during which samples and standards were analyzed. The end analysis may also serve as the beginning analysis of the subsequent 12-hour period. The use of the CS3 standard as a measure of instrument stability includes the evaluation of Gas Chromatograph (GC) Retention Times (RTS), relative ion abundance criteria, sensitivity, and calibration criteria.

C. Criteria:

The CS3 solution must meet the following Quality Control (QC) criteria:

1. Absolute RT criteria: The absolute RT of the first internal standard $^{13}C_{12}$-1,2,3,4-TCDD must be within ± 15 seconds of the absolute RTS of the identical compound obtained during initial calibration. If the RT of the first internal standard changes by more than ± 15 seconds, the laboratory must adjust the switching times of the descriptors and analyze the Window Defining Mixture (WDM) before proceeding with further analyses. Additionally, the absolute RT of the aforementioned first internal standard must exceed 25.0 minutes on the DB-5 column, and 15.0 minutes on the DB-225 column.

2. Relative Retention Time (RRT) criteria: The RRTs of the native and labeled chlorinated dibenzo-p-dioxins/chlorinated dibenzofurans (CDDs/CDFs) shall be within the limits described in Section VII and Table A.3.

3. Ion abundance ratio criteria: All native and labeled CDDs/CDFs in the CS3 standard must be within their respective ion abundance ratios (see Table A.4).

4. Instrument sensitivity criteria: The peaks representing both native and labeled analytes in the CS3 standard must have signal-to-noise (S/N) ratios ≥ 10:1.

5. Response criteria: The %D of the Relative Response (RR) must be within ± 25% of the RR of the initial calibration. The %D of the Relative Response Factor (RRF) must be within ± 35% of the initial calibration. Use the following equation to calculate the Percent Difference (%D):

$$\%D = \frac{Response_{ver} - Response_{INT}}{Response_{INT}} \times 100$$

Where,

$Response_{ver}$	=	Response (RR or RRF) established during calibration verification
$Response_{INT}$	=	Mean response ($\overline{RR}$ or $\overline{RRF}$) established during initial calibration according to DLM02.X, Exhibit D

D. Evaluation:

Verify that the CS3 standard meets the criteria for both RT and RRT, ion abundance ratio, S/N ratio, and response (%D associated with RR and RRF). An example of the measurement of S/N can be found in USEPA SW-846 Method 8290A (Revision 0) and can be obtained at: http://www.epa.gov/sw-846/pdfs/8290a.pdf

E. Action:

1. The RTS and RRTs of the CS3 internal standards will tell the reviewer much about the stability of the instrument. If the RT changes by more than ± 15 seconds when compared to previous calibration standards, the reviewer should carefully examine subsequent samples to determine if the change is an isolated occurrence or if the RT of the internal standard is consistent in the 12-hour period. The reviewer should use professional judgment to qualify the sample data if the CS3 internal standard RT changes by more than ± 15 seconds from subsequent sample internal standards (see Table 4). No qualification of sample data is necessary if the sample internal standard RTS are consistent.

2. The ion abundance, sensitivity, and calibration criteria are all critical indicators of instrument stability (see Table 4). Failure to satisfy the ion abundance criteria, S/N ratio 10:1 criteria, or the %D RR and RRF criteria each indicate significant problems with the instrument. Qualify detects as estimated "J" if any of these criteria fail. The S/N criteria are especially indicative of severely degraded instrument performance. For all affected analytes, qualify non-detects in associated samples as unusable "R" if the S/N ratio < 10:1 in the CS3 calibration verification standard.

Table 4. High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) Instrument Stability

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
RT changes > 15 seconds or RRT changes not within the values in Table A.3	Use professional judgment	
Relative ion abundance criteria is not within windows in CS3 (12-hour) standard	J	No qualification
S/N ratio < 10:1 in CS3 standard	J	R
%D greater than criteria in CS3 standard	J	No qualification

VII. High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) Initial Calibration

A. Review Items:

Form 6DFA (Form VI-HR CDD-1), Form 6DFB (Form VI-HR CDD-2), and raw data for all standards.

B. Objective:

Establish compliance requirements for satisfactory instrument calibration to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for the compounds on the Target Compound List (TCL).

The objective of the initial calibration is to establish a linear range and Mean Relative Responses ($\overline{RR}$s) and the Mean Relative Response Factors ($\overline{RRF}$s) for the instrumentation. The initial calibration is to be used for routine quantitation of samples using the $\overline{RR}$s and $\overline{RRF}$s established from the five Calibration Standards (CS1, CS2, CS3, CS4, and CS5). Subsequent calibration verifications occurring every 12 hours thereafter are not to be used for quantitation of samples, nor is the initial midpoint (CS3) solution to be used for this purpose.

C. Criteria:

The initial calibration criteria are strict because of their use in quantitation of sample data and the infrequency of initial calibration. Thus, the initial calibration affects the quality of the data based on it for an extended period of time.

Initial Calibration

Once the perfluorokerosene (PFK), Window Defining Mixture (WDM), Isomer Specificity Check (ISC), and Column Performance Solution (CPS) solutions have all been analyzed, and once the descriptor switching times have all been verified, the five CSs described in Table A.5 must be analyzed prior to any sample analysis.

The following criteria must be met for the initial calibration to be acceptable: Gas Chromatograph (GC) resolution; ion abundance ratio; Retention Time (RT); Relative Retention Time (RRT); instrument sensitivity [signal-to-noise (S/N)]; linearity of analyte response associated with Relative Response (RR) and Relative Response Factor (RRF); analyte concentration (ng/mL); and calibration frequency.

1. GC resolution criteria: Use DB-5, DB-225, or equivalent columns (see Section V).

2. Ion abundance criteria: The relative ion abundance criteria for chlorinated dibenzo-p-dioxins/ chlorinated dibenzofurans (CDDs/CDFs) listed in Table A.4, must be met for all CDD/CDF peaks, including the isotope-labeled peaks, in all solutions. The lower and upper limits of the ion abundance ratios represent a ± 15% window around the theoretical abundance ratio for each pair of selected ions (see Table A.1, for m/z types and exact m/z

ratios). The $^{37}Cl_4$-2,3,7,8-TCDD clean-up standard contains no ^{35}Cl, therefore the ion abundance ratio criteria do not apply to this compound.

3. Retention Time (RT) criteria: For all calibration solutions, the RTS of the isomers must fall within the appropriate RT windows established by the WDM analysis. In addition, the absolute RT of the internal standard $^{13}C_{12}$-1,2,3,4-TCDD must exceed 25 minutes on the DB-5 (or equivalent) column and 15 minutes on the DB-225 (or equivalent) column.

4. Mass Spectrometer sensitivity criteria: For all calibration solutions, including the CS1 solution, the S/N ratio must be $\geq$ 10:1.

5. Linearity criteria: The $\overline{RRF}$s and Percent Relative Standard Deviation (%RSD) of the five RRFs (CS1-CS5) for each compound applicable to RRF (internal standard) treatment is calculated. The %RSD of the five RRFs (CS1-CS5) must not exceed 35% for these compounds. Likewise, the $\overline{RR}$ and %RSD of the five RRs (CS1-CS5) for each compound applicable to RR (isotope dilution) treatment is calculated. The %RSD of the five RRs (CS1-CS5) must not exceed 20% for these compounds.

6. Concentration criteria: All initial Calibration Standards (CSs) must be analyzed at the correct concentration levels (see Table A.5).

7. Frequency criteria: Each HRGC/HRMS system must be initially calibrated to meet the terms of the contract whenever:

   - The laboratory takes corrective action which may change or affect the initial calibration criteria.

   - The calibration verification (CS3 calibration verification) acceptance criteria cannot be met even after corrective action (see Sections VI and VIII).

D. Evaluation:

1. Verify that the PFK, WDM, ISC, and CPS solutions were analyzed before the calibration standards.

2. Verify that all analytes in all calibration solutions are present at the correct concentrations (see Table A.5).

3. Verify that the requirements for frequency of initial calibration were observed.

4. Verify that the five RRF %RSDs are $\leq$ 35%.

5. Verify that the five RR %RSDs are $\leq$ 20%.

6. Verify that the ion abundance ratios in each CS are within $\pm$ 15% of the limits listed in Table A.4.

7. Verify that the GC resolution criteria are met [Percent Valley (% Valley) ≤ 25%].

8. Verify that the instrument sensitivity criteria are met (S/N ≥ 10) in all Selected Ion Current Profiles (SICPs).

9. Verify that the RT criteria involving the WDM and the internal standards are met.

E. Action:

1. Concentrations and Frequency

   All initial calibration standards must be analyzed at the concentrations described in the DLM02.X SOW. Initial calibrations must be performed when the contract is awarded, whenever significant instrument maintenance is performed (e.g., ion source cleaning, GC column replacement, etc.), or if calibration verification criteria are not met (see Table 5).

2. Ion Abundance Ratios

   If an analyte in a calibration standard failed the ion abundance ratio criteria, qualify sample results analyzed immediately after that initial calibration using the $\overline{\text{RRF}}$s or $\overline{\text{RR}}$ values for quantitation as unusable "R" for that analyte, because both the RRF and RR values depend on the areas used in the ion abundance ratio. Failed ion abundance ratio criteria for any analyte is a cause for concern, and may indicate that the Mass Spectrometer is not tuned correctly, the zero point is not correctly adjusted, or other problems.

   Use professional judgment for a more in-depth review to minimize the qualification of data which may be accomplished by considering the following hypothetical examples:

   - If the ion abundance ratio is not within the limits for an analyte in the CS1 solution (see Table A.4), qualify the low-end results for that analyte (below the CS2 concentration from Table A.5) as unusable "R".

   - If the ion abundance ratio is not within the limits for an analyte in the CS5 solution (see Table A.4), qualify the high-end results for that analyte (above the CS4 concentration from Table A.5) as unusable "R".

3. GC Resolution

   If failed resolution criteria involves tetrachlorinated dibenzo-p-dioxin (TCDD) isomers, qualify only those isomers as estimated "J". Request a reanalysis for all samples following a failed resolution to ensure the quantity of isomers present. When GC resolution capability is lacking, assume that 2,3,7,8-TCDD is the only isomer present.

4. Analyte Response

   If the %RSD is not within ± 20% and ± 35% for the RR and RRF, respectively, qualify the detects as estimated "J". The reviewer may discard either the CS1 or CS5 values for the initial calibration and recalculate the %RSD. If discarding either of these points brings the %RSD within the specified limits, qualify either the low- or high-end hits, depending on which point was discarded. Use professional judgment to perform reanalysis if either of these scenarios affect a majority of the data.

5. Sensitivity

   If the S/N ratio 10:1 sensitivity requirements are not met, qualify any detects as estimated "J" and non-detects as unusable "R" for all associated samples.

6. Retention Time

   Qualify all failed RT criteria from the initial calibration associated with the failed analyte(s) and reanalysis of all affected samples as unusable "R". No action is taken for non-detects. Systematic RT problems affecting all data require complete rejection of the entire data package, followed by reanalysis of all the samples.

Table 5. Initial Calibration

Criteria	Action	
	Detected Associated Compounds	**Non-Detected Associated Compounds**
Initial calibrations are not performed at the prescribed concentration and frequency	R	R
Ion Abundance Ratios is not within ± 15% of theoretical values, as described in Table A.4	R	R
GC Resolution (% Valley) of > 25%	J	No qualification
Linearity: RRF %RSDs is not within ± 35%; RR %RSDs is not within ± 20%	J	UJ
Sensitivity < 10:1 S/N ratio for all SICPs	J	R
RTs: Not within appropriate windows and absolute RT of internal standard $^{13}C_{12}$-1,2,3,4-TCDD or, > 25 minutes on DB-5 (or equivalent) column, or > 15 minutes on DB-225 (or equivalent) column	R	No qualification

VIII. High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) Calibration Verification

A. Review Items:

Form 7DFA (Form VII-HR CDD-1), Form 7DFB (Form VII-HR CDD-2), and raw data from the midpoint (CS3) standard.

B. Objective:

Establish compliance requirements for satisfactory calibration to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. Calibration verification is used to validate the Relative Responses (RRs) and Relative Response Factors (RRFs) of the initial calibration on which quantitations are based, and to check for satisfactory performance of the instrument on a day-to-day basis.

C. Criteria:

Calibration verification criteria: The laboratory must not proceed with sample analysis until an acceptable calibration verification has been performed and documented according to the following criteria: ion abundance ratios; Retention Times (RTS); Relative Retention Times (RRTs); instrument sensitivity [signal-to-noise (S/N)]; and analyte response [Percent Difference (%D) associated with the RR and RRF].

1. Ion abundance criteria: The ion abundance ratio criteria listed in Table A.4, must be met for all chlorinated dibenzo-p-dioxin/chlorinated dibenzofuran (CDD/CDF) peaks, including the labeled versions of native compounds and the internal standards.

2. Absolute Retention Time (RT) criteria: The RT of the first-eluting internal standard ($^{13}C_{12}$-1,2,3,4-TCDD) on the DB-5 (or equivalent) column and the DB-225 (or equivalent) column must meet the absolute RT criteria (see Section VI). In addition, the absolute RT of the internal standards must be within ± 15 seconds of the RTS obtained during the initial calibration.

3. Relative Retention Time (RRT) criteria: The RRTs of the native and labeled chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans (CDDs/CDFs) must be within the defined limits (see Section VII).

4. Instrument sensitivity criteria: For the CS3 solution, the signal-to-noise (S/N) ratio must be ≥ 10:1 for all CDD/CDF peaks, including the labeled versions of native compounds and the internal standards.

5. Analyte response criteria: The measured RRFs and RRs of each analyte and standard (labeled and internal) must be within ± 20% (RR) and ± 35% (RRF) of the mean values established during initial calibration:

$$\% \text{ Difference} = \frac{[(RRF_c - RRF_i) \times 100]}{RRF_i}$$

Where,

RRF_c = RRF established during calibration verification

RRF_i = RRF established during initial calibration

And:

$$\% \text{ Difference} = \frac{[(RR_c - RR_i) \times 100]}{RR_i}$$

Where,

RR_c = RR established during calibration verification

RR_i = RR established during initial calibration

D. Evaluation:

1. Verify that the calibration verification was run at the required frequency [following the Window Defining Mixture (WDM) or Column Performance Solution (CPS) in each 12-hour period] and that the calibration verification was compared to the correct initial calibration.

2. Verify from the raw data that the ion abundance ratios listed in Table A.4, were all met.

3. Verify from the raw data that the absolute RT criteria for the compound $^{13}C_{12}$-1,2,3,4-TCDD were met.

4. Verify from the raw data that the RRT criteria for the native and labeled CDDs/CDFs were met.

5. Verify from the raw Selected Ion Current Profile (SICP) data that the S/N ratio is ≥ 10:1 for the unlabeled CDD/CDF ions, labeled compounds, and internal standards.

6. Verify from the raw data that the measured RRs and RRFs of each analyte, labeled and otherwise, in the CS3 solution are within ± 25% (RRs) and within ± 35% (RRFs) of the mean values established during initial calibration.

E. Action:

If the calibration verification was not analyzed at the required frequency, contact the Task Order Project Officer (TOPO) to initiate sample reanalysis.

1. Use professional judgment to qualify any analyte in samples associated with a calibration verification not meeting the RT and/or RRT criteria (see Table 6).

2. Any detect in samples associated with a calibration verification not meeting the ion abundance criteria listed in Table A.4, is to be estimated "J" and non-detects estimated "UJ". The High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGS/HRMS) must be re-calibrated and the affected samples must be re-analyzed.

3. If the S/N ratio ≥ 10:1 limit is not met in a calibration verification, qualify all detects as estimated "J" and all non-detects as unusable "R".

4. Since the initial calibration is used to generate the RR and RRF values used for quantitation, the %D relative to the initial calibration's Mean RR ($\overline{RR}$) or Mean RRF ($\overline{RRF}$) is a crucial criterion for review. Qualify data associated with an analyte with a %D not within ± 20% (RR) and not within ± 35% (RRF) as estimated "J". Re-calibrate the HRGS/HRMS and re-analyze the affected samples.

Table 6. Calibration Verification Evaluation Actions

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
Ion abundance ratios not within ± 15% window	J	UJ
Absolute RT of internal standard $^{13}C_{12}$-1,2,3,4-TCDD > 25 minutes on DB-5 (or equivalent) column, or > 15 minutes on DB-225 (or equivalent) column	Use professional judgment	
Internal standards in the calibration verification not within 15 seconds of the RTS in the initial calibration	Use professional judgment	
RRTs in the calibration verification not within the limits defined in Table A.3	Use professional judgment	
Sensitivity: S/N < 10 for all compounds	J	R
%D for RRs not within ± 20% %D for RRFs not within ± 35%	J	No qualification

IX. Identification Criteria

A. Review Items:

Form 1DFA (Form I-HR CDD-1), Form 2DF (Form II-HR CDD), and raw data.

B. Objective:

Unambiguously identify a Gas Chromatographic (GC) peak as a chlorinated dibenzo-p-dioxin (CDD) or a chlorinated dibenzofuran (CDF).

C. Criteria:

For a GC peak to be unambiguously identified as a CDD or CDF, it must meet all of the following criteria:

1. Retention Times (RTS) and Relative Retention Times (RRTs)

   Retention Times (RTS) are required for all chromatograms; scan numbers are optional. For positive identifications, RTS for the two quantitation ions must maximize within 2 seconds. RTS must either be printed at the apex of each peak on the chromatogram, or each peak must be unambiguously labeled with an identifier that refers to the quantitation report. The chromatogram, the quantitation report, or a combination of both must contain the RT of each peak and its area.

   - To make a positive identification of the 2,3,7,8-substituted isomers for which an isotopically labeled counterpart or internal standard is present in the sample extract, the Relative Retention Time (RRT) at the maximum peak height of the analyte must be within the RRT window in Table A.3. The RRT is calculated as follows:

$$\text{RRT} = \frac{\text{RT of analyte}}{\text{RT of corresponding internal standard}}$$

   - To make a positive identification of the non-2,3,7,8-substituted isomers (tetra- through hepta-) for which a labeled standard is not available, the RT must be within the RT window established by the Window Defining Mixture (WDM) for the corresponding homologue.

2. Peak Identification

   Both of the specified ions listed in Table A.1, and on Forms I for each CDD/CDF homologue, must be present in the Selected Ion Current Profile (SICP). The ion current response for the two quantitation ions for the analyte in question must maximize simultaneously within the same 2 seconds. This requirement also applies to the labeled

versions of the native and internal standards. For the clean-up standard, only one ion is monitored.

3. Signal-to-Noise (S/N) Ratio

   The integrated ion current for each native analyte ion listed in Table A.1, must be at least 2.5 times (2.5x) the background noise and must not have saturated the detector (applies to sample extracts only). The labeled and internal standard ions, however, must be at least 10.0x the background noise and must also not have saturated the detector (applies to sample extracts only). In the case of the various calibration standard solutions, the S/N ratio must be ≥ 10:1 for all of the CDD/CDF compounds, whether or not they are labeled.

4. Ion Abundance Ratios

   The ion abundance ratio criteria listed in Table A.4, for native and labeled analytes and for internal standards must be met using peak areas to calculate ratios.

   If interferences are present and ion abundance ratios are not met using peak areas, but all other qualitative identification criteria are met (RT, S/N, presence of both ions), the laboratory may use peak heights to evaluate the ion ratio. If the peak is a CDD/CDF, the ion abundance ratios may be determined using peak heights instead of areas. Quantitate the peaks as "H" using peak heights rather than areas for both the target analyte and the labeled compound or internal standard.

5. Polychlorinated Diphenyl Ether (PCDPE) Interferences

   If PCDPE interferences are detected above the 2.5:1 S/N ratio limit, as indicated by the presence of peaks at the exact m/z(s) monitored for these interferents (see Table A.1), qualify all CDF sample results with a coeluting PCDPE interference as estimated "J".

D. Evaluation:

1. Verify that the RRTs for the 2,3,7,8-substituted compounds are within the RRT windows listed in Table A.3.

2. Verify that the RTS for the non-2,3,7,8-substituted compounds are within the RT windows established by the WDM for the corresponding homologues (Form 5DFA).

3. Verify from the SICPs that the ion current responses for the two quantitation ions for each analyte maximize simultaneously (within the same 2 seconds).

4. Verify from the SICPs that for each analyte ion listed in Table A.1, the S/N ratio is ≥ 2.5:1 and that the detector has not been saturated. Use professional judgment to verify the presence of the CDD/CDF if an analyte is flagged with an asterisk (*).

5. Verify from the Forms I that the ion abundance ratios are within the criteria listed in Table A.4.

6. Verify that no PCDPE interferences exist.

E. Action:

1. If a peak falls outside of the Table A.3 and/or the WDM windows, qualify the results as unusable "R" (see Table 7).

2. If ion current responses for the two quantitation ions for an analyte fail to maximize simultaneously (within 2 seconds), qualify the data as unusable "R".

3. If ion abundance criteria are not satisfied, qualify the detects as unusable "R" and use professional judgment to qualify non-detects.

4. If S/N criteria are not satisfied, qualify the detects as estimated "J" and non-detects as estimated "UJ".

5. If PCDPE interferences exist above the 2.5:1 S/N ratio limit, qualify associated CDFs as estimated "J" and non-detects as estimated "UJ".

Table 7. Identification Criteria Evaluation Actions

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
Signals do not maximize within 2 seconds	R	R
S/N < 2.5	J	UJ
Ion abundance ratios not within the limits in Table A.4, or not within 10% of the ratio in the most recent CS3 standard	R	R
RRTs for 2,3,7,8-substituted CDD and CDF not within the limits in Table A.3 The RT of non-substituted CDDs/CDFs not within the RTS established by the WDM	R	R
PCDPE ion S/N > 2.5	J	UJ

NOTE: Use professional judgment to determine the correct identification of analytes.

X. Method Blank Analysis

A. Review Items:

Form 4DF (Form IV-HR CDD) and raw data.

B. Objective:

Determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The criteria for evaluation of blanks apply to any method blank associated with samples. If problems with a blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. Acceptable laboratory method blanks must not contain any chemical interference or electronic noise at or above the Contract Required Quantitation Limit (CRQL) at the m/z of the specified unlabeled chlorinated dibenzo-p-dioxin/chlorinated dibenzofuran (CDD/CDF) ions. There must be at least one laboratory method blank for each batch of samples extracted.

2. A peak that meets identification criteria as a CDD/CDF in the method blank must not exceed the CRQL for that analyte except in the case of octachlorinated dibenzo-p-dioxin/octachlorinated dibenzofuran (OCDD/OCDF), where the maximum allowable amount is less than three times (< 3x) the CRQL.

3. If a group of samples and the method blank are contaminated, rerun the associated detects and any samples containing peaks that do not meet all of the qualitative identification criteria for a contaminated method blank.

   NOTE: Report results for all peaks with signal-to-noise (S/N) ratio > 2.5:1, even if they are < CRQL (see DLM02.X, Exhibit C for CDD/CDF CRQLs).

4. The method blank, like any other sample in the Sample Delivery Group (SDG), must meet the technical acceptance criteria for sample analysis (see DLM02.X, Exhibit D).

D. Evaluation:

1. Verify that at least one method blank is analyzed with each matrix-specific extraction procedure, including separatory funnel and continuous liquid-liquid extraction procedures.

2. Verify that, with the exception of OCDD and OCDF, the method blank(s) are free from contamination ≤ CRQL for the native compounds. The concentration of OCDD/OCDF in the method blank must be < 3x the CRQL.

E. Action:

1. If the method blank is contaminated with a CDD/CDF greater than or equal to the CRQLs listed in the DLM02.X SOW, or are greater than three times (> 3x) the CRQLs for OCDD/OCDF, qualify all detects as estimated "J" and non-detects for those analytes as estimated "UJ" (see Table 8).

2. Use professional judgment to qualify detects as unusable "R" that are below method blank contaminant concentrations and a sample/sample set with results at levels similar to the levels reported in the method blank.

Table 8. Method Blank Evaluation Actions

Method Blank Result	Sample Result	Action
< CRQL	Not detected	No qualification
	< CRQL	U
	≥ CRQL	Use professional judgment
> CRQL (> 3x CRQL for OCDD/OCDF)	Not detected	UJ
	< CRQL	U
	≥ CRQL and < Blank Result	U or J
	> CRQL and ≥ Blank Result	Use professional judgment
=CRQL	Not detected	UJ
	< CRQL	U
	≥ CRQL	Use professional judgment
Gross contamination	Positive	R

XI. Laboratory Control Sample (LCS) Analysis

A. Review Items:

Form 3DFA (Form III-HR CDD-1) and raw data.

B. Objective:

Provide data on the accuracy of the analytical method, and prepare and analyze a sample of spiked reference matrix [the Laboratory Control Sample (LCS)] for each matrix analyzed. If a matrix is not represented in a Sample Delivery Group (SDG), no spiked LCS is required for that matrix. USEPA has identified a number of reference matrices to be used for the spiked LCS, and the laboratory must use an aliquot of that matrix for its own LCS work (see DLM02.X, Exhibit D). When a reference matrix that simulates the sample matrix under test is not readily available, USEPA retains the option to supply the laboratory with a reference matrix containing the expected interferences for a particular project.

C. Criteria:

1. For each sample Delivery Group (SDG), the laboratory must prepare a spiked LCS for all of the matrix types that occur in that SDG (see DLM02.X, Exhibit D).

2. The recovery of each spiked analyte must be in the range in Table A.6.

3. The LCS must meet the technical acceptance criteria for sample analysis (see DLM02.X, Exhibit D).

D. Evaluation:

Confirm that the spiking solution was added to the LCS, and that the chlorinated-p-dioxin/chlorinated dibenzofuran (CDD/CDF) analytes were at their correct concentrations. Verify that calculations, and transcriptions from raw data, were performed correctly.

E. Action:

1. If LCS recovery results are greater than the upper acceptance limits, qualify all associated sample data for those analytes which fail in the LCS as estimated "J" (see Table 9). No qualification of the data is necessary if the laboratory failed to prepare and analyze the LCS at the required frequency. Note this in the Data Review Narrative and notify the Task Order Project Officer (TOPO).

2. If LCS results are < 10%, qualify those analytes and non-detects as unusable "R" in all of the associated samples. Notify the TOPO concerning samples associated with a non-compliant LCS to decide on re-extraction and reanalysis.

Table 9. Laboratory Control Sample (LCS) Recovery Actions

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
%R > Upper Acceptance Limit	J	No qualification
10% < %R < Lower Acceptance Limit	J	R
10% > %R	R	R

XII. Toxicity Equivalency Factor (TEF) and Isomer Specificity

A. Review Items:

Form 1DFB (Form I-HR CDD-2) and raw data.

B. Objective:

Isomer specificity for all 2,3,7,8-substituted chlorinated dibenzo-p-dioxins/chlorinated dibenzofurans (CDDs/CDFs) cannot be achieved on the 60 meter DB-5 column alone. Historically, problems have been associated with the separation of 2,3,7,8-TCDD from 1,2,3,7-/1,2,3,8-TCDD and 1,2,3,9-TCDD, and separation of 2,3,7,8-TCDF from 1,2,3,9-TCDF and 2,3,4,7-TCDF. There is toxicological concern associated with 2,3,7,8-TCDD and 2,3,7,8-TCDF; therefore additional analyses may be required for some samples, as described below.

The exclusion of homologues such as mono-, di-, tri-, and the non-2,3,7,8-substituted isomers in the higher homologues, does not mean that they are not toxic. Their toxicity, as estimated at this time, is much less than the toxicity of the native 2,3,7,8-substituted isomers listed in Table A.6. Hence, only the 2,3,7,8-substituted tetra- through octa- isomers are included in the Toxicity Equivalency Factor (TEF) calculations. The procedure for calculating the 2,3,7,8-TCDD TEFs for the Target Compound List (TCL) analytes is not claimed by the Chlorinated Dioxins Workgroup (CDWG) to be based on a thoroughly established scientific foundation. Rather, the procedure represents a "Consensus Recommendation on Science Policy."

The 2,3,7,8-TCDD TEF-adjusted concentration of a sample is used by the laboratory as an aid in determining when second column confirmation or re-extractions and re-analyses are required.

C. Criteria:

1. When calculating the 2,3,7,8-TCDD TEF-adjusted concentration of a sample, the laboratory must include only those 2,3,7,8-substituted isomers that were detected in the sample and that met all of the qualitative identification criteria. The laboratory does not include Estimated Maximum Possible Concentration (EMPC) or Estimated Detection Limit (EDL) values in the TEF calculations.

2. For each 2,3,7,8-substituted isomer positively identified in the sample, the TEF from 1DFB (Form I-HR CDD-2) is multiplied by the concentration from 1DFA (Form I-HR CDD-1) to give the TEF-adjusted concentration. The sum of the TEF-adjusted concentrations serves as an aid in determining when second column confirmation or re-extractions and re-analyses are required. Include the octachlorinated dibenzo-p-dioxin (OCDD) data in the TEF calculations only if the OCDD concentration in the sample is greater than the OCDD concentration in the blank.

D. Evaluation:

Verify that the TEF calculations were correctly performed.

NOTE: The *reviewer* may be required to recalculate the TEFs using EMPCs and EDLs. The *laboratory*, however, is not required to perform such calculations.

E. Action:

If calculations were not correctly performed by the laboratory, notify the Task Order Project Officer (TOPO) of the deficiency.

XIII. Dilution by Addition of Solvent

A. Review Items:

Raw data (quantitation reports and chromatograms).

B. Objective:

A calibrated range is defined by the initial calibration. All sample results must be within the calibrated range judged to be acceptable.

C. Criteria:

If the Selected Ion Current Profile (SICP) area at either quantitation m/z for any compound exceeds the calibration range of the system, a solvent dilution of the extract can be performed. The sample extract is diluted by a factor of up to 20 times (20x) with n-nonane, the instrument internal standard in the extract is adjusted to 100 pg/uL, and an aliquot of this diluted extract is analyzed by the internal standard method. If more than a dilution of 20 times (20x) is required, contact the Task Order Project Officer (TOPO).

D. Evaluation:

1. Verify that all reported sample values are within the calibration range.

2. Verify that the internal standard calculations used to determine analyte concentrations in the diluted sample were performed correctly.

3. Verify that a dilution factor of $\leq$ 20x was used and correctly documented.

4. Verify that the laboratory contacted the TOPO prior to diluting the sample by a factor of $>$ 20x.

E. Action:

1. Compare the original and diluted analyses of the sample. Use professional judgment to qualify results if substantial differences are noted.

2. Qualify all of the sample detects which are out of range as estimated "J" if a sample value is not within the calibration range, and appropriate dilution was not performed.

XIV. Dilution by Re-extraction and Reanalysis

A. Review Items:

Raw data (quantitation reports and chromatograms).

B. Objective:

A calibrated range is defined by the initial calibration. All sample results must be within the calibrated range to be acceptable.

C. Criteria:

If the Selected Ion Current Profile (SICP) area at either quantitation m/z for any compound exceeds the calibration range of the system, re-extract and re-analyze a smaller sample aliquot.

D. Evaluation:

1. Verify that all reported sample values are within the calibration range.

2. Verify that the internal standard and/or isotope dilution calculations used to determine analyte concentrations in the diluted sample were performed correctly.

3. Verify that a smaller sample size was used and correctly documented.

4. Verify that the Percent Solids (% Solids) procedure in DLM02.X, Exhibit D, was carried out for soil/sediment samples, even if no dilutions were subsequently required.

E. Action:

Qualify out-of-range sample data as estimated "J" if a sample value is not within the calibration range, and re-extraction with dilution was not performed.

XV. Second Column Confirmation

A. Review Items:

Form 1DFC (Form I-HR CDD-3) and raw data.

B. Objective:

Isomer specificity for all 2,3,7,8-substituted chlorinated-p-dioxins/chlorinated dibenzofurans (CDDs/CDFs) cannot be achieved on the 60-meter DB-5 column alone. Historically, problems have been associated with the separation of 2,3,7,8-TCDF from 1,2,3,9-TCDF and 2,3,4,7-TCDF. There is toxicological concern associated with 2,3,7,8-TCDF; therefore, a second column confirmation is used and additional analyses may be required for some samples.

C. Criteria:

1. Second column confirmation is required for any sample analyzed on a DB-5 (or equivalent) column in which 2,3,7,8-TCDF is reported, or where 2,3,7,8-TCDF is reported as an Estimated Maximum Possible Concentration (EMPC) at or above the Contract Required Quantitation Limit (CRQL). The laboratory may utilize one of the following options to achieve better isomer specificity than can be obtained on the DB-5 column alone.

    - The sample extract may be re-analyzed on a DB-225 (or equivalent) Gas Chromatograph (GC) column to achieve better GC resolution and, therefore, better identification and quantitation of the individual 2,3,7,8-substituted isomers.

    - The sample extract may be analyzed on a GC column capable of resolving all of the 2,3,7,8-substituted CDDs/CDFs from other isomers, but not necessarily capable of resolving all of the non-2,3,7,8-substituted isomers from one another.

2. Regardless of the GC column used, for a GC peak to be identified as a 2,3,7,8-substituted CDD/CDF isomer, it must meet all of the criteria listed in DLM02.X, Exhibit D, [ion abundance ratio, signal-to-noise (S/N) ratio, Retention Time (RT), etc.]. If using any GC column other than those specified (DB-5, DB-225), the laboratory shall clearly document in the Data Review Narrative, the elution order of all analytes of interest on any such column.

3. For any sample analyzed on a DB-5 (or equivalent) column in which 2,3,7,8-TCDF is reported as an EMPC, regardless of Toxicity Equivalency Factor (TEF)-adjusted concentration or matrix, analysis of the extract is required on a second GC column which provides better specificity for these two isomers.

D. Evaluation:

1. Verify that second column confirmation is used whenever 2,3,7,8-TCDF is detected in any sample at any level (S/N ratio for the peak must be ≥ 2.5:1).

2. Verify that quantitation is performed on both columns and reported on the appropriate page of
   Form I. The two concentrations should not be combined or averaged, especially if the second column confirmation analysis is performed on a different instrument.

3. Verify that second column confirmation analysis meets all criteria previously discussed in this document (initial calibration requirements, linearity specifications, etc.).

   NOTE: Second column confirmation analysis is usually performed on a different instrument than that used for primary analysis.

E. Action:

If second-column confirmation is required but was not performed, qualify the 2,3,7,8-TCDF detects as unusable "R".

XVI. Estimated Detection Limit (EDL) and Estimated Maximum Possible Concentration (EMPC)

A. Review Items:

Form 1DFA (Form I-HR CDD-1) and raw data.

B. Objective:

For each analyte that is not detected, calculate an Estimated Detection Limit (EDL). The sample-specific EDL is an estimate made by the laboratory of the concentration of a given analyte that must be present to produce a signal with a peak height of at least 2.5 times (2.5x) the background noise signal level. The estimate is specific to a particular analysis of the sample and will be affected by sample size, dilution, etc. There is toxicological significance of chlorinated-p-dioxins/chlorinated dibenzofurans (CDDs/CDFs); therefore, the EDL value is reported for non-detected analytes rather than simply reporting the respective Contract Required Quantitation Limit (CRQL).

The Estimated Maximum Possible Concentration (EMPC) value is applied to a sample when the signal-to-noise (S/N) ratio is at least 2.5:1 for both quantitation ions, but the ion abundance ratio criteria are not met.

C. Criteria:

1. EDL

The EDL is calculated for each 2,3,7,8-substituted isomer that is not identified, regardless of whether or not any non-2,3,7,8-substituted isomers in that homologue are present. The EDL is also calculated for those 2,3,7,8-substituted isomers where responses for both of the quantitation ions are less than 2.5 times (< 2.5x) the background level, and therefore do not meet the identification criteria.

The formulas below are used to calculate an EDL for each absent 2,3,7,8-substituted CDD/CDF. The background level (H_x) is determined by measuring the height of the noise at the expected Retention Times (RTS) of both of the quantitation ions of the particular 2,3,7,8-substituted isomer. The expected RT is determined from the most recent analysis of the midpoint standard (CS3) performed on the same High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) system that was used for the analysis of the samples that are associated with the EDL calculations.

All Matrices Other than Aqueous:

$$\text{Soil EDL (ng/kg)} = \frac{2.5 \times Q_{IS} \times (H_{x1}+H_{x2}) \times D}{W \times (H_{IS1}+H_{IS2}) \times \overline{RR}}$$

Where,

EDL = Estimated Detection Limit for 2,3,7,8-substituted CDDs/CDFs

Q_{IS} = Quantity (pg) of appropriate internal standard added prior to sample extraction

H_{x1},H_{x2} = Peak heights of the noise for both quantitation ions of the CDD/CDF

H_{IS1},H_{IS2} = Peak heights of the internal standard ions

D = Dilution Factor

W = Weight extracted in grams

$\overline{RR}$ = The Mean Relative Response for the isomer of interest from the initial calibration (see DLM02.X, Exhibit D)

Aqueous:

$$\text{Aqueous EDL (pg/L)} = \frac{2.5 \times Q_{IS} \times (H_{x1}+H_{x2}) \times D}{V \times (H_{IS1}+H_{IS2}) \times \overline{RR}}$$

Where,

EDL = Estimated Detection Limit for 2,3,7,8-substituted CDDs/CDFs

Q_{IS} = Quantity (pg) of appropriate internal standard added prior to sample extraction

H_{x1},H_{x2} = Peak heights of the noise for both quantitation ions of the CDD/CDF

H_{IS1},H_{IS2} = Peak heights of the internal standard ions

D = Dilution Factor

V = Volume extracted in liters

$\overline{RR}$ = The Mean Relative Response for the isomer of interest from the initial calibration (see DLM02.X, Exhibit D)

2. Estimated Maximum Possible Concentration

An EMPC is calculated for 2,3,7,8-substituted isomers that are characterized by a response with a S/N ratio of at least 2.5:1 for both of the quantitation ions, but that do not meet the ion abundance ratio criteria outlined in Section IX.

The EMPC is calculated according to one of the following formulas:

All Matrices Other than Aqueous:

$$\text{EMPC (ng/kg)} = \frac{(C_{EX} \times D)}{W_S}$$

Where,

D = Dilution Factor

W_S = Sample dry weight in kg

C_{EX} = The concentration of the native compound in the extract

Aqueous:

$$\text{EMPC (pg/L)} = \frac{(C_{EX} \times D)}{V_S}$$

Where,

D = Dilution Factor

V_S = Sample volume in liters

C_{EX} = The concentration of the native compound in the extract

D. Evaluation:

1. Verify that EDLs and EMPCs are correctly calculated.

2. An EDL must be reported for each undetected analyte. The EDL must be < CRQL, except when increased due to dilution of the extract.

3. Analytes reported as EMPCs must meet all of the identification criteria, except for ion abundance ratios, as outlined in Section IX.

E. Action:

Qualify all EDLs and EMPCs that were not correctly calculated as unusable "R".

XVII. Labeled Compound Recoveries

A. Review Items:

Form 1DFA (Form I-HR CDD-1) and raw data.

B. Objective:

The 15 labeled chlorinated-p-dioxins/chlorinated dibenzofurans (CDDs/CDFs) serve as the isotopic dilution quantitative mechanism in this method. The recovery of these compounds, along with the recovery of the clean-up standard, is a critical measure of the effectiveness of the laboratory and method to extract the compounds of interest.

C. Criteria:

1. If the original sample, prior to any dilutions, has any labeled compound or internal standard with a Percent Recovery (% Recovery) not within the limits specified in Table A.7, re-extract and re-analyze that sample.

   Values below 100% indicate loss of labeled and unlabeled compounds during the analytical process. Values over 100% indicate errors in the quantitation of the labeled compounds, or problems with the addition of the internal standards to the sample extracts. Within the limits, the use of isotope dilution or internal standard quantitation (depending on the analyte) will produce acceptable results for the target compounds. Outside the limits, the quantitation accuracy or precision of the results will be affected.

2. Re-extract and re-analyze if the labeled compounds are not present with at least a 10:1 signal-to-noise ratio (S/N) at their respective m/z(s).

3. If any of the labeled compound ion abundance ratios specified in Table A.4 are not within the contract-specified control limits, re-analyze the sample extract on the same Gas Chromatograph (GC) column and Mass Spectrometer used for the original analysis. If the problem corrects itself, use the data from the second analysis and disregard the data from the first analysis. No additional re-extraction and reanalysis are required. Re-extract and re-analyze if the failed ion abundance ratios persist through the second analysis.

4. If the absolute Retention Time (RT) of $^{13}C_{12}$-1,2,3,4-TCDD shifts by more than ± 15 seconds from the RTS of that standard in the initial calibration, re-analyze the sample extract after the laboratory has investigated the cause of the RT shift and taken corrective action. No re-extraction is required for such an analysis.

5. If $^{13}C_{12}$-2,3,7,8-TCDD is not resolved from $^{13}C_{12}$-1,2,3,4-TCDD with a valley of ≤ 25% on the DB-5 (or equivalent) column, or $^{13}C_{12}$-2,3,7,8-TCDD is not resolved from $^{13}C_{12}$-1,2,3,4-TCDD with a valley of ≤ 25% on the DB-225 (or equivalent) column, adjust the High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) operating conditions, re-calibrate the instrument, and re-analyze the

affected sample. This criterion applies to sample analysis; no re-extraction and reanalysis are required if the second analysis resolves the problem. If this criterion is not met for a calibration standard, re-analyze associated samples after instrument re-calibration. Re-extraction is not ordinarily required unless the resolution difficulties reappear after re-calibration.

D. Evaluation:

1. Verify that the labeled compound and the internal standard recoveries fall within the required limits.

2. Verify that the S/N ratio of the labeled compound is ≥ 10:1.

3. Verify that the ion abundance ratios of the labeled compounds are within the required limits.

E. Action:

1. If the recovery of the labeled compounds are not within the limits in Table A.7, qualify all associated sample results as estimated "J". If no reanalysis is found, contact the Task Order Project Officer (TOPO) to initiate reanalysis.

2. The ^{37}Cl-labeled clean-up standard is used to monitor the efficiency of the clean-up; it is added to the sample extracts after extraction and before any clean-up steps. Low recoveries of the labeled compounds and the clean-up standard suggest that losses may be due to the performance of the clean-up steps. Thus, re-extraction and reanalysis of the sample may yield better results. If the labeled compound recoveries are low (< 40%), and the clean-up standard recovery is not, the recovery problems may be associated with the extraction procedures or related to a particularly difficult matrix. In this case, reanalysis may only serve to confirm a "matrix effect".

XVIII. Regional Quality Assurance and Quality Control (QA/QC)

A. Review Items:

Form 1DFA (Form I-HR CDD-1), chromatograms, quantitation reports, Traffic Report/Chain of Custody (TR/COC) documentation, and raw data for Regional Quality Control (QC) samples.

B. Objective:

Evaluate the results of any Regional Quality Assurance (QA) and QC samples initiated by the Region, including field duplicates, Regional Performance Evaluation (PE) samples, blind spikes, and blind blanks. (It is highly recommended to adopt the use of these QA/QC samples.)

C. Criteria:

Criteria are determined by each Region.

1. The PE sample frequency may vary. A PE sample may be included as frequently as once per Sample Delivery Group (SDG).

2. The analytes present in the PE sample must be correctly identified and quantitated.

D. Evaluation:

Evaluation procedures must follow the Region's Standard Operating Procedure (SOP) for data review. Each Region will handle the evaluation of PE samples on an individual basis. If available, compare results for PE samples to the acceptance criteria for the specific PE samples.

E. Action:

Any action must be in accordance with Regional specifications and criteria for acceptable PE sample results. Note in the Data Review Narrative for Task Order Project Officer (TOPO) action any unacceptable PE sample results.

XIX. Overall Assessment of Data

A. Review Items:

Entire data package, data review results, Quality Assurance Project Plan (QAPP), if available, and the Sampling and Analysis Plan (SAP), if available.

B. Objective:

Assess the overall quality of the data.

C. Criteria:

The overall assessment of a data package is a brief narrative in which the data reviewer expresses their comments, concerns, and opinions about the quality and usability of the data.

D. Evaluation:

1. Evaluate any technical problems which have not been previously addressed.

2. Remember that analytical problems are often additive in nature.

3. Review all available information including, but not limited to, the QAPP [specifically, the Data Quality Objectives (DQOs)], the SAP, and any communications from the data user that concern the intended use and desired quality of the data.

4. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate application of the data.

E. Action:

1. Use professional judgment to determine if there is any need to qualify data which were not already qualified based on the Quality Control (QC) criteria previously discussed.

2. Write a brief narrative to give the data user an indication of the analytical limitations of the data. Note for Task Order Project Officer (TOPO) action any inconsistencies between data and the Data Review Narrative. If sufficient information on the intended use and required quality of the data is available, include an assessment of the data usability within the given context.

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Appendix A: Tables

Extracted From:

USEPA Statement of Work (SOW) for Analysis of Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs), Multi-Media, Multi-Concentration, DLM02.X, Dated May 2005

Table A.1. Descriptors, Exact Mass-to-Charge (m/z) Ratios, m/z Types, and Elemental Compositions of the CDDs/CDFs

Descriptor	Exact m/z[1]	m/z Type	Elemental Composition	Substance[2]
1	292.9825	Lock	$C_7 F_{11}$	PFK
	303.9016	M	$C_{12} H_4 {}^{35}Cl_4 O$	TCDF
	305.8987	M+2	$C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O$	TCDF
	315.9419	M	$^{13}C_{12} H_4 {}^{35}Cl_4 O$	TCDF[3]
	317.9389	M+2	$^{13}C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O$	TCDF[3]
	319.8965	M	$C_{12} H_4 {}^{35}Cl_4 O_2$	TCDD
	321.8936	M+2	$C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O_2$	TCDD
	327.8847	M	$C_{12} H_4 {}^{37}Cl_4 O_2$	TCDD[4]
	330.9792	QC	$C_7 F_{13}$	PFK
	331.9368	M	$^{13}C_{12} H_4 {}^{35}Cl_4 O_2$	TCDD[3]
	333.9339	M+2	$^{13}C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O_2$	TCDD[3]
	375.8364	M+2	$C_{12} H_4 {}^{35}Cl_5 {}^{37}Cl O$	HxCDPE
2	339.8597	M+2	$C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O$	PeCDF
	341.8567	M+4	$C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O$	PeCDF
	351.9000	M+2	$^{13}C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O$	PeCDF
	353.8970	M+4	$^{13}C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O$	PeCDF[3]
	354.9792	Lock	$C_9 F_{13}$	PFK
	355.8546	M+2	$C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O_2$	PeCDD
	357.8516	M+4	$C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O_2$	PeCDD[3]
	369.8919	M+4	$^{13}C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O_2$	PeCDD[3]
	409.7974	M+2	$C_{12} H_3 {}^{35}Cl_6 {}^{37}Cl O$	HpCDPE
3	373.8208	M+2	$C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O$	HxCDF
	375.8178	M+4	$C_{12} H_2 {}^{35}Cl_4 {}^{37}Cl_2 O$	HxCDF
	383.8639	M	$^{13}C_{12} H_2 {}^{35}Cl_6 O$	HxCDF[3]
	385.8610	M+2	$^{13}C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O$	HxCDF[3]
	389.8157	M+2	$C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O_2$	HxCDD
	391.8127	M+4	$C_{12} H_2 {}^{35}Cl_4 {}^{37}Cl_2 O_2$	HxCDD
	392.9760	Lock	$C_9 F_{15}$	PFK
	401.8559	M+2	$^{13}C_{12} H_2 {}^{35}Cl_5 {}^{37}Cl O_2$	HxCDD[3]
	403.8529	M+4	$^{13}C_{12} H_2 {}^{35}Cl_4 {}^{37}Cl_2 O_2$	HxCDD[3]
	430.9729	QC	$C_9 F_{17}$	PFK

Table A.1. Descriptors, Exact Mass-to-Charge (m/z) Ratios, m/z Types, and Elemental Compositions of the CDDs/CDFs (con't)

Descriptor	Exact m/z[1]	m/z Type	Elemental Composition	Substance[2]
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
4	407.7818	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H{}^{35}Cl_7O$	HpCDF[3]
	419.8220	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF[3]
	423.7766	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	430.9729	Lock	C_9F_{17}	PFK
	435.8169	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD[3]
	437.8140	M+4	$^{13}C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD[3]
	479.7165	M+4	$C_{12}H{}^{35}Cl_7{}^{37}Cl_2O$	NCDPE
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	442.9728	Lock	$C_{10}F_{17}$	PFK
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD[3]
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD[3]
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$	DCDPE

[1]Nuclidic masses used:

H = 1.007825 C = 12.00000 ^{13}C = 13.003355 F= 18.9984

O = 15.994915 ^{35}Cl = 34.968853 ^{37}Cl = 36.965903

[2]TCDD = Tetrachlorodibenzo-p-dioxin
TCDF = Tetrachlorodibenzofuran
PeCDD = Pentachlorodibenzo-p-dioxin
PeCDF = Pentachlorodibenzofuran
HxCDD = Hexachlorodibenzo-p-dioxin
HxCDF = Hexachlorodibenzofuran
HpCDD = Heptachlorodibenzo-p-dioxin
HpCDF = Heptachlorodibenzofuran
OCDD = Octachlorodibenzo-p-dioxin
OCDF = Octachlorodibenzofuran
HxCDPE = Hexachlorodiphenyl ether
HpCDPE = Heptachlorodiphenyl ether

OCDPE = Octachlorodiphenyl ether
NCDPE = Nonachlorodiphenyl ether
DCDPE = Decachlorodiphenyl ether
PFK = Perfluorokerosene

[3]Labeled compound.

[4]There is only one m/z for $^{37}Cl_4$-2,3,7,8,-TCDD (cleanup standard).

Table A.2. Gas Chromatography (GC) RT Window Defining Mixture (WDM) and Isomer Specificity Check Standard

CDD/CDF	First Eluted	Last Eluted
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

DB-5 Column TCDD Isomer Specificity Check Standard

1,2,3,7 and 1,2,3,8-TCDD
2,3,7,8-TCDD
1,2,3,9-TCDD

DB-225 Column TCDF Isomer Specificity Check Standard

2,3,4,7-TCDF
2,3,7,8-TCDF
1,2,3,9-TCDF

Sp-2331 Column TCDD Isomer Specificity Check Standard
2,3,7,8-TCDD
1,4,7,8-TCDD
1,2,3,7-TCDD
1,2,3,8-TCDD

Table A.3. Relative Retention Times and Quantitation Reference of the Native and Labeled Chlorinated Dibenzo-p-Dioxins/Chlorinated Dibenzofurans (CDDs/CDFs)

CDD/CDF	Retention Time and Quantitation Reference	Relative Retention Time
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the injection internal standard		
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0.999–1.003
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999–1.002
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999–1.002
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999–1.002
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999–1.002
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923–1.103
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976–1.043
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989–1.052
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000–1.425
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.011–1.526
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000–1.567
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the injection internal standard		
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999–1.001
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0.997–1.005
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999–1.001
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	0.999–1.001
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999–1.001
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.998–1.004
1,2,3,7,8,9-HxCDD[1]		1.000–1.019
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999–1.001
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999–1.001
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999–1.001
OCDF	$^{13}C_{12}$-OCDD	0.999–1.008
OCDD	$^{13}C_{12}$-OCDD	0.999–1.001
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.944–0.970
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.949–0.975
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977–1.047
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.959–1.021
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977–1.000

Table A.3. Relative Retention Times and Quantitation Reference of the Native and Labeled Chlorinated Dibenzo-p-Dioxins/Chlorinated Dibenzofurans (CDDs/CDFs) (con't)

CDD/CDF	Retention Time and Quantitation Reference	Relative Retention Time
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.981–1.003
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.043–1.085
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.057–1.151
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.086–1.110
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.032–1.311

[1]The retention time reference for 1,2,3,7,8,9-HxCDD is ^{13}C12-1,2,3,6,7,8-HxCDD.

1,2,3,7,8,9-HxCDD is quantified using the averaged responses of ^{13}C12-1,2,3,4,7,8-HxCDD and ^{13}C12-1,2,3,6,7,8-HxCDD.

Table A.4. Theoretical Ion Abundance Ratios and Quality Control (QC) Limits

Number of Chlorine Atoms	m/z's Forming Ratio	Theoretical Ratio	QC Limit[1]	
			Lower	Upper
4[2]	M/(M+2)	0.77	0.65	0.89
5	(M+2)/(M+4)	1.55	1.32	1.78
6	(M+2)/(M+4)	1.24	1.05	1.43
6[3]	M/(M+2)	0.51	0.43	0.59
7	(M+2)/(M+4)	1.05	0.88	1.20
7[4]	M/(M+2)	0.44	0.37	0.51
8	(M+2)/(M+4)	0.89	0.76	1.02

[1]QC limits represent ±15% windows around the theoretical ion abundance ratios.

[2]Does not apply to $^{37}Cl_4$-2,3,7,8-TCDD (cleanup standard).

[3]Used for $^{13}C_{12}$-HxCDF only.

[4]Used for $^{13}C_{12}$-HpCDF only.

Table A.5. Concentration of CDDs/CDFs in Calibration and Calibration Verification Solutions

CDD/CDF	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
2,3,7,8-TCDD	0.5	2	10	40	200
2,3,7,8-TCDF	0.5	2	10	40	200
1,2,3,7,8-PeCDD	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000
OCDD	5.0	20	100	400	2000
OCDF	5.0	20	100	400	2000
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100

Table A.5. Concentration of CDDs/CDFs in Calibration and Calibration Verification Solutions (con't)

CDD/CDF	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
$^{13}C_{12}$-OCDD	200	200	200	200	200
Cleanup Standard					
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2	10	40	200
Internal Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

Table A.6. Acceptance Criteria for Laboratory Control Sample (LCS)

CDD/CDF	Test conc (ng/mL)	LCS (% Recovery)
2,3,7,8-TCDD	10	67-158
2,3,7,8-TCDF	10	75-158
1,2,3,7,8-PeCDD	50	70–142
1,2,3,7,8-PeCDF	50	80-134
2,3,4,7,8-PeCDF	50	68-160
1,2,3,4,7,8-HxCDD	50	70-164
1,2,3,6,7,8-HxCDD	50	76-134
1,2,3,7,8,9-HxCDD	50	64-162
1,2,3,4,7,8-HxCDF	50	72-134
1,2,3,6,7,8-HxCDF	50	84-130
1,2,3,7,8,9-HxCDF	50	78-130
2,3,4,6,7,8-HxCDF	50	70–156
1,2,3,4,6,7,8-HpCDD	50	70–140
1,2,3,4,6,7,8-HpCDF	50	82-132
1,2,3,4,7,8,9-HpCDF	50	78-138
OCDD	100	78-144
OCDF	100	63-170

Table A.7. Labeled Compound Recovery in Samples When All CDDs/CDFs are Tested

Compound	Test conc (ng/mL)	Labeled Compound Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	25-164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24-169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25-181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24-185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21-178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32-141
$^{13}C_{12}$-1,2,3,6,7,8,-HxCDD	100	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26-152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26-123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29-147
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	100	28-136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23-140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28-143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26-138
$^{13}C_{12}$-OCDD	200	17-157
$^{37}Cl_4$-2,3,7,8-TCDD	10	35-197

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USEPA CONTRACT LABORATORY PROGRAM
NATIONAL FUNCTIONAL GUIDELINES
FOR
INORGANIC DATA REVIEW

FINAL

Office of Superfund Remediation and Technology Innovation (OSRTI)
U.S. Environmental Protection Agency
Washington, DC 20460

NOTICE

The policies and procedures set forth here are intended as guidance to the United States Environmental Protection Agency (hereafter referred to as USEPA) and other governmental employees. They do not constitute rule making by USEPA, and may not be relied upon to create a substantive or procedural right enforceable by any other person. The Government may take action that is at variance with the policies and procedures in this manual.

This document can be obtained from the USEPA's Contract Laboratory Program (CLP) Web site at:

http://www.epa.gov/superfund/programs/clp/guidance.htm

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ACRONYMS

AA	Atomic Absorption
ASB	Analytical Services Branch
CADRE	Computer-Aided Data Review and Evaluation
CCB	Continuing Calibration Blank
CCS	Contract Compliance Screening
CCV	Continuing Calibration Verification
CLP	Contract Laboratory Program
CO	Contracting Officer
CRI	CRQL Check Standard
CRQL	Contract Required Quantitation Limit
CSF	Complete SDG File
CVAA	Cold Vapor AA
DART	Data Assessment Rapid Transmittal
DAT	Data Assessment Tool
DF	Dilution Factor
DQO	Data Quality Objective
ICB	Initial Calibration Blank
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICS	Interference Check Sample
ICV	Initial Calibration Verification
LCS	Laboratory Control Sample
LRS	Linear Range Sample
MDL	Method Detection Limit
NIST	National Institute of Standards and Technology
OSRTI	Office of Superfund Remediation and Technology Innovation
OSWER	Office of Solid Waste and Emergency Response
PB	Preparation Blank
PE	Performance Evaluation
%D	Percent Difference
%R	Percent Recovery
%RI	Percent Relative Intensity
%RSD	Percent Relative Standard Deviation
%S	Percent Solids
PO	Project Officer
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
RSCC	Regional Sample Control Center
SDG	Sample Delivery Group
SMO	Sample Management Office
SOP	Standard Operating Procedure
SOW	Statement of Work
TAL	Target Analyte List
TR/COC	Traffic Report/Chain of Custody Documentation
USEPA	United States Environmental Protection Agency

TARGET ANALYTE LIST

Al	Aluminum
Sb	Antimony
As	Arsenic
Ba	Barium
Be	Beryllium
Cd	Cadmium
Ca	Calcium
Cr	Chromium
Co	Cobalt
Cu	Copper
CN	Cyanide
Fe	Iron
Pb	Lead
Mg	Magnesium
Mn	Manganese
Hg	Mercury
Ni	Nickel
K	Potassium
Se	Selenium
Ag	Silver
Na	Sodium
Tl	Thallium
V	Vanadium
Zn	Zinc

INTRODUCTION

This document is designed to offer the data reviewer guidance in determining the usability of analytical data generated through the USEPA Contract Laboratory Program (CLP) multi-media Inorganic Statement of Work (SOW), ILM05.X (ILM05.3 and any future editorial revisions of ILM05.3). This guidance is somewhat limited in scope and is intended to be used as an aid in the formal technical review process. It should not be used to establish specific contract compliance (use of this document to evaluate data generated under Inorganic SOWs other than ILM05.X is cautioned). Definitive guidance is provided where performance should be fully under a Laboratory's control [e.g., blanks, calibration verification standards, Interference Check Samples (ICSs), Quality Control (QC) audit samples, and instrument performance checks (tuning)], while general guidance is provided for evaluating subjective data that is affected by site conditions.

The guidelines presented in the document will aid the data reviewer in establishing (a) if data meets the specific technical and QC criteria established in the SOW, and (b) the usability and extent of bias of any data not meeting the specific technical and QC criteria established in the SOW. It must be understood by the reviewer that acceptance of data not meeting technical requirements is based upon many factors, including, but not limited to, site-specific technical requirements, the need to facilitate the progress of specific projects, and availability for re-sampling. To make judgments at this level requires the reviewer to have a complete understanding of the intended use of the data. The reviewer is strongly encouraged to establish a dialogue with the user prior to, and after data review, to discuss usability issues and to answer questions regarding the review. It should also be understood that in all Cases, data which do not meet specified criteria are never to be fully acceptable without qualification.

The reviewer should note that while this document is to be used as an aid in the formal data review process, other sources of guidance and information, as well as professional judgment, should also be used to determine the ultimate usability of data, especially in those Cases where all data does not meet specific technical criteria. The reviewer should also be aware that minor modifications to some of the analytical methods may be made through the "Modified Analysis Request" to meet site-specific requirements, and that these modifications could affect certain validation criteria such as Contract Required Quantitation Limits (CRQLs) and Target Analyte Lists (TALs). A copy of any modification request made to the analytical method should be included in the data package by the Laboratory.

Please visit the CLP Web site at http://www.epa.gov/superfund/programs/clp/index.htm for more information on how to obtain service through the CLP.

DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the national qualifiers assigned to results in the data review process. If the Regions choose to use additional qualifiers, a complete explanation of those qualifiers should accompany the data review.

U	The analyte was analyzed for, but was not detected above the level of the reported sample quantitation limit.
J	The result is an estimated quantity. The associated numerical value is the approximate concentration of the analyte in the sample.
J+	The result is an estimated quantity, but the result may be biased high.
J-	The result is an estimated quantity, but the result may be biased low.
R	The data are unusable. The sample results are rejected due to serious deficiencies in meeting Quality Control (QC) criteria. The analyte may or may not be present in the sample.
UJ	The analyte was analyzed for, but was not detected. The reported quantitation limit is approximate and may be inaccurate or imprecise.

DATA PACKAGE INSPECTION

For data obtained from the Contract Laboratory Program (CLP), the Data Assessment Tool (DAT) reports may be used as a tool in the validation process. The DAT report incorporates Contract Compliance Screening (CCS) and Computer-Aided Data Review and Evaluation (CADRE) results, and is transmitted via the Data Assessment Rapid Transmittal (DART) system. For more information about DAT, please refer to the following CLP Web site:

http://www.epa.gov/superfund/programs/clp/dat.htm

The DAT report will identify any missing and/or incorrect information in the data package. The CLP Laboratory may submit a reconciliation package for any missing items or to correct data.

To obtain the DAT report and/or the reconciliation package, or if there are any other concerns regarding the data package, contact the CLP Project Officer (CLP PO) from the Region where the samples were taken. Please refer to the following CLP Web site for the most recent list of Regional CLP POs:

http://www.epa.gov/superfund/programs/clp/contacts.htm

PRELIMINARY REVIEW

This document is for the review of analytical data generated through the USEPA CLP Inorganic Statement of Work (SOW), ILM05.X (ILM05.3 and any future editorial revisions of ILM05.3). To use this document effectively, the reviewer should have a general overview of the Sample Delivery Group (SDG) or sample Case at hand. The exact number of samples, their assigned numbers, their matrix, and the number of Laboratories involved in the analysis are essential information.

It is suggested that an initial review of the data package be performed taking into consideration all information specific to the sample data package (e.g., flexible analysis approval notices, Traffic Report/Chain of Custody (TR/COC) documentation, SDG Narratives, etc.).

The reviewer should also have a copy of the Quality Assurance Project Plan (QAPP) or similar document for the project for which the samples were analyzed. The reviewer should contact the appropriate Regional CLP PO to obtain copies of the QAPP and relevant site information. This information is necessary in determining the final usability of the analytical data.

The SDGs or Cases routinely have unique samples that require special attention by the reviewer. These include field blanks, field duplicates, and performance audit samples which must be identified. The sampling records (e.g., TR/COC documentation, field logs, and/or contractor tables) should identify:

1. The Region where the samples were taken, and
2. The complete list of samples with information on:
   a. Sample matrix;
   b. Field blanks*;
   c. Field duplicates*;
   d. Field spikes*;
   e. Quality Control (QC) audit samples*;
   f. Shipping dates;
   g. Preservatives;
   h. Types of analysis; and
   i. Laboratories involved.

   * If applicable.

The TR/COC documentation includes sample descriptions and date(s) of sampling. The reviewer must consider lag times between sampling and start of analysis when assessing technical sample holding times.

The Laboratory's SDG Narrative is another source of general information. Notable problems with matrices, insufficient sample volume for analysis or reanalysis, samples received in broken containers, preservation, and unusual events should be documented in the SDG Narrative. The reviewer should also inspect any telephone or communication logs detailing any discussion of sample or analysis issues between the Laboratory, the CLP Sample Management Office (SMO), and the USEPA Region.

DATA REVIEW NARRATIVE

A Data Review Narrative, including the Inorganic Data Review Summary form (see Appendix B), must accompany the Laboratory data forwarded to the intended data recipient (client) or user to promote communication. A copy of the Data Review Narrative should be submitted to the CLP PO assigned oversight responsibility for the Laboratory producing the data.

The Data Review Narrative should include comments that clearly identify the problems associated with a Case or SDG and state the limitations of the data. Documentation should also include the Sample Number, analytical method, extent of the problem, and assigned qualifiers.

ICP-AES DATA REVIEW

The inorganic data requirements for Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) to be reviewed during validation are listed below:

I. Preservation and Holding Times

II. Calibration
- A. Initial
- B. Initial and Continuing Calibration Verification (ICV/CCV)
- C. Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

III. Blanks

IV. Inductively Coupled Plasma - Interference Check Sample (ICP-ICS)

V. Laboratory Control Sample (LCS)

VI. Duplicate Sample Analysis

VII. Spike Sample Analysis

VIII. ICP Serial Dilution

IX. Field Duplicates

X. Overall Assessment

An Example Analytical Sequence for ICP-AES

S0
S
ICV
ICB
CRI
ICSA
ICSAB
CCV
CCB
ten samples
CCV
CCB
seven samples
CRI
ICSA
ICSAB
CCV
CCB
ten samples, etc.

I. Preservation and Holding Times

A. Review Items:

Form IA-IN, Form IB-IN, Form XII-IN, Form XIII-IN, Traffic Report/Chain of Custody (TR/COC) documentation, Form DC-1, raw data, and the Sample Delivery Group (SDG) Narrative checking for: pH; cooler temperature; holding time; and other sample conditions.

B. Objective:

The objective is to ascertain the validity of the analytical results based on the sample condition, and the holding time of the sample from the date of collection to the date of analysis.

C. Criteria:

1. Technical requirements for sample holding times have only been established for aqueous matrices. The addition of nitric acid to adjust the pH is only required for aqueous samples.

2. The technical holding time criteria for aqueous metal samples is 180 days, preserved (with nitric acid) to pH <2.

3. Aqueous samples shall be maintained at 4°C ±2°C until preparation and analysis to allow for re-preparation and for the direct analysis of dissolved metals.

4. Soil/sediment samples shall be maintained at 4°C ±2°C until preparation and analysis.

D. Evaluation:

Technical holding times are established by comparing the sampling date(s) on the TR/COC documentation with the dates of analysis on Form XIII-IN, and the raw data. Information contained in the Complete SDG File (CSF) should also be considered in the determination of holding times. Verify that the analysis dates on the Form XIIIs and the raw data are identical. Review the SDG Narrative and raw data preparation logs to determine if samples were properly preserved. If there is an indication that there were problems with the samples, the integrity of the samples may be compromised and professional judgment should be used to evaluate the effect of the problem on the sample results.

E. Action:

NOTE: Apply the action to each sample for which the preservation or holding time criteria was not met.

1. If the pH of aqueous metal samples was ≥2 at the time of sample receipt, use professional judgment to qualify the samples based on the pH of the sample and the chemistry of the metal(s) of interest. Qualify results that are ≥ Method Detection Limit (MDL) as estimated low (J-), and qualify non-detects as unusable (R).

2. If technical holding times were exceeded, use professional judgment to determine the reliability of the data, based on the magnitude of the additional time compared to the technical requirement and whether the samples were properly preserved. The expected bias

would be low. Qualify results that are ≥MDL as estimated low (J-), and qualify non-detects as unusable (R).

3. Due to limited information concerning holding times for soil samples, it is left to the discretion of the data reviewer whether to apply water holding time criteria to soil samples. If they are applied, it must be clearly documented in the Data Review Narrative.

4. When the holding times are exceeded, the reviewer should comment in the Data Review Narrative on any possible consequences for the analytical results.

5. When holding times are grossly exceeded, note it for Contract Laboratory Program Project Officer (CLP PO) action.

Table 1. Technical Holding Time Actions for ICP-AES Analysis

Preservation & Holding Time Results	Action for Samples
Aqueous metals samples received with pH ≥2	Use professional judgment Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as unusable (R)
Technical Holding Time exceeded: Metals > 180 days	Use professional judgment Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as unusable (R)

II. Calibration

A. Review Items:

Form II-IN (Parts A & B), Form XI-IN, Form XIII-IN, preparation logs, calibration standard logs, instrument logs, instrument printouts, and raw data.

B. Objective:

Method requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data for the metals on the Inorganic Target Analyte List (TAL). Initial Calibration Verification (ICV) demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical run. Continuing Calibration Verification (CCV) demonstrates that the initial calibration is still valid by checking the performance of the instrument on a continuing basis.

C. Criteria:

1. Initial Calibration

The instruments shall be successfully calibrated daily (or once every 24 hours), and each time the instrument is set up. The calibration date and time shall be included in the raw data.

a. A blank and at least one calibration standard shall be used to establish each analytical curve. All measurements shall be within the instrument linear working range where the interelement correction factors are valid. A minimum of two replicate exposures are required for standardization, all Quality Control (QC), and sample analyses. The average result of the multiple exposures for the standardization, QC, and sample analyses shall be used.

b. The instrumental calibration near the Contract Required Quantitation Limit (CRQL) must be verified for each analyte. A CRQL Check Standard (CRI) solution shall be prepared and analyzed at the beginning and end of each sample analysis run and every 20 analytical samples, immediately preceding the Interference Check Sample (ICS) analyses, but not before ICV analysis. The CRI at the beginning of the run must immediately follow the ICV/ICB analyses.

c. The CRI shall be run per Inductively Coupled Plasma (ICP) for every wavelength used for analysis, and for all analytes except for Al, Ba, Ca, Fe, Mg, Na, and K. All results and Percent Recoveries (%R) shall be reported on Form IIB-IN. If the results for the CRI do not fall within the fixed acceptance limits, the Laboratory shall immediately reanalyze the CRI for those analytes. If the results of the reanalysis do not fall within the acceptance limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the new calibration then reverified.

2. Initial and Continuing Calibration Verification (ICV and CCV)

The acceptance criteria for the ICVs, CCVs, and CRIs are presented in Table 2:

Table 2. Acceptance Criteria for ICVs, CCVs, and CRIs

Analytical Method	Inorganic Analytes	ICV/CCV Low Limit (% of True Value)	ICV/CCV High Limit (% of True Value)	CRI Low Limit (% of True Value)	CRI High Limit (% of True Value)
ICP-AES	Metals	90	110	70 (50 for Sb, Pb, Tl)	130 (150 for Sb, Pb, Tl)

a. Initial Calibration Verification (ICV)

1) Immediately after each system has been calibrated, the accuracy of the initial calibration must be verified and documented for each target analyte by the analysis of an ICV solution(s). If the ICV %R falls outside of the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and all affected samples reanalyzed.

2) If the ICV solution is not available from USEPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration level other than that used for instrument calibration (or the CRI), but within the calibrated range.

3) The ICV solution shall be run at each analytical wavelength used for analysis.

b. Continuing Calibration Verification (CCV)

1) To ensure accuracy during the course of each analytical run, the CCV shall be analyzed and reported for each wavelength used for the analysis of each analyte.

2) The CCV standard shall be analyzed at a frequency of 10% or every two hours during an analytical run, whichever is more frequent. The CCV standard shall also be analyzed at the beginning of the run, and again after the last analytical sample.

3) The analyte concentration(s) in the CCV standard(s) shall be different than the concentration used for the ICV, and shall be one of the following solutions at, or near, the mid-range levels of the calibration curve:

   A. USEPA solutions;
   B. National Institute of Standards and Technology (NIST) standards; or
   C. A Laboratory-prepared standard solution (self-prepared or commercially available).

4) The same CCV standard solution shall be used throughout the analysis runs for a Sample Delivery Group (SDG).

5) The CCV shall be analyzed in the same fashion as an actual sample. Operations such as the number of replicate analyses, the number and duration of the instrument rinses,

etc., affect the measured CCV result and are not to be applied to the CCV to an extent greater than was applied to the associated analytical samples. If the %R of the CCV was outside of the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification reanalyzed.

D. Evaluation:

1. Verify that the instrument was calibrated daily (once every 24 hours) and each time the instrument was set up, utilizing a blank and at least one calibration standard.

2. Confirm that the measurements were within the documented linear working range, and were the average result of at least two replicate exposures.

3. Evaluate the reported CRI to confirm that it was analyzed at the proper concentration, frequency, and location within the analytical run sequence. Verify that acceptable %R results were obtained.

4. Verify that the ICV and CCV standards were analyzed for each analyte at the proper frequency (10%) and at the appropriate concentration. Verify that acceptable %R results were obtained.

5. Recalculate one or more of the ICV, CCV, and CRI %R using the following equation and verify that the recalculated value agrees with the Laboratory-reported values on Forms II (A & B)-IN.

$$\%R = \frac{\text{Found(value)}}{\text{True(value)}} \times 100$$

Where,

Found(value) = Concentration (in µg/L) of each analyte measured in the analysis of the ICV, CCV, or CRI solution

True(value) = Concentration (in µg/L) of each analyte in the ICV, CCV, or CRI source

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTES: For initial calibrations or ICVs that do not meet the technical criteria, apply the action to all samples reported from the analytical run.

For CCVs or CRIs that do not meet the technical criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of the QC sample and a subsequent technically acceptable analysis of the QC sample in the analytical run.

1. If the instrument was not calibrated daily and each time the instrument was set up, qualify the data as unusable (R). If the instrument was not calibrated with at least the minimum number of standards, or if the calibration curve does not include standards at required concentrations (e.g., a blank), use professional judgment to qualify results that are ≥ Method Detection Limit (MDL) as estimated (J) or unusable (R), and non-detects as estimated (UJ) or unusable (R).

2. If the CRIs are outside the acceptance criteria, use professional judgment to qualify all associated data. If possible, indicate the bias in the review. The following guidelines are recommended:

   a. If the CRI %R is <50% (<30% for Sb, Pb, Tl), qualify all sample results that are ≥MDL but < two times (2x) the CRQL and all non-detects as unusable (R). Qualify detects that are ≥2x the CRQL as estimated (J).

   b. If the CRI %R falls within the range of 50-69% (30-49% for Sb, Pb, Tl), qualify all sample results that are ≥MDL but <2x the CRQL as estimated low (J-), and all non-detects as estimated (UJ). Detects ≥2x the CRQL should not be qualified based on this criterion.

   c. If the CRI %R is >130% but ≤180% (>150% but ≤200 for Sb, Pb, Tl), qualify all sample results that are ≥MDL but <2x the CRQL as estimated high (J+). Non-detects and detects ≥2x the CRQL should not be qualified based on this criterion.

   d. If the CRI %R is >180% (>200% for Sb, Pb, Tl), qualify all sample results that are ≥MDL as unusable (R).

3. If the ICV or CCV %R falls outside the acceptance windows, use professional judgment to qualify all associated data. If possible, indicate the bias in the review. The following guidelines are recommended:

   a. If the ICV or CCV %R is <75%, qualify non-detects as unusable (R). Use professional judgment to qualify all results that are ≥MDL as estimated low (J-) or unusable (R).

   b. If the ICV or CCV %R falls within the range of 75-89%, qualify sample results that are ≥MDL as estimated low (J-), and qualify non-detects as estimated (UJ).

   c. If the ICV or CCV %R falls within the range of 111-125%, qualify sample results that are ≥MDL as estimated high (J+).

d. If the ICV or CCV %R is within the range of 111-125%, non-detects should not be qualified.

e. If the ICV or CCV %R is >125%, use professional judgment to qualify results that are ≥MDL as estimated high (J+) or unusable (R). Non-detects should not be qualified.

f. If the %R is >160%, qualify all results that are ≥MDL as unusable (R).

4. If the Laboratory failed to provide adequate calibration information, the Region's designated representative should contact the Laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

5. Note the potential effects on the reported data due to exceeding the calibration criteria in the Data Review Narrative.

6. If calibration criteria are grossly exceeded, note this for CLP Project Officer (CLP PO) action.

NOTE: For truly critical samples, a further in-depth evaluation of the calibration curve may be warranted to determine if additional qualification is necessary.

Table 3. Calibration Actions for ICP-AES Analysis

Calibration Result	Action for Samples
Calibration not performed	Qualify all results as unusable (R)
Calibration incomplete	Use professional judgment Qualify results that are ≥MDL as estimated (J) or unusable (R) Qualify non-detects as estimated (UJ) or unusable (R)
CRI %R <50% (<30% for Sb, Pb, Tl)	Qualify results that are ≥MDL but <2x the CRQL and all non-detects as unusable (R) Qualify all results that are ≥2x the CRQL as estimated (J)
CRI %R 50-69% (30-49% for Sb, Pb, Tl)	Qualify results that are ≥MDL but <2x the CRQL as estimated low (J-) Qualify non-detects as estimated (UJ) Results that are ≥2x the CRQL are not qualified
CRI %R >130% but ≤180% (>150% but ≤200% for Sb, Pb, Tl)	Qualify results that are ≥MDL but <2x the CRQL as estimated high (J+) Non-detects and results that are ≥2x the CRQL are not qualified
CRI %R >180% (>200% for Sb, Pb, Tl)	Qualify results that are ≥MDL as unusable (R)
ICV/CCV %R <75%	Qualify results that are ≥MDL as estimated low (J-) or unusable (R) Qualify all non-detects as unusable (R)
ICV/CCV %R 75-89%	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
ICV/CCV %R 111-125%	Qualify results that are ≥MDL as estimated (J)
ICV/CCV %R >125%	Qualify results that are ≥MDL as estimated high (J+) or unusable (R)
ICV/CCV %R >160%	Qualify results that are ≥MDL as unusable (R)

III. Blanks

A. Review Items:

Form I-IN, Form III-IN, Form XII-IN, Form XIII-IN, preparation logs, calibration standard logs, instrument logs, and raw data.

B. Objective:

The objective of blank analysis results assessment is to determine the existence and magnitude of contamination resulting from Laboratory (or field) activities. The criteria for evaluation of blanks applies to any blank associated with the samples (e.g., method blanks, calibration blanks, field blanks, etc.). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. No contaminants should be found in the blank(s).

2. The Initial Calibration Blank (ICB) shall be analyzed after the analytical standards, but not before analysis of the Initial Calibration Verification (ICV) during the initial calibration of the instrument (see Section II.C.1).

3. A Continuing Calibration Blank (CCB) shall be analyzed at each wavelength used for the analysis, immediately after every ICV and Continuing Calibration Verification (CCV). The CCB shall be analyzed at a frequency of 10% or every two hours during the run, whichever is more frequent. The CCB shall be analyzed at the beginning of the run, and again after the last CCV that was analyzed after the last analytical sample of the run. The CCB result (absolute value) shall not exceed the Contract Required Quantitation Limit (CRQL) of each analyte for which analysis is performed.

4. At least one Preparation Blank (PB) shall be prepared and analyzed for each matrix, with every Sample Delivery Group (SDG), or with each batch of samples digested, whichever is more frequent. The PB consists of reagent water processed through the appropriate sample preparation and analysis procedure.

5. If any analyte concentration in the PB is >CRQL, the lowest concentration of that analyte in the associated samples must be 10 times (10x) the PB concentration. Otherwise, all samples associated with that PB with the analyte's concentration <10x the PB concentration, and >CRQL, should be redigested and reanalyzed for that analyte (except for an identified field blank). The Laboratory is not to correct the sample concentration for the blank value.

6. If the concentration of the PB for a certain analyte is <(−CRQL), all samples reported <10x the CRQL (associated with that analyte in that blank), should be redigested and reanalyzed.

D. Evaluation:

1. Verify that an ICB was analyzed after the calibration, the CCB was analyzed at the proper frequency and location during the run, and PBs were prepared and analyzed as appropriate for the SDG (e.g., total number of samples, various types of matrices present, number of digestion batches, etc.).

2. Review the results reported, as well as the raw data (e.g., instrument printouts, strip charts, printer tapes, bench sheets, etc.) for all blanks, and verify that the results were accurately reported.

3. Evaluate all of the associated blanks for the presence of target analytes. Verify that if target analytes were present in a PB, or if a concentration was <(−CRQL), the affected samples were redigested and reanalyzed. Verify that if target analytes were present in an ICB or a CCB, the analysis was terminated, the problem corrected, the instrument recalibrated, and the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration blank reanalyzed.

NOTE: For data obtained from the Contract Laboratory Program (CLP), many of the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTES: For ICBs that do not meet the technical criteria, apply the action to all samples reported from the analytical run.

For CCBs that do not meet the technical criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of the CCB and a subsequent technically acceptable analysis of the CCB in the analytical run.

For PBs that do not meet the technical criteria, apply the action to all samples prepared in the same preparation batch.

1. If the appropriate blanks were not analyzed with the correct frequency, the data reviewer should use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the Laboratory. The situation should then be recorded in the Data Review Narrative, and noted for CLP Project Officer (PO) action.

2. Action regarding unsuitable blank results depends on the circumstances and origin of the blank. The reviewer should note that in instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of contaminant.

3. Some general "technical" review actions include:

    a. Any blank (including PB) reported with a negative result, whose value is ≤(−MDL) but ≥(−CRQL), should be carefully evaluated to determine its effect on the sample data. The reviewer shall then use professional judgment to assess the data. For any blank (including PB) reported with a negative result, whose value is <(−CRQL), qualify results that are ≥CRQL as estimated low (J-) and non-detects as estimated (UJ).

    b. The blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. In particular, soil sample results reported on Form I-IN will not be on the same basis (units, dilution) as the calibration blank data reported on Form III-IN. The reviewer may find it easier to work with the raw data.

4. Specific "method" actions include:

    a. If the absolute value of an ICB or a CCB result is >CRQL, the analysis should be terminated. If the analysis was not terminated and the affected samples were not reanalyzed, report non-detects and results that are ≥MDL, but ≤CRQL as CRQL-U. For results that are >CRQL but < Blank Result, use professional judgment to qualify the data as unusable (R) or to report the results at the level of the blank with a "U" qualifier. Use professional judgment to qualify results that are > Blank Result. Note this situation for CLP PO action and record it in the Data Review Narrative.

    b. If the absolute value of the concentration of the PB is ≤CRQL, report non-detects and results tat are ≥MDL but ≤CRQL as CRQL-U. Use professional judgment to quality results that are >CRQL.

    c. If any analyte concentration in the PB is >CRQL, the lowest concentration of that analyte in the associated samples must be 10x the PB concentration. Otherwise, all samples associated with that blank with concentrations <10x the PB concentration and >CRQL should be redigested and reanalyzed. Raise the CRQL to the concentration found in the PB and report those samples that do not require redigestion (that are ≥MDL but ≤CRQL) as CRQL-U. Note for CLP PO action and record in the Data Review Narrative if the Laboratory failed to redigest and reanalyze the affected samples. The reviewer shall then use professional judgment to assess the data.

Table 4. Blank Actions for ICP-AES Analysis

Blank Type	Blank Result	Sample Result	Action for Samples
ICB/CCB	≥MDL but ≤CRQL	Non-detect	No action
		≥MDL but ≤CRQL	Report CRQL value with a"U"
		>CRQL	Use professional judgment
ICB/CCB	>CRQL	≥MDL but ≤CRQL	Report CRQL value with a "U"
		>CRQL but <Blank Result	Report at level of Blank Result with a "U" or qualify data as unusable (R)
		>Blank Result	Use professional judgment
ICB/CCB	≤(-MDL) but ≥(-CRQL)	≥MDL, or non-detect	Use professional judgment
ICB/CCB	<(-CRQL)	<10x the CRQL	Qualify results that are ≥CRQL as estimated low (J-) Qualify non-detects as estimated (UJ)
PB	>CRQL	≥MDL but ≤CRQL	Report CRQL value with a "U"
		>CRQL but <10x the Blank Result	Qualify results as unusable (R) or estimated high (J+)
		≥10x the Blank Result	No action
PB	≥MDL but ≤CRQL	Non-detect ≥MDL but ≤CRQL >CRQL	No action Report CRQL value with a "U" Use professional judgment
PB	<(-CRQL)	<10x the CRQL	Qualify results that are ≥CRQL as estimated low (J-) Qualify non-detects as estimated (UJ)

IV. Inductively Coupled Plasma - Interference Check Sample (ICP-ICS)

A. Review Items:

Form IVA-IN, Form IVB-IN, Form XIII-IN, instrument printouts, and raw data.

B. Objective:

The Inductively Coupled Plasma (ICP) Interference Check Sample (ICS) verifies the analytical instrument's ability to overcome interferences typical of those found in samples.

NOTE: The Laboratory should have analyzed and reported ICS results for all elements being reported from the analytical run and for all interferents (target and non-target) for these reported elements.

C. Criteria:

1. The ICS consists of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively, starting with Solution A, for all wavelengths used for each analyte reported by Inductively Coupled Plasma - Atomic Emissions Spectroscopy (ICP-AES).

2. An ICS must be run at the beginning and end of each sample analysis run and every 20 analytical samples. The ICS is not to be run prior to the Initial Calibration Verification (ICV), and is to be immediately followed by a Continuing Calibration Verification (CCV), which will be followed by a Continuing Calibration Blank (CCB).

3. Results for the analysis of ICS Solution A must fall within the control limits of ± two times (2x) the Contract Required Quantitation Limit (CRQL), or ±20% of the true value (whichever is greater) for the analytes and interferents.

4. Results for the analysis of ICS Solution AB must fall within the control limits of ±2x the CRQL, or ±20% of the true value (whichever is greater) for the analytes and interferents included in the solution.

5. If the value of an ICS result exceeds ±2x the CRQL, or ±20% of true value (whichever is greater) criteria, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the new calibration then reverified, and the affected samples reanalyzed.

6. The ICS should be obtained from USEPA if available, and analyzed according to the instructions supplied with the solutions. The ICS may be prepared with the interferents at 2x the level specified in the Statement of Work (SOW) if high levels of interferents are found in the field samples. If the ICS is not available from USEPA, an independent ICS solution shall be prepared with the interferent and analyte concentrations at the levels specified in the method.

D. Evaluation:

1. Verify using the raw data (ICP instrumental printout) that the ICS was analyzed at the proper frequency and location during the analytical run.

2. Evaluate the ICS raw data for results with an absolute value that is > Method Detection Limit (MDL) for those analytes which are not present in the ICS solution.

3. Recalculate using the raw data and the following equation, one or more of the analyte Percent Recoveries (%R), and verify that the recalculated value agrees with the Laboratory- reported values on Form IV-IN.

$$\%R = \frac{\text{Found(value)}}{\text{True(value)}} \times 100$$

Where,

Found(value) = Concentration (in µg/L) of each analyte interferent measured in the analysis of ICS Solution A or ICS Solution AB

True(value) = Concentration (in µg/L) of each analyte or interferent in ICS Solution A or ICS Solution AB

4. If the value of an ICS result exceeds the ±2x the CRQL, or ±20% of true value (whichever is greater) criteria, and the Laboratory failed to terminate the analysis, and take the appropriate corrective action, note this for Contract Laboratory Project Officer (CLP PO) action and record in the Data Review Narrative. Use professional judgment to assess the data.

NOTE: For data obtained from the CLP, the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTE: For an ICS that does not meet the technical criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of the ICS and a subsequent technically acceptable analysis of the ICS in the analytical run.

1. The raw data should, but may not, contain results for interferents. If not, the reviewer shall use professional judgment to qualify the data. If the data does contain results for interferents, the reviewer should apply the following actions to samples with concentrations of interferents that are comparable to, or greater than, their respective levels in the ICS:

   a. If the ICS %R for an analyte or interferent is >120% (or greater than the true value + 2x the CRQL, as applicable) and the sample results are non-detects, the data should not be qualified.

   b. If the ICS %R for an analyte or interferent is >120% (or greater than the true value + 2x the CRQL, as applicable) qualify sample results that are ≥MDL as estimated high (J+). If

the ICS %R (or true value) grossly exceeds the limits, use professional judgment to qualify the data.

c. If the ICS %R for an analyte or interferent falls within the range of 50-79% (or less than the true value - 2x the CRQL, as applicable) qualify sample results that are ≥MDL as estimated low (J-).

d. If the ICS recovery for an analyte falls within the range of 50-79% (or less than the true value - 2x the CRQL, as applicable), the possibility of false negatives exists. Qualify sample non-detects as estimated (UJ).

e. If the ICSAB %R for an analyte or interferent is <50%, qualify all sample results that are ≥MDL as estimated low (J-) and all sample non-detects as unusable (R).

2. If results that are ≥MDL are observed for analytes that are not present in the ICS solution, the possibility of false positives exists. An evaluation of the associated sample data for the affected elements should be made. For samples with comparable or higher levels of interferents and with analyte concentrations that approximate those levels found in the ICS, qualify sample results that are ≥MDL as estimated high (J+). Non-detects should not be qualified.

3. If negative results are observed for analytes that are not present in the ICS solution, and their absolute value is ≥MDL, the possibility of false negatives in the samples exists. An evaluation of the associated sample data for the affected analytes should be made. For samples with comparable or higher levels of interferents, qualify non-detects for the affected analytes as estimated (UJ), and results that are ≥MDL but <10x the absolute value of the negative result as estimated low (J-).

4. In general, ICP-AES sample data can be accepted if the concentrations of Al, Ca, Fe, and Mg in the sample are found to be less than or equal to their respective concentrations in the ICS. If these elements are present at concentrations greater than the level in the ICS, or other elements are present in the sample at >10 mg/L, the reviewer should investigate the possibility of other interference effects as given in the ICP-AES method or as indicated by the Laboratory's interelement correction factors reported on Forms XA-IN and XB-IN for that particular instrument. The analyte concentration equivalents presented in the method should be considered only as estimated values since the exact value of any analytical system is instrument-specific. Therefore, estimate the concentration produced by an interfering element. If the estimate is >2x the CRQL, and also >10% of the reported concentration of the affected element, qualify the affected results as estimated (J).

5. If the raw data does not contain results for the interferents, note it in the Data Review Narrative.

6. Actions regarding the interpretation and/or the subsequent qualification of ICP data due to the ICS analytical results can be extremely complex. Use professional judgment to determine the need for the associated sample data to be qualified. The reviewer may need to obtain additional information from the Laboratory. All interpretive situations should then be recorded in the Data Review Narrative.

7. If the ICS acceptance criteria are grossly exceeded, note the specifics for CLP PO action.

Table 5. Interference Check Actions for ICP-AES Analysis

Interference Check Sample Results	Action for Samples
ICS %R >120% (or greater than true value + 2x the CRQL)	Qualify results that are ≥MDL as estimated high (J+)
ICS %R 50-79% (or less than true value - 2x the CRQL)	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
ICSAB %R <50%	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as unusable (R)
Potential false positives in field samples with interferents	Qualify results that are ≥MDL as estimated high (J+)
Potential false negatives in field samples with interferents	Qualify results that are ≥MDL but <10x(|negative value|) as estimated low (J-) Qualify non-detects as estimated (UJ)

V. Laboratory Control Sample (LCS)

A. Review Items:

Form VII-IN, Form XII-IN, preparation logs, instrument printouts, and raw data.

B. Objective:

The Laboratory Control Sample (LCS) serves as a monitor of the overall performance of each step during the analysis, including the sample preparation.

C. Criteria:

1. Aqueous and solid LCSs shall be analyzed for each analyte utilizing the same sample preparations, analytical methods, and Quality Assurance/Quality Control (QA/QC) procedures as employed for the samples. The aqueous LCS solution shall be obtained from USEPA, if available. However, if the LCS is unavailable from USEPA, the Initial Calibration Verification (ICV) solution(s) may be used.

    a. One aqueous LCS shall be prepared and analyzed for every group of aqueous samples in a Sample Delivery Group (SDG), or with each batch of aqueous samples digested, whichever is more frequent.

    b. All aqueous LCS Percent Recoveries (%R) must fall within the control limits of 80-120%, except for Sb and Ag which have no fixed control limits. If the %R for the aqueous LCS falls outside of the control limits (except for Ag and Sb), the analysis should be terminated, the problem corrected, and the samples prepared with that LCS redigested and reanalyzed.

    c. A solid LCS shall be prepared and analyzed utilizing each of the preparation and analytical procedures applied to the soil/sediment samples received, with one exception: the Percent Solids (%S) determination is not required. If the solid LCS is not available from USEPA, other USEPA QA samples or certified materials may be used.

    d. One solid LCS shall be prepared and analyzed for each group of soil sediment samples in an SDG, for each batch of samples digested or distilled, whichever is more frequent.

    e. All solid LCS results shall fall within the control limits reported on Form VII-IN. If the results for the solid LCS fall outside of the control limits, the analyses should be terminated, the problem corrected, and the samples prepared with that LCS redigested and reanalyzed.

D. Evaluation:

1. Verify using Form VII-IN, Form XII-IN, and raw data that the appropriate number of required LCSs were prepared and analyzed for the SDG.

2. Evaluate Form VII-IN and verify that all results for each analyte fall within the established control limits.

NOTE: Certain elements have only advisory limits for the LCS. Professional judgment should be used when evaluating these elements.

3. Check the raw data (e.g., instrument printouts, strip charts, bench sheets, etc.) to verify that the %Rs on Form VII-IN were accurately transcribed. Recalculate one or more of the reported %Rs using the following equation:

$$\%R = \frac{\text{Found(value)}}{\text{True(value)}} \times 100$$

Where,

Found(value) = Concentration of each analyte (in µg/L or mg/kg) measured in the analysis of the LCS

True(value) = Concentration of each analyte (in µg/L or mg/kg) in the LCS

4. Verify that the LCS was prepared at the same time as the associated samples using the same procedures.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

If the LCS criteria are not met, the Laboratory performance and method accuracy are in question. Professional judgment should be used to determine if the data should be qualified or rejected. The following guidance is suggested for qualifying sample data associated with an LCS that does not meet the required criteria.

For an LCS that does not meet the technical criteria, apply the action to all samples in the same preparation batch.

1. Aqueous LCS:

a. If the LCS %R falls within the range of 50-79%, qualify sample results that are ≥ Method Detection Limit (MDL) as estimated low (J-). If the LCS %R is >120%, qualify sample results that are ≥MDL as estimated high (J+).

b. If the LCS recovery is >120% and the sample results are non-detects, the data should not be qualified.

c. If the LCS recovery falls within the range of 50-79%, qualify non-detects as estimated (UJ).

d. If LCS %R is <50%, qualify all results that are ≥MDL as estimated low (J-) and all non-detects as unusable (R).

e. If the LCS %R is >150%, qualify all affected data (both detects and non-detects) as unusable (R).

2. Solid LCS:

a. If the LCS results are greater than the reported control limits, qualify sample results that are ≥MDL as estimated high (J+). If the LCS results are less than the reported control limits, qualify sample results that are ≥MDL as estimated low (J-).

b. If the LCS results are greater than the reported control limits and the sample results are non-detects, the data should not be qualified.

c. If the LCS results are less than the reported control limits, qualify non-detects as estimated (UJ).

3. If a Laboratory fails to analyze an LCS with each SDG, or if a Laboratory consistently fails to generate acceptable LCS recoveries, note this for CLP Project Officer (CLP PO) action.

4. Whenever possible, the potential effects on the data due to out-of-control LCS results should be noted in the Data Review Narrative.

Table 6. LCS Actions for ICP-AES Analysis

LCS Result	Action for Samples
Aqueous %R 50-79%	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
Aqueous %R >120%	Qualify results that are ≥MDL as estimated high (J+)
Aqueous %R <50%	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as unusable (R)
Aqueous %R >150%	Qualify all results as unusable (R)
Soil result > upper limit	Qualify results that are ≥MDL as estimated high (J+)
Soil result < lower limit	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as estimated (UJ)

VI. Duplicate Sample Analysis

A. Review Items:

Cover Page, Form VI-IN, Form XII-IN, instrument printouts, and raw data.

B. Objective:

The objective of duplicate sample analysis is to demonstrate acceptable method precision by the Laboratory at the time of analysis. Duplicate analyses are also performed to generate data that determines the long-term precision of the analytical method on various matrices. Non-homogenous samples can impact the apparent method precision. However, aqueous samples are generally homogenous and most soil samples are homogenous within a factor of two or three.

C. Criteria:

1. Samples identified as field blanks or Performance Evaluation (PE) samples cannot be used for duplicate sample analysis.

2. At least one duplicate sample shall be prepared and analyzed from each group of samples of a similar matrix type (e.g., water or soil) or for each Sample Delivery Group (SDG). Duplicates cannot be averaged for reporting on Form I-IN. Additional duplicate sample analyses may be required by USEPA Regional request. Alternately, the Region may require that a specific sample be used for the duplicate sample analysis.

3. Duplicate sample analyses are required for Percent Solids (%S) determination.

4. A control limit of 20% for the Relative Percent Difference (RPD) shall be used for original and duplicate sample values ≥ five times (5x) the Contract Required Quantitation Limit (CRQL).

5. A control limit of the CRQL shall be used if either the sample or duplicate value is <5x the CRQL. The absolute value of the control limit (CRQL) shall be entered in the "Control Limit" column on Form VI-IN. If both samples are non-detects, the RPD is not calculated for Form VI-IN.

NOTE: The above control limits are **method requirements** for duplicate samples, regardless of the sample matrix type. However, it should be noted that Laboratory variability arising from the sub-sampling of non-homogenous soil samples is a common occurrence. Therefore, for **technical review purposes only**, Regional policy or project Data Quality Objectives (DQOs) may allow the use of less restrictive criteria (e.g., 35% RPD, 2x the CRQL) to be assessed against duplicate soil samples.

D. Evaluation:

1. Verify from the Cover Page, Form XII-IN, and the raw data that the appropriate number of required duplicate samples were prepared and analyzed for the SDG.

2. Evaluate Form VI-IN and the raw data to verify that all duplicate results for each analyte and method fall within the established control limits.

3. Verify that a field blank or PE sample was not used for duplicate analysis.

4. Check the raw data and recalculate one or more of the RPD values using the following equation to verify that the results were correctly reported on Form VI-IN:

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where,

RPD = Relative Percent Difference

S = Sample Result (original)

D = Duplicate Result

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with the above criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTE: For a duplicate sample analysis that does not meet the technical criteria, apply the action to all samples of the same matrix if the reviewer considers the samples to be sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data when determining similarity, including: site and sampling documentation (e.g., location and type of sample, descriptive data, soil classification); field test data (e.g., pH, Eh, conductivity, chlorine); and Laboratory data for other parameters [e.g., Total Suspended Solids (TSSs), Total Dissolved Solids (TDSs), Total Organic Carbon (TOC), alkalinity or buffering capacity, reactive sulfide, anions]. The reviewer should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the SDG. The reviewer may determine that only some of the samples in the SDG are similar to the duplicate sample, and that only these samples should be qualified. Or, the reviewer may determine that no samples are sufficiently similar to the sample used for the duplicate, and thus that only the field sample used to prepare the duplicate sample should be qualified.

1. If the appropriate number of duplicate samples was not analyzed for each matrix using the correct frequency, use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the Laboratory. Note the situation in the Data Review Narrative, and for CLP Project Officer (CLP PO) action.

2. If the results from a duplicate analysis for a particular analyte fall outside the appropriate control limits, qualify sample results that are ≥MDL as estimated (J) and non-detects as estimated (UJ).

3. If a field blank or PE sample was used for the duplicate sample analysis, note this for CLP PO action. All of the other Quality Control (QC) data must then be carefully checked, and professional judgment exercised by the data reviewer when evaluating the data.

4. Note the potential effects on the data due to out-of-control duplicate sample results in the Data Review Narrative.

Table 7. Duplicate Sample Actions for ICP-AES Analysis

Duplicate Sample Results	Action for Samples
Both original sample and duplicate sample >5x the CRQL and RPD >20%*	Qualify those results that are ≥MDL that professional judgment determines to be affected as estimated (J) and non-detects as estimated (UJ)
Original sample or duplicate sample ≤5x the CRQL (including non-detects) and absolute difference between sample and duplicate >CRQL*	Qualify those results that are ≥MDL that professional judgment determines to be affected as estimated (J) and non-detects as estimated (UJ)

*The above control limits are **method requirements** for duplicate samples, regardless of the sample matrix type. However, it should be noted that Laboratory variability arising from the sub-sampling of non-homogenous soil samples is a common occurrence. Therefore, for **technical review purposes only**, Regional policy or project DQOs may allow the use of less restrictive criteria (e.g., 35% RPD, 2x the CRQL) to be assessed against duplicate soil samples.

VII. Spike Sample Analysis

A. Review Items:

Cover Page, Form V-IN (Part A & B), Form XII-IN, instrument printouts, and raw data.

B. Objective:

The spiked sample analysis is designed to provide information about the effect of each sample matrix on the sample preparation procedures and the measurement methodology. Non-homogenous samples can impact the apparent method recovery. However, aqueous samples are generally homogenous and most soil samples are homogenous within a factor of two or three. If the spike is added to the sample prior to the digestion (e.g., prior to the addition of other reagents), it is referred to as a spiked sample, pre-digestion, or Matrix Spike. If the spike is added to the sample after the completion of the digestion procedures, it is referred to as a post-digestion spike, or analytical spike.

C. Criteria:

1. Samples identified as field blanks or Performance Evaluation (PE) samples cannot be used for spiked sample analysis.

2. At least one spiked sample (pre-digestion) shall be prepared and analyzed from each group of samples with a similar matrix type (e.g., water or soil), or for each Sample Delivery Group (SDG).

3. When the pre-digestion spike recovery falls outside of the control limits and the sample result is < four times (4x) the spike added, a post-digestion spike shall be performed for those analytes that do not meet the specified criteria. An aliquot of the remaining unspiked sample shall be spiked at 2x the indigenous level or 2x the Contract Required Quantitation Limit (CRQL), whichever is greater.

   NOTE: Post-digestion spikes are not required for Ag.

4. The spike Percent Recovery (%R) shall be within the established acceptance limits. However, spike recovery limits do not apply when the sample concentration is ≥4x the spike added. In such an event, the data shall be reported unflagged, even if the %R does not meet the acceptance criteria.

5. If the spiked sample analysis was performed on the same sample that was chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample". The average of the duplicate results cannot be used for the purpose of determining %R.

   NOTE: The final spike concentrations required for the various target analytes are presented in the methods described in the Statement of Work (SOW).

D. Evaluation:

1. Verify using the Cover Page, Form VA-IN, Form XII-IN, and raw data, that the appropriate number of required spiked samples were prepared and analyzed for the SDG.

2. Verify that a field blank or PE sample was not used for the spiked sample analysis.

3. Evaluate Form VA-IN and the raw data to verify that all pre-digestion spiked sample results for each required analyte fall within the established control limits. If not, verify that a post-digestion/post-distillation spike was prepared and analyzed.

4. Recalculate using the raw data, one or more of the %R using the following equation, and verify that the recalculated value agrees with the Laboratory-reported values on Forms V(A & B)-IN:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

NOTES: When the sample concentration is < Method Detection Limit (MDL), use SR = 0 only for the purpose of calculating the %R. The actual spiked sample results, sample results, and %R (positive or negative) shall still be reported on Forms VA-IN and VB-IN.

For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with the above criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTE: For a Matrix Spike that does not meet the technical criteria, apply the action to all samples of the same matrix, if the reviewer considers the samples sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data, including: site and sampling documentation (e.g., location and type of sample, descriptive data, soil classification); field test data (e.g., pH, Eh, conductivity, chlorine); and Laboratory data for other parameters [e.g., Total Suspended Solids (TSSs), Total Dissolved Solids (TDSs), Total Organic Carbon (TOC), alkalinity or buffering capacity, reactive sulfide, anions], in determining similarity. The reviewer should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the SDG. The reviewer may determine that only some of the samples in the SDG are similar to the Matrix Spike sample, and that only these samples should be qualified. Or, the reviewer may determine that no samples are sufficiently similar to the sample used for the Matrix Spike, and thus that only the field sample used to prepare the Matrix Spike sample should be qualified.

1. If the appropriate number of Matrix Spike samples was not analyzed for each matrix using the correct frequency, use professional judgment to determine if the associated sample data

should be qualified. The reviewer may need to obtain additional information from the Laboratory. Note the situation in the Data Review Narrative, and for CLP Project Officer (CLP PO) action.

2. If a field blank or PE sample was used for the spiked sample analysis, note this for CLP PO action. All of the other Quality Control (QC) data must then be carefully checked, and professional judgment exercised by the data reviewer when evaluating the data.

3. If the Matrix Spike recovery does not meet the evaluation criteria and a required post-digestion spike was not performed, note this for CLP PO action.

4. If the Matrix Spike %R is <30%, verify that a post-digestion spike was analyzed if required. If the post-digestion spike %R is <75% or is not performed, qualify sample results that are ≥ Method Detection Limit (MDL) as estimated low (J-) and non-detects as unusable (R). If the post-digestion spike %R is ≥75%, qualify sample results that are ≥MDL as estimated (J) and non-detects as estimated (UJ).

5. If the Matrix Spike %R is 30-74% and the sample results are ≥MDL, verify that a post-digestion spike was analyzed if required. If the %R for the post-digestion is also <75% or is not performed, qualify the affected data as estimated low (J-). If the %R for the post-digestion spike is ≥75%, qualify the affected data as estimated (J).

6. If the Matrix Spike %R falls within the range of 30-74% and the sample results are non-detects, qualify the affected data as estimated (UJ).

7. If the Matrix Spike %R is >125% and the reported sample results are non-detects, the sample data should not be qualified.

8. If the Matrix Spike %R is >125% and the sample results are ≥MDL, verify that a post-digestion spike was analyzed if required. If the %R for the post-digestion spike is also >125% or is not performed, qualify the affected data as estimated high (J+). If the %R for the post-digestion spike is ≤125%, qualify the affected data as estimated (J).

9. Note the potential effects on the data due to out-of-control spiked sample results in the Data Review Narrative.

Table 8. Spike Sample Actions for ICP-AES Analysis

Spike Sample Results	Action for Samples
Matrix Spike %R <30% Post-digestion spike %R <75%	Qualify affected results that are ≥MDL as estimated low (J-) and affected non-detects as unusable (R)
Matrix Spike %R <30% Post-digestion spike %R ≥75%	Qualify affected results that are ≥MDL as estimated (J) Qualify affected non-detects as estimated (UJ)
Matrix Spike %R 30-74% Post-digestion Spike %R <75%	Qualify affected results that are ≥MDL as estimated low (J-) and affected non-detects as estimated (UJ)
Matrix Spike %R 30-74% Post-digestion spike %R ≥75%	Qualify affected results that are ≥MDL as estimated (J) Qualify affected non-detects as estimated (UJ)
Matrix Spike %R >125% Post-digestion spike %R >125%	Qualify affected results that are ≥MDL as estimated high (J+)
Matrix Spike %R >125% Post-digestion spike %R ≤125%	Qualify affected results that are ≥MDL as estimated (J)
Matrix Spike %R <30% No post-digestion spike performed (e.g., not required for Ag)	Qualify affected results that are ≥MDL as estimated low (J-) and affected non detects as unusable (R)
Matrix Spike %R 30-74% No post-digestion spike performed (e.g., not required for Ag)	Qualify affected results that are ≥MDL as estimated low (J-) and non-detects as estimated (UJ)
Matrix Spike %R >125% No post-digestion spike performed (e.g., not required for Ag)	Qualify affected results that are ≥MDL as estimated high (J+) Non-detects are not qualified

VIII. ICP Serial Dilution

A. Review Items:

Form I-IN, Form VIII-IN, instrument printouts, and raw data.

B. Objective:

The serial dilution of samples quantitated by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) determines whether or not significant physical or chemical interferences exist due to sample matrix.

C. Criteria:

1. An ICP Serial Dilution analysis shall be performed on a sample from each group of samples with a similar matrix type (e.g., water or soil) or for each Sample Delivery Group (SDG), whichever is more frequent.

2. Samples identified as field blanks or Performance Evaluation (PE) samples cannot be used for the ICP Serial Dilution analysis.

3. If the analyte concentration is sufficiently high [concentration in the original sample is >50 times (50x) the Method Detection Limit (MDL)], the serial dilution analysis (a five-fold dilution) shall then agree within a 10 Percent Difference (%D) of the original determination after correction for dilution. Note that serial dilutions of soil samples are reported in µg/L, but the MDL is in mg/kg. The units will need to be adjusted.

D. Evaluation:

1. Verify that a field blank or PE sample was not used for the serial dilution analysis.

2. Check the raw data and recalculate the %D using the following equation. Verify that the serial dilution analysis results, and the calculated %D results agree with the values reported by the Laboratory on Form VIII-IN:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

Where,

I = Initial Sample Result (instrument reading)

S = Serial Dilution Result (instrument reading x5)

3. Check the raw data for any evidence of positive or negative interference (results from the diluted sample which are significantly different than the original sample), possibly due to high levels of dissolved solids in the sample, ionization effects, etc.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information

regarding the Laboratory's compliance with the above criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTE: For a serial dilution that does not meet the technical criteria, apply the action to all samples of the same matrix if the reviewer considers the samples sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data, including: site and sampling documentation (e.g., location and type of sample, descriptive data, soil classification); field test data (e.g., pH, Eh, conductivity, chlorine); and Laboratory data for other parameters [e.g., Total Suspended Solids (TSSs), Total Dissolved Solids (TDSs), Total Organic Carbon (TOC), alkalinity or buffering capacity, reactive sulfide, anions], in determining similarity. The reviewer should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the SDG. The reviewer may determine that only some of the samples in the SDG are similar to the serial dilution sample, and that only these samples should be qualified. Or, the reviewer may determine that no samples are sufficiently similar to the sample used for serial dilution, and thus that only the field sample used to prepare the serial dilution sample should be qualified.

1. If the required %D criteria are not met, qualify all affected results that are ≥MDL as estimated (J) and all affected non-detects as estimated (UJ).

2. If evidence of positive or negative interference is found, use professional judgment to qualify the associated sample data. Note the potential effects on the reported data in the Data Review Narrative.

3. It should be noted for CLP Project Officer (CLP PO) action and in the Data Review Narrative if a field blank or PE sample was used for the serial dilution analysis.

Table 9. Serial Dilution Actions for ICP-AES Analysis

Serial Dilution Result	Action for Samples
Sample concentration >50x MDL and %D >10	Qualify affected results that are ≥MDL as estimated (J) Qualify affected non-detects as estimated (UJ)
Interferences present	Use professional judgment

IX. Field Duplicates

A. Review Items:

Form I-IN, instrument printouts, and raw data.

B. Objective:

Field duplicate samples may be collected and analyzed as an indication of overall precision. These analyses measure both field and Laboratory precision. The results, therefore, may have more variability than Laboratory duplicates that measure only Laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

C. Criteria:

There are no "required" review criteria for determining comparability of field duplicate analyses.

D. Evaluation:

Identify samples that are field duplicates using Traffic Report/Chain of Custody (TR/COC) documentation or sample field sheets. Compare the results reported for each sample and calculate the Relative Percent Difference (RPD), if appropriate.

E. Action:

Provide any evaluation of the field duplicates in the Data Review Narrative.

X. Overall Assessment

A. Review Items:

Entire sample data package, data review results, preparation logs, calibration standard logs, instrument logs, instrument printouts, and raw data (including any confirmation data).

B. Objective:

The objective is to ensure that the reported sample quantitation results are accurate. It is appropriate for the data reviewer to make professional judgments and express concerns, as well as to comment on the validity of the overall data for a Case. This is particularly appropriate when there are several Quality Control (QC) criteria that are outside of the specification parameters. The additive nature of QC factors that fall outside of specification parameters is difficult to objectively assess. The reviewer has a responsibility to inform the user of data quality and data limitations to help the user to avoid inappropriate use of the data, while not precluding any consideration of the data. If qualifiers other than those used in this document are necessary to describe or qualify the data, it is necessary to thoroughly document/explain the additional qualifiers used. The data reviewer would be greatly assisted in this endeavor if the acceptance or performance criteria were provided. The Inorganic Review Summary (see Appendix B) and supplementary documentation must be included with the review.

C. Criteria:

1. Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

2. Reported analyte concentrations must be quantitated according to the appropriate analytical method, as listed in the method.

D. Evaluation:

Examine the raw data to verify that correct calculations of the sample results were reported by the Laboratory. Digestion and distillation logs, instrument printouts, strip charts, etc., should be compared to the reported sample results recorded on the appropriate Inorganic Summary Forms (Form I-IN through Form XIII-IN).

1. Evaluate any technical problems not previously addressed.

2. Examine the raw data for any anomalies (e.g., baseline shifts, negative absorbance, omissions, illegibility, etc.).

3 Verify that appropriate methods and amounts were used in preparing the samples for analysis.

4. Verify that there are no transcription or reduction errors [e.g., dilutions, Percent Solids (%S), sample weights, etc.] on one or more samples.

5. Verify that results fall within the linear range(s) of the Inductively Coupled Plasma (ICP) instrument(s) (Form XI).

6. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the Quality Assurance Project Plan (QAPP), focusing specifically on the acceptance or performance criteria, the Standard Operating Procedure(s) (SOPs), and communication with the user concerning the intended use and desired quality of these data.

E. Action:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC criteria previously discussed.

2. Write a brief Data Review Narrative to give the user an indication of the analytical limitations of the data. Note any discrepancies between the data and the SDG Narrative for Contract Laboratory Program Project Officer (CLP PO) action. If sufficient information on the intended use and required quality of the data are available, the reviewer should include an assessment of the data usability within the given context.

3. If any discrepancies are found, the Laboratory may be contacted by the Region's designated representative to obtain additional information for resolution. If a discrepancy remains unresolved, the reviewer may determine that qualification of the data is warranted.

Calculations for ICP-AES

Aqueous Samples by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES):

The concentrations determined in the digestate are to be reported in units of µg/L:

$$\text{Concentration } (\mu g/L) = C \times \frac{V_f}{V_i} \times DF$$

Where,

C = Instrument value in µg/L

V_f = Final digestion volume (mL)

V_i = Initial digestion volume (mL)

DF = Dilution Factor

Soil Samples by ICP-AES:

The concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample, in units of mg/kg:

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S} \times DF$$

Where,

C = Concentration (mg/L)

V = Final sample volume in Liters (L)

W = Wet sample weight (kg)

S = % Solids/100 (see SOW ILM05.3 Exhibit D - Introduction to Analytical Methods, Section 1.6)

DF = Dilution Factor

Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation:

To calculate the adjusted MDL or adjusted CRQL for water/aqueous samples, substitute the value of the MDL (µg/L) or CRQL (µg/L) into the "C" term in the equation above.

Calculate the adjusted MDL or adjusted CRQL for soil samples as follows:

$$\text{Adjusted Concentration (dry wt.)(mg/kg)} = C \times \frac{W_M}{W_R} \times \frac{V_R}{V_M} \times \frac{1}{S} \times DF$$

Where,

C	=	MDL or CRQL concentration (mg/kg)
W_M	=	Minimum method required wet sample weight (g)
W_R	=	Reported wet sample weight (g)
V_M	=	Method required final sample volume (mL)
V_R	=	Reported final sample volume (mL)
S	=	% Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)
DF	=	Sample Dilution Factor

ICP-MS DATA REVIEW

The inorganic data requirements for Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to be reviewed during validation are listed below:

I. Preservation and Holding Times

II. ICP-MS Tune Analysis

III. Calibration
- A. Initial
- B. Initial and Continuing Calibration Verification (ICV/CCV)
- C. Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

IV. Blanks

V. Inductively Coupled Plasma - Interference Check Sample (ICP-ICS)

VI. Laboratory Control Sample (LCS)

VII. Duplicate Sample Analysis

VIII. Spike Sample Analysis

IX. ICP Serial Dilution

X. ICP-MS Internal Standards

XI. Field Duplicates

XII. Overall Assessment

NOTE: At this time, the ICP-MS method in SOW ILM05.X is for water samples only. If soil samples are analyzed by a modified version of this method, the reviewer must use professional judgment to modify the review criteria [e.g., for duplicate sample analyses, spike sample analyses, serial dilution analyses, Laboratory Control Samples (LCSs), and internal standards]. These modifications must be detailed in the Data Review Narrative.

An Example Analytical Sequence for ICP-MS

Tune(s)
S0
S
ICV
ICB
CRI
ICSA
ICSAB
CCV
CCB
ten samples
CCV
CCB
seven samples
CRI
CCV
CCB
ten samples, etc.

I. Preservation and Holding Times

A. Review Items:

Form IA-IN, Form IB-IN, Form XII-IN, Form XIII-IN, Traffic Report/Chain of Custody (TR/COC) documentation, Form DC-1, raw data, and the Sample Delivery Group (SDG) Narrative checking for: pH; cooler temperature; holding time; and other sample conditions.

B. Objective:

The objective is to determine the validity of the analytical results based on the sample condition, and the holding time of the sample from the date of collection to the date of analysis.

C. Criteria:

1. The technical holding time criteria for aqueous metal samples is 180 days; preserved (with nitric acid) to pH <2.

2. Aqueous samples shall be maintained at 4°C ±2°C until preparation and analysis to allow for re-preparation and for the direct analysis of dissolved metals.

D. Evaluation:

Technical holding times are established by comparing the sampling date(s) on the TR/COC documentation with the dates of analysis on Form XIII-IN, and the raw data. Information contained in the Complete SDG File (CSF) should also be considered in the determination of holding times. Verify that the analysis dates on the Form XIIIs and the raw data are identical. Review the SDG Narrative and raw data preparation logs to determine if samples were properly preserved. If there is an indication that there were problems with the samples, the integrity of the samples may be compromised and professional judgment should be used to evaluate the effect of the problem on the sample results.

E. Action:

NOTE: Apply the action to each sample for which the preservation or holding time criteria was not met.

1. If the pH of aqueous metals samples is ≥2 at the time of sample receipt, use professional judgment to qualify the samples based on the pH of the sample and the chemistry of the metal(s) of interest. Qualify results that are ≥ Method Detection Limit (MDL) as estimated low (J-), and qualify non-detects as unusable (R).

2. If technical holding times are exceeded, use professional judgment to determine the reliability of the data based on the magnitude of the additional time compared to the technical requirement and whether the samples were properly preserved. The expected bias would be low. Qualify results that are ≥MDL as estimated low (J-), and qualify non-detects as unusable (R).

3. When the holding times are exceeded, the reviewer should comment in the Data Review Narrative on any possible consequences for the analytical results.

4. When holding times are grossly exceeded, note this for Contract Laboratory Program Project Officer (CLP PO) action.

Table 10. Technical Holding Time Actions for ICP-MS Analysis

Preservation & Holding Time Results	Action for Samples
Aqueous metals samples received with pH ≥2	Use professional judgment Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as unusable (R)
Technical Holding Time exceeded: Metals >180 days.	Use professional judgment Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as unusable (R)

II. ICP-MS Tune Analysis

A. Review Items:

Form XIV-IN, instrument printouts, and raw data.

B. Objective:

The Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) tune serves as an initial demonstration of instrument stability and precision.

C. Criteria:

1. Prior to calibration, the Laboratory shall analyze or scan the ICP-MS tuning solution at least five times (5x) consecutively. The tuning solution contains 100 µg/L of Be, Mg, Co, In, and Pb. The solution shall contain all required isotopes of the above elements. The Laboratory shall make any adjustments necessary to bring peak width within the instrument and to bring mass resolution to within 0.1 amu over manufacturer's specifications the range of 6-210 amu.

2. The Percent Relative Standard Deviation (%RSD) of the absolute signals for all analytes in the tuning solution must be <5%.

D. Evaluation:

1. Verify using the raw data and Form XIV-IN that the appropriate number of analyses or scans of the ICP-MS tuning solution were performed, and that the appropriate analytes were present in the solution.

2. Verify using the raw data and Form XIV-IN that the mass calibration falls within the limits for each isotope of each analyte.

3. Verify using the raw data and Form XIV-IN that the %RSD is <5% for each isotope of each analyte.

4. Check the raw data to verify that the reported average mass and %RSD on Form XIV-IN were accurately calculated. Recalculate one or more of the average masses and %RSDs for an isotope using the following equations:

$$\text{Mean} = \frac{\sum x}{n}$$

Where,

x = Mass from analysis

n = Number of analyses

$$\text{Percent Relative Standard Deviation} = \frac{\sigma_{n-1} \times 100}{\bar{x}}$$

Where,

$\bar{x}$ = Mean

σ_{n-1} = Standard Deviation

NOTE: For data obtained from the Contract Laboratory Program (CLP), many of the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with the above criteria can be obtained from the Data Assessment Tool (DAT) reports and may be used as part of the evaluation process.

E. Action:

NOTE: For ICP-MS tunes that does not meet the technical criteria, apply the action to all samples reported from the analytical run.

1. If the ICP-MS instrument was not tuned prior to calibration, the sample data should be qualified as unusable (R).

2. If the tuning solution was not analyzed or scanned at least 5x consecutively or the tuning solution does not contain the required analytes spanning the analytical range, the reviewer should use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the Laboratory. The situation should be recorded in the Data Review Narrative and noted for CLP Project Officer (CLP PO) action.

3. If the mass calibration is not within 0.1 amu for any isotope in the tuning solution, qualify all analyte results that are ≥MDL associated with that isotope as estimated (J), and all non-detects associated with that isotope as estimated (UJ). The situation should be recorded in the Data Review Narrative and noted for CLP PO action.

4. If the %RSD exceeds 5% for any isotope in the tuning solution, qualify all sample results that are ≥MDL associated with that tune as estimated (J), and all non-detects associated with that tune as estimated (UJ). The situation should be recorded in the Data Review Narrative and noted for CLP PO action.

Table 11. ICP-MS Tune Actions for ICP-MS Analysis

ICP-MS Tune Results	Action for Samples
Tune not performed	Qualify all results as unusable (R)
Tune not performed properly	Use professional judgment
Mass calibration not within 0.1 amu	Qualify results that are ≥MDL as estimated (J) Qualify non-detects as estimated (UJ)
%RSD >5%	Qualify results that are ≥MDL as estimated (J) Qualify non-detects as estimated (UJ)

III. Calibration

A. Review Items:

Form II-IN (Parts A & B), Form XI-IN, Form XIII-IN, preparation logs, calibration standard logs, instrument logs, instrument printouts, and raw data.

B. Objective:

Method requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data for the metals on the Inorganic Target Analyte List (TAL). Initial Calibration Verification (ICV) demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical run. Continuing Calibration Verification (CCV) demonstrates that the initial calibration is still valid by checking the performance of the instrument on a continual basis.

C. Criteria:

1. Initial Calibration

The instruments shall be successfully calibrated daily (or once every 24 hours), and each time the instrument is set up. The calibration date and time shall be included in the raw data.

a. A blank and at least one calibration standard shall be used to establish each analytical curve. All measurements shall be within the instrument linear working range. A minimum of three replicate scans are required for standardization and all Quality Control (QC) and sample analyses. The average result of the multiple scans for the standardization, QC, and sample analyses shall be used.

b. The instrumental calibration near the Contract Required Quantitation Limit (CRQL) must be verified for each analyte. A CRQL Check Standard (CRI) solution shall be prepared and analyzed at the beginning and end of each sample analysis run and every 20 analytical samples, but not before the ICV analysis. The initial CRI shall immediately precede the Interference Check Sample (ICS) analyses, and immediately follow the ICV/ICB analyses.

c. The CRI shall be run by ICP-MS for every mass used for analysis. All results and Percent Recoveries (%Rs) shall be reported on Form IIB-IN. If the results for the CRI do not fall within the fixed acceptance limits, the Laboratory shall immediately reanalyze the CRI for those analytes. If the results of the reanalysis do not fall within the acceptance limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the new calibration then reverified.

2. Initial and Continuing Calibration Verification (ICV and CCV)

The acceptance criteria for the ICVs, CCVs, and CRIs are presented in Table 12:

Table 12. Acceptance Criteria for ICV, CCV, and CRI Standards

Analytical Method	Inorganic Analytes	ICV/CCV Low Limit (% of True Value)	ICV/CCV High Limit (% of True Value)	CRI Low Limit (% of True Value)	CRI High Limit (% of True Value)
ICP-MS	Metals	90	110	70 (50 for Co, Mn, Zn)	130 (150 for Co, Mn, Zn)

a. Initial Calibration Verification (ICV)

1) Immediately after each ICP-MS system has been calibrated, the accuracy of the initial calibration must be verified and documented for each target analyte by the analysis of an ICV solution(s). If the ICV Percent Recovery (%R) falls outside of the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and all affected samples reanalyzed.

2) If the ICV is not available from USEPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration level other than that used for instrument calibration (or the CRI), but within the calibrated range.

3) The ICV solution shall be run at each analytical mass used for analysis.

b. Continuing Calibration Verification (CCV)

1) To ensure accuracy during the course of each analytical run, the CCV shall be analyzed and reported for each mass used for the analysis of each analyte.

2) The CCV standard shall be analyzed at a frequency of 10% or every two hours during an analytical run, whichever is more frequent. The CCV standard shall also be analyzed at the beginning of the run, and again after the last analytical sample.

3) The analyte concentration(s) in the CCV standard(s) shall be different than the concentration used for the ICV, and shall be one of the following solutions at, or near, the mid-range levels of the calibration curve:

   A. USEPA solutions;
   B. National Institute of Standards and Technology (NIST) standards; or
   C. A Laboratory-prepared standard solution (self-prepared or commercially available).

4) The same CCV standard solution shall be used throughout the analysis runs for a Sample Delivery Group (SDG).

5) The CCV shall be analyzed in the same fashion as an actual sample. Operations such as the number of replicate analyses, the number and duration of the instrument rinses, etc., affect the measured CCV result and are not to be applied to the CCV to an extent greater than was applied to the associated analytical samples. If the %R of the CCV was outside of the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification reanalyzed.

D. Evaluation:

1. Verify that the instrument was calibrated daily (once every 24 hours) and each time the instrument was set up, utilizing a blank and at least one calibration standard.

2. Confirm that the measurements were within the documented linear working range, and were the average result of at least three replicate exposures.

3. Evaluate the reported CRI to confirm that it was analyzed at the proper concentration, frequency, and location within the analytical run sequence. Verify that acceptable %R results were obtained.

4. Verify that the ICV and CCV standards were analyzed for each analyte at the proper frequency (10%) and at the appropriate concentration. Verify that acceptable %R results were obtained.

5. Recalculate one or more of the ICV, CCV, and CRI %Rs using the following equation and verify that the recalculated value agrees with the Laboratory-reported values on Forms II (A & B)-IN.

$$\%R = \frac{\text{Found(value)}}{\text{True(value)}} \times 100$$

Where,

Found(value) = Concentration (in µg/L) of each analyte measured in the analysis of the ICV, CCV, or CRI solution

True(value) = Concentration (in µg/L) of each analyte in the ICV, CCV, or CRI source

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTE: For initial calibrations or ICVs that does not meet the technical criteria, apply the action to all samples reported from the analytical run.

For CCVs or CRIs that does not meet the technical criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of the QC sample and a subsequent technically acceptable analysis of the QC sample in the analytical run.

1. If the instrument was not calibrated daily and each time the instrument was set up, qualify the data as unusable (R). If the instrument was not calibrated with at least the minimum number of standards, or if the calibration curve does not include standards at required concentrations (e.g., a blank), use professional judgment to qualify results that are ≥MDL as estimated (J) or unusable (R), and non-detects as estimated (UJ) or unusable (R).

2. If the CRIs are outside the acceptance criteria, use professional judgment to qualify all associated data. If possible, indicate the bias in the review. The following guidelines are recommended:

   a. If the CRI %R is <50% (<30% for Co, Mn, Zn), qualify all sample results that are ≥MDL but < two times (2x) the CRQL and all non-detects as unusable (R). Qualify detects that are ≥2x the CRQL as estimated (J).

   b. If the CRI %R falls within the range of 50-69% (30-49% for Co, Mn, Zn), qualify all sample results that are ≥MDL but <2x the CRQL as estimated low (J-), and all non-detects as estimated (UJ). Detects that are ≥2x the CRQL should not be qualified based on this criterion.

   c. If the CRI %R is >130% but ≤180% (>150% but ≤200% for Co, Mn, Zn), qualify all sample results that are ≥MDL but <2x the CRQL as estimated high (J+). Non-detects and detects that are ≥2x the CRQL should not be qualified based on this criterion.

   d. If the CRI %R is >180% (>200% for Co, Mn, Zn), qualify all sample results that are ≥MDL as unusable (R).

3. If the ICV or CCV %R falls outside the acceptance windows, use professional judgment to qualify all associated data. If possible, indicate the bias in the review. The following guidelines are recommended:

   a. If the ICV or CCV %R is <75%, qualify non-detects as unusable (R). Use professional judgment to qualify all results that are ≥MDL as estimated low (J-) or unusable (R).

   b. If the ICV or CCV %R falls within the range of 75-89%, qualify sample results that are ≥MDL as estimated low (J-), and qualify non-detects as estimated (UJ).

   c. If the ICV or CCV %R falls within the range of 111-125%, qualify sample results that are ≥MDL as estimated high (J+).

   d. If the ICV or CCV %R falls within the range of 111-125%, non-detects should not be qualified.

e. If the ICV or CCV %R is >125%, use professional judgment to qualify results that are ≥MDL as estimated high (J+) or unusable (R). Non-detects should not be qualified.

f. If the %R is >160%, qualify all results that are ≥MDL as unusable (R).

4. If the Laboratory failed to provide adequate calibration information, the USEPA Region's designated representative should contact the Laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

5. Note the potential effects on the reported data due to exceeding the calibration criteria in the Data Review Narrative.

6. If calibration criteria are grossly exceeded, note this for CLP Project Officer (CLP PO) action.

NOTE: For truly critical samples, a further in-depth evaluation of the calibration curve may be warranted to determine if additional qualification is necessary.

Table 13. Calibration Actions for ICP-MS Analysis

Calibration Result	Action for Samples
Calibration not performed	Qualify all results as unusable (R)
Calibration incomplete	Use professional judgment Qualify results that are ≥MDL as estimated (J) or unusable (R) Qualify non-detects as estimated (UJ) or unusable (R)
CRI %R <50% (<30% for Co, Mn, Zn)	Qualify all results that are ≥MDL but <2x the CRQL and all non-detects as unusable (R) Qualify all results that are ≥2x the CRQL as estimated (J)
CRI %R 50-69% (30-49% for Co, Mn, Zn)	Qualify results that are ≥MDL but <2x the CRQL as estimated low (J-) Qualify non-detects as estimated (UJ) Results that are ≥2x the CRQL are not qualified
CRI %R >130% but ≤180% (>150% but ≤200% for Co, Mn, Zn)	Qualify results that are ≥MDL but <2x the CRQL as estimated high (J+) Non-detects and results that are ≥2x the CRQL are not qualified

Table 13. Calibration Actions for ICP-MS Analysis (Con't)

Calibration Result	Action for Samples
CRI %R >180% (>200% for Co, Mn, Zn)	Qualify all results that are ≥MDL as unusable (R)
ICV/CCV %R <75%	Qualify results that are ≥MDL as estimated low (J-) or unusable (R) Qualify all non-detects as unusable (R)
ICV/CCV %R 75-89%	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
ICV/CCV %R 111-125%	Qualify results that are ≥MDL as estimated (J)
ICV/CCV %R >125%	Qualify results that are ≥MDL as estimated high (J+) or unusable (R)
ICV/CCV %R >160%	Qualify results that are ≥MDL as unusable (R)

IV. Blanks

A. Review Items:

Form I-IN, Form III-IN, Form XII-IN, Form XIII-IN, preparation logs, calibration standard logs, instrument logs, and raw data.

B. Objective:

The objective of blank analysis results assessment is to determine the existence and magnitude of contamination resulting from Laboratory (or field) activities. The criteria for evaluation of blanks applies to any blank associated with the samples (e.g., method blanks, calibration blanks, field blanks, etc.). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. No contaminants should be found in the blank(s).

2. The Initial Calibration Blank (ICB) shall be analyzed after the analytical standards, but not before analysis of the Initial Calibration Verification (ICV) during the initial calibration of the instrument (see Section II.C.1).

3. A Continuing Calibration Blank (CCB) shall be analyzed at each mass used for the analysis, immediately after every ICV and Continuing Calibration Verification (CCV). The CCB shall be analyzed at a frequency of 10% or every two hours during the run, whichever is more frequent. The CCB shall be analyzed at the beginning of the run, and again after the last CCV that was analyzed after the last analytical sample of the run. The CCB result (absolute value) shall not exceed the Contract Required Quantitation Limit (CRQL) of each analyte for which analysis is performed.

4. At least one Preparation Blank (PB) shall be prepared and analyzed, with every Sample Delivery Group (SDG), or with each batch of samples digested, whichever is more frequent. The PB consists of reagent water processed through the appropriate sample preparation and analysis procedure.

5. If any analyte concentration in the PB is >CRQL, the lowest concentration of that analyte in the associated samples must be 10 times (10x) the PB concentration. Otherwise, all samples associated with that PB with the analyte's concentration <10x the PB concentration, and >CRQL, should be redigested and reanalyzed for that analyte (except for an identified field blank). The Laboratory is not to correct the sample concentration for the blank value.

6. If the concentration of the PB for a certain analyte is <(−CRQL), all samples reported <10x the CRQL (associated with that analyte in that blank), should be redigested and reanalyzed.

D. Evaluation:

1. Verify that an ICB was analyzed after the calibration, the CCB was analyzed at the proper frequency and location during the run, and PBs were prepared and analyzed as appropriate for the SDG (e.g., total number of samples, various types of matrices present, number of digestion batches, etc.).

2. Review the results reported on the Blank Summary (Form III-IN), as well as the raw data (e.g., instrument printouts, strip charts, printer tapes, bench sheets, etc.) for all blanks, and verify that the results were accurately reported.

3. Evaluate all of the associated blanks for the presence of target analytes. Verify that if target analytes were present in a PB, or if a concentration was <(−CRQL), the affected samples were redigested and reanalyzed. Verify that if target analytes were present in an ICB or a CCB, the analysis was terminated, the problem corrected, the instrument recalibrated, and the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration blank reanalyzed.

NOTE: For data obtained from the Contract Laboratory Program (CLP), many of the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTES: For ICBs that does not meet the technical criteria, apply the action to all samples reported from the analytical run.

For CCBs that does not meet the technical criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of the CCB and a subsequent technically acceptable analysis of the CCB in the analytical run.

For PBs that does not meet the technical criteria, apply the action to all samples prepared in the same preparation batch.

1. If the appropriate blanks were not analyzed with the correct frequency, the data reviewer should use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the Laboratory. The situation should then be recorded in the Data Review Narrative, and noted for CLP Project Officer (CLP PO) action.

2. Action regarding unsuitable blank results depends on the circumstances and origin of the blank. The reviewer should note that in instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of contaminant.

3. Some general "technical" review actions include:

    a. Any blank (including PB) reported with a negative result, whose value is ≤(−Method Detection Limit) (MDL) but ≥(−CRQL), should be carefully evaluated to determine its effect on the sample data. The reviewer shall then use professional judgment to assess the data. For any blank (including PB) reported with a negative result, whose value is <(−CRQL), qualify results that are ≥CRQL as estimated low (J-) and non-detects as estimated (UJ).

4. Specific "method" actions include:

    a. If the absolute value of an ICB or a CCB result >CRQL, the analysis should be terminated. If the analysis was not terminated and the affected samples were not reanalyzed, report non-detect and results that are ≥MDL but ≤CRQL as CRQL-U. For results that are >CRQL but < Blank Result, use professional judgment to qualify the data as unusable or to report the results at the level of the blank with a "U" qualifier. Use professional judgment to qualify results that are > Blank Result. Note this situation for CLP PO action and record it in the Data Review Narrative.

    b. If the absolute value of the concentration of the PB is ≤CRQL, report non-detects and results that are ≥MDL but ≤CRQL as CRQL-U. Use professional judgment to qualify results that are >CRQL.

    c. If any analyte concentration in the PB is >CRQL, the lowest concentration of that analyte in the associated samples must be 10x the PB concentration. Otherwise, all samples associated with that blank with concentrations <10x the PB concentration and >CRQL should be redigested and reanalyzed. Raise the CRQL to the concentration found in the PB and report those samples that does not require redigestion (that are ≥MDL but ≤CRQL) as CRQL-U. Note for CLP PO action and record in the Data Review Narrative if the Laboratory failed to redigest and reanalyze the affected samples. The reviewer shall then use professional judgment to assess the data.

Table 14. Blank Actions for ICP-MS Analysis

Blank Type	Blank Result	Sample Result	Action for Samples
ICB/CCB	≥MDL but ≤CRQL	Non-Detect	No action
		≥MDL but ≤CRQL	Report CRQL value with a "U"
		>CRQL	Use professional judgment
ICB/CCB	>CRQL	≥MDL but ≤CRQL	Report CRQL value with a "U"
		>CRQL but <Blank Result	Report at level of Blank Result with a "U" or qualify data as unusable (R)
		>Blank Result	Use professional judgment
ICB/CCB	≤(-MDL), but ≥(-CRQL)	≥MDL, or non-detect	Use professional judgment
ICB/CCB	<(-CRQL)	<10x CRQL	Qualify results that are ≥CRQL as estimated low (J-) Qualify non-detects as estimated (UJ)
PB	>CRQL	≥MDL but ≤CRQL	Report CRQL value with a "U"
		>CRQL but <10x the Blank Result	Qualify results as unusable (R) or estimated high (J+)
		≥10x the Blank Result	No action
PB	≥MDL but ≤CRQL	Non-detect ≥MDL but ≤CRQL >CRQL	No action Report CRQL value with a "U" Use professional judgment
PB	<(-CRQL)	<10x CRQL	Qualify results that are ≥CRQL as estimated low (J-) Qualify non-detects as estimated (UJ)

V. Inductively Coupled Plasma-Interference Check Sample (ICP-ICS)

A. Review Items:

Form IVA-IN, Form IVB-IN, Form XIII-IN, instrument printouts, and raw data.

B. Objective:

The Inductively Coupled Plasma-Interference Check Sample (ICP-ICS) verifies the analytical instrument's ability to overcome isobaric interferences typical of those found in samples.

C. Criteria:

1. The ICS consists of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively, starting with Solution A, for all masses used for each analyte or interferent reported by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

2. An ICS must be run at the beginning of each analysis run. The ICS is not to be run prior to the Initial Calibration Verification (ICV), and shall be immediately followed by a Continuing Calibration Verification/Continuing Calibration Blank (CCV/CCB).

3. Results for the ICP-MS analysis of the ICS Solution A shall fall within the control limits of ±3x the CRQL, or ±20% of the true value (whichever is greater) for the analytes included in the solution.

4. Results for the ICP-MS analysis of the ICS Solution AB must fall within the control limits of ±3x the CRQL, or ±20% of the true value (whichever is greater) for the analytes included in the solution.

5. If the value of an ICS result exceeds ±3x the CRQL, or ±20% of true value (whichever is greater) criteria, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the new calibration then reverified, and all analytical samples analyzed since the last compliant ICS reanalyzed.

6. The ICS should be obtained from USEPA, if available, and analyzed according to the instructions supplied with the solutions. If the ICS is not available from USEPA, an independent ICS solution shall be prepared with the interferent and analyte concentrations at the levels specified in the method.

D. Evaluation:

1. Verify using the raw data (ICP instrumental printout) that the ICS was analyzed at the proper frequency and location during the analytical run.

2. Evaluate the ICS raw data for results with an absolute value that is > Method Detection Limit (MDL) for those analytes that are not present in the ICS solution.

3. Recalculate using the raw data and the following equation, one or more of the analyte Percent Recoveries (%R), and verify that the recalculated value agrees with the Laboratory- reported values on Form IV-IN.

$$\%R = \frac{\text{Found(value)}}{\text{True(value)}} \times 100$$

Where,

Found(value) = Concentration (in µg/L) of each analyte interferent measured in the analysis of ICS Solution A or ICS Solution AB

True(value) = Concentration (in µg/L) of each analyte or interferent in ICS Solution A or ICS Solution AB

4. If the value of an ICS result exceeds ±3x the CRQL, or ±20% of true value (whichever is greater) criteria, and the Laboratory failed to terminate the analysis and take the appropriate corrective action, note this for Contract Laboratory Program Project Officer (CLP PO) action and record in the Data Review Narrative. Use professional judgment to assess the data.

NOTE: For data obtained from the CLP, the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTE: For an ICS for ICP-MS that does not meet the technical criteria, apply the action to all samples reported from the analytical run.

1. The raw data may not contain results for interferents. In this case, the reviewer shall use professional judgment to qualify the data. If the data does contain results for interferents, the reviewer should apply the following actions to samples with concentrations of interferents that are comparable to, or greater than, their respective levels in the ICS:

   a. If the ICS %R for an analyte is >120% (or greater than the true value + 3x the CRQL as applicable) and the sample results are non-detects, the data should not be qualified.

   b. If the ICS %R for an analyte is >120% (or greater than the true value + 3x the CRQL as applicable) qualify sample results that are ≥MDL as estimated high (J+). If the ICS %R (or true value) grossly exceeds the limits, use professional judgment to qualify the data.

   c. If the ICS %R for an analyte falls within the range of 50-79% (or less than the true value - 3x the CRQL as applicable) qualify sample results that are ≥MDL as estimated low (J-).

   d. If the ICS recovery for an analyte falls within the range of 50-79% (or less than the true value - 3x the CRQL as applicable), the possibility of false negatives exists. Qualify sample non-detects as estimated (UJ).

e. If the ICSAB %R for an analyte or interferent is <50%, qualify all sample results that are ≥MDL and all sample non-detects as unusable (R).

2. If results that are ≥MDL are observed for analytes which are not present in the ICS solution, the possibility of false positives exists. An evaluation of the associated sample data for the affected elements should be made. For samples with comparable or higher levels of interferents and with analyte concentrations that approximate those levels found in the ICS, qualify sample results that are ≥MDL as estimated high (J+). Non-detects should not be qualified.

3. If negative results are observed for analytes that are not present in the ICS solution, and their absolute value is ≥MDL, the possibility of false negatives in the samples exists. An evaluation of the associated sample data for the affected analytes should be made. For samples with comparable or higher levels of interferents, qualify non-detects for the affected analytes as estimated (UJ), and results that are ≥MDL but <10x the absolute value of the negative result as estimated low (J-).

4. If the raw data does not contain results for the interferents, note this in the Data Review Narrative.

5. Actions regarding the interpretation and/or the subsequent qualification of ICP data due to the ICS analytical results can be extremely complex. Use professional judgment to determine the need for the associated sample data to be qualified. The reviewer may need to obtain additional information from the Laboratory. All interpretive situations should then be recorded in the Data Review Narrative.

6. If the ICS acceptance criteria are grossly exceeded, note the specifics for CLP PO action.

Table 15. Interference Check Actions for ICP-MS Analysis

Interference Check Sample Results	Action for Samples
ICS %R >120% (or > true value + 3x the CRQL)	Qualify results that are ≥MDL as estimated high (J+)
ICS %R 50-79% (or < true value - 3x the CRQL)	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
ICSAB %R <50%	Qualify all sample data as unusable (R)
Potential false positives in field samples with interferents	Qualify results that are ≥MDL as estimated high (J+)
Potential false negatives in field samples with interferents	Qualify results that are ≥MDL but <10x(|negative value|) as estimated low (J-) Qualify non-detects as estimated (UJ)

VI. Laboratory Control Sample (LCS)

A. Review Items:

Form VII-IN, Form XII-IN, preparation logs, instrument printouts, and raw data.

B. Objective:

The Laboratory Control Sample (LCS) serves as a monitor of the overall performance of each step during the analysis, including the sample preparation.

C. Criteria:

1. Aqueous LCSs shall be analyzed for each analyte utilizing the same sample preparations, analytical methods, and Quality Assurance/Quality Control (QA/QC) procedures as employed for the samples. The aqueous LCS solution shall be obtained from USEPA if available. However, if the LCS is unavailable from USEPA, the Initial Calibration Verification (ICV) solution(s) may be used.

    a. One aqueous LCS shall be prepared and analyzed for every group of aqueous samples in a Sample Delivery Group (SDG), or with each batch of aqueous samples digested, whichever is more frequent.

    b. All aqueous LCS Percent Recoveries (%R) must fall within the control limits of 80-120%. If the %R for the aqueous LCS falls outside of the control limits, the analysis should be terminated, the problem corrected, and the samples prepared with that LCS redigested and reanalyzed.

D. Evaluation:

1. Verify using Form VII-IN, Form XII-IN, and raw data that the appropriate number of required LCSs were prepared and analyzed for the SDG.

2. Evaluate Form VII-IN and verify that all results for each analyte fall within the established control limits.

3. Check the raw data (e.g., instrument printouts, strip charts, bench sheets, etc.) to verify that the %Rs on Form VII-IN were accurately transcribed. Recalculate one or more of the reported %Rs using the following equation:

$$\%R = \frac{\text{Found(value)}}{\text{True(value)}} \times 100$$

Where,

Found(value) = Concentration of each analyte (in µg/L) measured in the analysis of the LCS

True(value) = Concentration of each analyte (in µg/L) in the LCS

4. Verify that the LCS was prepared at the same time as the associated samples using the same procedures.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

If the LCS criteria are not met, the Laboratory performance and method accuracy are in question. Professional judgment should be used to determine if the data should be qualified or rejected. The following guidance is suggested for qualifying sample data associated with an LCS that does not meet the required criteria.

For an LCS that does not meet the technical criteria, apply the action to all samples in the same preparation batch.

1. If the LCS %R falls within the range of 50-79%, qualify sample results that are ≥ Method Detection Limit (MDL) as estimated low (J-). If the LCS %R is >120%, qualify sample results that are ≥MDL as estimated high (J+).

2. If the LCS recovery is >120% and the sample results are non-detects, the data should not be qualified.

3. If the LCS recovery falls within the range of 50-79%, qualify non-detects as estimated (UJ).

4. If LCS %R is <50%, qualify all results that are ≥MDL as estimated low (J-) and all non-detects as unusable (R).

5. If the LCS %R is >150%, qualify all affected data (both detects and non-detects) as unusable (R).

6. If a Laboratory fails to analyze an LCS with each SDG, or if a Laboratory consistently fails to generate acceptable LCS recoveries, note this for CLP Project Officer (PO) action

7. Whenever possible, the potential effects on the data due to out-of-control LCS results should be noted in the Data Review Narrative.

Table 16. LCS Actions for ICP-MS Analysis

LCS Result	Action for Samples
Aqueous %R 50-79%	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
Aqueous %R >120%	Qualify results that are ≥MDL as estimated high (J+)
Aqueous %R <50%	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as unusable (R)
Aqueous %R >150%	Qualify all results as unusable (R)

VII. Duplicate Sample Analysis

A. Review Items:

Cover Page, Form VI-IN, Form XII-IN, instrument printouts, and raw data.

B. Objective:

The objective of duplicate sample analysis is to demonstrate acceptable method precision by the Laboratory at the time of analysis. Duplicate analyses are also performed to generate data that determines the long-term precision of the analytical method on various matrices. Non-homogenous samples can impact the apparent method precision. However, aqueous samples are generally homogenous and most soil samples are homogenous within a factor of two or three.

C. Criteria:

1. Samples identified as field blanks or Performance Evaluation (PE) samples cannot be used for duplicate sample analysis.

2. At least one duplicate sample shall be prepared and analyzed from each group of samples of a similar matrix type or for each Sample Delivery Group (SDG). Duplicates cannot be averaged for reporting on Form I-IN. Additional duplicate sample analyses may be required by USEPA Regional request. Alternately, the Region may require that a specific sample be used for the duplicate sample analysis.

3. Duplicate sample analyses are required for Percent Solids (%S) determination.

4. A control limit of 20% for the Relative Percent Difference (RPD) shall be used for original and duplicate sample values $\geq$ five times (5x) the Contract Required Quantitation Limit (CRQL).

5. A control limit of the CRQL shall be used if either the sample or duplicate value is <5x the CRQL. The absolute value of the control limit (CRQL) shall be entered in the "Control Limit" column on Form VI-IN. If both samples are non-detects, the RPD is not calculated for Form VI-IN.

D. Evaluation:

1. Verify from the Cover Page, Form XII-IN, and the raw data that the appropriate number of required duplicate samples were prepared and analyzed for the SDG.

2. Evaluate Form VI-IN and the raw data to verify that all duplicate results for each analyte and method fall within the established control limits.

3. Verify that a field blank or PE sample was not used for duplicate analysis.

4. Check the raw data and recalculate one or more of the RPD values using the following equation to verify that the results were correctly reported on Form VI-IN:

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where,

RPD = Relative Percent Difference

S = Sample Result (original)

D = Duplicate Result

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with the above criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTE: For a duplicate sample analysis that does not meet the technical criteria, apply the action to all samples of the same matrix, if the reviewer considers the samples sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data, including: site and sampling documentation (e.g., location and type of sample, descriptive data); field test data (e.g., pH, Eh, conductivity, chlorine); and Laboratory data for other parameters [e.g., Total Suspended Solids (TSSs), Total Dissolved Solids (TDSs), Total Organic Carbon (TOC), alkalinity or buffering capacity, reactive sulfide, anions], in determining similarity. The reviewer should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the SDG. The reviewer may determine that only some of the samples in the SDG are similar to the duplicate sample, and that only these samples should be qualified. Or, the reviewer may determine that no samples are sufficiently similar to the sample used for the duplicate, and thus only the field sample used to prepare the duplicate sample should be qualified.

1. If the appropriate number of duplicate samples were not analyzed, use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the Laboratory. Note the situation in the Data Review Narrative, and for CLP Project Officer (PO) action.

2. If the results from a duplicate analysis for a particular analyte fall outside the appropriate control limits, qualify sample results that are ≥MDL as estimated (J) and non-detects as estimated (UJ).

3. If a field blank or PE sample was used for the duplicate sample analysis, note this for CLP PO action. All of the other Quality Control (QC) data must then be carefully checked, and professional judgment exercised by the data reviewer when evaluating the data.

4. Note the potential effects on the data due to out-of-control duplicate sample results in the Data Review Narrative.

Table 17. Duplicate Sample Actions for ICP-MS Analysis

Duplicate Sample Results	Action for Samples
Both original sample and duplicate sample >5x the CRQL and RPD>20%	Qualify those results that are ≥MDL that professional judgment determines to be affected as estimated (J) and non-detects as estimated (UJ)
Original sample or duplicate sample ≤5x the CRQL (including non-detects) and absolute difference between sample and duplicate >CRQL	Qualify those results that are ≥MDL that professional judgment determines to be affected as estimated (J) and non-detects as estimated (UJ)

*The above control limits are **method requirements** for duplicate samples, regardless of the sample matrix type. However, it should be noted that Laboratory variability arising from the sub-sampling of non-homogenous soil samples is a common occurrence. Therefore, for **technical review purposes only**, Regional policy or project Data Quality Objectives (DQOs) may allow the use of less restrictive criteria (e.g., 35% RPD, 2x the CRQL) to be assessed against duplicate soil samples.

VIII. Spike Sample Analysis

A. Review Items:

Cover Page, Form V-IN (Part A & B), Form XII-IN, instrument printouts, and raw data.

B. Objective:

The spiked sample analysis is designed to provide information about the effect of each sample matrix on the sample preparation procedures and the measurement methodology. Non-homogenous samples can impact the apparent method recovery. However, aqueous samples are generally homogenous. If the spike is added to the sample before the digestion (e.g., prior to the addition of other reagents), it is referred to as a spiked sample, pre-digestion spike, or Matrix Spike. If the spike is added to the sample after the completion of the digestion procedures, it is referred to as a post-digestion spike, or analytical spike.

C. Criteria:

1. Samples identified as field blanks or Performance Evaluation (PE) samples cannot be used for spiked sample analysis.

2. At least one spiked sample shall be prepared and analyzed for each Sample Delivery Group (SDG).

3. When the Matrix Spike recovery falls outside of the control limits and the sample result is < four times (4x) the spike added, a post-digestion spike shall be performed for those analytes that do not meet the specified criteria. An aliquot of the remaining unspiked sample shall be spiked at 2x the indigenous level or 2x the Contract Required Quantitation Limit (CRQL), whichever is greater.

4. The spike Percent Recovery (%R) shall be within the established acceptance limits. However, spike recovery limits do not apply when the sample concentration is ≥4x the spike added. In such an event, the data shall be reported unflagged, even if the %R does not meet the acceptance criteria.

5. If the spiked sample analysis was performed on the same sample that was chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample". The average of the duplicate results cannot be used for the purpose of determining %R.

NOTE: The final spike concentrations required for the various target analytes are presented in the methods described in the Statement of Work (SOW).

D. Evaluation:

1. Verify using the Cover Page, Form VA-IN, Form XII-IN, and raw data that the appropriate number of required spiked samples were prepared and analyzed for the SDG.

2. Verify that a field blank or PE sample was not used for the spiked sample analysis.

3. Evaluate Form VA-IN and the raw data to verify that all pre-digestion spiked sample results for each required analyte fall within the established control limits. If not, verify that a post-digestion spike was prepared and analyzed.

4. Recalculate using the raw data, one or more of the %R using the following equation, and verify that the recalculated value agrees with the Laboratory-reported values on Forms V(A & B)-IN:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

NOTES: When the sample concentration is < Method Detection Limit (MDL), use SR = 0 only for the purposes of calculating the %R. The actual spiked sample results, sample results, and %R (positive or negative) shall still be reported on Form V (A & B)-IN.

For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with the above criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTE: For a Matrix Spike that does not meet the technical criteria, apply the action to all samples of the same matrix, if the reviewer considers the samples sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data, including: site and sampling documentation (e.g., location and type of sample, descriptive data); field test data (e.g., pH, Eh, conductivity, chlorine); and Laboratory data for other parameters [e.g., Total Suspended Solids (TSSs), Total Dissolved Solids (TDSs), Total Organic Carbon (TOC), alkalinity or buffering capacity, reactive sulfide, anions], in determining similarity. The reviewer should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the SDG. The reviewer may determine that only some of the samples in the SDG are similar to the Matrix Spike sample, and that only these samples should be qualified. Or, the reviewer may determine that no samples are sufficiently similar to the sample used for the Matrix Spike, and thus that only the field sample used to prepare the Matrix Spike sample should be qualified.

1. If the appropriate number of Matrix Spike samples was not analyzed, use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the Laboratory. Note the situation in the Data Review Narrative, and for CLP Project Officer (CLP PO) action.

2. If a field blank or PE sample was used for the spiked sample analysis, note this for CLP PO action. All of the other Quality Control (QC) data must then be carefully checked, and professional judgment exercised by the data reviewer when evaluating the data.

3. If the Matrix Spike recovery does not meet the evaluation criteria and a required post-digestion spike was not performed, note this for CLP PO action.

4. If the Matrix Spike %R is <30%, verify that a post-digestion spike was analyzed if required. If the post-digestion spike %R is <75% or is not performed, qualify sample results that are ≥MDL as estimated low (J-) and non-detects as unusable (R). If the post-digestion spike %R is ≥75%, qualify sample results that are ≥MDL as estimated (J) and non-detects as estimated (UJ).

5. If the Matrix Spike %R is 30-74% and the sample results are ≥MDL, verify that a post-digestion spike was analyzed, if required. If the %R for the post-digestion spike is also <75% or is not performed, qualify the affected data as estimated low (J-). If the %R for the post-digestion spike is ≥75%, qualify the affected data as estimated (J).

6. If the Matrix Spike %R falls within the range of 30-74% and the sample results are non-detects, qualify the affected data as estimated (UJ).

7. If the Matrix Spike %R is >125% and the reported sample results are non-detects, the sample data should not be qualified.

8. If the Matrix Spike %R is >125% and the sample results are ≥MDL, verify that a post-digestion spike was analyzed, if required. If the %R for the post-digestion spike is also >125% or is not performed, qualify the affected data as estimated high (J+). If the %R for the post-digestion spike is ≤125%, qualify the affected data as estimated (J).

9. Note the potential effects on the data due to out-of-control spiked sample results in the Data Review Narrative.

Table 18. Spike Sample Actions for ICP-MS Analysis

Spike Sample Results	Action for Samples
Matrix Spike %R <30% Post-digestion spike %R <75%	Qualify affected results that are ≥MDL as estimated low (J-) Qualify affected non-detects as unusable (R)
Matrix Spike %R <30% Post-digestion spike %R ≥75%	Qualify affected results that are ≥MDL as estimated (J) Qualify affected non-detects as estimated (UJ)
Matrix Spike %R 30-74% Post-digestion spike %R <75%	Qualify affected results that are ≥MDL as estimated low (J-) Qualify affected non-detects as estimated (UJ)
Matrix Spike %R 30-74% Post-digestion spike %R ≥75%	Qualify affected results that are ≥MDL as estimated (J) Qualify affected non-detects as estimated (UJ)
Matrix Spike %R >125% Post-digestion spike %R >125%	Qualify affected results that are ≥MDL as estimated high (J+)
Matrix Spike %R >125% Post-digestion spike %R ≤125%	Qualify affected results that are ≥MDL as estimated (J)
Matrix Spike %R <30% No post-digestion spike performed	Qualify affected results that are ≥MDL as estimated low (J-) and affected non-detects as unusable (R)
Matrix Spike %R 30-74% No post-digestion spike performed	Qualify affected results that are ≥MDL as estimated low (J-) and affected non-detects as estimated (UJ)
Matrix Spike %R >125% No post-digestion spike performed	Qualify affected results that are ≥MDL as estimated high (J+) Non-detects are not qualified

IX. ICP Serial Dilution

A. Review Items:

Form I-IN, Form VIII-IN, instrument printouts, and raw data.

B. Objective:

The serial dilution of samples quantitated by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) determines whether or not significant physical or chemical interferences exist due to sample matrix.

C. Criteria:

1. An ICP serial dilution analysis shall be performed on a sample for each Sample Delivery Group (SDG), whichever is more frequent.

2. Samples identified as field blanks or Performance Evaluation (PE) samples cannot be used for the ICP serial dilution analysis.

3. If the analyte concentration is sufficiently high [concentration in the original sample is >50 times (50x) the Method Detection Limit (MDL)], the serial dilution analysis (a five-fold dilution) shall then agree within a 10 Percent Difference (%D) of the original determination after correction for dilution.

D. Evaluation:

1. Verify that a field blank or PE sample was not used for the serial dilution analysis.

2. Check the raw data and recalculate the %D using the following equation. Verify that the serial dilution analysis results, and the calculated %D results agree with the values reported by the Laboratory on Form VIII-IN:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

Where,

I = Initial sample result (instrument reading)

S = Serial dilution result (instrument reading x 5)

3. Check the raw data for any evidence of positive or negative interference (results from the diluted sample which are significantly different than the original sample), possibly due to high levels of dissolved solids in the sample, ionization effects, etc.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with the above criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTE: For a serial dilution that does not meet the technical criteria, apply the action to all samples of the same matrix if the reviewer considers the samples sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data, including: site and sampling documentation (e.g., location and type of sample, descriptive data); field test data (e.g., pH, Eh, conductivity, chlorine); and Laboratory data for other parameters [e.g., Total Suspended Solids (TSSs), Total Dissolved Solids (TDSs), Total Organic Carbon (TOC), alkalinity or buffering capacity, reactive sulfide, anions], in determining similarity. The reviewer should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the SDG. The reviewer may determine that only some of the samples in the SDG are similar to the serial dilution sample, and that only these samples should be qualified. Or, the reviewer may determine that no samples are sufficiently similar to the sample used for serial dilution, and thus only the field sample used to prepare the serial dilution sample should be qualified.

1. If the required %D criteria are not met, qualify all affected results that are ≥MDL as estimated (J) and all affected non-detects as estimated (UJ).

2. If evidence of positive or negative interference is found, use professional judgment to qualify the associated sample data. Note the potential effects on the reported data in the Data Review Narrative.

3. It should be noted for CLP Project Officer (CLP PO) action and in the Data Review Narrative if a field blank or PE sample was used for the serial dilution analysis.

Table 19. Serial Dilution Actions for ICP-MS Analysis

Serial Dilution Result	Action for Samples
Sample concentration >50x MDL and %D >10	Qualify affected results that are ≥MDL as estimated (J) Qualify affected non-detects as estimated (UJ)
Interferences present	Use professional judgment

X. ICP-MS Internal Standards

A. Review Items:

Form XIII-IN, Form XV-IN, instrument printouts, and raw data.

B. Objective:

The analysis of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) internal standards determines the existence and magnitude of instrument drift and physical interferences. The criteria for evaluation of internal standard results applies to all analytical and Quality Control (QC) samples analyzed during the run, beginning with the calibration.

C. Criteria:

1. All samples analyzed during a run, with the exception of the ICP-MS tune, shall contain internal standards. A minimum of five internal standards from the following list shall be added to each sample: Li (the Li^6 isotope); Sc; Y; Rh; In (the In^{115} isotope); Tb; Ho; Lu; and Bi. If the Laboratory uses lithium as an internal standard, the Laboratory shall use an Li^6-enriched standard. The masses of the internal standards shall bracket the masses of the target analytes. The laboratory shall monitor the same internal standards throughout the entire analytical run.

2. The intensity of the internal standard response in a sample is monitored and compared to the intensity of the response for that internal standard in the calibration blank. The Percent Relative Intensity (%RI) in the sample shall fall within 60-125% of the response in the calibration blank.

3. If the %RI of the response in the sample falls outside of these limits, the Laboratory shall reanalyze the original sample at a two-fold dilution.

D. Evaluation:

1. Verify using Form XV-IN and the raw data that a minimum of five internal standards from the specified list were used for the analysis, that the masses of the internal standards bracket the masses of the target analytes, and that the same internal standards were monitored for the entire run.

2. Verify using Form XV-IN and the raw data that these internal standards were added to each sample in the run, including calibrations, samples, and QC samples (except tune).

3. Verify using Form XV-IN that the %RI between an internal standard in a sample and the internal standard in the calibration blank was reported for each sample.

4. Verify using Form XIII-IN, Form XV-IN, and the raw data that if the %RI for a sample was outside the limits (60-125%), the sample was reanalyzed of a 2X dilution.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with the above criteria can be obtained from the Data Assessment Tool (DAT) reports and may be used as part of the evaluation process.

E. Action:

NOTE: Apply the action to the affected analytes for each sample that does not meet the internal standard criteria.

1. If no internal standards were analyzed with the run, the sample data should be qualified as unusable (R). Record this in the Data Review Narrative and note for CLP Project Officer (CLP PO) action.

2. If less than five of the required internal standards were analyzed with the run, or the masses of the internal standards does not bracket the masses of the target analytes, the analyte sample data not bracketed by the internal standard masses should be qualified as unusable (R). Record this in the Data Review Narrative and note for CLP PO action.

3. If the %RIs for all internal standards in a sample are within the 60-125% limit, the sample data should not be qualified.

4. If the %RI for an internal standard in a sample is not within the 60-125% limit, qualify the data for those analytes with atomic masses that fall between the atomic mass of the internal standard lighter than the affected internal standard, and the atomic mass of the internal standard heavier than the affected internal standard, or between the limit (upper or lower) of the mass range and the nearest unaffected internal standard, as follows:

   a. If the sample was reanalyzed at a two-fold dilution with internal standard %RI within the limits, report the result of the diluted analysis without qualification. If the %RI of the diluted analysis was not within the 60-125% limit, report the results of the original undiluted analyses and qualify the data for all analytes that are ≥ Method Detection Limit (MDL) in the sample associated with the internal standard as estimated (J), and non-detected analytes associated with the internal standard as estimated (UJ).

   b. If the sample was not reanalyzed at a two-fold dilution, the reviewer should use professional judgment to determine the reliability of the data. The reviewer may determine that the results are estimated (J) or unusable (R).

Table 20. Internal Standard Actions for ICP-MS Analysis

Internal Standard Results	Action for Samples
No internal standards	Qualify all results as unusable (R)
<5 of the required internal standards	Qualify all analyte results not bracketed by internal standard masses as unusable (R)
Masses of internal standards do not bracket masses of target analytes	Qualify all analyte results not bracketed by internal standard masses as unusable (R)
%RI <60% or >125%, and original sample reanalyzed at 2-fold dilution	If %RI of diluted sample analysis 60-125%, do not qualify the data If the %RI of the diluted sample analysis is outside the 60-125% limit, qualify results that are ≥MDL as estimated (J) and qualify non-detects as estimated (UJ)
Original sample not reanalyzed at 2-fold dilution	Use professional judgment Qualify sample results as estimated (J) or unusable (R)

XI. Field Duplicates

A. Review Items:

Form I-IN, instrument printouts, and raw data.

B. Objective:

Field duplicate samples may be collected and analyzed as an indication of overall precision. These analyses measure both field and Laboratory precision. The results, therefore, may have more variability than Laboratory duplicates that measure only Laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

C. Criteria:

There are no "required" review criteria for determining comparability of field duplicate analyses.

D. Evaluation:

Identify samples that are field duplicates using Traffic Report/Chain of Custody (TR/COC) documentation or sample field sheets. Compare the results reported for each sample and calculate the Relative Percent Difference (RPD), if appropriate.

E. Action:

Provide any evaluation of the field duplicates in the Data Review Narrative.

XII. Overall Assessment

A. Review Items:

Entire data package, data review results, preparation logs, calibration standard logs, instrument logs, instrument printouts, and raw data (including any confirmation data).

B. Objective:

The objective is to ensure that the reported sample quantitation results are accurate. It is appropriate for the data reviewer to make professional judgments and express concerns, as well as to comment on the validity of the overall data for a Case. This is particularly appropriate when there are several Quality Control (QC) criteria that are outside of the specification parameters. The additive nature of QC factors that fall outside of specification parameters is difficult to assess in an objective manner, but the reviewer has a responsibility to inform the user concerning data quality and data limitations to assist that user in avoiding inappropriate use of the data, while not precluding any consideration of the data at all. If qualifiers other than those used in this document are necessary to describe or qualify the data, it is necessary to thoroughly document/explain the additional qualifiers used. The data reviewer would be greatly assisted in this endeavor if the acceptance or performance criteria were provided. The Inorganic Review Summary (see Appendix B) and supplementary documentation must be included with the review.

C. Criteria:

1. Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

2. Reported analyte concentrations must be quantitated according to the appropriate analytical method, as listed in the method.

D. Evaluation:

Examine the raw data to verify that the correct calculation of the sample results was reported by the Laboratory. Digestion logs, instrument printouts, strip charts, etc., should be compared to the reported sample results recorded on the appropriate Inorganic Summary Forms (Form I-IN through Form XV-IN).

1. Evaluate any technical problems not previously addressed.

2. Examine the raw data for any anomalies (e.g., baseline shifts, negative absorbance, omissions, illegibility, etc.).

3 Verify that appropriate methods and volumes were used in preparing the samples for analysis. Verify that the turbidity was measured prior to method selection. If reduced volumes were used, verify that the Laboratory had received Contract Laboratory Program Project Officer (CLP PO) approval for the use of the reduced volume.

4. Verify that there are no transcription or reduction errors [e.g., dilutions, Percent Solids (%S), sample weights, etc.] on one or more samples.

5. Verify that results fall within the linear range(s) of the Inductively Coupled Plasma (ICP) instrument(s) (Form XI).

6. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the Quality Assurance Project Plan (QAPP), focusing specifically on the acceptance or performance criteria, the Standard Operating Procedure(s) (SOPs), and communication with the user concerning the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC criteria previously discussed.

2. Write a brief Data Review Narrative to give the user an indication of the analytical limitations of the data. Note any discrepancies between the data and the Sample Delivery Group (SDG) Narrative for CLP PO action. If sufficient information on the intended use and required quality of the data are available, the reviewer should include an assessment of the data usability within the given context.

3. If any discrepancies are found, the Laboratory may be contacted by the Region's designated representative to obtain additional information for resolution. If a discrepancy remains unresolved, the reviewer may determine that qualification of the data is warranted.

Calculations for ICP-MS

Prepared Sample Concentration (Method HW2):

$$\text{Concentration } (\mu g/L) = C \times \frac{V_f}{V_i} \times \frac{V_f}{20} \times DF$$

Where,

C = Instrument value in µg/L (the average of all replicate integrations)

V_f = Final digestion volume (50 mL)

V_i = Initial digestion volume (100 mL)

DF = Dilution Factor

Prepared Sample Concentration (Method HW3):

$$\text{Concentration } (\mu g/L) = C \times DF$$

Where,

C = Instrument value in µg/L (the average of all replicate integrations)

DF = Dilution Factor

MERCURY DATA REVIEW

The inorganic data requirements for mercury data review to be reviewed during validation are listed below:

I. Preservation and Holding Times

II. Calibration
   A. Initial
   B. Initial and Continuing Calibration Verification (ICV/CCV)
   C. Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

III. Blanks

IV. Laboratory Control Sample (LCS)

V. Duplicate Sample Analysis

VI. Spike Sample Analysis

VII. Field Duplicates

VIII. Overall Assessment

An Example Analytical Sequence for Mercury

S0
S0.2
S0.5
S1.0
S5.0
S10.0
ICV
ICB
CRI
CCV
CCB
ten samples
CCV
CCB
nine samples
CRI
CCV
CCB
ten samples, etc.

I. Preservation and Holding Times

A. Review Items:

Form IA-IN, Form IB-IN, Form XII-IN, Form XIII-IN, Traffic Report/Chain of Custody (TR/COC) documentation, Form DC-1, raw data, and the Sample Delivery Group (SDG) Narrative checking for: pH; cooler temperature; holding time; and other sample conditions.

B. Objective:

The objective is to ascertain the validity of the analytical results based on the sample condition, and the holding time of the sample from the date of collection to the date of analysis.

C. Criteria:

1. Technical requirements for sample holding times have only been established for aqueous matrices. The addition of nitric acid to adjust the pH is only required for aqueous samples.

2. The technical holding time criteria for aqueous mercury samples is 28 days; preserved (with nitric acid) to pH<2.

3. Aqueous samples shall be maintained at 4°C ±2°C until preparation and analysis to allow for re-preparation and for the direct analysis of dissolved metals.

4. The preservation for soil/sediment samples is maintenance at 4°C ±2°C until preparation and analysis.

D. Evaluation:

Technical holding times are established by comparing the sampling date(s) on the TR/COC documentation with the dates of analysis on Form XIII-IN, and the raw data. Information contained in the Complete SDG File (CSF) should also be considered in the determination of holding times. Verify that the analysis dates on the Form XIIIs and the raw data are identical. Review the SDG Narrative and raw data preparation logs to determine if samples were properly preserved. If there is an indication that there were problems with the samples, the integrity of the samples may be compromised and professional judgment should be used to evaluate the effect of the problem on the sample results.

E. Action:

NOTE: Apply the action to each sample for which the preservation or holding time criteria was not met.

1. If the pH of aqueous metals samples is ≥2 at the time of sample receipt, use professional judgment to qualify the samples based on the pH of the sample and the chemistry of the metal(s) of interest. Qualify results that are ≥MDL as estimated low (J-), and qualify non-detects as unusable (R).

2. If technical holding times are exceeded, use professional judgment to determine the reliability of the data based on the magnitude of the additional time compared to the technical

requirement and whether the samples were properly preserved. The expected bias would be low. Qualify results that are ≥MDL as estimated low (J-), and non-detects as unusable (R).

3. Due to limited information concerning holding times for soil samples, it is left to the discretion of the data reviewer whether to apply water holding time criteria to soil samples. If they are applied, it must be clearly documented in the Data Review Narrative.

4. When the holding times are exceeded, the reviewer should comment in the Data Review Narrative on any possible consequences for the analytical results.

5. When holding times are grossly exceeded, note this for Contract Laboratory Program Project Officer (CLP PO) action.

6. When shipping or storage temperatures grossly exceed the requirements, the loss of volatile mercury compounds or metallic mercury is possible. The expected bias would be low. Use professional judgment to qualify the samples and note for CLP PO action.

Table 21. Technical Holding Time Actions for Mercury Analysis

Preservation & Holding Time Results	Action for Samples
Aqueous metals samples received with pH ≥2	Use professional judgment Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as unusable (R)
Technical holding time exceeded: mercury >28 days	Use professional judgment Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as unusable (R)

II. Calibration

A. Review Items:

Form II-IN (Parts A & B), Form XI-IN, Form XIII-IN, preparation logs, calibration standard logs, instrument logs, instrument printouts, and raw data.

B. Objective:

Method requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data for mercury. Initial Calibration Verification (ICV) demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical run. Continuing Calibration Verification (CCV) demonstrates that the initial calibration is still valid by checking the performance of the instrument on a continuing basis.

C. Criteria:

1. Initial Calibration

The instruments shall be successfully calibrated daily (or once every 24 hours), and each time the instrument is set up. The calibration date and time shall be included in the raw data. The calibration curve shall be prepared by the same method used to prepare the samples for analysis.

a. Cold Vapor Mercury Analysis

1) A blank and at least four calibration standards shall be employed to establish the analytical curve. One of the calibration standards shall be at the Contract Required Quantitation Limit (CRQL). The calibration curves for mercury shall possess a correlation coefficient of ≥ 0.995 to ensure the linearity over the calibrated range. All sample results shall be reported from an analysis within the calibrated range.

2) The linearity of the analytical curve shall be verified near the CRQL. A CRQL Check Standard (CRI) solution shall be prepared and analyzed at the beginning and end of each sample analysis run and every 20 analytical samples, but not before the ICV analysis. The CRI at the beginning of the run must immediately follow the ICV/ICB analyses.

3) Analysis of the CRI for mercury is required for both the manual and automated cold vapor methods, and the results and Percent Recovery (%R) are to be reported on Form IIB-IN.

4) If the results for the CRI do not fall within the fixed acceptance limits, the Laboratory shall reanalyze a CRI. If the results of the reanalysis do not fall within the acceptance limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, the CRI and associated samples redigested if necessary, and the new calibration then reverified.

2. Initial and Continuing Calibration Verification (ICV and CCV)

The acceptance criteria for the ICVs, CCVs, and CRIs are presented in Table 22. These standards shall be prepared by the same method used to prepare the samples for analysis.

Table 22. Acceptance Criteria for ICVs, CCVs, and CRIs

Analytical Method	Inorganic Analyte	ICV/CCV Low Limit (% of True Value)	ICV/CCV High Limit (% of True Value)	CRI Low Limit (% of True Value)	CRI High Limit (% of True Value)
Cold Vapor AA	Mercury	80	120	70	130

a. Initial Calibration Verification (ICV)

1) Immediately after each Atomic Absorption (AA) system has been calibrated, the accuracy of the initial calibration must be verified and documented for mercury by the analysis of an ICV solution(s). If the ICV %R falls outside of the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and all affected samples reanalyzed.

2) If the ICV is not available from USEPA, or where a certified solution of the analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration level other than that used for instrument calibration (or the CRI), but within the calibrated range.

b. Continuing Calibration Verification (CCV)

1) To ensure accuracy during the course of each analytical run, the CCV shall be analyzed and reported.

2) The CCV standard shall be analyzed at a frequency of 10% or every two hours during an analytical run, whichever is more frequent. The CCV standard shall also be analyzed at the beginning of the run, and again after the last analytical sample.

3) The analyte concentration in the CCV standard shall be different than the concentration used for the ICV, and shall be one of the following solutions at, or near, the mid-range levels of the calibration curve:

   A. USEPA solutions;
   B. National Institute of Standards and Technology (NIST) standards; or
   C. A Laboratory-prepared standard solution (self-prepared or commercially available).

4) The same CCV standard solution shall be used throughout the analysis runs for a Sample Delivery Group (SDG).

5) The CCV shall be analyzed in the same fashion as an actual sample. Operations such as the number of replicate analyses, the number and duration of the instrument rinses, etc., affect the measured CCV result and are not to be applied to the CCV to an extent greater than was applied to the associated analytical samples. If the %R of the CCV

was outside of the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the preceding 10 analytical samples (or all analytical samples analyzed since the last compliant CCV) reanalyzed.

D. Evaluation

1. Verify that the instrument was calibrated daily (once every 24 hours) and each time the instrument was set up, utilizing a blank and at least four calibration standards. Confirm that one of the calibration standards was analyzed at the CRQL.

2. Evaluate the reported CRI to confirm that it was analyzed at the proper frequency, concentration, and location within the analytical run sequence. Verify that acceptable %R results were obtained.

3. Verify that the ICV and CCV standards were analyzed for mercury at the proper frequency (10%) and at the appropriate concentration. Verify that acceptable %R results were obtained.

4. Recalculate one or more of the ICV, CCV, or CRI %R using the following equation and verify that the recalculated value agrees with the Laboratory-reported values on Forms II (A & B)-IN.

$$\%R = \frac{\text{Found(value)}}{\text{True(value)}} \times 100$$

Where,

Found(value) = Concentration (in µg/L) of mercury measured in the analysis of the ICV, CCV, or CRI solution

True(value) = Concentration (in µg/L) of mercury in the ICV, CCV, or CRI source

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTES: For initial calibrations or ICVs that do not meet the technical criteria, apply the action to all samples reported from the analytical run.

For CCVs or CRIs that do not meet the technical criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of the QC sample and a subsequent technically acceptable analysis of the QC sample in the analytical run.

1. If the instrument was not calibrated daily and each time the instrument was set up, qualify the data as unusable (R). If the instrument was not calibrated with at least the minimum number of standards, or if the calibration curve does not include standards at required concentrations

(e.g., a blank, or a standard at the CRQL), use professional judgment to qualify results that are ≥ Method Detection Limit (MDL) as estimated (J) or unusable (R), and non-detects as estimated (UJ) or unusable (R).

2. If the correlation coefficient is <0.995, qualify sample results that are ≥MDL as estimated (J), and non-detects as estimated (UJ). Depending on the degree of the deviation from linearity, further qualification of the data may be required depending on the professional judgment of the reviewer [e.g., unusable data (R)].

3. If the CRIs are outside the acceptance criteria, use professional judgment to qualify all associated data. If possible, indicate the bias in the review. The following guidelines are recommended:

   a. If the CRI %R is <50%, qualify all sample results that are ≥MDL but < two times (2x) the CRQL and all non-detects as unusable (R). Qualify detects that are ≥2x the CRQL as estimated (J).

   b. If the CRI %R falls within the range of 50-69%, qualify all sample results that are ≥MDL but <2x the CRQL as estimated low (J-), and all non-detects as estimated (UJ). Detects that are ≥2x the CRQL should not be qualified based on this criterion.

   c. If the CRI %R is >130% but ≤180%, qualify all sample results that are ≥MDL but <2x the CRQL as estimated high (J+). Non-detects and detects that are ≥2x the CRQL should not be qualified based on this criterion.

   d. If the CRI %R is >180%, qualify all sample results that are ≥MDL as unusable (R).

4. If the ICV or CCV %R falls outside the acceptance windows, use professional judgment to qualify all associated data. If possible, indicate the bias in the review. The following guidelines are recommended:

   a. If the ICV or CCV %R is <65%, qualify non-detects as unusable (R). Use professional judgment to qualify all results that are ≥MDL as estimated low (J-) or unusable (R).

   b. If the ICV or CCV %R falls within the range of 65-79%, qualify sample results that are ≥MDL as estimated low (J-) and qualify non-detects as estimated (UJ).

   c. If the ICV or CCV %R falls within the range of 121-135%, qualify sample results that are ≥MDL as estimated high (J+).

   d. If the ICV or CCV %R falls within the range of 121-135%, non-detects should not be qualified.

   e. If the ICV or CCV %R is >135%, use professional judgment to qualify results that are ≥MDL as estimated high (J+) or unusable (R). Non-detects should not be qualified.

   f. If the %R is >170%, qualify all results that are ≥MDL as unusable (R).

5. If the Laboratory failed to provide adequate calibration information, the Region's designated representative should contact the Laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

6. Note the potential effects on the reported data due to exceeding the calibration criteria in the Data Review Narrative.

7. If calibration criteria are grossly exceeded, note this for CLP Project Officer (CLP PO) action.

NOTE: For truly critical samples, a further in-depth evaluation of the calibration curve may be warranted to determine if additional qualification is necessary.

Table 23. Calibration Actions for Mercury Analysis

Calibration Result	Action for Samples
Calibration not performed	Qualify all results as unusable (R)
Calibration incomplete	Use professional judgment Qualify results that are ≥MDL as estimated (J) or unusable (R) Qualify non-detects as estimated (UJ) or unusable (R)
Correlation coefficient <0.995	Qualify results that are ≥MDL as estimated (J) Qualify non-detects as estimated (UJ)
CRI %R <50%	Qualify all results that are ≥MDL but <2x the CRQL and all non-detects as unusable (R) Qualify all results that are ≥2x the CRQL as estimated (J)
CRI %R 50-69%	Qualify results that are ≥MDL but <2x the CRQL as estimated low (J-) Qualify non-detects as estimated (UJ) Results that are ≥2x the CRQL are not qualified
CRI %R >130% but ≤180%	Qualify results that are ≥MDL but <2x the CRQL as estimated high (J+) Non-detects and results that are ≥2x the CRQL are not qualified
CRI %R >180%	Qualify all results that are ≥MDL as unusable (R)
ICV/CCV %R <65%	Qualify results that are ≥MDL as estimated low (J-) or unusable (R) Qualify all non-detects as unusable (R)
ICV/CCV %R 65-79%	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
ICV/CCV %R 121-135%	Qualify results that are ≥MDL as estimated (J)
ICV/CCV %R >135%	Qualify results that are ≥MDL as estimated high (J+) or unusable (R)
ICV/CCV %R >170%	Qualify results that are ≥MDL as unusable (R)

III. Blanks

A. Review Items:

Form I-IN, Form III-IN, Form XII-IN, Form XIII-IN, preparation logs, calibration standard logs, instrument logs, and raw data.

B. Objective:

The objective of blank analysis results assessment is to determine the existence and magnitude of contamination resulting from Laboratory (or field) activities. The criteria for evaluation of blanks applies to any blank associated with the samples (e.g., method blanks, calibration blanks, field blanks, etc.). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. No contaminants should be found in the blank(s).

2. The Initial Calibration Blank (ICB) shall be analyzed after the analytical standards, but not before analysis of the Initial Calibration Verification (ICV) during the initial calibration of the instrument (see Section II.C.1). The ICB shall be prepared by the same method used to prepare the samples for analysis.

3. A Continuing Calibration Blank (CCB) shall be analyzed immediately after every ICV and Continuing Calibration Verification (CCV). The CCB shall be prepared by the same method used to prepare the samples for analysis. The CCB shall be analyzed at a frequency of 10%, or every two hours during the run, whichever is more frequent. The CCB shall be analyzed at the beginning of the run, and again after the last CCV that was analyzed after the last analytical sample of the run. The CCB result (absolute value) shall not exceed the Contract Required Quantitation Limit (CRQL) for mercury.

4. At least one Preparation Blank (PB) shall be prepared and analyzed for each matrix, with every Sample Delivery Group (SDG), or with each batch of samples digested, whichever is more frequent. The PB consists of reagent water processed through the appropriate sample preparation and analysis procedure.

5. If the mercury concentration in the PB is >CRQL, the lowest concentration of mercury in the associated samples must be 10 times (10x) the PB concentration. Otherwise, all samples associated with that PB with a mercury concentration <10x the PB concentration, and >CRQL, should be redigested and reanalyzed (except for an identified field blank). The Laboratory is not to correct the sample concentration for the blank value.

6. If the concentration of the PB for mercury is <(−CRQL), all samples reported <10x the CRQL (associated with that analyte in that blank), should be redigested and reanalyzed.

D. Evaluation:

1. Verify that an ICB was analyzed after the calibration, the CCB was analyzed at the proper frequency and location during the run, and PBs are prepared and analyzed as appropriate for the SDG (e.g., total number of samples, various types of matrices present, number of digestion batches, etc.).

2. Review the results reported on the Blank Summary (Form III-IN), as well as the raw data (e.g., instrument printouts, strip charts, printer tapes, bench sheets, etc.) for all blanks, and verify that the results are accurately reported.

3. Evaluate all of the associated blanks for the presence of mercury. Verify that if mercury was present in a PB, or if a concentration was <(−CRQL), the affected samples were redigested and reanalyzed. Verify that if mercury was present in an ICB or a CCB, the analysis was terminated, the problem corrected, the instrument recalibrated, and the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration blank reanalyzed.

NOTE: For data obtained from the Contract Laboratory Program (CLP), many of the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTES: For ICBs that do not meet the technical criteria, apply the action to all samples reported from the analytical run.

For CCBs that do not meet the technical criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of the CCB and a subsequent technically acceptable analysis of the CCB in the analytical run.

For PBs that do not meet the technical criteria, apply the action to all samples prepared in the same preparation batch.

1. If the appropriate blanks are not analyzed with the correct frequency, the data reviewer should use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the Laboratory. The situation should then be recorded in the Data Review Narrative, and noted for CLP Project Officer (PO) action.

2. Action regarding unsuitable blank results depends on the circumstances and origin of the blank. The reviewer should note that in instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of contaminant.

3. Some general "technical" review actions include:

   a. Any blank (including PB) reported with a negative result, whose value is ≤[−Method Detection Limit (MDL)] but ≥(−CRQL), should be carefully evaluated to determine its effect on the sample data. The reviewer shall then use professional judgment to assess the data. For any blank (including PB) reported with a negative result, whose value is <(−CRQL), qualify results that are ≥CRQL as estimated low (J-) and non-detects as estimated (UJ).

   b. The blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. In particular, soil sample results reported on Form I-IN will not be on the same basis (units, dilution) as the calibration blank data reported on Form III-IN. The reviewer may find it easier to work with the raw data.

4. Specific "method" actions include:

   a. If the absolute value of an ICB or a CCB result is >CRQL, the analysis should be terminated. If the analysis was not terminated and the affected samples are not reanalyzed, report non-detects and results that are ≥MDL but ≤CRQL as CRQL-U. For results that are >CRQL but < Blank Result, use professional judgment to qualify the data as unusable (R), or to report the results at the level of the blank with a "U" qualifier. Use professional judgment to qualify results that are > Blank Result. Note this situation for CLP PO action and record it in the Data Review Narrative.

   b. If the absolute value of the concentration of the PB is ≤CRQL, report non-detect and results ≥MDL but ≤CRQL as CRQL-U. Use professional judgment to qualify results that are >CRQL.

   c. If the mercury concentration in the PB is >CRQL, the lowest concentration of mercury in the associated samples must be 10x the PB concentration. Otherwise, all samples associated with that blank with concentrations <10x the PB concentration and >CRQL should be redigested and reanalyzed. Raise the CRQL to the concentration found in the PB and report those samples that do not require redigestion (that are ≥MDL but ≤CRQL) as CRQL-U. Note for CLP PO action and record in the Data Review Narrative if the Laboratory failed to redigest and reanalyze the affected samples. The reviewer shall then use professional judgment to assess the data.

Table 24. Blank Actions for Mercury Analysis

Blank Type	Blank Result	Sample Result	Action for Samples
ICB/CCB	Absolute value is ≥MDL but ≤CRQL	Non-detect	No action
		≥MDL but ≤CRQL	Report CRQL value with a "U"
		>CRQL	Use professional judgment
ICB/CCB	Absolute value is >CRQL	≥MDL but ≤CRQL	Report CRQL value with a "U"
		>CRQL but <Blank Result	Report at level of Blank Result with a "U" or qualify data as unusable (R)
		>Blank Result	Use professional judgment
ICB/CCB	≤(-MDL), but ≥(-CRQL)	≥MDL, or non-detect	Use professional judgment
ICB/CCB	<(-CRQL)	<10x the CRQL	Qualify results that are ≥CRQL as estimated low (J-) Qualify non-detects as estimated (UJ)
PB	>CRQL	≥MDL but ≤CRQL	Report CRQL value with a "U"
		>CRQL but <10x the Blank Result	Qualify results as unusable (R) or estimated high (J+)
		≥10x the Blank Result	No action
PB	≥MDL but ≤CRQL	Non-detect ≥MDL but ≤CRQL >CRQL	No action Report CRQL with a "U" Use professional judgment
PB	<(-CRQL)	<10x the CRQL	Qualify results that are ≥CRQL as estimated low (J-) Qualify non-detects as estimated (UJ)

IV. Laboratory Control Sample (LCS)

A. Review Items:

Form VII-IN, Form XII-IN, preparation logs, instrument printouts, and raw data.

B. Objective:

The Laboratory Control Sample (LCS) serves as a monitor of the overall performance of each step during the analysis, including the sample preparation.

C. Criteria:

1. Solid LCSs shall be analyzed utilizing the same sample preparations, analytical methods, and Quality Assurance/Quality Control (QA/QC) procedures as employed for the samples.

    a. A solid LCS shall be prepared and analyzed utilizing each of the preparation and analytical procedures applied to the soil/sediment samples received, with one exception: The Percent Solids (%S) determination is not required. If the solid LCS is not available from USEPA, other USEPA QA samples or certified materials may be used.

    b. One solid LCS shall be prepared and analyzed for each group of soil sediment samples in an Sample Delivery Group (SDG), or for each batch of samples digested, whichever is more frequent.

    c. All solid LCS results shall fall within the control limits reported on Form VII-IN. If the results for the solid LCS fall outside of the control limits, the analyses should be terminated, the problem corrected, and the samples prepared with that LCS redigested and reanalyzed.

D. Evaluation:

1. Verify using Form VII-IN, Form XII-IN, and raw data that the appropriate number of required LCSs were prepared and analyzed for the SDG.

2. Evaluate Form VII-IN and verify that all results for mercury fall within the established control limits.

3. Check the raw data (e.g., instrument printouts, strip charts, bench sheets, etc.) to verify that the Percent Recoveries (%Rs) on Form VII-IN were accurately transcribed. Recalculate one or more of the reported %Rs using the following equation:

$$\%R = \frac{\text{Found(value)}}{\text{True(value)}} \times 100$$

Where,

Found(value) = Concentration of mercury (in mg/kg) measured in the analysis of the LCS

True(value) = Concentration of mercury (in mg/kg) in the LCS

4. Verify that the LCS was prepared at the same time as the associated samples using the same procedures.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

If the LCS criteria are not met, the Laboratory performance and method accuracy are in question. Professional judgment should be used to determine if the data should be qualified or rejected. The following guidance is suggested for qualifying sample data associated with an LCS that does not meet the required criteria.

For an LCS that does not meet the technical criteria, apply the action to all samples in the same preparation batch.

1. Solid LCS:

   a. If the LCS results are greater than the reported control limits, qualify sample results that are ≥ Method Detection Limit (MDL) as estimated high (J+). If the LCS results are less than the reported control limits, qualify sample results that are ≥MDL as estimated low (J-).

   b. If the LCS results are greater than the reported control limits and the sample results are non-detects, the data should not be qualified.

   c. If the LCS results are less than the reported control limits, qualify non-detects as estimated (UJ).

   d. If a Laboratory fails to analyze an LCS with each SDG, or if a Laboratory consistently fails to generate acceptable LCS recoveries, note this for CLP Project Officer (PO) action.

   e. Whenever possible, the potential effects on the data due to out-of-control LCS results should be noted in the Data Review Narrative.

Table 25. LCS Actions for Mercury Analysis

LCS Result	Action for Samples
Soil Result > upper limit	Qualify results that are ≥MDL as estimated high (J+)
Soil Result < lower limit	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as estimated (UJ)

V. Duplicate Sample Analysis

A. Review Items:

Cover Page, Form VI-IN, Form XII-IN, instrument printouts, and raw data.

B. Objective:

The objective of duplicate sample analysis is to demonstrate acceptable method precision by the Laboratory at the time of analysis. Duplicate analyses are also performed to generate data that determines the long-term precision of the analytical method on various matrices. Non-homogenous samples can impact the apparent method precision. However, aqueous samples are generally homogenous and most soil samples are homogenous within a factor of two or three.

C. Criteria:

1. Samples identified as field blanks or Performance Evaluation (PE) samples cannot be used for duplicate sample analysis.

2. At least one duplicate sample shall be prepared and analyzed from each group of samples of a similar matrix type (e.g., water or soil) or for each Sample Delivery Group (SDG). Duplicates cannot be averaged for reporting on Form I-IN. Additional duplicate sample analyses may be required by USEPA Regional request. Alternately, the Region may require that a specific sample be used for the duplicate sample analysis.

3. Duplicate sample analyses are required for Percent Solids (%S) determination.

4. A control limit of 20% for the Relative Percent Difference (RPD) shall be used for original and duplicate sample values ≥ five times (5x) the Contract Required Quantitation Limit (CRQL).

5. A control limit of the CRQL shall be used if either the sample or duplicate value is <5x the CRQL. The absolute value of the control limit (CRQL) shall be entered in the "Control Limit" column on Form VI-IN. If both samples are non-detects, the RPD is not calculated for Form VI-IN.

NOTE: The above control limits are **method requirements** for duplicate samples, regardless of the sample matrix type. However, it should be noted that Laboratory variability arising from the sub-sampling of non-homogenous soil samples is a common occurrence. Therefore, for **technical review purposes only**, Regional policy or project Data Quality Objectives (DQOs) may allow the use of less restrictive criteria (e.g., 35% RPD, 2x the CRQL) to be assessed against duplicate soil samples.

D. Evaluation:

1. Verify from the Cover Page, Form XII-IN, and the raw data that the appropriate number of required duplicate samples were prepared and analyzed for the SDG.

2. Evaluate Form VI-IN and the raw data to verify that all mercury duplicate results for each method fall within the established control limits.

3. Verify that a field blank or PE sample was not used for duplicate analysis.

4. Check the raw data and recalculate one or more of the RPD values using the following equation to verify that the results were correctly reported on Form VI-IN:

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where,

RPD = Relative Percent Difference

S = Sample Result (original)

D = Duplicate Result

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with the above criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTE: For a duplicate sample analysis that does not meet the technical criteria, apply the action to all samples of the same matrix, if the reviewer considers the samples sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data, including: site and sampling documentation (e.g., location and type of sample, descriptive data, soil classification); field test data (e.g., pH, Eh, conductivity, chlorine); and Laboratory data for other parameters [e.g., Total Suspended Solids (TSSs), Total Dissolved Solids (TDSs), Total Organic Carbon (TOC), alkalinity or buffering capacity, reactive sulfide, anions], in determining similarity. The reviewer should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the SDG. The reviewer may determine that only some of the samples in the SDG are similar to the duplicate sample, and that only these samples should be qualified. Or, the reviewer may determine that no samples are sufficiently similar to the sample used for the duplicate, and thus that only the field sample used to prepare the duplicate sample should be qualified.

1. If the appropriate number of duplicate samples was not analyzed for each matrix using the correct frequency, use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the Laboratory. Note the situation in the Data Review Narrative, and for CLP Project Officer (PO) action.

2. If the results from a duplicate analysis for mercury fall outside the appropriate control limits, qualify sample results that are ≥ Method Detection Limit (MDL) as estimated (J) and non-detects as estimated (UJ).

3. If a field blank or PE sample was used for the duplicate sample analysis, note this for CLP PO action. All of the other Quality Control (QC) data must then be carefully checked, and professional judgment exercised by the data reviewer when evaluating the data.

4. Note the potential effects on the data due to out-of-control duplicate sample results in the Data Review Narrative.

Table 26. Duplicate Sample Actions for Mercury Analysis

Duplicate Sample Results	Action for Samples
Both original sample and duplicate sample >5x the CRQL and RPD>20%*	Qualify those results that are ≥MDL that professional judgment determines to be affected as estimated (J) and non-detects as estimated (UJ)
Original sample or duplicate sample ≤5x the CRQL (including non-detects) and absolute difference between sample and duplicate >CRQL*	Qualify those results that are ≥MDL that professional judgment determines to be affected as estimated (J) and non-detects as estimated (UJ)

*The above control limits are **method requirements** for duplicate samples, regardless of the sample matrix type. However, it should be noted that Laboratory variability arising from the sub-sampling of non-homogenous soil samples is a common occurrence. Therefore, for **technical review purposes only**, Regional policy or project DQOs may allow the use of less restrictive criteria (e.g., 35% RPD, 2x the CRQL) to be assessed against duplicate soil samples

VI. Spike Sample Analysis

A. Review Items:

Cover Page, Form V-IN (Part A & B), Form XII-IN, instrument printouts, and raw data.

B. Objective:

The spiked sample analysis is designed to provide information about the effect of each sample matrix on the sample preparation procedures and the measurement methodology. Non-homogenous samples can impact the apparent method recovery. However, aqueous samples are generally homogenous and most soil samples are homogenous within a factor of two or three. If the spike is added to the sample before the digestion (e.g., prior to the addition of other reagents), it is referred to as a spiked sample, pre-digestion spike, or Matrix Spike.

C. Criteria:

1. Samples identified as field blanks or Performance Evaluation (PE) samples cannot be used for spiked sample analysis.

2. At least one spiked sample (pre-digestion) shall be prepared and analyzed from each group of samples with a similar matrix type (e.g., water or soil), or for each Sample Delivery Group (SDG).

3. The spike Percent Recovery (%R) shall be within the established acceptance limits. However, spike recovery limits do not apply when the sample concentration is ≥ four times (4x) the spike added. In such an event, the data shall be reported unflagged, even if the %R does not meet the acceptance criteria.

4. If the spiked sample analysis was performed on the same sample that was chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample". The average of the duplicate results cannot be used for the purpose of determining %R.

NOTE: The final spike concentrations required for mercury are presented in the method described in the Statement of Work (SOW).

D. Evaluation:

1. Verify using the Cover Page, Form VA-IN, Form XII-IN, and raw data that the appropriate number of required spiked samples were prepared and analyzed for the SDG.

2. Verify that a field blank or PE sample was not used for the spiked sample analysis.

3. Evaluate Form VA-IN and the raw data to verify that all Matrix Spike sample results for mercury fall within the established control limits.

4. Recalculate using the raw data, one or more of the %R using the following equation, and verify that the recalculated value agrees with the Laboratory-reported values on Forms V(A & B)-IN:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

NOTES: When the sample concentration is < Method Detection Limit (MDL), use SR = 0 only for the purposes of calculating the %R. The actual spiked sample results, sample results, and %R (positive or negative) shall still be reported on Form V (A & B)-IN.

For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with the above criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTE: For a Matrix Spike that does not meet the technical criteria, apply the action to all samples of the same matrix, if the reviewer considers the samples sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data, including: site and sampling documentation (e.g., location and type of sample, descriptive data, soil classification); field test data (e.g., pH, Eh, conductivity, chlorine); and Laboratory data for other parameters [e.g., Total Suspended Solids (TSSs), Total Dissolved Solids (TDSs), Total Organic Carbon (TOC), alkalinity or buffering capacity, reactive sulfide, anions], in determining similarity. The reviewer should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the SDG. The reviewer may determine that only some of the samples in the SDG are similar to the Matrix Spike sample, and that only these samples should be qualified. Or, the reviewer may determine that no samples are sufficiently similar to the sample used for the Matrix Spike, and thus that only the field sample used to prepare the Matrix Spike sample should be qualified.

1. If the appropriate number of Matrix Spike samples was not analyzed for each matrix using the correct frequency, use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the Laboratory. Note the situation in the Data Review Narrative, and for CLP Project Officer (CLP PO) action.

2. If a field blank or PE sample was used for the spiked sample analysis, note this for CLP PO action. All of the other Quality Control (QC) data must then be carefully checked, and professional judgment exercised by the data reviewer when evaluating the data.

3. If the Matrix Spike %R is <30%, qualify affected results that are ≥MDL as estimated low (J-). Qualify affected non-detects as unusable (R).

4. If the Matrix Spike %R falls within the range of 30-74% and the sample results are ≥MDL, qualify the affected data as estimated low (J-).

5. If the Matrix Spike %R falls within the range of 30-74% and the sample results are non-detects, qualify the affected data as estimated (UJ).

6. If the Matrix Spike %R is >125% and the reported sample results are non-detects, the sample data should not be qualified.

7. If the Matrix Spike %R is >125% and the sample results are ≥MDL, qualify the affected data as estimated high (J+).

8. Note the potential effects on the data due to out-of-control spiked sample results in the Data Review Narrative.

Table 27. Spike Sample Actions for Mercury Analysis

Spike Sample Results	Action for Samples
Matrix Spike %R <30%	Qualify affected results that are ≥MDL as estimated low (J-) and affected non-detects as unusable (R)
Matrix Spike %R 30-74%	Qualify affected results that are ≥MDL as estimated low (J-) and affected non-detects as estimated (UJ)
Matrix Spike %R >125%	Qualify affected results that are ≥MDL as estimated high (J+) Non-detects are not qualified

VII. Field Duplicates

A. Review Items:

Form I-IN, instrument printouts, and raw data.

B. Objective:

Field duplicate samples may be collected and analyzed as an indication of overall precision. These analyses measure both field and Laboratory precision. The results, therefore, may have more variability than Laboratory duplicates that measure only Laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

C. Criteria:

There are no "required" review criteria for determining comparability of field duplicate analyses.

D. Evaluation:

Identify samples that are field duplicates using Traffic Report(s)/Chain of Custody (TR/COC) documentation or sample field sheets. Compare the results reported for each sample and calculate the Relative Percent Difference (RPD), if appropriate.

E. Action:

Provide any evaluation of the field duplicates in the Data Review Narrative.

VIII. Overall Assessment

A. Review Items:

Entire data package, data review results, preparation logs, calibration standard logs, instrument logs, instrument printouts, and raw data (including any confirmation data).

B. Objective:

The objective is to ensure that the reported sample quantitation results are accurate. It is appropriate for the data reviewer to make professional judgments and express concerns, as well as to comment on the validity of the overall data for a Case. This is particularly appropriate when there are several Quality Control (QC) criteria that are outside of the specification parameters. The additive nature of QC factors that fall outside of specification parameters is difficult to assess in an objective manner, but the reviewer has a responsibility to inform the user concerning data quality and data limitations to assist that user in avoiding inappropriate use of the data, while not precluding any consideration of the data at all. If qualifiers other than those used in this document are necessary to describe or qualify the data, it is necessary to thoroughly document/explain the additional qualifiers used. The data reviewer would be greatly assisted in this endeavor if the acceptance or performance criteria are provided. The Inorganic Review Summary (see Appendix B) and supplementary documentation must be included with the review.

C. Criteria:

1. Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

2. Reported analyte concentrations must be quantitated according to the appropriate analytical method, as listed in the method.

D. Evaluation:

Examine the raw data to verify that the correct calculation of the sample results was reported by the Laboratory. Digestion logs, instrument printouts, strip charts, etc., should be compared to the reported sample results recorded on the appropriate Inorganic Summary Forms (Form I-IN through Form XV-IN).

1. Evaluate any technical problems not previously addressed.

2. Examine the raw data for any anomalies (e.g., baseline shifts, negative absorbance, omissions, illegibility, etc.).

3. Verify that the appropriate methods and amounts were used to prepare samples and standards for analysis. If reduced volumes are used, verify that the Laboratory had received Contract Laboratory Program Project Officer (CLP PO) approval for the use of the reduced volume.

4. Verify that there are no transcription or reduction errors [e.g., dilutions, Percent Solids (%S), sample weights, etc.] on one or more samples.

5. Verify that results fall within the calibrated range for mercury.

6. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the Quality Assurance Project Plan (QAPP), focusing specifically on the acceptance or performance criteria, the Standard Operating Procedure(s) (SOPs), and communication with the user concerning the intended use and desired quality of these data.

E. Action:

1. Use professional judgment to determine if there is any need to qualify data which are not qualified based on the QC criteria previously discussed.

2. Write a brief Data Review Narrative to give the user an indication of the analytical limitations of the data. Note any discrepancies between the data and the SDG Narrative for CLP PO action. If sufficient information on the intended use and required quality of the data are available, the reviewer should include an assessment of the data usability within the given context.

3. If any discrepancies are found, the Laboratory may be contacted by the Region's designated representative to obtain additional information for resolution. If a discrepancy remains unresolved, the reviewer may determine that qualification of the data is warranted.

Calculations for Mercury

Aqueous Samples:

$$\text{Hg Concentration } (\mu g/L) = \frac{\mu g \text{ Hg, curve}}{\text{aliquot volume, mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

Soil Samples:

$$\text{Hg Concentration (mg/kg)} = \text{Hg } \mu g/g = \frac{C}{W \times S} \times (0.1L)$$

Where,

C = Concentration from curve (µg/L)

W = Wet sample weight (g)

S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)

Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation:

To calculate the adjusted MDL or adjusted CRQL for water/aqueous samples, multiply the value of the MDL (µg/L) or CRQL (µg/L) by the Dilution Factor (DF). Calculate the adjusted MDL or adjusted CRQL for soil samples as follows:

$$\text{Adjusted Concentration (dry wt.)(mg/kg)} = C \times \frac{W_M}{W_R} \times \frac{1}{S} \times DF$$

Where,

C = MDL or CRQL concentration (mg/kg)

W_M = Method required wet sample weight (g)

W_R = Reported wet sample weight (g)

S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)

DF = Dilution Factor

CYANIDE DATA REVIEW

The inorganic data requirements for cyanide data review to be reviewed during validation are listed below:

I. Preservation and Holding Times

II. Calibration
   A. Initial
   B. Initial and Continuing Calibration Verification (ICV/CCV)
   C. Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

III. Blanks

IV. Laboratory Control Sample (LCS)

V. Duplicate Sample Analysis

VI. Spike Sample Analysis

VII. Field Duplicates

VIII. Overall Assessment

An Example Analytical Sequence for Cyanide

S0
S10
S20
S50
S100
S200
S400
ICV (distilled)
ICB
CRI
CCV
CCB
MIDRANGE
nine samples
CCV
CCB
nine samples
CRI
CCV
CCB
ten samples, etc.

I. Preservation and Holding Times

A. Review Items:

Form IA-IN, Form IB-IN, Form XII-IN, Form XIII-IN, Traffic Report/Chain of Custody (TR/COC) documentation, Form DC-1, raw data, and the Sample Delivery Group (SDG) Narrative checking for: pH; cooler temperature; holding time; and other sample conditions.

B. Objective:

The objective is to ascertain the validity of the analytical results based on the sample condition, and the holding time of the sample from the date of collection to the date of analysis.

C. Criteria:

1. Technical requirements for sample holding times have only been established for aqueous matrices. The addition of sodium hydroxide to adjust the pH is only required for aqueous samples.

2. The technical holding time criteria for aqueous cyanide samples are 14 days; oxidizing agents removed, then preserved (with sodium hydroxide) to pH>12.

3. Aqueous samples shall be maintained at 4°C ±2°C until preparation and analysis to allow for re-preparation and for the direct analysis of dissolved metals.

4. The preservation for soil/sediment samples is maintenance at 4°C ±2°C until preparation and analysis.

D. Evaluation:

Technical holding times are established by comparing the sampling date(s) on the TR/COC documentation with the dates of analysis on Form XIII-IN, and the raw data. Information contained in the Complete SDG File (CSF) should also be considered in the determination of holding times. Verify that the analysis dates on the Form XIIIs and the raw data are identical. Review the SDG Narrative and raw data preparation logs to determine if samples were properly preserved. If there is an indication that there are problems with the samples, the integrity of the samples may be compromised and professional judgment should be used to evaluate the effect of the problem on the sample results. For aqueous cyanide samples, the reviewer should look for evidence that the samples were tested for the presence of sulfides or oxidizing agents, and whether the appropriate preservation steps were taken.

E. Action:

NOTE: Apply the action to each sample for which the preservation or holding time criteria were not met.

1. If oxidizing agents are detected in aqueous cyanide samples at the time of sample preparation, qualify results that are ≥ Method Detection Limit (MDL) as estimated low (J-) and non-detects as unusable (R). If sulfides are detected in aqueous cyanide samples at the time of sample preparation and there is no evidence that the Laboratory removed the sulfides (using precipitation and filtration), qualify results that are ≥MDL as estimated (J) and non-detects as unusable (R). If the pH of aqueous cyanide samples is ≤12 at the time of sample receipt, use professional judgment to qualify the samples based on the pH of the sample. Qualify results that are ≥MDL as estimated low (J-) and qualify non-detects as unusable (R).

2. If technical holding times are exceeded, use professional judgment to determine the reliability of the data based on the magnitude of the additional time compared to the technical requirement and whether the samples are properly preserved. The expected bias would be low. Qualify results that are ≥MDL as estimated low (J-) and non-detects as unusable (R).

3. Due to limited information concerning holding times for soil samples, it is left to the discretion of the data reviewer whether to apply water holding time criteria to soil samples. If they are applied, it must be clearly documented in the Data Review Narrative.

4. When the holding times are exceeded, the reviewer should comment in the Data Review Narrative on any possible consequences for the analytical results.

5. When holding times are grossly exceeded, note this for Contract Laboratory Program Project Officer (CLP PO) action.

Table 28. Technical Holding Time Actions for Cyanide Analysis

Preservation & Holding Time Results	Action for Samples
Aqueous cyanide samples received with oxidizing agents present.	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as unusable (R)
Aqueous cyanide samples received with sulfides present, and sulfides are not removed	Qualify results that are ≥MDL as estimated (J) Qualify non-detects as unusable (R)
Aqueous cyanide samples received with pH ≤12	Use professional judgment Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as unusable (R)
Technical holding time exceeded: Cyanide >14 days	Use professional judgment Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as unusable (R)

II. Calibration

A. Review Items:

Form II-IN (Parts A & B), Form XI-IN, Form XIII-IN, preparation logs, calibration standard logs, instrument logs, instrument printouts, and raw data.

B. Objective:

Method requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data for cyanide. Initial Calibration Verification (ICV) demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical run. Continuing Calibration Verification (CCV) demonstrates that the initial calibration is still valid by checking the performance of the instrument on a continuing basis.

C. Criteria:

1. Initial Calibration

The instruments shall be successfully calibrated daily (or once every 24 hours), and each time the instrument is set up. The calibration date and time shall be included in the raw data.

a. A blank and at least three calibration standards, one of which shall be at the Contract Required Quantitation Limit (CRQL), shall be employed to establish the analytical curve. The calibration curve for cyanide shall possess a correlation coefficient of ≥ 0.995 to ensure the linearity over the calibrated range.

b. All sample results shall be reported from an analysis within the calibrated range.

c. At least one calibration standard (mid-level) shall be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. The distilled standard shall agree within ±15% of the undistilled standard. This mid-level standard shall be prepared at least once for each distillation method used to prepare samples for analysis. This standard shall be analyzed immediately following the first CCV/CCB analyses.

d. The linearity of the analytical curve shall be verified near the CRQL. A CRQL Check Standard (CRI) solution shall be prepared and analyzed at the beginning and end of each sample analysis run and every 20 analytical samples, but not before the ICV analysis. The CRI of the beginning of the run must immediately follow the ICV/ICB analyses.

e. Analysis of the CRI for cyanide is required for both the manual and semi-automated spectrophotometric methods, and the results and Percent Recovery (%R) are to be reported on Form IIB-IN.

f. If the results for the CRI do not fall within the fixed acceptance limits, the Laboratory must reanalyze the CRI. If the results of the reanalysis do not fall within the acceptance limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the new calibration then reverified.

2. Initial and Continuing Calibration Verification (ICV and CCV)

The acceptance criteria for the ICVs, CCVs, and CRIs are presented in Table 29:

Table 29. Acceptance Criteria for ICVs, CCVs, and CRIs

Analytical Method	Inorganic Analyte	ICV/CCV Low Limit (% of True Value)	ICV/CCV High Limit (% of True Value)	CRI Low Limit (% of True Value)	CRI High Limit (% of True Value)
Other	Cyanide	85	115	70	130

a. Initial Calibration Verification (ICV)

1) Immediately after each cyanide system has been calibrated, the accuracy of the initial calibration must be verified and documented by the analysis of an ICV solution(s). If the ICV %R falls outside of the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and all affected samples reanalyzed.

2) If the ICV is not available from USEPA, or where a certified solution of the analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration level other than that used for instrument calibration (or the CRI), but within the calibrated range.

3) For cyanide analysis, the ICV standard solution shall be distilled with each batch of samples analyzed. An ICV distilled with a particular set of samples must be analyzed only with that sample set.

b. Continuing Calibration Verification (CCV)

1) To ensure accuracy during the course of each analytical run, the CCV shall be analyzed and reported.

2) The CCV standard shall be analyzed at a frequency of 10% or every two hours during an analytical run, whichever is more frequent. The CCV standard shall also be analyzed at the beginning of the run, and again after the last analytical sample.

3) The analyte concentration in the CCV standard shall be different from the concentration used for the ICV, and shall be one of the following solutions at, or near, the mid-range levels of the calibration curve:

   A. USEPA solutions;
   B. National Institute of Standards and Technology (NIST) standards; or
   C. A Laboratory-prepared standard solution (self-prepared or commercially available).

4) The same CCV standard solution shall be used throughout the analysis runs for a Sample Delivery Group (SDG).

5) The CCV shall be analyzed in the same fashion as an actual sample. Operations such as the number of replicate analyses, the number and duration of the instrument rinses, etc., affect the measured CCV result and are not to be applied to the CCV to an extent greater than was applied to the associated analytical samples. If the %R of the CCV was outside of the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification reanalyzed.

D. Evaluation:

1. Cyanide Analysis

a. Verify that the instrument was calibrated daily (once every 24 hours) and each time the instrument was set up, utilizing a blank and at least three calibration standards. Confirm that one of the calibration standards was analyzed at the CRQL.

b. Check the distillation log and verify that a mid-level cyanide standard and the ICV were distilled and analyzed. Verify that the distilled mid-level cyanide standard agrees within ±15% of the undistilled standard.

c. Evaluate the reported CRI to confirm that it was analyzed at the proper frequency, concentration, and location within the analytical run sequence. Verify that acceptable %R results were obtained.

d. Verify that the ICV and CCV standards were analyzed for cyanide at the proper frequency (10%) and at the appropriate concentration. Verify that acceptable %R results were obtained.

e. Recalculate one or more of the ICV, CCV, or CRI %R using the following equation and verify that the recalculated value agrees with the Laboratory-reported values on Forms II (A & B)-IN.

$$\%R = \frac{\text{Found(value)}}{\text{True(value)}} \times 100$$

Where,

Found(value) = Concentration (in µg/L) of cyanide measured in the analysis of the ICV, CCV, or CRI solution

True(value) = Concentration (in µg/L) of cyanide in the ICV, CCV, or CRI source

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTES: For initial calibrations or non-distilled ICVs that do not meet the technical criteria, apply the action to all samples reported from the analytical run. For distilled ICV, apply the action to all samples prepared in the same preparation batch.

For CCVs or CRIs that do not meet the technical criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of the QC sample and a subsequent technically acceptable analysis of the QC sample in the analytical run.

1. If the instrument was not calibrated daily and each time the instrument was set up, qualify the data as unusable (R). If the instrument was not calibrated with at least the minimum number of standards, or if the calibration curve does not include standards at required concentrations (e.g., a blank, or a standard at the CRQL), use professional judgment to qualify results that are ≥ Method Detection Limit (MDL) as estimated (J) or unusable (R), and non-detects as estimated (UJ) or unusable (R).

2. If the correlation coefficient is <0.995, qualify sample results that are ≥MDL as estimated (J), and non-detects as estimated (UJ). Depending on the degree of the deviation from linearity, further qualification of the data may be required depending on the professional judgment of the reviewer [e.g., unusable data (R)].

3. If one of the mid-range standards and the ICV are not distilled for cyanide, or the distilled standard(s) does not agree with the undistilled standard (>±15% but <±30%) qualify sample results that are ≥MDL as estimated (J). If the distilled standard disagrees with the undistilled standard by more than 30%, qualify sample results that are ≥MDL as unusable (R).

4. If the CRIs are outside the acceptance criteria, use professional judgment to qualify all associated data. If possible, indicate the bias in the review. The following guidelines are recommended:

   a. If the CRI %R is <50%, qualify all sample results are ≥MDL but < two times (2x) the CRQL and all non-detects as unusable (R). Qualify detects ≥2x the CRQL as estimated (J).

   b. If the CRI %R falls within the range of 50-69%, qualify all sample results that are ≥MDL but <2x the CRQL as estimated low (J-) and all non-detects as estimated (UJ). Detects that are ≥2x the CRQL should not be qualified based on this criterion.

   c. If the CRI %R is >130%, qualify all sample results that are ≥MDL but <2x the CRQL as estimated high (J+). Non-detects and detects ≥2x the CRQL should not be qualified based on this criterion.

   d. If the CRI %R is >180%, qualify all sample results that are ≥MDL as unusable (R).

5. If the ICV or CCV %R falls outside the acceptance windows, use professional judgment to qualify all associated data. If possible, indicate the bias in the review. The following guidelines are recommended:

a. If the ICV or CCV %R is <70%, qualify non-detects as unusable (R). Use professional judgment to qualify all results that are ≥MDL as estimated low (J-) or unusable (R).

b. If the ICV or CCV %R falls within the range of 70-84%, qualify sample results that are ≥MDL as estimated low (J-), qualify non-detects as estimated (UJ).

c. If the ICV or CCV %R falls within the range of 116-130%, qualify sample results that are ≥MDL as estimated high (J+).

d. If the ICV or CCV %R is within the range of 116-130%, non-detects should not be qualified.

e. If the ICV or CCV %R is >130%, use professional judgment to qualify results that are ≥MDL as estimated high (J+) or unusable (R). Non-detects should not be qualified.

f. If the %R is >165%, qualify all results that are ≥MDL as unusable (R).

6. If the Laboratory failed to provide adequate calibration information, the Region's designated representative should contact the Laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

7. Note the potential effects on the reported data due to exceeding the calibration criteria in the Data Review Narrative.

8. If calibration criteria are grossly exceeded, note this for Contract Laboratory Program Project Officer (CLP PO) action.

NOTE: For truly critical samples, a further in-depth evaluation of the calibration curve may be warranted to determine if additional qualification is necessary.

Table 30. Calibration Actions for Cyanide Analysis

Calibration Result	Action for Samples
Calibration not performed	Qualify all results as unusable (R)
Calibration incomplete	Use professional judgment Qualify results that are ≥MDL as estimated (J) or unusable (R) Qualify non-detects as estimated (UJ) or unusable (R)
Correlation coefficient <0.995	Qualify results that are ≥MDL as estimated (J) Qualify non-detects as estimated (UJ)
No distilled ICV or mid-range standard for cyanide, or distilled standards do not agree (>±15% but ≤±30%) with undistilled standard	Qualify results that are ≥MDL as estimated (J)
Distilled standards do not agree (>±30%) with undistilled standard	Qualify results that are ≥MDL as unusable (R)
CRI %R <50%	Qualify all results that are ≥MDL but <2x the CRQL and all non-detects as unusable (R) Qualify all results that are ≥2x the CRQL as estimated (J)
CRI %R 50-69%	Qualify results that are ≥MDL but <2x the CRQL as estimated low (J-) Qualify non-detects as estimated (UJ) Results that are ≥2x the CRQL are not qualified
CRI %R >130% but ≤165%	Qualify results that are ≥MDL but <2x the CRQL as estimated high (J+) Non-detects and results that are ≥2x the CRQL are not qualified
CRI %R >165%	Qualify all results that are ≥MDL as unusable (R)
ICV/CCV %R <70%	Qualify results that are ≥MDL as estimated low (J-) or unusable (R) Qualify all non-detects as unusable (R)
ICV/CCV %R 70-84%	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as estimated (UJ)
ICV/CCV %R 116-130%	Qualify results that are ≥MDL as estimated (J)
ICV/CCV %R >130%	Qualify results that are ≥MDL as estimated high (J+) or unusable (R)
ICV/CCV %R >165%	Qualify results that are ≥MDL as unusable (R)

III. Blanks

A. Review Items:

Form I-IN, Form III-IN, Form XII-IN, Form XIII-IN, preparation logs, calibration standard logs, instrument logs, and raw data.

B. Objective:

The objective of blank analysis results assessment is to determine the existence and magnitude of contamination resulting from Laboratory (or field) activities. The criteria for evaluation of blanks applies to any blank associated with the samples (e.g., method blanks, calibration blanks, field blanks, etc.). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. No contaminants should be found in the blank(s).

2. The Initial Calibration Blank (ICB) shall be analyzed after the analytical standards, but not before analysis of the Initial Calibration Verification (ICV) during the initial calibration of the instrument (see Section II.C.1).

3. A Continuing Calibration Blank (CCB) shall be analyzed immediately after every ICV and Continuing Calibration Verification (CCV). The CCB shall be analyzed at a frequency of 10% or every two hours during the run, whichever is more frequent. The CCB shall be analyzed at the beginning of the run, and again after the last CCV that was analyzed after the last analytical sample of the run. The CCB result (absolute value) shall not exceed the Contract Required Quantitation Limit (CRQL) of cyanide.

4. At least one Preparation Blank (PB) shall be prepared and analyzed for each matrix, with every Sample Delivery Group (SDG), or with each batch of samples distilled, whichever is more frequent. The PB consists of reagent water processed through the appropriate sample preparation and analysis procedure.

5. If the cyanide concentration in the PB is >CRQL, the lowest concentration of cyanide in the associated samples must be 10 times (10x) the PB concentration. Otherwise, all samples associated with that PB with a cyanide concentration <10x the PB concentration, and >CRQL, should be redistilled and reanalyzed cyanide (except for an identified field blank). The Laboratory is not to correct the sample concentration for the blank value.

6. If the concentration of the PB for cyanide is <(−CRQL), all samples reported <10x the CRQL (associated with that blank), should be redistilled and reanalyzed.

D. Evaluation:

1. Verify that an ICB was analyzed after the calibration, the CCB was analyzed at the proper frequency and location during the run, and PBs are prepared and analyzed as appropriate for the SDG (e.g., total number of samples, various types of matrices present, number of digestion batches, etc.).

2. Review the results reported on the Blank Summary (Form III-IN), as well as the raw data (e.g., instrument printouts, strip charts, printer tapes, bench sheets, etc.) for all blanks, and verify that the results were accurately reported.

3. Evaluate all of the associated blanks for the presence of cyanide. Verify that if cyanide was present in a PB, or if a concentration was <(−CRQL), the affected samples were redistilled and reanalyzed. Verify that if cyanide was present in an ICB or a CCB, the analysis was terminated, the problem corrected, the instrument recalibrated, and the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration blank reanalyzed.

NOTE: For data obtained from the Contract Laboratory Program (CLP), many of the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTES: For ICBs that do not meet the technical criteria, apply the action to all samples reported from the analytical run.

For CCBs that do not meet the technical criteria, apply the action to all samples analyzed between a previous technically acceptable analysis of the CCB and a subsequent technically acceptable analysis of the CCB in the analytical run.

For PBs that do not meet the technical criteria, apply the action to all samples prepared in the same preparation batch.

1. If the appropriate blanks are not analyzed with the correct frequency, the data reviewer should use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the Laboratory. The situation should then be recorded in the Data Review Narrative, and noted for CLP Project Officer (PO) action.

2. Action regarding unsuitable blank results depends on the circumstances and origin of the blank. The reviewer should note that in instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of contaminant.

3. Some general "technical" review actions include:

   a. Any blank (including PB) reported with a negative result, whose value is ≤[−Method Detection Limit (MDL)] but ≥(−CRQL), should be carefully evaluated to determine its effect on the sample data. The reviewer shall then use professional judgment to assess the data. For any blank (including PB) reported with a negative result, whose value is <(−CRQL), qualify results that are ≥CRQL as estimated low (J-) and non-detects as estimated (UJ).

   b. The blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. In particular, soil sample results reported on Form I-IN will not be on the same basis (units, dilution) as the calibration blank data reported on Form III-IN. The reviewer may find it easier to work with the raw data.

4. Specific "method" actions include:

   a. If the absolute value of an ICB or a CCB result is >CRQL, the analysis should be terminated. If the analysis was not terminated and the affected samples are not reanalyzed, report non-detects and results that are ≥MDL but ≤CRQL as CRQL-U. For results that are >CRQL but < Blank Result, use professional judgment to qualify the data as unusable (R), or report the results at the level of the blank with a "U" qualifier. Use professional judgment to qualify results that are > Blank Result. Note this situation for CLP PO action and record it in the Data Review Narrative.

   b. If the absolute value of the concentration of the PB is ≤CRQL, no correction of the sample results should be performed, report non-defects and results ≥MDL but ≤CRQL as CRQL-U. Use professional judgment to qualify results that are >CRQL.

   c. If the cyanide concentration in the PB is >CRQL, the lowest concentration of cyanide in the associated samples must be 10x the PB concentration. Otherwise, all samples associated with that blank with concentrations <10x the PB concentration and >CRQL should be redistilled and reanalyzed. Raise the CRQL to the concentration found in the PB and report those samples that do not require redigestion (≥MDL but ≤CRQL) as CRQL-U. Note for CLP PO action and record in the Data Review Narrative if the Laboratory failed to redistill and reanalyze the affected samples. The reviewer shall then use professional judgment to assess the data.

Table 31. Blank Actions for Cyanide Analysis

Blank Type	Blank Result	Sample Result	Action for Samples
ICB/CCB	Absolute value is ≥MDL but ≤CRQL	Non-detect	No action
		≥MDL but ≤CRQL	Report CRQL value with a"U"
		>CRQL	Use professional judgment
ICB/CCB	Absolute value is >CRQL	≥MDL but ≤CRQL	Report CRQL value with a "U"
		>CRQL but <Blank Result	Report at level of Blank Result with a "U" or qualify data as unusable (R)
		>Blank Result	Use professional judgment
ICB/CCB	≤(−MDL), but ≥(−CRQL)	≥MDL, or non-detects	Use professional judgment
ICB/CCB	<(−CRQL)	<10x the CRQL	Qualify results that are ≥CRQL as estimated low (J-) Qualify non-detects as estimated (UJ)
PB	>CRQL	≥MDL but ≤CRQL	Report CRQL value with a "U"
		>CRQL but <10x the Blank Result	Qualify results as unusable (R) or estimated high (J+)
		≥10x the Blank Result	No action
PB	≥MDL but ≤CRQL	Non-detect ≥MDL but ≤CRQL >CRQL	No action Report CRQL value with a "U" Use professional judgment
PB	<(−CRQL)	<10x the CRQL	Qualify results that are ≥CRQL as estimated low (J-) Qualify non-detects as estimated (UJ)

IV. Laboratory Control Sample (LCS)

A. Review Items:

Form VII-IN, Form XII-IN, preparation logs, instrument printouts, and raw data.

B. Objective:

The Laboratory Control Sample (LCS) serves as a monitor of the overall performance of each step during the analysis, including the sample preparation.

C. Criteria:

1. A solid LCS shall be prepared and analyzed utilizing each of the preparation and analytical procedures applied to the soil/sediment samples received, with one exception: The Percent Solids (%S) determination is not required. If the solid LCS is not available from USEPA, other USEPA Quality Assurance (QA) samples or certified materials may be used.

2. One solid LCS shall be prepared and analyzed for each group of soil sediment samples in a Sample Delivery Group (SDG), or for each batch of samples distilled, whichever is more frequent.

3. All solid LCS results shall fall within the control limits reported on Form VII-IN. If the results for the solid LCS fall outside of the control limits, the analyses should be terminated, the problem corrected, and the samples prepared with that LCS redistilled and reanalyzed.

D. Evaluation:

1. Verify using Form VII-IN, Form XII-IN, and raw data that the appropriate number of required LCSs were prepared and analyzed for the SDG.

2. Evaluate Form VII-IN and verify that all results for cyanide fall within the established control limits.

3. Check the raw data (e.g., instrument printouts, strip charts, bench sheets, etc.) to verify that the Percent Recoveries (%Rs) on Form VII-IN were accurately transcribed. Recalculate one or more of the reported %Rs using the following equation:

$$\%R = \frac{\text{Found(value)}}{\text{True(value)}} \times 100$$

Where,

Found(value) = Concentration of cyanide (in mg/kg) measured in the analysis of the LCS

True(value) = Concentration of cyanide (in mg/kg) in the LCS

4. Verify that the LCS was prepared at the same time as the associated samples using the same procedures

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

If the LCS criteria are not met, the Laboratory performance and method accuracy are in question. Professional judgment should be used to determine if the data should be qualified or rejected. The following guidance is suggested for qualifying sample data associated with an LCS that does not meet the required criteria.

For an LCS that does not meet the technical criteria, apply the action to all samples in the same preparation batch.

1. If the LCS results are greater than the reported control limits, qualify sample results that are ≥ Method Detection Limit (MDL) as estimated high (J+). If the LCS results are less than the reported control limits, qualify sample results that are ≥MDL as estimated low (J-).

2. If the LCS results are greater than the reported control limits and the sample results are non-detects, the data should not be qualified.

3. If the LCS results are less than the reported control limits, qualify non-detects as estimated (UJ).

4. If a Laboratory fails to analyze an LCS with each SDG, or if a Laboratory consistently fails to generate acceptable LCS recoveries, note this for CLP Project Officer (CLP PO) action.

5. Whenever possible, the potential effects on the data due to out-of-control LCS results should be noted in the Data Review Narrative.

Table 32. LCS Actions for Cyanide Analysis

LCS Result	Action for Samples
Soil Result > upper limit	Qualify results that are ≥MDL as estimated high (J+)
Soil Result < lower limit	Qualify results that are ≥MDL as estimated low (J-) Qualify non-detects as estimated (UJ)

V. Duplicate Sample Analysis

A. Review Items:

Cover Page, Form VI-IN, Form XII-IN, instrument printouts, and raw data.

B. Objective:

The objective of duplicate sample analysis is to demonstrate acceptable method precision by the Laboratory at the time of analysis. Duplicate analyses are also performed to generate data that determines the long-term precision of the analytical method on various matrices. Non-homogenous samples can impact the apparent method precision. However, aqueous samples are generally homogenous and most soil samples are homogenous within a factor of two or three.

C. Criteria:

1. Samples identified as field blanks or Performance Evaluation (PE) samples cannot be used for duplicate sample analysis.

2. At least one duplicate sample shall be prepared and analyzed from each group of samples of a similar matrix type (e.g., water or soil) or for each Sample Delivery Group (SDG). Duplicates cannot be averaged for reporting on Form I-IN. Additional duplicate sample analyses may be required by USEPA Regional request. Alternately, the Region may require that a specific sample be used for the duplicate sample analysis.

3. Duplicate sample analyses are required for Percent Solids (%S) determination.

4. A control limit of 20% for the Relative Percent Difference (RPD) shall be used for original and duplicate sample values ≥ five times (5x) the Contract Required Quantitation Limit (CRQL).

5. A control limit of the CRQL shall be used if either the sample or duplicate value is <5x the CRQL. The absolute value of the control limit (CRQL) shall be entered in the "Control Limit" column on Form VI-IN. If both samples are non-detects, the RPD is not calculated for Form VI-IN.

NOTE: The above control limits are **method requirements** for duplicate samples, regardless of the sample matrix type. However, it should be noted that Laboratory variability arising from the sub-sampling of non-homogenous soil samples is a common occurrence. Therefore, for **technical review purposes only**, Regional policy or project Data Quality Objectives (DQOs) may allow the use of less restrictive criteria (e.g., 35% RPD, 2x the CRQL) to be assessed against duplicate soil samples.

D. Evaluation:

1. Verify from the Cover Page, Form XII-IN, and the raw data that the appropriate number of required duplicate samples were prepared and analyzed for the SDG.

2. Evaluate Form VI-IN and the raw data to verify that all cyanide duplicate results for each method fall within the established control limits.

3. Verify that a field blank or PE sample was not used for duplicate analysis.

4. Check the raw data and recalculate one or more of the RPD values using the following equation to verify that the results were correctly reported on Form VI-IN:

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where,

RPD = Relative Percent Difference

S = Sample result (original)

D = Duplicate result

NOTE: For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with the above criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTE: For a duplicate sample analysis that does not meet the technical criteria, apply the action to all samples of the same matrix, if the reviewer considers the samples sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data, including: site and sampling documentation (e.g., location and type of sample, descriptive data, soil classification); field test data (e.g., pH, Eh, conductivity, chlorine); and Laboratory data for other parameters [e.g., Total Suspended Solids (TSSs), Total Dissolved Solids (TDSs), Total Organic Carbon (TOC), alkalinity or buffering capacity, reactive sulfide, anions], in determining similarity. The reviewer should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the SDG. The reviewer may determine that only some of the samples in the SDG are similar to the duplicate sample, and that only these samples should be qualified. Or, the reviewer may determine that no samples are sufficiently similar to the sample used for the duplicate, and thus that only the field sample used to prepare the duplicate sample should be qualified.

1. If the appropriate number of duplicate samples was not analyzed for each matrix using the correct frequency, use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the Laboratory. Note the situation in the Data Review Narrative, and for CLP Project Officer (PO) action.

2. If the results from a duplicate analysis for cyanide fall outside the appropriate control limits, qualify sample results that are ≥ Method Detection Limit (MDL) as estimated (J) and non-detects as estimated (UJ).

3. If a field blank or PE sample was used for the duplicate sample analysis, note this for CLP PO action. All of the other Quality Control (QC) data must then be carefully checked, and professional judgment exercised by the data reviewer when evaluating the data.

4. Note the potential effects on the data due to out-of-control duplicate sample results in the Data Review Narrative.

Table 33. Duplicate Sample Actions for Cyanide Analysis

Duplicate Sample Results	Action for Samples
Both original sample and duplicate sample >5x the CRQL and RPD>20%*	Qualify those results that are ≥MDL that professional judgment determines to be affected as estimated (J) and non-detects as estimated (UJ)
Original sample or duplicate sample ≤5x the CRQL (including non-detects) and absolute difference between sample and duplicate >CRQL*	Qualify those results that are ≥MDL that professional judgment determines to be affected as estimated (J) and non-detects as estimated (UJ)

*The above control limits are **method requirements** for duplicate samples, regardless of the sample matrix type. However, it should be noted that Laboratory variability arising from the sub-sampling of non-homogenous soil samples is a common occurrence. Therefore, for **technical review purposes only**, Regional policy or project Data Quality Objectives (DQOs) may allow the use of less restrictive criteria (e.g., 35% RPD, 2x the CRQL) to be assessed against duplicate soil samples.

VI. Spike Sample Analysis

A. Review Items:

Cover Page, Form V-IN (Part A & B), Form XII-IN, instrument printouts, and raw data.

B. Objective:

The spiked sample analysis is designed to provide information about the effect of each sample matrix on the sample preparation procedures and the measurement methodology. Non-homogenous samples can impact the apparent method recovery. However, aqueous samples are generally homogenous and most soil samples are homogenous within a factor of two or three. If the spike is added to the sample prior to any distillation steps (e.g., cyanide), it is referred to as a spiked sample, pre-distillation spike, or Matrix Spike. If the spike is added to the sample after the completion of the distillation procedures, it is referred to as a post-distillation spike, or analytical spike.

C. Criteria:

1. Samples identified as field blanks or Performance Evaluation (PE) samples cannot be used for spiked sample analysis.

2. At least one spiked sample (pre-distillation) shall be prepared and analyzed from each group of samples with a similar matrix type (e.g., water or soil), or for each Sample Delivery Group (SDG).

3. When the pre-distillation spike recovery falls outside of the control limits and the sample result is < four times (4x) the spike added, a post-distillation spike shall be performed An aliquot of the remaining unspiked sample shall be spiked at 2x the indigenous level or 2x the Contract Required Quantitation Limit (CRQL), whichever is greater.

4. The spike Percent Recovery (%R) shall be within the established acceptance limits. However, spike recovery limits do not apply when the sample concentration is ≥4x the spike added. In such an event, the data shall be reported unflagged, even if the %R does not meet the acceptance criteria.

5. If the spiked sample analysis was performed on the same sample that was chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample". The average of the duplicate results cannot be used for the purpose of determining %R.

NOTE: The final spike concentrations required are presented in the method described in the Statement of Work (SOW).

D. Evaluation:

1. Verify using the Cover Page, Form VA-IN, Form XII-IN, and raw data that the appropriate number of required spiked samples were prepared and analyzed for the SDG.

2. Verify that a field blank or PE sample was not used for the spiked sample analysis.

3. Evaluate Form VA-IN and the raw data to verify that all pre-distillation spiked sample results fall within the established control limits. If not, verify that a post-distillation spike was prepared and analyzed.

4. Recalculate using the raw data, one or more of the %R using the following equation, and verify that the recalculated value agrees with the Laboratory-reported values on Forms V(A & B)-IN:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

NOTES: When the sample concentration is < Method Detection Limit (MDL), use SR = 0 only for the purposes of calculating the %R. The actual spiked sample results, sample results, and %R (positive or negative) shall still be reported on Form V(A & B)-IN.

For data obtained from the Contract Laboratory Program (CLP), the above criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the Laboratory's compliance with the above criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

NOTE: For a Matrix Spike that does not meet the technical criteria, apply the action to all samples of the same matrix, if the reviewer considers the samples sufficiently similar. The reviewer will need to exercise professional judgment in determining sample similarity. The reviewer should make use of all available data, including: site and sampling documentation (e.g., location and type of sample, descriptive data, soil classification); field test data (e.g., pH, Eh, conductivity, chlorine); and Laboratory data for other parameters [e.g., Total Suspended Solids (TSSs), Total Dissolved Solids (TDSs), Total Organic Carbon (TOC), alkalinity or buffering capacity, reactive sulfide, anions], in determining similarity. The reviewer should also use the sample data (e.g., similar concentrations of analytes) in determining similarity between samples in the SDG. The reviewer may determine that only some of the samples in the SDG are similar to the Matrix Spike sample, and that only these samples should be qualified. Or, the reviewer may determine that no samples are sufficiently similar to the sample used for the Matrix Spike, and thus that only the field sample used to prepare the Matrix Spike sample should be qualified.

1. If the appropriate number of Matrix Spike samples was not analyzed for each matrix using the correct frequency, use professional judgment to determine if the associated sample data should be qualified. The reviewer may need to obtain additional information from the Laboratory. Note the situation in the Data Review Narrative, and for CLP Project Officer (CLP PO) action.

2. If a field blank or PE sample was used for the spiked sample analysis, note this for CLP PO action. All of the other Quality Control (QC) data must then be carefully checked, and professional judgment exercised by the data reviewer when evaluating the data.

3. If the Matrix Spike recovery does not meet the evaluation criteria and a required post-distillation spike was not performed, note this for CLP PO action.

4. If the Matrix Spike %R is <30%, verify that a post-distillation spike was analyzed if required. If the post-distillation spike %R is <75% or is not performed, qualify sample results that are ≥MDL as estimated low (J-) and non-detects as unusable (R). If the post-distillation spike %R is ≥75%, qualify sample results that are ≥MDL as estimated (J) and non-detects as estimated (UJ).

5. If the Matrix Spike %R falls within the range of 30-74% and the sample results are ≥MDL, verify that a post-distillation spike was analyzed if required. If the %R for the post-distillation spike is also <75% or not performed, qualify the affected data as estimated low (J-). If the %R for the post-distillation spike is ≥75%, qualify the affected data as estimated (J).

6. If the Matrix Spike %R falls within the range of 30-74% and the sample results are non-detects, qualify the affected data as estimated (UJ).

7. If the Matrix Spike %R is >125% and the reported sample results are non-detects, the sample data should not be qualified.

8. If the Matrix Spike %R is >125% and the sample results are ≥MDL, verify that a post-distillation spike was analyzed if required. If the %R for the post-distillation spike is also >125% or is not performed, qualify the affected data as estimated high (J+). If the %R for the post-distillation spike is ≤125%, qualify the affected data as estimated (J).

9. Note the potential effects on the data due to out-of-control spiked sample results in the Data Review Narrative.

Table 34. Spike Sample Actions for Cyanide Analysis

Spike Sample Results	Action for Samples
Matrix Spike %R <30% Post-distillation spike %R <75%	Qualify affected results that are ≥MDL as estimated low (J-) Qualify affected non-detects as unusable (R)
Matrix Spike %R <30% Post-distillation spike %R ≥75%	Qualify affected results that are ≥MDL as estimated (J) Qualify affected non-detects as estimated (UJ)
Matrix Spike %R 30-74% Post-distillation spike %R <75%	Qualify affected results that are ≥MDL as estimated low (J-) Qualify affected non-detects as estimated (UJ)
Matrix Spike %R 30-74% Post-distillation spike %R ≥75%	Qualify affected results that are ≥MDL as estimated (J) Qualify affected non-detects as estimated (UJ)
Matrix Spike %R >125% Post-distillation spike %R >125%	Qualify affected results that are ≥MDL as estimated high (J+)
Matrix Spike %R >125% Post-distillation spike %R ≤125%	Qualify affected results that are ≥MDL as estimated (J)
Matrix Spike %R <30% No post-distillation spike performed	Qualify affected results that are ≥MDL as estimated low (J-) and affected non-detects as unusable (R)
Matrix Spike %R 30-74 No post-distillation spike performed	Qualify affected results that are ≥MDL as estimated low (J-) and affected non-detects as estimated (UJ)
Matrix Spike %R >125% No post-distillation spike performed	Qualify affected results that are ≥MDL as estimated high (J+) Non-detects are not qualified

VII. Field Duplicates

A. Review Items:

Form I-IN, instrument printouts, and raw data.

B. Objective:

Field duplicate samples may be collected and analyzed as an indication of overall precision. These analyses measure both field and Laboratory precision. The results, therefore, may have more variability than Laboratory duplicates that measure only Laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

C. Criteria:

There are no "required" review criteria for determining comparability of field duplicate analyses.

D. Evaluation:

Identify samples that are field duplicates using Traffic Report/Chain of Custody (TR/COC) documentation or sample field sheets. Compare the results reported for each sample and calculate the Relative Percent Difference (RPD), if appropriate.

E. Action:

Provide any evaluation of the field duplicates in the Data Review Narrative.

VIII. Overall Assessment

A. Review Items:

Entire data package, data review results, preparation logs, calibration standard logs, instrument logs, instrument printouts, and raw data (including any confirmation data).

B. Objective:

The objective is to ensure that the reported sample quantitation results are accurate. It is appropriate for the data reviewer to make professional judgments and express concerns, as well as to comment on the validity of the overall data for a Case. This is particularly appropriate when there are several Quality Control (QC) criteria that are outside of the specification parameters. The additive nature of QC factors that fall outside of specification parameters is difficult to assess in an objective manner, but the reviewer has a responsibility to inform the user concerning data quality and data limitations to assist that user in avoiding inappropriate use of the data, while not precluding any consideration of the data at all. If qualifiers other than those used in this document are necessary to describe or qualify the data, it is necessary to thoroughly document/explain the additional qualifiers used. The data reviewer would be greatly assisted in this endeavor if the acceptance or performance criteria were provided. The Inorganic Review Summary (see Appendix B) and supplementary documentation must be included with the review.

C. Criteria:

1. Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

2. Reported analyte concentrations must be quantitated according to the appropriate analytical method, as listed in the method.

D. Evaluation:

Examine the raw data to verify that the correct calculation of the sample results was reported by the Laboratory. Distillation logs, instrument printouts, strip charts, etc., should be compared to the reported sample results recorded on the appropriate Inorganic Summary Forms (Form I-IN through Form XV-IN).

1. Evaluate any technical problems not previously addressed.

2. Examine the raw data for any anomalies (e.g., baseline shifts, negative absorbance, omissions, illegibility, etc.).

3 Verify that the appropriate methods and amounts were used to prepare samples for analysis. If reduced volumes were used, verify that the Laboratory had received Contract Laboratory Program Project Officer (CLP PO) approval for the use of the reduced volume.

4. Verify that there were no transcription or reduction errors [e.g., dilutions, Percent Solids (%S), sample weights, etc.] on one or more samples.

5. Verify that results fall within the calibrated range for cyanide.

6. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the Quality Assurance Project Plan (QAPP), focusing specifically on the acceptance or performance criteria, the Standard Operating Procedure(s) (SOPs), and communication with user concerning the intended use and desired quality of these data.

E. Action:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC criteria previously discussed.

2. Write a brief Data Review Narrative to give the user an indication of the analytical limitations of the data. Note any discrepancies between the data and the SDG Narrative for CLP PO action. If sufficient information on the intended use and required quality of the data are available, the reviewer should include an assessment of the data usability within the given context.

3. If any discrepancies are found, the Laboratory may be contacted by the Region's designated representative to obtain additional information for resolution. If a discrepancy remains unresolved, the reviewer may determine that qualification of the data is warranted.

Calculations for Cyanide

Aqueous Sample Concentration (Manual):

$$\text{CN Concentration } (\mu g/L) = \frac{A \times 1000 \text{ mL/L}}{B} \times \frac{50 \text{ mL}}{C}$$

Where,

A = µg cyanide read from standard curve (per 250 mL)

B = mL of original sample for distillation (see Exhibit D - Analytical Methods for Total Cyanide Analysis, Section 10.2.2.1.1)

C = mL taken for colorimetric analysis (see Exhibit D - Analytical Methods for Total Cyanide Analysis, Section 10.3.1.1)

50 mL = Standard volume taken for colorimetric determination (see Exhibit D - Analytical Methods for Total Cyanide Analysis, Section 10.3.1.1)

1000 mL/L = Conversion mL to L

NOTE: The minimum value that can be substituted for A is the Method Detection Limit (MDL) value adjusted for volume.

Soil Sample Concentration (Manual):

$$\text{CN Concentration (mg/kg)} = \frac{A \times \frac{50 \text{ mL}}{B}}{C \times \frac{\% \text{ solids}}{100}}$$

Where,

A = µg cyanide read from standard curve (per 250 mL)

B = mL of distillate taken for colorimetric determination (see Exhibit D - Analytical Methods for Total Cyanide Analysis, Section 10.3.1.1)

C = Wet weight of original sample in g (see Exhibit D - Analytical Methods for Total Cyanide Analysis, Section 10.2.4.1.1)

50 mL = Standard volume taken for colorimetric determination (see Exhibit D - Analytical Methods for Total Cyanide Analysis, Section 10.3.1.1)

% solids = % Solids (see Exhibit D - Introduction to Analytical Methods, Section 1.6)

Soil Sample Concentration (Semi-automated):

$$\text{CN Concentration (mg/kg)} = \frac{A \times .25}{C \times \frac{\%\ \text{solids}}{100}}$$

Where,

A = µg/L determined from standard curve

C = Wet weight of original sample in g (see Exhibit D - Analytical Methods for Total Cyanide Analysis, Section 10.2.4.1.1)

.25 = Conversion factor for distillate final volume (see Exhibit D - Analytical Methods for Total Cyanide Analysis, Section 10.2.2.1.5)
% Solids (see Exhibit D - Introduction to Analytical Methods, Section 1.6)

% solids = % Solids (see Exhibit D - Introduction to Analytical Methods, Section 1.6)

NOTE: The minimum value that can be substituted for A is the MDL value.

Calculations for Midi Distillation (Cyanide) of Waters and Soils:

Aqueous Sample Concentration (Midi):

$$\text{CN Concentration (µg/L)} = \frac{A \times D \times F}{B}$$

Where,

A = µg/L cyanide of sample from regression analysis

B = Volume of original sample for distillation (0.050 L) (see Exhibit D - Analytical Methods for Total Cyanide Analysis, Section 10.2.3.1.2)

D = Any Dilution Factor (DF) necessary to bracket sample value within standard values

F = Sample receiving solution volume (0.050 L)

NOTE: The minimum value that can be substituted for A is the MDL value.

Soil Sample Concentration (Midi):

$$\text{CN Concentration (mg/kg)} = \frac{A \times D \times F}{B \times E}$$

Where,

A = µg/L Cyanide of sample from regression analysis curve

B = Wet weight of original sample (see Exhibit D - Analytical Methods for Total Cyanide Analysis, Section 10.2.4.2.2)

D = Any dilution factor necessary to bracket sample value within standard values

E = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)

F = Sample receiving solution volume (0.050 L)

NOTE: The minimum value that can be substituted for A is the MDL value.

Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation:

To calculate the adjusted aqueous MDL or adjusted aqueous CRQL for the manual colorimetric method, multiply the MDL (µg/L) or CRQL (µg/L) by 0.25 and substitute the result for the "A" term in the appropriate equation above. To calculate the adjusted aqueous MDL or adjusted aqueous CRQL for all other methods, follow the instructions in Exhibit D - Data Analysis and Calculations, Section 11.1.1, or substitute the MDL (µg/L) or CRQL (µg/L) for the "A" term in the appropriate equation above.

The adjusted soil MDL or adjusted soil CRQL for all methods shall be calculated as follows:

$$\text{Adjusted Concentration (mg/kg)} = C \times \frac{W_M}{W_R} \times \frac{1}{S}$$

Where,

C = MDL or CRQL concentration (mg/kg)

W_M = Minimum method required wet sample weight (g)

W_R = Reported wet sample weight (g)

S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)

NOTE: For the midi-distillation, multiply the adjusted concentration value (mg/kg) obtained in the appropriate equation above by any applicable DF.

APPENDIX A: GLOSSARY

Analyte -- The element of interest, ion, or parameter an analysis seeks to determine.

Analytical Services Branch (ASB) -- Directs the Contract Laboratory Program (CLP) from within the Office of Superfund Remediation and Technical Innovation (OSRTI) in the Office of Solid Waste and Emergency Response (OSWER).

Analytical Sample -- Any solution or media introduced into an instrument on which an analysis is performed excluding instrument calibration, Initial Calibration Verification (ICV), Initial Calibration Blank (ICB), Continuing Calibration Verification (CCV), and Continuing Calibration Blank (CCB). Note that the following are all defined as analytical samples: undiluted and diluted samples (USEPA and non-USEPA); Matrix Spike samples; duplicate samples; serial dilution samples, analytical (post-digestion/post-distillation) spike samples; Interference Check Samples (ICSs); Contract Required Quantitation Limit (CRQL) Check Standards (CRIs); Laboratory Fortified Blanks (LFBs); Laboratory Control Samples (LCSs); Preparation Blanks (PBs), and Linear Range Samples (LRSs).

Associated Samples -- Any sample related to a particular Quality Control (QC) analysis. For example, for Initial Calibration Verification (ICV), all samples run under the same calibration curve. For duplicates, all Sample Delivery Group (SDG) samples digested/distilled of the same matrix.

Blank -- A sample designed to assess specific sources of contamination. See individual definitions for types of blanks.

Calibration -- The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards are to be prepared using the same type of reagents or concentration of acids as used in the sample preparation.

Calibration Blank -- A blank solution containing all of the reagents in the same concentration as those used in the analytical sample preparation. This blank is not subject to the preparation method.

Calibration Curve -- A plot of instrument response versus concentration of standards.

Calibration Standards -- A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). The solutions may or may not be subjected to the preparation method, but contain the same matrix (i.e., the same amount of reagents and/or preservatives) as the sample preparations to be analyzed.

Case -- A finite, usually predetermined number of samples collected over a given time period from a particular site. Case numbers are assigned by the Sample Management Office (SMO). A Case consists of one or more Sample Delivery Groups (SDGs).

Continuing Calibration Blank (CCB) -- A reagent water sample that is run every ten samples and designed to detect any carryover contamination.

Contract Compliance Screening (CCS) -- A screening of electronic and hardcopy data deliverables for completeness and compliance with the contract. This screening is performed under USEPA direction by the Contract Laboratory Program (CLP) Sample Management Office (SMO) contractor.

Continuing Calibration Verification (CCV) -- A single parameter or multi-parameter standard solution prepared by the analyst and used to verify the stability of the instrument calibration with time, and the

instrument performance during the analysis of samples. The CCV can be one of the calibration standards. However, all parameters being measured by the particular system must be represented in this standard and the standard must have the same matrix (i.e., the same amount of reagents and/or preservatives) as the samples. The CCV should have a concentration in the middle of the calibration range and shall be run every 10 analytical samples or every two hours, whichever is more frequent.

Contract Laboratory Program (CLP) -- Supports the USEPA's Superfund effort by providing a range of state-of-the-art chemical analytical services of known quality. This program is directed by the Analytical Services Branch (ASB) of the Office of Superfund Remediation and Technical Innovation (OSRTI) of USEPA.

Contract Laboratory Program Project Officer (CLP PO) -- The Regional USEPA official responsible for monitoring Laboratory performance and/or requesting analytical data or services from a CLP Laboratory.

Contract Required Quantitation Limit (CRQL) -- Minimum level of quantitation acceptable under the contract Statement of Work (SOW).

CRQL Check Standard (CRI) -- A single parameter or multi-parameter standard solution prepared at the Contract Required Quantitation Limit (CRQL) and used to verify the instrument calibration at low levels.

Duplicate -- A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

Field Blank -- Any sample that is submitted from the field and identified as a blank. A field blank is used to check for cross-contamination during sample collection, sample shipment, and in the Laboratory. A field blank includes trip blanks, rinsate blanks, bottle blanks, equipment blanks, preservative blanks, decontamination blanks, etc.

Field Duplicate -- A duplicate sample generated in the field, not in the Laboratory.

Holding Time -- The maximum amount of time samples may be held before they are processed.

Contractual -- The maximum amount of time that the Contract Laboratory Program (CLP) Laboratory may hold the samples from the sample receipt date until analysis and still be in compliance with the terms of the contract, as specified in the CLP Analytical Services Statement of Work (SOW). These times are the same or less than technical holding times to allow for sample packaging and shipping.

Technical -- The maximum amount of time that samples may be held from the collection date until analysis.

Initial Calibration -- Analysis of analytical standards for a series of different specified concentrations to define the quantitative response, linearity, and dynamic range of the instrument to target analytes.

Initial Calibration Blank (ICB) -- The first blank standard run to confirm the calibration curve.

Initial Calibration Verification (ICV) -- Solution(s) prepared from stock standard solutions, metals, or salts obtained from a source separate from that utilized to prepare the calibration standards. The ICV is used to verify the concentration of the calibration standards and the adequacy of the instrument calibration. The ICV should be traceable to National Institute of Standards and Technology (NIST) or other certified standard sources when USEPA ICV solutions are not available.

Internal Standard -- A non-target element added to a sample at a known concentration after preparation but prior to analysis. Instrument responses to internal standards are monitored as a means of assessing overall instrument performance.

Interference Check Sample (ICS) -- Verifies the contract Laboratory's ability to overcome interferences typical of those found in samples.

Laboratory Control Sample (LCS) -- A control sample of known composition. LCSs are processed using the same sample preparation, reagents, and analytical methods employed for the USEPA samples received.

Linear Range, Linear Dynamic Range -- The concentration range over which the instrument response remains linear.

Matrix -- The predominant material of which the sample to be analyzed is composed. For the purposes of this document, the matrices are water and soil.

Matrix Spike -- Introduction of a known concentration of analyte into a sample to provide information about the effect of the sample matrix on the digestion and measurement methodology (also identified as a pre-distillation/digestion spike).

Method Detection Limit (MDL) -- The concentration of a target parameter that, when a sample is processed through the complete method, produces a signal with 99% probability that it is different from the blank. For seven replicates of the sample, the mean value must be 3.14s above the blank, where "s" is the standard deviation of the seven replicates.

Narrative (SDG Narrative) -- Portion of the data package which includes Laboratory, contract, Case, Sample Number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution.

Office of Solid Waste and Emergency Response (OSWER) – The USEPA office that provides policy, guidance, and direction for the USEPA's solid waste and emergency response programs, including Superfund.

Percent Difference (%D) -- As used in this document and the Statement of Work (SOW), is used to compare two values. The difference between the two values divided by one of the values.

Performance Evaluation (PE) Sample -- A sample of known composition provided by USEPA for contractor analysis. Used by USEPA to evaluate Contractor performance.

Post Digestion Spike -- The addition of a known amount of standard after digestion or distillation (also identified as an analytical spike).

Preparation Blank -- An analytical control that contains reagent water and reagents, which is carried through the entire preparation and analytical procedure.

Relative Percent Difference (RPD) -- As used in this document and the Statement of Work (SOW) to compare two values, the RPD is based on the mean of the two values, and is reported as an absolute value (i.e., always expressed as a positive number or zero).

Regional Sample Control Center (RSCC) -- In USEPA Regions, coordinates sampling efforts and serves as the central point-of-contact for sampling questions and problems. Also assists in coordinating the level of Regional sampling activities to correspond with the monthly projected demand for analytical services.

Relative Standard Deviation (RSD) -- As used in this document and the Statement of Work (SOW), the mean divided by the standard deviation, expressed as a percentage.

Sample -- A single, discrete portion of material to be analyzed, which is contained in single or multiple containers and identified by a unique Sample Number.

Sample Delivery Group (SDG) -- A unit within a sample Case that is used to identify a group of samples for delivery. An SDG is defined by the following, whichever is most frequent:

a. Each Case of field samples received; or
b. Each 20 field samples [excluding Performance Evaluation (PE) samples] within a Case; or
c. Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).

In addition, all samples and/or sample fractions assigned to an SDG must be scheduled under the same contractual turnaround time. Preliminary Results have **no impact** on defining the SDG. Samples may be assigned to SDGs by matrix (i.e., all soil samples in one SDG, all water samples in another) at the discretion of the Laboratory.

Sample Management Office (SMO) -- A contractor-operated facility operated under the SMO contract, awarded and administered by the USEPA. Provides necessary management, operations, and administrative support to the Contract Laboratory Program (CLP).

Serial Dilution -- The dilution of a sample by a factor of five. When corrected by the Dilution Factor (DF), the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents [Inductively Coupled Plasma (ICP) only].

Statement of Work (SOW) -- A document which specifies how Laboratories analyze samples under a particular Contract Laboratory Program (CLP) analytical program.

Tune -- Analysis of a solution containing a range of isotope masses to establish Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) mass-scale accuracy, mass resolution, and precision prior to calibration.

APPENDIX B:
INORGANIC DATA REVIEW SUMMARY

CASE NO._____ SITE_____

LABORATORY_____ NO. OF SAMPLES/MATRIX_____

SDG NO._____ SOW NO._____ REGION_____

REVIEWER NAME_____ COMPLETION DATE_____

CLP PO: ACTION_____ FYI_____

REVIEW CRITERIA	METHOD/ANALYTE			
	ICP-AES	ICP-MS	Mercury	Cyanide
1. Preservation/Holding Time	_____	_____	_____	_____
2. Calibration	_____	_____	_____	_____
3. Blanks	_____	_____	_____	_____
4. Interference Check Sample	_____	_____		
5. Laboratory Control Sample	_____	_____	_____	_____
6. Duplicate Sample Analysis	_____	_____	_____	_____
7. Spike Sample Analysis	_____	_____	_____	_____
8. ICP Serial Dilution	_____	_____		
9 ICP-MS Tune Analysis		_____		
10. ICP-MS Internal Standards		_____		
11. Field Duplicates	_____	_____	_____	_____
12. Overall Assessment	_____	_____	_____	_____

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USEPA CONTRACT LABORATORY PROGRAM
NATIONAL FUNCTIONAL GUIDELINES
FOR
LOW CONCENTRATION ORGANIC DATA REVIEW

Final

Office of Emergency and Remedial Response (OERR)
U.S. Environmental Protection Agency (USEPA)
Washington, DC 20460

NOTICE

The polices and procedures set forth here are intended as guidance to the United States Environmental Protection Agency (hereafter referred to as USEPA) and other governmental employees. They do not constitute rule making by the USEPA, and may not be relied on to create a substantive or procedural right enforceable by any other person. The Government may take action that is at variance with the policies and procedures in this manual.

This document can be obtained from the USEPA's Contract Laboratory Program (CLP) Web site at:

http://www.epa.gov/superfund/programs/clp/guidance.htm

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Acronyms

BFB	Bromofluorobenzene
CCS	Contract Compliance Screening
CLP	Contract Laboratory Program
CLP PO	Contract Laboratory Program Project Officer
CRQL	Contract Required Quantitation Limit
DCB	Decachlorobiphenyl
DFTPP	Decafluorotriphenylphosphine
DMC	Deuterated Monitoring Compound
DQA	Data Quality Assessment
GC	Gas Chromatograph
GC/ECD	Gas Chromatograph/Electron Capture Detector
GC/MS	Gas Chromatograph/Mass Spectrometer
LCS	Laboratory Control Sample
%D	Percent Difference
PCBs	Polychlorinated Biphenyls
PE	Performance Evaluation
PEM	Performance Evaluation Mixture
QA	Quality Assurance
QAC	Quality Assurance Coordinator
QAPP	Quality Assurance Project Plan
QC	Quality Control
RIC	Reconstructed Ion Chromatogram
RPD	Relative Percent Difference
RRF	Relative Response Factor
RRT	Relative Retention Time
RSCC	Regional Sample Control Center
RSD	Relative Standard Deviation
SAP	Sampling and Analysis Plan
SDG	Sample Delivery Group
SMO	Sample Management Office
SOP	Standard Operating Procedure
SOW	Statement of Work
TCX	Tetrachloro-m-xylene
TIC	Tentatively Identified Compound
USEPA	United States Environmental Protection Agency
VTSR	Validated Time of Sample Receipt

INTRODUCTION

This document is designed to offer the data reviewer guidance in determining the usability of analytical data generated through the USEPA Contract Laboratory Program's (CLP) Low Concentration Organic Statement of Work (SOW), OLC03.X (OLC03.2 and any future editorial revisions of OLC03.2). The guidance is somewhat limited in scope and is intended to be used as an aid in the formal technical review process. It should not be used to establish specific contract compliance (use of this document to evaluate data generated under Organic SOWs other than OLC03.X is cautioned). Definitive guidance is provided where performance should be fully under a laboratory's control (e.g., blanks, calibration standards, instrument performance checks), while general guidance is provided for evaluating subjective data that is affected by the site conditions.

The guidelines presented in the document will aid the data reviewer in establishing (a) if data meets the specific technical and quality control criteria established in the SOW, and (b) the usability and extent of bias of any data not meeting the specific technical and quality criteria established in the SOW. It must be understood by the reviewer that acceptance of data not meeting technical requirements is based upon many factors, including, but not limited to, site-specific technical requirements, need to facilitate the progress of specific projects, and availability for re-sampling. To make judgements at this level requires the reviewer to have a complete understanding of the intended use of the data. The reviewer is strongly encouraged to establish a dialogue with the user, prior to, and after data review, to discuss usability issues and to answer questions regarding the review. It should also be understood that in all cases, data which do not meet specified criteria are never to be fully acceptable without qualification.

The data reviewer should note that while this document is to be used as an aid in the formal data review process, other sources of guidance and information, as well as professional judgement, should also be used to determine the ultimate usability of data, especially in those cases where all data does not meet specific technical criteria. The reviewer should also be aware that minor modifications to the analytical methods may be made through the SOW's "flexibility clause" to meet site-specific requirements, and that these modifications could affect certain validation criteria such as the Contract Required Quantitation Limits (CRQL), initial and continuing calibration levels, and Target Compound Lists (TCLs). A copy of any modification request made to the analytical method should be included in the data package by the laboratory.

DATA QUALIFIER DEFINITIONS

The following definitions provide brief explanations of the national qualifiers assigned to results in the data review process. If the Regions choose to use additional qualifiers, a complete explanation of those qualifiers should accompany the data review.

U	The analyte was analyzed for, but was not detected above the level of the adjusted Contract Required Quantitation Limit (CRQL) for sample and method.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
N	The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification".
NJ	The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.
UJ	The analyte was not detected above the adjusted CRQL. However, the reported adjusted CRQL is approximate and may be inaccurate or imprecise.
R	The sample results are unusable. The analyte may or may not be present in the sample.

DATA PACKAGE INSPECTION

For data obtained through the Contract Laboratory Program (CLP), the Data Assessment Tool (DAT) report is a useful tool in the data review process. The DAT report incorporates Contract Compliance Screening (CCS) and Computer-Aided Data Review and Evaluation (CADRE) results and is transmitted via the Data Assessment Rapid Transmittal (DART) system. For more information about DAT, please refer to the following USEPA Web site:

http://www.epa.gov/superfund/programs/clp/dat.htm

The DAT report will identify any missing and/or incorrect information in the data package. The CLP laboratory may submit a reconciliation package for any missing items or to correct data.

To obtain the DAT report and/or the reconciliation package, or if there are any other concerns regarding the data package, contact the CLP PO from the Region where the samples were taken.

http://www.epa.gov/superfund/programs/clp/contact.htm

PRELIMINARY REVIEW

This document is for the review of analytical data generated through the USEPA CLP Low Concentration Organic Statement of (SOW), OLC03.X (OLC03.2 and any future editorial revisions of OLC03.2). To use this document effectively, the reviewer should have an understanding of the analytical method used and a general overview of the Sample Delivery Group (SDG) or sample Case at hand. The exact number of samples, their assigned numbers, their matrix, and the number of laboratories involved in their analysis are essential information.

It is suggested that an initial review of the data package be performed taking into consideration all information specific to the data package (e.g., flexible analysis approval notices, traffic reports, SDG narratives, etc.).

The reviewer should also have a copy of the Quality Assurance Project Plan (QAPP) or similar document for the project for which samples were analyzed. The reviewer should contact the appropriate Regional CLP PO to obtain copies of the QAPP and relevant site information. This information is necessary in determining the final usability of the analytical data.

Sample cases (SDGs) routinely have unique samples which require special attention from the reviewer. These include field blanks, field duplicates, and performance evaluation samples which must be identified. The sampling records (e.g., Traffic Reports/Chain of Custody, field logs and/or contractor tables) should identify:

1. The Region where the samples were taken, and

2. The complete list of samples with information on:

    a. sample matrix,
    b. field blanks,
    c. field duplicates,
    d. field spikes,
    e. Quality Control (QC) audit samples,
    f. shipping dates,
    g. preservatives, and
    h. laboratories involved.

The Chain-of-Custody record includes sample descriptions and date(s) of sampling. The reviewer must consider lag times between sampling and start of analysis when assessing technical sample holding times.

The laboratory's SDG Narrative is another source of general information. Notable problems with matrices, insufficient sample volume for analysis or re-analysis, samples received in broken containers, preservation, and unusual events should be documented in the SDG Narrative. The reviewer should also inspect any telephone or other communication logs detailing any discussions of sample preparation and/or analysis issues between the laboratory, CLP Sample Management Office (SMO) and the USEPA Region.

DATA REVIEW NARRATIVE

A Data Review Narrative, including the Organic Data Review Summary form, (see Appendix B) must accompany the laboratory data forwarded to the intended data recipient (client) or user to promote communications. A copy of the Data Review Narrative should be submitted to the Contract Laboratory Program Project Officer (CLP PO) assigned oversight responsibility for the laboratory producing the data.

The Data Review Narrative should include comments that clearly identify the problems associated with a Case or SDG and state the limitations of the data. Documentation should include the sample number, analytical method, extent of the problem, and assigned qualifiers.

VOLATILE DATA REVIEW

The data requirements to be checked are listed below:

I. Preservation

II. Gas Chromatograph/Mass Spectrometer (GC/MS) Instrument Performance Check

III. Initial Calibration

IV. Continuing Calibration

V. Blanks

VI. Deuterated Monitoring Compounds (DMCs)

VII. Matrix Spikes/Matrix Spike Duplicates (MS/MSDs)

VIII. Regional Quality Assurance (QA) and Quality Control (QC)

IX. Internal Standards

X. Target Compound Identification

XI. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

XII. Tentatively Identified Compounds (TICs)

XIII. System Performance

XIV. Overall Assessment of Data

I. Preservation

A. Review Items:

Form I LCV-1 and Form I LCV-2, USEPA Sample Traffic Report (TR) and/or Chain-of-Custody, raw data, and the Sample Delivery Group (SDG) Narrative checking for:

1. pH
2. Sample temperature
3. Holding time
4. Other sample conditions (e.g., headspace)

B. Objective:

The objective is to ascertain the validity of the analytical results based on sample condition (i.e., preservation, temperature, headspace) and the holding time of the sample from the time of collection to the time of analysis.

C. Criteria:

The technical holding time criterion for water samples is that for volatile compounds in cooled (4°C ±2°C) water samples that are acid-preserved (with HCl to pH 2 or below), the maximum holding time is 14 days from sample collection.

D. Evaluation:

Technical holding times are established by comparing the sampling dates on the TR with the dates of analysis on Form I LCV-1, Form I LCV-2, and the raw data. Information contained in the complete SDG file should also be considered in the determination of holding times. Verify that the analysis dates on the Form Is and the raw data/SDG file are identical. Review the SDG Narrative to determine if samples were preserved. If there is no indication in the SDG Narrative or the sample records that there was a problem with the samples, then the integrity of samples can be assumed to be acceptable. If it is indicated that there were problems with the samples, then the integrity of the sample may have been compromised and professional judgment should be used to evaluate the effect of the problem on the sample results.

E. Action:

1. Qualify sample results using preservation and technical holding time information as follows:

    a. If there is no evidence that the samples were properly preserved, but were analyzed within the technical holding time (14 days from sample collection), qualify all positive results for non-halogenated compounds (including ketones and aromatics) with “J” and sample quantitation limits as unusable (R).

    b. If there is no evidence that the samples were properly preserved, but were analyzed within the technical holding time (14 days from sample collection), qualify all positive results for halogenated compounds with “J” and sample quantitation limits with “UJ”.

c. If there is no evidence that the samples were properly preserved, and the samples were analyzed outside of the technical holding time (14 days from sample collection), qualify positive results for all volatile compounds with "J" and quantitation limits as unusable (R).

d. If the samples were properly preserved, but were analyzed outside of the technical holding time (14 days from sample collection), qualify positive results with "J" and sample quantitation limits as unusable (R).

Table 1. Holding Time Actions for Volatile Analyses

Acid Preserved	Criteria	Action
No	# 14 days	Non-halogenated (including ketones & aromatics): Positives "J" Quantitation Limits "R"
		Halogenated Compounds: Positives "J" Quantitation Limits "UJ"
No	> 14 days	All Compounds: Positives "J" Quantitation Limits "R"
Yes	> 14 days	All Compounds: Positives "J" Quantitation Limits "R"

2. Whenever possible, the reviewer should comment on the effect of the holding time exceedance on the resulting data in the Data Review Narrative.

3. When technical holding times are exceeded, this should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

II. GC/MS Instrument Performance Check

A. Review Items:

Form V LCV, BFB mass spectra, and mass listing.

B. Objective:

Gas Chromatograph/Mass Spectrometer (GC/MS) instrument performance checks are performed to ensure mass resolution, identification, and to some degree, sensitivity. These criteria are not sample-specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.

C. Criteria:

50 ng of the instrument performance check solution must be injected at the beginning of each 12-hour period during which samples or standards are analyzed. The instrument performance check, bromofluorobenzene (BFB) for volatile analysis, must meet the ion abundance criteria listed in Table 2.

Table 2. Ion Abundance Criteria For Bromofluorobenzene (BFB)

m/z	ION ABUNDANCE CRITERIA
50	8.0 - 40.0% of m/z 95
75	30.0 - 66.0% of m/z 95
95	Base peak, 100% relative abundance
96	5.0 - 9.0% of m/z 95
173	Less than 2.0% of m/z 174
174	50.0 - 120.0% of m/z 95
175	4.0-9.0% of mass 174
176	93.0 - 101.0% of m/z 174
177	5.0 - 9.0% of m/z 176

NOTE: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95.

D. Evaluation:

1. Compare the data presented for each Instrument Performance Check (Form V LCV) with each mass listing submitted to ensure the following:

    a. Form V LCV is present and completed for each 12-hour period during which samples were analyzed.

b. The laboratory has not made transcription errors between the data and the form. If there are major differences between the mass listing and the Form Vs, a more in-depth review of the data is required. This may include obtaining and reviewing additional information from the laboratory.

c. The appropriate number of significant figures has been reported (number of significant figures given for each ion in the ion abundance criteria column) and that rounding is correct.

d. The laboratory has not made calculation errors.

2. Verify from the raw data (mass spectral listing) that the mass assignment is correct and that the mass listing is normalized to m/z 95.

3. Verify that the ion abundance criteria was met. The criteria for m/z 173, 175, 176, and 177 are calculated by normalizing to the specified m/z.

4. If possible, verify that spectra were generated using appropriate background subtraction techniques. Since the BFB spectrum is obtained from chromatographic peaks that should be free from coelution problems, background subtraction should be done in accordance with the following procedure:

   a. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.

   b. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not subtract the BFB peak as part of the background.

NOTE: All mass spectrometer instrument conditions must be identical to those used during the sample analysis. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the method specifications are contrary to the Quality Assurance (QA) objectives, and are therefore unacceptable.

E. Action:

1. If the laboratory has made minor transcription errors which do not significantly affect the data, the data reviewer should make the necessary corrections on a copy of the form.

2. If the laboratory has failed to provide the correct forms or has made significant transcription or calculation errors, the Region's designated representative should contact the laboratory and request corrected data. If the information is not available, the reviewer must use professional judgment to assess the data. The laboratory's Contract Laboratory Program Project Officer (CLP PO) should be notified.

3. If mass assignment is in error (e.g., m/z 96 is indicated as the base peak rather than m/z 95), classify all associated data as unusable (R).

4. If ion abundance criteria are not met, professional judgment may be applied to determine to what extent the data may be utilized. When applying professional judgment to this topic, the most important factors to consider are the empirical results that are relatively

insensitive to location on the chromatographic profile and the type of instrumentation. Therefore, the critical ion abundance criteria for BFB are the m/z 95/96, 174/175, 174/176, and 176/177 ratios. The relative abundances of m/z 50 and 75 are of lower importance. This issue is more critical for Tentatively Identified Compounds (TICs) than for target analytes.

5. Decisions to use analytical data associated with BFB instrument performance checks not meeting contract requirements should be clearly noted on the Data Review Narrative.

6. If the reviewer has reason to believe that instrument performance check criteria were achieved using techniques other than those described in Volatile Section II.D.4, additional information on the instrument performance checks should be obtained. If the techniques employed are found to be at variance with the contract requirements, the performance and procedures of the laboratory may merit evaluation. Concerns or questions regarding laboratory performance should be noted for CLP PO action. For example, if the reviewer has reason to believe that an inappropriate technique was used to obtain background subtraction (such as background subtracting from the solvent front or from another region of the chromatogram rather than from the BFB peak), then this should be noted for CLP PO action.

III. Initial Calibration

A. Review Items:

Form VI LCV-1, Form VI LCV-2, Form VI LCV-3, quantitation reports, and chromatograms.

B. Objective:

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for compounds on the volatile Target Compound List (TCL). Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run and of producing a linear calibration curve.

C. Criteria:

1. Initial calibration standards containing both volatile target compounds and Deuterated Monitoring Compounds (DMCs) are analyzed at concentrations of 0.50, 1.0, 5.0, 10.0, and 25.0 µg/L for non-ketones, and 5.0, 10.0, 25.0, 50.0, and 125 µg/L for ketones at the beginning of each analytical sequence, or as necessary if the calibration verification acceptance criteria are not met. The initial calibration (and any associated samples and blanks) must be analyzed within 12 hours of the associated instrument performance check.

2. Initial calibration Relative Response Factors (RRFs) for the volatile target compounds and DMCs listed in Table 3 must be greater than or equal to 0.01. The RRF for all other volatile target compounds and DMCs must be greater than or equal to 0.05.

3. The Percent Relative Standard Deviation (%RSD) of the initial calibration RRFs must be less than or equal to 50.0% for the volatile target compounds and DMCs listed in Table 3. The %RSD for all other volatile target compounds and DMCs must be less than or equal to 30.0%.

NOTE: The flexibility clause in the method may impact some of the criteria above. A copy of the flexibility clause should be present in the Sample Delivery Group (SDG). Refer to the Contract Laboratory Program (CLP) home page at http://www.epa.gov/superfund/programs/clp/ for the specific requirements.

D. Evaluation:

1. Verify that the correct concentrations of standards were used for the initial calibration (i.e., 0.50 1.0, 5.0, 10.0, and 25.0 µg/L for non-ketones, and 5.0, 10.0, 25.0, 50.0, and 125 µg/L for ketones).

2. If any sample results were calculated using an initial calibration standard, verify that the correct standard (i.e., 5 .0 µg/L for non-ketones, and 25.0 µg/L for ketones) was used for calculating sample results and the samples were analyzed within 12 hours of the associated instrument performance check.

3. Evaluate the initial calibration Relative Response Factors (RRFs) and the Mean Relative Response Factor (RRF) for all volatile target compounds and DMCs:

a. Check and recalculate the RRFs and $\overline{RRF}$ for at least one volatile target compound associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

b. Verify that for the volatile target compounds and DMCs listed in Table 3, the initial calibration RRFs are greater than or equal to 0.010, and for all other volatile target compounds and DMCs, RRFs are greater than or equal to 0.05.

Table 3. Volatile Compounds Exhibiting Poor Response

Volatile Compounds	
Acetone	1,2-Dichloropropane
2-Butanone	1,2-Dibromo-3-chloropropane
Carbon Disulfide	4-Methyl-2-pentanone
Chloroethane	2-Hexanone
Chloromethane	1,2-Dichloropropane-d6 (DMC)
Cyclohexane	2-Hexanone-d5 (DMC)
Chloroethane-d5 (DMC)	2-Butanone-d5 (DMC)

4. Evaluate the %RSD for all volatile target compounds and DMCs:

   a. Check and recalculate the %RSD for one or more volatile target compound(s). Verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. If the %RSD is greater than 50.0% for the volatile target compounds and DMCs listed in Table 3 and greater than 30.0% for all other volatile target compounds and DMCs, then the reviewer should use professional judgment to determine the need to check the points on the curve for the cause of the non-linearity. This is checked by eliminating either the high point or the low point and recalculating the %RSD (see Volatile Section III.E.2).

5. If errors are detected in the calculations of either the RRFs or the %RSD, perform a more comprehensive recalculation.

E. Action:

1. All volatile target compounds, including the "poor performers" listed in Table 3, will be qualified using the following criteria:

   a. If any of the volatile target compounds listed in Table 3 has %RSD greater than 50.0%, qualify positive results with "J", and non-detected compounds using professional judgment (see Item 2 below).

b. For all other volatile target compounds, if %RSD is greater than 30.0%, qualify positive results with "J", and non-detected compounds using professional judgment (see Item 2 below).

c. If any volatile target compound has an RRF value less than the minimum criterion (0.01 for the "poor performers" listed in Table 3, and 0.05 for all other volatile compounds), use professional judgment for positive results based on mass spectral identification to qualify the data as "J" or unusable (R).

d. If any volatile target compound has an RRF value less than the minimum criterion (0.01 for the "poor performers" listed in Table 3, and 0.05 for all other volatile compounds), qualify non-detected compounds as unusable (R).

e. No action is taken on the DMC %RSD and RRF data alone. However, using professional judgment and following the guidelines in Item 2 below, the data reviewer may use the DMC %RSD and RRF data in conjunction with the DMC recoveries to determine the need for qualification of data.

2. At the reviewer's discretion, and based on the project-specific data quality objectives, a more in-depth review may be considered using the following guidelines:

   a. If any volatile target compound has a %RSD greater than the maximum criterion (50.0% for the "poor performers" and 30.0% for all other volatile compounds), and if eliminating either the high or the low point of the curve does not restore the %RSD to less than or equal to the required maximum:

      i. Qualify positive results for that compound(s) with "J".

      ii. Qualify non-detected volatile target compounds using professional judgment.

   b. If the high point of the curve is outside of the linearity criteria (e.g., due to saturation):

      i. No qualifiers are required for positive results in the linear portion of the curve.

      ii. Qualify positive results outside of the linear portion of the curve with a "J".

      iii. No qualifiers are needed for volatile target compounds that were not detected.

   c. If the low end of the curve is outside of the linearity criteria:

      i. No qualifiers are required for positive results in the linear portion of the curve.

      ii. Qualify low level positive results in the area of non-linearity with a "J".

      iii. For non-detected volatile compounds use the lowest point of the valid curve to determine the new quantitation limit.

3. If the laboratory has failed to provide adequate calibration information, the Region's designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

4. Whenever possible, the potential effects on the data due to calibration criteria exceedance should be noted in the Data Review Narrative.

5. If calibration criteria are grossly exceeded, this should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

Table 4. Initial Calibration Actions for Volatiles Analyses

Criteria	Action
%RSD > 50.0 (poor performers) %RSD > 30.0 (all other target compounds)	Positives "J" Non-detects: Professional Judgment
RRF < 0.01 (poor performers) RRF < 0.05 (all other target compounds)	Positives "J" or "R" (based on mass spectral identification) Non-detects "R"

IV. Continuing Calibration

A. Review Items:

Form VII LCV-1, Form VII LCV-2, Form VII LCV-3, quantitation reports, and chromatograms.

B. Objective:

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. Continuing calibration establishes the 12-hour Relative Response Factors (RRFs) on which the quantitations are based and checks satisfactory performance of the instrument on a day-to-day basis.

C. Criteria:

1. Continuing calibration standards containing both target compounds and Deuterated Monitoring Compounds (DMCs) are analyzed at the beginning of each 12-hour analysis period following the analysis of the instrument performance check and prior to the analysis of the method blank and samples. If time remains in the 12-hour time period after initial calibration and samples are to be analyzed, the mid-point standard from the initial calibration can be used as a continuing calibration.

2. Continuing calibration Relative Response Factors (RRFs) for the volatile target compounds and DMCs listed in Table 3 must be greater than or equal to 0.01. The RRF for all other volatile target compounds and DMCs must be greater than or equal to 0.05.

3. The Percent Difference (%D) between the initial calibration $\overline{\text{RRF}}$ and the continuing calibration RRF must be within ±50.0 % for the volatile target compounds and DMCs listed in Table 3. The %D for all other volatile target compounds and DMCs must be within ±30.0%.

D. Evaluation:

1. Verify that the continuing calibration was run at the required frequency and the continuing calibration was compared to the correct initial calibration. If the mid-point standard from the initial calibration is used as a continuing calibration, verify that the result of the mid-point standard was compared to the correct initial calibration.

2. Evaluate the continuing calibration RRF for all volatile target compounds and DMCs:

   a. Check and recalculate the continuing calibration RRF for at least one volatile target compound associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. Verify that for the volatile target compounds and DMCs listed in Table 3, the continuing calibration RRF is greater than or equal to 0.01, and for all other volatile target compounds and DMCs, RRF is greater than or equal to 0.05.

3. Evaluate the %D between initial calibration $\overline{RRF}$ and continuing calibration RRF for all volatile target compounds and DMCs:

    a. Check and recalculate the %D for one or more volatile target compound(s) associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

    b. Verify that the %D is within ±50.0% for the volatile target compounds and DMCs listed in Table 3 and within ±30.0% for all other volatile target compounds and DMCs.

4. If errors are detected in the calculations of either the continuing calibration RRF or the %D, perform a more comprehensive recalculation.

E . Action:

1. All volatile target compounds, including the "poor performers" listed in Table 3, will be qualified using the following criteria:

    a. If %D value for any of the volatile target "poor performers" is outside the ±50.0% criterion, qualify positive results with "J" and non-detected compounds "UJ".

    b. If %D value for any other volatile target compound is outside the ±30.0% criterion, qualify positive results with "J", and non-detected compounds "UJ".

    c. If any volatile target compound has an RRF value less than the minimum criterion (0.01 for the "poor performers" and 0.05 for all other volatile compounds), use professional judgment for positive results, based on mass spectral identification, to qualify the data as "J" or unusable (R).

    d. If any volatile target compound has an RRF value less than the minimum criterion (0.01 for the "poor performers" and 0.05 for all other volatile compounds), qualify non-detected compounds as unusable (R).

    e. No action is taken on the DMC %D and RRF data alone. However, using professional judgment, the data reviewer may use the DMC %D and RRF data in conjunction with the DMC recoveries to determine the need for qualification of data.

2. If the laboratory has failed to provide adequate calibration information, the Region's designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

3. Whenever possible, the potential effects on the data due to calibration criteria exceedance should be noted in the Data Review Narrative.

4. If calibration criteria are grossly exceeded, this should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

Table 5. Continuing Calibration Actions for Volatiles Analyses

Criteria	Action
%D > 50.0 or < -50.0 (poor performers) %D > 30.0 or < -30.0 (all other target compounds)	Positives "J" Non-detects "UJ"
RRF < 0.01 (poor performers) RRF < 0.05 (all other target compounds)	Positives "J" or "R" (based on mass spectral identification) Non-detects "R"

V. Blanks

A. Review Items:

Form I LCV-1, Form I LCV-2, Form IV LCV, chromatograms, and quantitation reports.

B. Objective:

The purpose of laboratory or field blank analyses is to determine the existence and magnitude of contamination resulting from laboratory or field activities. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks, instrument blanks, storage blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. A method blank analysis must be performed after the calibration standards and once for every 12-hour time period, beginning with the injection of bromofluorobenzene (BFB).

2. The method blank must be analyzed on each Gas Chromatograph/Mass Spectrometer (GC/MS) system used to analyze samples.

3. A storage blank must be prepared upon receipt of the first samples from a Sample Delivery Group (SDG), and stored with the samples until analysis. The storage blank must be analyzed once per SDG.

4. An instrument blank must be analyzed after any sample that has saturated ions from a given compound to check that the blank is free of interference and the system is not contaminated.

5. The concentration of each target compound found in the storage and method blanks must be less than its Contract Required Quantitation Limit (CRQL) listed in the method, except for methylene chloride and cyclohexane which must be less than 10 times (10x) their respective CRQLs, and acetone and 2-butanone which must be less than 2x their respective CRQLs.

6. The concentration of each target compound in the instrument blank must be less than its CRQL listed in the method.

7. The concentration of non-target compounds in all blanks must be less than 2.0 µg/L.

D . Evaluation:

1. Review the results of all associated blanks on the forms and raw data (chromatograms and quantitation reports) to evaluate the presence of target and non-target compounds in the blanks.

2. Verify that a method blank analysis has been reported for each 12-hour time period on each GC/MS system used to analyze volatile samples. The reviewer can use the Method Blank Summary (Form IV LCV) to identify the samples associated with each method blank.

3. Verify that a storage blank has been analyzed and included with each SDG.

4. Verify that the instrument blank analysis has been performed following any sample analysis where a target analyte(s) is/are reported at high concentration(s).

E. Action:

Action regarding unsuitable blank results depends on the circumstances and origin of the blank. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results must not be corrected by subtracting any blank value.

1. If a volatile compound is found in a method blank, but not found in the sample, no action is taken.

2. If the method blank concentration is less than the CRQL (<10x CRQL for methylene chloride and cyclohexane and <2x CRQL for 2-butanone and acetone):

   a. and the sample concentration is less than the CRQL, report the CRQL value with a "U".

   b. and the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.

3. If the method blank concentration is greater than the CRQL (>10x CRQL for methylene chloride and cyclohexane and >2x CRQL for 2-butanone and acetone) and:

   a. the sample concentration is less than the CRQL, report the CRQL value with a "U".

   b. the sample concentration is greater than the CRQL, but less than the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank and qualify with a "U", or the reviewer may elect to qualify the data as unusable (R).

   c. the sample concentration is greater than the CRQL and greater than the blank concentration, use professional judgment to qualify the data.

4. If the method blank concentration is equal to the CRQL (equal to 10x CRQL for methylene chloride and cyclohexane, and equal to 2x CRQL for 2-butanone and acetone) and:

   a. the sample concentration is less than the CRQL, report the CRQL value with a "U".

   b. the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.

5. If gross contamination exists (i.e., saturated peaks by GC/MS), all affected compounds in the associated samples should be qualified as unusable (R) due to interference. This should be noted for Contract Laboratory Program Project Officer (CLP PO) action if the contamination is suspected of having an effect on the sample results.

6. The same consideration given to the target compounds should also be given to Tentatively Identified Compounds (TICs), which are found in both the sample and associated blank(s) (see Volatile Section XII for TIC guidance).

7. If the contaminants found in the blank are interfering non-target compounds at concentrations >2 µg/L, the reviewer may use professional judgment to qualify the data.

8. Additionally, there may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, they should qualify the data. Contamination introduced through dilution water is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but are absent in the undiluted sample result.

9. If an instrument blank was not analyzed following a sample analysis which contained an analyte(s) at high concentration(s), sample analysis results after the high concentration sample must be evaluated for carryover. Professional judgment should be used to determine if instrument cross-contamination has affected any positive compound identification(s). If instrument cross-contamination is suggested, this should be noted for CLP PO action if the cross-contamination is suspected of having an effect on the sample results.

10. If contaminants are found in the storage blanks, the following action is recommended:

    a. The associated method blank data should be reviewed to determine if the contaminant(s) was also present in the method blank. If the analyte was present at a comparable level in the method blank, the source of the contamination may be in the analytical system and the action recommended for the method blank would apply.

       If the analyte was not present in the method blank, the source of contamination may be in the storage area and all associated samples should be considered for possible cross-contamination.

    b. If the storage blank contains a volatile Target Compound List (TCL) compound(s) at a concentration greater than or equal to the CRQL, all positive results for that compound(s) should be qualified with “J”. If the concentration level in the blank is significantly high, then positive sample results may require rejection and be qualified with “R”. Non-detected volatile target compounds should not require qualification unless the contamination is so high that it interferes with the analysis of the non-detected compounds.

Table 6. Blank Actions for Volatiles Analyses

Blank Type	Blank Result	Sample Result	Action for Samples
Method	< CRQL *	Not detected	No action
Method	< CRQL *	< CRQL	Report CRQL value with a "U"
		$ CRQL	Professional judgment
Method	> CRQL *	< CRQL	Report CRQL value with a "U"
		$ CRQL but < Blank Result	Report the blank concentration for the sample with a "U" or qualify the data as unusable (R)
		> CRQL and $ Blank Result	Professional judgment
Method	= CRQL*	< CRQL	Report CRQL value with a "U"
		$CRQL	Professional judgment
Method	Gross contamination	Positive	Qualify results as unusable (R)
Method	TIC >2 µg/L	Positive	Professional judgment
Storage	$ CRQL *	Positive	Qualify results with a "J"
Storage	Grossly above CRQL *	Positive	Qualify results as unusable (R)

* 10x CRQL for methylene chloride and cyclohexane and 2x CRQL for 2-butanone and acetone.

VI. Deuterated Monitoring Compounds

A. Review Items:

Form II LCV-1, Form II LCV-2, quantitation reports, and chromatograms.

B. Objective:

Laboratory performance on individual samples is established by means of spiking activities. All samples are spiked with Deuterated Monitoring Compounds (DMCs) just prior to sample purging. The evaluation of the results of these DMCs is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and requires analytical experience and professional judgment. Accordingly, this section consists primarily of guidelines, in some cases with several optional approaches suggested.

C. Criteria:

1. Fourteen DMCs listed in Table 7 below are added to all samples and blanks to measure their recovery in environmental samples.

Table 7. Volatile Deuterated Monitoring Compounds (DMCs) and Recovery Limits

DMC	Recovery Limits (%)	DMC	Recovery Limits (%)
Vinyl Chloride-d3	49 - 138	1,2-Dichloropropane-d6	84 - 123
Chloroethane-d5	60 - 126	Toluene-d8	77 - 120
1,1-Dichloroethene-d2	65 - 130	trans-1,3-Dichloropropene-d4	80 - 128
2-Butanone-d5	42 - 171	2-Hexanone-d5	37 - 169
Chloroform-d	80 - 123	Bromoform-d	76 - 135
1,2-Dichloroethane-d4	78 - 129	1,1,2,2-Tetrachloroethane-d2	75 - 131
Benzene-d6	78 - 121	1,2-Dichlorobenzene-d4	50 - 150

2. Recoveries for DMCs in volatile samples and blanks must be within the limits specified in Table 7.

D. Evaluation:

1. Check raw data (e.g., chromatograms and quantitation reports) to verify the recoveries on the Deuterated Monitoring Compound Recovery Forms (Form II LCV-1 and Form II LCV-2). Check for any calculation or transcription errors.

2. Verify that the DMC recoveries were calculated correctly. The equation can be found in the method.

3. Whenever there are two or more analyses for a particular sample, the reviewer must determine which are the most acceptable data to report. Considerations should include, but are not limited to:

    a. DMC recovery (marginal versus gross deviation).

    b. Technical holding times.

    c. Comparison of the values of the target compounds reported in each sample analysis.

    d. Other Quality Control (QC) information, such as performance of internal standards.

E . Action:

Table 9 lists the volatile DMCs and their associated target compounds. If any DMC recovery in the volatiles fraction is out of specification, data should be qualified to include the consideration of the existence of interference in the raw data. Considerations should include, but are not limited to::

1. For any recovery greater than the upper acceptance limit:

    a. Detected associated volatile target compounds are qualified as “J”.

    b. Non-detected associated volatile target compounds should not be qualified.

2. For any recovery greater than or equal to 20%, but less than the lower acceptance limit:

    a. Detected associated volatile target compounds are qualified as “J”.

    b. The sample quantitation limit for non-detected associated volatile target compounds are qualified as approximated (UJ).

3. For any recovery less than 20%:

    a. Detected associated volatile target compounds are qualified as “J”.

    b. Non-detected associated volatile target compounds may be qualified as unusable (R).

4. In the special case of a blank analysis having DMCs out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable DMC recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, analytical problems should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

Table 8. DMC Recovery Actions For Volatiles Analyses

Criteria	Action	
	Detected Associated Compounds	Non-detected Associated Compounds
%R > Upper Acceptance Limit	"J"	No Qualification
20% #%R < Lower Acceptance Limit	"J"	"UJ"
%R < 20%	"J"	"R"

Table 9. Volatile Deuterated Monitoring Compounds and the Associated Target Compounds

Chloroethane-d5 (DMC)	**1,2-Dichloropropane-d6 (DMC)**	**1,2-Dichlorobenzene-d4 (DMC)**
Dichlorodifluoromethane	Cyclohexane	Chorobenzene
Chloromethane	Methylcyclohexane	1,3-Dichlorobenzene
Bromomethane	1,2-Dichloropropane	1,4-Dichlorobenzene
Chloroethane	Bromodichloromethane	1,2-Dichlorobenzene
Carbon Disulfide		1,2,4-Trichlorobenzene
		1,2,3-Trichlorobenzene

Bromoform-d (DMC)	**trans-1,3-Dichloropropene-d4 (DMC)**	**Chloroform-d (DMC)**
Dibromochloromethane	cis-1,3-Dichloropropene	1,1-Dichloroethane
1,2-Dibromoethane	trans-1,3-Dichloropropene	Bromochloromethane
Bromoform	1,1,2-Trichloroethane	Chloroform

2-Butanone-d5 (DMC)	**1,1-Dichloroethene-d2 (DMC)**	**2-Hexanone-d5 (DMC)**
Acetone	trans-1,2-Dichloroethene	4-Methyl-2-pentanone
2-Butanone	cis-1,2-Dichloroethene	2-Hexanone

Table 9. Volatile Deuterated Monitoring Compounds and the Associated Target Compounds, con't.

Vinyl Chloride-d3 (DMC)	Benzene-d6 (DMC)	1,1,2,2-Tetrachloroethane-d2 (DMC)
Vinyl Chloride	Benzene	1,1,2,2,-Tetrachlororethane
		1,2-Dibromo-3-chloropropane
1,2-Dichloroethane-d4 (DMC)	**Toulene-d8 (DMC)**	
Trichlorofluoromethane	Trichloroethene	
1,1-Dichloroethene	Toluene	
1,1,2-Trichloro-1,2,2-trifluoroethane	Tetrachloroethene	
Methyl Acetate	Ethylbenzene	
Methylene Chloride	Xylenes (total)	
Methyl tert-Butyl Ether	Styrene	
1,1,1-Trichloroethane	Isopropylbenzene	
Carbon Tetrachloride		
1,2-Dichloroethane		

VII. Matrix Spikes/Matrix Spike Duplicates

A. Review Items:

Form III LCV, chromatograms, and quantitation reports.

NOTE: Data for Matrix Spike/Matrix Spike Duplicates (MS/MSDs) will not be present unless requested by the Region.

B. Objective:

Data for MS/MSDs are generated to determine long-term precision and accuracy of the analytical method on the sample matrix and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone cannot be used to evaluate the precision and accuracy of individual samples. However, when exercising professional judgment, this data should be used in conjunction with other available Quality Control (QC) information.

C. Criteria:

1. **If requested**, MS/MSD samples are analyzed at a frequency of one MS and MSD per 20 or fewer samples.

2. Spike recoveries should be within the advisory limits provided on Form III LCV.

3. Relative Percent Difference (RPD) between MS and MSD recoveries must not exceed the advisory limits provided on Form III LCV.

D. Evaluation:

1. Verify that requested MS and MSD samples were analyzed at the required frequency and results are provided for each sample.

2. Inspect results for the MS/MSD Recovery on Form III LCV and verify that the results for recovery and RPD are within the advisory limits.

3. Verify transcriptions from raw data and check calculations.

4. Verify that the MS recoveries and RPD were calculated correctly.

5. Calculate Percent Relative Standard Deviation (%RSD) results of non-spiked compounds between the original sample, MS, and MSD samples. Provide this information in the Data Review Narrative.

E. Action:

1. No action is taken on MS/MSD data alone. However, using informed professional judgment, the data reviewer may use the MS and MSD results in conjunction with other QC criteria and determine the need for some qualification of the data.

2. The data reviewer should first try to determine to what extent the results of the MS/MSD affect the associated data. This determination should be made with regard to the MS/MSD sample itself, as well as specific analytes for all samples associated with the MS/MSD.

3. In those instances where it can be determined that the results of the MS/MSD affect only the sample spiked, qualification should be limited to this sample only. However, it may be determined through the MS/MSD results that a laboratory is having a systematic problem in the analysis of one or more analytes that affects all associated samples.

4. The reviewer must use professional judgment to determine the need for qualification of positive results of non-spiked compounds.

NOTE: If a field blank was used for the MS/MSD, the Contract Laboratory Program Project Officer (CLP PO) must be notified.

VIII. Regional Quality Assurance and Quality Control

A. Review Items:

Form I LCV-1, Form I LCV-2, chromatograms, Sample Traffic Reports (TRs), and quantitation reports.

B. Objective:

Regional Quality Assurance and Quality Control (QA/QC) samples refer to any QA and/or QC samples initiated by the Region, including field duplicates, Performance Evaluation (PE) samples, blind spikes, and blind blanks. The use of these QA/QC samples are highly recommended (e.g., the use of field duplicates can provide information on sampling precision and homogeneity).

C. Criteria:

Criteria are determined by each Region.

1. PE sample frequency may vary.

2. The analytes present in the PE sample must be correctly identified and quantified.

D. Evaluation:

1. Evaluation procedures must follow the Region's Standard Operating Procedure (SOP) for data review. Each Region will handle the evaluation of PE samples on an individual basis. Results for PE samples should be compared to the acceptance criteria for the specific PE samples, if available.

2. Calculate Relative Percent Difference (RPD) between field duplicates. Provide this information in the Data Review Narrative.

E. Action:

Any action must be in accordance with Regional specifications and the criteria for acceptable PE sample results. Unacceptable results for PE samples should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

IX. Internal Standards

A. Review Items:

Form VIII LCV, quantitation reports, and chromatograms.

B. Objective:

Internal standard performance criteria ensures that Gas Chromatograph/Mass Spectrometer (GC/MS) sensitivity and response are stable during each analysis.

C. Criteria:

1. The internal standard area counts must not vary by more than a factor of ±40.0% from the associated 12-hour calibration standard.

2. The retention time of the internal standard must not vary more than ±20 seconds from the retention time of the associated 12-hour calibration standard.

D. Evaluation:

1. Check raw data (e.g., chromatograms and quantitation lists) to verify the internal standard retention times and areas reported on the Internal Standard Area Summary (Form VIII LCV).

2. Verify that all retention times and internal standard areas are within criteria.

3. If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations should include:

    a. Magnitude and direction of the internal standard area shift.

    b. Magnitude and direction of the internal standard retention time shift.

    c. Technical holding times.

    d. Comparison of the values of the target compounds reported in each fraction.

    e. Other Quality Control (QC).

E. Action:

1. If an internal standard area count for a sample or blank is greater than +40.0% of the area for the associated standard:

    a. Positive results for compounds quantitated using that internal standard should be qualified with a “J”.

    b. Non-detected associated compounds should not be qualified.

2. If an internal standard area count for a sample or blank is less than -40.0% of the area for the associated standard:

a. Positive results for compounds quantitated using that internal standard should be qualified with a "J".

b. Non-detected associated compounds should be qualified as unusable (R).

3. If an internal standard retention time varies by more than 20.0 seconds:

   The chromatographic profile for that sample must be examined to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection of the data for that sample fraction. Positive results should not need to be qualified as "R" if the mass spectral criteria are met.

4. If the internal standard performance criteria are grossly exceeded, this should be noted for Contract Laboratory Program Project Officer (CLP PO) action. Potential effects on the data resulting from unacceptable internal standard performance should be noted in the Data Review Narrative.

Table 10. Internal Standards Actions for Volatiles Analyses

Criteria	Action	
	Detected Associated Compounds*	Non-detected Associated Compounds*
Area counts > 40% of 12-hour standard	"J"	No action
Area counts < 40% of 12-hour standard	"J"	"R"

* See Table D-3 in the method for volatile compounds associated to each internal standard.

X. Target Compound Identification

A. Review Items:

Form I LCV-1, Form I LCV-2, quantitation reports, mass spectra, and chromatograms.

B. Objective:

The objective of the criteria for Gas Chromatograph/Mass Spectrometer (GC/MS) qualitative analysis is to minimize the number of erroneous compound identifications. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).

The identification criteria can be applied more easily in detecting false positives than false negatives. More information is available for false positives due to the requirement for submittal of data supporting positive identifications. Negatives, or non-detected compounds, on the other hand, represent an absence of data and are, therefore, more difficult to assess. One example of the detection of false negatives is not reporting a target compound that is reported as a Tentatively Identified Compound (TIC).

C. Criteria:

1. The Relative Retention Times (RRTs) must be within ±0.06 RRT units of the standard RRT.

2. Mass spectra of the sample compound and a current laboratory-generated standard (i.e., the mass spectrum from the associated calibration standard) must match according to the following criteria:

   a. All ions present in the standard mass spectrum at a relative intensity greater than 10% must be present in the sample spectrum.

   b. The relative intensities of these ions must agree within ±20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30-70 %).

   c. Ions present at greater than 10% in the sample mass spectrum, but not present in the standard spectrum, must be evaluated by a reviewer experienced in mass spectral interpretation.

D. Evaluation:

1. Check that the RRT of reported compounds is within ±0.06 RRT units of the standard RRT.

2. Check the sample compound spectra against the laboratory standard spectra to verify that it meets the specified criteria.

3. The reviewer should be aware of situations when sample carryover is a possibility and should use judgment to determine if instrument cross-contamination has affected any positive compound identification. The method specifies that an instrument blank must be run after samples which contain target compounds at levels exceeding the initial calibration range (25 µg/L for non-ketones, 125 µg/L for ketones), or non-target compounds at concentrations greater

than 100 µg/L, or saturated ions from a compound (excluding the compound peaks in the solvent front).

4. Check the chromatogram to verify that peaks are identified. Major peaks are either identified as target compounds, TICs, Deuterated Monitoring Compounds (DMCs), or internal standards.

E. Action:

1. The application of qualitative criteria for GC/MS analysis of target compounds requires professional judgment. It is up to the reviewer's discretion to obtain additional information from the laboratory. If it is determined that incorrect identifications were made, all such data should be qualified as not detected (U) or unusable (R).

2. Professional judgment must be used to qualify the data if it is determined that cross-contamination has occurred.

3. Any changes made to the reported compounds or concerns regarding target compound identifications should be clearly indicated in the Data Review Narrative. The necessity for numerous or significant changes should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

XI. Compound Quantitation and Reported CRQLs

A. Review Items:

Forms I LCV-1, Form I LCV-2, sample preparation sheets, Sample Delivery Group (SDG) Narrative, quantitation reports, and chromatograms.

B. Objective:

The objective is to ensure that the reported quantitation results and Contract Required Quantitation Limits (CRQLs) are accurate.

C. Criteria:

1. Compound quantitation, as well as the adjustment of the CRQLs, must be calculated according to the correct equation.

2. Compound Relative Response Factors (RRFs) must be calculated based on the internal standard associated with that compound, as listed in the method. Quantitation must be based on the quantitation ion (m/z) specified in the method for both the internal standards and target analytes. The compound quantitation must be based on the RRF from the appropriate daily standard.

D. Evaluation:

1. For all fractions, raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Quantitation lists and chromatograms should be compared to the reported positive sample results and quantitation limits. Check the reported values.

2. Verify that the correct internal standard, quantitation ion, and RRF were used to quantitate the compound. Verify that the same internal standard, quantitation ion, and RRF are used consistently throughout, in both the calibration as well as the quantitation process.

3. Verify that the CRQLs have been adjusted to reflect all sample dilutions.

E. Action:

1. If any discrepancies are found, the laboratory may be contacted by the Region's designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, the reviewer must use professional judgment to decide which value is the most accurate value. Under these circumstances, the reviewer may determine that qualification of data is warranted. A description of the reasons for data qualification and the qualification that is applied to the data should be documented in the Data Review Narrative.

2. Numerous or significant failures to accurately quantify the target compounds or to properly evaluate and adjust CRQLs should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

XII. Tentatively Identified Compounds

A. Review Items:

Form I LCV-TIC, chromatograms, library search printouts, and spectra for the Tentatively Identified Compound (TIC) candidates.

B. Objective:

Chromatographic peaks in volatile fraction analyses that are not target analytes, Deuterated Monitoring Compounds (DMCs), or internal standards are potential TICs. TICs must be qualitatively identified via a forward search of the NIST/USEPA/NIH (May 1992 release or later) mass spectral library, and/or Wiley (1991 release or later) mass spectral library, or the equivalent. The identifications must be assessed by the data reviewer.

C. Criteria:

For each sample, the laboratory must conduct a mass spectral search of the NIST/USEPA/NIH, and/or Wiley, or equivalent mass spectral library, and report the possible identity for the appropriate number of the largest volatile fraction peaks which are not DMCs, internal standards, or target compounds, but which have an area or height greater than 10% of the area or height of the nearest internal standard. Estimated concentrations for TICs are calculated similarly to the Target Compound List (TCL) compounds, using total ion areas for the TIC and the internal standard, and assuming a Relative Response Factor (RRF) of 1.0. TIC results are reported for each sample on the Organic Analyses Data Sheet (Form I LCV-TIC).

D. Evaluation:

1. Guidelines for tentative identification are as follows:

    a. Major ions (greater than 10% Relative Intensity) in the reference spectrum should be present in the sample spectrum.

    b. The relative intensities of the major ions should agree within ±20% between the sample and the reference spectra.

    c. Molecular ions present in the reference spectrum should be present in the sample spectrum.

    d. Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination, interference, or presence of coeluting compounds.

    e. Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting compounds. Data system library reduction programs can sometimes create these discrepancies.

    f. Non-target compounds receiving a library search match of 85% or higher should be considered a “likely match”. The compound should be reported unless the mass spectral interpretation specialist feels there is evidence not to report the compound as identified by the library search program. The laboratory should include in the Sample Delivery Group

(SDG) Narrative the justification for not reporting a compound as listed by the search program.

g. If the library search produces more than one compound at or above 85%, report the compound with the highest percent match (report first compound if percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels that the highest match compound should not be reported or another compound with a lower match should be reported. The laboratory should include the justification for not reporting the compound with the highest spectral match within the SDG Narrative.

h. If the library search produces a series of obvious isomer compounds with library search matches greater than 85% (e.g., tetramethyl naphthalenes), the compound with the highest library search percent match should be reported (or the first compound if the library search matches are the same). A note should be placed in the SDG Narrative indicating that the exact isomer configuration, as reported, may not be accurate.

i. If the library search produces no matches at or above 85%, and in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (e.g., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

j. Straight-chain, branched, or cyclic alkanes are not to be reported as TICs on Form I LCV-TIC. When the above alkanes are tentatively identified, the concentration(s) are to be estimated and reported in the SDG Narrative as alkanes by class (i.e., straight-chain, branched, cyclic, as a series, or as applicable).

2. Check the raw data to verify that the laboratory has generated a library search for all required peaks in the chromatograms for samples and blanks.

3. Blank chromatograms should be examined to verify that TIC peaks present in samples are not found in blanks. When a low-level, non-target compound that is a common artifact or laboratory contaminant is detected in a sample, a thorough check of blank chromatograms may require looking for peaks which are less than 10% of the internal standard height, but present in the blank chromatogram at a similar Relative Retention Time (RRT).

4. All mass spectra for every sample and blank must be examined.

5. Since TIC library searches often yield several candidate compounds having a close matching score, all reasonable choices must be considered.

6. The reviewer should be aware of common laboratory artifacts/contaminants and their sources (e.g., Aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.

   Examples:

   a. Common laboratory contaminants: $C0_2$ (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons, and phthalates at levels less than 100 µg/L.

b. Solvent preservatives such as cyclohexene, which is a methylene chloride preservative. Related by-products include cyclohexanone, cyclohexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.

c. Aldol condensation reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

7. Occasionally, a target compound may be identified in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list (false negative). If the total area quantitation method was used, the reviewer should request that the laboratory recalculate the result using the proper quantitation ion and Relative Response Factor (RRF).

   In certain situations, a non-target compound may be incorrectly identified by the instrument's target analyte data processor as a target compound (false positive). When this happens, the non-target library search procedure will not detect the false positive as a TIC. In this case the reviewer should request that the laboratory properly identify the compound and recalculate the result using the total area quantitation method and a RRF of 1.0.

   In addition, the reviewer should evaluate other sample chromatograms and check for both false negatives and false positives to determine if the occurrence is isolated or systematic.

8. Target compounds could be identified in more than one fraction. Verify that quantitation is made from the proper fraction.

9. Library searches should not be performed on internal standards or DMCs.

10. TIC concentration should be estimated assuming an RRF of 1.0.

E . Action:

1. All TIC results should be qualified as "NJ", tentatively identified, with approximated concentrations.

2. General actions related to the review of TIC results are as follows:

   a. If it is determined that a tentative identification of a non-target compound is not acceptable, the tentative identification should be changed to "unknown" or another appropriate identification.

   b. If all contractually-required peaks were not library searched and quantitated, the Region's designated representative may request these data from the laboratory.

3. In deciding whether a library search result for a TIC represents a reasonable identification, professional judgment must be exercised. If there is more than one possible match, the result may be reported as "either compound X or compound Y". If there is a lack of isomer specificity, the TIC result may be changed to a non-specific isomer result (e.g., 1,3,5-trimethyl benzene to trimethyl benzene isomer) or to a compound class (e.g., 2-methyl, 3-ethyl benzene to a substituted aromatic compound).

4. The reviewer may elect to report all similar compounds as a total (e.g., all alkanes may be summarized and reported as total hydrocarbons).

5. Other case factors may influence TIC judgments. If a sample TIC match is poor, but other samples have a TIC with a valid library match, similar (RRT), and the same ions, identification information may be inferred from the other sample TIC results.

6. Any changes made to the reported data or any concerns regarding TIC identifications should be indicated in the Data Review Narrative.

7. Failure to properly evaluate and report TICs should be noted for CLP Project Officer (CLP PO) action.

XIII. System Performance

A. Review Items:

Form VIII LCV and chromatograms.

B. Objective:

During the period following Instrument Performance Quality Control (QC) checks (e.g., blanks, tuning, calibration), changes may occur in the system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC runs, a thorough review of the ongoing data acquisition can yield indicators of instrument performance.

C. Criteria:

There are no specific criteria for system performance. Professional judgment should be applied to assess the system performance.

D. Evaluation:

1. Abrupt discrete shifts in the Reconstructed Ion Chromatogram (RIC) baseline may indicate a change in the instrument's sensitivity or the zero setting. A baseline “shift” could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds at, or near, the detection limit to miss detection. A baseline “rise” could indicate problems such as a change in the instrument zero, a leak, or degradation of the column.

2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

    a. High RIC background levels or shifts in absolute retention times of internal standards.

    b. Excessive baseline rise at elevated temperature.

    c. Extraneous peaks.

    d. Loss of resolution.

    e. Peak tailing or peak splitting that may result in inaccurate quantitation.

3. A drift in instrument sensitivity may occur during the 12-hour time period. This could be discerned by examination of the internal standard area on Form VIII LCV for trends such as a continuous or near-continuous increase or decrease in the internal standard area over time.

E. Action:

Professional judgment must be used to qualify the data if it is determined that system performance has degraded during sample analyses. Any degradation of system performance which significantly affected the data should be documented for Contract Laboratory Program Project Officer (CLP PO) action.

XIV. Overall Assessment of Data

A. Review Items:

Entire data package, data review results, and (if available) the Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP).

B. Objective:

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria:

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation:

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to help the data user avoid inappropriate use of the data. Review all available information, including the QAPP (specifically the acceptance and performance criteria), SAP, and communication with the data user that concerns the intended use and desired quality of these data.

E. Action:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the Quality Control (QC) criteria previously discussed.

2. Write a brief narrative to give the user an indication of the analytical limitations of the data. Any inconsistency of the data with the Sample Delivery Group (SDG) Narrative should be noted for Contract Laboratory Program Project Officer (CLP PO) action. If sufficient information on the intended use and required quality of the data are available, the reviewer should include their assessment of the usability of the data within the given context. This may be used as part of a formal Data Quality Assessment (DQA).

SEMIVOLATILE DATA REVIEW

The semivolatile data requirements to be checked are listed below:

I. Preservation

II. Gas Chromatograph/Mass Spectrometer (GC/MS) Instrument Performance Check

III. Initial Calibration

IV. Continuing Calibration

V. Blanks

VI. Deuterated Monitoring Compounds (DMCs)

VII. Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

VIII. Regional Quality Assurance (QA) and Quality Control (QC)

IX. Internal Standards

X. Target Compound Identification

XI. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

XII. Tentatively Identified Compounds (TICs)

XIII. System Performance

XIV. Overall Assessment of Data

I. Preservation

A. Review Items:

Form I LCSV-1, Form I LCSV-2, USEPA Sample Traffic Report (TR) and/or Chain-of-Custody, raw data, sample extraction sheets, and the Sample Delivery Group (SDG) Narrative checking for:

1. pH
2. Sample temperature
3. Holding time
4. Other sample conditions

B. Objective:

The objective is to ascertain the validity of the analytical results based on sample condition (i.e., preservation and temperature) and the holding time of the sample from time of collection to time of sample extraction and analysis.

C. Criteria:

The technical holding time criteria for water samples are as follows:

For semivolatile compounds in cooled (4°C ± 2°C) water samples, the maximum holding time for extraction is seven (7) days from sample collection, and the maximum holding time for analysis is 40 days from sample extraction.

D. Evaluation:

Technical holding times for sample extraction are established by comparing the sampling date on the TR with the dates of extraction on Form I LCSV-1, Form I LCSV-2, and the sample extraction sheets. To determine if the samples were analyzed within the holding time after extraction, compare the dates of extraction on the sample extraction sheets with the dates of analysis on Form I LCSV-1 and Form I LCSV-2.

Verify that the TR indicates that the samples were received intact and iced. If it is indicated that there were problems with the samples, then the integrity of the sample may have been compromised and professional judgment should be used to evaluate the effect of the problem on the sample results.

E. Action:

1. If technical holding times are exceeded, document in the Data Review Narrative that holding times were exceeded and qualify all positive results as estimated "J", and sample quantitation limits as estimated "UJ".

2. If technical holding times are grossly exceeded, either on the first analysis or upon re-analysis, the reviewer must use professional judgment to determine the reliability of the data and the effect of additional storage on the sample results. The reviewer may determine that positive results or the associated quantitation limits are approximates and should be

qualified with “J” or “UJ”, respectively, or the reviewer may determine that non-detected data are unusable (R).

3. Whenever possible, the reviewer should comment on the effect of the holding time exceedance on the resulting data in the Data Review Narrative.

4. When technical holding times are grossly exceeded, this should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

Table 11. Holding Time Actions for Semivolatile Analyses

Holding Time	Action
> 7 days (for extraction), or > 40 days (for analysis)	Positives “J” Quantitation Limits “UJ”
Grossly exceeded	Using professional judgment: Positives “J” Quantitation Limits “UJ” or “R”

II. GC/MS Instrument Performance Check

A. Review Items:

Form V LCSV, DFTPP mass spectra, and mass listing.

B. Objective:

Gas Chromatograph/Mass Spectrometer (GC/MS) instrument performance checks are performed to ensure mass resolution, identification, and to some degree, sensitivity. These criteria are not sample-specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.

C. Criteria:

50 ng of the instrument performance check solution must be injected at the beginning of each 12-hour period during which samples or standards are analyzed. The instrument performance check, decafluorotriphenylphosphine (DFTPP) for semivolatile analysis, must meet the ion abundance criteria provided in Table 12.

Table 12. Ion Abundance Criteria For Decafluorotriphenylphosphine (DFTPP)

m/z	ION ABUNDANCE CRITERIA
51	30.0 - 80.0% of m/z 198
68	Less than 2.0% of m/z 69
69	Mass 69 relative abundance
70	Less than 2.0% of m/z 69
127	25.0 - 75.0% of m/z 198
197	Less than 1.0% of m/z 198
198	Base peak, 100% relative abundance
199	5.0 - 9.0% of m/z 198
275	10.0 - 30.0% of m/z 198
365	Greater than 0.75% of m/z 198
441	Present, but less than m/z 443
442	40.0 - 110.0% of m/z 198
443	15.0 - 24.0% of m/z 442

NOTE: All ion abundances must be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z 442 may be up to 110% that of m/z 198.

D. Evaluation:

1. Compare the data presented on each GC/MS Instrument Performance Check (Form V LCSV) with each mass listing submitted and ensure the following:

    a. Form V LCSV is present and completed for each 12-hour period during which samples were analyzed.

    b. The laboratory has not made any transcription errors between the data and the form. If there are major differences between the mass listing and the Form Vs, a more in-depth review of the data is required. This may include obtaining and reviewing additional information from the laboratory.

    c. The appropriate number of significant figures has been reported (number of significant figures given for each ion in the ion abundance criteria column) and that rounding is correct.

    d. The laboratory has not made any calculation errors.

2. Verify from the raw data (mass spectral listing) that the mass assignment is correct and the mass is normalized to m/z 198.

3. Verify that the ion abundance criteria was met. The criteria for m/z 68, 70, 441, and 443 are calculated by normalizing to the specified m/z.

4. If possible, verify that spectra were generated using appropriate background subtraction techniques. Since the DFTPP spectrum is obtained from chromatographic peaks that should be free from coelution problems, background subtraction should be done in accordance with the following procedure:

    a. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.

    b. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. Do not subtract the DFTPP peak as part of the background.

NOTE: All mass spectrometer instrument conditions must be identical to those used during the sample analysis. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the contract specifications are contrary to the Quality Assurance (QA) objectives and are, therefore, unacceptable.

E. Action:

1. If the laboratory has made minor transcription errors that do not significantly affect the data, the data reviewer should make the necessary corrections on a copy of the form.

2. If the laboratory has failed to provide the correct forms or has made significant transcription or calculation errors, the Region's designated representative should contact the laboratory and request corrected data. If the information is not available, then the reviewer

must use professional judgment to assess the data. The laboratory's Contract Laboratory Program Project Officer (CLP PO) should be notified.

3. If mass assignment is in error (e.g., m/z 199 is indicated as the base peak rather than m/z 198), classify all associated data as unusable (R).

4. If ion abundance criteria are not met, professional judgment may be applied to determine to what extent the data may be utilized. Guidelines to aid in the application of professional judgment in evaluating ion abundance criteria are discussed below:

    a. Some of the most critical factors in the DFTPP criteria are the non-instrument specific requirements that are also not unduly affected by the location of the spectrum on the chromatographic profile. The m/z ratios for 198/199 and 442/443 are critical. These ratios are based on the natural abundances of carbon 12 and carbon 13 and should always be met. Similarly, the relative abundances for m/z 68, 70, 197, and 441 indicate the condition of the instrument and the suitability of the resolution adjustment. Note that all of the foregoing abundances relate to adjacent ions; they are relatively insensitive to differences in instrument design and position of the spectrum on the chromatographic profile.

    b. For the ions at m/z 51, 127, and 275, the actual relative abundance is not as critical. For instance, if m/z 275 has 40% relative abundance (criteria: 10.0-30.0%) and other criteria are met, then the deficiency is minor.

    c. The relative abundance of m/z 365 is an indicator of suitable instrument zero adjustment. If relative abundance for m/z 365 is zero, minimum detection limits may be affected. On the other hand, if m/z 365 is present, but less than the 0.75% minimum abundance criteria, the deficiency is not as serious.

5. Decisions to use analytical data associated with DFTPP instrument performance checks not meeting method requirements should be clearly noted in the Data Review Narrative.

6. If the reviewer has reason to believe that instrument performance check criteria were achieved using techniques other than those specified in Semivolatile Section II.D.4, additional information on the DFTPP instrument performance checks should be obtained. If the techniques employed are found to be at variance with contract requirements, the procedures of the laboratory may merit evaluation. Concerns or questions regarding laboratory performance should be noted for CLP PO action. For example, if the reviewer has reason to believe that an inappropriate technique was used to obtain background subtraction (such as background subtracting from the solvent front or from another region of the chromatogram rather than from the DFTPP peak), then this should be noted for CLP PO action.

III. Initial Calibration

A. Review Items:

Form VI LCSV-1, Form VI LCSV-2, Form VI LCSV-3 quantitation reports, and chromatograms.

B. Objective:

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for compounds on the semivolatile Target Compound List (TCL). Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run and of producing a linear calibration curve.

C. Criteria:

1. Initial calibration standards containing both semivolatile target compounds and Deuterated Monitoring Compounds (DMCs) are analyzed. All target compounds (except the seven compounds listed below) and the DMCs are analyzed at concentrations of 5.0, 10.0, 20.0, 50.0, and 80.0 ng/uL at the beginning of each analytical sequence or as necessary if the calibration verification acceptance criteria are not met. The seven compounds are: 2,4-dinitrophenol; 2,4,5-trichlorophenol; 2-nitroaniline; 3-nitroaniline; 4-nitroaniline; 4-nitrophenol, and 4,6-dinitro-2-methylphenol. These compounds require calibration at 20.0, 50.0, 80.0, 100.0, and 120.0 ng/uL. The initial calibration (and any associated samples and blanks) must be analyzed within 12 hours of the associated instrument performance check.

2. Initial calibration standard Relative Response Factors (RRFs) for the semivolatile target compounds and DMCs listed in Table 13 must be greater than or equal to 0.010. The RRF for all other semivolatile target compounds and DMCs must be greater than or equal to 0.05.

3. The Percent Relative Standard Deviation (%RSD) of the initial calibration RRFs must be less than or equal to 50.0% for the semivolatile target compounds and DMCs listed in Table 13. The %RSD must be less than or equal to 30.0% for 2,4-dinitrotoluene, 2-nitrophenol, and 2,4-dimethyphenol, and less than or equal to 20.5% for all other semivolatile target compounds and DMCs.

   NOTE: The flexibility clause in the method may impact some of the criteria listed above. A copy of the flexibility clause should be present in the SDG. Refer to the CLP Web Site at http://www.epa.gov/superfund/programs/clp/methflex.htm for the specific requirements.

D. Evaluation:

1. Verify that the correct concentrations of standards were used for the initial calibration (i.e., 5.0, 10.0, 20.0, 50.0, and 80.0 ng/uL). For the seven compounds listed in Semivolatile Section III.C.1 with higher CRQLs, verify that a five-point initial calibration at 20.0, 50.0, 80.0, 100.0, and 120.0 ng/uL was performed.

2. If any sample results were calculated using an initial calibration standard, verify that the correct standard (i.e., 80.0 ng/uL for the seven compounds listed in Semivolatile Section III.C.1 and 20.0 ng/uL for all other target compounds) was used for calculating sample results. Also verify that the samples were analyzed within 12 hours of the associated instrument performance check.

3. Evaluate the initial calibration RRFs and the Mean Relative Response Factors ($\overline{RRFs}$) for all semivolatile target compounds and DMCs:

   a. Check and recalculate the RRFs and $\overline{RRFs}$ for at least one semivolatile target compound associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. Verify that for the semivolatile target compounds and DMCs listed in Table 13, the initial calibration RRFs are greater than or equal to 0.01, and for all other semivolatile target compounds and DMCs, RRFs are greater than or equal to 0.05.

Table 13. Semivolatile Compounds Exhibiting Poor Response

Semivolatile Compounds	
2,2'-oxybis(1-Chloropropane)	Benzaldehyde
4-Chloroaniline	Pentachlorophenol
Hexachlorobutadiene	4-Nitroaniline
Hexachlorocyclopentadiene	4,6-Dinitro-2-methylphenol
2-Nitroaniline	N-Nitrosodiphenylamine
3-Nitroaniline	3-3'-Dichlorobenzidine
2,4-Dinitrophenol	4-Chloroaniline-d4 (DMC)
4-Nitrophenol	4,6-Dinitro-2-methylphenol-d2 (DMC)
Acetophenone	4-Nitrophenol-d4 (DMC)
Caprolactam	

4. Evaluate the %RSD for all semivolatile target compounds and DMCs:

   a. Check and recalculate the %RSD for one or more semivolatile target compound(s). Verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. If the %RSD is greater than the maximum criteria (50.0% for the semivolatile target compounds and DMCs listed in Table 13, 30.0 % for 2,4-dinitrotoluene, 2-nitrophenol, and 2,4-dimethyphenol, and 20.5% for all other semivolatile target compounds and DMCs), then the reviewer should use professional judgment to determine the need to check the points on the curve for the cause of the non-linearity.

This is checked by eliminating either the high point or the low point and re-calculating the %RSD (see Semivolatile Section III.E.2).

5. If errors are detected in the calculations of either the RRF or the %RSD, perform a more comprehensive recalculation.

E. Action:

1. All semivolatile target compounds, including the "poor performers" listed in Table 13 will be qualified using the following criteria:

   a. If any of the semivolatile target compounds listed in Table 13 has %RSD greater than 50.0%, qualify positive results with a "J", and non-detected compounds using professional judgment (see Item 2 below).

   b. For 2,4-dinitrotoluene, 2-nitrophenol, and 2,4-dimethyphenol, if %RSD is greater than 30.0%, qualify positive results with "J", and non-detected compounds using professional judgment (see Item 2 below).

   c. For all other semivolatile target compounds, if %RSD is greater than 20.5%, qualify positive results with "J", and non-detected compounds using professional judgment (see Item 2 below).

   d. If any semivolatile target compound has an RRF value less than the minimum criterion (0.01 for the "poor performers" listed in Table 13, and 0.05 for all other semivolatile compounds), use professional judgment for positive results, based on mass spectral identification, to qualify the data as "J" or unusable (R).

   e. If any semivolatile target compound has an RRF value less than the minimum criterion (0.01 for the "poor performers" listed in Table 13, and 0.05 for all other semivolatile compounds), qualify non-detected compounds as unusable (R).

   f. No action is taken on the DMC %RSD and RRF data alone. However, using professional judgment and following the guidelines in Item 2 below, the data reviewer may use the DMC %RSD and RRF data in conjunction with the DMC recoveries to determine the need for qualification of data.

2. At the reviewer's discretion, and based on the project specific data quality objectives, a more in-depth review may be considered using the following guidelines:

   a. If any semivolatile target compound has a %RSD greater than the maximum criterion (50.0% for the "poor performers", 30.0% for 2,4-dinitrotoluene, 2-nitrophenol, and 2,4-dimethyphenol, and 20.5% for all other semivolatile compounds), and if eliminating either the high or the low point of the curve does not restore the %RSD to less than or equal to the required maximum:

      i. Qualify positive results for that compound(s) with a "J".

      ii. Qualify non-detected semivolatile target compounds using professional judgment.

b. If the high point of the curve is outside of the linearity criteria (e.g., due to saturation):

   i. No qualifiers are required for positive results in the linear portion of the curve.

   ii. Qualify positive results outside of the linear portion of the curve with a "J".

   iii. No qualifiers are needed for semivolatile target compounds that were not detected.

c. If the low end of the curve is outside of the linearity criteria:

   i. No qualifiers are required for positive results in the linear portion of the curve.

   ii. Qualify low level positive results in the area of non-linearity with a "J".

   iii. For non-detected semivolatile compounds use the lowest point of the valid curve to determine the new quantitation limit.

3. If the laboratory has failed to provide adequate calibration information, the Region's designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

4. Whenever possible, the potential effects on the data due to calibration criteria exceedance should be noted in the Data Review Narrative.

5. If calibration criteria are grossly exceeded, this should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

Table 14. Initial Calibration Actions for Semivolatile Analyses

Criteria	Action
%RSD > maximum criteria*	Positives "J" Non-detects: Professional Judgment
RRF < 0.01 (poor performers) RRF < 0.05 (all other target compounds)	Positives "J" or "R" (based on mass spectral identification) Non-detects "R"

*50.0% for the "poor performers", 30.0 % for 2,4-dinitrotoluene, 2-nitrophenol, and 2,4-dimethyphenol, and 20.5% for all other semivolatile compounds

IV. Continuing Calibration

A. Review Items:

Form VII LCSV-1, Form VII LCSV-2, Form VII LCSV-3, quantitation reports, and chromatograms.

B. Objective:

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. Continuing calibration establishes the 12-hour Relative Response Factors (RRFs) on which the quantitations are based and checks satisfactory performance of the instrument on a day-to-day basis.

C. Criteria:

1. Continuing calibration standards containing both target compounds and Deuterated Monitoring Compounds (DMCs) are analyzed at the beginning of each 12-hour analysis period following the analysis of the instrument performance check, and prior to the analysis of the method blank and samples. If time remains in the 12-hour time period after initial calibration and samples are to be analyzed, the mid-point standard from the initial calibration can be used as a continuing calibration.

2. Continuing calibration RRFs for the semivolatile target compounds and DMCs listed in Table 13 must be greater than or equal to 0.01. The RRF for all other semivolatile target compounds and DMCs must be greater than or equal to 0.05.

3. The Percent Difference (%D) between the initial calibration $\overline{\text{RRF}}$ and the continuing calibration RRF must be within ± 50.0 % for the semivolatile target compounds and DMCs listed in Table 13. The %D for all other semivolatile target compounds and DMCs must be within ±25.0%, except for 2,4-dinitrotoluene, 2-nitrophenol, and 2,4-dimethylphenol, for which the %D must be within ±30.0%.

D. Evaluation:

1. Verify that the calibration verification was run at the required frequency and that the continuing calibration was compared to the correct initial calibration. If the mid-point standard from the initial calibration is used as a continuing calibration, verify that the result of the mid-point standard was compared to the correct initial calibration.

2. Evaluate the continuing calibration RRF for all semivolatile target compounds and DMCs:

   a. Check and recalculate the continuing calibration RRF for at least one semivolatile target compound associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. Verify that for all semivolatile target compounds and DMCs listed in Table 13, the continuing calibration RRF is greater than or equal to 0.01, and for all other semivolatile target compounds and DMCs, RRF is greater than or equal to 0.05.

3. Evaluate the %D between initial calibration $\overline{RRF}$ and continuing calibration RRF for one or more semivolatile target compound(s) and DMCs.

    a. Check and recalculate the %D for one or more semivolatile target compound(s) associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory-reported value(s).

    b. Verify that the %D is within ±50.0% for the semivolatile target compounds and DMCs listed in Table 13, ±30.0% for 2,4-dinitrotoluene, 2-nitrophenol, and 2,4-dimethyphenol, and ±25.0% for all other semivolatile target compounds and DMCs.

4. If errors are detected in the calculations of either the continuing calibration RRF or the %D, perform a more comprehensive recalculation.

E. Action:

1. All semivolatile target compounds, including the "poor performers" listed in Table 13, will be qualified using the following criteria:

    a. If %D value for any of the semivolatile target "poor performers" is outside the ±50.0% criterion, qualify positive results with "J" and non-detected compounds "UJ".

    b. If %D value for 2,4-dinitrotoluene, 2-nitrophenol, and 2,4-dimethylphenol is outside the ±30.0% criterion, qualify positive results with "J" and non-detected compounds "UJ".

    c. If %D value for any other semivolatile target compound is outside the ±25.0% criterion, qualify positive results with "J", and non-detected compounds "UJ".

    d. If any semivolatile target compound has an RRF value less than the minimum criterion (0.01 for the "poor performers" and 0.05 for all other semivolatile compounds), use professional judgment for positive results, based on mass spectral identification, to qualify the data as "J" or unusable (R).

    e. If any semivolatile target compound has an RRF value less than the minimum criterion (0.01 for the "poor performers" and 0.05 for all other volatile compounds), qualify non-detected compounds as unusable (R).

    f. No action is taken on the DMC %D and RRF data alone. However, using professional judgment, the data reviewer may use the DMC %D and RRF data in conjunction with the DMC recoveries to determine the need for qualification of data.

2. If the laboratory has failed to provide adequate calibration information, the Region's designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

3. Whenever possible, the potential effects on the data due to calibration criteria exceedance should be noted in the Data Review Narrative.

4. If calibration criteria are grossly exceeded, this should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

Table 15. Continuing Calibration Actions for Semivolatile Analyses

Criteria	Action
%D outside allowable limits*	Positives "J" Non-detects "UJ"
RRF < 0.01 (poor performers) RRF < 0.05 (all other target compounds)	Positives "J" or "R" (based on mass spectral identification) Non-detects "R"

*±50.0% for the "poor performers", ±30.0 % for 2,4-dinitrotoluene, 2-nitrophenol, and 2,4-dimethyphenol, and ±20.5% for all other semivolatile compounds.

V. Blanks

A. Review Items:

Form I LCSV-1, Form I LCSV-2, Form IV LCSV, chromatograms, and quantitation reports.

B. Objective:

The purpose of laboratory or field blank analyses is to determine the existence and magnitude of contamination resulting from laboratory or field activities. If problems exist with a blank, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. A method blank must be extracted each time samples are extracted.

2. The number of samples extracted with each method blank shall not exceed 20 field samples (excluding Matrix Spike/Matrix Spike Duplicates (MS/MSDs) and Performance Evaluation (PE) samples).

3. The method blank must be analyzed on each Gas Chromatograph/Mass Spectrometer (GC/MS) system used to analyze the set of samples prepared with the method blank.

4. The concentration of each target compound (except the phthalate esters - see Table 16) found in the method blank must be less than its Contract Required Quantitation Limit (CRQL) listed in the method. The concentration of each phthalate ester found in the method blank must be less than five times (5x) its respective CRQL listed in the method.

5. The concentration of non-target compounds in all blanks must be less than or equal to 10 µg/L.

Table 16. Phthalate Esters

Phthalate Esters
Dimethylphthalate
Diethylphthalate
Di-n-butylphthalate
Butylbenzylphthalate
bis(2-Ethylhexyl)phthalate
Di-n-octylphthalate

D. Evaluation:

1. Review the results of all associated blanks on the forms and raw data (chromatograms and quantitation reports) to evaluate the presence of target and non-target compounds in the blanks.

2. Verify that a method blank analysis has been reported for each extraction batch and for each GC/MS system used to analyze semivolatile samples. The reviewer can use the Method Blank Summary (Form IV LCSV) to identify the samples associated with each method blank.

E. Action:

The sample results must not be corrected by subtracting any blank value.

1. If a semivolatile compound is found in a method blank but not found in the sample, no action is taken.

2. If the method blank concentration is less than the CRQL (<5x CRQL for phthalate esters) and:

   a. the sample concentration is less than the CRQL, report the CRQL value with a "U".

   b. the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.

3. If the method blank concentration is greater than the CRQL (>5x CRQL for phthalate esters) and:

   a. the sample concentration is less than the CRQL, report the CRQL value with a "U".

   b. the sample concentration is greater than or equal to the CRQL, but less than the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank with a "U", or the reviewer may elect to qualify the data as unusable (R).

   c. the sample concentration is greater than the CRQL and greater than or equal to the blank concentration, use professional judgment to qualify the data.

4. If the method blank concentration is equal to the CRQL (equal to 5x CRQL for phthalate esters), and:

   a. the sample concentration is less than the CRQL, report the CRQL value with a "U".

   b. the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.

5. If gross contamination exists (i.e., saturated peaks by GC/MS), all affected compounds in the associated samples should be qualified as unusable (R), due to interference. This should be noted for Contract Laboratory Program Project Officer (CLP PO) action if the contamination is suspected of having an effect on the sample results.

6. The same consideration given to the target compounds should also be given to Tentatively Identified Compounds (TICs), which are found in both the sample and associated blank(s) (see Semivolatile Section XII for TIC guidance).

7. If the contaminants found in the blank are interfering non-target compounds at concentrations >10 µg/L, the reviewer may use professional judgment to qualify the data.

8. Additionally, there may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, they should qualify the data. Contamination introduced through dilution water is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but are absent in the undiluted sample result.

Table 17. Blank Actions for Semivolatiles Analyses

Method Blank Result	Sample Result	Action for Samples
< CRQL *	Not detected	No action
< CRQL *	< CRQL	Report CRQL value with a "U"
	$CRQL	Professional judgment
> CRQL *	< CRQL	Report CRQL value with a "U"
	$ CRQL but < Blank Result	Report the blank concentration for the sample with a "U" or qualify the data as unusable (R)
	> CRQL and $ Blank Result	Professional judgment
= CRQL*	< CRQL	Report CRQL with a "U"
	$ CRQL	Professional judgment
Gross contamination	Positive	Qualify results as unusable (R)
TIC >10 µg/L	Positive	Professional judgment

* 5x CRQL for phthalate esters.

VI. Deuterated Monitoring Compounds

A. Review Items:

Form II LCSV-1, Form II LCSV-2 , chromatograms, and quantitation reports.

B. Objective:

Laboratory performance on individual samples is established by means of spiking activities. All samples are spiked with Deuterated Monitoring Compounds (DMCs) prior to sample preparation. The evaluation of the results of these DMCs is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences. Since the effects of the sample matrix are frequently outside laboratory control and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and requires analytical experience and professional judgment. Accordingly, this section consists primarily of guidelines, in some cases with several optional approaches suggested.

C. Criteria:

1. Sixteen DMCs (seven acid compounds and nine base/neutral compounds) listed in Table 18 below are added to all samples and blanks to measure their recovery in environmental samples.

Table 18. Semivolatile Deuterated Monitoring Compounds (DMCs) and Recovery Limits

DMC	Recovery Limits (%)	DMC	Recovery Limits (%)
Phenol-d5	10 - 110	Dimethylphthalate-d6	62 - 102
bis-(2-Chloroethyl) ether-d8	41 - 94	Acenaphthylene-d8	49 - 98
2-Chlorophenol-d4	33 - 110	4-Nitrophenol-d4	9 - 181
4-Methylphenol-d8	38 - 95	Fluorene-d10	50 - 97
Nitrobenzene-d5	35 - 114	4,6-Dinitro-methylphenol-d2	53 - 153
2-Nitrophenol-d4	40 - 106	Anthracene-d10	55 - 116
2,4-Dichlorophenol-d3	42 - 98	Pyrene-d10	47 - 114
4-Chloroaniline-d4	8 - 70	Benzo(a)pyrene-d12	54 - 120

2. Recoveries for DMCs in semivolatile samples and blanks must be within the limits specified in Table 18.

D. Evaluation:

1. Check raw data (e.g., chromatograms and quantitation reports) to verify the recoveries on the Deuterated Monitoring Compound Recovery Forms (Form II LCSV-1 and Form II LCSV-2). Check for any calculation or transcription errors.

2. Verify that the DMC recoveries were calculated correctly. The equation can be found in the method.

3. Whenever there are two or more analyses for a particular sample, the reviewer must determine which are the most accurate data to report. Considerations should include, but are not limited to:

    a. DMC recovery (marginal versus gross deviation).

    b. Technical holding times.

    c. Comparison of the values of the target compounds reported in each sample analysis.

    d. Other Quality Control (QC) information, such as performance of internal standards.

E. Action:

Table 20 lists the semivolatile DMCs and their associated target compounds. If any DMC recovery in the semivolatiles fraction is out of specification, data should be qualified considering the existence of interference in the raw data and using professional judgment as follows:

1. For any recovery greater than the upper acceptance limit:

    a. Detected associated semivolatile target compounds are qualified as "J."

    b. Non-detected associated semivolatile target compounds should not be qualified.

2. For any recovery less than the lower acceptance limit:

    a. Detected associated semivolatile target compounds are qualified as "J".

    b. Use professional judgment to qualify the sample quantitation limit for non-detected associated semivolatile target compounds as approximated (UJ) or unusable (R).

3. In the special case of a blank analysis with DMCs out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable DMC recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, analytical problems should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

Table 19. DMCs Actions For Semivolatile Analyses

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
%R >Upper Acceptance Limit	"J"	No qualification
%R <Lower Acceptance Limit	"J"	Professional judgment: "UJ" or "R"

Table 20. Semivolatile Deuterated Monitoring Compounds and the Associated Target Compounds

Phenol-d5 (DMC)	**2-Chlorophenol-d4 (DMC)**	**2-Nitrophenol-d4**
Benzaldehyde	2-Chlorophenol	Isophorone
Phenol		2-Nitrophenol

bis-(2-Chloroethyl) ether-d8 (DMC)	**4-Methylphenol-d8 (DMC)**	**4-Chloroaniline-d4 (DMC)**
bis-(2-Chloroethyl) ether	2-Methylphenol	4-Chloroaniline
2,2'-oxybis(1-Chloropropane)	4-Methylphenol	Hexachlorocyclopentadiene
bis(2-Chloroethoxy) methane	2,4-Dimethylphenol	3,3'-Dichlorobenzidine

Nitrobenzene-d5 (DMC)	**2,4-Dichlorophenol-d3 (DMC)**	**Dimethylphthalate-d6 (DMC)**
Acetophenone	2,4-Dichlorophenol	Caprolactam
N-Nitroso-di-n-propylamine	Hexachlorobutadiene	1,1'-Biphenyl
Hexachloroethane	4-Chloro-3-methylphenol	Dimethylphthalate
Nitrobenzene	2,4,6-Trichlorophenol	Diethylphthalate
2,6-Dinitrotoluene	2,4,5-Trichlorophenol	Di-n-butylphthalate
2,4-Dinitrotoluene	1,2,4,5-Tetrachlorobenzene	Butylbenzylphthalate
N-Nitrosodiphenylamine	Pentachlorophenol	bis(2-Ethylhexyl) phthalate
		Di-n-octylphthalate

Table 20. Semivolatile Deuterated Monitoring Compounds and the Associated Target Compounds, con't.

Fluorene-d10 (DMC)	Anthracene-d10 (DMC)	Pyrene-d10 (DMC)
Dibenzofuran	Hexachlorobenzene	Fluoranthene
Fluorene	Atrazine	Pyrene
4-Chlorophenyl-phenylether	Phenanthrene	Benzo(a)anthracene
4-Bromophenyl-phenylether	Anthracene	Chrysene

Acenaphthylene-d8 (DMC)	4-Nitrophenol-d4	Benzo (a) pyrene-d12 (DMC)
Naphthalene	2-Nitroaniline	Benzo(b)fluoranthene
2-Methylnaphthalene	3-Nitroaniline	Benzo(k)fluoranthene
2-Chloronaphthalene	2,4-Dinitrophenol	Benzo(a)pyrene
Acenaphthylene	4-Nitrophenol	Indeno(1,2,3-cd)pyrene
Acenaphthene	4-Nitroaniline	Dibenzo(a,h)anthracene
		Benzo(g,h,i)perylene

4,6-Dinitro-2-methylphenol-d2 (DMC)
4,6-Dinitro-2-methylphenol

VII. Matrix Spikes/Matrix Spike Duplicates

A. Review Items:

Form III LCSV, chromatograms, and quantitation reports.

NOTE: Data for Matrix Spike/Matrix Spike Duplicates (MS/MSDs) will not be present unless requested by the Region.

B. Objective:

Data for MS/MSDs are generated to determine long-term precision and accuracy of the analytical method on the sample matrix and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone cannot be used to evaluate the precision and accuracy of individual samples. However, when exercising professional judgment, this data should be used in conjunction with other available Quality Control (QC) information.

C. Criteria:

1. **If requested**, MS and MSD samples are analyzed at a frequency of one MS and MS per 20 or fewer samples.

2. Spike recoveries should be within the advisory limits provided on Form III LCSV.

3. Relative Percent Differences (RPD) between MS and MSD recoveries must not exceed the advisory limits provided on Form III LCSV.

D. Evaluation:

1. Verify that requested MS and MSD samples were analyzed at the required frequency and that results are provided for each sample.

2. Inspect results for the MS/MSD Recovery on Form III LCSV and verify that the results for recovery and RPD are within the advisory limits.

3. Verify transcriptions from raw data and verify calculations.

4. Check that the MS recoveries and RPD were calculated correctly.

5. Calculate Percent Relative Standard Deviation (%RSD) results of non-spiked compounds between the original sample, MS, and MSD sample. Provide this information in the Data Review Narrative.

E. Action:

1. No action is taken on MS/MSD data alone. However, using informed professional judgment, the data reviewer may use the MS and MSD results in conjunction with other QC criteria and determine the need for some qualification of the data.

2. The data reviewer should first try to determine to what extent the results of the MS/MSD affect the associated data. This determination should be made with regard to the MS/MSD sample itself, as well as specific analytes for all samples associated with the MS/MSD.

3. In those instances where it can be determined that the results of the MS/MSD affect only the sample spiked, qualification should be limited to this sample only. However, it may be determined through the MS/MSD results that a laboratory is having a systematic problem in the analysis of one or more analytes, which affects all associated samples.

4. The reviewer must use professional judgment to determine the need for qualification of positive results of non-spiked compounds.

NOTE: If a field blank was used for the MS/MSD, the Contract Laboratory Program Project Officer (CLP PO) must be notified.

VIII. Regional Quality Assurance and Quality Control

A. Review Items:

Form I LCSV-1, Form I LCSV-2 , chromatograms, Sample Traffic Reports (TRs), and quantitation reports.

B. Objective:

Regional Quality Assurance and Quality Control (QA/QC) refer to any QA and/or QC samples initiated by the Region, including field duplicates, Performance Evaluation (PE) samples, blind spikes, and blind blanks. The use of these QA/QC samples are highly recommended (e.g., the use of field duplicates can provide information on sampling precision and homogeneity).

C. Criteria:

Criteria are determined by each Region.

1. PE sample frequency may vary.

2. The analytes present in the PE sample must be correctly identified and quantified.

D. Evaluation:

1. Evaluation procedures must follow the Region's Standard Operating Procedure (SOP) for data review. Each Region will handle the evaluation of PE samples on an individual basis. Results for PE samples should be compared to the acceptance criteria for the specific PE samples, if available.

2. Calculate Relative Percent Difference (RPD) between field duplicates. Provide this information in the Data Review Narrative.

E. Action:

Any action must be in accordance with Regional specifications and the criteria for acceptable PE sample results. Unacceptable results for PE samples should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

IX. Internal Standards

A. Review Items:

Form VIII LCSV-1, Form VIII LCSV-2, quantitation reports, and chromatograms.

B. Objective:

Internal standards performance criteria ensure that Gas Chromatograph/Mass Spectrometer (GC/MS) sensitivity and response are stable during each analysis.

C. Criteria:

1. Internal standard area counts must not vary by more than a factor of two (-50% to +100%) from the associated 12-hour calibration standard.

2. The retention time of the internal standard must not vary by more than ±20 seconds from the retention time of the associated 12-hour calibration standard.

D. Evaluation:

1. Check raw data (e.g., chromatograms and quantitation lists) to verify the internal standard retention times and areas reported on the Internal Standard Area Summary (Form VIII LCSV-1 and Form VIII LCSV-2).

2. Verify that all retention times and internal standard areas are within the required criteria.

3. If there are two analyses for a particular fraction, the reviewer must determine which are the most accurate data to report. Considerations should include:

    a. Magnitude and direction of the internal standard area shift.

    b. Magnitude and direction of the internal standard retention time shift.

    c. Technical holding times.

    d. Comparison of the values of the target compounds reported in each fraction.

    e. Other Quality Control (QC) information.

E. Action:

1. If an internal standard area count for a sample or blank is greater than +100% of the area for the associated standard:

    a. Positive results for compounds quantitated using that internal standard should be qualified “J”.

    b. Non-detected associated compounds should not be qualified.

2. If an internal standard area count for a sample or blank is less than 50% of the area for the associated standard:

   a. Positive results for compounds quantitated using that internal standard should be qualified with a "J".

   b. Non-detected associated compounds should be qualified as unusable (R).

3. If an internal standard retention time varies by more than 20 seconds:

   The chromatographic profile for that sample must be examined to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection of the data for that sample fraction. Positive results should not need to be qualified with "R" if the mass spectral criteria are met.

4. If the internal standard performance criteria are grossly exceeded, then this should be noted for Contract Laboratory Program Project Officer (CLP PO) action. Potential effects on the data resulting from unacceptable internal standard performance should be noted in the Data Review Narrative.

Table 21. Internal Standards Actions For Semivolatiles Analyses

Criteria	Action	
	Detected Associated Compounds*	Non-Detected Associated Compounds*
Area counts >100% of 12-hour standard	"J"	No action
Area counts <50% of 12-hour standard	"J"	"R"

* See Table D-2 in the method for semivolatile compounds associated to each internal standard.

X. Target Compound Identification

A. Review Items:

Form I LCSV-1, Form I LCSV-2, quantitation reports, mass spectra, and chromatograms.

B. Objective:

The objective of the criteria for Gas Chromatograph/Mass Spectrometer (GC/MS) qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).

The identification criteria can be applied much more easily in detecting false positives than false negatives. More information is available for false positives due to the requirement for submittal of data supporting positive identifications. However, negatives, or non-detected compounds, represent an absence of data and are, therefore, much more difficult to assess. One example of the detection of false negatives is not reporting a target compound that is reported as a Tentatively Identified Compound (TIC).

C. Criteria:

1. The Relative Retention Times (RRTs) must be within ±0.06 RRT units of the standard RRT.

2. Mass spectra of the sample compound and a current laboratory-generated standard (i.e., the mass spectrum from the associated calibration standard) must match according to the following criteria:

    a. All ions present in the standard mass spectrum at a relative intensity greater than 10% must be present in the sample spectrum.

    b. The relative intensities of these ions must agree within ±20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30-70%).

    c. Ions present at greater than 10% in the sample mass spectrum, but not present in the standard spectrum, must be evaluated by a reviewer experienced in mass spectral interpretation.

D. Evaluation:

1. Check that the RRT of reported compounds is within ±0.06 RRT units of the standard RRT.

2. Check the sample compound spectra against the laboratory standard spectra to verify that it meets the specified criteria.

3. The reviewer should be aware of situations when sample carryover is a possibility and should use professional judgment to determine if instrument cross-contamination has affected any positive compound identification.

4. Check the chromatogram to verify that peaks are identified. Major peaks are either identified as target compounds, TICs, Deuterated Monitoring Compounds (DMCs), or internal standards.

E. Action:

1. The application of qualitative criteria for GC/MS analysis of target compounds requires professional judgment. It is up to the reviewer's discretion to obtain additional information from the laboratory. If it is determined that incorrect identifications were made, all such data should be qualified as not detected (U) or unusable (R).

2. Professional judgment must be used to qualify the data if it is determined that cross-contamination has occurred.

3. Any changes made to the reported compounds or concerns regarding target compound identifications should be clearly indicated in the Data Review Narrative. The necessity for numerous or significant changes should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

XI. Compound Quantitation and Reported CRQLS

A. Review Items:

Form I LCSV-1, Form I LCSV-2 , sample preparation sheets, Sample Delivery Group (SDG) Narrative, quantitation reports, and chromatograms.

B. Objective:

The objective is to ensure that the reported quantitation results and Contract Required Quantitation Limits (CRQLs) are accurate.

C. Criteria:

1. Compound quantitation, as well as the adjustment of the CRQL, must be calculated according to the correct equation.

2. Compound Relative Response Factors (RRFs) must be calculated based on the internal standard associated with that compound, as listed in the method. Quantitation must be based on the quantitation ion (m/z) specified in the method for both the internal standard and target analytes. The compound quantitation must be based on the RRF from the appropriate daily calibration standard.

D. Evaluation:

1. For all fractions, raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Quantitation lists and chromatograms should be compared to the reported positive sample results and quantitation limits. Check the reported values.

2. Verify that the correct internal standard, quantitation ion, and RRF were used to quantitate the compound. Verify that the same internal standard, quantitation ion, and RRF are used consistently throughout, in both the calibration as well as quantitation process.

3. Verify that the CRQLs have been adjusted to reflect all sample dilutions.

E. Action:

1. If any discrepancies are found, the laboratory may be contacted by the Region's designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, the reviewer must use professional judgment to decide which value is the most accurate value. Under these circumstances, the reviewer may determine that qualification of data is warranted. A description of the reasons for data qualification and the qualification that is applied to the data should be documented in the Data Review Narrative.

2. Numerous or significant failures to accurately quantify the target compound or to properly evaluate and adjust CRQLs should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

XII. Tentatively Identified Compounds

A. Review Items:

Form I LCSV-TIC , chromatograms, library search printouts, and spectra for the Tentatively Identified Compound (TIC) candidates.

B. Objective:

Chromatographic peaks in semivolatile fraction analyses that are not target analytes, Deuterated Monitoring Compounds (DMCs), or internal standards are potential TICs. TICs must be qualitatively identified via a forward search of the NIST/USEPA/NIH (May 1992 release or later) mass spectral library, and/or Wiley (1991 release or later) mass spectral library, or equivalent. The identification must be assessed by the data reviewer.

C. Criteria:

For each sample, the laboratory must conduct a mass spectral search of the NIST/USEPA/NIH, and/or Wiley, or equivalent mass spectral library, and report the possible identity for the appropriate number of the largest semivolatile fraction peaks which are not DMCs, internal standards, or target compounds, but which have area or height greater than 10% of the area or height of the nearest internal standard. Estimated concentrations for TICs are calculated similarly to the Target Compound List (TCL) compounds, using total ion areas for the TIC and the internal standard, and assuming a Relative Response Factor (RRF) of 1.0. TIC results are reported for each sample on the Organic Analyses Data Sheet (Form I LCSV-TIC).

D. Evaluation:

1. Guidelines for tentative identification are as follows:

    a. Major ions (greater than 10% relative intensity) in the reference spectrum should be present in the sample spectrum.

    b. The relative intensities of the major ions should agree within ±20% between the sample and the reference spectra.

    c. Molecular ions present in the reference spectrum should be present in the sample spectrum.

    d. Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination, interference, or presence of coeluting compounds.

    e. Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting compounds. Data system library reduction programs can sometimes create these discrepancies.

    f. Non-target compounds receiving a library search match of 85% or higher should be considered a “likely match”. The compound should be reported unless the mass spectral interpretation specialist feels there is evidence to support not reporting the

compound as identified by the library search program. The lab should include the justification for not reporting a compound as listed by the search program in the Sample Delivery Group (SDG) Narrative.

g. If the library search produces more than one compound at or above 85%, report the compound with the highest percent match (report the first compound if percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels that the highest match compound should not be reported or another compound with a lower match should be reported. The laboratory should include the justification for not reporting the compound with the highest spectral match within the SDG Narrative.

h. If the library search produces a series of obvious isomer compounds with library search matches greater than 85% (e.g., tetramethyl naphthalenes), the compound with the highest library search percent match should be reported (or the first compound if the library search matches are the same). A note should be placed in the SDG Narrative indicating the exact isomer configuration, as reported, may not be accurate.

i If the library search produces no matches at or above 85% and in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (e.g., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

j. Straight-chained, branched, or cyclic alkanes are not to be reported as TICs on Form I LCSV-TIC. When these alkanes are tentatively identified, the concentration(s) are to be estimated and reported in the SDG Narrative as alkanes by class (i.e., straight-chain, branched, cyclic, as a series, or as applicable).

2. Check the raw data to verify that the laboratory has generated a library search for all required peaks in the chromatograms for samples and blanks.

3. Blank chromatograms should be examined to verify that TIC peaks present in samples are not found in blanks. When a low-level, non-target compound that is a common artifact or laboratory contaminant is detected in a sample, a thorough check of blank chromatograms may require looking for peaks which are less than 10% of the internal standard height, but present in the blank chromatogram at a similar Relative Retention Time (RRT).

4. All mass spectra for each sample and blank must be examined.

5. Since TIC library searches often yield several candidate compounds having a close matching score, all reasonable choices should be considered.

6. The reviewer should be aware of common laboratory artifacts/contaminants and their sources (e.g., Aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.

Examples:

a. Common laboratory contaminants: CO_2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons, and phthalates at levels less than 100 µg/L.

b. Solvent preservatives, such as cyclohexene which is a methylene chloride preservative. Related by-products include cyclohexanone, cyclohexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.

c. Aldol reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

7. Occasionally, a target compound may be identified in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list (false negative). If the total area quantitation method was used, the reviewer should request that the laboratory recalculate the result using the proper quantitation ion and Relative Response Factor (RRF).

   In certain situations, a non-target compound may be incorrectly identified by the instrument's target analyte data processor as a target compound (false positive). When this happens, the non-target library search procedure will not detect the false positive as a TIC. In this case the reviewer should request that the laboratory properly identify the compound and recalculate the result using the total area quantitation method and a RRF of 1.0.

   In addition, the reviewer should evaluate other sample chromatograms and check for both false negatives and false positives to determine if the occurrence is isolated or systematic.

8. Target compounds may be identified in more than one fraction. Verify that quantitation is made from the proper fraction.

9. Library searches should not be performed on internal standards or DMCs.

10. TIC concentration should be estimated assuming an RRF of 1.0.

E. Action:

1. All TIC results should be qualified as "NJ", tentatively identified, with approximated concentrations.

2. General actions related to the review of TIC results are as follows:

   a. If it is determined that a tentative identification of a non-target compound is not acceptable, the tentative identification should be changed to "unknown" or another appropriate identification.

   b. If all contractually-required peaks were not library searched and quantitated, the Region's designated representative could request these data from the laboratory.

3. In deciding whether a library search result for a TIC represents a reasonable identification, professional judgment must be exercised. If there is more than one possible match, the result may be reported as "either compound X or compound Y". If there is a lack of isomer specificity, the TIC result may be changed to a non-specific isomer result (e.g., 1,3,5-trimethyl benzene to trimethyl benzene isomer), or to a compound class (e.g., 2-methyl, 3-ethyl benzene to a substituted aromatic compound).

4. The reviewer may elect to report all similar isomers as a total (e.g., all alkanes may be summarized and reported as total hydrocarbons).

5. Other case factors may influence TIC judgments. If a sample TIC match is poor, but other samples have a TIC with a good library match, similar Relative Retention Time (RRT), and the same ions, identification information may be inferred from the other sample TIC results.

6. Any changes made to the reported data or any concerns regarding TIC identifications should be indicated in the Data Review Narrative.

7. Failure to properly evaluate and report TICs should be noted for CLP Project Officer (CLP PO) action.

XIII. System Performance

A. Review Items:

Form VIII LCSV-1, Form VIII LCSV-2 , and chromatograms.

B. Objective:

During the period following Instrument Performance Quality Control (QC) checks (e.g., blanks, tuning, calibration), changes may occur in the system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC runs, a thorough review of the ongoing data acquisition can yield indicators of instrument performance.

C. Criteria:

There are no specific criteria for system performance. Professional judgment should be used to assess the system performance.

D. Evaluation:

1. Abrupt discrete shifts in the Reconstructed Ion Chromatogram (RIC) baseline may indicate a change in the instrument's sensitivity or the zero setting. A baseline “shift” could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds, at or near the detection limit, to miss detection. A baseline “rise” could indicate problems such as a change in the instrument zero, a leak, or degradation of the column.

2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

    a. High RIC background levels or shifts in absolute retention times of internal standards.

    b. Excessive baseline rise at elevated temperature.

    c. Extraneous peaks.

    d. Loss of resolution.

    e. Peak tailing or peak splitting that may result in inaccurate quantitation.

3. A drift in instrument sensitivity may occur during the 12-hour time period. This could be discerned by examination of the internal standards area on Form VIII LCSV-1 and Form VIII LCSV-2 for trends such as a continuous or near-continuous increase or decrease in the internal standard area over time.

E. Action:

Professional judgment must be used to qualify the data if it is determined that system performance has degraded during sample analyses. Any degradation of system performance which significantly affected the data should be documented for Contract Laboratory Program Project Officer (CLP PO) action.

XIV. Overall Assessment of Data

A. Review Items:

Entire data package, data review results, and (if available) Quality Assurance Project Plan (QAPP), and Sampling and Analysis Plan (SAP).

B. Objective:

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria:

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation:

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the QAPP (specifically the acceptance or performance criteria), SAP, and communication with the data user that concerns the intended use and desired quality of these data.

E. Action:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the Quality Control (QC) criteria previously discussed.

2. Write a brief narrative to give the user an indication of the analytical limitations of the data. Any inconsistency of the data with the Sample Delivery Group (SDG) Narrative should be noted for Contract Laboratory Program Project Officer (CLP PO) action. If sufficient information on the intended use and required quality of the data are available, the reviewer should include their assessment of the usability of the data within the given context. This may be used as part of a formal Data Quality Assessment (DQA).

PESTICIDE/AROCLOR (PCB) DATA REVIEW

The Pesticide/Aroclor (PCB) data requirements to be checked are listed below.

I. Preservation

II. Gas Chromatograph/Electron Capture Detector (GC/ECD) Instrument Performance Check

III. Initial Calibration

IV. Calibration Verification

V. Blanks

VI. Surrogate Spikes

VII. Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

VIII. Laboratory Control Samples (LCSs)

IX. Regional Quality Assurance (QA) and Quality Control (QC)

X. Florisil Cartridge Performance Check

XI. Target Compound Identification

XII. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

XIII. Overall Assessment of Data

I. Preservation

A. Review Items:

Form I LCP, USEPA Sample Traffic Report (TR) and/or Chain-of-Custody, raw data, sample extraction sheets, and Sample Delivery Group (SDG) Narrative checking for :

1. pH
2. Sample temperature
3. Holding time
4. Other sample conditions

B. Objective:

The objective is to ascertain the validity of results based on sample condition (i.e., preservation and temperature) and the holding time of the sample from time of collection to time of sample extraction and analysis.

C. Criteria:

The technical holding time criteria for water samples are as follows:

For pesticides and Aroclors in cooled (4°C ± 2°C) water samples, the maximum holding time for extraction is seven (7) days from sample collection, and the maximum holding time for analysis is 40 days from sample extraction.

D. Evaluation:

Technical holding times for sample extraction are established by comparing the sample collection date on the TR with the dates of extraction on Form I LCP and the sample extraction sheets. To determine if the samples were analyzed within the holding time after extraction, compare the dates of extraction on the sample extraction sheets with the dates of analysis on Form I LCP.

Review the SDG Narrative and the TR to determine if the samples were received intact and iced. If there is no indication in the SDG Narrative, the TR, or other sample records that there was a problem with the samples, then the integrity of the samples can be assumed to be acceptable. If it is indicated that there were problems with the samples, then the integrity of the sample may have been compromised and professional judgment should be used to evaluate the effect of the problem on the sample results.

E. Action:

1. If technical holding times are exceeded, qualify all positive results as estimated "J", and sample quantitation limits as estimated "UJ". Document in the Data Review Narrative that holding times were exceeded.

2. If technical holding times are grossly exceeded, either on the first analysis or upon re-analysis, the reviewer must use professional judgment to determine the reliability of the data and the effect of additional storage on the sample results. The reviewer may determine that detected compound results and non-detected compound quantitation

limits are approximates and should be qualified with "J" or "UJ", respectively, or the reviewer may determine that non-detected compound data are unusable (R).

3. Whenever possible, the reviewer should comment on the effect of exceeding the holding time on the resulting data in the Data Review Narrative.

4. When technical holding times are grossly exceeded, this should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

Table 22. Holding Time Actions for Pesticide/Aroclor (PCB) Analyses

Holding Time	Action
> 7 days (for extraction), or > 40 days (for analysis)	Positives "J," Quantitation Limits "UJ"
Grossly exceeded	Using professional judgment: Positives "J" Quantitation Limits "UJ" or "R"

II. GC/ECD Instrument Performance Check

A. Review Items:

Form VI LCP-4, Form VI LCP-5, Form VI LCP-6, Form VI LCP-7, Form VII LCP-1, chromatograms, and data system printouts.

B. Objective:

Performance checks on the Gas Chromatograph with Electron Capture Detector (GC/ECD) system are performed to ensure adequate resolution and instrument sensitivity. These criteria are not sample-specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.

C. Criteria:

1. Resolution Check Mixture

   a. The Resolution Check Mixture is analyzed at the beginning of every initial calibration sequence, on each Gas Chromatograph (GC) column and instrument used for analysis. The Resolution Check Mixture contains the following pesticides and surrogates:

Resolution Check Mixture Components

gamma-Chlordane	Endrin ketone
Endosulfan I	Methoxychlor
4,4'-DDE	Tetrachloro-m-xylene (surrogate)
Dieldrin	Decachlorobiphenyl (surrogate)
Endosulfan sulfate	

   b. The resolution between any two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 60% on each GC column.

2. Performance Evaluation Mixture

   a. The Performance Evaluation Mixture (PEM) is analyzed at the beginning (following the resolution check mixture) and at the end of the initial calibration sequence. The PEM is also analyzed at the beginning of every other 12-hour analytical period. The PEM contains the following pesticides and surrogates:

Performance Check Mixture Components

gamma-BHC	Endrin
alpha-BHC	Methoxychlor
4,4'-DDT	Tetrachloro-m-xylene (surrogate)
beta-BHC	Decachlorobiphenyl (surrogate)

b. The resolution between any two adjacent peaks in the initial calibration and calibration verification PEMs must be greater than or equal to 90% on each GC column.

c. The percent breakdown is the amount of decomposition that 4,4'-DDT and Endrin undergo when analyzed on the GC column. For Endrin, the percent breakdown is determined by the presence of Endrin aldehyde and/or Endrin ketone in the PEM. For 4,4-DDT, the percent breakdown is determined by the presence of 4,4'-DDD and/or 4,4'-DDE in the PEM.

i. The percent breakdown of 4,4'-DDT and Endrin in the PEMs must each be less than or equal to 20.0% on each GC column.

ii. The combined percent breakdown for 4,4'-DDT and Endrin in PEMs must be less than or equal to 30.0% on each GC column.

3. Midpoint Individual Standard Mixtures A and B

a. The mid-point Individual Standard Mixtures A and B (INDA/INDB) are analyzed as part of the initial calibration. The mid-point INDA and INDB are also analyzed at the beginning of every other 12-hour analytical period. The Individual Standard Mixtures contain the following pesticides and surrogates:

Individual Standard Mixtures Components

Individual Standard Mix A	**Individual Standard Mix B**
alpha-BHC	beta-BHC
Heptachlor	delta-BHC
gamma-BHC	Aldrin
Endosulfan I	Heptachlor-epoxide
Dieldrin	alpha-Chlordane
Endrin	gamma-Chlordane
4,4'-DDD	4,4'-DDE
4,4'-DDT	Endosulfan sulfate

Individual Standard Mixtures Components, con't.

Individual Standard Mix A	Individual Standard Mix B
Methoxychlor	Endrin aldehyde
Tetrachloro-m-xylene (surrogate)	Endrin ketone
Decachlorobiphenyl (surrogate)	Endosulfan II
	Tetrachloro-m-xylene (surrogate)
	Decachlorobiphenyl (surrogate)

b. The resolution between any two adjacent peaks in the mid-point concentration of Individual Standard Mixtures A and B in the initial calibration and calibration verification must be greater than or equal to 90.0% on each column.

D. Evaluation:

1. Resolution Check Mixture

   Check the Resolution Check Mixture data and Form VI LCP-4 to verify that the resolution between two adjacent peaks for the required compounds is greater than or equal to 60% on both GC columns.

2. Performance Evaluation Mixture

   a. Check the initial calibration and calibration verification Performance Evaluation Mixture (PEM) data and Form VI LCP-5 to verify that the resolution between adjacent peaks is greater than or equal to 90% on both GC columns.

   b. Check Form VII LCP-1 to verify that the breakdown of 4,4'-DDT is less than or equal to 20.0%, the breakdown of Endrin is less than or equal to 20.0%, and the combined breakdown of 4,4'-DDT and Endrin is less than or equal to 30.0% in all PEMs on both GC columns.

3. Midpoint Individual Standard Mixture A and B

   Check the initial calibration and calibration verification mid-point Individual Standard Mixtures A and B data on Form VI LCP-6 and Form VI LCP-7 to verify that the resolution between adjacent peaks is greater than or equal to 90% on both GC columns.

E. Action:

1. Resolution Check Mixture

   If resolution criteria are not met, the quantitative results may not be accurate due to inadequate resolution. Qualitative identifications may also be questionable if coelution exists.

a. Detected target compounds that were not adequately resolved should be qualified with a "J".

b. Use professional judgment to determine the need to qualify undetected data as unusable (R).

2. Performance Evaluation Mixture

a. If PEM resolution criteria are not met, the quantitative results may not be accurate due to inadequate resolution. Qualitative identifications may be questionable if coelution exists.

i. Positive sample results should be qualified with a "J".

ii. Use professional judgment to determine the need to qualify undetected data as unusable (R).

b. If 4,4'-DDT breakdown is greater than 20.0%:

i. Qualify positive results for 4,4'-DDT "J".

ii. Qualify positive results for 4,4'-DDT and/or 4,4'-DDE "J".

iii. If 4,4'-DDT was not detected, but 4,4'-DDD and/or 4,4'-DDE are detected, qualify the quantitation limit for 4,4'-DDT as unusable (R), and qualify positive results for 4,4'-DDD and/or 4,4'-DDE as presumptively present at an approximated quantity (NJ).

c. If Endrin breakdown is greater than 20.0%:

i. Qualify positive results for Endrin "J".

ii. Qualify positive results for Endrin aldehyde and/or Endrin ketone "J".

iii. If Endrin was not detected, but Endrin aldehyde and/or Endrin ketone are detected, qualify the quantitation limit for Endrin as unusable (R), and qualify positive results for Endrin aldehyde and/or Endrin ketone as presumptively present at an approximated quantity (NJ).

d. If the combined 4,4'-DDT and Endrin breakdown is greater than 30.0%, the reviewer should consider the degree of individual breakdown of 4,4'-DDT and Endrin and apply qualifiers as described above.

3. Midpoint Individual Standard Mixtures A and B

   If mid-point Individual Standard Mixtures A and/or B resolution criteria are not met, the quantitative results may not be accurate due to inadequate resolution. Qualitative identifications may be questionable if coelution exists.

   a. Detected target compounds that were not adequately resolved should be qualified with a "J".

   b. Use professional judgment to determine the need to qualify undetected data as unusable (R).

4. Potential effects on the sample data resulting from the instrument performance check criteria should be noted in the Data Review Narrative. If the data reviewer has knowledge that the laboratory has repeatedly failed to comply with the requirements for linearity, resolution, or 4,4'-DDT/Endrin breakdown, the data reviewer should notify the Contract Laboratory Program Project Officer (CLP PO).

Table 23. GC/ECD Instrument Performance Check Actions

Criteria	Action
Resolution Check Mixture %Resolution <60.0	Positives "J" Non-detects "R" (using professional judgment)
PEM %Resolution <90.0	Positives "J" Non-detects "R" (using professional judgment)
4,4'-DDT % breakdown >20.0% and 4,4'-DDT is detected	Positive 4,4'-DDT "J" Positive 4,4'-DDD "J" Positive 4,4'-DDE "J"
Endrin % breakdown >20.0% and Endrin is detected	Positive Endrin "J" Positive Endrin aldehyde "J" Positive Endrin ketone "J"
4,4'-DDT % breakdown >20.0% and 4,4'-DDT is not detected	Non-detect 4,4'-DDT "R" Positive 4,4'-DDD "NJ" Positive 4,4'-DDE "NJ"
Endrin % breakdown >20.0% and Endrin is not detected	Non-detect Endrin "R" Positive Endrin aldehyde "NJ" Positive Endrin ketone "NJ"
Combined % breakdown >30%	Apply qualifiers as described above considering degree of individual breakdown.
Midpoint Individual Standard Mixture A and B %Resolution <90.0	Positives "J" Non-detects "R" (using professional judgment)

III. Initial Calibration

A. Review Items:

Form VI LCP-1, Form VI LCP-2, Form VI LCP-3, chromatograms, and data system printouts.

B. Objective:

Compliance requirements for satisfactory initial calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for pesticide and Aroclor compounds on the Target Compound List (TCL). Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical sequence, and capable of producing a linear calibration curve.

C. Criteria:

1. Individual Standard Mixtures A and B (containing all of the single component pesticides and surrogates) must be analyzed at low, mid-point, and high levels during the initial calibration, on each Gas Chromatograph (GC) column and instrument used for analysis.

    a. The mean retention times of each of the single component pesticides and surrogates are determined from the three-point initial calibration. The mean retention time for the surrogates are measured from each Individual Standard Mixture A.

    b. A retention time window must be calculated for each single component analyte and surrogate according to Table D-1 of the pesticides fraction in the method.

    c. At least one chromatogram from each of the Individual Standard Mixtures A and B must yield peaks that give recorder deflections between 50-100% of full scale.

    d. The concentrations of the low, medium, and high level standards containing all of the single component pesticides and surrogates are as follows:

        i. The low point corresponds to the Contract Required Quantitation Limits (CRQL) for each analyte.

        ii. The mid-point concentration must be four times (4x) the low point.

        iii. The high point must be at least 16 times (16x) the low point, but a higher concentration may be chosen.

    e. Mean calibration factor must be calculated for each single component analyte and surrogate over the initial calibration range.

    f. The Percent Relative Standard Deviation (RSD) of the calibration factors for each of the single component target compounds must be less than or equal to 20.0%, except for alpha-BHC and delta-BHC. The Percent RSD of the calibration factors for alpha-BHC and delta-BHC must be less than or equal to 25.0%. The Percent RSD of the calibration factors for the two surrogates must be less than or equal to 30.0%.

NOTE: Either peak area or peak height may be used to calculate the calibration factors that are, in turn, used to calculate %RSD. However, the type of peak measurement used to calculate each calibration factor for a given compound must be consistent. For example, if peak area is used to calculate the low point calibration factor for Endrin, then the mid-point and high point calibration factors for Endrin must also be calculated using peak area.

2. Multi-component Target Compounds

   a. The multi-component target compounds (the seven Aroclors and Toxaphene) must be analyzed separately (except for Aroclor 1260 and Aroclor 1016, which may be combined in one standard mixture, Aroclor 1660) at a single concentration level during the initial calibration sequence. The analysis of the multi-component target compounds must also contain the pesticide surrogates.

   b. For each multi-component analyte, the retention times are determined for three to five peaks. The retention time window is calculated as ±0.07 minutes around the absolute retention times.

   c. A calibration factor must be determined for each peak selected for the multi-component analytes.

D. Evaluation:

1. Individual Standard Mixtures A and B

   a. Check the raw data (chromatograms and data system printouts) for each standard to verify that each of the standards was analyzed at the required concentration levels.

   c. Check the Individual Standard Mixtures A and B data and Form VI LCP-1 and review the calculated retention time windows for calculation and transcription errors.

   d. Check the chromatograms and verify that at least one chromatogram from each of the Individual Standard Mixtures A and B yields peaks registering recorder/printer deflections between 50-100% of full scale.

   e. Verify that the concentrations of the low, medium, and high level standards of Individual Standard Mixtures A and B meet the criteria defined in Pesticide Section III.C.1.d.

   f. Check the Individual Standard Mixtures A and B data and Form VI LCP-2 to verify that the %RSD for the calibration factors are in compliance with the criteria defined in Pesticide Section III.C.

   g. Check and recalculate the calibration factors and %RSD for one or more pesticides. Verify that the recalculated values agree with the reported values. If errors are detected, more comprehensive recalculation and review should be performed.

2. Multi-component Target Compounds

   a. Check the raw data for the standards to verify that the multi-component analytes were analyzed at the required concentration.

   b. Check the data for the multi-component target compounds and Form VI LCP-3 to verify that at least three peaks were used for identification, and retention time windows were calculated as required.

   c. Check the data to verify that calibration factors have been determined for each selected peak.

E . Action:

1. If retention time windows are not calculated correctly, recalculate the windows and use the corrected values for all evaluations.

2. If the chromatogram display (recorder deflection) criteria are not met, use professional judgment to evaluate the effect on the data.

3. If the standard concentration criteria are not met, use professional judgment to evaluate the effect on the data and notify the Contract Laboratory Program Project Officer (CLP PO). This is especially critical for the low level standards and non-detects.

4. If the %RSD criteria are not met, qualify positive results with a "J" and the quantitation limits for non-detected target compounds with "UJ".

5. Potential effects on the sample data due to problems with calibration should be noted in the Data Review Narrative. If the data reviewer has knowledge that the laboratory has repeatedly failed to comply with the requirements for frequency, linearity, retention time, or resolution, the data reviewer should notify the CLP PO.

Table 24. Initial Calibration Action for Pesticide/Aroclor (PCB) Analyses

Criteria	Action
%RSD exceeds allowable limits*	Positives "J" Non-detects "UJ"

* %RSD # 20% for single component target compounds except delta-BHC and alpha-BHC.
%RSD # 25% for delta-BHC and alpha-BHC.
%RSD # 30.0% for surrogates (tetrachloro-m-xylene and decachlorobiphenyl).

IV. Calibration Verification

A. Review Items:

Form VII LCP-1, Form VII LCP-2, chromatograms, and data system printouts.

B . Objective:

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. Calibration verification checks and documents satisfactory performance of the instrument over specific time periods during sample analysis. To confirm the calibration and evaluate instrument performance, calibration verification is performed, consisting of the analyses of instrument blanks, the Performance Evaluation Mixture (PEM), and the mid-point concentration of Individual Standard Mixtures A and B.

C. Criteria:

1. The absolute retention time for each single component pesticide and surrogate in the PEM and the mid-point concentration of Individual Standard Mixtures A and B used for calibration verification must be within the retention time windows determined from the initial calibration.

2. The Percent Difference (%D) between the calculated amount and the nominal amount (amount added) for each of the single component pesticides and surrogates in the PEM and the mid-point concentration of the Individual Standard Mixtures A and B used for calibration verification must be greater than or equal to -25.0% and less than or equal to 25.0%.

D . Evaluation:

1. Check the data for each of the single component pesticides and surrogates in the PEM, the mid-point concentration of Individual Standard Mixtures A and B, Form VII LCP-1, and Form VII LCP-2 to verify that the absolute retention times are within the retention time windows.

2. Check the data from the PEM, the mid-point concentration of Individual Standard Mixtures A and B, Form VII LCP-1, and Form VII LCP-2 to verify that the %D between the calculated amount and the true amount for each of the pesticides and surrogates are within ±25.0%.

E. Action:

1. Retention time windows are used in qualitative identification. If the standards do not fall within the retention time windows, the associated sample results should be carefully evaluated. All samples injected after the last in-control standard are potentially affected.

    a. For non-detected target compounds in the affected samples, check to see if the sample chromatograms contain any peaks that are close to the expected retention time window of the pesticide of interest.

i. If no peaks are present, non-detected values can be considered valid and no action is necessary.

ii. If any peaks are present close to the expected retention time window of the pesticide of interest, the reviewer may choose to qualify the non-detected values as "N".

b. For detected compounds in the affected samples, if the peaks are within the retention time window, no action is necessary. However, if the peaks are close to the expected retention time window of the pesticide of interest, the reviewer may take additional effort to determine if sample peaks represent the compounds of interest.

For example, the reviewer can examine the data package for the presence of three or more standards containing the pesticide of interest that were run within a 72-hour period during which the sample was analyzed. If three or more such standards are present, the retention time window can be re-evaluated using the mean retention times of the standards.

i. If the peaks in the affected sample fall within the revised window, the detected target compounds may be qualified as "NJ".

ii. If the reviewer cannot do anything with the data to resolve the problem of concern, all quantitation limits should be qualified unusable "R".

2. If the %D is not within ±25%, qualify associated positive results "J" and quantitation limits for non-detects "UJ".

3. Potential effects on the sample data due to problems with calibration should be noted in the Data Review Narrative.

Table 25. Calibration Verification Action for Pesticide/Aroclor (PCB) Analyses

Criteria	Action
RT out of RT window	Use professional judgment (see Pesticide Section IV.E.1 above)
%D not within ±25%	Positives "J" Non-detects "UJ"

V. Blanks

A. Review Items:

Form I LCP, Form IV LCP, chromatograms, and data system printouts.

B. Objective:

The purpose of laboratory or field blank analyses is to determine the existence and magnitude of contamination resulting from laboratory or field activities. The criteria for evaluation of laboratory blanks apply to any blank associated with the samples (e.g., method blanks, instrument blanks, and sulfur cleanup blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. Method Blanks

   A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples (excluding Matrix Spike/Matrix Spike Duplicate (MS/MSDs), Performance Evaluation (PE) samples, and Laboratory Control Samples (LCSs)). In addition, a method blank shall be extracted by the same procedure used to extract samples.

2. Instrument Blanks

   An acceptable instrument blank must be run at least once every 12 hours and immediately prior to the analysis of either the Performance Evaluation Mixture (PEM) or mid-point Individual Standard Mixtures A and B, used for calibration verification. All groups of acceptable sample analyses are to be preceded and followed by acceptable instrument blanks.

3. Sulfur Cleanup Blanks

   A sulfur cleanup blank must be analyzed whenever part of a set of samples extracted together requires sulfur cleanup. If the entire set of samples associated with a method blank requires sulfur cleanup, the method blank also serves the purpose of a sulfur blank and no separate sulfur blank is required.

4. The concentration of each target analyte in the method, sulfur, and instrument blanks must be less than its Contract Required Quantitation Limits (CRQL) listed in the method.

D. Evaluation:

1. Review the results of all associated blanks, Form I LCP, Form IV LCP, and raw data (chromatograms and data system printouts) to evaluate presence of target or non-target analytes in the blanks.

2. Verify that method blank analysis has been reported per Sample Delivery Group (SDG), per extraction batch, and per extraction procedure. The reviewer can use Form IV LCP to identify samples associated with each blank.

3. Verify that the method blank analysis(es) contains less than the CRQL of any target pesticide or Aroclor/Toxaphene, or any interfering peak.

4. Verify that the instrument blank analysis has been performed every 12 hours as the first analysis of the calibration verification sequence. Evaluate the results from the various instrument blanks to verify that target analyte concentrations are less than the CRQL (assuming a 1 Liter extraction of a water sample).

5. Verify that the sulfur cleanup blanks were analyzed at the required frequency and the sulfur blanks do not contain any target compounds at or above the CRQL (assuming a 1 Liter extraction of a water sample). If a separate sulfur cleanup blank was prepared, one version of Form IV LCP should be completed associating all the samples with the method blank, and a second version of Form IV LCP should be completed listing only those samples associated with the separate sulfur cleanup blank.

E. Action:

Action regarding unsuitable blank results depends on the circumstances and the origin of the blank. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results must <u>not</u> be corrected by subtracting the blank value.

1. If a target pesticide compound or Aroclor/Toxaphene is found in the blank but <u>not</u> found in the sample, no qualification is required.

2. If a target pesticide compound or Aroclor/Toxaphene concentration in a blank is less than the CRQL, and:

   a. the sample concentration is less than the CRQL, report the CRQL value with a “U”.

   b. the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.

3. If a target pesticide compound or Aroclor/Toxaphene concentration in a blank is greater than the CRQL, and:

   a. the sample concentration is less than the CRQL, report the CRQL value with a “U”.

   b the sample concentration is greater than or equal to the CRQL, but less than the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank with a “U”, or the reviewer may elect to qualify the data as unusable (R).

   c. the sample concentration is greater than the CRQL, and greater than the blank concentration, use professional judgment to qualify the data.

4. If a target pesticide compound or Aroclor/Toxaphene concentration in a blank is equal to the CRQL, and:

   a. the sample concentration is less than the CRQL, report the CRQL value with a "U".

   b. the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.

5. If gross contamination exists (e.g., saturated peaks, "hump-o-grams", "junk" peaks), all affected compounds in the associated samples should be qualified as unusable (R), due to interference. This should be noted for Contract Laboratory Program Project Officer (CLP PO) action if the contamination is suspected of having an effect on the sample results.

6. Additionally, there may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, they should qualify the data. Contamination introduced through dilution is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but absent in the undiluted sample result.

Table 26. Blank Actions for Pesticide/Aroclor (PCB) Analyses

Blank Result	Sample Result	Action for Samples
< CRQL	Not detected	No action
< CRQL	< CRQL	Report CRQL value with a "U"
	$ CRQL	Professional Judgment
> CRQL	< CRQL	Report CRQL value with a "U"
	$ CRQL but < Blank Result	Report the blank concentration for the sample with a "U", or qualify the data as unusable (R)
	> CRQL and $ Blank Result	Professional judgment
= CRQL	< CRQL	Report CRQL values with a "U"
	$CRQL	Professional judgment
Gross contamination	Positive	Qualify results as unusable (R)

VI. Surrogate Spikes

A. Review Items:

Form II LCP, Form VIII LCP, chromatograms, and data system printouts.

B. Objective:

Laboratory performance on individual samples is established by means of spiking activities. All samples are spiked with surrogate compounds prior to sample extraction. The evaluation of the recovery results of these surrogate spikes is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and requires analytical experience and professional judgment. Accordingly, this section consists primarily of guidelines, in some cases with several optional approaches suggested.

C. Criteria:

1. Two surrogate spikes, tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DCB), are added to all samples, including Matrix Spike/Matrix Spike Duplicates (MS/MSDs), Laboratory Control Samples (LCSs) and blanks to measure their recovery. The surrogates are also added to all the standards to monitor retention times.

2. The recovery limits for the surrogates TCX and DCB are 30-150% for all samples, including MS/MSDs, LCSs and blanks.

3. The retention times of the surrogates in each Performance Evaluation Mixture (PEM), mid-point Individual Standard Mixtures A and B used for calibration verification, and samples must be within the calculated retention time windows. TCX must be within ±0.05 minutes, and DCB must be within ±0.10 minutes of the mean retention time determined from the initial calibration.

D. Evaluation:

1. Check the raw data (e.g., chromatograms and data system printouts) to verify the recoveries on the Surrogate Recovery Form (Form II LCP). Check for any calculation or transcription errors.

2. Verify that the surrogate recoveries were calculated correctly using the equation in the method.

3. Check the raw data (e.g., chromatograms and data system printouts) to verify that the retention times on Form VIII LCP are accurate and within the retention time windows determined from the initial calibration.

4. Whenever there are two or more analyses for a particular sample, the reviewer must determine which are the most accurate data to report. Considerations should include, but are not limited to:

a. Surrogate recovery (marginal versus gross deviation).

b. Technical holding times.

c. Comparison of the values of the target compounds reported in each sample analysis.

d. Other Quality Control (QC) information, such as surrogate recoveries and/or retention times in blanks and standards.

E. Action:

If either surrogate spike recovery is outside the acceptance limits, the reviewer must consider the existence of coelution and interference in the raw data and use professional judgment to qualify data as described below, as surrogate recovery problems may not directly apply to target analytes.

1. For any surrogate recovery greater than 150%:

   a. Detected associated target compounds are qualified as "J".

   b. Non-detected associated target compounds should not be qualified.

2. For any surrogate recovery greater than or equal to 10%, but less than 30%:

   a. Detected associated target compounds are qualified as "J".

   b. Non-detected associated target compounds are qualified as "UJ".

3. For any surrogate recovery less than 10%, the reviewer should examine the sample chromatogram to assess the qualitative validity of the analysis. If low surrogate recoveries are found to be due to sample dilution, professional judgment should be used to determine if the resulting data should be qualified. If sample dilution is not a factor, qualify:

   a. Detected associated target compounds as "J".

   b. Non-detected associated target compounds as unusable (R).

4. In the special case of a blank analysis with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, analytical problems should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

5. If surrogate retention times in PEMs, Individual Standard Mixtures, samples and blanks are outside of the retention time windows, the reviewer must use professional judgment to qualify data.

Table 27. Surrogate Actions for Pesticide/Aroclor (PCB) Analyses

Criteria	Action*	
	Detected Associated Compounds	Non-detected Associated Compounds
%R > 150%	"J"	No qualification
10% # %R < 30%	"J"	"UJ"
%R < 10% (sample dilution not a factor)	"J"	"R"
RT out of RT window	Professional Judgment	

*Use professional judgment in qualifying data as surrogate recovery problems may not directly apply to target analytes.

Table 28. Pesticides Surrogates and Associated Target Compounds

Tetrachloro-m-xylene (surrogate)	**Decachlorobiphenyl (surrogate)**	
alpha-BHC	alpha-Chlordane	4,4'-DDE
beta-BHC	gamma-Chlordane	4,4'-DDT
gamma-BHC	Heptachlor epoxide	Endosulfan I
delta-BHC	Dieldrin	Endosulfan II
Heptachlor	Endrin	Endosulfan sulfate
Aldrin	Endrin aldehyde	Methoxychlor
	Endrin ketone	Aroclors
	4,4'-DDD	Toxaphene

VII. Matrix Spikes/Matrix Spike Duplicates

A. Review Items:

Form III LCP-1, chromatograms, and data system printouts.

NOTE: Data for Matrix Spike/Matrix Spike Duplicates (MS/MSDs) will not be present unless requested by the Region.

B. Objective:

Data for MS/MSDs are generated to determine long-term precision and accuracy of the analytical method on the sample matrix and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone cannot be used to evaluate the precision and accuracy of individual samples. However, when exercising professional judgment, this data should be used in conjunction with other available Quality Control (QC) information.

C. Criteria:

1. **If requested**, MS/MSD samples are extracted and analyzed at a frequency of one MS and MSD per 20 or fewer field samples.

2. MS/MSD recoveries should be within the advisory limits provided on Form III LCP-1.

3. Relative Percent Difference (RPD) between MS and MSD recoveries should not exceed the advisory limits provided on Form III LCP-1.

D. Evaluation:

1. Verify that requested MS and MSD samples were analyzed at the required frequency and that results are provided for each sample.

2. Check the raw data and Form III LCP-1 to verify that the results for MS and MSD recoveries were calculated and transcribed correctly.

3. Check that the MS and MSD recoveries and the RPD were calculated correctly.

4. Calculate the Percent Relative Standard Deviation (%RSD) of non-spiked compounds between the original sample, MS, and MSD sample results. Provide this information in the Data Review Narrative.

E . Action:

1. No action is taken on MS/MSD data alone. However, using informed professional judgment, the data reviewer may use the MS and MSD results in conjunction with other Quality Control (QC) criteria and determine the need for some qualification of the data.

2. The data reviewer should first try to determine to what extent the results of the MS/MSD affect the associated sample data. This determination should be made with

regard to the MS/MSD sample itself, as well as specific analytes for all samples associated with the MS/MSD.

3. In those instances where it can be determined that the results of the MS/MSD affect only the sample spiked, qualification should be limited to this sample only. However, it may be determined through the MS/MSD results that a laboratory is having a systematic problem in the analysis of one or more analytes, which affects all associated samples.

4 The reviewer must use professional judgment to determine the need for qualification of positive results of non-spiked compounds.

NOTE: If a field blank was used for the MS/MSD, unless designated as such by the Region, the Contract Laboratory Program Project Officer (CLP PO) must be notified.

VIII. Laboratory Control Samples

A. Review Items:

Form I LCP, Form III LCP-2, LCS chromatograms, and data system printouts.

B. Objective:

Data for Laboratory Control Samples (LCSs) are generated to provide information on the accuracy of the analytical method and laboratory performance.

C. Criteria:

1. The LCS contains the pesticides target compounds and surrogates listed in Table 29 below.

Table 29. Pesticides Laboratory Control Sample (LCS) Spike Compounds and Recovery Limits

LCS Spike Compound	Recovery Limits (%)	LCS Spike Compound	Recovery Limits (%)
gamma-BHC	50 - 120	Endosulfan sulfate	50 - 120
Heptachlor epoxide	50 - 150	gamma-chlordane	30 - 130
Dieldrin	30 - 130	Tetrachloro-m-xylene (surrogate)	30 - 150
4,4-DDE	50 - 150	Decachlorobiphenyl (surrogate)	30 - 150
Endrin	50 - 120		

2. The percent recoveries for the LCS compounds must be within the limits specified in Table 29.

NOTE: All samples prepared and analyzed with an LCS that does not meet the technical acceptance criteria in the method will require re-extraction and re-analysis.

D. Evaluation:

1. Check the raw data (e.g., chromatograms and data system printouts) to verify the recoveries on the Laboratory Control Sample Recovery Form (Form III LCP-2). Check for any calculation or transcription errors.

2. Verify that the LCS recoveries reported on Form III LCP-2 are within the QC limits.

E. Action:

If the LCS criteria are not met, laboratory performance and method accuracy are in question. Professional judgment should be used to determine if the data should be qualified or rejected. The following guidance is suggested for qualifying sample data for which the associated LCS does not meet the required criteria.

1. If the LCS recovery criteria are not met, the LCS results should be used to qualify sample data for the specific compounds that are included in the LCS solution.

    a. If the LCS recovery exceeds the upper acceptance limit, detected target compounds may be qualified as "J". Non-detected target compounds should not be qualified.

    b. If the LCS recovery is less than the lower acceptance limit, detected target compounds may be qualified as "J" and non-detects may be qualified as unusable (R).

    c. Professional judgment should be used to qualify data for compounds other than those compounds that are included in the LCS. Professional judgment to qualify non-LCS compounds should take into account the compound class, compound recovery efficiency, analytical problems associated with each compound, and comparability in the performance of the LCS compound to the non-LCS compound.

4. It should be noted for Contract Laboratory Program Project Officer (CLP PO) action if a laboratory fails to analyze an LCS with each SDG, or if the reviewer has knowledge that a laboratory consistently fails to generate acceptable LCS recoveries.

Table 30. LCS Recovery Actions

Criteria	Action
> Upper Acceptance Limit	Positives "J" Non-Detects: No qualification
< Lower Acceptance Limit	Positives "J" Non-Detects "R"

IX. Regional Quality Assurance and Quality Control

A. Review Items:

Form I LCP, chromatograms, data system printouts, Sample Traffic Reports (TRs), and raw data for Regional Quality Control (QC) samples.

B. Objective:

Regional Quality Assurance (QA) and QC refers to any QA and/or QC samples initiated by the Region, including field duplicates, Performance Evaluation (PE) samples, blind spikes, and blind blanks. The use of these QA/QC samples are highly recommended (e.g., the use of field duplicates can provide information on sampling precision and sample homogeneity).

C. Criteria:

Criteria are determined by each Region.

1. PE sample frequency may vary.

2. The analytes present in the PE sample must be correctly identified and quantified.

D. Evaluation:

1. Evaluation procedures must follow the Region's Standard Operating Procedure (SOP) for data review. Each Region will handle the evaluation of PE samples on an individual basis. Results for PE samples should be compared to the acceptance criteria for the specific PE samples, if available.

2. Calculate Relative Percent Difference (RPD) between field duplicates. Provide this information in the Data Review Narrative.

E. Action:

Any action must be in accordance with Regional specifications and the criteria for acceptable PE sample results. Unacceptable results for PE samples should be noted for Contract Laboratory Program Project Officer (CLP PO) action.

X. Florisil Cartridge Performance Check

A. Review Items:

Form IX LCP, Florisil raw data, chromatograms, and data system printouts.

B. Objective:

The Florisil cartridge cleanup procedure is used to remove matrix interferences from sample extracts prior to analysis. The use of the Florisil cartridge cleanup procedure significantly reduces matrix interferences caused by polar compounds. The performance of each lot of Florisil cartridges used for sample cleanup is checked by running a spiked reagent through a cartridge, and calculating the recoveries of the spiked compounds through the cartridge.

C. Criteria:

1. The performance of each lot of Florisil cartridges used for sample cleanup must be checked at least once, or every six months, whichever is most frequent. The performance of the Florisil cartridges is checked with a spiking solution contain 2,4,5-trichlorophenol and the mid-point concentration of Individual Standard Mixture A.

2. The limits for recovery of the target pesticide compounds and surrogates in the Individual Standard Mixture A are 80-120%, and the recovery limit for 2,4,5-trichlorophenol is less than 5%.

D. Evaluation:

1. Check the raw data for the Florisil cartridge performance check analysis and the results on Form IX LCP. Recalculate some of the percent recoveries to verify that there are no calculation or transcription errors.

2. Verify that the percent recoveries of the target pesticides and surrogates in the performance check solution are within 80-120%, and the recovery of 2,4,5-trichlorophenol is less than 5%.

E. Action:

1. If the Florisil Cartridge Performance Check criteria are not met, the raw data should be examined for the presence of polar interferences and professional judgment should be used in qualifying the data as follows:

    a. If percent recovery is greater than 120% for any of the pesticide target compounds in the Florisil Cartridge Performance Check, use professional judgment to qualify detected target compounds. Non-detected target compounds do not require qualification.

    b. If percent recovery is less than 80%, but greater than 10%, for any of the pesticide target compounds in the Florisil Cartridge Performance Check, qualify detected target compounds “J” and non-detected target compounds “UJ”.

c. If percent recovery is less than 10% for any of the pesticide target compounds in the Florisil Cartridge Performance Check, non-detected target compounds may be qualified as unusable (R). Detected target compounds do not require qualification.

d. If percent recovery of 2,4,5-trichlorophenol in the Florisil Cartridge Performance Check is greater than or equal to 5%, use professional judgment to qualify detected and non-detected target compounds, considering interference on the sample chromatogram.

4. Potential effects on the sample data resulting from the Florisil Cartridge Performance Check analysis not yielding acceptable results should be noted in the Data Review Narrative.

Table 31. Florisil Cartridge Performance Check Actions

Criteria	Action
%R > 120% (pesticide target compounds)	Positives: Professional Judgment Non-detects: No action
10% < %R < 80% (pesticide target compounds)	Positives: "J" Non-detects: "UJ"
%R < 10% (pesticide target compounds)	Positives: Professional Judgment Non-detects: "R"
%R > 5% (2,4,5-trichlorophenol)	Professional Judgment

XI. Target Compound Identification

A. Review Items:

Form I LCP, Form X LCP-1, Form X LCP-2, chromatograms, and data system printouts.

B. Objective:

Qualitative criteria for compound identification have been established to minimize the number of false positives (reporting a compound present when it is not) and false negatives (not reporting a compound that is present).

C. Criteria:

1. The retention times of both of the surrogates, and reported target compounds in each sample must be within the calculated retention time windows on both columns. Tetrachloro-m-xylene (TCX) must be within ±0.05 minutes of the mean retention time determined from the initial calibration and Decachlorobiphenyl (DCB) must be within ±0.10 minutes of the mean retention time determined from the initial calibration.

2. When no analytes are identified in a sample, the chromatograms from the analyses of the sample extract must use the same scaling factor as was used for the low point standard of the initial calibration associated with those analyses.

3. Chromatograms must display single component pesticides detected in the sample and the largest peak of any multi-component analyte detected in the sample at less than full scale.

4. If an extract must be diluted, chromatograms must display single component pesticides between 10-100% of full scale, and multi-component analytes between 25-100% of full scale.

5. For any sample, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and also return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of DCB.

6. If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram, and both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

D. Evaluation:

1. Review Form I LCP, the associated raw data (chromatograms and data system printouts) and Form X LCP-1 and Form X LCP-2. Confirm reported detected analytes by comparing the sample chromatograms to the tabulated results and verifying peak measurements and retention times. Confirm reported non-detected analytes by a review of the sample chromatograms. Check the associated blank data for potential interferences (to evaluate sample data for false positives) and check the calibration data for adequate retention time windows (to evaluate sample data for false positives and false negatives).

2. For multi-component target compounds (Aroclors and Toxaphene), the retention times and relative peak height ratios of major component peaks should be compared against the appropriate standard chromatograms.

E. Action:

1. If the qualitative criteria for both columns were not met, all target compounds that are reported as detected should be considered non-detected. The reviewer should use professional judgment to assign an appropriate quantitation limit using the following guidance:

   a. If the detected target compound peak was sufficiently outside the pesticide retention time window, the reported values may be a false positive and should be replaced with the sample Contract Required Quantitation Limits (CRQL) value.

   b. If the detected target compound peak poses an interference with potential detection of another target peak, then the reported value should be considered and qualified as unusable (R).

2. If the data reviewer identifies a peak in both Gas Chromatograph (GC) column analyses that falls within the appropriate retention time windows, but was reported as a non-detect, the compound may be a false negative. Professional judgment should be used to decide if the compound should be included. All conclusions made regarding target compound identification should be included in the Data Review Narrative.

3. If target compounds were detected on both GC columns, and the Percent Difference (%D) between the two results is greater than 25.0%, the potential for coelution should be considered and the reviewer should use professional judgment to decide whether a much larger concentration obtained on one column versus the other indicates the presence of an interfering compound. If an interfering compound is indicated, professional judgment must be used to determine how best to report, and if necessary, qualify the data.

4. If multi-component target compounds exhibit marginal pattern-matching quality, professional judgment should be used to establish whether the differences are due to environmental “weathering” (i.e., degradation of the earlier eluting peaks relative to the later eluting peaks). If the presence of a multi-component pesticide is strongly suggested, results should be reported as presumptively present (N).

5. If an observed pattern closely matches more than one Aroclor, professional judgment should be used to decide whether the neighboring Aroclor is a better match, or if multiple Aroclors are present.

XII. Compound Quantitation and Reported CRQLS

A. Review Items:

Form I LCP, Form X LCP-1, Form X LCP-2, sample preparation log sheets, chromatograms, Sample Delivery Group (SDG) Narrative, and data system printouts.

B . Objective:

The objective is to ensure that the reported quantitative results and Contract Required Quantitation Limits (CRQLs) are accurate.

C. Criteria:

Compound quantitation, as well as the adjustment of the CRQL, must be calculated according to the equations provided in the method.

D. Evaluation:

1. Raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Data system printouts, chromatograms, and sample preparation log sheets should be compared to the reported positive sample results and quantitation limits. Verify that the sample values are reported correctly.

2. Verify that the CRQLs have been adjusted to reflect all sample dilutions, clean-up activities, and other factors that are not accounted for by the method.

E. Action:

1. Quantitation limits affected by large, off-scale peaks should be qualified as unusable (R). If the interference is on-scale, the reviewer can provide an approximated quantitation limit (UJ) for each affected compound.

2. If there are any discrepancies found, the laboratory may be contacted by the Region's designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, the reviewer must decide which value is the best value. Under these circumstances, the reviewer may determine if qualification of the data is warranted. A description of the reasons for data qualification and the qualification that is applied to the data should be documented in the Data Review Narrative.

XIII. Overall Assessment of Data

A. Review Items:

Entire data package, data review results, and (if available) Quality Assurance Project Plan (QAPP), and Sampling and Analysis Plan (SAP).

B . Objective:

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C . Criteria:

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation:

1 . Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the QAPP (specifically the acceptance or performance criteria), SAP, and communication with data user that concerns the intended use and desired quality of these data.

E . Action:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the Quality Control (QC) criteria previously discussed.

2. Write a brief narrative to give the user an indication of the analytical limitations of the data. Any inconsistency of that data with the Sample Delivery Group (SDG) Narrative should be noted for Contract Laboratory Program Project Officer (CLP PO) action. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his/her assessment of the usability of the data within the given context. This may be used as part of a formal Data Quality Assessment (DQA).

APPENDIX A: GLOSSARY

Analysis Date/time - The date and military time (24-hour clock) of the injection of the sample, standard, or blank into the GC/MS or GC system.

Blank - An analytical sample designed to assess specific sources of contamination. See individual definitions for types of blanks.

Breakdown - A measure of the decomposition of certain analytes (DDT and Endrin) into by-products.

4-Bromofluorobenzene (BFB) - The compound chosen to establish mass spectrometer instrument performance for volatile analyses.

Calibration Factor - A measure of the Gas Chromatographic response of a target analyte to the mass injected.

Case - A finite, usually predetermined, number of samples collected over a given time period from a particular site. Case numbers are assigned by the Sample Management Office (SMO). A Case consists of one or more Sample Delivery Groups (SDGs).

Contract Compliance Screening (CCS) - A screening of electronic and hardcopy data deliverables for completeness and compliance with the contract. This screening is performed under USEPA direction by the SMO Contractor.

Contamination - A component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

Continuing Calibration - Analytical standard run every 12 hours to verify that the instrument response at the concentration of the standard is within acceptable limits.

Contract Laboratory Program (CLP) - Supports the USEPA's Superfund effort by providing a range of state-of-the-art chemical analytical services of known and documented quality. This program is directed by the Analytical Operations/Data Quality Center (AOC) of the Office of Emergency and Remedial Response (OERR) of USEPA.

Contract Laboratory Program Project Officer (CLP PO) - The Regional USEPA official responsible for monitoring laboratory performance and/or requesting analytical data or services from a CLP laboratory.

Decafluorotriphenylphosphine (DFTPP) - Compound chosen to establish mass spectrometer instrument performance for semivolatile analysis.

Deuterated Monitoring Compounds (DMCs) - Compounds added to every volatile and semivolatile calibration standard, blank, and sample used to evaluate the efficiency of the extraction/purge and trap procedures, and the performance of the Gas Chromatograph/Mass Spectrometer (GC/MS) systems. DMCs are isotopically labeled (deuterated) analogs of native target compounds. DMCs are not expected to be naturally detected in the environmental media.

Field Sample - A portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

Gas Chromatograph (GC) - The instrument used to separate analytes on a stationary phase within a chromatographic column. The analytes are volatized directly from the sample (volatile), or injected as extracts (semivolatile and pesticide). In volatile and semivolatile analyses, the compounds are detected by a Mass Spectrometer. In Pesticide analysis, the compounds are detected by an Electron Capture Detector.

Holding Time - The maximum amount of time samples may be held before they are processed.

> **Technical** – The maximum length of time that a sample may be held from the collection date until extraction and/or analysis.

Initial Calibration - Analysis of analytical standards at different concentrations to define the linear range of an analytical instrument (e.g., GC/MS, GC/ECD).

Internal Standards - Compounds added to every volatile and semivolatile standard, blank, sample, or sample extract, including the Laboratory Control Sample, at a known concentration, prior to analysis. Internal standards are used to monitor instrument performance and quantitation of target compounds.

Instrument Blank - A blank designed to determine the level of contamination either associated with the analytical instruments, or resulting from carryover.

Laboratory Control Sample (LCS) - The LCS is an internal laboratory Quality Control sample designed to assess (on an SDG-by-SDG basis) the capability of the contractor to perform the analytical method.

m/z - Mass to charge ratio, synonymous with "m/e".

Matrix - The predominant material of which the sample to be analyzed is composed. For the purpose of this document, the sample matrix is water.

Matrix Effect - In general, the effect of a particular matrix (water) on the constituents with which it contacts. Matrix effects may prevent efficient purging/extraction of target analytes, and may affect DMC and surrogate recoveries. In addition, non-target analytes may be extracted from the matrix causing interferences.

Matrix Spike (MS) - Aliquot of the water sample fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

Matrix Spike Duplicate (MSD) - A second aliquot of the same water sample that is fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to determine precision of the method.

Method Blank - A reagent water sample spike with internal standards, and surrogate standards (or DMCs for volatile and semivolatile), that is carried throughout the entire analytical procedure. The method blank is used to define the level of contamination associated with the processing and analysis of samples.

Narrative (SDG Narrative) - Portion of the data package which includes laboratory, contract, Case and sample number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution

Percent Difference (%D) -The difference between two values (usually a true value and a found value), calculated as a percentage of the true value. The Percent Difference indicates both the direction and the magnitude of the difference (i.e., the Percent Difference may be either negative, positive, or zero).

Performance Evaluation Mixture - A calibration solution of specific analytes used to evaluate both recovery and percent breakdown as measures of performance.

Polychlorinated Biphenyls (PCBs) - A group of toxic, persistent chemicals used in electrical transformers and capacitors for insulating purposes, and in gas pipeline systems as a lubricant. The sale and new use of PCBs were banned by law in 1979.

Purge and Trap (Device) - Analytical technique (device) used to isolate volatile (purgeable) organics by stripping the compounds from water by a stream of inert gas, trapping the compounds on an adsorbent such as a porous polymer trap, and thermally desorbing the trapped compounds onto the Gas Chromatographic column.

Reconstructed Ion Chromatogram (RIC) - A mass spectral graphical representation of the separation achieved by a Gas Chromatograph; a plot of total ion current versus retention time.

Relative Percent Difference (RPD) -The difference between two values, calculated as a percent relative to the mean of the two values.

Relative Response Factor (RRF) - A measure of the mass spectral response of an analyte relative to its associated internal standard. RRFs are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

Relative Retention Time (RRT) - The ratio of the retention time of a compound to that of a standard (such as an internal standard).

Resolution - Also termed separation or percent resolution, the separation between peaks on a chromatogram, calculated by dividing the depth of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.

Resolution Check Mixture - A solution of specific analytes used to determine resolution of adjacent peaks; used to assess instrumental performance.

Retention Time (RT) - The time a target analyte is retained on a GC column before elution. The identification of a target analyte is dependent on a target compound's retention time falling within the specified retention time window established for that compound. Retention time is dependent on the nature of the column's stationary phase, column diameter, temperature, flow rate, and other parameters.

Sample Delivery Group (SDG) - A unit within a sample Case that is used to identify a group of samples for delivery. An SDG is defined by the following, whichever is most frequent:

- Each Case of field samples received, or;
- Each 20 field samples (excluding Performance Evaluation (PE) samples) within a Case, or;
- Each 7 calendar day period during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).

In addition, all samples and/or sample fractions assigned to an SDG must have been scheduled under the same contractual turnaround time. Preliminary Results have no impact on defining the SDG.

Sample Management Office (SMO) - A contractor operated facility operated under the Contract Laboratory Analytical Services Support (CLASS) contract, awarded and administered by USEPA.

Sample Number (EPA Sample Number) - A unique identification number designated by USEPA to each sample. The EPA sample number appears on the sample Traffic Report (TR) which documents information on that sample.

Semivolatile Compounds - Compounds amenable to analysis by extraction of the sample with an organic solvent. Used synonymously with Base/Neutral/Acid (BNA) compounds.

Statement of Work (SOW) – A document which specifies how laboratories analyze samples under a particular CLP analytical program.

Storage Blank - Reagent water (two 40.0 mL aliquots) stored with volatile samples in an SDG. It is analyzed after all samples in that SDG have been analyzed; and it is used to determine the level of contamination acquired during storage.

Sulfur Cleanup Blank - A modified method blank that is prepared only when some of the samples in a batch are subjected to sulfur cleanup. It is used to determine the level of contamination associated with the sulfur cleanup procedure. When all of the samples are subjected to sulfur cleanup, then the method blank serves this purpose. When none of the samples are subjected to sulfur cleanup, no sulfur cleanup blank is required.

Surrogates (Surrogate Standard) - For pesticides/Aroclors, compounds added to every blank, sample, including Laboratory Control Sample, requested Matrix Spike/Matrix Spike Duplicate, and standard; used to evaluate analytical efficiency by measuring recovery. Surrogates are not expected to be detected in environmental media.

Target Compound List (TCL) - A list of compounds designated by the Statement of Work (Exhibit C) for analysis.

Tentatively Identified Compounds (TIC) - Compounds detected in samples that are not target compounds, internal standards, Deuterated Monitoring Compounds, or surrogates. Up to 30 peaks, not including those identified as alkanes (those greater than 10% of the peak area or height of the nearest internal standard), are subjected to mass spectral library searches for tentative identification.

Traffic Report (TR) - A USEPA sample identification form filled out by the sampler, which accompanies the sample during shipment to the laboratory and which documents sample condition and receipt by the laboratory.

Twelve-hour Time Period - The twelve (12)-hour time period for GC/MS system instrument performance check, standards calibration (initial or continuing calibration), and method blank analysis begins at the moment of injection of the DFTPP or BFB analysis that the laboratory submits as documentation of instrument performance. The time period ends after 12 hours have elapsed according to the system clock. For Pesticide/Aroclor (PCB) analyses performed by GC/EC, the 12-hour time period in the analytical sequence begins at the moment of injection of the instrument blank that precedes sample analyses, and ends after twelve hours have elapsed according to the system clock.

Validated Time of Sample Receipt (VTSR) - The date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and Sample Traffic Report.

Volatile Compounds - Compounds amenable to analysis by the purge and trap technique. Used synonymously with purgeable compounds.

APPENDIX B:
ORGANIC DATA REVIEW SUMMARY

CASE NO. _____ SITE _____

LABORATORY _____ NO. OF SAMPLES/MATRIX _____

SDG NO. _____ SOW NO. _____ REGION _____

REVIEWER NAME _____ COMPLETION DATE _____

CLP PO: ACTION _____ FYI _____

REVIEW CRITERIA		FRACTION		
		VOA	BNA	PEST/PCB
1.	PRESERVATION	_____	_____	_____
2.	GC/MS OR GC/ECD INSTRUMENT PERFORMANCE CHECK	_____	_____	_____
3.	INITIAL CALIBRATION	_____	_____	_____
4.	CONTINUING CALIBRATION OR CALIBRATION VERIFICATION	_____	_____	_____
5.	BLANKS	_____	_____	_____
6.	DEUTERATED MONITORING COMPOUND SURROGATE SPIKES	_____	_____	_____
7.	MATRIX SPIKES/MATRIX SPIKE DUPLICATES	_____	_____	_____
8.	LABORATORY CONTROL SAMPLE			_____
9.	REGIONAL QA/QC	_____	_____	_____
10.	INTERNAL STANDARDS	_____	_____	
11.	FLORISIL CARTRIDE PERFORMANCE CHECK			_____
12.	TARGET COMPOUND IDENTIFICATION	_____	_____	_____
13.	COMPOUND QUANTITATION AND REPORTED CRQLS	_____	_____	_____
14.	TENTATIVELY IDENTIFIED COMPOUNDS	_____	_____	
15.	SYSTEM PERFORMANCE	_____	_____	

Office of Superfund Remediation and Technology Innovation (OSRTI)
United States Environmental Protection Agency (USEPA)
Washington, DC 20460

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USEPA Contract Laboratory Program

National Functional Guidelines

for Superfund Organic Methods Data Review

Final

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NOTICE

The policies and procedures set forth here are intended as guidance to the United States Environmental Protection Agency (hereafter referred to as USEPA) and other Governmental employees. They do not constitute rule-making by the USEPA, and may not be relied on to create a substantive or procedural right enforceable by any other person. The Government may take action that is at a variance with the policies and procedures in this manual.

This document can be obtained from the USEPA's Contract Laboratory Program (CLP) Web site at:

http://www.epa.gov/superfund/programs/clp/guidance.htm

Table of Contents

List of Tables

Acronyms

%D	Percent Difference
%RSD	Percent Relative Standard Deviation
ARO	Aroclor
BFB	Bromofluorobenzene
CCS	Contract Compliance Screening
CCV	Continuing Calibration Verification
CF	Calibration Factor
CLP	Contract Laboratory Program
CLP PO	Contract Laboratory Program Project Officer
COC	Chain of Custody
CRQL	Contract Required Quantitation Limit
CSF	Complete SDG File
DART	Data Assessment Rapid Transmittal
DAT	Data Assessment Tool
DCB	Decachlorobiphenyl
DFTPP	Decafluorotriphenylphosphine
DMC	Deuterated Monitoring Compound
DQA	Data Quality Assessment
DQO	Data Quality Objective
GC	Gas Chromatograph
GC/ECD	Gas Chromatograph/Electron Capture Detector
GC/MS	Gas Chromatograph/Mass Spectrometer
GPC	Gel Permeation Chromatography
INDA	Individual Standard Mixture A
INDB	Individual Standard Mixture B
INDC	Individual Standard Mixture C
LCS	Laboratory Control Sample
MS	Matrix Spike
MSD	Matrix Spike Duplicate
OSRTI	Office of Superfund Remediation and Technology Innovation

Acronyms

PCBs	Polychlorinated Biphenyls
PE	Performance Evaluation
PEM	Performance Evaluation Mixture
QA	Quality Assurance
QAC	Quality Assurance Coordinator
QAPP	Quality Assurance Project Plan
QC	Quality Control
RIC	Reconstructed Ion Chromatogram
RPD	Relative Percent Difference
RRF	Relative Response Factor
$\overline{RRF}$	Mean Relative Response Factor
RRT	Relative Retention Time
RSCC	Regional Sample Control Center
RSD	Relative Standard Deviation
RT	Retention Time
SAP	Sampling and Analysis Plan
SCP	Single Component Pesticide
SDG	Sample Delivery Group
SIM	Selected Ion Monitoring
SMO	Sample Management Office
SOP	Standard Operating Procedure
SOW	Statement of Work
TCL	Target Compound List
TCX	Tetrachloro-m-xylene
TIC	Tentatively Identified Compound
TR	Traffic Report/Chain of Custody Record
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
VTSR	Validated Time of Sample Receipt

Introduction

This document is designed to offer the data reviewer guidance in determining the usability of analytical data generated through the Contract Laboratory Program's (CLP) Statement of Work (SOW) for Multi-Media, Multi-Concentration Organics Analysis (SOM01.2), and any future editorial revisions of SOM01.2, hereinafter referred to as the SOM01.2 SOW. The guidance is somewhat limited in scope and is intended to be used as an aid in the formal technical review process. It should not be used to establish specific contract compliance (use of this document to evaluate data generated under Organic SOWs other than the SOM01.2 SOW is cautioned). Definitive guidance is provided where performance should be fully under a laboratory's control (e.g., blanks, calibration standards, instrument performance checks), while general guidance is provided for evaluating subjective data that is affected by the site conditions.

The guidelines presented in the document will aid the data reviewer in establishing: (a) if data meets the specific technical and quality control (QC) criteria established in the SOW; and (b) the usability of any data not meeting the specific technical and QC criteria established in the SOW. It must be understood by the reviewer that acceptance of data not meeting technical requirements is based upon many factors, including, but not limited to, site-specific technical requirements, the need to facilitate the progress of specific projects, and availability for resampling. To make judgments at this level requires the reviewer to have a complete understanding of the intended use of the data. The reviewer is strongly encouraged to establish a dialogue with the user to discuss usability issues and to answer questions regarding the review, prior to, and after data review. It should also be understood that in all cases, data which do not meet specified criteria are never to be fully acceptable without qualification.

The data reviewer should note that while this document is to be used as an aid in the formal data review process, other sources of guidance and information, as well as professional judgment, should also be used to determine the ultimate usability of data, especially in those cases where all data does not meet specific technical criteria. The reviewer should also be aware that minor modifications to the analytical methods may be made through the CLP's Request For Quote For Modified Analysis form to meet site-specific requirements, and that these modifications could affect certain validation criteria such as the Contract Required Quantitation Limits (CRQLs), initial calibration levels, Continuing Calibration Verification (CCV) levels, and Target Compound Lists (TCLs). A full copy of a request for modified analysis made to the analytical method should be included in the data package by the laboratory.

Data Qualifier Definitions

The following definitions provide brief explanations of the national qualifiers assigned to results in the data review process. If the Regions choose to use additional qualifiers, a complete explanation of those qualifiers should accompany the data review.

U	The analyte was analyzed for, but was not detected at a level greater than or equal to the level of the adjusted Contract Required Quantitation Limit (CRQL) for sample and method.
J	The analyte was positively identified and the associated numerical value is the approximate concentration of the analyte in the sample (due either to the quality of the data generated because certain quality control criteria were not met, or the concentration of the analyte was below the CRQL).
NJ	The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.
UJ	The analyte was not detected at a level greater than or equal to the adjusted CRQL. However, the reported adjusted CRQL is approximate and may be inaccurate or imprecise.
R	The sample results are unusable due to the quality of the data generated because certain criteria were not met. The analyte may or may not be present in the sample.
C	This qualifier applies to pesticide and Aroclor results when the identification has been confirmed by Gas Chromatograph/Mass Spectrometer (GC/MS).
X	This qualifier applies to pesticide and Aroclor results when GC/MS analysis was attempted but was unsuccessful.

Data Package Inspection

For data obtained through the CLP, the Data Assessment Tool (DAT) report is a useful tool in the data review process. The DAT report incorporates Contract Compliance Screening (CCS) and computer-aided data evaluation results and is transmitted via the Data Assessment Rapid Transmittal (DART) system. For more information about the DAT report, please refer to the following USEPA Web site:

http://www.epa.gov/superfund/programs/clp/dat.htm

The DAT report will identify any missing and/or incorrect information in the data package. The CLP laboratory may submit a reconciliation package for any missing items or to correct data.

To obtain the DAT report and/or the reconciliation package, or if there are any other concerns regarding the data package, contact the Contract Laboratory Program Project Officer (CLP PO) from the Region where the samples were taken. For personnel contact information, refer to the following USEPA Web site:

http://www.epa.gov/superfund/programs/clp/contacts.htm

Preliminary Review

This document is for the review of analytical data generated through the SOM01.2 SOW and any future editorial revisions of SOM01.2. To use this document effectively, the reviewer should have an understanding of the analytical method used and a general overview of the Sample Delivery Group (SDG) or sample Case at hand. The exact number of samples, their assigned numbers, their matrix, and the number of laboratories involved in their analyses are essential information.

It is suggested that an initial review of the data package be performed, taking into consideration all information specific to the data package (flexible analysis approval notices, Traffic Report/Chain of Custody Records (TR/COCs), SDG Narratives, etc.).

The reviewer should also have a copy of the Quality Assurance Project Plan (QAPP) or similar document for the project for which samples were analyzed. The reviewer should contact the appropriate Regional Contract Laboratory Program Project Officer (CLP PO) to obtain copies of the QAPP and relevant site information. This information is necessary in determining the final usability of the analytical data.

Sample Cases (SDGs) routinely have unique field quality control (QC) samples which require special attention from the reviewer. These include field and trip blanks, field duplicates, and Performance Evaluation (PE) samples which must be identified. The sampling records (e.g., TR/COC Records, field logs, and/or contractor tables) should identify:

1. The Region where the samples were taken,
2. The Case number,
3. The complete list of samples, with information on:
    a. Sample matrix;
    b. Field Blanks (i.e., equipment blanks or rinsate blanks) and trip blanks;
    c. Field duplicates;
    d. Field spikes;
    e. QC audit samples;
    f. Shipping dates;
    g. Preservatives; and
    h. Laboratories involved.

The TR/COC Record includes sample descriptions and date(s) of sampling. The reviewer must consider lag times between sampling and start of analysis when assessing technical sample holding times.

The laboratory's SDG Narrative is another source of general information. Notable problems with matrices, insufficient sample volume for analysis or re-analysis, samples received in broken containers, preservation, and unusual events should be documented in the SDG Narrative. The reviewer should also inspect any email correspondence, telephone, or other communication logs detailing any discussions of sample preparation and/or analysis issues between the laboratory, CLP Sample Management Office (SMO) and the USEPA Region.

Data Review Narrative

A Data Review Narrative, including the Organic Data Review Summary form, (see Appendix B) must accompany the laboratory data forwarded to the intended data recipient (client) or user to promote communications. A copy of the Data Review Narrative should be submitted to the Contract Laboratory Program Project Officer (CLP PO) assigned oversight responsibility for the laboratory producing the data.

The Data Review Narrative should include comments that clearly identify the problems associated with a Case or SDG and state the limitations of the data. Documentation should include the CLP Sample Number, analytical method, extent of the problem, and assigned qualifiers.

TRACE VOLATILE DATA REVIEW

The data requirements to be checked are:

I. Preservation

II. Gas Chromatograph/Mass Spectrometer (GC/MS) Instrument Performance Check

III. Initial Calibration

IV. Continuing Calibration Verification (CCV)

V. Blanks

VI. Deuterated Monitoring Compounds (DMCs)

VII. Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

VIII. Regional Quality Assurance (QA) and Quality Control (QC)

IX. Internal Standards

X. Target Compound Identification

XI. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

XII. Tentatively Identified Compounds (TICs)

XIII. System Performance

XIV. Overall Assessment of Data

NOTE: *Language specific to Selective Ion Monitoring (SIM) analyses is shown in italic.*

I. Preservation

A. Review Items:

Form I VOA-1, Form I VOA-2, *Form I VOA-SIM*, Form I VOA-TIC, Traffic Report/Chain of Custody Records (TR/COCs), raw data, and the Sample Delivery Group (SDG) Narrative checking for:

1. pH
2. Sample temperature
3. Holding time
4. Other sample conditions (e.g., headspace)

B. Objective:

The objective is to ascertain the validity of the analytical results based on sample condition (e.g., preservation, temperature, headspace) and the holding time of the sample from the time of collection to the time of analysis.

C. Criteria:

The technical holding time criterion for aqueous samples are as follows:

For volatile compounds in properly cooled (4°C ± 2°C) aqueous samples that are acid-preserved (with HCl to a pH of 2 or below), the maximum holding time is 14 days from sample collection. For aqueous samples that were properly cooled (4°C ± 2°C), but which have no indication of being preserved, the maximum holding time is seven (7) days from sample collection.

D. Evaluation:

Technical holding times are established by comparing the sample collection dates on the TR/COC Record with the dates of analysis on Form I VOA-1, Form I VOA-2, *Form I VOA-SIM*, Form I VOA-TIC and the raw data. Information contained in the Complete SDG File (CSF) should also be considered in the determination of holding times. Verify that the analysis dates on Form I(s) and the raw data/SDG file are identical. Review the SDG Narrative to determine if the samples were preserved and arrived at the laboratory in proper condition (e.g., received intact, appropriate sample temperature at receipt, pH, absence of air bubbles or detectable headspace). If there is no indication in the SDG Narrative, the TR/COC, or the sample records that there was a problem with the samples, the integrity of samples can be assumed to be acceptable. If it is indicated that there were problems with the samples, the integrity of the sample may have been compromised and professional judgment should be used to evaluate the effect of the problem on the sample results.

E. Action:

1. Qualify sample results using preservation and technical holding time information as follows (see Table 1):
   a. If there is no evidence that the samples were properly preserved, but the samples were analyzed within the technical holding time [seven (7) days from sample collection], no qualification of the data is necessary.

b. If there is no evidence that the samples were properly preserved, and the samples were analyzed outside of the technical holding time [seven (7) days from sample collection], qualify detects for all volatile compounds with a "J" and non-detects as unusable "R".

c. If the samples were properly preserved, and the samples were analyzed within the technical holding time [14 days from sample collection], no qualification of the data is necessary.

d. If the samples were properly preserved, but were analyzed outside of the technical holding time [14 days from sample collection], qualify detects with a "J" and non-detects as unusable "R".

Table 1. Holding Time Actions for Trace Volatile Analyses

Matrix	Preserved	Criteria	Action	
			Detected Associated Compounds	Non-Detected Associated Compounds
Aqueous	No	≤ 7 days	No qualification	
Aqueous	No	> 7 days	J	R
Aqueous	Yes	≤ 14 days	No qualification	
Aqueous	Yes	> 14 days	J	R

2. Whenever possible, the reviewer should comment on the effect of the holding time exceedance on the resulting data in the Data Review Narrative.

3. Use professional judgment to qualify samples whose temperature upon receipt at the laboratory is either below 2 degrees centigrade or above 6 degrees centigrade.

4. Note, for Contract Laboratory Program Project Officer (CLP PO) action, when technical holding times are exceeded.

II. Gas Chromatograph/Mass Spectrometer (GC/MS) Instrument Performance Check

A. Review Items:

Form V VOA, bromofluorobenzene (BFB) mass spectra, and mass listing.

B. Objective:

GC/MS instrument performance checks are performed to ensure adequate mass resolution, identification, and to some degree, sensitivity. These criteria are not sample-specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.

NOTE: This requirement does not apply when samples are analyzed by the Selected Ion Monitoring (SIM) technique.

C. Criteria:

1. The 12-hour clock begins with either the injection of BFB, or in cases where a closing Continuing Calibration Verification (CCV) can be used as an opening CCV, the 12-hour clock begins with the injection of the opening CCV.
2. Listed below are some, but not necessarily all, examples of acceptable analytical sequences incorporating the use of the opening and/or closing CCV. Use these examples as a guide for the possible analytical sequences that can be expected. The criteria associated with these analytical sequences have been evaluated as part of the Contract Compliance Screening (CCS) process.

Conditions for When Example Sequence is Appropriate:	Acceptable Criteria That Must Be Met:	Notes:
Use Example 1 if time remains on the 12-hour clock after the initial calibration sequence.	• BFB tunes meet instrument performance criteria. • The five Initial Calibration standards meet initial calibration criteria. • CCV A meets both opening and closing CCV criteria. • CCV B meets closing CCV criteria.	The requirement of starting the new 12-hour clock for Analytical Sequence 2 with a new BFB tune is waived if CCV A meets opening CCV criteria. If CCV B meets opening CCV criteria, a method blank and subsequent samples may be analyzed immediately after CCV B.
Use Example 2 if time remains on the 12-hour clock after the initial calibration sequence.	• BFB tunes meet instrument performance criteria. • The five Initial Calibration standards meet initial calibration criteria. • CCV A meets closing CCV criteria (but does not meet opening CCV criteria). • CCV B meets opening CCV criteria. • CCV C meets closing CCV criteria.	CCV A does not meet opening CCV criteria, therefore a new BFB tune must be performed, immediately followed by CCV B before a method blank and any samples may be analyzed. In this case, the new 12-hour clock and Analytical Sequence 2 begins with the injection of the new BFB tune.

Conditions for When Example Sequence is Appropriate:	Acceptable Criteria That Must Be Met:	Notes:
Use Example 3 if more than 12-hours have elapsed since the most recent initial calibration or closing CCV, OR if the most recent closing CCV was not or could not be used as an opening CCV.	• BFB tunes meet instrument performance criteria. • CCV A meets opening CCV criteria. • CCV B meets both opening and closing CCV criteria. • CCV C meets both opening and closing CCV criteria.	The requirement of starting the new 12-hour clock for Analytical Sequence 2 with a new BFB tune is waived if CCV B meets opening CCV criteria. If CCV C meets opening CCV criteria, a method blank and subsequent samples may be analyzed immediately after CCV C.
Use Example 4 if more than 12-hours have elapsed since the most recent initial calibration or closing CCV, OR if the most recent closing CCV was not or could not be used as an opening CCV.	• BFB tunes meet instrument performance criteria. • CCV A meets opening CCV criteria. • CCV B meets closing CCV criteria (but does not meet opening CCV criteria). • CCV C meets opening CCV criteria. • CCV D meets both opening and closing CCV criteria.	CCV B does not meet opening CCV criteria, therefore a new BFB tune must be performed, immediately followed by CCV C before a method blank and any samples may be analyzed. In this case, the new 12-hour clock and Analytical Sequence 2 begins with the injection of the new BFB tune. The requirement of starting the new 12-hour clock for Analytical Sequence 3 with a new BFB tune is waived if CCV D meets opening CCV criteria. If CCV D meets opening CCV criteria, a method blank and subsequent samples may be analyzed immediately after CCV D.

Example 1:	**Time**	**Material Injected**	**Analytical Sequence #**
Start of 12-hour clock for Analytical Sequence 1	0 hr	BFB	1
		Initial Calibration 0.5	1
		Initial Calibration 1.0	1
		Initial Calibration 5.0	1
		Initial Calibration 10	1
		Initial Calibration 20	1
		Method Blank	1
		Subsequent Samples	1
		•	1
		•	1
		•	1
		•	1
End of 12-hour clock for Analytical Sequence 1/ Beginning of 12-hour clock for Analytical Sequence 2	12 hr	CCV A (meets opening CCV criteria)	1/2
		Method Blank	2
		Subsequent Samples	2
		•	2
		•	2
		•	2
		•	2
End of 12-hour clock for Analytical Sequence 2/ Beginning of 12-hour clock for Analytical Sequence 3	24 hr	CCV B (meets opening CCV criteria)	2/3

Example 2:	**Time**	**Material Injected**	**Analytical Sequence #**
Start of 12-hour clock for Analytical Sequence 1	0 hr	BFB	1
		Initial Calibration 0.5	1
		Initial Calibration 1.0	1
		Initial Calibration 5.0	1
		Initial Calibration 10	1
		Initial Calibration 20	1
		Method Blank	1
		Subsequent Samples	1
		•	1
		•	1
		•	1
		•	1
End of 12-hour clock for Analytical Sequence 1	12 hr	CCV A (meets closing CCV criteria; fails opening CCV criteria)	1
Beginning of 12-hour clock for Analytical Sequence 2	13 hr	BFB	2
		CCV B (meets opening CCV criteria)	2
		Method Blank	2
		Subsequent Samples	2
		•	2
		•	2
		•	2
		•	2
End of 12-hour clock for Analytical Sequence 2	25 hr	CCV C (meets closing CCV criteria)	2

Example 3:	**Time**	**Material Injected**	**Analytical Sequence #**
Start of 12-hour clock for Analytical Sequence 1	0 hr	BFB	1
		CCV A (meets opening CCV criteria)	1
		Method Blank	1
		Subsequent Samples	1
		•	1
		•	1
		•	1
		•	1
End of 12-hour clock for Analytical Sequence 1/ Beginning of 12-hour clock for Analytical Sequence 2	12 hr	CCV B (meets opening CCV criteria)	1/2
		Method Blank	2
		Subsequent Samples	2
		•	2
		•	2
		•	2
End of 12-hour clock for Analytical Sequence 2/ Beginning of 12-hour clock for Analytical Sequence 3	24 hr	CCV C (meets opening CCV criteria)	2/3

Example 4:	**Time**	**Material Injected**	**Analytical Sequence #**
Start of 12-hour clock for Analytical Sequence 1	0 hr	BFB	1
		CCV A (meets opening CCV criteria)	1
		Method Blank	1
		Subsequent Samples	1
		•	1
		•	1
		•	1
End of 12-hour clock for Analytical Sequence 1	12 hr	CCV B (meets closing CCV criteria; fails opening CCV criteria)	1
Beginning of 12-hour clock for Analytical Sequence 2	13 hr	BFB	2
		CCV C (meets opening CCV criteria)	2
		Method Blank	2
		Subsequent Samples	2
		•	2
		•	2
		•	2
End of 12-hour clock for Analytical Sequence 2/ Beginning of 12-hour clock for Analytical Sequence 3	25 hr	CCV D (meets opening CCV criteria)	2/3

3. Inject a sufficient amount of the instrument performance check solution (up to 50 ng BFB on-column) at the beginning of each 12-hour period during which samples or standards are analyzed. The instrument performance check, BFB for trace volatile analysis, must meet the ion abundance criteria listed in Table 2. This criteria is waived in cases where a closing CCV can be used as an opening CCV (i.e., a BFB instrument performance check analysis is not required when a closing CCV analysis meets the requirements of an opening CCV analysis).

Table 2. Ion Abundance Criteria For Bromofluorobenzene (BFB)

Mass	Ion Abundance Criteria
50	15.0 - 40.0% of mass 95
75	30.0 - 80.0% of mass 95
95	Base peak, 100% relative abundance
96	5.0 - 9.0% of mass 95*
173	Less than 2.0% of mass 174
174	50.0% - 120% of mass 95
175	5.0 - 9.0% of mass 174
176	95.0 - 101% of mass 174
177	5.0 - 9.0% of mass 176

* All ion abundances must be normalized to mass to charge (m/z) 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95.

D. Evaluation:

1. Compare the data presented for each Instrument Performance Check (Form V VOA) with each mass listing submitted to ensure the following:
   a. Form V VOA is present and completed for each 12-hour period during which samples were analyzed. In cases where a closing CCV is used as an opening CCV for the next 12-hour period, an additional Form V VOA is not required.
   b. The laboratory has not made transcription errors between the data and the form. If there are major differences between the mass listing and the Form Vs, a more in-depth review of the data is required. This may include obtaining and reviewing additional information from the laboratory.
   c. The appropriate number of significant figures has been reported (number of significant figures given for each ion in the ion abundance criteria column) and that rounding is correct.
   d. The laboratory has not made any calculation errors.
2. Verify that samples were not analyzed before a valid instrument performance check or were not analyzed 12 hours after the injection of the Instrument Performance Check Solution. This evaluation is not to be performed in cases where a closing CCV is used as an opening CCV.
3. Verify from the raw data (mass spectral listing) that the mass assignment is correct and that the mass listing is normalized to m/z 95.
4. Verify that the ion abundance criteria was met. The criteria for m/z 173, 175, 176, and 177 are calculated by normalizing to the specified m/z.

5. If possible, verify that spectra were generated using appropriate background subtraction techniques. Since the BFB spectrum is obtained from chromatographic peaks that should be free from coelution problems, background subtraction should be done in accordance with the following procedure:

   a. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.

   b. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not subtract the BFB peak as part of the background.

   NOTE: All mass spectrometer instrument conditions must be identical to those used during the sample analysis. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the method specifications are contrary to the Quality Assurance (QA) objectives, and are therefore unacceptable.

   For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the CCS process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. If samples are analyzed without a preceding valid instrument performance check or are analyzed 12 hours after the Instrument Performance Check and are not preceded by an analysis of a closing CCV that meets the opening CCV criteria, qualify all data in those samples as unusable "R".
2. If the laboratory has made minor transcription errors which do not significantly affect the data, the data reviewer should make the necessary corrections on a copy of the form.
3. If the laboratory has failed to provide the correct forms or has made significant transcription or calculation errors, the Region's designated representative should contact the laboratory and request corrected data. If the information is not available, the reviewer must use professional judgment to assess the data. Notify the laboratory's Contract Laboratory Program Project Officer (CLP PO).
4. If mass assignment is in error (e.g., m/z 96 is indicated as the base peak rather than m/z 95), classify all associated data as unusable "R".
5. If ion abundance criteria are not met, professional judgment may be applied to determine to what extent the data may be utilized. When applying professional judgment to this topic, the most important factors to consider are the empirical results that are relatively insensitive to location on the chromatographic profile and the type of instrumentation. Therefore, the critical ion abundance criteria for BFB are the m/z 95/96, 174/175, 174/176, and 176/177 ratios. The relative abundances of m/z 50 and 75 are of lower importance. This issue is more critical for Tentatively Identified Compounds (TICs) than for target analytes.
6. Note, in the Data Review Narrative, decisions to use analytical data associated with BFB instrument performance checks not meeting contract requirements.
7. If the reviewer has reason to believe that instrument performance check criteria were achieved using techniques other than those described in Trace Volatiles Organic Analysis, Section II.D.5, obtain additional information on the instrument performance checks. If the techniques employed are found to be at variance with the contract requirements, the performance and procedures of the laboratory may merit evaluation. Note, for CLP PO action, concerns or questions regarding laboratory performance. For example, if the reviewer has reason to believe that an inappropriate technique was used to obtain background subtraction (such as background subtracting from the solvent front or from another region of the chromatogram rather than from the BFB peak), note this for CLP PO action.

III. Initial Calibration

A. Review Items:

Form VI VOA-1, Form VI VOA-2, Form VI VOA-3, Form VI VOA-SIM, quantitation reports, and chromatograms.

B. Objective:

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for compounds on the volatile Target Compound List (TCL). Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run and of producing a linear calibration curve and provides the Mean Relative Response Factors ($\overline{\text{RRFs}}$) used for quantitation.

C. Criteria:

1. Initial calibration standards containing both volatile target compounds and Deuterated Monitoring Compounds (DMCs) are analyzed at concentrations of 0.50, 1.0, 5.0, 10, and 20 µg/L for non-ketones, 5.0, 10, 50, 100 and 200 µg/L for ketones at the beginning of each analytical sequence, or as necessary if the continuing calibration verification acceptance criteria are not met. The initial calibration (and any associated samples and blanks) must be analyzed within 12 hours of the associated instrument performance check. All three xylene isomers (o-, m-, and p-xylene) must be present in calibration standards. The o-xylene calibration standard concentrations must be at 0.50, 1.0, 5.0, 10 and 20 µg/L, while the concentration of the m-, plus the p-xylene isomers must **total** 0.50, 1.0, 5.0, 10, and 20 µg/L.

   If analysis by the SIM technique is requested for compounds of interest, prepare calibration standards containing the compounds of interest and their associated DMCs at concentrations of 0.05, 0.1, 0.5, 1.0, and 2.0 µg/L.

2. Initial calibration Relative Response Factors (RRFs) for the volatile target compounds listed in Table 3 and all DMCs must be greater than or equal to 0.010. The RRF for all other volatile target compounds must be greater than or equal to 0.050.

3. The Percent Relative Standard Deviation (%RSD) of the initial calibration RRFs must be less than or equal to 40.0% for the volatile target compounds listed in Table 3 and the associated DMCs (see Table 9). The %RSD for all other volatile target compounds and associated DMCs must be less than or equal to 30.0%.

   NOTE: **The flexibility clause in the method may impact some of the preceding criteria. A copy of the flexibility clause should be present in the Sample Delivery Group (SDG). Refer to the Contract Laboratory Program (CLP) home page at http://www.epa.gov/oerrpage/superfund/programs/clp/modifiedanalyses.htm for the specific method flexibility requirements.**

D. Evaluation:

1. Verify that the correct concentrations of standards were used for the initial calibration (i.e., 0.50, 1.0, 5.0, 10, and 20 µg/L for non-ketones, 5.0, 10, 50, 100, and 200 µg/L for ketones).

   If analysis by the SIM technique is requested, verify that the correct concentrations of standards were used for the initial calibration (i.e., 0.05, 0.1, 0.5, 1.0, and 2.0 µg/L for all compounds and associated DMCs).

2. Verify that the $\overline{RRF}$ obtained from the associated initial calibration was used for calculating sample results and the samples were analyzed within 12 hours of the associated instrument performance check.

3. Evaluate the initial calibration RRFs and the $\overline{RRF}$s for all volatile target compounds and DMCs:

   a. Check and recalculate the RRFs and $\overline{RRF}$ for at least one volatile target compound associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. Verify that for the volatile target compounds listed in Table 3 and for all DMCs, the initial calibration RRFs are greater than or equal to 0.010, and for all other volatile target compounds, RRFs are greater than or equal to 0.050.

Table 3. Volatile Compounds Exhibiting Poor Response

Volatile Compounds	
Acetone	Isopropylbenzene
2-Butanone	Methyl acetate
Carbon disulfide	Methylene chloride
Chloroethane	Methylcyclohexane
Chloromethane	Methyl tert-butyl ether
Cyclohexane	trans-1,2-Dichloroethene
1,2-Dibromoethane	4-Methyl-2-pentanone
Dichlorodifluoromethane	2-Hexanone
cis-1,2-Dichloroethene	Trichlorofluoromethane
1,2-Dichloropropane	1,1,2-Trichloro-1,2,2-trifluoroethane
1,2-Dibromo-3-chloropropane	

4. Evaluate the %RSD for all volatile target compounds and DMCs:

   a. Check and recalculate the %RSD for one or more volatile target compound(s) and DMCs. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. If the %RSD is greater than the maximum criteria [40.0% for the volatile target compounds listed in Table 3 and associated DMCs listed in Table 9, and 30.0% for all other volatile target compounds and associated DMCs], the reviewer should use professional judgment to determine the need to check the points on the curve for the cause of the non-linearity. This is checked by eliminating either the high-point or the low-point and recalculating the %RSD (see Trace Volatiles Organic Analysis, Section III.E.2).

5. If errors are detected in the calculations of either the RRFs or the %RSD, perform a more comprehensive recalculation.

   NOTE: For data obtained from the CLP, the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. Qualify all volatile target compounds, including the compounds exhibiting poor response listed in Table 3, using the following criteria (see Table 4):

   a. If any volatile target compound has an RRF value less than the minimum criterion (0.010 for the compounds exhibiting poor response listed in Table 3, and 0.050 for all other volatile compounds), use professional judgment for detects, based on mass spectral identification, to qualify the data as a "J" or unusable "R".

   b. If any volatile target compound has an RRF value less than the minimum criterion (0.010 for the compounds exhibiting poor response listed in Table 3, and 0.050 for all other volatile compounds), qualify non-detected compounds as unusable "R".

   c. If any of the volatile target compounds listed in Table 3 has %RSD greater than 40.0%, qualify detects with a "J", and non-detected compounds using professional judgment (see Trace Volatiles Organic Analysis, Section III.E.2).

   d. For all other volatile target compounds, if %RSD is greater than 30.0%, qualify detects with a "J", and non-detected compounds using professional judgment (see Trace Volatiles Organic Analysis, Section III.E.2).

   e. If the volatile target compounds meet the acceptance criteria for RRF and the %RSD, no qualification of the data is necessary.

   f. No qualification of the data is necessary on the DMC RRF and %RSD data alone. Use professional judgment and follow the guidelines in Trace Volatiles Organic Analysis, Section III.E.2, to evaluate the DMC RRF and %RSD data in conjunction with the DMC recoveries to determine the need for qualification of data.

2. At the reviewer's discretion, and based on the project-specific Data Quality Objectives (DQOs), a more in-depth review may be considered using the following guidelines:

   a. If any volatile target compound has a %RSD greater than the maximum criterion (40.0% for the compounds listed in Table 3, and 30.0% for all other volatile compounds), and if eliminating either the high or the low-point of the curve does not restore the %RSD to less than or equal to the required maximum:

      i. Qualify detects for that compound(s) with a "J".

      ii. Qualify non-detected volatile target compounds using professional judgment.

   b. If the high-point of the curve is outside of the linearity criteria (e.g., due to saturation):

      i. Qualify detects outside of the linear portion of the curve with a "J".

      ii. No qualifiers are required for detects in the linear portion of the curve.

      iii. No qualifiers are required for volatile target compounds that were not detected.

   c. If the low-point of the curve is outside of the linearity criteria:

      i. Qualify low-level detects in the area of non-linearity with a "J".

      ii. No qualifiers are required for detects in the linear portion of the curve.

      iii. For non-detected volatile compounds, use the lowest point of the linear portion of the curve to determine the new quantitation limit.

3. If the laboratory has failed to provide adequate calibration information, the Region's designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

4. Note in the Data Review Narrative, whenever possible, the potential effects on the data due to calibration criteria exceedance.
5. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if calibration criteria are grossly exceeded.

Table 4. Initial Calibration Actions for Trace Volatiles Analyses

Criteria for Trace Analysis	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
RRF < 0.010 (target compounds listed in Table 3) RRF < 0.050 (all other target compounds)	J or R (based on mass spectral identification)	R
RRF ≥ 0.010 (target compounds listed in Table 3) RRF ≥ 0.050 (all other target compounds)	No qualification	
% RSD ≤ 40.0 (target compounds listed in Table 3) % RSD ≤ 30.0 (all other target compounds)	No qualification	
% RSD > 40.0 (target compounds listed in Table 3) % RSD > 30.0 (all other target compounds)	J	Use professional judgment

IV. Continuing Calibration Verification (CCV)

A. Review Items:

Form VII VOA-1, Form VII VOA-2, Form VII VOA-3, *Form VII VOA-SIM*, quantitation reports, and chromatograms.

B. Objective:

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. The CCV checks satisfactory performance of the instrument on a day-to-day basis, however, quantitations are based on the Mean Relative Response Factors ($\overline{RRF}$s) obtained from the initial calibration.

C. Criteria:

1. The 12-hour clock begins with either the injection of Bromofluorobenzene (BFB) or in cases where a closing CCV can be used as an opening CCV, the 12-hour clock begins with the injection of the opening CCV.
2. CCV standards containing both target compounds and Deuterated Monitoring Compounds (DMCs) are analyzed both at the beginning (opening CCV) and end (closing CCV) of each 12-hour analysis period following the analysis of the instrument performance check and prior to the analysis of the method blank and samples. An instrument performance check is not required prior to the analysis of a closing CCV or prior to a closing CCV which can be used as an opening CCV for the next 12-hour period. If time remains in the 12-hour time period after initial calibration and samples are to be analyzed, the mid-point standard from the initial calibration can be used as an opening CCV.
3. For an opening CCV, the Relative Response Factors (RRFs) for the volatile target compounds listed in Table 3, and for all DMCs, must be greater than or equal to 0.010. The RRF for all other volatile target compounds must be greater than or equal to 0.050.
4. For a closing CCV, the RRFs for all volatile target compounds and DMCs must be greater than or equal to 0.010.
5. The Percent Difference (%D) between the initial calibration RRF and the opening CCV RRF must be within ±40.0% for the volatile target compounds listed in Table 3 and associated DMCs listed in Table 9. The Percent Difference for all other volatile target compounds and associated DMCs must be within ±30.0%.
6. For a closing CCV, the Percent Difference between the initial calibration $\overline{RRF}$ and the CCV RRF must be within ±50.0% for all volatile target compounds and associated DMCs.

D. Evaluation:

1. Verify that the CCV was run at the required frequency (an opening and closing CCV must be run within a 12-hour period) and the CCV was compared to the correct initial calibration. If the mid-point standard from the initial calibration is used as an opening CCV, verify that the result (RRF) of the mid-point standard was compared to the $\overline{RRF}$ from the correct initial calibration.
2. Evaluate the CCV RRF for all volatile target compounds and DMCs:

a. Check and recalculate the CCV RRF for at least one volatile target compound and DMC associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

b. For an opening CCV, verify that all volatile target compounds listed in Table 3 and all DMCs have CCV RRFs of greater than or equal to 0.010, and all other volatile target compounds have RRFs greater than or equal to 0.050.

c. For a closing CCV, verify that all volatile target compounds and DMCs have CCV RRFs of greater than or equal to 0.010.

3. Evaluate the Percent Difference between initial calibration $\overline{RRF}$ and CCV RRF (both opening and closing RRF) for all volatile target compounds and DMCs:

a. Check and recalculate the Percent Difference for one or more volatile target compound(s) and DMCs associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory-reported value(s).

b. For an opening CCV, verify that the Percent Difference is within ±40.0% for the volatile target compounds listed in Table 3 and DMCs listed in Table 9, and within ±30.0% for all other volatile target compounds and associated DMCs.

c. For a closing CCV, verify that the Percent Difference is within ±50.0% for all volatile target compounds and associated DMCs.

4. If errors are detected in the calculations of either the CCV (both opening and closing) RRF or the Percent Difference, perform a more comprehensive recalculation.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. If a CCV (opening and closing) was not run at the appropriate frequency, qualify all data as unusable "R" (see Table 5).

2. Qualify all volatile target compounds, including the compounds exhibiting poor response listed in Table 3 using the following criteria:

a. For an opening CCV, if any volatile target compound has an RRF value less than the minimum criterion (0.010 for the compounds exhibiting poor response, and 0.050 for all other volatile compounds), use professional judgment for detects, based on mass spectral identification, to qualify the data as a "J" or unusable "R".

b. For a closing CCV, if any volatile target compound has an RRF value less than 0.010, use professional judgment for detects based on mass spectral identification to qualify the data as a "J" or unusable "R".

c. For an opening CCV, if any volatile target compound has an RRF value less than the minimum criterion (0.010 for the compounds exhibiting poor response, and 0.050 for all other volatile compounds), qualify non-detected compounds as unusable "R".

d. For a closing CCV, if any volatile target compound has an RRF value less than 0.010, qualify non-detected compounds as unusable "R".

e. For an opening CCV, if the Percent Difference value for any of the volatile target compounds listed in Table 3 is outside the ±40.0% criterion, qualify detects with a "J" and non-detected compounds with an approximated "UJ".

f. For a closing CCV, if the Percent Difference value for any of the volatile target compounds listed in Table 3 is outside the ±50.0% criterion, qualify detects with a "J" and non-detected compounds with an approximated "UJ".

g. For an opening CCV, if the Percent Difference value for any other volatile target compound is outside the ±30.0% criterion, qualify detects with a "J" and non-detected compounds with an approximated "UJ".

h. For a closing CCV, if the Percent Difference value for any other volatile target compound is outside the ±50.0% criterion, qualify detects with a "J" and non-detected compounds with an approximated "UJ".

i. If the volatile target compounds meet the acceptable criteria for RRF and the Percent Difference, no qualification of the data is necessary.

j. No qualification of the data is necessary on the DMC RRF and the Percent Difference data alone. Use professional judgment to evaluate the DMC RRF and Percent Difference data in conjunction with the DMC recoveries to determine the need for qualification of data.

3. If the laboratory has failed to provide adequate calibration information, the Region's designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

4. Note in the Data Review Narrative, whenever possible, the potential effects on the data due to calibration criteria exceedance.

5. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if calibration criteria are grossly exceeded.

Table 5. Continuing Calibration Verification (CCV) Actions for Trace Volatiles Analyses

Criteria for Opening CCV	Criteria for Closing CCV	Action	
		Detected Associated Compounds	Non-Detected Associated Compounds
RRF < 0.010 (volatile target compounds listed in Table 3) RRF < 0.050 (all other volatile target compounds)	RRF < 0.010 (all volatile target compounds)	J or R (based on mass spectral identification)	R
RRF ≥ 0.010 (volatile target compounds listed in Table 3) RRF ≥ 0.050 (all other volatile target compounds)	RRF ≥ 0.010 (all volatile target compounds)	No qualification	
%D > 40.0 or < -40.0 (volatile target compounds listed in Table 3) %D > 30.0 or < -30.0 (all other volatile target compounds)	%D > 50.0 or < -50.0 (all volatile target compounds)	J	UJ
%D ≤ 40.0 and ≥ -40.0 (volatile target compounds listed in Table 3) %D ≤ 30.0 and ≥ -30.0 (all other volatile target compounds)	%D ≤ 50.0 and ≥ -50.0 (all volatile target compounds)	No qualification	

Criteria for Opening CCV	Criteria for Closing CCV	Action	
		Detected Associated Compounds	Non-Detected Associated Compounds
Opening CCV not performed at required frequency (see Trace Volatiles Organic Analysis, Section IV.C.1)	Closing CCV not performed at required frequency (see Trace Volatile Organic Analysis, Section IV.C.1)	R	

V. Blanks

A. Review Items:

Form I VOA-1, Form I VOA-2, Form I VOA-TIC, Form I VOA-SIM, Form IV VOA, Form IV VOA-SIM, chromatograms, and quantitation reports.

B. Objective:

The purpose of laboratory, field, or trip blank analyses is to determine the existence and magnitude of contamination resulting from laboratory, field, or sample transport activities. The purpose of the method blank is to determine the levels of contamination associated with the processing and analysis of the samples. The storage blank indicates whether contamination may have occurred during storage of samples. The results from the instrument blank analysis indicate whether there is contamination from the analysis of a previous sample. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks, instrument blanks, storage blanks, field blanks, or trip blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. Method Blanks

   A method blank analysis must be performed after the calibration standards and once for every 12-hour time period.

   The method blank must be analyzed on each Gas Chromatograph/Mass Spectrometer (GC/MS) system used to analyze samples.

2. Storage Blanks

   A storage blank must be prepared upon receipt of the first samples from a Sample Delivery Group (SDG), and stored with the samples until analysis. The storage blank must be analyzed once per SDG.

3. Instrument Blanks

   An instrument blank must be analyzed immediately after any sample that has saturated ions (target compounds that exceed the calibration range or non-target compounds that exceed 100 µg/L) from a given compound to check that the blank is free of interference and the system is not contaminated. The concentration of each target compound in the instrument blank must be less than its Contract Required Quantitation Limit (CRQL) listed in the method.

   NOTE: The concentration of each target compound found in the storage, method, field, or trip blanks must be less than its CRQL listed in the method, except for methylene chloride, acetone, and 2-butanone, which must be less than 2x their respective CRQLs. The concentration of non-target compounds in all blanks must be less than 2.0 µg/L.

D. Evaluation:

1. Review the results of all associated blanks on the forms and raw data (chromatograms and quantitation reports) to evaluate the presence of target and non-target compounds in the blanks.

2. Verify that a method blank analysis has been reported for each 12-hour time period on each GC/MS system used to analyze volatile samples. The reviewer can use the Method Blank Summary (Form IV VOA and Form IV VOA-SIM) to identify the samples associated with each method blank.
3. Verify that a storage blank has been analyzed and included with each SDG.
4. Verify that the instrument blank analysis has been performed following any sample analysis where a target analyte(s) is/are reported at high concentration(s).

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process. Data concerning the field or trip blanks are not evaluated as part of the CCS process. If field or trip blanks are present, the data reviewer should evaluate this data in a similar fashion as the method blanks.**

E. Action:

Action regarding unsuitable blank results depends on the circumstances and origin of the blank. In instances where more than one of the same type of blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. Do not correct the results by subtracting any blank value.

1. If a volatile compound is found in a method blank, but not found in the sample, no qualification of the data is necessary (see Table 6).
2. If the method blank concentration is less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone, and acetone) and:
   a. the sample concentration is less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone, and acetone), report the CRQL value with a "U".
   b. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone), and less than 2x the CRQL (less than 4x the CRQL for methylene chloride, 2-butanone, and acetone), use professional judgment.
   c. the sample concentration is greater than or equal to 2x the CRQL (greater than or equal to 4x the CRQL for methylene chloride, 2-butanone, and acetone), no qualification of the data is necessary.
3. If the method blank concentration is greater than the CRQL (greater than 2x the CRQL for methylene chloride, 2-butanone, and acetone) and:
   a. the sample concentration is less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone, and acetone), report the CRQL value with a "U".
   b. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone), and less than the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank and qualify with a "U", or the reviewer may elect to qualify the data as unusable "R".
   c. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone) and greater than or equal to the blank concentration, use professional judgment to qualify the data.
4. If the method blank concentration is equal to the CRQL (equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone) and:
   a. the sample concentration is less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone, and acetone), report the CRQL value with a "U".

b. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone), use professional judgment to qualify the data.

5. If gross contamination exists (i.e., saturated peaks by GC/MS), qualify all affected compounds in the associated samples as unusable "R" due to interference. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if the contamination is suspected of having an effect on the sample results.

6. Give the same consideration as the target compounds to the Tentatively Identified Compounds (TICs), which are found in both the sample and associated blank(s) (see Trace Volatiles Organic Analysis, Section XII, for TIC guidance).

7. If the contaminants found in the blank are interfering non-target compounds at concentrations greater than 2 µg/L, use professional judgment to qualify the data.

   NOTE: There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, they should qualify the data. Contamination introduced through dilution water is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but are absent in the undiluted sample result.

8. If an instrument blank was not analyzed following a sample analysis which contained an analyte(s) at high concentration(s), evaluate the sample analysis results immediately after the high concentration sample for carryover. Use professional judgment to determine if instrument cross-contamination has affected any positive compound identification(s). Note, for CLP PO action, if instrument cross-contamination is suggested and suspected of having an effect on the sample results.

9. If contaminants are found in the storage, field, or trip blanks, the following is recommended:

   a. Review the associated method blank data to determine if the contaminant(s) was also present in the method blank.

      i. If the analyte was present at a comparable level in the method blank, the source of the contamination may be in the analytical system and the action recommended for the method blank would apply.

      ii. If the analyte was not present in the method blank, the source of contamination may be in the storage area, in the field, or during sample transport. Consider all associated samples for possible cross-contamination.

   b. If the storage, field, or trip blanks contain a volatile Target Compound List (TCL) compound(s) at a concentration less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone, and acetone), and:

      i. the sample concentration is less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone and acetone), report the CRQL value with a "U".

      ii. the sample concentration is greater than or equal to 2x the CRQL (greater than or equal to 4x the CRQL for methylene chloride, 2-butanone and acetone), no qualification of the data is necessary.

      iii. the sample concentration is greater than or equal to the CRQL and less than 2x the CRQL (less than 4x the CRQL for methylene chloride, 2-butanone and acetone), use professional judgment to qualify the data.

   c. If the storage, field, or trip blanks contain a volatile TCL compound(s) at a concentration equal to the CRQL (2x the CRQL for methylene chloride, 2-butanone and acetone) and:

i. the sample concentration is less than or equal to the CRQL (less than or equal to 2x the CRQL for methylene chloride, 2-butanone and acetone), report the CRQL value with a "U".

ii. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone and acetone), use professional judgment to qualify the data.

d. If the storage, field, or trip blanks contain a volatile TCL compound(s) at a concentration greater than the CRQL (greater than 2x the CRQL for methylene chloride, 2-butanone, and acetone), and:

i. the sample concentration is less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone, and acetone), report the CRQL value with a "U".

ii. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone), and less than the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank and qualify with a "U", or the reviewer may elect to qualify the data as unusable "R".

iii. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone), and greater than or equal to the blank concentration, use professional judgment to qualify the data.

e. If gross contamination [greater than 2x the CRQL (greater than 4x the CRQL for methylene chloride, 2-butanone and acetone)] exists in the storage, field, or trip blank, positive sample results may require rejection and be qualified as unusable "R". Non-detected volatile target compounds do not require qualification unless the contamination is so high that it interferes with the analyses of non-detected compounds.

f. If the contaminants found in the blank are interfering non-target compounds at concentrations greater than 2 µg/L, use professional judgment to qualify the data.

Table 6. Blank Actions for Trace Volatiles Analyses

Blank Type	Blank Result	Sample Result	Action for Samples
Method, Storage, Field, Trip, Instrument***	Detects	Not detected	No qualification
	< CRQL *	< CRQL*	Report CRQL value with a U
		≥ CRQL* and < 2x the CRQL**	Use professional judgment
		≥ 2x the CRQL**	No qualification
	> CRQL *	< CRQL*	Report CRQL value with a U
		≥ CRQL* and < blank concentration	Report the blank concentration for the sample with a U or qualify the data as unusable R
		≥ CRQL* and ≥ blank concentration	Use professional judgment
	= CRQL*	< CRQL*	Report CRQL value with a U
		≥ CRQL*	Use professional judgment
	TIC >2 µg/L	Detects	Use professional judgment

* 2x the CRQL for methylene chloride, 2-butanone and acetone.

** 4x the CRQL for methylene chloride, 2-butanone, and acetone.

*** Qualifications based on instrument blank results affect only the sample analyzed immediately after the sample that has target compounds that exceed the calibration range or non-target compounds that exceed 100 µg/L.

VI. Deuterated Monitoring Compounds (DMCs)

A. Review Items:

Form II VOA-1, Form II VOA-2, *Form II VOA-SIM1*, *Form II VOA-SIM2*, quantitation reports, and chromatograms.

B. Objective:

Laboratory performance on individual samples is established by means of spiking activities. All samples are spiked with DMCs just prior to sample purging. The evaluation of the results of these DMCs is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and requires analytical experience and professional judgment. Accordingly, this section consists primarily of guidelines, in some cases with several optional approaches suggested.

C. Criteria:

The DMCs listed in Table 7 are added to all samples and blanks to measure their recovery in environmental samples.

Table 7. Volatile Deuterated Monitoring Compounds (DMCs) and Recovery Limits

DMC	Recovery Limits (%)	DMC	Recovery Limits (%)
Vinyl chloride-d_3	65 - 131	1,2-Dichloropropane-d_6	79 - 124
Chloroethane-d_5	71 - 131	Toluene-d_8	77 - 121
1,1-Dichloroethene-d_2	55 - 104	trans-1,3-Dichloropropene-d_4	73 - 121
2-Butanone-d_5	49 - 155	2-Hexanone-d_5	28 - 135
Chloroform-d	78 - 121	1,1,2,2-Tetrachloroethane-d_2	73 - 125
1,2-Dichloroethane-d_4	78 - 129	1,2-Dichlorobenzene-d_4	80 - 131
Benzene-d_6	77 - 124		

Recoveries for DMCs in volatile samples and blanks must be within the limits specified in Table 7.

NOTE: The recovery limits for any of the compounds listed in Table 7 may be expanded at any time during the period of performance if USEPA determines that the limits are too restrictive.

D. Evaluation:

1. Check raw data (e.g., chromatograms and quantitation reports) to verify the recoveries on the Deuterated Monitoring Compound Recovery Forms (Form II VOA-1, Form II VOA-2, Form II VOA-3, Form II VOA-4, *Form II VOA-SIM, and Form II VOA SIM2*).

   Check for any calculation or transcription errors; verify that the DMC recoveries were calculated correctly using the equation in the method.

2. Whenever there are two or more analyses for a particular sample, the reviewer must determine which are the most acceptable data to report. Considerations include, but are not limited to:

a. DMC recovery (marginal versus gross deviation).

b. Technical holding times.

c. Comparison of the values of the target compounds reported in each sample analysis.

d. Other Quality Control (QC) information, such as performance of internal standards.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

Table 9 lists the volatile DMCs and their associated target compounds. If any DMC recovery in the volatiles fraction is out of specification, qualify the data considering the existence of interference in the raw data (see Table 8). Considerations include, but are not limited to:

1. For any recovery greater than the upper acceptance limit:
   a. Qualify detected associated volatile target compounds as a "J".
   b. Do not qualify non-detected associated volatile target compounds.
2. For any recovery greater than or equal to 20%, and less than the lower acceptance limit:
   a. Qualify detected associated volatile target compounds as a "J".
   b. Qualify non-detected associated volatile target compounds as approximated "UJ".
3. For any recovery less than 20%:
   a. Qualify detected associated volatile target compounds as a "J".
   b. Qualify non-detected associated volatile target compounds as unusable "R".
4. For any recovery within acceptance limits, no qualification of the data is necessary.
5. In the special case of a blank analysis having DMCs out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable DMC recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, note analytical problems for Contract Laboratory Program Project Officer (CLP PO) action.

Table 8. Deuterated Monitoring Compound (DMC) Recovery Actions For Trace Volatiles Analyses

Criteria	Action	
	Detected Associated Compounds	Non-detected Associated Compounds
%R > Upper Acceptance Limit	J	No qualification
20% %R < Lower Acceptance Limit	J	UJ
%R < 20%	J	R
Lower Acceptance Limit ≤ %R ≤ Upper Acceptance Limit	No qualification	

Table 9. Volatile Deuterated Monitoring Compounds (DMCs) and the Associated Target Compounds

Chloroethane-d_5 (DMC)	1,2-Dichloropropane-d_6 (DMC)	1,2-Dichlorobenzene-d_4 (DMC)
Dichlorodifluoromethane	Cyclohexane	Chlorobenzene
Chloromethane	Methylcyclohexane	1,3-Dichlorobenzene
Bromomethane	1,2-Dichloropropane	1,4-Dichlorobenzene
Chloroethane	Bromodichloromethane	1,2-Dichlorobenzene
Carbon disulfide		1,2,4-Trichlorobenzene
		1,2,3-Trichlorobenzene
trans-1,3-Dichloropropene-d4 (DMC)	Chloroform-d (DMC)	2-Hexanone-d_5 (DMC)
cis-1,3-Dichloropropene	1,1-Dichloroethane	4-Methyl-2-pentanone
trans-1,3-Dichloropropene	Bromochloromethane	2-Hexanone
1,1,2-Trichloroethane	Chloroform	
	Dibromochloromethane	
	Bromoform	
2-Butanone-d_5 (DMC)	1,1-Dichloroethene-d_2 (DMC)	1,1,2,2-Tetrachloroethane-d_2 (DMC)
Acetone	trans-1,2-Dichloroethene	1,1,2,2,-Tetrachlororethane
2-Butanone	1,1-Dichloroethene	1,2-Dibromo-3-chloropropane
	cis-1,2-Dichloroethene	
Vinyl chloride-d_3 (DMC)	Benzene-d_6 (DMC)	Toluene-d_8 (DMC)
Vinyl chloride	Benzene	Trichloroethene
		Toluene
		Tetrachloroethene
		Ethylbenzene
		o-Xylene
		m,p-Xylene
		Styrene
		Isopropylbenzene
1,2-Dichloroethane-d_4 (DMC)		
Trichlorofluoromethane		
1,1,2-Trichloro-1,2,2-trifluoroethane		
Methyl acetate		
Methylene chloride		
Methyl-tert-butyl ether		
1,1,1-Trichloroethane		
Carbon tetrachloride		
1,2-Dibromoethane		
1,2-Dichloroethane		

VII. Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

A. Review Items:

Form III VOA-1, chromatograms, and quantitation reports.

NOTE: Data for MS and MSDs will not be present unless requested by the Region.

B. Objective:

Data for MS and MSDs are generated to determine long-term precision and accuracy of the analytical method on the sample matrix and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone cannot be used to evaluate the precision and accuracy of individual samples. However, when exercising professional judgment, this data should be used in conjunction with other available Quality Control (QC) information.

C. Criteria:

1. **If requested**, MS and MSD samples are analyzed at a frequency of one MS and MSD per 20 or fewer samples.
2. Spike recoveries should be within the advisory limits provided on Form III VOA-1.
3. Relative Percent Difference (RPD) between MS and MSD recoveries must be within the advisory limits provided on Form III VOA-1.

D. Evaluation:

1. Verify that requested MS and MSD samples were analyzed at the required frequency and results are provided for each sample.
2. Inspect results for the MS and MSD Recovery on Form III VOA-1 and verify that the results for recovery and RPD are within the advisory limits.
3. Verify transcriptions from raw data and check calculations.
4. Verify that the MS and MSD recoveries and RPD were calculated correctly.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. No qualification of the data is necessary on MS and MSD data alone. However, using informed professional judgment, the data reviewer may use the MS and MSD results in conjunction with other QC criteria to determine the need for some qualification of the data. Table 11 lists the volatile target compounds that are spiked into samples to test for matrix effects. If any MS and MSD Percent Recovery or RPD in the volatiles fraction is out of specification, qualify data to include the consideration of the existence of interference in the raw data (see Table 10). Considerations include, but are not limited to:
   a. For any recovery or RPD greater than the upper acceptance limit:
      i. Qualify detected spiked volatile target compounds as a "J".

ii. Do not qualify non-detected spiked volatile target compounds.

b. For any recovery greater than or equal to 20%, and less than the lower acceptance limit:

i. Qualify detected spiked volatile target compounds as a "J".

ii. Qualify non-detected spiked volatile target compounds as approximated "UJ".

c. For any recovery less than 20%:

i. Qualify detected spiked volatile target compounds as a "J".

ii. Qualify non-detected spiked volatile target compounds using professional judgment.

d. For any recovery or RPD within acceptance limits, no qualification of the data is necessary.

2. The data reviewer should first try to determine to what extent the results of the MS and MSD affect the associated data. This determination should be made with regard to the MS and MSD sample itself, as well as specific analytes for all samples associated with the MS and MSD.

3. In those instances where it can be determined that the results of the MS and MSD affect only the sample spiked, limit qualification to this sample only. However, it may be determined through the MS and MSD results that a laboratory is having a systematic problem in the analysis of one or more analytes that affects all associated samples and the reviewer should use professional judgment to qualify the data from all associated samples.

4. The reviewer must use professional judgment to determine the need for qualification of detects of non-spiked compounds.

NOTE: **Notify the Contract Laboratory Program Project Officer (CLP PO) if a field or trip blank was used for the MS and MSD.**

Table 10. Matrix Spike/Matrix Spike Duplicate (MS/MSD) Actions for Trace Volatiles Analysis

Criteria	Action	
	Detected Spiked Compounds	Non-detected Spiked Compounds
%R or RPD> Upper Acceptance Limit	J	No qualification
20% ≤ %R< Lower Acceptance Limit	J	UJ
%R < 20%	J	Use professional judgment
Lower Acceptance Limit ≤ %R; RPD ≤ Upper Acceptance Limit	No qualification	

Table 11. Matrix Spike (MS) Recovery and Relative Percent Difference (RPD) Limits

Compound	Percent Recovery	RPD
1,1-Dichloroethene	61 - 145	0 - 14
Benzene	76 - 127	0 - 11
Trichloroethene	71 - 120	0 - 14
Toluene	76 - 125	0 - 13
Chlorobenzene	75 - 130	0 - 13

VIII. Regional Quality Assurance (QA) and Quality Control (QC)

A. Review Items:

Form I VOA-1, Form I VOA-2, *Form I VOA-SIM*, chromatograms, Traffic Report/Chain of Custody Record (TR/COC), quantitation reports, and other raw data from QA/QC samples.

B. Objective:

Regional QA/QC samples refer to any QA and/or QC samples initiated by the Region, including field duplicates, Performance Evaluation (PE) samples, blind spikes, and blind blanks. The use of these QA/QC samples is highly recommended (e.g., the use of field duplicates can provide information on sampling precision and homogeneity).

C. Criteria:

Criteria are determined by each Region.

1. PE sample frequency may vary.
2. The analytes present in the PE sample must be correctly identified and quantified.

D. Evaluation:

1. Evaluation procedures must follow the Region's Standard Operating Procedure (SOP) for data review. Each Region will handle the evaluation of PE samples on an individual basis. Compare results for PE samples to the acceptance criteria for the specific PE samples, if available.
2. Calculate Relative Percent Difference (RPD) between field duplicates. Provide this information in the Data Review Narrative.

E. Action:

Any action must be in accordance with Regional specifications and the criteria for acceptable PE sample results. Note, for Contract Laboratory Program Project Officer (CLP PO) action, unacceptable results for PE samples.

IX. Internal Standards

A. Review Items:

Form VIII VOA, *Form VIII VOA-SIM*, quantitation reports, and chromatograms.

B. Objective:

Internal standard performance criteria ensures that Gas Chromatograph/Mass Spectrometer (GC/MS) sensitivity and response are stable during each analysis.

C. Criteria:

1. The internal standard area counts for all samples [including Matrix Spike and Matrix Spike Duplicate (MS/MSD), and Performance Evaluation (PE) samples] and all blanks must not vary more than ±40.0% from the associated 12-hour calibration standard [opening Continuing Calibration Verification (CCV) or mid-point standard from initial calibration].
2. The Retention Time (RT) of the internal standard in the sample or blank must not vary more than ±20 seconds from the RT of the internal standard in the associated 12-hour calibration standard (opening CCV or mid-point standard from initial calibration).

D. Evaluation:

1. Check raw data (e.g., chromatograms and quantitation lists) to verify the internal standard RTs and areas reported on the Internal Standard Area Summary (Form VIII VOA, *Form VIII VOA-SIM*).
2. Verify that all RTs and internal standard areas are within criteria for all samples and blanks.
3. If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations include, but are not limited to:
   a. Magnitude and direction of the internal standard area shift.
   b. Magnitude and direction of the internal standard RT shift.
   c. Technical holding times.
   d. Comparison of the values of the target compounds reported in each fraction.
   e. Other Quality Control (QC) information.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. If an internal standard area count for a sample or blank is greater than 140.0% of the area for the associated standard (opening CCV or mid-point standard from initial calibration) (see Table 12):
   a. Qualify detects for compounds quantitated using that internal standard with a "J".
   b. Do not qualify non-detected associated compounds.
2. If an internal standard area count for a sample or blank is less than 60.0% of the area for the associated standard (opening CCV or mid-point standard from initial calibration):

a. Qualify detects for compounds quantitated using that internal standard with a "J".

b. Qualify non-detected associated compounds as unusable "R".

3. If an internal standard area count for a sample or blank is greater than or equal to 60.0%, and less than 140% of the area for the associates standard opening CCV or mid-point standard from initial calibration, no qualification of the data is necessary.

4. If an internal standard RT varies by more than 20.0 seconds:

   Examine the chromatographic profile for that sample to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection of the data for that sample fraction. Detects should not need to be qualified as unusable "R" if the mass spectral criteria are met.

5. If an internal standard RT varies by less than or equal to 20.0 seconds, no qualification of the data is necessary.

6. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if the internal standard performance criteria are grossly exceeded. Note in the Data Review Narrative potential effects on the data resulting from unacceptable internal standard performance.

Table 12. Internal Standard Actions for Trace Volatiles Analyses

Criteria	Action	
	Detected Associated Compounds*	Non-detected Associated Compounds*
Area counts > 140% of 12-hour standard (opening CCV or mid-point standard from initial calibration)	J	No qualification
Area counts < 60% of 12-hour standard (opening CCV or mid-point standard from initial calibration)	J	R
Area counts ≥ 60% but ≤ 140% of 12-hour standard (opening CCV or mid-point standard from initial calibration)	No qualification	
RT difference > 20.0 seconds between samples and 12-hour standard (opening CCV or mid-point standard from initial calibration)	R **	
RT difference ≤ 20.0 seconds between samples and 12-hour standard (opening CCV or mid-point standard from initial calibration)	No qualification	

* For volatile compounds associated to each internal standard, see Table 3 - Trace Volatile Target Compounds and Deuterated Monitoring Compounds with Corresponding Internal Standards for Quantitation in SOM01.2, Exhibit D, available at: http://www.epa.gov/superfund/programs/clp/som1.htm

** See Trace Volatiles Organic Analysis, Section IX.E.4.

X. Target Compound Identification

A. Review Items:

Form I VOA-1, Form I VOA-2, *Form I VOA-SIM*, quantitation reports, mass spectra, and chromatograms.

B. Objective:

The objective of the criteria for Gas Chromatograph/Mass Spectrometer (GC/MS) qualitative analysis is to minimize the number of erroneous compound identifications. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).

The identification criteria can be applied more easily in detecting false positives than false negatives. More information is available for false positives due to the requirement for submittal of data supporting positive identifications. Negatives, or non-detected compounds, on the other hand, represent an absence of data and are, therefore, more difficult to assess. One example of the detection of false negatives is not reporting a target compound that is reported as a Tentatively Identified Compound (TIC).

C. Criteria:

1. The Relative Retention Times (RRTs) must be within ±0.06 RRT units of the standard RRT [opening Continuing Calibration Verification (CCV) or mid-point standard from initial calibration].
2. Mass spectra of the sample compound and a current laboratory-generated standard [i.e., the mass spectrum from the associated calibration standard (opening CCV or mid-point standard from initial calibration)] must match according to the following criteria:
    a. All ions present in the standard mass spectrum at a relative intensity greater than 10% must be present in the sample spectrum.
    b. The relative intensities of these ions must agree within ±20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30-70%).
    c. Ions present at greater than 10% in the sample mass spectrum, but not present in the standard spectrum, must be evaluated by a reviewer experienced in mass spectral interpretation.

D. Evaluation:

1. Check that the RRT of reported compounds is within ±0.06 RRT units of the standard RRT (opening CCV or mid-point standard from the initial calibration).
2. Check the sample compound spectra against the laboratory standard spectra to verify that it meets the specified criteria.
3. The reviewer should be aware of situations when sample carryover is a possibility and should use professional judgment to determine if instrument cross-contamination has affected any positive compound identification. The method specifies that an instrument blank must be run after samples which contain target compounds at levels exceeding the initial calibration range (20 µg/L for non-ketones, 200 µg/L for ketones), or non-target compounds at concentrations greater than 100 µg/L, or saturated ions from a compound (excluding the compound peaks in the solvent front).

4. Check the chromatogram to verify that peaks are identified. Major peaks are either identified as target compounds, TICs, Deuterated Monitoring Compounds (DMCs), or internal standards.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

1. The application of qualitative criteria for GC/MS analysis of target compounds requires professional judgment. It is up to the reviewer's discretion to obtain additional information from the laboratory. If it is determined that incorrect identifications were made, qualify all such data as not detected "U" or unusable "R".
2. Use professional judgment to qualify the data if it is determined that cross-contamination has occurred.
3. Note in the Data Review Narrative any changes made to the reported compounds or concerns regarding target compound identifications. Note, for Contract Laboratory Program Project Officer (CLP PO) action, the necessity for numerous or significant changes.

XI. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

A. Review Items:

Forms I VOA-1, Form I VOA-2, *Form I VOA-SIM*, sample preparation sheets, Sample Delivery Group (SDG) Narrative, quantitation reports, and chromatograms.

B. Objective:

The objective is to ensure that the reported quantitation results and CRQLs are accurate.

C. Criteria:

1. Compound quantitation, as well as the adjustment of the CRQLs, must be calculated according to the correct equation.
2. Compound Relative Response Factors (RRFs) must be calculated based on the internal standard associated with that compound, as listed in the method. Quantitation must be based on the quantitation ion (m/z) specified in the method for both the internal standards and target analytes. The compound quantitation must be based on the average RRF from the associated initial calibration.

D. Evaluation:

1. Examine raw data to verify the correct calculation of all sample results reported by the laboratory. Compare quantitation lists and chromatograms to the reported detects and non-detects sample results. Check the reported values.
2. Verify that the correct internal standard, quantitation ion, and Mean Relative Response Factor ($\overline{RRF}$) were used to quantitate the compound. Verify that the same internal standard, quantitation ion, and $\overline{RRF}$ are used consistently throughout, in both the calibration as well as the quantitation process.
3. Verify that the CRQLs have been adjusted to reflect all sample dilutions.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

1. If any discrepancies are found, the Region's designated representative may contact the laboratory to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, the reviewer must use professional judgment to decide which value is the most accurate. Under these circumstances, the reviewer may determine that qualification of data is warranted. Note in the Data Review Narrative a description of the reasons for data qualification and the qualification that is applied to the data.
2. Note, for Contract Laboratory Program Project Officer (CLP PO) action, numerous or significant failures to accurately quantify the target compounds or to properly evaluate and adjust CRQLs.

XII. Tentatively Identified Compounds (TICs)

A. Review Items:

Form I VOA-TIC, chromatograms, library search printouts, and spectra for the TIC candidates.

B. Objective:

Chromatographic peaks in volatile fraction analyses that are not target analytes, Deuterated Monitoring Compounds (DMCs), or internal standards are potential TICs. TICs must be qualitatively identified via a forward search of the NIST/USEPA/NIH Mass Spectral Library (May 2002 release or later)[1], and/or Wiley Mass Spectral Library (1998 release or later)[2], or the equivalent. The identifications must be assessed by the data reviewer.

C. Criteria:

For each sample, the laboratory must conduct a mass spectral search of the NIST/USEPA/NIH (May 2002 release or later), and/or Wiley (1998 release or later), or equivalent mass spectral library, and report the possible identity for 30 of the largest volatile fraction peaks which are not DMCs, internal standards, or target compounds, but which have an area or height greater than 10% of the area or height of the nearest internal standard. Estimated concentrations for TICs are calculated similarly to the Target Compound List (TCL) compounds, using total ion areas for the TIC and the internal standard, and assuming a Relative Response Factor (RRF) of 1.0. TIC results are reported for each sample on the Organic Analyses Data Sheet (Form I VOA-TIC).

D. Evaluation:

1. Guidelines for tentative identification are as follows:
   a. Major ions (greater than 10% Relative Intensity) in the reference spectrum should be present in the sample spectrum.
   b. The relative intensities of the major ions should agree within ±20% between the sample and the reference spectra.
   c. Molecular ions present in the reference spectrum should be present in the sample spectrum.
   d. Review ions present in the sample spectrum, but not in the reference spectrum, for possible background contamination, interference, or presence of coeluting compounds.
   e. Review ions present in the reference spectrum, but not in the sample spectrum, for possible subtraction from the sample spectrum because of background contamination or coeluting compounds. Data system library reduction programs can sometimes create these discrepancies.
   f. Non-target compounds receiving a library search match of 85% or higher are considered a "likely match". Report the compound unless the mass spectral interpretation specialist feels there is evidence not to report the compound as identified by the library search program. Note in the Sample Delivery Group (SDG) Narrative the justification for not reporting a compound as listed by the search program.

[1]NIST/USEPA/NIH Mass Spectral Library (May 2002 release or later), National Institute of Standards and Technology, Gaithersburg, Maryland.

[2]Wiley Mass Spectral Library (1998 release or later) John Wiley & Sons, Inc., Hoboken, New Jersey.

g. If the library search produces more than one compound greater than or equal to 85%, report the compound with the highest percent match (report first compound if percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels that the highest match compound should not be reported or another compound with a lower match should be reported. The laboratory should include the justification for not reporting the compound with the highest spectral match within the SDG Narrative. Do not report DMCs, internal standards, and volatile target compounds as TICs, unless the only compounds having a percent match of greater than 85% are DMCs, internal standards, or volatile target compounds.

h. If the library search produces a series of obvious isomer compounds with library search matches greater than or equal to 85%, report the compound with the highest library search percent match (or the first compound if the library search matches are the same). Note in the SDG Narrative that the exact isomer configuration, as reported, may not be accurate.

i. If the library search produces no matches greater than or equal to 85%, and in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, report the compound as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (e.g., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

j. Alkanes are not to be reported as TICs on Form I VOA-TIC. An alkane is defined as any hydrocarbon with the generic formula C_nH_{2n+2} that contains only C-H and C-C single bonds. When the preceding alkanes are tentatively identified, estimate the concentration(s) and report them in the SDG Narrative as alkanes by class (i.e., straight-chain, branched, cyclic, as a series, or as applicable). Report total alkanes concentration on Form I VOA-TIC.

2. Check the raw data to verify that the laboratory has generated a library search for all required peaks in the chromatograms for samples and blanks.

3. Examine blank chromatograms to verify that TIC peaks present in samples are not found in blanks. When a low-level, non-target compound that is a common artifact or laboratory contaminant is detected in a sample, a thorough check of blank chromatograms may require looking for peaks which are less than 10% of the internal standard height, but present in the blank chromatogram at a similar Relative Retention Time (RRT).

4. Examine all mass spectra for every sample and blank.

5. Consider all reasonable choices, since TIC library searches often yield several candidate compounds having a close matching score.

6. Be aware of common laboratory artifacts/contaminants and their sources (e.g., Aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.

   Examples:

   Common laboratory contaminants include CO2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons, and phthalates at levels less than 100 µg/L.

   Solvent preservatives include cyclohexene, (a methylene chloride preservative). Related by-products include cyclohexanone, cyclohexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.

   Aldol condensation reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

7. A target compound may be identified in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list (false negative). If the total area quantitation method was used, request that the laboratory recalculate the result using the proper quantitation ion and Relative Response Factor (RRF).

   A non-target compound may be incorrectly identified by the instrument's target analyte data processor as a target compound (false positive). When this happens, the non-target library search procedure will not detect the false positive as a TIC. In this case, request that the laboratory properly identify the compound and recalculate the result using the total area quantitation method and a RRF of 1.0.

   Evaluate other sample chromatograms and check for both false negatives and false positives to determine if the occurrence is isolated or systematic.

8. Target compounds may be identified in more than one fraction. Verify that quantitation is made from the proper fraction.
9. Do not perform library searches on internal standards or DMCs.
10. Estimate TIC concentration assuming an RRF of 1.0.

E. Action:

1. Qualify all TIC results for which there is presumptive evidence of a match (e.g. greater than or equal to 85% match) as "NJ", tentatively identified, with approximated concentrations.
2. General actions related to the review of TIC results are as follows:
   a. If it is determined that a tentative identification of a non-target compound is unacceptable, change the tentative identification to "unknown" or another appropriate identification, and qualify the result with a "J".
   b. If all contractually-required peaks were not library searched and quantitated, the Region's designated representative may request these data from the laboratory.
3. In deciding whether a library search result for a TIC represents a reasonable identification, use professional judgment. If there is more than one possible match, report the result as "either compound X or compound Y". If there is a lack of isomer specificity, change the TIC result to a non-specific isomer result (e.g., 1,3,5-trimethyl benzene to trimethyl benzene isomer) or to a compound class (e.g., 2-methyl, 3-ethyl benzene to a substituted aromatic compound).
4. The reviewer may elect to report all similar compounds as a total (e.g., all alkanes may be summarized and reported as total hydrocarbons).
5. Other Case factors may influence TIC judgments. If a sample TIC match is poor, but other samples have a TIC with a valid library match, similar RRT, and the same ions, infer identification information from the other sample TIC results.
6. Note in the Data Review Narrative any changes made to the reported data or any concerns regarding TIC identifications.
7. Note, for Contract Laboratory Program Project Officer (CLP PO) action, failure to properly evaluate and report TICs.

XIII. System Performance

A. Review Items:

Form VIII VOA, *Form VIII VOA-SIM*, and chromatograms.

B. Objective:

During the period following Instrument Performance Quality Control (QC) checks (e.g., blanks, tuning, calibration), changes may occur in the system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC runs, a thorough review of the ongoing data acquisition can yield indicators of instrument performance.

C. Criteria:

There are no specific criteria for system performance. Use professional judgment to assess the system performance.

D. Evaluation:

1. Abrupt discrete shifts in the Reconstructed Ion Chromatogram (RIC) baseline may indicate a change in the instrument's sensitivity or the zero setting. A baseline "shift" could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds at or near the detection limit to miss detection. A baseline "rise" could indicate problems such as a change in the instrument zero, a leak, or degradation of the column.
2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:
    a. High RIC background levels or shifts in Absolute Retention Times (RTs) of internal standards.
    b. Excessive baseline rise at elevated temperature.
    c. Extraneous peaks.
    d. Loss of resolution.
    e. Peak tailing or peak splitting that may result in inaccurate quantitation.
3. A drift in instrument sensitivity may occur during the 12-hour time period and may be an indication of possible internal standard spiking problems. This could be discerned by examination of the internal standard area on Form VIII VOA for trends such as a continuous or near-continuous increase or decrease in the internal standard area over time.

E. Action:

Use professional judgment to qualify the data if it is determined that system performance has degraded during sample analyses. Note, for Contract Laboratory Program Project Officer (CLP PO) action, any degradation of system performance which significantly affected the data.

XIV. Overall Assessment of Data

A. Review Items:

Entire data package, data review results, and (if available), the Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP).

B. Objective:

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria:

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation:

1. Evaluate any technical problems which have not been previously addressed.
2. If appropriate information is available, the reviewer may assess the usability of the data to help the data user avoid inappropriate use of the data. Review all available information, including the QAPP (specifically the acceptance and performance criteria), SAP, and communication with the data user that concerns the intended use and desired quality of these data.

E. Action:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the Quality Control (QC) criteria previously discussed.
2. Write a brief narrative to give the user an indication of the analytical limitations of the data. Note, for Contract Laboratory Program Project Officer (CLP PO) action, any inconsistency of the data with the Sample Delivery Group (SDG) Narrative. If sufficient information on the intended use and required quality of the data are available, the reviewer should include their assessment of the usability of the data within the given context. This may be used as part of a formal Data Quality Assessment (DQA).

LOW/MEDIUM VOLATILE DATA REVIEW

The data requirements to be checked are:

I. Preservation

II. Gas Chromatograph/Mass Spectrometer (GC/MS) Instrument Performance Check

III. Initial Calibration

IV. Continuing Calibration Verification (CCV)

V. Blanks

VI. Deuterated Monitoring Compounds (DMCs)

VII. Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

VIII. Regional Quality Assurance (QA) and Quality Control (QC)

IX. Internal Standards

X. Target Compound Identification

XI. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

XII. Tentatively Identified Compounds (TICs)

XIII. System Performance

XIV. Overall Assessment of Data

I. Preservation

A. Review Items:

Form I VOA-1, Form I VOA-2, Form I VOA-TIC, Traffic Report/Chain of Custody Record (TR/COC), raw data, and the Sample Delivery Group (SDG) Narrative checking for:

1. pH
2. Sample temperature
3. Holding time
4. Other sample conditions (e.g., headspace)

B. Objective:

The objective is to ascertain the validity of the analytical results based on sample condition (i.e., preservation, temperature, headspace) and the holding time of the sample from the time of collection to the time of analysis.

C. Criteria:

The technical holding time criterion for aqueous samples are as follows:

For volatile compounds in properly cooled (4°C ± 2°C) aqueous samples that are acid-preserved (with HCl to a pH of 2 or below), the maximum holding time is 14 days from sample collection.

For aqueous samples that were properly cooled (4°C ± 2°C), but which have no indication of being preserved, the maximum holding time is 7 days from sample collection.

The technical holding time criterion for non-aqueous samples are as follows:

For volatile components that are frozen (less than -7°C) or are properly cooled (4°C ± 2°C) and preserved with $NaHSO_4$, the maximum holding time is 14 days from sample collection.

D. Evaluation:

Technical holding times are established by comparing the sample collection dates on the TR/COC Record with the dates of analysis on Form I VOA-1, Form I VOA-2, Form I VOA-TIC, and the raw data. Information contained in the Complete SDG File (CSF) should also be considered in the determination of holding times. Verify that the analysis dates on Form I(s) and the raw data/SDG file are identical. Review the SDG Narrative to determine if samples were preserved and arrived at the laboratory in proper condition (e.g., received intact, appropriate sample temperature at receipt, pH, absence of air bubbles or detectable headspace). If there is no indication in the SDG Narrative, the TR/COC Record, or the sample records that there was a problem with the samples, the integrity of samples can be assumed to be acceptable. If it is indicated that there were problems with the samples, the integrity of the sample may have been compromised and professional judgment should be used to evaluate the effect of the problem on the sample results.

E. Action:

1. Qualify aqueous sample results using preservation and technical holding time information as follows (see Table 13):
   a. If there is no evidence that the samples were properly preserved, and the samples were analyzed within the technical holding time (7 days from sample collection), no qualification of the data is necessary.
   b. If there is no evidence that the samples were properly preserved, and the samples were analyzed outside of the technical holding time (7 days from sample collection), qualify detects for all volatile compounds with a "J" and non-detects as unusable "R".
   c. If the samples were properly preserved, and the samples were analyzed within the technical holding time (14 days from sample collection), no qualification of the data is necessary.
   d. If the samples were properly preserved, and were analyzed outside of the technical holding time (14 days from sample collection), qualify detects with a "J" and non-detects as unusable "R".
2. Qualify non-aqueous sample results using the preservation and technical holding time information as follows (see Table 13):
   a. If there is no evidence that the samples were properly preserved, and the samples were analyzed within technical holding time (14 days from sample collection) qualify detects for all volatile compounds with a "J" and non-detects as unusable "R".
   b. If the samples were properly preserved and the samples were analyzed within the technical holding time (14 days from sample collection), no qualification of the data is necessary.
   c. If there is no evidence that the samples were properly preserved, and the samples were analyzed outside the technical holding time (14 days from sample collection), qualify detects for all volatile compounds with a "J" and non-detects as unusable "R".
   d. If the samples were properly preserved, and the samples were analyzed outside the technical holding time (14 days from sample collection), qualify detects for all volatile compounds with a "J" and non-detects as unusable "R".

Table 13. Holding Time Actions for Low/Medium Volatile Analyses

Matrix	Preserved	Criteria	Action	
			Detected Associated Compounds	Non-Detected Associated Compounds
Aqueous	No	≤ 7 days	No qualification	
	No	> 7 days	J	R
	Yes	≤ 14 days	No qualification	
	Yes	> 14 days	J	R
Non-Aqueous	No	≤ 14 days	J	R
	Yes	≤ 14 days	No qualification	
	Yes/No	> 14 days	J	R

3. Use professional judgment to qualify samples whose temperature upon receipt at the laboratory is either below 2 degrees centigrade or above 6 degrees centigrade.

4. Due to limited information concerning holding times for non-aqueous samples, it is left to the discretion of the data reviewer to apply aqueous holding times or other information that is available.
5. Note in the Data Review Narrative, whenever possible, the effect of the holding time exceedance on the resulting data.
6. Note, for Contract Laboratory Program Project Officer (CLP PO) action, when technical holding times are exceeded.

II. Gas Chromatograph/Mass Spectrometer (GC/MS) Instrument Performance Check

A. Review Items:

Form V VOA, bromofluorobenzene (BFB) mass spectra, and mass listing.

B. Objective:

GC/MS instrument performance checks are performed to ensure adequate mass resolution, identification, and to some degree, sensitivity. These criteria are not sample-specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.

C. Criteria:

1. The 12-hour clock begins with either the injection of BFB, or in cases where a closing Continuing Calibration Verification (CCV) can be used for an opening CCV, the 12-hour clock begins with the injection of the opening CCV.
2. Listed below are some, but not necessarily all, examples of acceptable analytical sequences incorporating the use of the opening and/or closing CCV. Use these examples as a guide for possible analytical sequences that can be expected. The criteria associated with these analytical sequences have been evaluated as part of the Contract Compliance Screening (CCS) process.

Conditions for When Example Sequence is Appropriate:	Acceptable Criteria That Must Be Met:	Notes:
Use Example 1 if time remains on the 12-hour clock after the initial calibration sequence.	• BFB tunes meet instrument performance criteria. • The five Initial Calibration standards meet initial calibration criteria. • CCV A meets both opening and closing CCV criteria. • CCV B meets closing CCV criteria.	The requirement of starting the new 12-hour clock for Analytical Sequence 2 with a new BFB tune is waived if CCV A meets opening CCV criteria. If CCV B meets opening CCV criteria, a method blank and subsequent samples may be analyzed immediately after CCV B.
Use Example 2 if time remains on the 12-hour clock after the initial calibration sequence.	• BFB tunes meet instrument performance criteria. • The five Initial Calibration standards meet initial calibration criteria. • CCV A meets closing CCV criteria (but does not meet opening CCV criteria). • CCV B meets opening CCV criteria. • CCV C meets closing CCV criteria.	CCV A does not meet opening CCV criteria, therefore, a new BFB tune must be performed, immediately followed by CCV B before the method blank and any samples may be analyzed. In this case, the new 12-hour clock and Analytical Sequence 2 begins with the injection of the new BFB tune.

Conditions for When Example Sequence is Appropriate:	Acceptable Criteria That Must Be Met:	Notes:
Use Example 3 if more than 12-hours have elapsed since the most recent initial calibration or closing CCV, OR if the most recent closing CCV was not or could not be used as an opening CCV.	• BFB tunes meet instrument performance criteria. • CCV A meets opening CCV criteria. • CCV B meets both opening and closing CCV criteria. • CCV C meets both opening and closing CCV criteria.	The requirement of starting the new 12-hour clock for Analytical Sequence 2 with a new BFB tune is waived if CCV B meets opening CCV criteria. If CCV C meets opening CCV criteria, a method blank and subsequent samples may be analyzed immediately after CCV C.
Use Example 4 if more than 12-hours have elapsed since the most recent initial calibration or closing CCV, OR if the most recent closing CCV was not or could not be used as an opening CCV.	• BFB tunes meet instrument performance criteria. • CCV A meets opening CCV criteria. • CCV B meets closing CCV criteria (but does not meet opening CCV criteria). • CCV C meets opening CCV criteria. • CCV D meets both opening and closing CCV criteria.	Because CCV B does not meet opening CCV criteria before the method blank and any samples may be analyzed, a new BFB tune must be performed, immediately followed by CCV C. In this case, the new 12-hour clock and Analytical Sequence 2 begins with the injection of the new BFB tune. The requirement of starting the new 12-hour clock for Analytical Sequence 3 with a new BFB tune is waived if CCV D meets opening CCV criteria. If CCV D meets opening CCV criteria, a method blank and subsequent samples may be analyzed immediately after CCV D.

Example 1:	**Time**	**Material Injected**	**Analytical Sequence #**
Start of 12-hour clock for Analytical Sequence 1	0 hr	BFB	1
		Initial Calibration 5.0	1
		Initial Calibration 10	1
		Initial Calibration 50	1
		Initial Calibration 100	1
		Initial Calibration 200	1
		Method Blank	1
		Subsequent Samples	1
		•	1
		•	1
		•	1
		•	1
End of 12-hour clock for Analytical Sequence 1/ Beginning of 12-hour clock for Analytical Sequence 2	12 hr	CCV A (meets opening CCV criteria)	1/2
		Method Blank	2
		Subsequent Samples	2
		•	2
		•	2
		•	2
		•	2
End of 12-hour clock for Analytical Sequence 2/ Beginning of 12-hour clock for Analytical Sequence 3	24 hr	CCV B (meets opening CCV criteria)	2/3

Example 2:	**Time**	**Material Injected**	**Analytical Sequence #**
Start of 12-hour clock for Analytical Sequence 1	0 hr	BFB	1
		Initial Calibration 5.0	1
		Initial Calibration 10	1
		Initial Calibration 50	1
		Initial Calibration 100	1
		Initial Calibration 200	1
		Method Blank	1
		Subsequent Samples	1
		•	1
		•	1
		•	1
		•	1
End of 12-hour clock for Analytical Sequence 1	12 hr	CCV A (meets closing CCV criteria, fails opening CCV criteria)	1
Beginning of 12-hour clock for Analytical Sequence 2	13 hr	BFB	2
		CCV B (meets opening CCV criteria)	2
		Method Blank	2
		Subsequent Samples	2
		•	2
		•	2
		•	2
		•	2
End of 12-hour clock for Analytical Sequence 2	25 hr	CCV C (meets closing CCV criteria)	2

Example 3:	**Time**	**Material Injected**	**Analytical Sequence #**
Start of 12-hour clock for Analytical Sequence 1	0 hr	BFB	1
		CCV A (meets opening CCV criteria)	1
		Method Blank	1
		Subsequent Samples	1
		•	1
		•	1
		•	1
		•	1
End of 12-hour clock for Analytical Sequence 1/ Beginning of 12-hour clock for Analytical Sequence 2	12 hr	CCV B (meets opening CCV criteria)	1/2
		Method Blank	2
		Subsequent Samples	2
		•	2
		•	2
		•	2
End of 12-hour clock for Analytical Sequence 2/ Beginning of 12-hour clock for Analytical Sequence 3	24 hr	CCV C (meets opening CCV criteria)	2/3

Example 4:	**Time**	**Material Injected**	**Analytical Sequence #**
Start of 12-hour clock for Analytical Sequence 1	0 hr	BFB	1
		CCV A (meets opening CCV criteria)	1
		Method Blank	1
		Subsequent Samples	1
		•	1
		•	1
		•	1
		•	1
End of 12-hour clock for Analytical Sequence 1	12 hr	CCV B (meets closing CCV criteria, fails opening CCV criteria)	1
Beginning of 12-hour clock for Analytical Sequence 2	13 hr	BFB	2
		CCV C (meets opening CCV criteria)	2
		Method Blank	2
		Subsequent Samples	2
		•	2
		•	2
		•	2
End of 12-hour clock for Analytical Sequence 2/ Beginning of 12-hour clock for Analytical Sequence 3	25 hr	CCV D (meets opening CCV criteria)	2/3

3. Inject a sufficient amount of the instrument performance check solution (50 ng BFB on-column) at the beginning of each 12-hour period during which samples or standards are analyzed. The instrument performance check, BFB for volatile analysis, must meet the ion abundance criteria listed in Table 14. This criteria is waived in cases where a closing CCV can be used as an opening CCV (i.e., a BFB instrument performance check analysis is not required when a closing CCV analysis meets the requirements of an opening CCV analysis).

Table 14. Ion Abundance Criteria For Bromofluorobenzene (BFB)

Mass	Ion Abundance Criteria
50	15.0 - 40.0% of mass 95
75	30.0 - 80.0% of mass 95
95	Base peak, 100% relative abundance
96	5.0 - 9.0% of mass 95*
173	Less than 2.0% of mass 174
174	50.0% - 120% of mass 95
175	5.0 - 9.0% of mass 174
176	95.0 - 101% of mass 174
177	5.0 - 9.0% of mass 176

* All ion abundances must be normalized to mass to charge (m/z) 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95.

D. Evaluation:

1. Compare the data presented for each Instrument Performance Check (Form V VOA) with each mass listing submitted to ensure the following:
   a. Form V VOA is present and completed for each 12-hour period during which samples were analyzed. In cases where a closing CCV is used as an opening CCV for the next 12-hour period, an additional Form V VOA is not required.
   b. The laboratory has not made transcription errors between the data and the form. If there are major differences between the mass listing and the Form Vs, a more in-depth review of the data is required. This may include obtaining and reviewing additional information from the laboratory.
   c. The appropriate number of significant figures has been reported (number of significant figures given for each ion in the ion abundance criteria column) and that rounding is correct.
   d. The laboratory has not made any calculation errors.
2. Verify that samples were not analyzed before a valid instrument performance check or were not analyzed 12 hours after the injection of the Instrument Performance Check Solution. This evaluation is not to be performed in cases where a closing CCV is used as an opening CCV.
3. Verify from the raw data (mass spectral listing) that the mass assignment is correct and that the mass listing is normalized to m/z 95.
4. Verify that the ion abundance criteria were met. The criteria for m/z 173, 175, 176, and 177 are calculated by normalizing to the specified m/z.

5. If possible, verify that spectra were generated using appropriate background subtraction techniques. Since the BFB spectrum is obtained from chromatographic peaks that should be free from coelution problems, background subtraction should be done in accordance with the following procedure:

   a. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.

   b. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not subtract the BFB peak as part of the background.

   NOTE: All mass spectrometer instrument conditions must be identical to those used during the sample analysis. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the contract specifications are contrary to the Quality Assurance (QA) objectives and are, therefore, unacceptable.

   For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the CCS process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. If samples are analyzed without a preceding valid instrument check or are analyzed 12 hours after the Instrument Performance Check and are not preceded by an analysis of a closing CCV that meets opening CCV criteria, qualify all data for those samples as unusable "R".
2. If the laboratory has made minor transcription errors which do not significantly affect the data, the data reviewer should make the necessary corrections on a copy of the form.
3. If the laboratory has failed to provide the correct forms or has made significant transcription or calculation errors, the Region's designated representative should contact the laboratory and request corrected data. If the information is not available, the reviewer must use professional judgment to assess the data. Notify the laboratory's Contract Laboratory Program Project Officer (CLP PO).
4. If mass assignment is in error (e.g., m/z 96 is indicated as the base peak rather than m/z 95), classify all associated data as unusable "R".
5. If ion abundance criteria are not met, professional judgment may be applied to determine to what extent the data may be utilized. When applying professional judgment to this topic, the most important factors to consider are the empirical results that are relatively insensitive to location on the chromatographic profile and the type of instrumentation. Therefore, the critical ion abundance criteria for BFB are the m/z 95/96, 174/175, 174/176, and 176/177 ratios. The relative abundances of m/z 50 and 75 are of lower importance. This issue is more critical for Tentatively Identified Compounds (TICs) than for target analytes.
6. Note in the Data Review Narrative decisions to use analytical data associated with BFB instrument performance checks not meeting contract requirements.
7. If the reviewer has reason to believe that instrument performance check criteria were achieved using techniques other than those described in Low/Medium Volatiles Organic Analysis, Section II.D.5, obtain additional information on the instrument performance checks. If the techniques employed are found to be at variance with the contract requirements, the procedures of the laboratory may merit evaluation. Note, for CLP PO action, concerns or questions regarding laboratory performance. For example, if the reviewer has reason to believe that an inappropriate technique was used to obtain background subtraction (such as background subtracting from the solvent front or from another region of the chromatogram rather than from the BFB peak), this should be noted for CLP PO action.

III. Initial Calibration

A. Review Items:

Form VI VOA-1, Form VI VOA-2, Form VI VOA-3, quantitation reports, and chromatograms.

B. Objective:

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for compounds on the volatile Target Compound List (TCL). Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run and of producing a linear calibration curve and provides the Mean Relative Response Factors ($\overline{\text{RRF}}$s) used for quantitation.

C. Criteria:

1. Initial calibration standards containing both volatile target compounds and Deuterated Monitoring Compounds (DMCs) are analyzed at concentrations of 5.0, 10, 50, 100, and 200 µg/L for non-ketones, 10, 20, 100, 200, and 400 µg/L for ketones, and 100, 200, 1250, 2000, and 4000 µg/L for 1,4-Dioxane at the beginning of each analytical sequence, or as necessary if the continuing calibration verification acceptance criteria are not met. All three xylene isomers (o-, m-, and p-xylene) must be present in the calibration standards. The o-xylene calibration standard concentrations must be at 5.0, 10, 50, 100, and 200 µg/L, while the concentration of the m- plus the p-xylene isomers must **total** 5.0, 10, 50, 100, and 200 µg/L. The initial calibration (and any associated samples and blanks) must be analyzed within 12 hours of the associated instrument performance check.
2. Initial calibration standard Relative Response Factors (RRFs) for the volatile target compounds listed in Table 15 and all DMCs must be greater than or equal to 0.010, except for 1,4-Dioxane and its associated DMC (≥ 0.0050 advisory). The RRF for all other volatile target compounds must be greater than or equal to 0.050.
3. The Percent Relative Standard Deviation (%RSD) of the initial calibration RRFs must be less than or equal to 40.0% for the volatile target compounds and DMCs listed in Table 15 except for 1,4-Dioxane and its associated DMC (50.0%). The %RSD for all other volatile target compounds and associated DMCs must be less than or equal to 20.0%.

NOTE: **The flexibility clause in the method may impact some of the criteria preceding. A copy of the flexibility clause should be present in the Sample Delivery Group (SDG). Refer to the Contract Laboratory Program (CLP) Web site at http://www.epa.gov/oerrpage/superfund/programs/clp/modifiedanalyses.htm for the specific method flexibility requirements.**

D. Evaluation:

1. Verify that the correct concentrations of standards were used for the initial calibration (i.e. 5.0, 10, 50, 100, and 200 µg/L for non-ketones, 10, 20, 100, 200, and 400 µg/L for ketones, and 100, 200, 1250, 2000, and 4000 µg/L for 1,4-Dioxane).
2. Verify that the $\overline{\text{RRF}}$ obtained from the associated initial calibration was used for calculating sample results and the samples were analyzed within 12 hours of the associated instrument performance check.
3. Evaluate the initial calibration RRFs and the $\overline{\text{RRF}}$ for all volatile target compounds and DMCs:

a. Check and recalculate the RRFs and $\overline{RRF}$ for at least one volatile target compound associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

b. Verify that for all volatile target compounds listed in Table 15 and for all DMCs, the initial calibration RRFs are greater than or equal to 0.010, except for 1,4-Dioxane and its associated DMC (≥ 0.0050 advisory), and for all other volatile target compounds, RRFs are greater than or equal to 0.050.

Table 15. Volatile Compounds Exhibiting Poor Response

Volatile Compounds	
Acetone	1,2-Dibromo-3-chloropropane
2-Butanone	Isopropylbenzene
Carbon disulfide	Methyl acetate
Chloroethane	Methylene chloride
Chloromethane	Methylcyclohexane
Cyclohexane	Methyl tert-butyl ether
1,2-Dibromoethane	trans-1,2-Dichloroethene
Dichlorodifluoromethane	4-Methyl-2-pentanone
1,2-Dichloropropane	2-Hexanone
cis-1,2-Dichloroethene	Trichlorofluoromethane
1,4-Dioxane	1,1,2-Trichloro-1,2,2-trifluoroethane

4. Evaluate the %RSD for all volatile target compounds and DMCs:

   a. Check and recalculate the %RSD for one or more volatile target compound(s) and DMCs. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. If the %RSD is greater than the maximum criteria [40.0% for the volatile target compounds listed in Table 15, and associated DMCs (see Table 21) except for 1,4-Dioxane (50.0%) and its associated DMC, and 20.0% for all other volatile target compounds and associated DMCs], the reviewer should use professional judgment to determine the need to check the points on the curve for the cause of the non-linearity. This is checked by eliminating either the high-point or the low-point and recalculating the %RSD (see Low/Medium Volatiles Organic Analysis, Section III.E.2).

5. If errors are detected in the calculations of either the RRFs or the %RSD, perform a more comprehensive recalculation.

NOTE: **For data obtained from the CLP, the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

1. Qualify all volatile target compounds, including the compounds exhibiting poor response listed in Table 15, using the following criteria (see Table 16):

a. If any volatile target compound has an RRF value less than the minimum criterion [0.010 for the compounds exhibiting poor response listed in Table 15, except for 1,4-Dioxane (0.0050 advisory) and 0.050 for all other volatile compounds], use professional judgment for detects, based on mass spectral identification, to qualify the data as a "J" or unusable "R".

b. If any volatile target compound has an RRF value less than the minimum criterion [0.010 for the compounds exhibiting poor response listed in Table 15, except for 1,4-Dioxane (0.0050 advisory) and 0.050 for all other volatile compounds], qualify non-detected compounds as unusable "R".

c. If any of the volatile target compounds listed in Table 15 has %RSD greater than 40.0%, except for 1,4-Dioxane (50.0%), qualify detects with a "J" and non-detected compounds using professional judgment (see Low/Medium Volatiles Organic Analysis, Section III.E.2).

d. For all other volatile target compounds, if %RSD is greater than 20.0%, qualify detects with a "J" and non-detected compounds using professional judgment (see Low/Medium Volatiles Organic Analysis, Section III.E.2).

e. If the volatile target compounds meet the acceptance criteria for RRF and %RSD, no qualification of the data is necessary.

f. No qualification of the data is necessary on the DMC RRF and %RSD data alone. Use professional judgment and follow the guidelines in Low/Medium Volatiles Organic Analysis, Section III.E.2, to evaluate the DMC RRF and %RSD data in conjunction with the DMC recoveries for determination of the need for qualification of the data.

2. At the reviewer's discretion, and based on the project-specific Data Quality Objectives (DQOs), a more in-depth review may be considered using the following guidelines:

   a. If any volatile target compound has a %RSD greater than the maximum criterion [40.0% for the compounds listed in Table 15, except for 1,4-Dioxane (50.0%), and 20.0% for all other volatile compounds], and if eliminating either the high or the low-point of the curve does not restore the %RSD to less than or equal to the required maximum:

      i. Qualify detects for that compound(s) with a "J".

      ii. Qualify non-detected volatile target compounds using professional judgment.

   b. If the high-point of the curve is outside of the linearity criteria (e.g., due to saturation):

      i. Qualify detects outside of the linear portion of the curve with a "J".

      ii. No qualifiers are required for detects in the linear portion of the curve.

      iii. No qualifiers are required for volatile target compounds that were not detected.

   c. If the low-point of the curve is outside of the linearity criteria:

      i. Qualify low-level detects in the area of non-linearity with a "J".

      ii. No qualifiers are required for detects in the linear portion of the curve.

      iii. For non-detected volatile compounds, use the lowest point of the linear portion of the curve to determine the new quantitation limit.

3. If the laboratory has failed to provide adequate calibration information, the Region's designated representative should contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

4. Note in the Data Review Narrative, whenever possible, the potential effects on the data due to calibration criteria exceedance.

5. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if calibration criteria are grossly exceeded.

Table 16. Initial Calibration Actions for Low/Medium Volatiles Analyses

Criteria for Low/Med Analysis	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
RRF < 0.0050 (advisory for 1,4-Dioxane) RRF < 0.010 (target compounds listed in Table 15) RRF < 0.050 (all other target compounds)	J or R (based on mass spectral identification)	R
RRF ≥ 0.0050 (advisory for 1,4-Dioxane) RRF ≥ 0.010 (target compounds listed in Table 15) RRF ≥ 0.050 (all other target compounds)	No qualification	
%RSD ≤ 50.0 (1,4-Dioxane) %RSD ≤ 40.0 (target compounds listed in Table 15) %RSD ≤ 20.0 (all other target compounds)	No qualification	
%RSD > 50.0 (1,4-Dioxane) %RSD > 40.0 (target compounds listed in Table 15) %RSD > 20.0 (all other target compounds)	J	Use professional judgment

IV. Continuing Calibration Verification (CCV)

A. Review Items:

Form VII VOA-1, Form VII VOA-2, Form VII VOA-3, quantitation reports, and chromatograms.

B. Objective:

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. The CCV checks satisfactory performance of the instrument on a day-to-day basis, however, quantitations are based on the Mean Relative Response Factors ($\overline{RRF}$s) obtained from the initial calibration.

C. Criteria:

1. The 12-hour clock begins with either the injection of Bromofluorobenzene (BFB), or in cases where a closing CCV can be used in an opening CCV, the 12-hour clock begins with the injection of the opening CCV.
2. CCV standards containing both target compounds and associated Deuterated Monitoring Compounds (DMCs) are analyzed both at the beginning (opening CCV) and end (closing CCV) of each 12-hour analysis period following the analysis of the instrument performance check, and prior to the analysis of the method blank and samples. An instrument performance check is not required prior to the analysis of a closing CCV or prior to a closing CCV which can be used as an opening CCV for the next 12-hour period. If time remains in the 12-hour time period after initial calibration and samples are to be analyzed, the mid-point standard from the initial calibration can be used as the opening CCV.
3. For an opening CCV, the Relative Response Factors (RRFs) for the volatile target compounds listed in Table 15, and for all DMCs, must be greater than or equal to 0.010, except for 1,4-Dioxane and its associated DMC ($\geq$ 0.0050 advisory). The RRF for all other volatile target compounds must be greater than or equal to 0.050.
4. For a closing CCV, the RRFs for all volatile target compounds and DMCs must be greater than or equal to 0.010, except for 1,4-Dioxane and its associated DMC ($\geq$ 0.0050 advisory).
5. The Percent Difference (%D) between the initial calibration $\overline{RRF}$ and the opening CCV RRF must be within ±40.0% for the volatile target compounds listed in Table 15 and associated DMCs listed in Table 21, except for 1,4_Dioxane and its associated DMC (±50.0%). The Percent Difference for all other volatile target compounds and associated DMCs must be within ±25.0%.
6. For the closing CCV, the Percent Difference between the initial calibration $\overline{RRF}$ and the CCV RRF must be with ±50.0% for all volatile target compounds and associated DMCs.

D. Evaluation:

1. Verify that the CCV was run at the required frequency (an opening and closing CCV must be run within a 12-hour period) and the CCV was compared to the correct initial calibration. If the mid-point standard from the initial calibration is used as an opening CCV, verify that the result (RRF) of the mid-point standard was compared to the $\overline{RRF}$ from the correct initial calibration.
2. Evaluate the CCV RRF for all volatile target compounds and DMCs:

a. Check and recalculate the CCV RRF for at least one volatile target compound and DMC associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

b. For an opening CCV, verify that all volatile target compounds listed in Table 15 and all DMCs have CCV RRFs of greater than or equal to 0.010, except for 1,4-Dioxane and its associated DMC (≥ 0.0050 advisory), and all other volatile target compounds have RRFs greater than or equal to 0.050.

c. For a closing CCV, verify that all volatile target compounds and DMCs have CCV RRFs of greater than or equal to 0.010, except for 1,4-Dioxane and its associated DMC (≥ 0.0050 advisory).

3. Evaluate the Percent Difference between initial calibration $\overline{RRF}$ and CCV RRF (both opening and closing) for all volatile target compounds and DMCs:

a. Check and recalculate the Percent Difference for one or more volatile target compound(s) and DMCs associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory-reported value(s).

b. For an opening CCV, verify that the Percent Difference is within ±40.0% for the volatile target compounds listed in Table 15 and associated DMCs listed in Table 21, except for 1,4-Dioxane and its associated DMC (±50.0%), and within ±25.0% for all other volatile target compounds and associated DMCs.

c. For a closing CCV, verify that the Percent Difference is within ±50.0% for all volatile target compounds and DMCs.

4. If errors are detected in the calculations of either the CCV (both opening and closing) RRF or the Percent Difference, perform a more comprehensive recalculation.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. If a CCV (opening and closing) was not run at the appropriate frequency, qualify all data as unusable "R" (see Table 17).

2. Qualify all volatile target compounds, including the compounds exhibiting poor response listed in Table 15 using the following criteria:

a. For an opening CCV, if any volatile target compound has an RRF value less than the minimum criterion [0.010 for the compounds listed in Table 15, except 1,4-Dioxane (0.0050 advisory), and 0.050 for all other volatile compounds], use professional judgment for detects, based on mass spectral identification, to qualify the data as a "J" or unusable "R".

b. For a closing CCV, if any volatile target compound has an RRF value less than 0.010, except 1,4-Dioxane (< 0.0050 advisory), use professional judgment for detects based on mass spectral identification to qualify the data as a "J" or unusable "R".

c. For an opening CCV, if any volatile target compound has an RRF value less than the minimum criterion [0.010 for the compounds exhibiting poor response, except for 1,4-Dioxane (0.0050 advisory), and 0.050 for all other volatile compounds], qualify non-detected compounds as unusable "R".

d. For a closing CCV, if any volatile target compound has an RRF value less than 0.010, except 1,4-Dioxane (< 0.0050 advisory), qualify non-detected compounds as unusable "R".

e. For an opening CCV, if the Percent Difference value for any of the volatile target compounds listed in Table 15 is outside the ±40.0% criterion, except for 1,4-Dioxane (±50.0%), qualify detects with a "J" and non-detected compounds with an approximated "UJ".

f. For a closing CCV, if the Percent Difference value for any of the volatile target compounds listed in Table 15 is outside the ±50.0% criterion, qualify detects with a "J" and non-detected compounds with an approximated "UJ".

g. For an opening CCV, if the Percent Difference value for any other volatile target compound is outside the ±25.0% criterion, qualify detects with a "J" and non-detected compounds with an approximated "UJ".

h. For a closing CCV, if the Percent Difference value for any other volatile target compound is outside the ±50.0% criterion, qualify detects with a "J" and non-detected compounds with an approximated "UJ".

i. If the volatile target compounds meet the acceptance criteria for RRF and Percent Difference, no qualification of the data is necessary.

j. No qualification of the data is necessary on the DMC RRF and Percent Difference data alone. However, use professional judgment to evaluate the DMC RRF and Percent Difference data in conjunction with the DMC recoveries to determine the need for qualification of data.

3. If the laboratory has failed to provide adequate calibration information, the Region's designated representative may contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

4. Note in the Data Review Narrative, whenever possible, the potential effects on the data due to calibration criteria exceedance.

5. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if calibration criteria are grossly exceeded.

Table 17. Continuing Calibration Verification (CCV) Actions for Low/Medium Volatiles Analyses

Criteria for Opening CCV	Criteria for Closing CCV	Action	
		Detected Associated Compounds	Non-Detected Associated Compounds
RRF < 0.0050 (advisory for 1,4-Dioxane) RRF < 0.010 (target compounds listed in Table 15) RRF < 0.050 (all other target compounds)	RRF < 0.0050 (advisory for 1,4-Dioxane) RRF < 0.010 (all volatile target compounds)	J or R (based on mass spectral identification)	R
RRF ≥ 0.0050 (advisory for 1,4-Dioxane) RRF ≥ 0.010 (target compounds listed in Table 15) RRF ≥ 0.050 (all other target compounds)	RRF ≥ 0.0050 (advisory for 1,4-Dioxane) RRF ≥ 0.010 (all volatile target compounds)	No qualification	

Criteria for Opening CCV	Criteria for Closing CCV	Action	
		Detected Associated Compounds	Non-Detected Associated Compounds
%D > 50.0 or < -50.0 (1,4-Dioxane) %D > 40.0 or < -40.0 (target compounds listed in Table 15) %D > 25.0 or < -25.0 (all other target compounds)	%D > 50.0 or <-50.0 (all volatile target compounds)	J	UJ
%D ≤ 50.0 and ≥ -50.0 (1,4-Dioxane) %D ≤ 40.0 and ≥ -40.0 (target compounds listed in Table 15) %D ≤ 25.0 and ≥ -25.0 (all other target compounds)	%D ≤ 50.0 and ≥ -50.0 (all volatile target compounds)	No qualification	
Opening CCV not performed at required frequency (see Low/Medium Volatiles Organic Analysis, Section IV.C.1)	Closing CCV not performed at required frequency (see Low/Medium Volatiles Organic Analysis, Section IV.C.1)	R	

V. Blanks

A. Review Items:

Form I VOA-1, Form I VOA-2, Form I VOA-TIC, Form IV VOA, chromatograms, and quantitation reports.

B. Objective:

The purpose of laboratory, field, or trip blank analyses is to determine the existence and magnitude of contamination resulting from laboratory, field, or sample transport activities. The purpose of the method blank is to determine the levels of contamination associated with the processing and analysis of samples. The storage blank indicates whether contamination may have occurred during storage of samples. The results from the instrument blank analysis indicate whether there is contamination from the analysis of a previous sample. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks, instrument blanks, storage blanks, field blanks, or trip blanks). If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. Method Blanks

   A method blank analysis must be performed after the calibration standards and once for every 12-hour time period.

   The method blank must be analyzed on each Gas Chromatograph/Mass Spectrometer (GC/MS) system used to analyze samples. The method blank must be matrix specific (i.e., a non-aqueous method blank is required for non-aqueous samples, and an aqueous method blank is required for aqueous samples).

2. Storage Blanks

   A storage blank must be prepared upon receipt of the first samples from a Sample Delivery Group (SDG), and stored with the samples until analysis. The storage blank must be analyzed once per SDG.

3. Instrument Blank

   An instrument blank must be analyzed after any sample that has saturated ions from a given compound to check that the blank is free of interference and the system is not contaminated. The concentration of each target compound in the instrument blank must be less than its Contract Required Quantitation Limit (CRQL) listed in the method.

   NOTE: The concentration of each target compound found in the storage, method, field, or trip blanks must be less than its CRQL listed in the method, except for methylene chloride, acetone, and 2-butanone which must be less than 2 times (2x) their respective CRQLs.

D. Evaluation:

1. Review the results of all associated blanks on the forms and raw data (chromatograms and quantitation reports) to evaluate the presence of target and non-target compounds in the blanks.

2. Verify that a method blank analysis has been reported for each 12-hour time period on each GC/MS system used to analyze volatile samples. The reviewer can use the Method Blank Summary (Form IV VOA) to identify the samples associated with each method blank.
3. Verify that a method blank has been analyzed for each matrix present (i.e. if non-aqueous samples are present, verify that there is a non-aqueous method blank).
4. Verify that a storage blank has been analyzed and included with each SDG.
5. Verify that the instrument blank analysis has been performed following any sample analysis where a target analyte(s) is/are reported at high concentration(s).

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process. Data concerning the field or trip blanks are not evaluated as part of the CCS process. If field or trip blanks are present, the data reviewer should evaluate this data in a similar fashion as method blanks.**

E. Action:

Action regarding unsuitable blank results depends on the circumstances and origin of the blank. In instances where more than one of the same type of blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. Do not correct the results by subtracting any blank value (see Table 18).

1. If a volatile compound is found in a method blank, but not found in the sample, no qualification of the data is necessary.
2. If the method blank concentration is less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone, and acetone) and:
   a. the sample concentration is less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone, and acetone), report the CRQL value with a "U".
   b. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone), use professional judgment to qualify the data.
3. If the method blank concentration is greater than the CRQL (greater than 2x the CRQL for methylene chloride, 2-butanone, and acetone) and:
   a. the sample concentration is less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone, and acetone), report the CRQL value with a "U".
   b. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone), and less than the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank and qualify with a "U", or the reviewer may elect to qualify the data as unusable "R".
   c. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone), and greater than or equal to the blank concentration, use professional judgment to qualify the data.
4. If the method blank concentration is equal to the CRQL (equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone) and:
   a. the sample concentration is less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone, and acetone), report the CRQL value with a "U".

b. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone), use professional judgment to qualify the data.

5. If gross contamination exists (i.e., saturated peaks by GC/MS), qualify all affected compounds in the associated samples as unusable "R" due to interference. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if the contamination is suspected of having an effect on the sample results.

6. Give the same consideration as the target compounds to the Tentatively Identified Compounds (TICs), which are found in both the sample and associated blank(s) (see Low/Medium Volatiles Organic Analysis, Section XII, for TIC guidance).

7. If the contaminants found in the blank are interfering non-target compounds at concentrations greater than 10 µg/L, use professional judgment to qualify the data.

   NOTE: There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, they should qualify the data. Contamination introduced through dilution water is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but are absent in the undiluted sample result.

8. If an instrument blank was not analyzed following a sample analysis which contained an analyte(s) at high concentration(s), evaluate the sample analysis results immediately after the high concentration sample for carryover. Use professional judgment to determine if instrument cross-contamination has affected any positive compound identification(s). Note, for CLP PO action, if instrument cross-contamination is suggested and is suspected of having an effect on the sample results.

9. If contaminants are found in the storage, field, or trip blanks, the following is recommended:

   a. Review the associated method blank data to determine if the contaminant(s) was also present in the method blank.

      i. If the analyte was present at a comparable level in the method blank, the source of the contamination may be in the analytical system and the action recommended for the method blank would apply.

      ii. If the analyte was not present in the method blank, the source of contamination may be in the storage area, in the field, or during sample transport, consider all associated samples for possible cross-contamination.

   b. If the storage, field, or trip blanks contain a volatile Target Compound List (TCL) compound(s) at a concentration less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone, and acetone) and:

      i. the sample concentration is less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone, and acetone), report the CRQL value with a "U".

      ii. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone), use professional judgment to qualify the data.

   c. If the storage, field, or trip blanks contain a volatile TCL compound(s) at a concentration greater than the CRQL (greater than 2x the CRQL for methylene chloride, 2-butanone, and acetone) and:

      i. the sample concentration is less than the CRQL (less than 2x the CRQL for methylene chloride, 2-butanone, and acetone), report the CRQL value with a "U".

ii. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone), and less than the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank and qualify with a "U", or the reviewer may elect to qualify the data as unusable "R".

iii. the sample concentration is greater than or equal to the CRQL (greater than or equal to 2x the CRQL for methylene chloride, 2-butanone, and acetone) and greater than or equal to the blank concentration, use professional judgment to qualify the data.

d. If the storage, field, or trip blanks contain a volatile TCL compound(s) at a concentration equal to the CRQL (2x the CRQL for methylene chloride, 2-butanone, and acetone) and:

i. the sample concentration is less than the CRQL (2x the CRQL for methylene chloride, 2-butanone, and acetone), report the CRQL value with a "U".

ii. the sample concentration is greater than or equal to the CRQL (2x the CRQL for methylene chloride, 2-butanone, and acetone), use professional judgment to qualify the data.

e. If gross contamination (i.e., saturated by GC/MS) exists in the storage, field or trip blank, positive sample results may require rejection and be qualified as unusable "R". Non-detected volatile target compounds do not require qualification unless the contamination is so high that it interferes with the analyses of non-detected compounds.

Table 18. Blank Actions for Low/Medium Volatiles Analyses

Blank Type	Blank Result	Sample Result	Action for Samples
Method, Storage, Field, Trip, Instrument **	Detects	Not detected	No qualification
	< CRQL*	< CRQL*	Report CRQL value with a U
		≥ CRQL*	Use professional judgment
	> CRQL*	< CRQL*	Report CRQL value with a U
		≥ CRQL* and < blank concentration	Report the blank concentration for the sample with a U or qualify the data as unusable R
		≥ CRQL* and ≥ blank concentration	Use professional judgment
	= CRQL*	< CRQL*	Report CRQL value with a U
		≥ CRQL*	Use professional judgment
	Gross contamination	Detects	Qualify results as unusable R

* 2x the CRQL for methylene chloride, 2-butanone, and acetone.

** Qualifications based on instrument blank results affect only the sample analyzed immediately after the sample that has target compounds that exceed the calibration range or non-target compounds that exceed 100 µg/L.

VI. Deuterated Monitoring Compounds (DMCs)

A. Review Items:

Form II VOA-1, Form II VOA-2, Form II VOA-3, Form II VOA-4, quantitation reports, and chromatograms.

B. Objective:

Laboratory performance on individual samples is established by means of spiking activities. All samples are spiked with DMCs just prior to sample purging. The evaluation of the results of these DMCs is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and requires analytical experience and professional judgment. Accordingly, this section consists primarily of guidelines, in some cases with several optional approaches suggested.

C. Criteria:

1. The DMCs listed in Table 19 are added to all samples and blanks to measure their recovery in environmental samples.

Table 19. Volatile Deuterated Monitoring Compounds (DMCs) and Recovery Limits

DMC	Recovery Limits (%) for Water Samples	Recovery Limits (%) for Soil Samples
Vinyl chloride-d_3	65 - 131	68 - 122
Chloroethane-d_5	71 - 131	61 - 130
1,1-Dichloroethene-d_2	55 - 104	45 - 132
2-Butanone-d_5	49 - 155	20 - 182
Chloroform-d	78 - 121	72 - 123
1,2-Dichloroethane-d_4	78 - 129	79 - 122
Benzene-d_6	77 - 124	80 - 121
1,2-Dichloropropane-d_6	79 - 124	74 - 124
Toluene-d_8	77 - 121	78 - 121
trans-1,3-Dichloropropene-d_4	73 - 121	72 - 130
2-Hexanone-d_5	28 - 135	17 - 184
1,4-Dioxane-d_8	50 - 150	50 -150
1,1,2,2-Tetrachloroethane-d_2	73 - 125	56 - 161
1,2-Dichlorobenzene-d_4	80 - 131	70 - 131

2. Recoveries for DMCs in volatile samples and blanks must be within the limits specified in Table 19.

   NOTE: The recovery limits for any of the compounds listed in Table 19 may be expanded at any time during the period of performance if USEPA determines that the limits are too restrictive.

D. Evaluation:

1. Check raw data (e.g., chromatograms and quantitation reports) to verify the recoveries on the Deuterated Monitoring Compound Recovery Forms (Form II VOA-1, Form II VOA-2, Form II VOA-3, and Form II VOA-4).

   Check for any calculation or transcription errors; verify that the DMC recoveries were calculated correctly using the equation in the method.

2. Whenever there are two or more analyses for a particular sample, the reviewer must determine which are the most acceptable data to report. Considerations include, but are not limited to:

   a. DMC recovery (marginal versus gross deviation).

   b. Technical holding times.

   c. Comparison of the values of the target compounds reported in each sample analysis.

   d. Other Quality Control (QC) information, such as performance of internal standards.

   NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

Table 21 lists the volatile DMCs and their associated target compounds. If any DMC recovery in the volatiles fraction is out of specification, qualify data considering the existence of interference in the raw data (see Table 20). Considerations include, but are not limited to:

1. For any recovery greater than the upper acceptance limit:

   a. Qualify detected associated volatile target compounds as a "J".

   b. Do not qualify non-detected associated volatile target compounds.

2. For any recovery greater than or equal to 20%, and less than the lower acceptance limit:

   a. Qualify detected associated volatile target compounds as a "J".

   b. Qualify non-detected associated volatile target compounds as approximated "UJ".

3. For any recovery less than 20%:

   a. Qualify detected associated volatile target compounds as a "J".

   b. Qualify non-detected associated volatile target compounds as unusable "R".

4. For any recovery within acceptance limits, no qualification of the data is necessary.

5. In the special case of a blank analysis having DMCs out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable DMC recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. However, even if this judgment allows some use of the affected data, note analytical problems for Contract Laboratory Program Project Officer (CLP PO) action.

Table 20. Deuterated Monitoring Compound (DMC) Recovery Actions For Low/Medium Volatiles Analyses

Criteria	Action	
	Detected Associated Compounds	Non-detected Associated Compounds
%R > Upper Acceptance Limit	J	No qualification
20% ≤ %R < Lower Acceptance Limit	J	UJ
%R < 20%	J	R
Lower Acceptance Limit ≤ %R ≤ Upper Acceptance Limit	No qualification	

Table 21. Volatile Deuterated Monitoring Compounds (DMCs) and the Associated Target Compounds

Chloroethane-d_5 (DMC)	1,2-Dichloropropane-d_6 (DMC)	1,2-Dichlorobenzene-d_4 (DMC)
Dichlorodifluoromethane	Cyclohexane	Chlorobenzene
Chloromethane	Methylcyclohexane	1,3-Dichlorobenzene
Bromomethane	1,2-Dichloropropane	1,4-Dichlorobenzene
Chloroethane	Bromodichloromethane	1,2-Dichlorobenzene
Carbon disulfide		1,2,4-Trichlorobenzene
		1,2,3-Trichlorobenzene
1,4-Dioxane-d_8 (DMC)	trans-1,3-Dichloropropene-d_4 (DMC)	Chloroform-d (DMC)
1,4-Dioxane	cis-1,3-Dichloropropene	1,1-Dichloroethane
	trans-1,3-Dichloropropene	Bromochloromethane
	1,1,2-Trichloroethane	Chloroform
		Dibromochloromethane
		Bromoform
2-Butanone-d_5 (DMC)	1,1-Dichloroethene-d_2 (DMC)	2-Hexanone-d_5 (DMC)
Acetone	trans-1,2-Dichloroethene	4-Methyl-2-pentanone
2-Butanone	1,1-Dichloroethene	2-Hexanone
	cis-1,2-Dichloroethene	
Vinyl chloride-d_3 (DMC)	Benzene-d_6 (DMC)	1,1,2,2-Tetrachloroethane-d_2 (DMC)
Vinyl chloride	Benzene	1,1,2,2,-Tetrachlororethane
		1,2-Dibromo-3-chloropropane
1,2-Dichloroethane-d_4 (DMC)		Toluene-d_8 (DMC)
Trichlorofluoromethane		Trichloroethene
1,1,2-Trichloro-1,2,2-trifluoroethane		Toluene
Methyl acetate		Tetrachloroethene
Methylene chloride		Ethylbenzene
Methyl-tert-butyl ether		o-Xylene
1,1,1-Trichloroethane		m,p-Xylene
Carbon tetrachloride		Styrene
1,2-Dibromoethane		Isopropylbenzene
1,2-Dichloroethane		

VII. Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

A. Review Items:

Form III VOA-1, Form III VOA-2, chromatograms, and quantitation reports.

NOTE: Data for MS and MSDs will not be present unless requested by the Region.

B. Objective:

Data for MS and MSDs are generated to determine long-term precision and accuracy of the analytical method on the sample matrix and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone cannot be used to evaluate the precision and accuracy of individual samples. However, when exercising professional judgment, this data should be used in conjunction with other available Quality Control (QC) information.

C. Criteria:

1. **If requested**, MS and MSD samples are analyzed at a frequency of one MS and MSD per 20 or fewer samples per sample matrix and concentration level.
2. Spike recoveries should be within the advisory limits provided on Form III VOA-1 and Form III VOA-2.
3. Relative Percent Difference (RPD) between MS and MSD recoveries must be within the advisory limits provided on Form III VOA-1 and Form III VOA-2.

D. Evaluation:

1. Verify that requested MS and MSD samples were analyzed at the required frequency and results are provided for each sample.
2. Inspect results for the MS and MSD Recovery on Form III VOA-1 and Form III VOA-2 and verify that the results for recovery and RPD are within the advisory limits.
3. Verify transcriptions from raw data and check calculations.
4. Verify that the MS recoveries and RPD were calculated correctly.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. No qualification of the data is necessary on MS and MSD data alone. However, using informed professional judgment, the data reviewer may use the MS and MSD results in conjunction with other QC criteria to determine the need for some qualification of the data. Table 23 lists the volatile target compounds that are spiked into samples to test for matrix effects. If any MS and MSD Percent Recovery or RPD in the volatiles fraction is out of specification, qualify data to include the consideration of the existence of interference in the raw data (see Table 22). Considerations include, but are not limited to:
   a. For any recovery or RPD greater than the upper acceptance limit:
      i. Qualify detected spiked volatile target compounds as a "J".

ii. Do not qualify non-detected spiked volatile target compounds.

b. For any recovery greater than or equal to 20%, and less than the lower acceptance limit:

i. Qualify detected spiked volatile target compounds as a "J".

ii. Qualify non-detected spiked volatile target compounds as approximated "UJ".

c. For any recovery less than 20%:

i. Qualify detected spiked volatile target compounds as a "J".

ii. Use professional judgment to qualify non-detected spiked volatile target compounds.

d. For any recovery or RPD within acceptance limits, no qualification of the data is necessary.

2. The data reviewer should first try to determine to what extent the results of the MS and MSD affect the associated data. This determination should be made with regard to the MS and MSD sample itself, as well as specific analytes for all samples associated with the MS and MSD.

3. In those instances where it can be determined that the results of the MS and MSD affect only the sample spiked, limit qualification to this sample only. However, it may be determined through the MS and MSD results that a laboratory is having a systematic problem in the analysis of one or more analytes that affects all associated samples, and the reviewer must use professional judgment to qualify the data from all associated samples.

4. The reviewer must use professional judgment to determine the need for qualification of detects of non-spiked compounds.

NOTE: Notify the Contract Laboratory Program Project Officer (CLP PO) if a field or trip blank was used for the MS and MSD.

Table 22. Matrix Spike/Matrix Spike Duplicate (MS/MSD) Actions for Low/Medium Volatiles Analysis

Criteria	Action	
	Detected Spiked Compounds	Non-detected Spiked Compounds
%R or RPD > Upper Acceptance Limit	J	No qualification
20% ≤ %R < Lower Acceptance Limit	J	UJ
%R < 20%	J	Use professional judgment
Lower Acceptance Limit ≤ %R; RPD ≤ Upper Acceptance Limit	No qualification	

Table 23. Matrix Spike (MS) Recovery and Relative Percent Difference (RPD) Limits

Compound	% Recovery for Water Samples	RPD for Water Samples	% Recovery for Soil/Sediment Samples	RPD for Soil/Sediment Samples
1,1-Dichloroethene	61 - 145	0 - 14	59 - 172	0 - 22
Trichloroethene	71 - 120	0 - 14	62 - 137	0 - 24
Benzene	76 - 127	0 - 11	66 - 142	0 - 21
Toluene	76 - 125	0 - 13	59 - 139	0 - 21
Chlorobenzene	75 - 130	0 - 13	60 - 133	0 - 21

VIII. Regional Quality Assurance (QA) and Quality Control (QC)

A. Review Items:

Form I VOA-1, Form I VOA-2, chromatograms, Traffic Report/Chain of Custody Record (TR/COC), quantitation reports, and other raw data from QA/QC samples.

B. Objective:

Regional QA/QC samples refer to any QA and/or QC samples initiated by the Region, including field duplicates, Performance Evaluation (PE) samples, blind spikes, and blind blanks. The use of these QA/QC samples is highly recommended (e.g., the use of field duplicates can provide information on sampling precision and homogeneity).

C. Criteria:

Criteria are determined by each Region.

1. PE sample frequency may vary.
2. The analytes present in the PE sample must be correctly identified and quantified.

D. Evaluation:

1. Evaluation procedures must follow the Region's Standard Operating Procedure (SOP) for data review. Each Region will handle the evaluation of PE samples on an individual basis. Compare results for PE samples to the acceptance criteria for the specific PE samples, if available.
2. Calculate Relative Percent Difference (RPD) between field duplicates. Provide this information in the Data Review Narrative.

E. Action:

Any action must be in accordance with Regional specifications and the criteria for acceptable PE sample results. Note, for Contract Laboratory Program Project Officer (CLP PO) action, unacceptable results for PE samples.

IX. Internal Standards

A. Review Items:

Form VIII VOA, quantitation reports, and chromatograms.

B. Objective:

Internal standard performance criteria ensures that Gas Chromatograph/Mass Spectrometer (GC/MS) sensitivity and response are stable during each analysis.

C. Criteria:

1. The internal standard area counts for all samples [including Matrix Spike/Matrix Spike Duplicate (MS/MSD) and Performance Evaluation (PE) samples] and all blanks must be within the inclusive range of 50.0% and 200% of its response from the associated 12-hour calibration standard [opening Continuing Calibration Verification (CCV) or mid-point standard from the initial calibration].
2. The Retention Time (RT) of the internal standard in the sample or blank must not vary more than ±30 seconds from the RT of the internal standard in the associated 12-hour calibration standard (opening CCV or mid-point standard from initial calibration).

D. Evaluation:

1. Check raw data (e.g., chromatograms and quantitation lists) to verify the internal standard RTs and areas reported on the Internal Standard Area Summary (Form VIII VOA).
2. Verify that all RTs and internal standard areas are within criteria for all samples and blanks.
3. If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations include, but are not limited to:
   a. Magnitude and direction of the internal standard area shift.
   b. Magnitude and direction of the internal standard RT shift.
   c. Technical holding times.
   d. Comparison of the values of the target compounds reported in each fraction.
   e. Other Quality Control (QC) information.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

1. If an internal standard area count for a sample or blank is greater than 200% of the area for the associated standard (opening CCV or mid-point standard from the initial calibration) (see Table 24):
   a. Qualify detects for compounds quantitated using that internal standard with a "J".
   b. Do not qualify non-detected associated compounds.
2. If an internal standard area count for a sample or blank is less than 50.0% of the area for the associated standard (opening CCV or mid-point standard from initial calibration):
   a. Qualify detects for compounds quantitated using that internal standard with a "J".
   b. Qualify non-detected associated compounds as unusable "R".
3. If an internal standard area count for a sample or blank is greater than or equal to 50.0%, and less than or equal to 200% of the area for the associated standard opening CCV or mid-point standard from initial calibration, no qualification of the data is necessary.
4. If an internal standard RT varies by more than 30.0 seconds:

   Examine the chromatographic profile for that sample to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection of the data for that sample fraction. Detects should not need to be qualified as unusable "R" if the mass spectral criteria are met.
5. If an internal standard RT varies by less than or equal to 30.0 seconds, no qualification of the data is necessary.
6. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if the internal standard performance criteria are grossly exceeded. Note in the Data Review Narrative potential effects on the data resulting from unacceptable internal standard performance.

Table 24. Internal Standard Actions for Low/Medium Volatiles Analyses

Criteria	Action	
	Detected Associated Compounds*	Non-Detected Associated Compounds*
Area counts < 50.0% of 12-hour standard (opening CCV or mid-point standard from the initial calibration)	J	R
Area counts ≥ 50.0% and ≤ 200% of 12-hour standard (opening CCV or mid-point standard from the initial calibration)	No qualification	
Area counts > 200% of 12-hour standard (opening CCV or mid-point standard from the initial calibration)	J	No qualification
RT Difference ≤ 30.0 seconds between samples and 12-hour standard (opening CCV or mid-point standard from the initial calibration)	No qualification	
RT Difference > 30.0 seconds between samples and 12-hour standard (opening CCV or mid-point standard from the initial calibration)	R **	R

* For volatile compounds associated with each internal standard, see Table 3 - Volatile Target Compounds and Deuterated Monitoring Compounds with Corresponding Internal Standards for Quantitation in SOM01.2, Exhibit D, available at:

http://www.epa.gov/superfund/programs/clp/som1.htm

** See Low/Medium Volatiles Organic Analysis, Section IX.E.4 for exceptions.

X. Target Compound Identification

A. Review Items:

Form I VOA-1, Form I VOA-2, quantitation reports, mass spectra, and chromatograms.

B. Objective:

The objective of the criteria for Gas Chromatograph/Mass Spectrometer (GC/MS) qualitative analysis is to minimize the number of erroneous compound identifications. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).

The identification criteria can be applied more easily in detecting false positives than false negatives. More information is available for false positives due to the requirement for submittal of data supporting positive identifications. Negatives, or non-detected compounds, on the other hand, represent an absence of data and are, therefore, more difficult to assess. One example of the detection of false negatives is not reporting a target compound that is reported as a Tentatively Identified Compound (TIC).

C. Criteria:

1. The Relative Retention Times (RRTs) must be within ±0.06 RRT units of the standard RRT [opening Continuing Calibration Verification (CCV) or mid-point standard from the initial calibration].
2. Mass spectra of the sample compound and a current laboratory-generated standard [i.e., the mass spectrum from the associated calibration standard (opening CCV or mid-point standard from initial calibration)] must match according to the following criteria:
    a. All ions present in the standard mass spectrum at a relative intensity greater than 10% must be present in the sample spectrum.
    b. The relative intensities of these ions must agree within ±20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30-70%).
    c. Ions present at greater than 10% in the sample mass spectrum, but not present in the standard spectrum, must be evaluated by a reviewer experienced in mass spectral interpretation.

D. Evaluation:

1. Check that the RRT of reported compounds is within ±0.06 RRT units of the standard RRT (opening CCV or mid-point standard from the initial calibration).
2. Check the sample compound spectra against the laboratory standard spectra to verify that it meets the specified criteria.
3. Be aware of situations when sample carryover is a possibility and use professional judgment to determine if instrument cross-contamination has affected any positive compound identification. The method specifies that an instrument blank must be run after samples which contain target compounds at levels exceeding the initial calibration range (200 µg/L for non-ketones, 400 µg/L for ketones, and 4000 µg/L for 1,4-Dioxane).
4. Check the chromatogram to verify that peaks are identified. Major peaks are either identified as target compounds, TICs, Deuterated Monitoring Compounds (DMCs), or internal standards.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

1. The application of qualitative criteria for GC/MS analysis of target compounds requires professional judgment. It is up to the reviewer's discretion to obtain additional information from the laboratory. If it is determined that incorrect identifications were made, qualify all such data as not detected "U" or unusable "R".
2. Use professional judgment to qualify the data if it is determined that cross-contamination has occurred.
3. Note in the Data Review Narrative any changes made to the reported compounds or concerns regarding target compound identifications. Note, for Contract Laboratory Program Project Officer (CLP PO) action, the necessity for numerous or significant changes.

XI. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

A. Review Items:

Forms I VOA-1, Form I VOA-2, sample preparation sheets, Sample Delivery Group (SDG) Narrative, quantitation reports, and chromatograms.

B. Objective:

The objective is to ensure that the reported quantitation results and CRQLs are accurate.

C. Criteria:

1. Compound quantitation, as well as the adjustment of the CRQLs, must be calculated according to the correct equation.
2. Compound Relative Response Factors (RRFs) must be calculated based on the internal standard associated with that compound, as listed in the method. Quantitation must be based on the quantitation ion (m/z) specified in the method for both the internal standards and target analytes. The compound quantitation must be based on the average RRF from the associated initial calibration.

D. Evaluation:

1. Examine raw data to verify the correct calculation of all sample results reported by the laboratory. Compare quantitation lists and chromatograms to the reported detects and non-detects sample results. Check the reported values.
2. Verify that the correct internal standard, quantitation ion, and Mean Relative Response Factor ($\overline{RRF}$) were used to quantitate the compound. Verify that the same internal standard, quantitation ion, and $\overline{RRF}$ were used consistently throughout, in both the calibration as well as the quantitation process.
3. Verify that the CRQLs have been adjusted to reflect all sample dilutions and dry weight factors (for non-aqueous samples).

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

1. If any discrepancies are found, the Region's designated representative may contact the laboratory to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, the reviewer must use professional judgment to decide which value is the most accurate value. Under these circumstances, the reviewer may determine that qualification of data is warranted. Note in the Data Review Narrative a description of the reasons for data qualification and the qualification that is applied to the data.
2. For non-aqueous samples, if the Percent Moisture is less than 70.0%, no qualification of the data is necessary. If the Percent Moisture is greater than or equal to 70.0% and less than 90.0%, qualify detects as "J" and non-detects as approximated "UJ". If the Percent Moisture is greater than or equal to 90.0%, qualify detects as "J" and non-detects as unusable "R" (see Table 25).

Table 25. Percent Moisture Actions for Low/Medium Volatiles Analysis For Non-Aqueous Samples

Criteria	Action	
	Detected Associated Compounds	Non-detected Associated Compounds
% Moisture < 70.0	No qualification	
70.0 ≤ % Moisture < 90.0	J	UJ
% Moisture ≥ 90.0	J	R

NOTE: For Contract Laboratory Program Project Officer (CLP PO) action, numerous or significant failures to accurately quantify the target compounds or to properly evaluate and adjust CRQLs.

XII. Tentatively Identified Compounds (TICs)

A. Review Items:

Form I VOA-TIC, chromatograms, library search printouts, and spectra for the TIC candidates.

B. Objective:

Chromatographic peaks in volatile fraction analyses that are not target analytes, Deuterated Monitoring Compounds (DMCs), or internal standards are potential TICs. TICs must be qualitatively identified via a forward search of the NIST/USEPA/NIH Mass Spectral Library (May 2002 release or later)3, and/or Wiley Mass Spectral Library (1998 release or later)4, or the equivalent. The identifications must be assessed by the data reviewer.

C. Criteria:

For each sample, the laboratory must conduct a mass spectral search of the NIST/USEPA/NIH (May 2002 release or later), and/or Wiley (1998 release or later), or equivalent mass spectral library, and report the possible identity for 30 of the largest volatile fraction peaks which are not DMCs, internal standards, or target compounds, but which have an area or height greater than 10% of the area or height of the nearest internal standard. Estimated concentrations for TICs are calculated similarly to the Target Compound List (TCL) compounds, using total ion areas for the TIC and the internal standard, and assuming a Relative Response Factor (RRF) of 1.0. TIC results are reported for each sample on the Organic Analyses Data Sheet (Form I VOA-TIC).

D. Evaluation:

1. Guidelines for tentative identification are as follows:
   a. Major ions (greater than 10% Relative Intensity) in the reference spectrum should be present in the sample spectrum.
   b. The relative intensities of the major ions should agree within ±20% between the sample and the reference spectra.
   c. Molecular ions present in the reference spectrum should be present in the sample spectrum.
   d. Review ions present in the sample spectrum, but not in the reference spectrum, for possible background contamination, interference, or presence of coeluting compounds.
   e. Review ions present in the reference spectrum, but not in the sample spectrum, for possible subtraction from the sample spectrum because of background contamination or coeluting compounds. Data system library reduction programs can sometimes create these discrepancies.
   f. Non-target compounds receiving a library search match of 85% or higher are considered a "likely match". Report the compound unless the mass spectral interpretation specialist feels there is evidence not to report the compound as identified by the library search program. Note in the Sample Delivery Group (SDG) Narrative the justification for not reporting a compound as listed by the search program.

[3]NIST/USEPA/NIH Mass Spectral Library (May 2002 release or later), National Institute of Standards and Technology, Gaithersburg, Maryland.

[4]Wiley Mass Spectral Library (1998 release or later), John Wiley & Sons, Inc., Hoboken, New Jersey.

g. If the library search produces more than one compound greater than or equal to 85%, report the compound with the highest percent match (report first compound if percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels that the highest match compound should not be reported or another compound with a lower match should be reported. The laboratory should include the justification for not reporting the compound with the highest spectral match within the SDG Narrative. Do not report DMCs, internal standards, and volatile target compounds as TICs, unless the only compounds having a percent match of greater than 85% are DMCs, internal standards, or volatile target compounds.

h. If the library search produces a series of obvious isomer compounds with library search matches greater than or equal to 85%, report the compound with the highest library search percent match (or the first compound if the library search matches are the same). Note in the SDG Narrative that the exact isomer configuration, as reported, may not be accurate.

i. If the library search produces no matches greater than or equal to 85%, and in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, report the compound as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (e.g., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

j. Alkanes are not to be reported as TICs on Form I VOA-TIC. An alkane is defined as any hydrocarbon with the generic formula C_nH_{2n+2} that contains only C-H and C-C single bonds. When the preceding alkanes are tentatively identified, estimate the concentration(s) and report them in the SDG Narrative as alkanes by class (i.e., straight-chain, branched, cyclic, as a series, or as applicable). Report total alkanes concentration on Form I VOA-TIC.

2. Check the raw data to verify that the laboratory has generated a library search for all required peaks in the chromatograms for samples and blanks.

3. Examine blank chromatograms to verify that TIC peaks present in samples are not found in blanks. When a low-level, non-target compound that is a common artifact or laboratory contaminant is detected in a sample, a thorough check of blank chromatograms may require looking for peaks which are less than 10% of the internal standard height, but present in the blank chromatogram at a similar Relative Retention Time (RRT).

4. Examine all mass spectra for every sample and blank.

5. Consider all reasonable choices since TIC library searches often yield several candidate compounds having a close matching score.

6. Be aware of common laboratory artifacts/contaminants and their sources (e.g., Aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.

   a. Examples:

      i. Common laboratory contaminants include CO2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons, and phthalates at levels less than 100 µg/L.

      ii. Solvent preservatives include cyclohexene (a methylene chloride preservative). Related by-products include cyclohexanone, cyclohexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.

      iii. Aldol condensation reaction products of acetone include 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

7. A target compound may be identified in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list (false negative). If the total area quantitation method was used, request that the laboratory recalculate the result using the proper quantitation ion and Relative Response Factor (RRF).

   A non-target compound may be incorrectly identified by the instrument's target analyte data processor as a target compound (false positive). When this happens, the non-target library search procedure will not detect the false positive as a TIC. In this case, request that the laboratory properly identify the compound and recalculate the result using the total area quantitation method and a RRF of 1.0.

   Evaluate other sample chromatograms and check for both false negatives and false positives to determine if the occurrence is isolated or systematic.

8. Target compounds may be identified in more than one fraction. Verify that quantitation is made from the proper fraction.
9. Do not perform library searches on internal standards or DMCs.
10. Estimate TIC concentration assuming an RRF of 1.0.

E. Action:

1. Qualify all TIC results for which there is presumptive evidence of a match (e.g., greater than or equal to 85% match) as "NJ", tentatively identified, with approximated concentrations.
2. General actions related to the review of TIC results are as follows:
   a. If it is determined that a tentative identification of a non-target compound is unacceptable, change the tentative identification to "unknown" or another appropriate identification, and qualify the result with a "J".
   b. If all contractually-required peaks were not library searched and quantitated, the Region's designated representative may request these data from the laboratory.
3. In deciding whether a library search result for a TIC represents a reasonable identification, use professional judgment. If there is more than one possible match, report the result as "either compound X or compound Y". If there is a lack of isomer specificity, change the TIC result to a non-specific isomer result (e.g., 1,3,5-trimethyl benzene to trimethyl benzene isomer) or to a compound class (e.g., 2-methyl, 3-ethyl benzene to a substituted aromatic compound).
4. The reviewer may elect to report all similar compounds as a total (e.g., all alkanes may be summarized and reported as total hydrocarbons).
5. Other Case factors may influence TIC judgments. If a sample TIC match is poor, but other samples have a TIC with a valid library match, similar RRT, and the same ions, infer identification information from the other sample TIC results.
6. Note in the Data Review Narrative any changes made to the reported data or any concerns regarding TIC identifications.
7. Note, for Contract Laboratory Program Project Officer (CLP PO) action, failure to properly evaluate and report TICs.

XIII. System Performance

A. Review Items:

Form VIII VOA and chromatograms.

B. Objective:

During the period following Instrument Performance Quality Control (QC) checks (e.g., blanks, tuning, calibration), changes may occur in the system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC runs, a thorough review of the ongoing data acquisition can yield indicators of instrument performance.

C. Criteria:

There are no specific criteria for system performance. Professional judgment should be applied to assess the system performance.

D. Evaluation:

1. Abrupt discrete shifts in the Reconstructed Ion Chromatogram (RIC) baseline may indicate a change in the instrument's sensitivity or the zero setting. A baseline "shift" could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds, at or near the detection limit, to miss detection. A baseline "rise" could indicate problems such as a change in the instrument zero, a leak, or degradation of the column.
2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:
    a. High RIC background levels or shifts in Absolute Retention Times (RTs) of internal standards.
    b. Excessive baseline rise at elevated temperature.
    c. Extraneous peaks.
    d. Loss of resolution.
    e. Peak tailing or peak splitting that may result in inaccurate quantitation.
3. A drift in instrument sensitivity may occur during the 12-hour time period and may be an indication of internal standard spiking problems. This could be discerned by examination of the internal standard area on Form VIII VOA for trends such as a continuous or near-continuous increase or decrease in the internal standard area over time.

E. Action:

Use professional judgment to qualify the data if it is determined that system performance has degraded during sample analyses. Note, for Contract Laboratory Program Project Officer (CLP PO) action, any degradation of system performance which significantly affected the data.

XIV. Overall Assessment of Data

A. Review Items:

Entire data package, data review results, and (if available) the Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP).

B. Objective:

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria:

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation:

1. Evaluate any technical problems which have not been previously addressed.
2. If appropriate information is available, the reviewer may assess the usability of the data to help the data user avoid inappropriate use of the data. Review all available information, including the QAPP (specifically the acceptance and performance criteria), SAP, and communication with the data user that concerns the intended use and desired quality of these data.

E. Action:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the Quality Control (QC) criteria previously discussed.
2. Write a brief narrative to give the user an indication of the analytical limitations of the data. Note, for Contract Laboratory Program Project Officer (CLP PO) action, any inconsistency of the data with the Sample Delivery Group (SDG) Narrative. If sufficient information on the intended use and required quality of the data are available, the reviewer should include their assessment of the usability of the data within the given context. This may be used as part of a formal Data Quality Assessment (DQA).

SEMIVOLATILE DATA REVIEW

The semivolatile data requirements to be checked are:

I. Preservation

II. Gas Chromatograph/Mass Spectrometer (GC/MS) Instrument Performance Check

III. Initial Calibration

IV. Continuing Calibration Verification (CCV)

V. Blanks

VI. Deuterated Monitoring Compounds (DMCs)

VII. Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

VIII. Regional Quality Assurance (QA) and Quality Control (QC)

IX. Gel Permeation Chromatography (GPC) Performance Check

X. Internal Standards

XI. Target Compound Identification

XII. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

XIII. Tentatively Identified Compounds (TICs)

XIV. System Performance

XV. Overall Assessment of Data

NOTE: *Language specific to Selective Ion Monitoring (SIM) analyses is shown in italic.*

I. Preservation

A. Review Items:

Form I SV-1, Form I SV-2, *Form SV-SIM*, Form I SV-TIC, Traffic Report/Chain of Custody Record (TR/COC), raw data, sample extraction sheets, and the Sample Delivery Group (SDG) Narrative checking for:

1. pH
2. Sample temperature
3. Holding time
4. Other sample conditions

B. Objective:

The objective is to ascertain the validity of the analytical results based on sample condition (e.g., preservation and temperature) and the holding time of the sample from time of collection to time of sample extraction and analysis.

C. Criteria:

The technical holding time criteria for aqueous samples are as follows:

For semivolatile compounds in properly cooled (4°C ± 2°C) aqueous samples, the maximum holding time for extraction is seven (7) days from sample collection, and the maximum holding time for analysis is 40 days from sample extraction.

The technical holding time criteria for non-aqueous samples are as follows:

For semivolatile compounds in properly cooled (4°C ± 2°C) non-aqueous samples, the maximum holding time for extraction is 14 days from sample collection, and the maximum holding time for analysis is 40 days from sample extraction.

D. Evaluation:

Technical holding times for sample extraction are established by comparing the sample collection dates on the TR/COC Record with the dates of extraction on Form I SV-1, Form I SV-2, *Form I SV-SIM*, Form I SV-TIC, and the sample extraction sheets. To determine if the samples were analyzed within the holding time after extraction, compare the dates of extraction on the sample extraction sheets with the dates of analysis on Form I SV-1, Form I SV-2, *Form I SV-SIM* and Form I SV-TIC. Verify that the analysis dates on Form I(s) and the raw data/SDG File are identical. Review the SDG Narrative and the TR/COC Record to determine if the samples were received intact and iced. If there is no indication in the SDG Narrative, the TR/COC Record, or the sample records that there was a problem with the samples, the integrity of the samples can be assumed to be acceptable. If it is indicated that there were problems with the samples, the integrity of the sample may have been compromised and professional judgment should be used to evaluate the effect of the problem on the sample results.

E. Action:

1. Qualify aqueous sample results using preservation and technical holding time information as follows (see Table 26):

   a. If there is no evidence that the samples were properly preserved (e.g., if the sample temperature has exceeded the allowable limits or if the integrity of the sample has been compromised), and the samples were extracted or analyzed within the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], use professional judgment to qualify the data.

   b. If there is no evidence that the samples were properly preserved (e.g., if the sample temperature has exceeded the allowable limits or if the integrity of the sample has been compromised), and the samples were extracted or analyzed outside the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], use professional judgment to qualify the data.

   c. If the samples were properly preserved, and were extracted and analyzed within the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], no qualification of the data is necessary.

   d. If the samples were properly preserved, and were extracted or analyzed outside the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], qualify detects with a "J" and non-detects as estimated with an approximated "UJ". Note in the Data Review Narrative that holding times were exceeded and the effect of exceeding the holding time on the resulting data.

2. Qualify non-aqueous sample results using preservation and technical holding time information as follows (see Table 26):

   a. If there is no evidence that the samples were properly preserved (e.g., if the sample temperature has exceeded the allowable limits or if the integrity of the sample has been compromised), and the samples were extracted or analyzed within the technical holding time [14 days from sample collection for extraction; 40 days from sample collection for analysis], use professional judgment to qualify the data.

   b. If there is no evidence that the samples were properly preserved (e.g., if the sample temperature has exceeded the allowable limits or if the integrity of the sample has been compromised), and the samples were extracted or analyzed outside the technical holding time [14 days from sample collection for extraction; 40 days from sample collection for analysis], use professional judgment to qualify the data.

   c. If the samples were properly preserved, and were extracted and analyzed within the technical holding time [14 days from sample collection for extraction; 40 days from sample collection for analysis], no qualification of the data is necessary.

   d. If the samples were properly preserved, and were extracted or analyzed outside the technical holding time [14 days from sample collection for extraction; 40 days from sample collection for analysis], qualify detects with a "J" and non-detects as estimated with an approximated "UJ". Note in the Data Review Narrative that holding times were exceeded and the effect of exceeding the holding time on the resulting data.

3. Use professional judgment to qualify samples whose temperature upon receipt at the laboratory is either below 2 degrees centigrade or above 6 degrees centigrade.

4. If technical holding times are grossly exceeded, qualify all detects as estimated with a "J" and use professional judgment to qualify sample non-detects as "UJ" or "R".

5. Note in the Data Review Narrative, whenever possible, the effect of exceeding the holding time on the resulting data.
6. Note, for Contract Laboratory Program Project Officer (CLP PO) action, when technical holding times are grossly exceeded.

Table 26. Holding Time Actions for Semivolatile Analyses

Matrix	Preserved	Criteria	Action	
			Detected Associated Compounds	Non-Detected Associated Compounds
Aqueous	No	≤ 7 days (for extraction) and ≤ 40 days (for analysis)	Use professional judgment	
	No	> 7 days (for extraction) and > 40 days (for analysis)	Use professional judgment	
	Yes	≤ 7 days (for extraction) and ≤ 40 days (for analysis)	No qualification	
	Yes	> 7 days (for extraction) and > 40 days (for analysis)	J	UJ
	Yes/No	Grossly Exceeded	J	UJ or R
Non-aqueous	No	≤ 14 days (for extraction) and ≤ 40 days (for analysis)	Use professional judgment	
	No	> 14 days (for extraction) and > 40 days (for analysis)	Use professional judgment	
	Yes	≤ 14 days (for extraction) and ≤ 40 days (for analysis)	No qualification	
	Yes	> 14 days (for extraction) and > 40 days (for analysis)	J	UJ
	Yes/No	Grossly Exceeded	J	UJ or R

II. Gas Chromatograph/Mass Spectrometer (GC/MS) Instrument Performance Check

A. Review Items:

Form V SV, decafluorotriphenylphosphine (DFTPP) mass spectra, and mass listing.

B. Objective:

GC/MS instrument performance checks are performed to ensure adequate mass resolution, identification, and to some degree, sensitivity. These criteria are not sample-specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.

NOTE: This requirement does not apply when samples are analyzed by the Selected Ion Monitoring (SIM) technique.

C. Criteria:

1. The 12-hour clock begins with either the injection of DFTPP or in cases where a closing Continuing Calibration Verification (CCV) can be used as an opening CCV, the 12-hour clock begins with the injection of the opening CCV.
2. Listed below are some, but not necessarily all, examples of acceptable analytical sequences incorporating the use of the opening and/or closing CCV. Use these examples as a guide for possible analytical sequences that can be expected. The criteria associated with these analytical sequences have been evaluated as part of the Contract Compliance Screening (CCS) process.

Conditions for When Example Sequence is Appropriate:	Acceptable Criteria That Must Be Met:	Notes:
Use Example 1 if time remains on the 12-hour clock after the initial calibration sequence.	• DFTPP tunes meet instrument performance criteria. • The five Initial Calibration standards meet initial calibration criteria. • CCV A meets both opening and closing CCV criteria. • CCV B meets closing CCV criteria.	The requirement of starting the new 12-hour clock for Analytical Sequence 2 with a new DFTPP tune is waived if CCV A meets opening CCV criteria. If CCV B meets opening CCV criteria, a method blank and subsequent samples may be analyzed immediately after CCV B.
Use Example 2 if time remains on the 12-hour clock after the initial calibration sequence.	• DFTPP tunes meet instrument performance criteria. • The five Initial Calibration standards meet initial calibration criteria. • CCV A meets closing CCV criteria (but does not meet opening CCV criteria). • CCV B meets opening CCV criteria. • CCV C meets closing CCV criteria.	CCV A does not meet opening CCV criteria, therefore a new DFTPP tune must be performed, immediately followed by CCV B, before the method blank and any samples may be analyzed. In this case, the new 12-hour clock and Analytical Sequence 2 begins with the injection of the new DFTPP tune.

Conditions for When Example Sequence is Appropriate:	Acceptable Criteria That Must Be Met:	Notes:
Use Example 3 if more than 12-hours have elapsed since the most recent initial calibration or closing CCV, OR if the most recent closing CCV was not or could not be used as an opening CCV.	• DFTPP tunes meet instrument performance criteria. • CCV A meets opening CCV criteria. • CCV B meets both opening and closing CCV criteria. • CCV C meets both opening and closing CCV criteria.	The requirement of starting the new 12-hour clock for Analytical Sequence 2 with a new DFTPP tune is waived if CCV B meets opening CCV criteria. If CCV C meets opening CCV criteria, a method blank and subsequent samples may be analyzed immediately after CCV C.
Use Example 4 if more than 12-hours have elapsed since the most recent initial calibration or closing CCV, OR if the most recent closing CCV was not or could not be used as an opening CCV.	• DFTPP tunes meet instrument performance criteria. • CCV A meets opening CCV criteria. • CCV B meets closing CCV criteria (but does not meet opening CCV criteria). • CCV C meets opening CCV criteria. • CCV D meets both opening and closing CCV criteria.	CCV B does not meet opening CCV criteria, therefore a new DFTPP tune must be performed, immediately followed by CCV C, before the method blank and any samples may be analyzed. In this case, the new 12-hour clock and Analytical Sequence 2 begins with the injection of the new DFTPP tune. The requirement of starting the new 12-hour clock for Analytical Sequence 3 with a new DFTPP tune is waived if CCV D meets opening CCV criteria. If CCV D meets opening CCV criteria, a method blank and subsequent samples may be analyzed immediately after CCV D.

Example 1:	**Time**	**Material Injected**	**Analytical Sequence #**
Start of 12-hour clock for Analytical Sequence 1	0 hr	DFTPP	1
		Initial Calibration 5.0	1
		Initial Calibration 10	1
		Initial Calibration 20	1
		Initial Calibration 40	1
		Initial Calibration 80	1
		Method Blank	1
		Subsequent Samples	1
		•	1
		•	1
		•	1
		•	1
End of 12-hour clock for Analytical Sequence 1/ Beginning of 12-hour clock for Analytical Sequence 2	12 hr	CCV A (meets opening CCV criteria)	1/2
		Method Blank	2
		Subsequent Samples	2
		•	2
		•	2
		•	2
		•	2
End of 12-hour clock for Analytical Sequence 2/ Beginning of 12-hour clock for Analytical Sequence 3	24 hr	CCV B (meets opening CCV criteria)	2/3

Example 2:	**Time**	**Material Injected**	**Analytical Sequence #**
Start of 12-hour clock for Analytical Sequence 1	0 hr	DFTPP	1
		Initial Calibration 5.0	1
		Initial Calibration 10	1
		Initial Calibration 20	1
		Initial Calibration 40	1
		Initial Calibration 80	1
		Method Blank	1
		Subsequent Samples	1
		•	1
		•	1
		•	1
		•	1
End of 12-hour clock for Analytical Sequence 1	12 hr	CCV A (meets closing CCV criteria, fails opening CCV criteria)	1
Beginning of 12-hour clock for Analytical Sequence 2	13 hr	DFTPP	2
		CCV B (meets opening CCV criteria)	2
		Method Blank	2
		Subsequent Samples	2
		•	2
		•	2
		•	2
		•	2
End of 12-hour clock for Analytical Sequence 2	25 hr	CCV C (meets closing CCV criteria)	2

Example 3:	**Time**	**Material Injected**	**Analytical Sequence #**
Start of 12-hour clock for Analytical Sequence 1	0 hr	DFTPP	1
		CCV A (meets opening CCV criteria)	1
		Method Blank	1
		Subsequent Samples	1
		•	1
		•	1
		•	1
		•	1
End of 12-hour clock for Analytical Sequence 1/ Beginning of 12-hour clock for Analytical Sequence 2	12 hr	CCV B (meets opening CCV criteria)	1/2
		Method Blank	2
		Subsequent Samples	2
		•	2
		•	2
		•	2
End of 12-hour clock for Analytical Sequence 2/ Beginning of 12-hour clock for Analytical Sequence 3	24 hr	CCV C (meets opening CCV criteria)	2/3

Example 4:	**Time**	**Material Injected**	**Analytical Sequence #**
Start of 12-hour clock for Analytical Sequence 1	0 hr	DFTPP	1
		CCV A (meets opening CCV criteria)	1
		Method Blank	1
		Subsequent Samples	1
		•	1
		•	1
		•	1
End of 12-hour clock for Analytical Sequence 1	12 hr	CCV B (meets closing CCV criteria, fails opening CCV criteria)	1
Beginning of 12-hour clock for Analytical Sequence 2	13 hr	DFTPP	2
		CCV C (meets opening CCV criteria)	2
		Method Blank	2
		Subsequent Samples	2
		•	2
		•	2
		•	2
End of 12-hour clock for Analytical Sequence 2/ Beginning of 12-hour clock for Analytical Sequence 3	25 hr	CCV D (meets opening CCV criteria)	2/3

3. Inject a sufficient amount of the instrument performance check solution (50 ng DFTPP on-column) at the beginning of each 12-hour period during which samples or standards are analyzed. This requirement is waived if a closing CCV can be used as an opening CCV. The instrument performance check, DFTPP for semivolatile analysis, must meet the ion abundance criteria provided in Table 27.

Table 27. Ion Abundance Criteria For Decafluorotriphenylphosphine (DFTPP)

Mass	Ion Abundance Criteria
51	10.0 - 80.0% of mass 198
68	Less than 2.0% of mass 69
69	Present
70	Less than 2.0% of mass 69
127	10.0 - 80.0% of mass 198
197	Less than 2.0% of mass 198
198	Base peak, 100% relative abundance*
199	5.0 - 9.0% of mass 198
275	10.0 - 60.0% of mass 198
365	Greater than 1.0% of mass 198
441	Present, but less than mass 443
442	50.0 - 100% of mass 198
443	15.0 - 24.0% of mass 442

* All ion abundances must be normalized to m/z 198, the nominal base peak, even though the ion abundance of m/z 442 may be up to 100% that of m/z 198.

D. Evaluation:

1. Compare the data presented on each GC/MS Instrument Performance Check (Form V SV) with each mass listing submitted and ensure the following:

   a. Form V SV is present and completed for each 12-hour period during which samples were analyzed. In cases where a closing CCV is used as an opening CCV for the next 12-hour period, an additional Form V SV is not required.

   b. The laboratory has not made any transcription errors between the data and the form. If there are major differences between the mass listing and the Form Vs, a more in-depth review of the data is required. This may include obtaining and reviewing additional information from the laboratory.

   c. The appropriate number of significant figures has been reported (number of significant figures given for each ion in the ion abundance criteria column) and that rounding is correct.

   d. The laboratory has not made any calculation errors.

2. Verify that samples were not analyzed before a valid instrument performance check or were not analyzed 12 hours after the injection of the Instrument Performance Check Solution. This evaluation is not to be performed in cases where a closing CCV is used as an opening CCV.

3. Verify from the raw data (mass spectral listing) that the mass assignment is correct and the mass is normalized to m/z 198.
4. Verify that the ion abundance criteria were met. The criteria for m/z 68, 70, 441, and 443 are calculated by normalizing to the specified m/z.
5. If possible, verify that spectra were generated using appropriate background subtraction techniques. Since the DFTPP spectrum is obtained from chromatographic peaks that should be free from coelution problems, background subtraction should be done in accordance with the following procedure:
   a. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.
   b. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. Do not subtract the DFTPP peak as part of the background.

NOTE: **All mass spectrometer instrument conditions must be identical to those used during the sample analysis. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the contract specifications are contrary to the Quality Assurance (QA) objectives and are, therefore, unacceptable.**

For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the CCS process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. If samples are analyzed without a preceding valid instrument performance check or are analyzed 12 hours after the Instrument Performance Check and are not preceded by an analysis of a closing CCV that meets the opening CCV criteria, qualify all data in those samples as unusable "R".
2. If the laboratory has made minor transcription errors that do not significantly affect the data, the data reviewer should make the necessary corrections on a copy of the form.
3. If the laboratory has failed to provide the correct forms or has made significant transcription or calculation errors, the Region's designated representative should contact the laboratory and request corrected data. If the information is not available, the reviewer must use professional judgment to assess the data. Notify the laboratory's Contract Laboratory Program Project Officer (CLP PO).
4. If mass assignment is in error (e.g., m/z 199 is indicated as the base peak rather than m/z 198), classify all associated data as unusable "R".
5. If ion abundance criteria are not met, use professional judgment to determine to what extent the data may be utilized. Guidelines to aid in the application of professional judgment in evaluating ion abundance criteria are discussed as follows:
   a. Some of the most critical factors in the DFTPP criteria are the non-instrument specific requirements that are also not unduly affected by the location of the spectrum on the chromatographic profile. The m/z ratios for 198/199 and 442/443 are critical. These ratios are based on the natural abundances of carbon 12 and carbon 13 and should always be met. Similarly, the relative abundances for m/z 68, 70, 197, and 441 indicate the condition of the instrument and the suitability of the resolution adjustment. Note that all of the foregoing abundances relate to adjacent ions; they are relatively insensitive to differences in instrument design and position of the spectrum on the chromatographic profile.

b. For the ions at m/z 51, 127, and 275, the actual relative abundance is not as critical. For instance, if m/z 275 has 80.0% relative abundance (criteria: 10.0-60.0%) and other criteria are met, the deficiency is minor.

c. The relative abundance of m/z 365 is an indicator of suitable instrument zero adjustment. If relative abundance for m/z 365 is zero, minimum detection limits may be affected. On the other hand, if m/z 365 is present, but less than the 0.75% minimum abundance criteria, the deficiency is not as serious.

6. Note in the Data Review Narrative decisions to use analytical data associated with DFTPP instrument performance checks not meeting method requirements.

7. If the reviewer has reason to believe that instrument performance check criteria were achieved using techniques other than those specified in Semivolatiles Organic Analysis, Section II.D.5, obtain additional information on the DFTPP instrument performance checks. If the techniques employed are found to be at variance with contract requirements, the procedures of the laboratory may merit evaluation. Note, for CLP PO action, concerns or questions regarding laboratory performance. For example, if the reviewer has reason to believe that an inappropriate technique was used to obtain background subtraction (such as background subtracting from the solvent front or from another region of the chromatogram rather than from the DFTPP peak), this should be noted for CLP PO action.

III. Initial Calibration

A. Review Items:

Form VI SV-1, Form VI SV-2, Form VI SV-3, *Form VI SV-SIM*, quantitation reports, and chromatograms.

B. Objective:

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for compounds on the semivolatile Target Compound List (TCL). Initial calibration demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run and of producing a linear calibration curve, and provides the Mean Relative Response Factors ($\overline{\text{RRF}}$s) used for quantitation.

C. Criteria:

1. Initial calibration standards containing both semivolatile target compounds and Deuterated Monitoring Compounds (DMCs) are analyzed. All target compounds (except the seven compounds listed below) and the DMCs are analyzed at concentrations of 5.0, 10, 20, 40, and 80 ng/µL at the beginning of each analytical sequence or as necessary if the continuing calibration verification acceptance criteria are not met. The seven compounds are: 2,4-dinitrophenol; pentachlorophenol; 2-nitroaniline; 3-nitroaniline; 4-nitroaniline; 4-nitrophenol, and 4,6-dinitro-2-methylphenol. These compounds require a 4-point calibration at 10, 20, 40, and 80 ng/µL. The initial calibration (and any associated samples and blanks) must be analyzed within 12 hours of the associated instrument performance check.

   If analysis by the Selected Ion Monitoring (SIM) technique is requested for PAHs/pentachlorophenols, calibration standards are analyzed at 0.10, 0.20, 0.40, 0.80, and 1.0 ng/µL for each target compound of interest and the associated DMCs (see Table 34). Pentachlorophenol will require only a four-point initial calibration at 0.20, 0.40, 0.80, and 1.0 ng/µL.

2. Initial calibration standard Relative Response Factors (RRFs) for the semivolatile target compounds listed in Table 28 and for all DMCs must be greater than or equal to 0.010. The RRF for all other semivolatile target compounds must be greater than or equal to 0.050.

3. The Percent Relative Standard Deviation (%RSD) of the initial calibration RRFs must be less than or equal to 40.0% for the semivolatile target compounds and associated DMCs listed in Table 28. The %RSD for all other semivolatile target compounds and associated DMCs must be less than or equal to 20.0%.

NOTE: **The flexibility clause in the method may impact some of the preceding criteria. A copy of the flexibility clause should be present in the Sample Delivery Group (SDG). Refer to the Contract Laboratory Program (CLP) Web site at http://www.epa.gov/oerrpage/superfund/programs/clp/modifiedanalyses.htm for the specific method flexibility requirements.**

D. Evaluation:

1. Verify that the correct concentrations of standards were used for the initial calibration (i.e., 5.0, 10, 20, 40, and 80 ng/µL). For the seven compounds with higher Contract Required Quantitation Limits (CRQLs) listed in Semivolatiles Organic Analysis, Section III.C.1, verify that a four-point initial calibration at 10, 20, 40, 80 ng/µL was performed.

   If analysis by the SIM technique is requested, verify that the correct concentrations of standards were used for the initial calibration (i.e., 0.10, 0.20, 0.40, 0.80, and 1.0 ng/µL. The 0.10 standard is not required for pentachlorophenol).

2. Verify that the $\overline{RRF}$ obtained from the associated initial calibration was used for calculating sample results and the samples were analyzed within 12 hours of the associated instrument performance check.

3. Evaluate the initial calibration RRFs and the $\overline{RRF}$s for all semivolatile target compounds and DMCs:

   a. Check and recalculate the RRFs and $\overline{RRF}$s for at least one semivolatile target compound associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. Verify that for the semivolatile target compounds listed in Table 28 and for all DMCs, the initial calibration RRFs are greater than or equal to 0.010, and for all other semivolatile target compounds, RRFs are greater than or equal to 0.050.

Table 28. Semivolatile Target Compounds Exhibiting Poor Response

Compounds	
2,2'-Oxybis-(1-chloropropane)	Benzaldehyde
4-Chloroaniline	4-Nitroaniline
Hexachlorobutadiene	4,6-Dinitro-2-methylphenol
Hexachlorocyclopentadiene	N-Nitrosodiphenylamine
2-Nitroaniline	3-3'-Dichlorobenzidine
3-Nitroaniline	1,1'-Biphenyl
2,4-Dinitrophenol	Dimethylphthalate
4-Nitrophenol	Diethylphthalate
Acetophenone	1,2,4,5-Tetrachlorobenzene
Caprolactam	Carbazole
Atrazine	Butylbenzylphthalate
Di-n-butylphthalate	Di-n-octylphthalate
Bis(2-ethylhexyl)phthalate	

4. Evaluate the %RSD for all semivolatile target compounds and DMCs:

   a. Check and recalculate the %RSD for one or more semivolatile target compound(s) and DMCs. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

   b. If the %RSD is greater than the maximum criteria (40.0% for the semivolatile target compounds listed in Table 28 and associated DMCs (see Table 34), and 20.0% for all other semivolatile

target compounds and associated DMCs), the reviewer should use professional judgment to determine the need to check the points on the curve for the cause of the non-linearity. This is checked by eliminating either the high-point or the low-point and re-calculating the %RSD (see Semivolatiles Organic Analysis, Section III.E.2).

5. If errors are detected in the calculations of either the RRF or the %RSD, perform a more comprehensive recalculation.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. Qualify all semivolatile target compounds, including the compounds exhibiting poor response listed in Table 28, using the following criteria (see Table 29):
   a. If any semivolatile target compound has an RRF value less than the minimum criterion (0.010 for the target compounds exhibiting poor response listed in Table 28, and 0.050 for all other semivolatile compounds), use professional judgment for detects, based on mass spectral identification, to qualify the data as a "J" or unusable "R".
   b. If any semivolatile target compound has an RRF value less than the minimum criterion (0.010 for the target compounds exhibiting poor response listed in Table 28, and 0.050 for all other semivolatile compounds), qualify non-detected compounds as unusable "R".
   c. If any of the semivolatile target compounds listed in Table 28 has %RSD greater than 40.0%, qualify detects with a "J" and non-detected compounds using professional judgment (see Semivolatiles Organic Analysis, Section III.E.2).
   d. For all other semivolatile target compounds, if %RSD is greater than 20.0%, qualify detects with a "J" and non-detected compounds using professional judgment (see Semivolatiles Organic Analysis, Section III.E.2).
   e. If the semivolatile target compounds meet the acceptance criteria for RRF and %RSD, no qualification of the data is necessary.
   f. No qualification of the data is necessary on the DMC RRF and %RSD data alone. However, use professional judgment and follow the guidelines in Semivolatiles Organic Analysis, Section III.E.2, to evaluate the DMC RRF and %RSD data in conjunction with the DMC recoveries to determine the need for qualification of data.
2. At the reviewer's discretion, and based on the project-specific data quality objectives, a more in-depth review may be considered using the following guidelines:
   a. If any semivolatile target compound has a %RSD greater than the maximum criterion (40.0% for the target compounds listed in Table 28, and 20.0% for all other semivolatile compounds), and if eliminating either the high or the low-point of the curve does not restore the %RSD to less than or equal to the required maximum:
      i. Qualify detects for that compound(s) with a "J".
      ii. Qualify non-detected semivolatile target compounds using professional judgment.
   b. If the high-point of the curve is outside of the linearity criteria (e.g., due to saturation):
      i. Qualify detects outside of the linear portion of the curve with a "J".
      ii. No qualifiers are required for detects in the linear portion of the curve.

iii. No qualifiers are required for semivolatile target compounds that were not detected.

c. If the low-point of the curve is outside of the linearity criteria:

i. Qualify low-level detects in the area of non-linearity with a "J".

ii. No qualifiers are required for detects in the linear portion of the curve.

iii. For non-detected semivolatile compounds, use the lowest point of the linear portion of the curve to determine the new quantitation limit.

3. If the laboratory has failed to provide adequate calibration information, the Region's designated representative may contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

4. Note in the Data Review Narrative, whenever possible, the potential effects on the data due to calibration criteria exceedance.

5. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if calibration criteria are grossly exceeded.

Table 29. Initial Calibration Actions for Semivolatile Analyses

Criteria for Semivolatile Analysis	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
RRF < 0.010 (target compounds listed in Table 28) RRF < 0.050 (all other target compounds)	J or R (based on mass spectral identification)	R
RRF ≥ 0.010 (target compounds listed in Table 28) RRF ≥ 0.050 (all other target compounds)	No qualification	
%RSD ≤ 40.0 (target compounds listed in Table 28) %RSD ≤ 20.0 (all other target compounds)	No qualification	
%RSD > 40.0 (target compounds listed in Table 28) %RSD > 20.0 (all other target compounds)	J	Use professional judgment

IV. Continuing Calibration Verification (CCV)

A. Review Items:

Form VII SV-1, Form VII SV-2, Form VII SV-3, *Form VII SV-SIM*, quantitation reports, and chromatograms.

B. Objective:

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. The CCV checks satisfactory performance of the instrument on a day-to-day basis, however quantitations are based on the Mean Relative Response Factors ($\overline{RRFs}$) obtained from the initial calibration.

C. Criteria:

1. The 12-hour clock begins with either the injection of Decafluorotriphenylphosphine (DFTPP), or in cases where a closing CCV can be used as on opening CCV, the 12-hour clock begins with the injection of the opening CCV.
2. CCV standards containing both target compounds and associated Deuterated Monitoring Compounds (DMCs) are analyzed both at the beginning (opening CCV) and end (closing CCV) of each 12-hour analysis period following the analysis of the instrument performance check, and prior to the analysis of the method blank and samples. An instrument performance check is not required prior to the analysis of a closing CCV or prior to a closing CCV which can be used as an opening CCV for the next 12-hour period. If time remains in the 12-hour time period after initial calibration and samples are to be analyzed, the mid-point standard from the initial calibration can be used as an opening CCV.
3. For an opening CCV, the Relative Response Factors (RRFs) for the semivolatile target compounds listed in Table 28, and for all associated DMCs, must be greater than or equal to 0.010. The RRF for all other semivolatile target compounds must be greater than or equal to 0.050.
4. For a closing CCV, RRFs must be greater than or equal to 0.010 for all semivolatile target compounds and associated DMCs.
5. For an opening CCV, the Percent Difference (%D) between the initial calibration $\overline{RRF}$ and the opening CCV RRF must be within ±40.0% for the semivolatile target compounds and associated DMCs listed in Table 28. For an opening CCV, the Percent Difference for all other semivolatile target compounds and associated DMCs must be within ±25.0%.
6. For a closing CCV, the Percent Difference between the initial calibration $\overline{RRF}$ and the opening CCV RRF must be within ±50.0% for all semivolatile target compounds and associated DMCs.

D. Evaluation:

1. Verify that the CCV was run at the required frequency (an opening and closing CCV must be run within a 12-hour period) and the CCV was compared to the correct initial calibration. If the mid-point standard from the initial calibration is used as an opening CCV, verify that the result (RRF) of the mid-point standard was compared to the $\overline{RRF}$ from the correct initial calibration.
2. Evaluate the CCV RRF for all semivolatile target compounds and DMCs:

a. Check and recalculate the CCV RRF for at least one semivolatile target compound and DMC associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory reported value(s).

b. For an opening CCV, verify that all semivolatile target compounds listed in Table 28 and all DMCs have CCV RRFs of greater than or equal to 0.010, and all other semivolatile target compounds have RRFs of greater than or equal to 0.050.

c. For a closing CCV, verify that all semivolatile target compounds and DMCs have CCV RRFs of greater than or equal to 0.010.

3. Evaluate the Percent Difference between initial calibration $\overline{RRF}$ and CCV (both opening and closing) RRF for one or more semivolatile target compound(s) and DMCs:

a. Check and recalculate the Percent Difference for one or more semivolatile target compound(s) and DMCs associated with each internal standard. Verify that the recalculated value(s) agrees with the laboratory-reported value(s).

b. For an opening CCV, verify that the Percent Difference is within ±40.0% for the semivolatile target compounds and associated DMCs listed in Table 28, and within ±25.0% for all other semivolatile target compounds and associated DMCs.

c. For a closing CCV, verify that the Percent Difference is within ±50.0% for all semivolatile target compounds and DMCs.

4. If errors are detected in the calculations of either the CCV (both opening and closing) RRF or the Percent Difference, perform a more comprehensive recalculation.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. If a CCV (opening and closing) was not run at the appropriate frequency, qualify all data as unusable "R" (see Table 30).

2. Qualify all semivolatile target compounds, including the compounds exhibiting poor response listed in Table 28, using the following criteria:

a. For an opening CCV, if any semivolatile target compound has an RRF value less than the minimum criterion (0.010 for the compounds listed in Table 28 and 0.050 for all other semivolatile compounds), use professional judgment for detects, based on mass spectral identification, to qualify the data as a "J" or unusable "R".

b. For a closing CCV, if any semivolatile target compound has an RRF value less than 0.010, use professional judgment for detects based on mass spectral identification to qualify the data as a "J" or unusable "R".

c. For an opening CCV, if any semivolatile target compound has an RRF value less than the minimum criterion (0.010 for the compounds listed in Table 28 and 0.050 for all other semivolatile compounds), qualify non-detected compounds as unusable "R".

d. For a closing CCV, if any semivolatile target compound has an RRF of less than 0.010, qualify non-detected compounds as unusable "R".

e. For an opening CCV, if the Percent Difference value for any of the semivolatile target compounds listed in Table 28 is outside the ±40.0% criterion, qualify detects with a "J" and non-detected compounds with an approximated "UJ".

f. For a closing CCV, if the Percent Difference value for any of the semivolatile target compounds exhibiting poor response is outside the ±50.0% criterion, qualify detects with a "J" and non-detected compounds with an approximated "UJ".

g. For an opening CCV, if the Percent Difference value for any other semivolatile target compound is outside the ±25.0% criterion, qualify detects with a "J" and non-detected compounds with an approximated "UJ".

h. For a closing CCV, if the Percent Difference value for any other semivolatile target compound is outside the ±50.0% criterion, qualify detects with a "J" and non-detected compounds with an approximated "UJ".

i. No qualification of the data is necessary on the DMC RRF and Percent Difference data alone. However, use professional judgment to evaluate the DMC RRF and Percent Difference data in conjunction with the DMC recoveries to determine the need for qualification of data.

j. If the semivolatile target compounds meet the acceptance criteria for RRF and the Percent Difference, no qualification of the data is necessary.

3. If the laboratory has failed to provide adequate calibration information, the Region's designated representative may contact the laboratory and request the necessary information. If the information is not available, the reviewer must use professional judgment to assess the data.

4. Note in the Data Review Narrative, whenever possible, the potential effects on the data due to calibration criteria exceedance.

5. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if calibration criteria are grossly exceeded.

Table 30. Continuing Calibration Verification (CCV) Actions for Semivolatile Analyses

Criteria for Opening CCV	Criteria for Closing CCV	Action	
		Detected Associated Compounds	Non-Detected Associated Compounds
Opening CCV not performed at required frequency (see Semivolatile Organic Analysis, Section IV C.1)	Closing CCV not performed at required frequency (see Semivolatile Organic Analysis, Section IV C.1)	R	
RRF < 0.010 (target compounds listed in Table 28) RRF < 0.050 (all other target compounds)	RRF < 0.010 (all target compounds)	J or R	R
RRF ≥ 0.010 (target compounds listed in Table 28) RRF ≥ 0.050 (all other target compounds)	RRF ≥ 0.010 (all target compounds)	No qualification	
% D ≤ 40.0 or ≥ -40.0 (target compounds listed in Table 28) %D ≤ 25.0 or ≥-25.0 (all other target compounds)	% D ≤ 50.0 or ≥ -50.0 (all target compounds)	No qualification	
% D > 40.0 or < -40.0 (target compounds listed in Table 28) %D > 25.0 or < -25.0 (all other target compounds)	% D > 50.0 or < -50.0 (all target compounds)	J	UJ

V. Blanks

A. Review Items:

Form I SV-1, Form I SV-2, Form I SV-TIC, *Form I SV-SIM*, Form IV SV, *Form IV SV-SIM*, chromatograms, and quantitation reports.

B. Objective:

The purpose of laboratory or field blank analyses is to determine the existence and magnitude of contamination resulting from laboratory, field, or sample transport activities. The purpose of the method blank is to determine the levels of contamination associated with the processing and analysis of the samples. The criteria for evaluation of blanks apply to any blank associated with samples (e.g., method blanks and field blanks). If problems with a blank exist, all associated data must be carefully evaluated to determine whether or not there is any variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. Method Blanks

   A method blank must be extracted each time samples are extracted. A method blank is required per matrix (e.g., a non-aqueous method blank is required for non-aqueous samples and an aqueous method blank is required for aqueous samples) and concentration level (e.g., low or medium). The number of samples extracted with each method blank shall not exceed 20 field samples [excluding Matrix Spike/Matrix Spike Duplicates (MS/MSDs) and Performance Evaluation (PE) samples]. The method blank must be analyzed on each Gas Chromatograph/Mass Spectrometer (GC/MS) system used to analyze the set of samples prepared with the method blank.

   For low-level non-aqueous and aqueous samples, the concentration of each target compound [except bis(2-ethylhexyl)phthalate] found in the method blank must be less than its Contract Required Quantitation Limit (CRQL) listed in the method. The concentration of bis(2-ethylhexyl)phthalate found in the method blank must be less than five times (5x) its respective CRQL listed in the method. For medium-level non-aqueous samples, the concentration of each target compound found in the method blank must be less than its CRQL listed in the method.

   NOTE: The concentration of non-target compounds in all blanks must be less than or equal to 10 µg/L.

D. Evaluation:

1. Review the results of blanks on the forms and raw data (chromatograms and quantitation reports) to evaluate the presence of target and non-target compounds in the blanks.
2. Verify that a method blank analysis has been reported for each extraction batch and for each GC/MS system used to analyze semivolatile samples. There must be a method blank per sample matrix (i.e., if non-aqueous samples are present, verify that there is a non-aqueous method blank) and concentration level. The reviewer may use the Method Blank Summary (Form IV SV and *Form IV SV-SIM*) to identify the samples associated with each method blank.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process. Data concerning the field blanks are not evaluated as part of the CCS process. If field blanks are present, the data reviewer should evaluate this data in a similar fashion as the method blanks.**

E. Action:

Action regarding unsuitable blank results depends on the circumstances and origin of the blank. In instances where more than one of the same type of blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. Do not correct the sample results by subtracting any blank value (see Table 31).

1. If a semivolatile compound is found in a method blank, but not found in the sample, no qualification of the data is necessary.
2. If the method blank concentration is less than the CRQL [less than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples] and:
   a. the sample concentration is less than the CRQL [less than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples], report the CRQL value with a "U".
   b. the sample concentration is greater than or equal to the CRQL [greater than or equal to 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples], use professional judgment to qualify the data.
3. If the method blank concentration is greater than the CRQL [greater than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples] and:
   a. the sample concentration is less than the CRQL [less than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples], report the CRQL value with a "U".
   b. the sample concentration is greater than or equal to the CRQL [greater than or equal to 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples], and less than the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank with a "U", or the reviewer may elect to qualify the data as unusable "R".
   c. the sample concentration is greater than or equal to the CRQL [greater than or equal to 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples] and greater than or equal to the blank concentration, use professional judgment to qualify the data.
4. If the method blank concentration is equal to the CRQL [equal to 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples], and:
   a. the sample concentration is less than the CRQL [less than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples], report the CRQL value with a "U".
   b. the sample concentration is greater than or equal to the CRQL [greater than or equal to 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples], use professional judgment to qualify the data.
5. If gross contamination exists (i.e., saturated peaks by GC/MS), qualify all affected compounds in the associated samples as unusable "R", due to interference. Note, for Contract Laboratory Program

Project Officer (CLP PO) action, if the contamination is suspected of having an effect on the sample results.

6. Give the same consideration as the target compounds to the Tentatively Identified Compounds (TICs), which are found in both the sample and associated blank(s) (see Semivolatiles Organic Analysis, Section XIII, for TIC guidance).

7. If the contaminants found in the blank are interfering non-target compounds at concentrations greater than 10 µg/L, the reviewer may use professional judgment to qualify the data.

   NOTE: There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, they should qualify the data. Contamination introduced through dilution water is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but are absent in the undiluted sample result.

8. If contaminants are found in the field blanks, the following is recommended:

   a. Review the associated method blank data to determine if the contaminant(s) was also present in the method blank.

      i. If the analyte was present at a comparable level in the method blank, the source of the contamination may be in the analytical system and the action recommended for the method blank would apply.

      ii. If the analyte was not present in the method blank, the source of contamination may be in the field. Consider all associated samples for possible cross-contamination.

   b. If the field blank contains a semivolatile Target Compound List (TCL) compound(s) at a concentration greater than the CRQL [greater than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples], and:

      i. the sample concentration is less than the CRQL [less than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples], report the CRQL value with a "U".

      ii. the sample concentration is greater than or equal to the CRQL [greater than or equal to 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples], and less than the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank and qualify with a "U", or the reviewer may elect to qualify the data as unusable "R".

      iii. the sample concentration is greater than the CRQL [greater than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples]and greater than or equal to the blank concentration, use professional judgment to qualify the data.

   c. If the field blanks contain a semivolatile TCL compound(s) at a concentration less than the CRQL [less than 5x the CRQL for bis(2-ethylhexyl)phthalate in low-level non-aqueous and aqueous samples], and:

      i. the sample concentration is less than the CRQL [less than 5x the CRQL for bis(2-ethylhexyl)phthalate for low-level non-aqueous and aqueous samples], report the CRQL value with a "U".

      ii. the sample concentration is greater than or equal to the CRQL [greater than or equal to 5x the CRQL for bis(2-ethylhexyl)phthalate for low-level non-aqueous and aqueous samples], no qualification of the data is necessary.

d. If the field blanks contain a semivolatile TCL compound(s) at a concentration equal to the CRQL [equal to 5x the CRQL for bis(2-ethylhexyl)phthalate for low-level non-aqueous and aqueous samples] and:

   i. the sample concentration is less than the CRQL [less than 5x the CRQL for bis(2-ethylhexyl)phthalate for low-level non-aqueous and aqueous samples], report the CRQL value with a "U".

   ii. the sample concentration is greater than or equal to the CRQL [greater than or equal to 5x the CRQL for bis(2-ethylhexyl)phthalate for low-level non-aqueous and aqueous samples], use professional judgment to qualify the data.

e. If gross contamination (i.e., saturated peaks by GC/MS) exists in the field blank, positive sample results may require rejection and be qualified as unusable "R". Non-detected semivolatile target compounds do not require qualification unless the contamination is so high that it interferes with the analyses of non-detected compounds.

f. If the contaminants found in the field blank are interfering non-target compounds at concentrations greater than 10 µg/L (for aqueous blanks) or 330 µg/kg (for non-aqueous blanks), use professional judgment to qualify the data.

Table 31. Blank Actions for Semivolatiles Analyses

Blank Type	Blank Result	Sample Result	Action for Samples
Method, Field	Detects	Not detected	No qualification
	< CRQL*	< CRQL*	Report CRQL value with a U
		≥ CRQL*	Use professional judgment
	> CRQL*	< CRQL*	Report CRQL value with a U
		≥ CRQL* and <blank concentration	Report the blank concentration for the sample with a U or qualify the data as unusable R
		≥ CRQL* and ≥ blank concentration	Use professional judgment
	= CRQL*	< CRQL*	Report CRQL with a U
		≥ CRQL*	Use professional judgment
	Gross contamination	Detects	Qualify results as unusable R
	TIC > 10 µg/L (for aqueous blanks) TIC > 330 µg/kg (for non-aqueous blanks)	Detects	Use professional judgment

* 5x the CRQL for bis(2-ethylhexyl)phthalate for low-level non-aqueous and aqueous samples.

VI. Deuterated Monitoring Compounds (DMCs)

A. Review Items:

Form II SV-1, Form II SV-2, Form II SV-3, Form II SV-4, *Form II SV-SIM1, Form II SV-SIM2*, chromatograms, and quantitation reports.

B. Objective:

Laboratory performance on individual samples is established by means of spiking activities. All samples are spiked with DMCs prior to sample preparation. The evaluation of the results of these DMCs is not necessarily straightforward. The sample itself may produce effects due to factors such as interferences. Since the effects of the sample matrix are frequently outside laboratory control and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and requires analytical experience and professional judgment. Accordingly, this section consists primarily of guidelines, in some cases with several optional approaches suggested.

C. Criteria:

1. The DMCs listed in Table 32 are added to all samples and blanks to measure their recovery in environmental samples.

Table 32. Semivolatile Deuterated Monitoring Compound (DMC) and Recovery Limits

DMC	Recovery Limits (%) for Water Samples	Recovery Limits (%) for Soil/Sediment Samples
Phenol-d_5	39 - 106	17 -103
Bis-(2-chloroethyl) ether-d_8	40 - 105	12 - 98
2-Chlorophenol-d_4	41 - 106	13 - 101
4-Methylphenol-d_8	25 - 111	8 - 100
Nitrobenzene-d_5	43 - 108	16 - 103
2-Nitrophenol-d_4	40 - 108	16 - 104
2,4-Dichlorophenol-d_3	37 - 105	23 - 104
4-Chloroaniline-d_4	1 - 145	1 - 145
Dimethylphthalate-d_6	47 - 114	43 - 111
Acenaphthylene-d_8	41 - 107	20 - 97
4-Nitrophenol-d_4	33 - 116	16 - 166
Fluorene-d_{10}	42 - 111	40 - 108
4,6-Dinitro-2-methylphenol-d_2	22 - 104	1 - 121
Anthracene-d_{10}	44 - 110	22 - 98
Pyrene-d_{10}	52 - 119	51 - 120
Benzo(a)pyrene-d_{12}	32 - 121	43 - 111
Fluoranthene-d_{10} (SIM)	50 - 150	50 - 150
2-Methylnaphthalene-d_{10} (SIM)	50 - 150	50 - 150

2. Recoveries for DMCs in semivolatile samples and blanks must be within the limits specified in Table 32.

   NOTE: The recovery limits for any of the compounds listed in Table 32 may be expanded at any time during the period of performance if USEPA determines that the limits are too restrictive.

D. Evaluation:

1. Check raw data (e.g., chromatograms and quantitation reports) to verify the recoveries on the Deuterated Monitoring Compound Recovery Forms (Form II SV-1, Form II SV-2, Form II SV-3, Form II SV-4, *Form II SV-SIM1, and Form II SV-SIM2*).

   Check for any calculation or transcription errors; verify that the DMC recoveries were calculated correctly using the equation in the method.

2. Whenever there are two or more analyses for a particular sample, the reviewer must determine which are the most acceptable data to report. Considerations include, but are not limited to:

   a. DMC recovery (marginal versus gross deviation).

   b. Technical holding times.

c. Comparison of the values of the target compounds reported in each sample analysis.

d. Other Quality Control (QC) information, such as performance of internal standards.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

Table 34 and Table 35 (*SIM Analysis)* list the semivolatile DMCs and their associated target compounds. If any DMC recovery in the semivolatiles fraction is out of specification, qualify data considering the existence of interference in the raw data (see Table 33). Considerations include, but are not limited to:

1. For any recovery greater than the upper acceptance limit:
   a. Qualify detected associated semivolatile target compounds as a "J".
   b. Do not qualify non-detected associated semivolatile target compounds.
2. For any recovery less than the lower acceptance limit:
   a. Qualify detected associated semivolatile target compounds as a "J".
   b. Qualify non-detected associated semivolatile target compounds as approximated "UJ" or unusable "R".
3. For any recovery within acceptance limits, no qualification of the data is necessary.
4. In the special case of a blank analysis having DMCs out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable DMC recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. Note, for Contract Laboratory Program Project Officer (CLP PO) action, analytical problems, even if this judgment allows some use of the affected data.

Table 33. Deuterated Monitoring Compound (DMC) Recovery Actions For Semivolatile Analyses

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
%R > Upper Acceptance Limit	J	No qualification
%R < Lower Acceptance Limit	J	UJ or R
Lower Acceptance $\leq$ %R $\leq$ Upper Acceptance Limit	No qualification	

Table 34. Semivolatile Deuterated Monitoring Compounds (DMCs) and the Associated Target Compounds

Phenol-d_5 (DMC)	**2-Chlorophenol-d_4 (DMC)**	**2-Nitrophenol-d_4 (DMC)**
Benzaldehyde	2-Chlorophenol	Isophorone
Phenol		2-Nitrophenol
bis(2-Chloroethyl) ether-d_8 (DMC)	**4-Methylphenol-d_8 (DMC)**	**4-Chloroaniline-d_4 (DMC)**
bis-(2-Chloroethyl) ether	2-Methylphenol	4-Chloroaniline
2,2'-oxybis(1-Chloropropane)	4-Methylphenol	Hexachlorocyclopentadiene
bis(2-Chloroethoxy) methane	2,4-Dimethylphenol	3,3'-Dichlorobenzidine
Nitrobenzene-d_5 (DMC)	**2,4-Dichlorophenol-d_3 (DMC)**	**Dimethylphthalate-d_6 (DMC)**
Acetophenone	2,4-Dichlorophenol	Caprolactam
N-Nitroso-di-n-propylamine	Hexachlorobutadiene	1,1'-Biphenyl
Hexachloroethane	4-Chloro-3-methylphenol	Dimethylphthalate
Nitrobenzene	2,4,6-Trichlorophenol	Diethylphthalate
2,6-Dinitrotoluene	2,4,5-Trichlorophenol	Di-n-butylphthalate
2,4-Dinitrotoluene	1,2,4,5-Tetrachlorobenzene	Butylbenzylphthalate
N-Nitrosodiphenylamine	Pentachlorophenol	bis(2-ethylhexyl)phthalate
	2,3,4,6-Tetrachlorophenol	Di-n-octylphthalate
Fluorene-d_{10} (DMC)	**Anthracene-d_{10} (DMC)**	**Pyrene-d_{10} (DMC)**
Dibenzofuran	Hexachlorobenzene	Fluoranthene
Fluorene	Atrazine	Pyrene
4-Chlorophenyl-phenylether	Phenanthrene	Benzo(a)anthracene
4-Bromophenyl-phenylether	Anthracene	Chrysene
Carbazole		
Acenaphthylene-d_8 (DMC)	**4-Nitrophenol-d_4 (DMC)**	**Benzo (a) pyrene-d_{12} (DMC)**
Naphthalene	2-Nitroaniline	Benzo(b)fluoranthene
2-Methylnaphthalene	3-Nitroaniline	Benzo(k)fluoranthene
2-Chloronaphthalene	2,4-Dinitrophenol	Benzo(a)pyrene
Acenaphthylene	4-Nitrophenol	Indeno(1,2,3-cd)pyrene
Acenaphthene	4-Nitroaniline	Dibenzo(a,h)anthracene
		Benzo(g,h,i)perylene
4,6-Dinitro-2-methylphenol-d_2 (DMC)		
4,6-Dinitro-2-methylphenol		

Table 35. Semivolatile Deuterated Monitoring Compounds (DMCs) for Selective Ion Monitoring (SIM) and the Associated Target Compounds

Fluoranthene-d_{10} (DMC)	**2-Methylnapthalene-d_{10} (DMC)**
Fluoranthene	Napthalene
Pyrene	2-Methylnapthalene
Benzo(a)anthracene	Acenapthylene
Chrysene	Acenaphthene
Benzo(b)fluoranthene	Fluorene
Benzo(k)fluoranthene	Pentachlorophenol
Benzo(a)pyrene	Phenanthrene
Indeno(1,2,3-cd)pyrene	Anthracene
Dibenzo(a,h)anthracene	
Benzo(g,h,i)perylene	

VII. Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

A. Review Items:

Form III SV-1, Form III SV-2, *Form III SV-SIM1 and Form III SV-SIM2*, chromatograms, and quantitation reports.

NOTE: Data for MS and MSDs will not be present unless requested by the Region.

B. Objective:

Data for MS and MSDs are generated to determine long-term precision and accuracy of the analytical method on the sample matrix and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone cannot be used to evaluate the precision and accuracy of individual samples. However, when exercising professional judgment, this data should be used in conjunction with other available Quality Control (QC) information.

C. Criteria:

1. **If requested**, MS and MSD samples are analyzed at a frequency of one MS and MSD per 20 or fewer samples per sample matrix and concentration level.
2. Spike recoveries should be within the advisory limits provided on Form III SV-1, Form III SV-2, *Form III SV-SIM*, and *Form III SV-SIM2.*
3. Relative Percent Differences (RPDs) between MS and MSD recoveries must be within the advisory limits provided on Form III SV-1, Form III SV-2, *Form III SV-SIM*, and *Form III SV-SIM2.*

D. Evaluation:

1. Verify that requested MS and MSD samples were analyzed at the required frequency and that results are provided for each sample.
2. Inspect results for the MS and MSD Recovery on Form III SV, Form III SV-1, Form III SV-2, *Form III SV-SIM* and *Form III SV-SIM2* and verify that the results for recovery and RPD are within the advisory limits.
3. Verify transcriptions from raw data and verify calculations.
4. Check that the MS recoveries and RPD were calculated correctly.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. No qualification of the data is necessary on MS and MSD data alone. However, using informed professional judgment, the data reviewer may use the MS and MSD results in conjunction with other QC criteria to determine the need for some qualification of the data (see Table 36). Table 37 lists the semivolatile target compounds that are spiked into samples to test for matrix effects. If any MS and MSD Percent Recovery or RPD in the semivolatiles fraction is out of specification (see Table 37), qualify data to include the consideration of the existence of interference in the raw data. Considerations include, but are not limited to:

a. For any recovery or RPD greater than the upper acceptance limit:
   i. Qualify detected spiked semivolatile target compounds as a "J".
   ii. Do not qualify non-detected spiked semivolatile target compounds.
b. For any recovery less than the lower acceptance limit:
   i. Qualify detected spiked semivolatile target compounds as a "J".
   ii. Use professional judgment to qualify non-detected spiked semivolatile target compounds.
c. For any recovery or RPD within acceptance limits, no qualification of the data is necessary.

2. The data reviewer should first try to determine to what extent the results of the MS and MSD affect the associated data. This determination should be made with regard to the MS and MSD sample itself, as well as specific analytes for all samples associated with the MS and MSD.
3. In those instances where it can be determined that the results of the MS and MSD affect only the sample spiked, limit qualification to this sample only. However, it may be determined through the MS and MSD results that a laboratory is having a systematic problem in the analysis of one or more analytes, that affects all associated samples. Use professional judgment to qualify the data from all associated samples.
4. Use professional judgment to determine the need for qualification of detects of non-spiked compounds.

NOTE: Note, for Contract Laboratory Program Project Officer (CLP PO) action, if a field blank was used for the MS and MSD.

Table 36. Matrix Spike/Matrix Spike Duplicate (MS/MSD) Actions for Semivolatiles Analysis

Criteria	Action	
	Detected Spiked Compounds	Non-detected Spiked Compounds
%R or RPD > Upper Acceptance Limit	J	No qualification
%R < Lower Acceptance Limit	J	Use professional judgment
Lower Acceptance Limit ≤ %R; RPD ≤ Upper Acceptance Limit	No qualification	

Table 37. Matrix Spike (MS) Recovery and Relative Percent Difference (RPD)

Compound	% Recovery for Water Samples	RPD for Water Samples	% Recovery for Soil/Sediment Samples	RPD for Soil/Sediment Samples
Phenol	12 - 110	0 - 42	26 - 90	0 - 35
2-Chlorophenol	27 - 123	0 - 40	25 - 102	0 - 50
N-Nitroso-di-n-propylamine	41 - 116	0 - 38	41 - 126	0 - 38
4-Chloro-3-methylphenol	23 - 97	0 - 42	26 - 103	0 - 33
Acenaphthene	46 - 118	0 - 31	31 - 137	0 - 19
4-Nitrophenol	10 - 80	0 - 50	11 - 114	0 - 50
2,4-Dinitrotoluene	24 - 96	0 - 38	28 - 89	0 - 47
Pentachlorophenol	9 - 103	0 - 50	17 - 109	0 - 47
Pyrene	26 - 127	0 - 31	35 - 142	0 - 36

VIII. Regional Quality Assurance (QA) and Quality Control (QC)

A. Review Items:

Form I SV-1, Form I SV-2, *Form I SV-SIM*, chromatograms, Traffic Report/Chain of Custody Record (TR/COC), quantitation reports, and other raw data from QA/QC samples.

B. Objective:

Regional QA/QC refers to any QA and/or QC samples initiated by the Region, including field duplicates, Performance Evaluation (PE) samples, blind spikes, and blind blanks. The use of these QA/QC samples is highly recommended (e.g., the use of field duplicates can provide information on sampling precision and homogeneity).

C. Criteria:

Criteria are determined by each Region.

1. PE sample frequency may vary.
2. The analytes present in the PE sample must be correctly identified and quantified.

D. Evaluation:

1. Evaluation procedures must follow the Region's Standard Operating Procedure (SOP) for data review. Each Region will handle the evaluation of PE samples on an individual basis. Compare results for PE samples to the acceptance criteria for the specific PE samples, if available.
2. Calculate Relative Percent Difference (RPD) between field duplicates. Provide this information in the Data Review Narrative.

E. Action:

Any action must be in accordance with Regional specifications and the criteria for acceptable PE sample results. Note, for Contract Laboratory Program Project Officer (CLP PO) action, unacceptable results for PE samples.

IX. Gel Permeation Chromatography (GPC) Performance Check

A. Review Items:

Two ultraviolet (UV) traces, GPC cleanup blank quantitation reports, and chromatograms.

B. Objective:

GPC is used to remove high molecular weight contaminants that can interfere with the analysis of target analytes. GPC cleanup procedures are checked by adding the GPC calibration mixture to the GPC cleanup columns and setting the appropriate elution window, and verifying the recovery of target compounds through the cleanup procedure by the analysis of a cleanup blank.

C. Criteria:

1. GPC is used for the cleanup of all non-aqueous sample extracts and for aqueous sample extracts that contain high molecular weight components that interfere with the analysis of the target analytes.
2. At least once every seven (7) days, the calibration of the GPC unit must be checked by injecting the calibration solution.
3. The GPC calibration is acceptable if the two UV traces meet the following requirements:
    a. Peaks must be observed and symmetrical for all compounds in the calibration solution.
    b. Corn oil and the phthalate peaks exhibit greater than 85% resolution.
    c. The phthalate and methoxychlor peaks exhibit greater than 85% resolution.
    d. Methoxychlor and perylene peaks exhibit greater than 85% resolution.
    e. Perylene and sulfur peaks must not be saturated and should exhibit greater than 90% baseline resolution.
    f. The Retention Time (RT) shift is less than 5% between UV traces for bis(2-ethylhexyl)phthalate and perylene.
4. A GPC blank must be analyzed after each GPC calibration and is acceptable if the blank does not exceed the Contract Required Quantitation Limits (CRQL) for any target analytes, except for bis(2-ethylhexyl)phthalate, which must be less than 5x the CRQL.

D. Evaluation

1. Verify that there are two UV traces present and that the RT shift for bis(2-ethylhexyl)phthalate and perylene is less than 5%.
2. Verify that the compounds listed in Semivolatiles Organic Analysis, Section IX.C.3, are present and symmetrical in both UV traces and that the compound pairs meet the minimum resolution requirements.
3. Verify that no target compound exceeds the CRQL except for bis(2-ethylhexyl)phthalate, which must not exceed 5x the CRQL.

E. Action:

1. If GPC criteria are not met, examine the raw data for the presence of high molecular weight contaminants; examine subsequent sample data for unusual peaks; and use professional judgment in qualifying the data. Notify the Contract Laboratory Program Project Officer (CLP PO) if the laboratory chooses to analyze samples under unacceptable GPC criteria.
2. Note in the Data Review Narrative potential effects on the sample data resulting from the GPC cleanup analyses not yielding acceptable results.

X. Internal Standards

A. Review Items:

Form VIII SV-1, Form VIII SV-2, *Form VIII SV-SIM1*, *Form VIII SV-SIM2*, quantitation reports, and chromatograms.

B. Objective:

Internal standards performance criteria ensure that Gas Chromatograph/Mass Spectrometer (GC/MS) sensitivity and response are stable during each analysis.

C. Criteria:

1. Internal standard area counts for all samples [including Matrix Spike/Matrix Spike Duplicate (MS/MSD), or Performance Evaluation (PE) samples] and all blanks must be within the inclusive range of 50.0% and 200% of its response from the associated 12-hour calibration standard [opening Continuing Calibration Verification (CCV) or mid-point standard from the initial calibration].
2. The Retention Time (RT) of the internal standard in the sample or blank must not vary by more than ±30.0 seconds from the RT of the internal standard in the associated 12-hour calibration standard [opening CCV or mid-point standard from the initial calibration].

D. Evaluation:

1. Check raw data (e.g., chromatograms and quantitation lists) to verify the internal standard RTs and areas reported on the Internal Standard Area Summary (Form VIII SV-1, Form VIII SV-2, *Form VIII SV-SIM1*, and *Form VIII SV-SIM2*).
2. Verify that all RTs and internal standard areas are within the required criteria for all samples and blanks.
3. If there are two analyses for a particular fraction, the reviewer must determine which are the most accurate data to report. Considerations include, but are not limited to:
   a. Magnitude and direction of the internal standard area shift.
   b. Magnitude and direction of the internal standard RT shift.
   c. Technical holding times.
   d. Comparison of the values of the target compounds reported in each fraction.
   e. Other Quality Control (QC) information.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

1. If an internal standard area count for a sample or blank is greater than 200% of the area for the associated standard (opening CCV or mid-point standard from the initial calibration) (see Table 38):
   a. Qualify detects for compounds quantitated using that internal standard with a "J".

b. Do not qualify non-detected associated compounds.

2. If an internal standard area count for a sample or blank is less than 50.0% of the area for the associated standard (opening CCV or mid-point standard from the initial calibration):

   a. Qualify detects for compounds quantitated using that internal standard with a "J".

   b. Qualify non-detected associated compounds as unusable "R**".

3. If an internal standard area count for a sample or a blank is greater than or equal to 50.0%, and less than or equal to 200% of the area for the associated standard opening CCV or mid-point standard from the initial calibration, no qualification is necessary.

4. Absolute RTs of internal standards should not vary dramatically between samples and the associated 12-hour calibration standard (opening CCV or mid-point standard from the initial calibration). Examine the chromatographic profile for that sample to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection of the data for that sample fraction. Detects should not need to be qualified as unusable "R" if the mass spectral criteria are met.

5. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if the internal standard performance criteria are grossly exceeded. Note in the Data Review Narrative potential effects on the data resulting from unacceptable internal standard performance.

Table 38. Internal Standard Actions For Semivolatiles Analyses

Criteria	Action	
	Detected Associated Compounds*	**Non-Detected Associated Compounds***
Area counts >200% of 12-hour standard (opening CCV or mid-point standard from the initial calibration)	J	No qualification
Area counts <50.0% of 12-hour standard (opening CCV or mid-point standard from the initial calibration)	J	R**
Area counts $\geq$ 50.0% and $\leq$ 200% of 12-hour standard (opening CCV or mid-point standard from the initial calibration)	No qualification	
RT difference > 30.0 seconds between samples and 12-hour standard (opening CCV or mid-point standard from the initial calibration)	R	
RT difference $\leq$ 30.0 seconds between samples and 12-hour standard (opening CCV or mid-point standard from the initial calibration)	No qualification	

* For semivolatile compounds associated to each internal standard, see Table 2 - Semivolatile Internal Standards with Corresponding Target and Deuterated Monitoring Compounds Assigned for Quantitation in SOM01.2, Exhibit D, available at:
http://www.epa.gov/superfund/programs/clp/som1.htm

****** For area counts in the range of 20-50%, nondetected compounds may be qualified as UJ based on further evaluations on the data. The evaluations may include but are not limited to review of the chromatograms, mass spectra and statistical studies of signal-to-noise ratios. Such data qualifications shall be performed on a project-by-project basis.

XI. Target Compound Identification

A. Review Items:

Form I SV-1, Form I SV-2, *Form I SV-SIM*, quantitation reports, mass spectra, and chromatograms.

B. Objective:

The objective of the criteria for Gas Chromatograph/Mass Spectrometer (GC/MS) qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).

The identification criteria can be applied much more easily in detecting false positives than false negatives. More information is available for false positives due to the requirement for submittal of data supporting positive identifications. Negatives, or non-detected compounds, represent an absence of data and are, therefore, much more difficult to assess. One example of the detection of false negatives is not reporting a target compound that is reported as a Tentatively Identified Compound (TIC).

C. Criteria:

1. The Relative Retention Times (RRTs) must be within ±0.06 RRT units of the standard RRT [opening Continuing Calibration Verification (CCV) or mid-point standard from the initial calibration].
2. Mass spectra of the sample compound and a current laboratory-generated standard [i.e., the mass spectrum from the associated calibration standard (opening CCV or mid-point standard from initial calibration)] must match according to the following criteria:
    a. All ions present in the standard mass spectrum at a relative intensity greater than 10% must be present in the sample spectrum.
    b. The relative intensities of these ions must agree within ±20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30-70%).
    c. Ions present at greater than 10% in the sample mass spectrum, but not present in the standard spectrum, must be evaluated by a reviewer experienced in mass spectral interpretation.

D. Evaluation:

1. Check that the RRT of reported compounds is within ±0.06 RRT units of the standard RRT (opening CCV or mid-point standard from the initial calibration).
2. Check the sample compound spectra against the laboratory standard spectra to verify that it meets the specified criteria.
3. Be aware of situations when sample carryover is a possibility and use professional judgment to determine if instrument cross-contamination has affected any positive compound identification.
4. Check the chromatogram to verify that peaks are identified. Major peaks are either identified as target compounds, TICs, Deuterated Monitoring Compounds (DMCs), or internal standards.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

1. The application of qualitative criteria for GC/MS analysis of target compounds requires professional judgment. It is up to the reviewer's discretion to obtain additional information from the laboratory. If it is determined that incorrect identifications were made, qualify all such data as not detected "U" or unusable "R".
2. Use professional judgment to qualify the data if it is determined that cross-contamination has occurred.
3. Note in the Data Review Narrative any changes made to the reported compounds or concerns regarding target compound identifications. Note, for Contract Laboratory Program Project Officer (CLP PO) action, the necessity for numerous or significant changes.

XII. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

A. Review Items:

Form I SV-1, Form I SV-2, *Form I SV-SIM*, sample preparation sheets, Sample Delivery Group (SDG) Narrative, quantitation reports, and chromatograms.

B. Objective:

The objective is to ensure that the reported quantitation results and CRQLs are accurate.

C. Criteria:

1. Compound quantitation, adjustment of the CRQL, and Percent Moisture (for non-aqueous samples) must be calculated according to the correct equation.
2. Compound Relative Response Factors (RRFs) must be calculated based on the internal standard associated with that compound, as listed in the method. Quantitation must be based on the quantitation ion (m/z) specified in the method for both the internal standard and target analytes. The compound quantitation must be based on the average RRF from the associated initial calibration.

D. Evaluation:

1. Examine raw data to verify the correct calculation of all sample results reported by the laboratory. Compare quantitation lists and chromatograms to the reported detect and non-detect sample results. Check the reported values.
2. Verify that the correct internal standard, quantitation ion, and Mean Relative Response Factor ($\overline{RRF}$) were used to quantitate the compound. Verify that the same internal standard, quantitation ion, and $\overline{RRF}$ are used consistently throughout, in both the calibration as well as quantitation process.
3. Verify that the CRQLs have been adjusted to reflect all sample dilutions and Percent Moisture factors (for non-aqueous samples).

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

1. For non-aqueous samples, if the Percent Moisture is less the 70.0%, no qualification of the data is necessary. If the Percent Moisture is greater than or equal to 70.0% and less than 90.0%, qualify detects as "J" and non-detects as approximated "UJ". If the Percent Moisture is greater than or equal to 90.0%, qualify detects as "J" and non-detects as unusable "R" (see Table 39).
2. If any discrepancies are found, the Region's designated representative may contact the laboratory to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, the reviewer must use professional judgment to decide which value is the most accurate value. Under these circumstances, the reviewer may determine that qualification of data is warranted. Note in the Data Review Narrative a description of the reasons for data qualification and the qualification that is applied to the data.

3. Note, for Contract Laboratory Program Project Officer (CLP PO) action, numerous or significant failures to accurately quantify the target compound or to properly evaluate and adjust CRQLs.

Table 39. Percent Moisture Actions for Semivolatiles Analyses for Non-Aqueous Samples

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
%Moisture < 70.0%	No qualification	
70.0% ≤ %Moisture < 90.0%	J	UJ
%Moisture ≥ 90.0%	J	R

XIII. Tentatively Identified Compounds (TICs)

A. Review Items:

Form I SV-TIC, chromatograms, library search printouts, and spectra for the TIC candidates.

B. Objective:

Chromatographic peaks in semivolatile fraction analyses that are not target analytes, Deuterated Monitoring Compounds (DMCs), or internal standards are potential TICs. TICs must be qualitatively identified via a forward search of the NIST/USEPA/NIH Mass Spectral Library (May 2002 release or later)[5], and/or Wiley Mass Spectral Library (1998 release or later)[6], or equivalent. The identifications must be assessed by the data reviewer.

C. Criteria:

For each sample, the laboratory must conduct a mass spectral search of the NIST/USEPA/NIH (May 2002 release or later), and/or Wiley (1998 release or later), or equivalent mass spectral library, and report the possible identity for 30 of the largest semivolatile fraction peaks which are not DMCs, internal standards, or target compounds, but which have area or height greater than 10% of the area or height of the nearest internal standard. Estimated concentrations for TICs are calculated similarly to the Target Compound List (TCL) compounds, using total ion areas for the TIC and the internal standard, and assuming a Relative Response Factor (RRF) of 1.0. TIC results are reported for each sample on the Organic Analyses Data Sheet (Form I SV-TIC).

D. Evaluation:

1. Guidelines for tentative identification are as follows:
   a. Major ions (greater than 10% Relative Intensity) in the reference spectrum should be present in the sample spectrum.
   b. The relative intensities of the major ions should agree within ±20% between the sample and the reference spectra.
   c. Molecular ions present in the reference spectrum should be present in the sample spectrum.
   d. Review ions present in the sample spectrum, but not in the reference spectrum, for possible background contamination, interference, or presence of coeluting compounds.
   e. Review ions present in the reference spectrum, but not in the sample spectrum, for possible subtraction from the sample spectrum because of background contamination or coeluting compounds. Data system library reduction programs can sometimes create these discrepancies.
   f. Non-target compounds receiving a library search match of 85% or higher are a "likely match". Report the compound unless the mass spectral interpretation specialist feels there is evidence not to report the compound as identified by the library search program. Note in the Sample Delivery Group (SDG) Narrative the justification for not reporting a compound as listed by the search program.

[5]NIST/USEPA/NIH Mass Spectral Library (May 2002 release or later), National Institute of Standards and Technology, Gaithersburg, Maryland.

[6]Wiley Mass Spectral Library (1998 release or later) John Wiley & Sons, Inc., Hoboken, New Jersey.

g. If the library search produces more than one compound greater than or equal to 85%, report the compound with the highest percent match (report first compound if percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels that the highest match compound should not be reported or another compound with a lower match should be reported. The laboratory should include the justification for not reporting the compound with the highest spectral match within the SDG Narrative. Do not report DMCs, internal standards, and volatile target compounds as TICs, unless the only compounds having a percent match of greater than 85% are DMCs, internal standards, or volatile target compounds.

h. If the library search produces a series of obvious isomer compounds with library search matches greater than or equal to 85% (e.g., tetramethyl naphthalenes), report the compound with the highest library search percent match (or the first compound if the library search matches are the same). Note in the SDG Narrative that the exact isomer configuration, as reported, may not be accurate.

i. If the library search produces no matches greater than or equal to 85%, and in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, report the compound as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (e.g., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

j. Alkanes are not to be reported as TICs on Form I SVOA-TIC. An alkane is defined as any hydrocarbon with the generic formula C_nH_{2n+2} that contains only C-H and C-C single bonds. When the preceding alkanes are tentatively identified, estimate the concentration(s) and report them in the SDG Narrative as alkanes by class (i.e., straight-chain, branched, cyclic, as a series, or as applicable). Report total alkanes concentration on Form I VOA-TIC.

2. Check the raw data to verify that the laboratory has generated a library search for all required peaks in the chromatograms for samples and blanks.

3. Examine blank chromatograms to verify that TIC peaks present in samples are not found in blanks. When a low-level, non-target compound that is a common artifact or laboratory contaminant is detected in a sample, a thorough check of blank chromatograms may require looking for peaks which are less than 10% of the internal standard height, but present in the blank chromatogram at a similar Relative Retention Time (RRT).

4. Examine all mass spectra for each sample and blank.

5. Consider all reasonable choices since TIC library searches often yield several candidate compounds having a close matching score.

6. Be aware of common laboratory artifacts/contaminants and their sources (e.g., Aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.

   a. Examples:

      i. Common laboratory contaminants include CO2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons, and phthalates at levels less than 100 µg/L.

      ii. Solvent preservatives include cyclohexene (a methylene chloride preservative). Related by-products include cyclohexanone, cyclohexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.

      iii. Aldol condensation reaction products of acetone include 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

7. A target compound may be identified in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list (false negative). If the total area quantitation method was used, request that the laboratory recalculate the result using the proper quantitation ion and Relative Response Factor (RRF).

   A non-target compound may be incorrectly identified by the instrument's target analyte data processor as a target compound (false positive). When this happens, the non-target library search procedure will not detect the false positive as a TIC. In this case, request that the laboratory properly identify the compound and recalculate the result using the total area quantitation method and a RRF of 1.0.

   Evaluate other sample chromatograms and check for both false negatives and false positives to determine if the occurrence is isolated or systematic.

8. Target compounds may be identified in more than one fraction. Verify that quantitation is made from the proper fraction.
9. Do not perform library searches on internal standards or DMCs.
10. Estimate TIC concentration assuming an RRF of 1.0.

E. Action:

1. Qualify all TIC results for which there is presumptive evidence of a match (i.e., greater than or equal to 85% match) as "NJ", tentatively identified, with approximated concentrations.
2. General actions related to the review of TIC results are as follows:
   a. If it is determined that a tentative identification of a non-target compound is unacceptable, change the tentative identification to "unknown" or another appropriate identification and qualify the result with a "J".
   b. If all contractually-required peaks were not library searched and quantitated, the Region's designated representative may request these data from the laboratory.
3. In deciding whether a library search result for a TIC represents a reasonable identification, use professional judgment. If there is more than one possible match, report the result as "either compound X or compound Y". If there is a lack of isomer specificity, change the TIC result to a non-specific isomer result (e.g., 1,3,5-trimethyl benzene to trimethyl benzene isomer), or to a compound class (e.g., 2-methyl, 3-ethyl benzene to a substituted aromatic compound).
4. The reviewer may elect to report all similar isomers as a total (e.g., all alkanes may be summarized and reported as total hydrocarbons).
5. Other Case factors may influence TIC judgments. If a sample TIC match is poor, but other samples have a TIC with a good library match, similar RRT, and the same ions, infer identification information from the other sample TIC results.
6. Note in the Data Review Narrative any changes made to the reported data or any concerns regarding TIC identifications.
7. Note, for Contract Laboratory Program Project Officer (CLP PO) action, failure to properly evaluate and report TICs.

XIV. System Performance

A. Review Items:

Form VIII SV-1, Form VIII SV-2, *Form VIII SV-SIM1*, *Form VIII SV-SIM2*, and chromatograms.

B. Objective:

During the period following Instrument Performance Quality Control (QC) checks (e.g., blanks, tuning, calibration), changes may occur in the system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC runs, a thorough review of the ongoing data acquisition can yield indicators of instrument performance.

C. Criteria:

There are no specific criteria for system performance. Use professional judgment to assess the system performance.

D. Evaluation:

1. Abrupt discrete shifts in the Reconstructed Ion Chromatogram (RIC) baseline may indicate a change in the instrument's sensitivity or the zero setting. A baseline "shift" could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds, at or near the detection limit, to miss detection. A baseline "rise" could indicate problems such as a change in the instrument zero, a leak, or degradation of the column.
2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:
    a. High RIC background levels or shifts in Absolute Retention Times (RTs) of internal standards.
    b. Excessive baseline rise at elevated temperature.
    c. Extraneous peaks.
    d. Loss of resolution.
    e. Peak tailing or peak splitting that may result in inaccurate quantitation.
3. A drift in instrument sensitivity may occur during the 12-hour time period and may be an indication of internal standard spiking problems. This could be discerned by examination of the internal standards area on Form VIII SV-1, Form VIII SV-2, Form VIII SV-SIM1, and Form VIII SV-SIM2, for trends such as a continuous or near-continuous increase or decrease in the internal standard area over time.

E. Action:

Use professional judgment to qualify the data if it is determined that system performance has degraded during sample analyses. Note, for Contract Laboratory Program Project Officer (CLP PO) action, any degradation of system performance which significantly affected the data.

XV. Overall Assessment of Data

A. Review Items:

Entire data package, data review results, and (if available) Quality Assurance Project Plan (QAPP), and Sampling and Analysis Plan (SAP).

B. Objective:

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria:

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation:

1. Evaluate any technical problems that have not been previously addressed.
2. If appropriate information is available, the reviewer may assess the usability of the data to help the data user in avoiding inappropriate use of the data. Review all available information, including the QAPP (specifically the acceptance or performance criteria), SAP, and communication with the data user that concerns the intended use and desired quality of these data.

E. Action:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the Quality Control (QC) criteria previously discussed.
2. Write a brief narrative to give the user an indication of the analytical limitations of the data. Note, for Contract Laboratory Program Project Officer (CLP PO) action, any inconsistency of the data with the Sample Delivery Group (SDG) Narrative. If sufficient information on the intended use and required quality of the data are available, the reviewer should include their assessment of the usability of the data within the given context. This may be used as part of a formal Data Quality Assessment (DQA).

PESTICIDE DATA REVIEW

The pesticide data requirements to be checked are:

I. Preservation

II. Gas Chromatograph/Electron Capture Detector (GC/ECD) Instrument Performance Check

III. Initial Calibration

IV. Continuing Calibration Verification (CCV)

V. Blanks

VI. Surrogate Spikes

VII. Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

VIII. Laboratory Control Samples (LCSs)

IX. Regional Quality Assurance (QA) and Quality Control (QC)

X. Florisil Cartridge Performance Check

XI. Gel Permeation Chromatography (GPC) Performance Check

XII. Target Compound Identification

XIII. Gas Chromatograph/Mass Spectrometer (GC/MS) Confirmation

XIV. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

XV. Overall Assessment of Data

I. Preservation

A. Review Items:

Form I PEST, Traffic Report/Chain of Custody Record (TR/COC), raw data, sample extraction sheets, and Sample Delivery Group (SDG) Narrative checking for:

1. pH
2. Sample temperature
3. Holding time
4. Other sample conditions

B. Objective:

The objective is to ascertain the validity of the analytical results based on sample condition (e.g., preservation and temperature) and the holding time of the sample from time of collection to time of sample extraction and analysis.

C. Criteria:

The technical holding time criteria for aqueous samples are as follows:

> For pesticides in properly cooled (4°C ± 2°C) aqueous samples, the maximum holding time for extraction is seven (7) days from sample collection, and the maximum holding time for analysis is 40 days from sample extraction.

The technical holding time criteria for non-aqueous samples are as follows:

> For pesticides in properly cooled (4°C ± 2°C) non-aqueous samples, the maximum holding time for extraction is 14 days from sample collection, and the maximum holding time for analysis is 40 days from sample extraction.

D. Evaluation:

Technical holding times for sample extraction are established by comparing the sample collection dates on the TR/COC Record with the dates of extraction on Form I PEST and the sample extraction sheets. Information contained in the Complete SDG File (CSF) should also be considered in the determination of holding times. To determine if the samples were analyzed within the holding time after extraction, compare the dates of extraction on the sample extraction sheets with the dates of analysis on Form I PEST. Verify that the analysis dates on Form I(s) and the raw data/SDG file are identical. Review the SDG Narrative and the TR/COC Record to determine if the samples were received intact and iced. If there is no indication in the SDG Narrative, the TR/COC Record, or the sample records that there was a problem with the samples, assume the integrity of the samples is acceptable. If it is indicated that there were problems with the samples, the integrity of the sample may have been compromised. Use professional judgment to evaluate the effect of the problem on the sample results.

E. Action:

1. Qualify aqueous sample results using preservation and technical holding time information as follows (see Table 40):

   a. If there is no evidence that the samples were properly preserved (e.g., if the sample temperature has exceeded the allowable limits or if the integrity of the sample has been compromised), and the samples were extracted or analyzed within the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], use professional judgment to qualify the data.

   b. If there is no evidence that the samples were properly preserved (e.g., if the sample temperature has exceeded the allowable limits or if the integrity of the sample has been compromised), and the samples were extracted or analyzed outside the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], use professional judgment to qualify the data.

   c. If the samples were properly preserved, and were extracted and analyzed within the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], no qualification of the data is necessary.

   d. If the samples were properly preserved, and were extracted or analyzed outside the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], qualify detects with a "J" and non-detects as estimated with an approximated "UJ" or unusable "R". Note in the Data Review Narrative that holding times were exceeded and the effect of exceeding the holding time on the resulting data.

2. Qualify non-aqueous sample results using preservation and technical holding time information as follows (see Table 40):

   a. If there is no evidence that the samples were properly preserved (e.g., if the sample temperature has exceeded the allowable limits or if the integrity of the sample has been compromised), and the samples were extracted or analyzed within the technical holding times [14 days from sample collection for extraction; 40 days from sample collection for analysis], use professional judgment to qualify the data.

   b. If there is no evidence that the samples were properly preserved (e.g., if the sample temperature has exceeded the allowable limits or if the integrity of the sample has been compromised), and the samples were extracted or analyzed outside the technical holding times [14 days from sample collection; 40 days from sample collection for analysis], use professional judgment to qualify the data.

   c. If the samples were properly preserved, and were extracted and analyzed within the technical holding times [14 days from sample collection; 40 days from sample collection for analysis], no qualification of the data is necessary.

   d. If the samples were properly preserved, and were extracted or analyzed outside the technical holding times [14 days from sample collection; 40 days from sample collection for analysis], qualify detects with a "J" and non-detects as estimated with an approximated "UJ" or unusable "R". Note in the Data Review Narrative that holding times were exceeded and the effect of exceeding the holding time on the resulting data.

3. Use professional judgment to qualify samples whose temperature upon receipt at the laboratory is either below 2 degrees centigrade or above 6 degrees centigrade.

4. If technical holding times are grossly exceeded, qualify all detects as estimated with a "J" and use professional judgment to qualify sample non-detects.
5. Note in the Data Review Narrative, whenever possible, the effect of exceeding the holding time on the resulting data.
6. Note, for Contract Laboratory Program Project Officer (CLP PO) action, when technical holding times are grossly exceeded.

Table 40. Holding Time Actions for Pesticide Analyses

Matrix	Preserved	Criteria	Action	
			Detected Associated Compounds	Non-Detected Associated Compounds
Aqueous	No	≤ 7 days (for extraction) and ≤ 40 days (for analysis)	Use professional judgment	
	No	> 7 days (for extraction) and > 40 days (for analysis)	Use professional judgment	
	Yes	≤ 7 days (for extraction) and ≤ 40 days (for analysis)	No qualification	
	Yes	> 7 days (for extraction) and > 40 days (for analysis)	J	UJ
	Yes/No	Grossly Exceeded	J	UJ or R
Non-aqueous	No	≤ 14 days (for extraction) and ≤ 40 days (for analysis)	Use professional judgment	
	No	> 14 days (for extraction) and > 40 days (for analysis)	Use professional judgment	
	Yes	≤ 14 days (for extraction) and ≤ 40 days (for analysis)	No qualification	
	Yes	> 14 days (for extraction) and > 40 days (for analysis)	J	UJ
	Yes/No	Grossly Exceeded	J	UJ or R

II. Gas Chromatograph with Electron Capture Detector (GC/ECD) Instrument Performance Check

A. Review Items:

Form VI PEST-5, Form VI PEST-6, Form VI PEST-7, Form VI PEST-8, Form VI PEST-9, Form VI PEST-10, Form VII PEST-1, chromatograms, and data system printouts.

B. Objective:

GC/ECD instrument performance checks are performed to ensure adequate resolution and instrument sensitivity. These criteria are not sample-specific. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.

C. Criteria:

1. Resolution Check Mixture

   a. The Resolution Check Mixture is analyzed at the beginning of every initial calibration sequence, on each Gas Chromatograph (GC) column and instrument used for analysis. The Resolution Check Mixture contains the following pesticides and surrogates (see Table 41):

Table 41. Resolution Check Mixture Components

Compounds	
gamma-Chlordane	Endrin ketone
Endosulfan I	Methoxychlor
4,4'-DDE	Endosulfan II
Dieldrin	Heptachlor-epoxide
Endosulfan sulfate	alpha-Chlordane
alpha-BHC	4,4'-DDD
beta-BHC	4,4'-DDT
delta-BHC	Endrin
gamma-BHC	Endrin aldehyde
Aldrin	Tetrachloro-m-xylene (surrogate)
Heptachlor	Decachlorobiphenyl (surrogate)

   b. The resolution between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 80.0% for all analytes for the primary column and greater than or equal to 50.0% for the confirmation column in order to use one Individual Standard Mixture (C). If two Individual Standard Mixtures (A and B) are to be used, the resolution between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 60.0%.

2. Performance Evaluation Mixture (PEM)

   a. The PEM is analyzed at the beginning (following the Resolution Check Mixture) and at the end of the initial calibration sequence. The PEM analysis must bracket one end of each 12-hour analytical period. The PEM contains the following pesticides and surrogates (see Table 42):

Table 42. Performance Evaluation Mixture (PEM) Components

Compounds	
gamma-BHC	Endrin
alpha-BHC	Methoxychlor
4,4'-DDT	Tetrachloro-m-xylene (surrogate)
beta-BHC	Decachlorobiphenyl (surrogate)

   b. The resolution between any two adjacent peaks in the initial calibration and continuing calibration verification PEMs must be greater than or equal to 90% on each GC column.

   c. The Percent Breakdown is the amount of decomposition that 4,4'-DDT and Endrin undergo when analyzed on the GC column. For Endrin, the percent breakdown is determined by the presence of Endrin aldehyde and/or Endrin ketone in the PEM. For 4,4-DDT, the percent breakdown is determined by the presence of 4,4'-DDD and/or 4,4'-DDE in the PEM.

      i. The Percent Breakdown of 4,4'-DDT and Endrin in the PEMs must each be less than or equal to 20.0% on each GC column.

      ii. The combined Percent Breakdown for 4,4'-DDT and Endrin in PEMs must be less than or equal to 30.0% on each GC column.

3. Mid-point Individual Standard Mixtures (A and B) or (C)

   a. The resolution capabilities of the GC/ECD system used will dictate whether two Individual Standard Mixtures (A and B) (see Table 43) or one Individual Mixture (C) (see Table 44) can be used. This is determined by the analysis of the Resolution Check Mixture to see if the criteria in II.C.1.b are met. If Individual Standard Mixtures (A and B) are used, follow the procedure in 3b. If Individual Standard Mixture (C) is used, follow the procedure in 3c.

   b. Mid-point Individual Standard Mixtures (A and B)

      i. The mid-point Individual Standard Mixtures (A and B; INDA/INDB) are analyzed as part of the initial calibration. The mid-point INDA and INDB analysis must bracket one end of each 12-hour analytical period. The Individual Standard Mixtures contain the following pesticides and surrogates:

Table 43. Individual Standard Mixtures A and B Components

Individual Standard Mixture A	Individual Standard Mixture B
Compounds	
alpha-BHC	beta-BHC
Heptachlor	delta-BHC
gamma-BHC	Aldrin
Endosulfan I	Heptachlor-epoxide
Dieldrin	alpha-Chlordane
Endrin	gamma-Chlordane
4,4'-DDD	4,4'-DDE
4,4'-DDT	Endosulfan sulfate
Methoxychlor	Endrin aldehyde
Tetrachloro-m-xylene (surrogate)	Endrin ketone
Decachlorobiphenyl (surrogate)	Endosulfan II
	Tetrachloro-m-xylene (surrogate)
	Decachlorobiphenyl (surrogate)

ii. The resolution between any two adjacent peaks in the mid-point concentration of Individual Standard Mixtures (A and B) in the initial calibration and continuing calibration verification must be greater than or equal to 90.0% on each column.

c. Mid-point Individual Standard Mixture (C)

i. The mid-point Individual Standard Mixture (C; INDC) is analyzed as part of the initial calibration. The mid-point INDC analysis must bracket one end of each 12-hour analytical period. The Individual Standard Mixture (C) contains the pesticides and surrogates listed in Table 44.

ii. The resolution between any two adjacent peaks in the mid-point concentration of Individual Standard Mixture (C) in the initial calibration and continuing calibration verification must be greater than or equal to 80.0% for the primary column and greater than or equal to 50.0% for the secondary column.

Table 44. Individual Standard Mixture C Components

Compounds	
alpha-BHC	4,4'-DDD
beta-BHC	4,4'-DDE
delta-BHC	4,4'-DDT
gamma-BHC	Dieldrin
Aldrin	Endrin
Heptachlor	Endosulfan sulfate
Heptachlor-epoxide	Endrin ketone
alpha-Chlordane	Endrin aldehyde
gamma-Chlordane	Methoxychlor
Endosulfan I	Tetrachloro-m-xylene
Endosulfan II	Decachlorobiphenyl

D. Evaluation:

1. Resolution Check Mixture

   Check the Resolution Check Mixture data and Form VI PEST-5 to verify that if two Individual Standard Mixtures (A and B) are used, the resolution between two adjacent peaks for the required compounds in the Resolution Check Mixture is greater than or equal to 60.0% on both GC columns. Verify that if one Individual Standard Mixture (C) is used, the resolution between two adjacent peaks for the required compounds in the Resolution Check Mixture is greater than or equal 80.0% on the primary column and greater than or equal to 50.0% on the secondary column.

2. PEM

   a. Check the initial calibration and continuing calibration verification PEM data and Form VI PEST-6 to verify that the resolution between adjacent peaks is greater than or equal to 90.0% on both GC columns.

   b. Check Form VII PEST-1 to verify that the breakdown of 4,4'-DDT is less than or equal to 20.0%, the breakdown of Endrin is less than or equal to 20.0%, and the combined breakdown of 4,4'-DDT and Endrin is less than or equal to 30.0% in all PEMs on both GC columns.

3. Mid-point Individual Standard Mixtures (A and B)

   a. Check the initial calibration and continuing calibration verification mid-point Individual Standard Mixtures (A and B) data on Form VI PEST-7 and Form VI PEST-8 to verify that the resolution between adjacent peaks is greater than or equal to 90.0% on both GC columns.

4. Mid-point Individual Standard Mixture (C)

   a. Check the initial calibration and continuing calibration verification mid-point Individual Standard Mixture (C) data on Form VI PEST-9 and Form VI PEST-10 to verify that the resolution between adjacent peaks is greater than or equal to 80.0% for the primary column and 50.0% for the secondary column.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

1. Resolution Check Mixture
   a. If resolution criteria are not met, the quantitative results may not be accurate due to inadequate resolution. Qualitative identifications may also be questionable if coelution exists.
      i. Qualify detects for target compounds that were not adequately resolved with an "NJ" (see Table 45).
      ii. Qualify non-detected compounds as unusable "R".
2. PEM
   a. If PEM analysis is not performed at the required frequency (see Pesticides Organic Analysis, Section II.C.2.a), qualify all associated sample and blank results as unusable "R".
   b. If PEM resolution criteria are not met, the quantitative results may not be accurate due to inadequate resolution. Qualitative identifications may be questionable if coelution exists.
      i. Qualify detects with an "NJ".
      ii. Qualify non-detects as unusable "R".
   c. If 4,4'-DDT breakdown is greater than 20.0%:
      i. Qualify detects for 4,4'-DDT with a "J".
      ii. Qualify detects for 4,4'-DDD and/or 4,4'-DDE with a "J".
      iii. If 4,4'-DDT was not detected, but 4,4'-DDD and/or 4,4'-DDE were detected, qualify non-detects for 4,4'-DDT as unusable "R", and qualify detects for 4,4'-DDD and/or 4,4'-DDE as presumptively present at an approximated quantity "NJ".
   d. If Endrin breakdown is greater than 20.0%:
      i. Qualify detects for Endrin with a "J".
      ii. Qualify detects for Endrin aldehyde and/or Endrin ketone with a "J".
      iii. If Endrin was not detected, but Endrin aldehyde and/or Endrin ketone were detected, qualify the non-detects for Endrin as unusable "R", and qualify detects for Endrin aldehyde and/or Endrin ketone as presumptively present at an approximated quantity "NJ".
   e. If the combined 4,4'-DDT and Endrin breakdown is greater than 30.0%, the reviewer should consider the degree of individual breakdown of 4,4'-DDT and Endrin and apply qualifiers as described in this section.
3. Mid-point Individual Standard Mixtures (A and B) or (C)
   a. If mid-point Individual Standard Mixture analysis is not performed at the required frequency (see Pesticides Organic Analysis, Sections II.C.3.b and II.C.3.c), qualify all associated sample and blank results as unusable "R".
   b. If mid-point Individual Standard Mixtures (A and B) or (C) resolution criteria are not met, the quantitative results may not be accurate due to inadequate resolution. Qualitative identifications may be questionable if coelution exists.

i. Qualify detected target compounds that were not adequately resolved with an "NJ".

ii. Qualify non-detects as unusable "R".

4. Note in the Data Review Narrative the potential effects on the sample data resulting from the instrument performance check criteria. Notify the Contract Laboratory Program Project Officer (CLP PO) if the laboratory has repeatedly failed to comply with the requirements for linearity, resolution, or 4,4'-DDT/Endrin breakdown.

Table 45. Gas Chromatograph with Electron Capture Detector (GC/ECD) Instrument Performance Check Actions

Criteria [(Individual Standard Mixtures (A and B)]	Criteria (Individual Standard Mixture C)	Action
Resolution Check Mixture % Resolution <60.0%	Resolution Check Mixture % Resolution <80.0% (primary column) % Resolution <50.0% (secondary column)	Detects: NJ Non-detects: R
PEM % Resolution <90.0%		Detects: NJ Non-detects: R
PEM: 4,4'-DDT % Breakdown >20.0% and 4,4'-DDT is detected		Detects for 4,4'-DDT: J Detects for 4,4'-DDD: J Detects for 4,4'-DDE: J
PEM: 4,4'-DDT % Breakdown >20.0% and 4,4'-DDT is not detected		Non-detects for 4,4'- DDT: R Detects for 4,4'-DDD: NJ Detects for 4,4'-DDE: NJ
PEM: Endrin % Breakdown >20.0% and Endrin is detected		Detects for Endrin: J Detects for Endrin aldehyde: J Detects for Endrin ketone: J
PEM: Endrin % Breakdown >20.0% and Endrin is not detected		Non-detects for Endrin: R Detects for Endrin aldehyde: NJ Detects for Endrin ketone: NJ
PEM: Combined % Breakdown >30%		Apply qualifiers as described above considering degree of individual breakdown.
Mid-point Individual Standard Mixtures (A and B) % Resolution <90.0%	Mid-point Individual Standard Mixture (C) % Resolution <80.0% (primary column) Mid-point Individual Standard Mixture (C) % Resolution <50.0% (secondary column)	Detects: NJ Non-detects: R
PEM analysis not performed at the required frequency (see Pesticides, Section II.C.2.a.)		All results: R
Mid-point Individual Standard Mixtures analysis not performed at the required frequency (see Pesticides, Sections II.C.3.b.1 and II.C.3.c.1)		All results: R

III. Initial Calibration

A. Review Items:

Form VI PEST-1, Form VI PEST-2, Form VI PEST-3, Form VI PEST-4, chromatograms, and data system printouts.

B. Objective:

Compliance requirements for satisfactory initial calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for pesticide compounds on the Target Compound List (TCL). Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical sequence, and capable of producing a linear calibration curve.

C. Criteria:

1. Individual Standard Mixtures (A and B) or (C) (containing all of the pesticides and surrogates) must be analyzed at five concentration levels during the initial calibration, on each Gas Chromatograph (GC) column and instrument used for analysis.

   a. The Mean Retention Times ($\overline{RTs}$) of each of the Single Component Pesticides (SCPs) and surrogates are determined from the five-point initial calibration. The Retention Time (RT) for the surrogates is measured from each Individual Standard Mixtures (A and B).

   b. An RT Window must be calculated for each single component analyte and surrogate according to SOM01.2, Exhibit D - Pesticides, Table 1 - Retention Time Windows for Single Component Analytes, Toxaphene, and Surrogates, available at:

      http://www.epa.gov/superfund/programs/clp/som1.htm

      NOTE: At least one chromatogram from each of the Individual Standard Mixtures (A and B) or (C) must yield peaks that give recorder deflections between 50-100% of full scale.

   c. The five concentration level standards containing all of the Single Component Pesticides (SCPs) and surrogates should be prepared in either two mixtures (A and B) or one mixture (C) at the following concentration levels listed in Table 46.

Table 46. Concentration Levels of Calibration Standards

Compound	Concentration (ng/mL)				
	CS1	CS2	CS3	CS4	CS5
alpha-BHC	5.0	10	20	40	80
gamma-BHC	5.0	10	20	40	80
Heptachlor	5.0	10	20	40	80
Endosulfan I	5.0	10	20	40	80
Dieldrin	10	20	40	80	160
Endrin	10	20	40	80	160
4,4'-DDD	10	20	40	80	160
4,4'-DDT	10	20	40	80	160
Methoxychlor	50	100	200	400	800
beta-BHC	5.0	10	20	40	80
delta-BHC	5.0	10	20	40	80
Aldrin	5.0	10	20	40	80
Heptachlor-epoxide	5.0	10	20	40	80
4,4'-DDE	10	20	40	80	160
Endosulfan II	10	20	40	80	160
Endosulfan sulfate	10	20	40	80	160
Endrin ketone	10	20	40	80	160
Endrin aldehyde	10	20	40	80	160
alpha-Chlordane	5.0	10	20	40	80
gamma-Chlordane	5.0	10	20	40	80
Tetrachloro-m-xylene	5.0	10	20	40	80
Decachlorobiphenyl	10	20	40	80	160
Toxaphene	500	1000	2000	4000	8000

d. Mean Calibration Factor ($\overline{CF}$) must be calculated for each single component analyte and surrogate over the initial calibration range.

e. The Percent Relative Standard Deviation (%RSD) of the Calibration Factors (CFs) for each of the single component target compounds must be less than or equal to 20.0%, except for alpha-BHC and delta-BHC. The %RSD of the CFs for alpha-BHC and delta-BHC must be less than or equal to 25.0%. The %RSD of the CFs for the two surrogates (tetrachloro-m-xylene and decachlorobiphenyl) must be less than or equal to 30.0%.

NOTE: Either peak area or peak height may be used to calculate the CFs that are, in turn, used to calculate %RSD. However, the type of peak measurement used to calculate each CF for a given compound must be consistent. For example, if peak area is used to calculate the low-point CF for Endrin, the mid-point and high-point CFs for Endrin must also be calculated using peak area.

2. Toxaphene

   a. Toxaphene must be analyzed separately at a minimum of five different concentration levels during the initial calibration sequence. The analysis of Toxaphene compounds must also contain the pesticide surrogates.

   b. For each Toxaphene, the Retention Times (RTs) are determined for three to five peaks. The peaks chosen must not share the same RT Window as any SCP in any Individual Standard Mixture. The RT Window is calculated as ±0.07 minutes around the Absolute RTs.

   c. A CF must be determined for each peak selected for Toxaphene.

   d. The %RSD of the CFs for each of the Toxaphene peaks must be less than or equal to 30.0%; the %RSD of the CFs for the two surrogates (tetrachloro-m-xylene and decachlorobiphenyl) must be less than or equal to 30.0%.

   e. The five concentration level standards containing Toxaphene and surrogates should be prepared at the concentration levels listed in Table 46.

3. Initial Calibration Sequence

   The initial calibration must be performed following a specific sequence, depending upon whether one Individual Standard Mixture (C) (Initial Calibration Sequence 1) (see Table 47) or two Individual Standard Mixtures (A and B) (Initial Calibration Sequence 2) are used (see Table 48).

Table 47. Initial Calibration Sequence 1

Initial Calibration Sequence 1	
1.	Resolution Check
2.	Performance Evaluation Mixture (PEM)
3.	Toxaphene CS1
4.	Toxaphene CS2
5.	Toxaphene CS3
6.	Toxaphene CS4
7.	Toxaphene CS5
8.	CS1 Individual Standard Mixture C
9.	CS2 Individual Standard Mixture C
10.	CS3 Individual Standard Mixture C
11.	CS4 Individual Standard Mixture C
12.	CS5 Individual Standard Mixture C
13.	Instrument Blank
14.	PEM

Table 48. Initial Calibration Sequence 2

Initial Calibration Sequence 2	
1.	Resolution Check
2.	Performance Evaluation Mixture (PEM)
3.	Toxaphene CS1
4.	Toxaphene CS2
5.	Toxaphene CS3
6.	Toxaphene CS4
7.	Toxaphene CS5
8.	CS1 Individual Standard Mixture A
9.	CS1 Individual Standard Mixture B
10.	CS2 Individual Standard Mixture A
11.	CS2 Individual Standard Mixture B
12.	CS3 Individual Standard Mixture A
13.	CS3 Individual Standard Mixture B
14.	CS4 Individual Standard Mixture A
15.	CS4 Individual Standard Mixture B
16.	CS5 Individual Standard Mixture A
17.	CS5 Individual Standard Mixture B
18.	Instrument Blank
19.	PEM

NOTE: For Initial Calibration Sequence 2, Individual Standards for Mixture B may be analyzed before corresponding Individual Standards for Mixture A.

D. Evaluation:

For SCPs, follow the procedure in D.1 if either two Individual Standard Mixtures (A and B) or one Individual Standard Mixture (C) are used. For Toxaphene, follow the procedure in Pesticides Organic Analysis, Section III.D.2.

1. Individual Standard Mixtures (A and B) or (C)
   a. Check the raw data (chromatograms and data system printouts) for each standard to verify that each of the standards was analyzed at the required concentration levels.
   b. Check the Individual Standard Mixtures (A and B) data and Form VI PEST-1 and review the calculated RT Windows for calculation and transcription errors.
   c. Check the chromatograms and verify that at least one chromatogram from each of the Individual Standard Mixtures (A and B) or (C) yields peaks registering recorder/printer deflections between 50-100% of full scale.

d. Verify that the concentrations of the five standards of Individual Standard Mixtures (A and B) or (C) meet the criteria defined in Pesticides Organic Analysis, Section III.C.1.d.

e. Check the Individual Standard Mixtures (A and B) or (C) data and Form VI PEST-2 to verify that the %RSD for the CFs are in compliance with the criteria defined in Pesticides Organic Analysis, Section III.C.

f. Check and recalculate the CFs, $\overline{CFs}$, and %RSD for one or more pesticides in Individual Mixtures (A and B) or (C). Verify that the recalculated values agree with the reported values. If errors are detected, perform a more comprehensive recalculation and review.

2. Toxaphene

a. Check the raw data for the standards to verify that Toxaphene was analyzed at the required concentration.

b. Check the data for Toxaphene and Form VI PEST-3 to verify that at least three peaks were used for identification, and RT Windows were calculated as required. Verify that the peaks chosen do not share the same RT Window as any SCP in any Individual Standard Mixture.

c. Check the data to verify that CFs have been determined for each selected peak.

d. Check the chromatograms and verify that at least one chromatogram from each of the Toxaphene standards yields peaks registering recorder/printer deflections between 50-100% of full scale.

e. Verify that the concentrations of the Toxaphene standards meet the criteria defined in Pesticides Organic Analysis, Section III.C.1.d.

f. Check the Toxaphene data and Form VI PEST-4 to verify that the %RSD for the CFs are in compliance with the criteria defined in Pesticides Organic Analysis, Section III.C.

g. Check and recalculate the CFs, $\overline{CFs}$, and %RSD for one or more Toxaphene peaks. Verify that the recalculated values agree with the reported values. If errors are detected, perform a more comprehensive recalculation and review.

3. Initial Calibration Sequence

a. Verify that the proper initial calibration sequence (1 or 2) is used depending on if one (C) or two Individual Standard Mixtures (A and B) are used.

b. Verify that the steps of initial calibration is followed in the proper sequence.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. If the proper initial calibration sequence is not performed, or the steps of the initial calibration are not followed in the proper sequence, use professional judgment to evaluate the effect on the data and notify the Contract Laboratory Program Project Officer (CLP PO) (see Table 49). This is especially critical for the low-level standards and non-detects.

2. If RT Windows are not calculated correctly, recalculate the windows and use the corrected values for all evaluations.

3. If the chromatogram display (recorder deflection) criteria are not met, use professional judgment to evaluate the effect on the data.

4. If the standard concentration criteria are not met, use professional judgment to evaluate the effect on the data and notify the CLP PO. This is especially critical for the low-level standards and non-detects.
5. If the %RSD criteria are not met, qualify detects with a "J" and use professional judgment to qualify non-detected target compounds.
6. If the %RSD criteria are within allowable limits, no qualification of the data is necessary.
7. At the reviewer's discretion, and based on the project-specific data quality objectives, consider a more in-depth review using the following guidelines:
   a. If any pesticide target compound has a %RSD greater than the maximum criterion, and if eliminating either the high or the low-point of the curve does not restore the %RSD to less than or equal to the required maximum:
      i. Qualify detects for that compound(s) with a "J".
      ii. Qualify non-detected pesticide target compounds using professional judgment.
   b. If the high-point of the curve is outside of the linearity criteria (e.g., due to saturation):
      i. No qualifiers are required for detects in the linear portion of the curve.
      ii. Qualify detects outside of the linear portion of the curve with a "J".
      iii. No qualifiers are required for pesticide target compounds that were not detected.
   c. If the low-point of the curve is outside of the linearity criteria:
      i. No qualifiers are required for detects in the linear portion of the curve.
      ii. Qualify low-level detects in the area of non-linearity with a "J".
      iii. For non-detected pesticide compounds, use the lowest point of the linear portion of the curve to determine the new quantitation limit.
8. Note in the Data Review Narrative potential effects on the sample data due to problems with calibration. Notify the CLP PO if the laboratory has repeatedly failed to comply with the requirements for frequency, linearity, RT, or resolution.
9. Qualify data for Toxaphene sharing the same RT Window with any SCP in any Individual Standard Mixture using professional judgment.

Table 49. Initial Calibration Action for Pesticide Analyses

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
Initial calibration is not performed or not performed in the proper sequence	Use professional judgment	
%RSD exceeds allowable limits*	J	Use professional judgment
%RSD within allowable limits*	No qualification	

* %RSD ≤ 20.0% for single component target compounds except alpha-BHC and delta-BHC.
%RSD ≤ 25.0% for alpha-BHC and delta-BHC.
%RSD ≤ 30.0% for Toxaphene peaks.
%RSD ≤ 30.0% for surrogates (tetrachloro-m-xylene and decachlorobiphenyl).

IV. Continuing Calibration Verification (CCV)

A. Review Items:

Form VII PEST-1, Form VII PEST-2, Form VII PEST-3, Form VII PEST-4, chromatograms, and data system printouts.

B. Objective:

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. CCV checks and documents satisfactory performance of the instrument over specific time periods during sample analysis. To confirm the calibration and evaluate instrument performance, continuing calibration verification is performed, consisting of the analyses of instrument blanks, the Performance Evaluation Mixture (PEM), and the mid-point concentration of Individual Standard Mixtures (A and B) or (C). A CCV must be performed at the beginning (opening CCV) and end (closing CCV) of the analytical sequence. The opening and closing CCVs consist of an injection of an instrument blank followed by either an injection of an PEM or mid-point concentration of Individual Standard Mixtures (A and B) or (C) in an alternating fashion [i.e. if the PEM is part of the opening CCV, the mid-point concentration of Individual Standard Mixtures (A and B) or (C) must be part of the closing CCV]. A continuing calibration verification for Toxaphene is only required if Toxaphene is detected in a sample.

C. Criteria:

1. The Absolute Retention Time (RT) for each Single Component Pesticide (SCP) and surrogate in the PEM and the mid-point concentration of Individual Standard Mixtures (A and B) or (C) used for continuing calibration verification must be within the RT Windows determined from the initial calibration. If a continuing calibration verification is required for Toxaphene because of its detection in a sample, the Absolute RT for each Toxaphene peak must be within the RT Windows determined from the initial calibration.
2. The Percent Difference (%D) between the calculated amount and the nominal amount (amount added) for each of the SCP and surrogates in the PEM used for continuing calibration verification must be greater than or equal to -25.0% and less than or equal to 25.0%.
3. The Percent Difference between the Calibration Factor (CF) for each of the SCP and surrogates in the Calibration Verification Standard (CS3) and the Mean Calibration Factor ($\overline{CF}$) from the initial calibration must be greater than or equal to -20.0% and less than or equal to 20.0%. If a continuing calibration verification is required for Toxaphene because of its detection in a sample, the Percent Difference between the CF for each of the peaks used to identify Toxaphene in the Calibration Verification Standard (CS3) and the $\overline{CF}$ from the initial calibration must be greater than or equal to -20.0% and less than or equal to 20.0%.
4. No more than 14 hours may elapse from the injection of the instrument blank that begins an analytical sequence (opening CCV) and the injection of either a PEM or mid-point concentration of the Individual Standard Mixtures (A and B) or (C) that ends an analytical sequence (closing CCV).
5. No more than 12 hours may elapse from the injection of the instrument blank that begins an analytical sequence (opening CCV) and the injection of the last sample or blank that is part of the same analytical sequence.

6. No more than 72 hours may elapse from the injection of the sample with a Toxaphene detection and the Toxaphene Calibration Verification Standard (CS3).

D. Evaluation:

1. Check the data for each of the SCPs and surrogates in the PEM, the mid-point concentration of Individual Standard Mixtures (A and B) or (C), Form VII PEST-1, and Form VII PEST-2, Form VII PEST-3, to verify that the Absolute RTs are within the RT Windows. If a Toxaphene Calibration Verification is required, check the data for each Toxaphene peak and surrogates in the Toxaphene Calibration Verification Standard (CS3) and Form VII PEST-4 to verify that the Absolute RTs are within the RT Windows.
2. Check the data from the PEM, Form VII PEST-1, to verify that the Percent Difference between the calculated amount and the true amount for each of the pesticides and surrogates are within ±25.0%.
3. Check the data from the mid-point concentration of Individual Standard Mixtures (A and B) or (C), Form VII PEST-2, and Form VII PEST-3 to verify that the Percent Difference between the CF for each of the SCP and surrogates in the Calibration Verification Standard (CS3) and the CF from the initial calibration are within the inclusive range of ±20.0%. If a continuing calibration verification is required for Toxaphene because of its detection in a sample, check the data from the mid-point concentration of Toxaphenes, Form VII PEST-4 and verify that the Percent Difference between the CF for each of the peaks used to identify Toxaphene in the Calibration Verification Standard (CS3) and the CF from the initial calibration are within the inclusive range of ±20.0%.
4. Check the length of time that has elapsed from the beginning injection of the opening CCV (instrument blank) and the ending injection of the closing CCV [PEM or Individual Standard Mixtures (A and B) or (C)] to verify that no more than 14 hours has elapsed.
5. Check the length of time that has elapsed from the beginning injection of the opening CCV (instrument blank) and the injection of the last sample or method blank to verify that no more than 12 hours has elapsed.
6. If a continuing calibration verification is required for Toxaphene because of its detection in a sample, check the length of time that has elapsed from the injection of the sample with a Toxaphene detection and the Toxaphene Calibration Verification Standard (CS3) to verify that no more than 72 hours has elapsed.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. The RT Windows are used in qualitative identification. If the standards do not fall within the RT Windows, carefully evaluate the associated sample results (see Table 50). All samples injected after the last in-control standard are potentially affected.
   a. For non-detected target compounds in the affected samples, check to see if the sample chromatograms contain any peaks that are close to the expected RT Window of the pesticide of interest.
      i. If no peaks are present, consider non-detected values to be valid and no qualification of the data is necessary.
      ii. If any peaks are present close to the expected RT Window of the pesticide of interest, use professional judgment to qualify the non-detects as presumptively present "NJ".

b. For detected compounds in the affected samples, if the peaks are within the RT Window, no qualification of the data is necessary. However, if the peaks are close to the expected RT Window of the pesticide of interest, the reviewer may take additional effort to determine if sample peaks represent the compounds of interest.

   For example, the reviewer can examine the data package for the presence of three or more standards containing the pesticide of interest that were run within the analytical sequence during which the sample was analyzed. If three or more such standards are present, the RT Window can be re-evaluated using the Mean Retention Times ($\overline{RTs}$) of the standards.

   i. If the peaks in the affected sample fall within the revised window, qualify detects as "NJ".

   ii. If the reviewer cannot do anything with the data to resolve the problem of concern, qualify all non-detects as unusable "R".

2. For the PEM, if the Percent Difference is not within ±25.0% as defined in Pesticides Organic Analysis, Section IV.C.2, qualify associated detects with a "J" and non-detects with an approximated "UJ".
3. For the Calibration Verification Standard (CS3), if the Percent Difference is not within ±20.0% as defined in Pesticides Organic Analysis, Section IV.C.3, qualify associated detects with a "J" and non-detects with an approximated "UJ".
4. If more than 14 hours has elapsed as defined in Pesticides Organic Analysis, Section IV.C.4, qualify all data as unusable "R".
5. If more than 12 hours has elapsed as defined in Pesticides Organic Analysis, Section IV.C.5, qualify all data as unusable "R".
6. If more than 72 hours has elapsed as defined in Pesticides Organic Analysis, Section IV.C.6, qualify all data as unusable "R".
7. If the Percent Difference, time elapsed, and RTs are within acceptable limits, no qualification of the data is necessary.
8. Note in the Data Review Narrative potential effects on the sample data due to problems with calibration.

Table 50. Continuing Calibration Verification (CCV) Action for Pesticide Analyses

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
RT out of RT window	Use professional judgment (see Pesticides, Section IV.E.1)	
Percent Difference not within limits as defined in Pesticides Organic Analysis, Sections IV.C.2 and C.3	J	UJ
Time elapsed is greater than acceptable limits, as defined in Pesticides Organic Analysis, Sections IV.C.4, C.5, and C.6	R	
Percent Difference, time elapsed, and RT are within acceptable limits	No qualification	

V. Blanks

A. Review Items:

Form I PEST, Form IV PEST, chromatograms, and data system printouts.

B. Objective:

The purpose of laboratory or field blank analyses is to determine the existence and magnitude of contamination resulting from laboratory, field, or sample transport activities. The purpose of the method blank is to determine the levels of contamination associated with the processing and analysis of samples. The results from the instrument blank analysis indicate whether there is contamination from the analysis of a previous sample. The criteria for evaluation of blanks apply to any blank associated with the samples (e.g., method blanks, sulfur cleanup blanks, instrument blanks, and field blanks). If problems with any blank exist, carefully evaluate all associated data to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. Method Blanks

   A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples [excluding Matrix Spike/Matrix Spike Duplicate (MS/MSDs), Performance Evaluation (PE) samples, and Laboratory Control Samples (LCSs)]. In addition, a method blank shall be extracted by the same procedure used to extract samples and be analyzed on the same Gas Chromatograph/Electron Capture Detector (GC/ECD) system used to analyze associated samples.

2. Instrument Blanks

   An acceptable instrument blank must be run at the beginning and ending of an analytical sequence in which samples are analyzed, immediately prior to the analysis of the Performance Evaluation Mixture (PEM) or mid-point Individual Standard Mixtures (A and B) or (C), used for continuing calibration verification. All groups of acceptable sample analyses are to be preceded and followed by acceptable instrument blanks.

3. Sulfur Cleanup Blanks

   A sulfur cleanup blank must be analyzed whenever part of a set of samples extracted together requires sulfur cleanup. If the entire set of samples associated with a method blank requires sulfur cleanup, the method blank also serves the purpose of a sulfur blank and no separate sulfur blank is required.

   The concentration of each target analyte in the method, sulfur cleanup, instrument, and field blanks must be less than its Contract Required Quantitation Limits (CRQL) listed in the method.

D. Evaluation:

1. Review the results of all associated blanks, Form I PEST, Form IV PEST, and raw data (chromatograms and data system printouts) to evaluate the presence of target or non-target analytes in the blanks.
2. Verify that a method blank analysis has been reported per Sample Delivery Group (SDG), per extraction batch, and per extraction procedure. The reviewer can use Form IV PEST to identify samples associated with each blank.

3. Verify that the method blank analysis(es) contains less than the CRQL of any target SCP or Toxaphene, or any interfering peak.
4. Verify that the instrument blank analysis has been performed every 12 hours as the first analysis of the continuing calibration verification sequence. Evaluate the results from the various instrument blanks to verify that target analyte concentrations are less than the CRQL (assuming a 1 L extraction of a aqueous sample).
5. Verify that the sulfur cleanup blanks were analyzed at the required frequency and the sulfur blanks do not contain any target compounds greater than or equal to the CRQL (assuming a 1 L extraction of an aqueous sample). If a separate sulfur cleanup blank was prepared, one version of Form IV PEST should be completed associating all the samples with the method blank, and a second version of Form IV PEST should be completed listing only those samples associated with the separate sulfur cleanup blank.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process. Data concerning the field blanks are not evaluated as part of the CCS process. If field blanks are present, evaluate this data in a similar fashion as the method blanks.**

E. Action:

Action regarding unsuitable blank results depends on the circumstances and the origin of the blank. In instances where more than one of the same type of blank is associated with a given sample, base qualification upon a comparison with the associated blank having the highest concentration of a contaminant. Do not correct the results by subtracting the blank value.

1. If a target SCP or Toxaphene is found in the blank but not found in the sample, no qualification is required (see Table 51).
2. If a target SCP or Toxaphene concentration in a blank is less than the CRQL, and:
   a. the sample concentration is less than the CRQL, report the CRQL value with a "U".
   b. the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.
3. If a target SCP or Toxaphene concentration in a blank is greater than the CRQL, and:
   a. the sample concentration is less than the CRQL, report the CRQL value with a "U".
   b. the sample concentration is greater than or equal to the CRQL, and less than the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank with a "U", or the reviewer may elect to qualify the data as unusable "R".
   c. the sample concentration is greater than or equal to the CRQL, and greater than or equal to the blank concentration, use professional judgment to qualify the data.
4. If a target SCP or Toxaphene concentration in a blank is equal to the CRQL, and:
   a. the sample concentration is less than the CRQL, report the CRQL value with a "U".
   b. the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.
5. If gross contamination exists (e.g., saturated peaks, "hump-o-grams", " junk" peaks), all affected compounds in the associated samples should be qualified as unusable "R", due to interference. Note,

for Contract Laboratory Program Project Officer (CLP PO) action, if the contamination is suspected of having an effect on the sample results.

6. There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, they should qualify the data. Contamination introduced through dilution is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but absent in the undiluted sample result.
7. If contaminants are found in the field blanks, the following is recommended:
   a. Review the associated method blank data to determine if the contaminant(s) was also present in the method blank. If the analyte was present at a comparable level in the method blank, the source of the contamination may be in the analytical system and the action recommended for the method blank would apply.

      If the analyte was not present in the method blank, the source of contamination may have occurred in the field or during sample transport. Consider all associated samples for possible cross-contamination.
   b. If the field blank contains a pesticide Target Compound List (TCL) compound(s) at a concentration greater than the CRQL, and:
      i. the sample concentration is less than the CRQL, report the CRQL value with a "U".
      ii. the sample concentration is greater than or equal to the CRQL, but less than the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank and qualify with a "U", or use professional judgment to qualify the data as unusable "R".
      iii. the sample concentration is greater than the CRQL and greater than or equal to the blank concentration, use professional judgment to qualify the data.
   c. If gross contamination (e.g., saturated, "hump-o-grams", "junk" peaks) exists in the field blank, positive sample results may require rejection. Qualify as unusable "R". Non-detected pesticide target compounds do not require qualification unless the contamination is so high that it interferes with the analyses of non-detected compounds.
   d. If the field blank contains a pesticide TCL compound(s) at a concentration less than the CRQL and:
      i. the sample concentration is less than the CRQL, report the CRQL value with a "U".
      ii. the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.
   e. If the field blank contains a pesticide TCL compound(s) at a concentration equal to the CRQL and:
      i. the sample concentration is less than the CRQL, report the CRQL value with a "U".
      ii. the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.

Table 51. Blank Actions for Pesticide Analyses

Blank Type	Blank Result	Sample Result	Action for Samples
Method, Sulfur Cleanup, Instrument, Field	Detects	Not detected	No qualification
	< CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL	Use professional judgment
	> CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL and < blank concentration	Report the blank concentration for the sample with a U, or qualify the data as unusable R
		≥ CRQL and ≥ blank concentration	Use professional judgment
	= CRQL	< CRQL	Report CRQL values with a U
		≥ CRQL	Use professional judgment
	Gross contamination	Detects	Qualify results as unusable R

VI. Surrogate Spikes

A. Review Items:

Form II PEST-1, Form II PEST-2, Form VIII PEST, chromatograms, and data system printouts.

B. Objective:

Laboratory performance on individual samples is established by means of spiking activities. All samples are spiked with surrogate compounds prior to sample extraction. The evaluation of the recovery results of these surrogate spikes is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and requires analytical experience and professional judgment. Accordingly, this section consists primarily of guidelines, in some cases with several optional approaches suggested.

C. Criteria:

1. Two surrogate spikes, tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DCB), are added to all samples, including Matrix Spike/Matrix Spike Duplicates (MS/MSDs), Laboratory Control Samples (LCSs), and blanks to measure their recovery. The surrogates are also added to all the standards to monitor Retention Times (RTs).
2. The recovery limits for the surrogates TCX and DCB are 30-150% for all samples, including MS and MSDs, LCSs and all blanks.
3. The RTs of the surrogates in each Performance Evaluation Mixture (PEM), mid-point Individual Standard Mixtures (A and B) or (C) used for continuing calibration verification, all samples (including MS and MSD, LCS), and all blanks must be within the calculated RT Windows. TCX must be within ±0.05 minutes, and DCB must be within ±0.10 minutes of the Mean Retention Time ($\overline{RTs}$) determined from the initial calibration.

D. Evaluation:

1. Check the raw data (e.g., chromatograms and data system printouts) to verify the recoveries on the Surrogate Recovery Form (Form II PEST).
2. Check for any calculation or transcription errors; verify that the surrogate recoveries were calculated correctly using the equation in the method.
3. Check the raw data (e.g., chromatograms and data system printouts) to verify that the RTs on Form VIII PEST are accurate and within the RT Windows determined from the initial calibration.
4. Whenever there are two or more analyses for a particular sample, the reviewer must determine which are the most accurate data to report. Considerations include, but are not limited to:
   a. Surrogate recovery (marginal versus gross deviation).
   b. Technical holding times.
   c. Comparison of the values of the target compounds reported in each sample analysis.
   d. Other Quality Control (QC) information, such as surrogate recoveries and/or RTs in blanks and standards.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

If either surrogate spike recovery is outside the acceptance limits, the reviewer must consider the existence of coelution and interference in the raw data and use professional judgment to qualify data, as surrogate recovery problems may not directly apply to target analytes.

1. For any surrogate recovery greater than 200% (see Table 52):
   a. Qualify detected target compounds as "J".
   b. Use professional judgment to qualify non-detected target compounds.
2. For any surrogate recovery greater than 150% and less than or equal to 200%:
   a. Qualify detected target compounds as a "J".
   b. Do not qualify non-detected target compounds.
3. If both surrogate recoveries are greater than or equal to 30%, and less than or equal to 150%, no qualification of the data is necessary.
4. For any surrogate recovery greater than or equal to 10%, and less than 30%:
   a. Qualify detected target compounds as a "J".
   b. Qualify non-detected target compounds as an approximated "UJ".
5. For any surrogate recovery less than 10%, the reviewer should examine the sample chromatogram to assess the qualitative validity of the analysis. If low surrogate recoveries are from sample dilution, professional judgment should be used to determine if the resulting data should be qualified. If sample dilution is not a factor:
   a. Qualify detected target compounds as a "J".
   b. Qualify non-detected target compounds as unusable "R".
6. In the special case of a blank analysis with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. Note, for Contract Laboratory Program Project Officer (CLP PO) action, analytical problems even if this judgment allows some use of the affected data.
7. If surrogate RTs in PEMs, Individual Standard Mixtures, samples, and blanks are outside of the RT Windows, the reviewer must use professional judgment to qualify data.
8. If surrogate RTs are within RT windows, no qualification of the data is necessary.

Table 52. Surrogate Actions for Pesticide Analyses

Criteria	Action*	
	Detected Target Compounds	Non-detected Target Compounds
%R > 200%	J	Use professional judgment
150% < %R ≤ 200%	J	No qualification
30% ≤ %R ≤ 150%	No qualification	
10% ≤ %R < 30%	J	UJ
%R < 10% (sample dilution not a factor)	J	R
%R < 10% (sample dilution is a factor)	Use professional judgment	
RT out of RT window	Use professional judgment	
RT within RT window	No qualification	

* Use professional judgment in qualifying data, as surrogate recovery problems may not directly apply to target analytes.

VII. Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

A. Review Items:

Form III PEST-1, Form III PEST-2, chromatograms, and data system printouts.

NOTE: Data for MS and MSDs will not be present unless requested by the Region.

B. Objective:

Data for MS and MSDs are generated to determine long-term precision and accuracy of the analytical method on the sample matrix and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone cannot be used to evaluate the precision and accuracy of individual samples. However, when exercising professional judgment, this data should be used in conjunction with other available Quality Control (QC) information.

C. Criteria:

1. **If requested**, MS and MSD samples are extracted and analyzed at a frequency of one MS and MSD per 20 or fewer field samples per sample matrix.
2. MS and MSD recoveries should be within the advisory limits provided on Form III PEST-1, Form III PEST-2.
3. Relative Percent Differences (RPDs) between MS and MSD recoveries must be within the advisory limits provided on Form III PEST-1 and Form III PEST-2.

D. Evaluation:

1. Verify that requested MS and MSD samples were analyzed at the requested frequency and that results are provided for each sample.
2. Check the raw data and Form III PEST-1 and Form III PEST-2 to verify that the results for MS and MSD recoveries were calculated and transcribed correctly.
3. Check that the RPDs were calculated correctly.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. No qualification of the data is necessary on MS and MSD data alone. Use professional judgment to use the MS and MSD results in conjunction with other QC criteria to determine the need for some qualification of the data. Table 54 lists the pesticide target compounds that are spiked into samples to test for matrix effects. If any MS and MSD Percent Recovery, or RPD in the pesticides fraction is out of specification, qualify data to include the consideration of the existence of interference in the raw data. Considerations include, but are not limited to (see Table 53):
   a. For any recovery or RPD greater than the upper acceptance limit:
      i. Qualify detected spiked Single Component Pesticide (SCP) target compounds as a "J".
      ii. Do not qualify non-detected spiked SCP target compounds.

b. For any recovery greater than or equal to 20% and less than the lower acceptance limit:

   i. Qualify detected spiked SCP target compounds as a "J".

   ii. Qualify the sample quantitation limit for non-detected spiked SCP target compounds as approximated "UJ".

c. For any recovery less than 20%:

   i. Qualify detected spiked SCP target compounds as a "J".

   ii. Use professional judgment to qualify non-detected spiked SCP target compounds.

d. If recoveries and RPD are within acceptance limits, no qualification of the data is necessary.

2. The data reviewer should first try to determine to what extent the results of the MS and MSD affect the associated sample data. This determination should be made with regard to the MS and MSD sample itself, as well as specific analytes for all samples associated with the MS and MSD.

3. In those instances where it can be determined that the results of the MS and MSD affect only the sample spiked, limit qualification to this sample only. However, it may be determined through the MS and MSD results, that a laboratory is having a systematic problem in the analysis of one or more analytes that affects all associated samples. Use professional judgment to qualify the data from all associated samples.

4. Use professional judgment to determine the need for qualification of detects of non-spiked compounds.

NOTE: Notify the Contract Laboratory Program Project Officer (CLP PO) if a field blank was used for the MS and MSD, unless designated as such by the Region.

Table 53. Matrix Spike/Matrix Spike Duplicate (MS/MSD) Actions for Pesticide Analysis

Criteria	Action	
	Detected Spiked Compounds	Non-detected Spiked Compounds
%R or RPD > Upper Acceptance Limit	J	No qualification
20% ≤ %R < Lower Acceptance Limit	J	UJ
%R < 20%	J	Use professional judgment
Lower Acceptance Limit ≤ %R; RPD ≤ Upper Acceptance Limit	No qualification	

Table 54. Matrix Spike (MS) Recovery and Relative Percent Difference (RPD)

Compound	Percent Recovery Water	RPD Water	Percent Recovery Soil	RPD Soil
gamma-BHC (Lindane)	56 - 123	0 - 15	46 - 127	0 - 50
Heptachlor	40 - 131	0 - 20	35 - 130	0 - 31
Aldrin	40 - 120	0 - 22	34 - 132	0 - 43
Dieldrin	52 - 126	0 - 18	31 - 134	0 - 38
Endrin	56 - 121	0 - 21	42 - 139	0 - 45
4,4'-DDT	38 - 127	0 - 27	23 - 134	0 - 50

VIII. Laboratory Control Samples (LCSs)

A. Review Items:

Form I PEST, Form II PEST-1, Form II PEST-2, Form III PEST-3, Form III PEST-4, LCS chromatograms, and data system printouts.

B. Objective:

Data for LCSs are generated to provide information on the accuracy of the analytical method and laboratory performance.

C. Criteria:

The LCS contains the pesticides target compounds and surrogates listed in Table 55.

Table 55. Pesticides Laboratory Control Sample (LCS) Spike Compounds and Recovery Limits

LCS Spike Compound	Recovery Limits (%)	LCS Spike Compound	Recovery Limits (%)
gamma-BHC	50 - 120	Endosulfan sulfate	50 - 120
Heptachlor epoxide	50 - 150	gamma-Chlordane	30 - 130
Dieldrin	30 - 130	Tetrachloro-m-xylene (surrogate)	30 - 150
4,4'-DDE	50 - 150	Decachlorobiphenyl (surrogate)	30 - 150
Endrin	50 - 120		

NOTE: The recovery limits for any of the compounds in the LCS may be expanded at any time during the period of performance is USEPA determines that the limits are too restrictive.

All samples prepared and analyzed with an LCS that does not meet the technical acceptance criteria in the method will require re-extraction and re-analysis.

D. Evaluation:

Check the raw data (e.g., chromatograms and data system printouts) to verify the recoveries on the Laboratory Control Sample Recovery Forms (Form III PEST-3, Form III PEST-4). For surrogate recoveries check the Surrogate Recovery Forms (Form II PEST-1, Form II PEST-2).

Check for any calculation or transcription errors; verify that the LCS recoveries reported on Form II PEST-1, Form II PEST-2, Form III PEST-3, and Form III PEST-4 are within the Quality Control (QC) limits.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

If the LCS criteria are not met, laboratory performance and method accuracy are in question. Use professional judgment to determine if the data should be qualified or rejected. The following guidance is suggested for qualifying sample data for which the associated LCS does not meet the required criteria.

1. If the LCS recovery criteria are not met, use the LCS results to qualify sample data for the specific compounds that are included in the LCS solution (see Table 56).
   a. If the LCS recovery exceeds the upper acceptance limit, qualify detected target compounds as a "J". Do not qualify non-detected target compounds.
   b. If the LCS recovery is less than the lower acceptance limit, qualify detected target compounds as a "J" and non-detects as unusable "R".
   c. Use professional judgment to qualify data for compounds other than those compounds that are included in the LCS.
   d. Use professional judgment to qualify non-LCS compounds. Take into account the compound class, compound recovery efficiency, analytical problems associated with each compound, and comparability in the performance of the LCS compound to the non-LCS compound.
2. If the LCS recovery is within allowable limits, no qualification of the data is necessary.
3. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if a laboratory fails to analyze an LCS with each Sample Delivery Group (SDG), or if the reviewer has knowledge that a laboratory consistently fails to generate acceptable LCS recoveries.

Table 56. Laboratory Control Sample (LCS) Recovery Actions

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
%R > Upper Acceptance Limit	J	No qualification
%R < Lower Acceptance Limit	J	R
Lower Acceptance Limit $\leq$ %R $\leq$ Upper Acceptance Limit	No qualification	

IX. Regional Quality Assurance (QA) and Quality Control (QC)

A. Review Items:

Form I PEST, chromatograms, data system printouts, Traffic Report/Chain of Custody Record (TR/COC), quantitation reports and other raw data from Regional QA/QC samples.

B. Objective:

Regional QA/QC refers to any QA and/or QC samples initiated by the Region, including field duplicates, Performance Evaluation (PE) samples, blind spikes, and blind blanks. The use of these QA/QC samples are highly recommended (e.g., the use of field duplicates can provide information on sampling precision and sample homogeneity).

C. Criteria:

Criteria are determined by each Region.

1. PE sample frequency may vary.
2. The analytes present in the PE sample must be correctly identified and quantified.

D. Evaluation:

1. Evaluation procedures must follow the Region's Standard Operating Procedure (SOP) for data review. Each Region will handle the evaluation of PE samples on an individual basis. Compare results for PE samples to the acceptance criteria for the specific PE samples, if available.
2. Calculate Relative Percent Difference (RPD) between field duplicates. Provide this information in the Data Review Narrative.

E. Action:

Any action must be in accordance with Regional specifications and the criteria for acceptable PE sample results. Note, for Contract Laboratory Program Project Officer (CLP PO) action, unacceptable results for PE samples.

X. Florisil Cartridge Performance Check

A. Review Items:

Form IX PEST-1, Florisil raw data, chromatograms, and data system printouts.

B. Objective:

The Florisil cartridge cleanup procedure is used to remove matrix interferences from sample extracts prior to analysis. The use of the Florisil cartridge cleanup procedure significantly reduces matrix interferences caused by polar compounds. The performance of each lot of Florisil cartridges used for sample cleanup is checked by running a spiked reagent through a cartridge, and calculating the recoveries of the spiked compounds through the cartridge.

C. Criteria:

1. The performance of each lot of Florisil cartridges used for sample cleanup must be checked at least once, or every six months, whichever is most frequent. The performance of the Florisil cartridges is checked with a spiking solution contain 2,4,5-trichlorophenol and the mid-point concentration of Individual Standard Mixture (A). If calibration with one standard mixture is used, the mid-point concentration of Individual Standard Mixture (C) may also be used.
2. The limits for recovery of the target pesticide compounds and surrogates in the Individual Standard Mixture (A) are 80-120%, and the recovery limit for 2,4,5-trichlorophenol is less than 5%. If Individual Standard Mixture (C) is used, check the limits for recovery for the target compounds and surrogates present in the Individual Standard Mixture (A) only.

D. Evaluation:

1. Check the raw data for the Florisil cartridge performance check analysis and the results on Form IX PEST-1. Verify that there are no calculation or transcription errors.
2. Verify that the percent recoveries of the target pesticides and surrogates in the performance check solution are within 80-120%, and the recovery of 2,4,5-trichlorophenol is less than 5%.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

1. If the Florisil Cartridge Performance Check criteria are not met, examine the raw data for the presence of polar interferences and use professional judgment in qualifying the data as follows (see Table 57):
   a. If the Percent Recovery is greater than 120% for any of the pesticide target compounds in the Florisil Cartridge Performance Check, use professional judgment to qualify detected target compounds. Do not qualify non-detected target compounds.
   b. If the Percent Recovery is greater than or equal to 80% and less than or equal to 120% for all the pesticide target compounds, no qualification of the data is necessary.

c. If the Percent Recovery is greater than or equal to 10% and less than 80% for any of the pesticide target compounds in the Florisil Cartridge Performance Check, qualify detected target compounds with a "J" and non-detected target compounds with an approximated "UJ".

d. If the Percent Recovery is less than 10% for any of the pesticide target compounds in the Florisil Cartridge Performance Check, use professional judgment to qualify detected target compounds and qualify non-detected target compounds as unusable "R".

e. If the Percent Recovery of 2,4,5-trichlorophenol in the Florisil Cartridge Performance Check is greater than or equal to 5%, use professional judgment to qualify detected and non-detected target compounds, considering interference on the sample chromatogram.

2. Note in the Data Review Narrative potential effects on the sample data resulting from the Florisil Cartridge Performance Check analysis not yielding acceptable results.

Table 57. Florisil Cartridge Performance Check Actions

Criteria	Action	
	Detected Associated Compounds	**Non-Detected Associated Compounds**
%R > 120% (pesticide target compounds)	Use professional judgment	No qualification
80% ≤ %R ≤ 120%	No qualification	
10% ≤ %R < 80% (pesticide target compounds)	J	UJ
%R < 10% (pesticide target compounds)	Use professional judgment	R
%R > 5% (2,4,5-trichlorophenol)	Use professional judgment	

XI. Gel Permeation Chromatography (GPC) Performance Check

A. Review Items:

Form IX PEST-2, GPC raw data, chromatograms, and data system printouts.

B. Objective:

GPC is used to remove high molecular weight contaminants that can interfere with the analysis of target analytes. GPC cleanup procedures are checked by adding the GPC calibration mixture to the GPC cleanup columns and setting the appropriate elution window, and verifying the recovery of target compounds through the cleanup procedure by the analysis of a cleanup blank.

C. Criteria:

1. GPC is a mandatory cleanup method for non-aqueous samples and is an optional cleanup method for aqueous samples and sample extracts that contain high molecular weight components that interfere with the analysis of the target analytes.
2. At least once every seven (7) days, the calibration of the GPC unit must be checked by injecting with the GPC continuing calibration verification solution.
3. The GPC calibration is acceptable if the recovery of the pesticides in the GPC continuing calibration verification solution are within 80 to 110%.
    a. Peaks must be observed and symmetrical for all compounds in the calibration solution.
    b. Corn oil and the phthalate peaks exhibit greater than 85% resolution.
    c. The phthalate and methoxychlor peaks exhibit greater than 85% resolution.
    d. Methoxychlor and perylene peaks exhibit greater than 85% resolution.
    e. Perylene and sulfur peaks must not be saturated and should exhibit greater than 90% baseline resolution.
    f. The Retention Time (RT) shift is less than 5% between ultraviolet (UV) traces for bis(2-ethylhexyl)phthalate and perylene.
4. A GPC blank must be analyzed after each GPC calibration and is acceptable if the blank does not exceed the Contract Required Quantitation Limit (CRQL) for any target analytes listed in SOM01.2, Exhibit C - Pesticides, Target Component List and Contract Required Quantitation Limits, available at: http://www.epa.gov/superfund/programs/clp/som1.htm.

D. Evaluation:

1. Verify that there are two UV traces present and that the RT shift for bis(2-ethylhexyl)phthalate and perylene is less than 5%.
2. Verify that the compounds listed in Pesticides Organic Analysis, Section XI.C.3, are present and symmetrical in both UV traces and that the compound pairs meet the minimum resolution requirements.
3. Verify that no target compound in the GPC blank exceeds the CRQL.
4. Check the data from the GPC calibration check analyses and the Form IX PEST-2, and recalculate some of the percent recoveries to verify that the percent recoveries of the pesticides in the matrix

spike solution are within 80 to 110%. The Region may devise other means to compare this information. Check to make sure that no transcription errors have occurred.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. If GPC criteria are not met, examine the raw data for the presence of high molecular weight contaminants. Examine the subsequent sample data for unusual peaks, and use professional judgment in qualifying the data. Notify the Contract Laboratory Program Project Officer (CLP PO) if a laboratory chooses to analyze samples under unacceptable GPC criteria.
2. If the Percent Recovery is less than 10% for the pesticide compounds and surrogates during the GPC calibration check, the non-detected target compounds may be suspect. Use professional judgment to qualify the detected target compounds (see Table 58). Qualify all non-detected target compounds as unusable "R".
3. If the Percent Recovery is greater than or equal to 10% and is less than 80% for any of the pesticide target compounds in the GPC calibration, qualify detected target compounds with a "J" and non-detected target compounds with an approximated "UJ".
4. If the Percent Recovery is greater than or equal to 80% and less than or equal to 110% for all the pesticide target compounds, no qualification of the data is necessary.
5. If high recoveries (i.e., greater than 110%) were obtained for the pesticides and surrogates during the GPC calibration check, use professional judgment to qualify detected target compounds. Do not qualify non-detected target compounds.
6. Note in the Data Review Narrative potential effects on the sample data resulting from the GPC cleanup analyses not yielding acceptable results.

Table 58. Gel Permeation Chromatography (GPC) Performance Check Actions

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
%R < 10% (pesticide target compounds)	Use professional judgment	R
10% ≤ %R < 80%	J	UJ
80% ≤ %R ≤ 110%	No qualification	
%R > 110% (pesticide target compounds)	Use professional judgment	No qualification

XII. Target Compound Identification

A. Review Items:

Form I PEST, Form X PEST-1, Form X PEST-2, chromatograms, and data system printouts.

B. Objective:

Qualitative criteria for compound identification have been established to minimize the number of false positives (reporting a compound present when it is not) and false negatives (not reporting a compound that is present).

C. Criteria:

1. The Retention Times (RTs) of both of the surrogates and reported target compounds in each sample must be within the calculated RT Windows on both columns. Tetrachloro-m-xylene (TCX) must be within ±0.05 minutes of the Mean RT ($\overline{RT}$) determined from the initial calibration and Decachlorobiphenyl (DCB) must be within ±0.10 minutes of the $\overline{RT}$ determined from the initial calibration.
2. The Percent Difference (%D) for the detected mean concentrations of a pesticide target compound between the two Gas Chromatograph (GC) columns must be within the inclusive range of ±25.0.
3. When no analytes are identified in a sample, the chromatograms from the analyses of the sample extract must use the same scaling factor as was used for the low-point standard of the initial calibration associated with those analyses.
4. Chromatograms must display Single Component Pesticides (SCPs) detected in the sample and the largest peak of any multi-component analyte detected in the sample at less than full scale.
5. If an extract must be diluted, chromatograms must display SCPs peaks between 10-100% of full scale, and multi-component analytes between 25-100% of full scale.
6. For any sample, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and also return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of DCB.
7. If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram, and both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

D. Evaluation:

1. Review Form I PEST, the associated raw data (chromatograms and data system printouts) and Form X PEST-1 and Form X PEST-2. Confirm reported detected analytes by comparing the sample chromatograms to the tabulated results and verifying peak measurements and RTs. Confirm reported non-detected analytes by a review of the sample chromatograms. Check the associated blank data for potential interferences (to evaluate sample data for false positives) and check the calibration data for adequate RT Windows (to evaluate sample data for false positives and false negatives).
2. For Toxaphene, compare the RTs and relative peak height ratios of major component peaks the appropriate standard chromatograms.

3. Compare the Toxaphene peaks identified in the sample to determine that the RTs do not overlap with the RTs of any SCPs or with chromatographic interferences from the sample matrix.
4. Check that the Percent Difference results were calculated correctly.

E. Action:

1. If the qualitative criteria for both columns were not met, all target compounds that are reported as detected should be considered non-detected. The reviewer should use professional judgment to assign an appropriate quantitation limit using the following guidance:
   a. If the detected target compound peak was sufficiently outside the pesticide RT Window, the reported values may be a false positive and should be replaced with the sample Contract Required Quantitation Limits (CRQL) value.
   b. If the detected target compound peak poses an interference with potential detection of another target peak, the reported value should be considered and qualified as unusable "R".
2. If the data reviewer identifies a peak in both GC column analyses that falls within the appropriate RT Windows, but was reported as a non-detect, the compound may be a false negative. Use professional judgment to decide if the compound should be included. Note in the Data Review Narrative all conclusions made regarding target compound identification.
3. If the Toxaphene peak RT windows determined from the calibration overlap with SCPs or chromatographic interferences, use professional judgment to qualify the data.
4. If target compounds were detected on both GC columns, and the Percent Difference between the two results is greater than 25.0%, consider the potential for coelution and use professional judgment to decide whether a much larger concentration obtained on one column versus the other indicates the presence of an interfering compound. If an interfering compound is indicated, use professional judgment to determine how best to report, and if necessary, qualify the data.
5. If Toxaphene exhibits a marginal pattern-matching quality, use professional judgment to establish whether the differences are due to environmental "weathering" (i.e., degradation of the earlier eluting peaks relative to the later eluting peaks). If the presence of Toxaphene is strongly suggested, report results as presumptively present "N".

XIII. Gas Chromatograph/Mass Spectrometer (GC/MS) Confirmation

A. Review Items:

Form I PEST, Form X PEST-1, Form X PEST-2, chromatograms, and data system printouts.

B. Objective:

If GC/MS confirmation is required by the Region for all detected Single Component Pesticides (SCPs) and Toxaphene that have at least one individual peak with a sufficient on-column concentration on both columns (greater than or equal to 5.0 ng/µL for SCPs and 125 ng/µL for Toxaphene), GC/MS confirmation for purposes of qualitative identification is required. GC/MS confirmation may be accomplished by one of three general means:

1. Examination of the semivolatile GC/MS library search results [i.e., Tentatively Identified Compound (TIC) data]
2. A second analysis of the semivolatile extract; or
3. Analysis of the pesticide extract, following any solvent exchange and concentration steps that may be necessary.

C. Criteria:

The on-column concentration for any individual peak must be greater than or equal to 5.0 ng/µL for SCPs and greater than or equal to 125 ng/µL for Toxaphene on both GC columns.

D. Evaluation:

Review Form I PEST, the associated raw data (chromatograms and data system printouts) and Form X PEST-1 and Form X PEST-2. Confirm that GC/MS confirmation was required by ensuring that an individual peak has an on-column concentration greater than or equal to 5.0 ng/µL for a SCP and greater than or equal to 125 ng/µL for Toxaphene on both GC columns by looking at the quantitation reports.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. If the quantitative criteria for both columns were met ($\geq$5.0 ng/µL for SCPs and $\geq$125 ng/µL for Toxaphene), determine whether GC/MS confirmation was performed. If it was performed, qualify the data using the following guidance (see Table 59):
   a. If GC/MS confirmation was not required because the quantitative criteria for both columns was not met, but it was still performed, use professional judgment when evaluating the data to decide whether the detect should be qualified with "C".
   b. If GC/MS confirmation was performed, but unsuccessful for a target compound detected by GC/ECD analysis, qualify those detects as "X".

Table 59. Gas Chromatograph/Mass Spectrometer (GC/MS) Confirmation Actions

Criteria	Action
SCP/Toxaphene was confirmed by GC/MS	Detects C
SCP/Toxaphene was not confirmed by GC/MS	Detects X

XIV. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

A. Review Items:

Form I PEST, Form X PEST-1, Form X PEST-2, sample preparation log sheets, chromatograms, Sample Delivery Group (SDG) Narrative, and data system printouts.

B. Objective:

The objective is to ensure that the reported quantitative results, CRQLs, and Percent Moisture determination (for non-aqueous samples) are accurate.

C. Criteria:

Compound quantitation, as well as the adjustment of the CRQL, must be calculated according to the equations provided in the method.

D. Evaluation:

1. Examine raw data to verify the correct calculation of all sample results reported by the laboratory. Compare data system printouts, chromatograms, and sample preparation log sheets to the reported detects and non-detects sample results. Verify that the sample values are reported correctly.
2. Verify that the CRQLs have been adjusted to reflect all sample dilutions, cleanup activities, Percent Moisture factors (for non-aqueous samples) and other factors that are not accounted for by the method.

E. Action:

1. Qualify non-detect results affected by large, off-scale peaks as unusable "R". If the interference is on-scale, the reviewer can provide an approximated quantitation limit "UJ" for each affected compound.
2. For non-aqueous samples, if the Percent Moisture is less than 70.0%, no qualification of the data is necessary (see Table 60). If the Percent Moisture is greater than or equal to 70.0% and less than 90.0%, qualify detects as "J" and non-detects as "UJ". If the Percent Moisture is greater than or equal to 90.0%, qualify detects as "J" and non-detects as unusable "R".
3. If there are any discrepancies found, the Region's designated representative may contact the laboratory to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, the reviewer must decide which value is the best value. Under these circumstances, the reviewer may determine if qualification of the data is warranted. Note in the Data Review Narrative a description of the reasons for data qualification and the qualification that is applied to the data.

Table 60. Percent Moisture Actions for Pesticides Analyses for Non-Aqueous Samples

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
%Moisture < 70.0%	No qualification	
70.0% ≤ %Moisture < 90.0%	J	UJ
%Moisture ≥ 90.0%	J	R

XV. Overall Assessment of Data

A. Review Items:

Entire data package, data review results, and (if available) Quality Assurance Project Plan (QAPP), and Sampling and Analysis Plan (SAP).

B. Objective:

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria:

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation:

1. Evaluate any technical problems which have not been previously addressed.
2. If appropriate information is available, the reviewer may assess the usability of the data to help the data user in avoiding inappropriate use of the data. Review all available information, including the QAPP (specifically the acceptance or performance criteria), SAP, and communication with data user that concerns the intended use and desired quality of these data.

E. Action:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the Quality Control (QC) criteria previously discussed.
2. Write a brief narrative to give the user an indication of the analytical limitations of the data. Note, for Contract Laboratory Program Project Officer (CLP PO) action, any inconsistency of that data with the Sample Delivery Group (SDG) Narrative. If sufficient information on the intended use and required quality of the data are available, include an assessment of the usability of the data within the given context. This may be used as part of a formal Data Quality Assessment (DQA).

AROCLOR DATA REVIEW

The Aroclor data requirements to be checked are:

I. Preservation

II. Initial Calibration

III. Continuing Calibration Verification (CCV)

IV. Blanks

V. Surrogate Spikes

VI. Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

VII. Laboratory Control Samples (LCSs)

VIII. Regional Quality Assurance (QA) and Quality Control (QC)

IX. Gel Permeation Chromatography (GPC) Performance Check

X. Target Compound Identification

XI. Gas Chromatograph/Mass Spectrometer (GC/MS) Confirmation

XII. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

XIII. Overall Assessment of Data

I. Preservation

A. Review Items:

Form I ARO, Traffic Report/Chain of Custody Record (TR/COC), raw data, sample extraction sheets, and Sample Delivery Group (SDG) Narrative checking for:

1. pH
2. Sample temperature
3. Holding time
4. Other sample conditions

B. Objective:

The objective is to ascertain the validity of the analytical results based on sample condition (e.g., preservation and temperature) and the holding time of the sample from time of collection to time of sample extraction and analysis.

C. Criteria:

The technical holding time criteria for aqueous samples are as follows:

> For Aroclors in properly cooled (4°C ± 2°C) aqueous samples, the maximum holding time for extraction is seven (7) days from sample collection, and the maximum holding time for analysis is 40 days from sample extraction.

The technical holding time criteria for non-aqueous samples are as follows:

> For Aroclors in properly cooled (4°C ± 2°C) non-aqueous samples, the maximum holding time is 14 days from sample collection, and the maximum holding time for analysis is 40 days from sample extraction.

D. Evaluation:

Technical holding times for sample extraction are established by comparing the sample collection dates on the TR/COC Record with the dates of extraction on Form I ARO and the sample extraction sheets. Information contained in the Complete SDG File (CSF) should also be considered in the determination of holding times. To determine if the samples were analyzed within the holding time after extraction, compare the dates of extraction on the sample extraction sheets with the dates of analysis on Form I ARO. Verify that the analysis dates on Form I(s) and the raw data/SDG File are identical. Review the SDG Narrative and the TR/COC Record to determine if the samples were received intact and iced. If there is no indication in the SDG Narrative, the TR/COC Record, or the sample records that there was a problem with the samples, assume the integrity of the samples to be acceptable. If it is indicated that there were problems with the samples, the integrity of the sample may have been compromised; use professional judgment to evaluate the effect of the problem on the sample results.

E. Action:

1. Qualify aqueous sample results using preservation and technical holding time information as follows (see Table 61):

   a. If there is no evidence that the samples were properly preserved (e.g., if the sample temperature has exceeded the allowable limits or if the integrity of the sample has been compromised), and the samples were extracted or analyzed within the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], use professional judgment to qualify the data.

   b. If there is no evidence that the samples were properly preserved (e.g., if the sample temperature has exceeded the allowable limits or if the integrity of the sample has been compromised), and the samples were extracted or analyzed outside the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], use professional judgment to qualify the data.

   c. If the samples were properly preserved, and were extracted and analyzed within the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], no qualification of the data is necessary.

   d. If the samples were properly preserved, and were extracted or analyzed outside the technical holding times [seven (7) days from sample collection for extraction; 40 days from sample collection for analysis], qualify detects with a "J" and non-detects as estimated with an approximated "UJ" or unusable "R". Note in the Data Review Narrative that holding times were exceeded and the effect of exceeding the holding time on the resulting data.

2. Qualify non-aqueous sample results using preservation and technical holding time information as follows (see Table 61):

   a. If there is no evidence that the samples were properly preserved (e.g., if the sample temperature has exceeded the allowable limits or if the integrity of the sample has been compromised), and the samples were extracted or analyzed within the technical holding times [14 days from collection for extraction; 40 days from sample collection for analysis], use professional judgment to qualify the data.

   b. If there is no evidence that the samples were properly preserved (e.g., if the sample temperature has exceeded the allowable limits or if the integrity of the sample has been compromised), and the samples were extracted or analyzed outside the technical holding times [14 days from sample collection for extraction; 40 days from sample collection for analysis], use professional judgment to qualify the data.

   c. If the samples were properly preserved, and were extracted and analyzed within the technical holding times [14 days from sample collection for extraction; 40 days from sample collection for analysis], no qualification of the data is necessary.

   d. If the samples were properly preserved, and were extracted or analyzed outside the technical holding times [14 days from sample collection for extraction; 40 days from sample collection for analysis], qualify detects with a "J" and non-detects as estimated with an approximated "UJ" or unusable "R". Note in the Data Review Narrative that holding times were exceeded and the effect of exceeding the holding time on the resulting data.

3. Use professional judgment to qualify samples whose temperature upon receipt at the laboratory is either below 2 degrees centigrade or above 6 degrees centigrade.

4. If technical holding times are grossly exceeded, qualify all detects as estimated with a "J" and use professional judgment to qualify sample non-detects.

5. Note in the Data Review Narrative, whenever possible, the effect of exceeding the holding time on the resulting data.
6. Note, for Contract Laboratory Program Project Officer (CLP PO) action, when technical holding times are grossly exceeded.

Table 61. Holding Time Actions for Aroclor Analysis

Matrix	Preserved	Criteria	Action	
			Detected Associated Compounds	Non-Detected Associated Compounds
Aqueous	No	≤ 7 days (for extraction) and ≤ 40 days (for analysis)	Use professional judgment	
	No	> 7 days (for extraction) and > 40 days (for analysis)	Use professional judgment	
	Yes	≤ 7 days (for extraction) and ≤ 40 days (for analysis)	No qualification	
	Yes	> 7 days (for extraction) and > 40 days (for analysis)	J	UJ
	Yes/No	Grossly Exceeded	J	UJ or R
Non-aqueous	No	≤ 14 days (for extraction) and ≤ 40 days (for analysis)	Use professional judgment	
	No	> 14 days (for extraction) and > 40 days (for analysis)	Use professional judgment	
	Yes	≤ 14 days (for extraction) and ≤ 40 days (for analysis)	No qualification	
	Yes	> 14 days (for extraction) and > 40 days (for analysis)	J	UJ
	Yes/No	Grossly Exceeded	J	UJ or R

II. Initial Calibration

A. Review Items:

Form VI ARO-1, Form VI ARO-2, Form VI ARO-3, chromatograms, and data system printouts.

B. Objective:

Compliance requirements for satisfactory initial calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for Aroclor compounds on the Target Compound List (TCL). Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analytical sequence, and capable of producing a linear calibration curve.

C. Criteria:

1. An initial five-point calibration is performed using Aroclors 1016 and 1260 to demonstrate the linearity of the detector response. These Aroclors may be analyzed in a single standard mixture. The other seven Aroclors, 1221, 1232, 1242, 1248, 1254, 1262 or 1268, are calibrated at a single mid-point for pattern recognition. If Aroclors 1221, 1232, 1242, 1248, 1254, 1262 or 1268 are detected in a sample, a five-point initial calibration is required for the detected Aroclor.

   a. The Mean Retention Times ($\overline{RT}$s) of each of the three to five major peaks of Aroclors 1016 and 1260 and the Retention Time (RT) of the surrogates are determined from the five-point initial calibration. For the other seven Aroclors, 1221, 1232, 1242, 1248, 1254, 1262 or 1268, the $\overline{RT}$s of each of the three to five major peaks and the RT of the surrogates are determined from the single-point standard initial calibration. If Aroclors 1221, 1232, 1242, 1248, 1254, 1262 or 1268, are detected in a sample, the $\overline{RT}$s of each of the three to five major peaks and the RT of the surrogates are determined from the five-point initial calibration.

   b. An RT Window must be calculated as ±0.07 for each of the three to five Aroclor peaks and ±0.05 and ±0.10 for the surrogates tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DCB) respectively.

   c. At least one chromatogram from each of the Aroclor Standards must yield peaks that give recorder deflections between 50-100% of full scale.

   d. The concentrations of the five concentration level standards containing the Aroclors should be prepared at the following concentrations 100; 200; 400; 800; and 1600 ng/mL and surrogates at 5.0, 10, 20, 40 and 80 ng/mL for TCX and 10, 20, 40, 80 and 160 ng/mL for DCB.

   e. Mean Calibration Factor ($\overline{CF}$) must be calculated for the three to five major peaks of each Aroclor, as well as for the surrogates, over the initial calibration range.

   f. The Percent Relative Standard Deviation (%RSD) of the Calibration Factors (CFs) for the three to five major peaks of each of the Aroclor compounds must be less than or equal to 20.0%. The Percent RSD of the CFs for the two surrogates must be less than or equal to 20.0%.

      NOTE: Either peak area or peak height may be used to calculate the CFs that are, in turn, used to calculate %RSD. However, the type of peak measurement used to calculate each CF for a given compound must be consistent. For example, if peak area is used to calculate the CS1 CF for a given peak of a certain Aroclor, the remaining CFs for the same peak in the remaining standards (CS2-CS5) for that Aroclor must also be calculated using peak area.

2. Initial Calibration Sequence

The initial calibration must be performed following a specific sequence (see Table 62).

Table 62. Initial Calibration Sequence

Initial Calibration Sequence	
1.	Aroclor 1221 CS3
2.	Aroclor 1232 CS3
3.	Aroclor 1242 CS3
4.	Aroclor 1248 CS3
5.	Aroclor 1254 CS3
6.	Aroclor 1262 CS3
7.	Aroclor 1268 CS3
8.	Aroclor 1016/1260 (100 ng/mL) CS1
9.	Aroclor 1016/1260 (200 ng/mL) CS2
10.	Aroclor 1016/1260 (400 ng/mL) CS3
11.	Aroclor 1016/1260 (800 ng/mL) CS4
12.	Aroclor 1016/1260 (1600 ng/mL) CS5
13.	Instrument blank

D. Evaluation:

1. Check the raw data (chromatograms and data system printouts) for each standard to verify that each of the standards was analyzed at the required concentration levels.
2. Check the Aroclor Standards data and Form VI ARO-1 and Form VI ARO-3 and review the calculated RT Windows for calculation and transcription errors.
3. Check the chromatograms and verify that at least one chromatogram from each of the Aroclor Standards yields peaks registering recorder/printer deflections between 25-100% of full scale.
4. Verify that the concentrations of the Aroclor Standards meet the criteria defined in Aroclors Organic Analysis, Section II.C.1.d.
5. Check the Aroclor Standards data and Form VI ARO-2 to verify that the %RSD for the CFs are in compliance with the criteria defined in Aroclors Organic Analysis, Section II.C.
6. Check and recalculate the CFs and %RSD for one or more Aroclors. Verify that the recalculated values agree with the reported values. If errors are detected, more comprehensive recalculation and review should be performed.
7. Verify that if Aroclors 1221, 1232, 1242, 1248, 1254, 1262, or 1268 were detected in a sample, a valid 5-point calibration for that Aroclor using proper concentrations was performed.
8. Verify that the steps of initial calibration are followed in the proper sequence defined in Table 62.

E. Action:

1. If the proper initial calibration sequence is not performed, or the steps of the initial calibration are not followed in the proper sequence, use professional judgment to evaluate the effect on the data and notify the Contract Laboratory Program Project Officer (CLP PO) (see Table 63). This is especially critical for the low-level standards and non-detects.
2. If RT Windows are not calculated correctly, recalculate the windows and use the corrected values for all evaluations.
3. If the chromatogram display (recorder deflection) criteria are not met, use professional judgment to evaluate the effect on the data.
4. If the standard concentration criteria are not met, use professional judgment to evaluate the effect on the data and notify the CLP PO. This is especially critical for the low-level standards and non-detects.
5. If the %RSD criteria are not met, qualify detects with a "J" and non-detected target compounds with an approximated "UJ".
6. If the %RSD criteria are within allowable limits, no qualification of the data is necessary.
7. At the reviewer's discretion, and based on the project-specific data quality objectives, consider a more in-depth review using the following guidelines:
    a. If any Aroclor peak has a %RSD greater than the maximum criterion, and if eliminating either the high or the low-point of the curve does not restore the %RSD to less than or equal to the required maximum:
        i. Qualify detects for that Aroclor with a "J".
        ii. Qualify non-detected Aroclor using professional judgment.
    b. If the high-point of the curve is outside of the linearity criteria (e.g., due to saturation):
        i. No qualifiers are required for detects in the linear portion of the curve.
        ii. Qualify detects outside of the linear portion of the curve with a "J".
        iii. No qualifiers are needed for Aroclors that were not detected.
    c. If the low-point of the curve is outside of the linearity criteria:
        i. No qualifiers are required for detects in the linear portion of the curve.
        ii. Qualify low-level detects in the area of non-linearity with a "J".
        iii. For non-detected Aroclors, use the lowest point of the valid curve to determine the new quantitation limit.
8. Note in the Data Review Narrative potential effects on the sample data due to problems with calibration. Notify the CLP PO if the laboratory has repeatedly failed to comply with the requirements for frequency, linearity, RT, or resolution.

Table 63. Initial Calibration Action for Aroclor Analyses

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
Initial calibration is not performed or not performed in the proper sequence	Use professional judgment	
%RSD exceeds allowable limits*	J	UJ
%RSD within allowable limits*	No qualification	

* %RSD $\leq$ 20.0% for Aroclors.
%RSD $\leq$ 20.0% for surrogates (tetrachloro-m-xylene and decachlorobiphenyl).

III. Continuing Calibration Verification (CCV)

A. Review Items:

Form VII ARO-1, chromatograms, and data system printouts.

B. Objective:

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data. CCV checks and documents satisfactory performance of the instrument over specific time periods during sample analysis. To confirm the calibration and evaluate instrument performance, CCV is performed, consisting of the analyses of instrument blanks, and the mid-point concentration (CS3) of Aroclor standards. A CCV must be performed at the beginning (opening CCV) and end (closing CCV) of the analytical sequence. The opening and closing CCVs consist of an injection of an instrument blank followed by an injection of mid-point concentration (CS3) of Aroclor 1016/1260 Standard Mixture. If an Aroclor other than 1016 or 1260 is detected in any samples, that Aroclor must have a mid-point concentration (CS3) standard analyzed as part of the opening and closing CCV.

C. Criteria:

1. The Absolute Retention Time (RT) for each Aroclor and surrogate in the mid-point concentration (CS3) of the Aroclor Standards used for CCV must be within the RT Windows determined from the initial calibration.
2. For the opening CCV, or closing CCV that is used as an opening CCV for the next 12-hour period, the Percent Difference (%D) between the CF of each of the three to five peaks used to identify an Aroclor and surrogates in the mid-point concentration (CS3) of the Aroclor Standards and the CF from the initial calibration must be within ±15.0%.
3. For a closing CCV, the Percent Difference between the CF of each of the three to five peaks used to identify an Aroclor and surrogates in the mid-point concentration (CS3) of the Aroclor Standards and the CF from the initial calibration must be within ±50.0%.
4. No more than 14 hours may elapse from the injection of the instrument blank that begins an analytical sequence (opening CCV) and the injection of the last mid-point concentration (CS3) of the Aroclor Standards that ends an analytical sequence (closing CCV).
5. No more than 12 hours may elapse from the injection of the instrument blank that begins an analytical sequence (opening CCV) and the injection of the last sample or blank that is part of the same analytical sequence.

D. Evaluation:

1. Check the data for each of the Aroclors and surrogates in the mid-point concentration (CS3) of the Aroclor Standards on Form VII ARO-1 to verify that the Absolute RTs are within the RT Windows.
2. For an opening CCV, or closing CCV that is used as an opening CCV for the next analytical sequence, check the data for each of the Aroclors and surrogates in the mid-point concentration (CS3) of the Aroclor Standards on Form VII ARO-1 to verify that the Percent Difference between the CF of each of the three to five peaks used to identify an Aroclor and surrogates in the mid-point concentration (CS3) of the Aroclor Standards and the CF from the initial calibration is within ±15.0%.

3. For a closing CCV, check the data for each of the Aroclors and surrogates in the mid-point concentration (CS3) of the Aroclor Standards on Form VII ARO-1 to verify that the Percent Difference between the CF of each of the three to five peaks used to identify an Aroclor and surrogates in the mid-point concentration (CS3) of the Aroclor Standards and the CF from the initial calibration is within ±50.0%.
4. Check the length of time that has elapsed from the beginning injection of the instrument that belongs to the opening CCV and the ending injection of the last Aroclor Standard that is part of the closing CCV to verify that no more than 14 hours has elapsed.
5. Check the length of time that has elapsed from the beginning injection of the instrument blank that belongs to the opening CCV (instrument blank) and the injection of the last sample or method blank to verify that no more than 12 hours has elapsed.

E. Action:

1. RT Windows are used in qualitative identification. If the standards do not fall within the RT Windows, use professional judgment to evaluate the associated sample results (see Table 64). All samples injected after the last in-control standard are potentially affected.
   a. For non-detected target compounds in the affected samples, check to see if the sample chromatograms contain any peaks that are close to the expected RT Window of the Aroclor of interest.
      i. If no peaks are present, consider the non-detected values to be valid and no qualification of the data is necessary.
      ii. If any peaks are present close to the expected RT Window of the Aroclor of interest, qualify the non-detected values as presumptively present "N".
   b. For detected compounds in the affected samples, if the peaks are within the RT Window, no qualification of the data is necessary. If the peaks are close to the expected RT Window of the Aroclor of interest, the reviewer may take additional effort to determine if sample peaks represent the compounds of interest.

      For example, the reviewer can examine the data package for the presence of three or more standards containing the Aroclor of interest that were run within the analytical sequence during which the sample was analyzed. If three or more such standards are present, the RT Window can be re-evaluated using the Mean Retention Times ($\overline{RT}s$) of the standards.
      i. If the peaks in the affected sample fall within the revised window, qualify the detected target compounds as "NJ".
      ii. If the reviewer cannot do anything with the data to resolve the problem of concern, qualify all non-detects as unusable "R".
2. If the Percent Difference is not within ±15% as specified in Aroclors Organic Analysis, Section III.C.2, qualify associated detects with a "J" and non-detects with an approximated "UJ".
3. If the Percent Difference is not within ±50% as specified in Aroclors Organic Analysis, Section III.C.3, qualify associated detects with a "J" and non-detects with an approximated "UJ".
4. If more than 14 hours has elapsed as defined in Aroclors Organic Analysis, Section III.C.4, qualify associated as unusable "R".
5. If more than 12 hours has elapsed as defined in Aroclors Organic Analysis, Section III.C.5, qualify associated data as unusable "R".

6. If RT, Percent Difference, and time elapsed are within acceptable limits, no qualification of the data is necessary.
7. Note in the Data Review Narrative potential effects on the sample data due to problems with calibration.

Table 64. Continuing Calibration Verification (CCV) Action for Aroclor Analyses

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
RT out of RT window	Use professional judgment (see Aroclors, Section III.E.1)	
Percent Difference not within ±15% as specified in Aroclors, Section IV.C.2	J	UJ
Percent Difference not within ±50% as specified in Aroclors, Section IV.C.3	J	UJ
Time elapsed is greater than acceptable limits as defined in Aroclors, Sections IV.C.4, and C.5	R	
RT, Percent Difference, time elapsed are within acceptable limits	No qualification	

IV. Blanks

A. Review Items:

Form I ARO, Form IV ARO, chromatograms, and data system printouts.

B. Objective:

The purpose of laboratory or field blank analyses is to determine the existence and magnitude of contamination resulting from laboratory, field, or sample transport activities. The purpose of the method blank is to determine the level of contamination associated with the processing and analysis of samples. The results from the instrument blank indicate whether there is contamination from a previous sample. The purpose of the sulfur cleanup blank is to determine the level of contamination associated with the sulfur cleanup process. The criteria for evaluation of laboratory blanks apply to any blank associated with the samples (e.g., method blanks, sulfur cleanup blanks, instrument blanks, and field blanks). If problems with any blank exist, evaluate all associated data carefully to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting other data.

C. Criteria:

1. Method Blanks

   A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples [excluding Matrix Spike/Matrix Spike Duplicate (MS/MSDs), Performance Evaluation (PE) samples, and Laboratory Control Samples (LCSs)]. In addition, a method blank shall be extracted by the same procedure used to extract samples and be analyzed on the same Gas Chromatograph/Electron Capture Detector (GC/ECD) system used to analyze associated samples.

2. Instrument Blanks

   An acceptable instrument blank must be run at the end of the initial calibration sequence. An acceptable instrument blank must be run at the beginning and ending of an analytical sequence in which samples are analyzed, immediately prior to the analysis of the mid-point concentration (CS3) Aroclor Standard 1016/1260 Mixture, used for continuing calibration verification. All groups of acceptable sample analyses are to be preceded and followed by acceptable instrument blanks.

3. Sulfur Cleanup Blanks

   A sulfur cleanup blank must be analyzed whenever part of a set of samples extracted together requires sulfur cleanup. If the entire set of samples associated with a method blank requires sulfur cleanup, the method blank also serves the purpose of a sulfur blank and no separate sulfur blank is required.

   The concentration of each target analyte in the method, sulfur cleanup, instrument blanks, and field blanks must be less than its Contract Required Quantitation Limits (CRQL) listed in the method.

D. Evaluation:

1. Review the results of all associated blanks, Form I ARO, Form IV ARO, and raw data (chromatograms and data system printouts) to evaluate the presence of target or non-target analytes in the blanks.

2. Verify that a method blank analysis has been reported per Sample Delivery Group (SDG), per extraction batch, and per extraction procedure. The reviewer can use Form IV ARO to identify samples associated with each blank.
3. Verify that the method blank analysis(es) contains less than the CRQL of any target Aroclor or any interfering peak.
4. Verify that the instrument blank analysis has been performed at the beginning and end of every 12-hour period in which samples were analyzed, immediately before the analysis of the mid-point concentration (CS3) Aroclor Standard 1016/1260 Mixture or Aroclor of interest detected in a sample. Evaluate the results from the various instrument blanks to verify that target analyte concentrations are less than the CRQL (assuming a 1 L extraction of an aqueous sample).
5. Verify that the sulfur cleanup blanks were analyzed at the required frequency and the sulfur blanks do not contain any target compounds greater than or equal to the CRQL (assuming a 1 L extraction of an aqueous sample and 30g of a non-aqueous sample). If a separate sulfur cleanup blank was prepared, one version of Form IV ARO should be completed associating all the samples with the method blank, and a second version of Form IV ARO should be completed listing only those samples associated with the separate sulfur cleanup blank.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process. Data concerning the field blanks are not evaluated as part of the CCS process. If field blanks are present, the data reviewer should evaluate this data in a similar fashion as the method blanks.

E. Action:

Action regarding unsuitable blank results depends on the circumstances and the origin of the blank. In instances where more than one of the same type of blank is associated with a given sample, base qualification upon a comparison with the associated blank having the highest concentration of a contaminant. Do not correct the results by subtracting the blank value.

1. If a target Aroclor compound is found in the blank but not found in the sample, no qualification is required (see Table 65).
2. If a target Aroclor compound concentration in a blank is less than the CRQL, and:
   a. the sample concentration is less than the CRQL, report the CRQL value with a "U".
   b. the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.
3. If a target Aroclor compound concentration in a blank is greater than the CRQL, and:
   a. the sample concentration is less than the CRQL, report the CRQL value with a "U".
   b. the sample concentration is greater than or equal to the CRQL, and less than the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank with a "U", or the reviewer may elect to qualify the data as unusable "R".
   c. the sample concentration is greater than or equal to the CRQL, and greater than or equal to the blank concentration, use professional judgment to qualify the data.
4. If a target Aroclor compound concentration in a blank is equal to the CRQL, and:
   a. the sample concentration is less than the CRQL, report the CRQL value with a "U".

b. the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.

5. If gross contamination exists (e.g., saturated peaks, "hump-o-grams", "junk" peaks), all affected compounds in the associated samples should be qualified as unusable "R", due to interference. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if the contamination is suspected of having an effect on the sample results.

6. There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample is deemed necessary. If the reviewer determines that the contamination is from a source other than the sample, they should qualify the data. Contamination introduced through dilution is one example. Although it is not always possible to determine, instances of this occurring can be detected when contaminants are found in the diluted sample result, but absent in the undiluted sample result.

7. If contaminants are found in the field blanks, the following is recommended:

   a. Review the associated method blank data to determine if the contaminant(s) was also present in the method blank. If the analyte was present at a comparable level in the method blank, the source of the contamination may be in the analytical system and the action recommended for the method blank would apply.

      If the analyte was not present in the method blank, the source of contamination may have occurred in the field or during sample transport. Consider all associated samples for possible cross-contamination.

   b. If the field blank contains an Aroclor Target Compound List (TCL) compound(s) at a concentration greater than the CRQL and:

      i. the sample concentration is less than the CRQL, report the CRQL value with a "U".

      ii. the sample concentration is greater than or equal to the CRQL, and less than the blank concentration, report the concentration of the compound in the sample at the same concentration found in the blank and qualify with a "U", or use professional judgment to qualify the data as unusable "R".

      iii. the sample concentration is greater than the CRQL and greater than or equal to the blank concentration, use professional judgment to qualify the data.

   c. If gross contamination (e.g., saturated peaks, "hump-o-grams", "junk" peaks) exists in the storage or field blank, positive sample results may require rejection. Qualify as unusable "R". Non-detected Aroclor target compounds do not require qualification unless the contamination is so high that it interferes with the analyses of non-detected compounds.

   d. If the field blank contains an Aroclor volatile TCL compound(s) at a concentration less than the CRQL and:

      i. the sample concentration is less than the CRQL, report the CRQL value with a "U".

      ii. the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.

   e. If the field blank contains an Aroclor TCL compound(s) at a concentration equal to the CRQL and:

      i. the sample concentration is less than the CRQL, report the CRQL value with a "U".

      ii. the sample concentration is greater than or equal to the CRQL, use professional judgment to qualify the data.

Table 65. Blank Actions for Aroclor Analyses

Blank Type	Blank Result	Sample Result	Action for Samples
Method, Sulfur Cleanup, Instrument, Field	Detects	Not detected	No qualification
	< CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL	Use professional judgment
	> CRQL	< CRQL	Report CRQL value with a U
		≥ CRQL and < blank concentration	Report the blank concentration for the sample with a U, or qualify the data as unusable R
		≥ CRQL and ≥ blank concentration	Use professional judgment
	= CRQL	< CRQL	Report CRQL values with a U
		≥ CRQL	Use professional judgment
	Gross contamination	Detects	Qualify results as unusable R

V. Surrogate Spikes

A. Review Items:

Form II ARO-1, Form II ARO-2, Form VIII ARO, chromatograms, and data system printouts.

B. Objective:

Laboratory performance on individual samples is established by means of spiking activities. All samples are spiked with surrogate compounds prior to sample extraction. The evaluation of the recovery results of these surrogate spikes is not necessarily straightforward. The sample itself may produce effects due to such factors as interferences. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present relatively unique problems, the evaluation and review of data based on specific sample results is frequently subjective and requires analytical experience and professional judgment. Accordingly, this section consists primarily of guidelines, in some cases with several optional approaches suggested.

C. Criteria:

1. Two surrogate spikes, tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DCB), are added to all samples, including Matrix Spike/Matrix Spike Duplicates (MS/MSDs), Laboratory Control Samples (LCSs) and blanks to measure their recovery. The surrogates are also added to all the standards to monitor Retention Times (RTs).
2. The recovery limits for the surrogates TCX and DCB are 30-150% for all samples, including MS and MSDs, LCSs and all blanks.
3. The RTs of the surrogates in each Performance Evaluation Mixture (PEM), mid-point Aroclor standards used for continuing calibration verification, all samples [including MS and MSD, LCS, and Performance Evaluation (PE) samples] and all blanks must be within the calculated RT Windows. TCX must be within ±0.05 minutes, and DCB must be within ±0.10 minutes of the Mean Retention Time ($\overline{RT}$) determined from the initial calibration.

D. Evaluation:

1. Check the raw data (e.g., chromatograms and data system printouts) to verify the recoveries on the Surrogate Recovery Form (Form II ARO).
2. Check for any calculation or transcription errors; verify that the surrogate recoveries were calculated correctly using the equation in the method.
3. Check the raw data (e.g., chromatograms and data system printouts) to verify that the RTs on Form VIII ARO are accurate and within the RT Windows determined from the initial calibration.
4. Whenever there are two or more analyses for a particular sample, the reviewer must determine which are the most accurate data to report. Considerations include, but are not limited to:
   a. Surrogate recovery (marginal versus gross deviation).
   b. Technical holding times.
   c. Comparison of the values of the target compounds reported in each sample analysis.
   d. Other Quality Control (QC) information, such as surrogate recoveries and/or RTs in blanks and standards.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

If either surrogate spike recovery is outside the acceptance limits, consider the existence of coelution and interference in the raw data and use professional judgment to qualify data, as surrogate recovery problems may not directly apply to target analytes.

1. For any surrogate recovery greater than 200% (see Table 66):
   a. Qualify detected target compounds are qualified as "J".
   b. Use professional judgment to qualify non-detected target compounds.
2. For any surrogate recovery greater than 150%, and less than or equal to 200%:
   a. Qualify detected target compounds are qualified as a "J".
   b. Do not qualify non-detected target compounds.
3. If both surrogate recoveries are greater than or equal to 30% and less than or equal to 150%, no qualification of the data is necessary.
4. For any surrogate recovery greater than or equal to 10% and less than 30%:
   a. Qualify detected target compounds as a "J".
   b. Qualify non-detected target compounds as an approximated "UJ".
5. For any surrogate recovery less than 10%, the reviewer should examine the sample chromatogram to assess the qualitative validity of the analysis. If low surrogate recoveries are from sample dilution, use professional judgment to determine if the resulting data should be qualified. If sample dilution is not a factor:
   a. Qualify detected target compounds as a "J".
   b. Qualify non-detected target compounds as unusable "R".
6. In the special case of a blank analysis with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. The basic concern is whether the blank problems represent an isolated problem with the blank alone, or whether there is a fundamental problem with the analytical process. For example, if one or more samples in the batch show acceptable surrogate recoveries, the reviewer may choose to consider the blank problem to be an isolated occurrence. Note, for Contract Laboratory Program Project Officer (CLP PO) action, analytical problems even if this judgment allows some use of the affected data.
7. If surrogate RTs in PEMs, mid-point Aroclor standards used for Continuing Calibration Verification (CCV), samples, and blanks are outside of the RT Windows, use professional judgment to qualify data.
8. If surrogate RTs are within the RT windows, no qualification is necessary.

Table 66. Surrogate Actions for Aroclor Analyses

Criteria	Action*	
	Detected Target Compounds	Non-detected Target Compounds
%R > 200%	J	Use professional judgment
150% < %R ≤ 200%	J	No qualification
30% ≤ %R ≤ 150%	No qualification	
10% ≤ %R < 30%	J	UJ
%R < 10% (sample dilution not a factor)	J	R
%R < 10% (sample dilution is a factor)	Use professional judgment	
RT out of RT window	Use professional judgment	
RT within RT window	No qualification	

* Use professional judgment in qualifying data, as surrogate recovery problems may not directly apply to target analytes.

VI. Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

A. Review Items:

Form III ARO-1, Form III ARO-2, chromatograms, and data system printouts.

NOTE: Data for MS and MSDs will not be present unless requested by the Region.

B. Objective:

Data for MS and MSDs are generated to determine long-term precision and accuracy of the analytical method on the sample matrix and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone cannot be used to evaluate the precision and accuracy of individual samples. However, when exercising professional judgment, use this data in conjunction with other available Quality Control (QC) information.

C. Criteria:

1. **If requested**, MS and MSD samples are extracted and analyzed at a frequency of one MS and MSD per 20 or fewer field samples.
2. MS and MSD recoveries should be within the advisory limits provided on Form III ARO-1.
3. Relative Percent Difference (RPD) between MS and MSD recoveries should not exceed the advisory limits provided on Form III ARO-1.

D. Evaluation:

1. Verify that requested MS and MSD samples were analyzed at the requested frequency and that results are provided for each sample.
2. Check the raw data and Form III ARO-1 to verify that the results for MS and MSD recoveries were calculated and transcribed correctly.
3. Check that the RPD was calculated correctly.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with this criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

1. No qualification of the data is necessary on MS and MSD data alone. Use professional judgment to use the MS and MSD results in conjunction with other QC criteria to determine the need for some qualification of the data. Table 68 lists the Aroclor target analytes that are spiked into samples to test for matrix effects. If any MS and MSD, Percent Recovery, or RPD in the Aroclor fraction is out of specification, qualify data to include the consideration of the existence of interference in the raw data. Considerations include, but are not limited to (see Table 67):
    a. For any recovery or RPD greater than the upper acceptance limit:
        i. Qualify detected spiked Aroclor target compounds as a "J".
        ii. Do not qualify non-detected Aroclor target compounds.

b. For any recovery greater than or equal to 20% and less than the lower acceptance limit:

   i. Qualify detected spiked Aroclor target compounds as a "J".

   ii. Qualify the sample quantitation limit for non-detected spiked Aroclor target compounds as approximated "UJ".

c. For any recovery less than 20%:

   i. Qualify detected spiked Aroclor target compounds as a "J".

   ii. Use professional judgment to qualify non-detected spiked Aroclor target compounds.

d. If recoveries are within the acceptance limits, no qualification of the data is required.

2. The data reviewer should first try to determine to what extent the results of the MS and MSD affect the associated sample data. This determination should be made with regard to the MS and MSD sample itself, as well as specific analytes for all samples associated with the MS and MSD.

3. In those instances where it can be determined that the results of the MS and MSD affect only the sample spiked, limit qualification to this sample only. However, it may be determined through the MS and MSD results, that a laboratory is having a systematic problem in the analysis of one or more analytes that affects all associated samples. Use professional judgment to qualify the data from all associated samples.

4. Use professional judgment to determine the need for qualification of detects of non-spiked compounds.

NOTE: Notify the Contract Laboratory Program Project Officer (CLP PO) if a field blank was used for the MS and MSD, unless designated as such by the Region.

Table 67. Matrix Spike/Matrix Spike Duplicate (MS/MSD) Actions for Aroclor Analysis

Criteria	Action	
	Detected Spiked Compounds	Non-detected Spiked Compounds
%R or RPD > Upper Acceptance Limit	J	No qualification
20% ≤%R < Lower Acceptance Limit	J	UJ
%R < 20%	J	Use professional judgment
Lower Acceptance Limit ≤ %R ≤ Upper Acceptance Limit	No qualification	

Table 68. Matrix Spike (MS) Recovery and Relative Percent Difference (RPD) Limits

Compound	Percent Recovery QC Limits	RPD
AR1016	29 - 135	0 - 15
AR1260	29 - 135	0 - 20

VII. Laboratory Control Samples (LCSs)

A. Review Items:

Form I ARO, Form II ARO-1, Form II ARO-2, Form III ARO-3, Form III ARO-4, LCS chromatograms, and data system printouts.

B. Objective:

Data for LCSs are generated to provide information on the accuracy of the analytical method and laboratory performance.

C. Criteria:

1. The LCS contains the Aroclors target compounds and surrogates listed in Table 69.

Table 69. Aroclor Laboratory Control Sample (LCS) Recovery

Compound	% Recovery QC Limits
Aroclor 1016	50 - 150
Aroclor 1260	50 - 150
Tetrachloro-m-xylene (surrogate)	30 - 150
decachlorobiphenyl (surrogate)	30 - 150

2. The Percent Recoveries (%R) for the LCS compounds must be within the limits specified in Table 69.

NOTE: All samples prepared and analyzed with an LCS that does not meet the technical acceptance criteria in the method will require re-extraction and re-analysis.

D. Evaluation:

Check the raw data (e.g., chromatograms and data system printouts) to verify the recoveries on the Laboratory Control Sample Recovery Form (Form III ARO-3, Form III ARO-4). Check the raw data to verify the recoveries on the Surrogate Recovery Forms (Form II ARO-1, Form II ARO-2).

Check for any calculation or transcription errors; verify that the LCS recoveries reported on Form II ARO-1, Form II ARO-2, Form III ARO-3, and Form III ARO-4 are within the QC limits.

NOTE: For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.

E. Action:

If the LCS criteria are not met, laboratory performance and method accuracy are in question. Use professional judgment to determine if the data should be qualified or rejected. The following guidance is suggested for qualifying sample data for which the associated LCS does not meet the required criteria (see Table 70).

1. If the LCS recovery criteria are not met, use the LCS results to qualify sample data for the specific compounds that are included in the LCS solution.
   a. If the LCS recovery exceeds the upper acceptance limit, qualify detected target compounds as a "J". Do not qualify non-detected target compounds.
   b. If the LCS recovery is less than the lower acceptance limit, qualify detected target compounds as a "J" and non-detects as unusable "R".
   c. Use professional judgment to qualify data for compounds other than those compounds that are included in the LCS.
   d. Use professional judgment to qualify non-LCS compounds. Take into account the compound class, compound recovery efficiency, analytical problems associated with each compound, and comparability in the performance of the LCS compound to the non-LCS compound.
2. If the LCS recovery criteria are within the acceptance limit, no qualification of the data is necessary.
3. Note, for Contract Laboratory Program Project Officer (CLP PO) action, if a laboratory fails to analyze an LCS with each Sample Delivery Group (SDG), or if a laboratory consistently fails to generate acceptable LCS recoveries.

Table 70. Laboratory Control Sample (LCS) Recovery Actions

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
%R > Upper Acceptance Limit	J	No qualification
%R < Lower Acceptance Limit	J	R
Lower Acceptance Limit ≤ %R ≤ Upper Acceptance Limit	No qualification	

VIII. Regional Quality Assurance (QA) and Quality Control (QC)

A. Review Items:

Form I ARO, chromatograms, data system printouts, Traffic Report/Chain of Custody Record (TR/COC), quantitation reports, and other raw data from Regional QA/QC samples.

B. Objective:

Regional QA/QC refers to any QA and/or QC samples initiated by the Region, including field duplicates, Performance Evaluation (PE) samples, blind spikes, and blind blanks. The use of these QA/QC samples are highly recommended (e.g., the use of field duplicates can provide information on sampling precision and sample homogeneity).

C. Criteria:

Criteria are determined by each Region.

1. PE sample frequency may vary.
2. The analytes present in the PE sample must be correctly identified and quantified.

D. Evaluation:

1. Evaluation procedures must follow the Region's Standard Operating Procedure (SOP) for data review. Each Region will handle the evaluation of PE samples on an individual basis. Compare results for PE samples to the acceptance criteria for the specific PE samples, if available.
2. Calculate Relative Percent Difference (RPD) between field duplicates. Provide this information in the Data Review Narrative.

E. Action:

Any action must be in accordance with Regional specifications and the criteria for acceptable PE sample results. Note, for Contract Laboratory Program Project Officer (CLP PO) action, any unacceptable results for PE samples.

IX. Gel Permeation Chromatography (GPC) Performance Check

A. Review Items:

Two ultraviolet (UV) traces, GPC cleanup blank quantitation reports, and chromatograms.

B. Objective:

GPC is used to remove high molecular weight contaminants that can interfere with the analysis of target analytes. GPC cleanup procedures are checked by adding the GPC calibration mixture to the GPC cleanup columns and setting the appropriate elution window, and verifying the recovery of target compounds through the cleanup procedure by the analysis of a cleanup blank.

C. Criteria:

1. GPC is an optional cleanup method for both aqueous and non-aqueous samples and is used for the cleanup of all non-aqueous and aqueous sample extracts that contain high molecular weight components that interfere with the analysis of the target analytes.
2. At least once every seven (7) days, the calibration of the GPC unit must be checked by injecting with the GPC calibration verification solution.
3. The GPC calibration is acceptable if the two UV traces meet the following requirements:
   a. Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
   b. Corn oil and the phthalate peaks should exhibit greater than 85% resolution.
   c. The phthalate and methoxychlor peaks should exhibit greater than 85% resolution.
   d. Methoxychlor and perylene peaks should exhibit greater than 85% resolution.
   e. Perylene and sulfur peaks must not be saturated and should exhibit greater than 90% baseline resolution.
   f. The Retention Time (RT) shift is less than 5% between UV traces for bis(2-ethylhexyl)phthalate and perylene.
4. A GPC blank must be analyzed after each GPC calibration and it is acceptable if the blank does not exceed the Contract Required Quantitation Limit (CRQL) for any target analytes listed in SOM01.2, Exhibit C - Aroclors Target Compound List and Contract Required Quantitation Limits, available at:

http://www.epa.gov/superfund/programs/clp/som1.htm

D. Evaluation

1. Verify that there are two UV traces present and that the RT shift for bis(2-ethylhexyl)phthalate and perylene is less than 5%.
2. Verify that the compounds listed in IX.C.3 are present and symmetrical in both UV traces and that the compound pairs meet the minimum resolution requirements.
3. Verify that no target compound exceeds the CRQL.

NOTE: **For data obtained from the Contract Laboratory Program (CLP), the preceding criteria are evaluated as part of the Contract Compliance Screening (CCS) process. Information regarding the laboratory's compliance with these criteria can be obtained from the Data Assessment Tool (DAT) reports, and may be used as part of the evaluation process.**

E. Action:

1. If GPC criteria are not met, examine the raw data for the presence of high molecular weight contaminants. Examine the subsequent sample data for unusual peaks and use professional judgment in qualifying the data. Notify the Contract Laboratory Program Project Officer (CLP PO) if a laboratory chooses to analyze samples under unacceptable GPC criteria.
2. Note in the Data Review Narrative potential effects on the sample data resulting from the GPC cleanup analyses not yielding acceptable results.

X. Target Compound Identification

A. Review Items:

Form I ARO, Form X ARO, chromatograms, and data system printouts.

B. Objective:

Qualitative criteria for compound identification have been established to minimize the number of false positives (reporting a compound present when it is not) and false negatives (not reporting a compound that is present).

C. Criteria:

1. The Retention Times (RTs) of both of the surrogates and reported target compounds in each sample must be within the calculated RT Windows on both columns. Tetrachloro-m-xylene (TCX) must be within ±0.05 minutes of the Mean Retention Time ($\overline{RT}$) determined from the initial calibration and Decachlorobiphenyl (DCB) must be within ±0.10 minutes of the $\overline{RT}$ determined from the initial calibration.
2. The Percent Difference (%D) for the detected mean concentrations of an Aroclor target compound between the two Gas Chromatograph (GC) columns must be within the inclusive range of ±25.0.
3. When no analytes are identified in a sample, the chromatograms from the analyses of the sample extract must use the same scaling factor as was used for the low-point standard of the initial calibration associated with those analyses.
4. Chromatograms must display the largest peak of any Aroclors detected in the sample at less than full scale.
5. If an extract must be diluted, chromatograms must display Aroclors peaks between 25-100% of full scale.
6. If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram, and both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

D. Evaluation:

1. Review Form I ARO, the associated raw data (chromatograms and data system printouts) and Form X ARO. Confirm reported detected analytes by comparing the sample chromatograms to the tabulated results and verifying peak measurements and RTs. Confirm reported non-detected analytes by a review of the sample chromatograms. Check the associated blank data for potential interferences (to evaluate sample data for false positives) and check the calibration data for adequate RT Windows (to evaluate sample data for false positives and false negatives).
2. Compare the Aroclor peaks identified in the sample to determine that the RTs do not overlap with the RTs of any chromatographic interferences from the sample matrix.
3. Check that the Percent Difference results were calculated correctly.

E. Action:

1. If the qualitative criteria for both columns were not met, all target compounds that are reported as detected should be considered non-detected. The reviewer should use professional judgment to assign an appropriate quantitation limit using the following guidance:
   a. If the detected target compound peak was sufficiently outside the Aroclor RT Window, the reported values may be a false positive and should be replaced with the sample Contract Required Quantitation Limits (CRQL) value.
   b. If the detected target compound peak poses an interference with potential detection of another target peak, the reported value should be considered and qualified as unusable "R".
2. If the data reviewer identifies a peak in both GC column analyses that falls within the appropriate RT Windows, but was reported as a non-detect, the compound may be a false negative. Use professional judgment to decide if the compound should be included. Note in the Data Review Narrative all conclusions made regarding target compound identification.
3. If the Aroclor peak RT Windows determined from the calibration overlap with chromatographic interferences, use professional judgment to qualify the data.
4. If Aroclors were detected on both GC columns, and the Percent Difference between the two results is greater than 25.0%, consider the potential for coelution and use professional judgment to decide whether a much larger concentration obtained on one column versus the other indicates the presence of an interfering compound. If an interfering compound is indicated, use professional judgment to determine how best to report, and if necessary, qualify the data.
5. If Aroclors exhibit marginal pattern-matching quality, use professional judgment to establish whether the differences are due to environmental "weathering" (i.e., degradation of the earlier eluting peaks relative to the later eluting peaks). If the presence of an Aroclor is strongly suggested, report results as presumptively present "N".

XI. Gas Chromatograph/Mass Spectrometer (GC/MS) Confirmation

A. Review Items:

Form I ARO, Form X ARO, chromatograms, and data system printouts.

B. Objective:

If GC/MS confirmation is required by the Region for all detected Aroclors that have at least one individual peak with a sufficient on-column concentration on both columns (greater than or equal to 10 ng/µL), GC/MS confirmation for purposes of qualitative identification is required. GC/MS confirmation may be accomplished by one of three general means:

1. Examination of the semivolatile GC/MS library search results [i.e., Tentatively Identified Compound (TIC) data];
2. A second analysis of the semivolatile extract; or
3. Analysis of the Aroclor extract, following any solvent exchange and concentration steps that may be necessary.

C. Criteria:

The on-column concentration for any individual peak belonging to an Aroclor must be greater than or equal to 10 ng/µL on both GC columns. If the on-column concentration to run GC/MS confirmation is adequate, the laboratory must have permission from the Region before GC/MS performing confirmation.

D. Evaluation:

1. Review Form I ARO, the associated raw data (chromatograms and data system printouts) and Form X ARO-1 and Form X ARO-2. Confirm that GC/MS confirmation was required by ensuring that an individual peak belonging to an Aroclor has an on-column concentration greater than or equal to 10 ng/µL on both GC columns by looking at the quantitation reports.

E. Action:

1. If the quantitative criteria for both columns were met (≥10 ng/µL), determine whether GC/MS confirmation was performed. If it was performed, qualify the data using the following guidance (see Table 71):
   a. If GC/MS confirmation was not required because the quantitative criteria for both columns was not met, but it was still performed, the reviewer should use professional judgment when evaluating the data to decide whether the detect should be qualified with "C".
   b. If GC/MS confirmation was requested and performed, but not successful for a target compound detected by GC/ECD analyses, qualify those detects as "X".

Table 71. Gas Chromatograph/Mass Spectrometer (GC/MS) Confirmation Actions

Criteria	Action
Aroclor peak was confirmed by GC/MS	Detects C
Aroclor peak was not confirmed by GC/MS	Detects X

XII. Compound Quantitation and Reported Contract Required Quantitation Limits (CRQLs)

A. Review Items:

Form I ARO, Form X ARO-1, sample preparation log sheets, chromatograms, Sample Delivery Group (SDG) Narrative, and data system printouts.

B. Objective:

The objective is to ensure that the reported quantitative results and CRQLs are accurate.

C. Criteria:

Compound quantitation, as well as the adjustment of the CRQL, must be calculated according to the equations provided in the method.

D. Evaluation:

1. Examine raw data to verify the correct calculation of all sample results reported by the laboratory. Compare data system printouts, chromatograms, and sample preparation log sheets to the reported detects and non-detects sample results. Verify that the sample values are reported correctly.
2. Verify that the CRQLs have been adjusted to reflect all sample dilutions, cleanup activities, Percent Moisture determination (for non-aqueous samples) and other factors that are not accounted for by the method.

E. Action:

1. Qualify non-detect results affected by large, off-scale peaks as unusable "R". If the interference is on-scale, provide an approximated quantitation limit "UJ" for each affected compound.
2. For non-aqueous samples, if the Percent Moisture is less than 70.0%, no qualification of the data is necessary (see Table 72). If the Percent Moisture is greater than or equal to 70.0% and less than 90.0%, qualify detects as "J" and non-detects as "UJ". If the Percent Moisture is greater than or equal to 90.0%, qualify detects as "J" and non-detects as unusable "R".
3. If there are any discrepancies found, the Region's designated representative may contact the laboratory to obtain additional information that could resolve any differences. If a discrepancy remains unresolved, the reviewer must decide which value is the best value. Under these circumstances, determine if qualification of the data is warranted. Note in the Data Review Narrative a description of the reasons for data qualification and the qualification that is applied to the data.

Table 72. Percent Moisture Actions for Aroclors Analyses for Non-Aqueous Samples

Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
%Moisture < 70.0%	No qualification	
70.0% ≤ %Moisture < 90.0%	J	UJ
%Moisture ≥ 90.0%	J	R

XIII. Overall Assessment of Data

A. Review Items:

Entire data package, data review results, and (if available) Quality Assurance Project Plan (QAPP), and Sampling and Analysis Plan (SAP).

B. Objective:

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria:

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation:

1. Evaluate any technical problems which have not been previously addressed.
2. If appropriate information is available, assess the usability of the data to help the data user avoid inappropriate use of the data. Review all available information, including the QAPP (specifically the acceptance or performance criteria), SAP, and communication with data user that concerns the intended use and desired quality of these data.

E. Action:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the Quality Control (QC) criteria previously discussed.
2. Write a brief narrative to give the user an indication of the analytical limitations of the data. Note, for Contract Laboratory Program Project Officer (CLP PO) action, any inconsistency of that data with the Sample Delivery Group (SDG) Narrative. If sufficient information on the intended use and required quality of the data are available, include an assessment of the usability of the data within the given context. This may be used as part of a formal Data Quality Assessment (DQA).

APPENDIX A: GLOSSARY

Analysis Date/Time - The date and military time (24-hour clock) of the injection of the sample, standard, or blank into the Gas Chromatograph/Mass Spectrometer (GC/MS) or Gas Chromatograph (GC) system.

Aroclor - A trademarked name for a mixture of polychlorinated biphenyls (PCBs) used in a variety of applications including additives in lubricants, heat transfer dielectric fluids, adhesives, etc.

Blank - An analytical sample designed to assess specific sources of contamination. See individual definitions for types of blanks.

Breakdown - A measure of the decomposition of certain analytes (DDT and Endrin) into by-products.

4-Bromofluorobenzene (BFB) - The compound chosen to establish mass spectrometer instrument performance for volatile analyses.

Calibration Factor (CF) - A measure of the Gas Chromatographic response of a target analyte to the mass injected.

Case - A finite, usually predetermined number of samples collected over a given time period from a particular site. Case Numbers are assigned by the Sample Management Office (SMO). A Case consists of one or more Sample Delivery Groups (SDGs).

Contract Compliance Screening (CCS) - A screening of electronic and hardcopy data deliverables for completeness and compliance with the contract. This screening is performed under the United States Environmental Protection Agency (USEPA) direction by the Sample Management Office (SMO) Contractor.

Contamination - A component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

Continuing Calibration Verification (CCV) - Analytical standard run every 12 hours to verify that the instrument response at the concentration of the standard is within acceptable limits.

Contract Laboratory Program (CLP) - Supports the USEPA's Superfund effort by providing a range of state-of-the-art chemical analytical services of known and documented quality. This program is directed by the Analytical Services Branch (ASB) of the Office of Superfund Remediation and Technology Innovation (OSRTI) of USEPA.

Contract Laboratory Program Project Officer (CLP PO) - The Regional USEPA official responsible for monitoring laboratory performance and/or requesting analytical data or services from a Contract Laboratory Program (CLP) laboratory.

Decafluorotriphenylphosphine (DFTPP) - Compound chosen to establish mass spectrometer instrument performance for semivolatile analysis.

Deuterated Monitoring Compounds (DMCs) - Compounds added to every volatile and semivolatile calibration standard, blank, and sample used to evaluate the efficiency of the extraction/purge and trap procedures, and the performance of the Gas Chromatograph/Mass Spectrometer (GC/MS) systems.

DMCs are isotopically labeled (deuterated) analogs of native target compounds. DMCs are not expected to be naturally detected in the environmental media.

Field Blank - A blank used to provide information about contaminants that may be introduced during sample collection.

Field Sample - A portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

14-Hour Time Period - For pesticide and Aroclor analyses, the fourteen-hour time period begins at the injection of the beginning of the sequence for an opening Continuing Calibration Verification (CCV) (instrument blank) and must end with the injection of the closing sequence of the closing CCV [Individual standard A, B, or C or Performance Evaluation Mixture (PEM)]. The time period ends after 14 hours have elapsed according to the system clock.

Gas Chromatograph (GC) - The instrument used to separate analytes on a stationary phase within a chromatographic column. The analytes are volatized directly from the sample (volatile), or injected as extracts (semivolatile, pesticides, and Aroclors). In volatile and semivolatile analyses, the compounds are detected by a Mass Spectrometer. In pesticide and Aroclors analyses, the compounds are detected by an Electron Capture Detector (ECD).

Gas Chromatograph/Electron Capture Detector (GC/ECD) - A Gas Chromatograph (GC) equipped with an Electron Capture Detector (ECD). This is one of the most sensitive gas chromatographic detectors or halon-containing compounds such as organochlorine pesticides and polychlorinated biphenyls.

Initial Calibration - Analysis of analytical standards at different concentrations to define the linear range of an analytical instrument [e.g., Gas Chromatograph/Mass Spectrometer (GC/MS), Gas Chromatograph/Electron Capture Detector (GC/ECD)].

Internal Standards - Compounds added to every volatile and semivolatile standard, blank, sample, or sample extract, including the Laboratory Control Sample (LCS), at a known concentration, prior to analysis. Internal standards are used to monitor instrument performance and quantitation of target compounds.

Instrument Blank - A blank designed to determine the level of contamination either associated with the analytical instruments, or resulting from carryover.

Laboratory Control Sample (LCS) - The LCS is an internal laboratory Quality Control (QC) sample designed to assess [on a Sample Delivery Group (SDG)-by-SDG basis] the capability of the contractor to perform the analytical method.

m/z - Mass to charge ratio, synonymous with "m/e".

Matrix - The predominant material of which the sample to be analyzed is composed. For the purpose of this document, the sample matrix is either aqueous or non-aqueous.

Matrix Effect - In general, the effect of a particular matrix on the constituents with which it contacts. Matrix effects may prevent efficient purging/extraction of target analytes, and may affect DMC and surrogate recoveries. In addition, non-target analytes may be extracted from the matrix causing interferences.

Matrix Spike (MS) - Aliquot of the sample fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

Matrix Spike Duplicate (MSD) - A second aliquot of the same sample that is fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to determine precision of the method.

Method Blank - A reagent aqueous sample spiked with internal standards, and surrogate standards (or DMCs for volatile and semivolatile), that is carried throughout the entire analytical procedure. The method blank is used to define the level of contamination associated with the processing and analysis of samples.

Narrative (SDG Narrative) - Portion of the data package which includes laboratory, contract, Case and sample number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution

Percent Difference (%D) - The difference between two values (usually a true value and a found value), calculated as a percentage of the true value. The Percent Difference indicates both the direction and the magnitude of the difference (i.e., the Percent Difference may be either negative, positive, or zero).

Percent Relative Standard Deviation (%RSD) - The Percent Relative Standard Deviation is calculated from the standard deviation and mean measurement of either RRFs or CF from initial calibration standards. Percent Relative Standard Deviation indicates precision of a set of measurements.

Performance Evaluation Mixture (PEM) - A calibration solution of specific analytes used to evaluate both recovery and Percent Breakdown as measures of performance.

Polychlorinated Biphenyls (PCBs) - A group of toxic, persistent chemicals used in electrical transformers and capacitors for insulating purposes, and in gas pipeline systems as a lubricant. The sale and new use of PCBs were banned by law in 1979.

Purge-and-Trap (Device) - Analytical technique (device) used to isolate volatile (purgeable) organics by stripping the compounds from aqueous by a stream of inert gas, trapping the compounds on an adsorbent such as a porous polymer trap, and thermally desorbing the trapped compounds onto the Gas Chromatographic column.

Reconstructed Ion Chromatogram (RIC) - A mass spectral graphical representation of the separation achieved by a Gas Chromatograph; a plot of total ion current versus Retention Time (RT).

Relative Percent Difference (RPD) - The difference between two values, calculated as a percent relative to the mean of the two values.

Relative Response Factor (RRF) - A measure of the mass spectral response of an analyte relative to its associated internal standard. RRFs are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

Relative Retention Time (RRT) - The ratio of the Retention Time (RT) of a compound to that of a standard (such as an internal standard).

Resolution - Also termed *separation* or *percent resolution*, the separation between peaks on a chromatogram, calculated by dividing the depth of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.

Resolution Check Mixture - A solution of specific analytes used to determine resolution of adjacent peaks; used to assess instrumental performance.

Retention Time (RT) - The time a target analyte is retained on a Gas Chromatograph (GC) column before elution. The identification of a target analyte is dependent on a target compound's RT falling within the specified RT Window established for that compound. The RT is dependent on the nature of the column's stationary phase, column diameter, temperature, flow rate, and other parameters.

Sample Delivery Group (SDG) - A unit within a sample Case that is used to identify a group of samples for delivery. An SDG is defined by the following, whichever is most frequent:

- Each Case of field samples received, or;
- Each twenty (20) field samples (excluding Performance Evaluation (PE) samples) within a Case, or;
- Each seven (7) calendar day period [three (3) calendar day period for seven (7) day turnaround] during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).

In addition, all samples and/or sample fractions assigned to an SDG must have been scheduled under the same contractual turnaround time. Preliminary Results have no impact on defining the SDG.

Sample Management Office (SMO) - A contractor-operated facility operated under the Contract Laboratory Analytical Services Support (CLASS) contract, awarded and administered by USEPA.

Sample Number (USEPA Sample Number) - A unique identification number designated by USEPA to each sample. USEPA Sample Number appears on the Traffic Report/Chain of Custody Record (TR/COC) which documents information on that sample.

Semivolatile Compounds - Compounds amenable to analysis by extraction of the sample with an organic solvent. Used synonymously with Base/Neutral/Acid (BNA) compounds.

Statement of Work (SOW) - A document which specifies how laboratories analyze samples under a particular Contract Laboratory Program (CLP) analytical program.

Storage Blank - Reagent water (two 40.0 mL aliquots) or clean sand stored with volatile samples in a Sample Delivery Group (SDG). It is analyzed after all samples in that SDG have been analyzed; and it is used to determine the level of contamination acquired during storage.

Sulfur Cleanup Blank - A modified method blank that is prepared only when some of the samples in a batch are subjected to sulfur cleanup. It is used to determine the level of contamination associated with the sulfur cleanup procedure. When all of the samples are subjected to sulfur cleanup, the method blank serves this purpose. When none of the samples are subjected to sulfur cleanup, no sulfur cleanup blank is required.

Surrogates (Surrogate Standard) - For pesticides and Aroclors, compounds added to every blank, sample [including Laboratory Control Sample (LCS)], Matrix Spike/Matrix Spike Duplicate (MS/MSD), and standard; used to evaluate analytical efficiency by measuring recovery. Surrogates are not expected to be detected in environmental media.

Target Compound List (TCL) - A list of compounds designated by the Statement of Work (SOW) for analysis.

Technical Holding Time - The maximum length of time that a sample may be held from the collection date until extraction and/or analysis.

Tentatively Identified Compounds (TIC) - Compounds detected in samples that are not target compounds, internal standards, Deuterated Monitoring Compounds (DMCs), or surrogates. Up to thirty (30) peaks, not including those identified as alkanes (those greater than 10% of the peak area or height of the nearest internal standard), are subjected to mass spectral library searches for tentative identification.

Traffic Report/Chain of Custody Record (TR/COC) - A USEPA sample identification form filled out by the sampler, which accompanies the sample during shipment to the laboratory and which documents sample condition and receipt by the laboratory.

Trip Blank - A blank used to provide information about contaminants that may be introduced during sample transport.

Twelve-hour Time Period - The twelve (12)-hour time period for Gas Chromatograph/Mass Spectrometer (GC/MS) system instrument performance check, standards calibration [initial or Continuing Calibration Verification (CCV)], and method blank analysis begins at the moment of injection of the Decafluorotriphenylphosphine (DFTPP) or 4-Bromofluorobenzene (BFB) analysis that the laboratory submits as documentation of instrument performance. The time period ends after 12 hours have elapsed according to the system clock. For pesticide analyses performed by Gas Chromatograph/Electron Capture Detector (GC/ECD), the 12-hour time period in the analytical sequence begins at the moment of injection of the instrument blank that precedes sample analyses, and ends after twelve hours have elapsed according to the system clock.

Validated Time of Sample Receipt (VTSR) - The date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and Traffic Report/Chain of Custody Record (TR/COC).

Volatile Compounds - Compounds amenable to analysis by the purge-and-trap technique. Used synonymously with purgeable compounds.

APPENDIX B: ORGANIC DATA REVIEW SUMMARY

CASE NO.	SITE	
LABORATORY	NO. OF SAMPLES/MATRIX	
SDG NO.	SOW NO.	REGION
REVIEWER NAME	COMPLETION DATE	
CLP PO: ACTION	FYI	

Review Criteria	Fraction				
	TRACE	LOW/MED	SVOA	PEST	AROCLOR
Preservation					
GC/MS or GC/ECD Instrument Performance Check					
Initial Calibration					
Continuing Calibration Verification					
Blanks					
Deuterated Monitoring Compound Surrogate Spikes					
Matrix Spike/Matrix Spike Duplicate					
Laboratory Control Sample					
Regional QA/QC					
Internal Standards					
GPC Performance Check					
Florisil Cartridge Performance Check					
Target Compound Identification					
GC/MS Confirmation					
Compound Quantitation and Reported CRQLS					
Tentatively Identified Compounds					
System Performance					
Overall Assessment of Data					

§ 141.54 Maximum residual disinfectant level goals for disinfectants.

MRDLGs for disinfectants are as follows:

Disinfectant residual	MRDLG(mg/L)
Chlorine	4 (as Cl_2).
Chloramines	4 (as Cl_2).
Chlorine dioxide	0.8 (as ClO_2)

[63 FR 69465, Dec. 16, 1998]

§ 141.55 Maximum contaminant level goals for radionuclides.

MCLGs for radionuclides are as indicated in the following table:

Contaminant	MCLG
1. Combined radium-226 and radium-228	Zero.
2. Gross alpha particle activity (excluding radon and uranium).	Zero.
3. Beta particle and photon radioactivity	Zero.
4. Uranium	Zero.

[65 FR 76748, Dec. 7, 2000]

EFFECTIVE DATE NOTE: At 65 FR 76748, Dec. 7, 2000, § 141.55 was added, effective Dec. 8, 2003.

Subpart G—National Revised Primary Drinking Water Regulations: Maximum Contaminant Levels and Maximum Residual Disinfectant Levels

EFFECTIVE DATE NOTE: At 65 FR 76748, Dec. 7, 2000, the heading of subpart G was revised to read ''National Primary Drinking Water Regulations: Maximum Contaminant Levels and Maximum Residual Disinfectant Levels'', effective Dec. 8, 2003.

§ 141.60 Effective dates.

(a) The effective dates for § 141.61 are as follows:

(1) The effective date for paragraphs (a)(1) through (a)(8) of § 141.61 is January 9, 1989.

(2) The effective date for paragraphs (a)(9) through (a)(18) and (c)(1) through (c)(18) of § 141.61 is July 30, 1992.

(3) The effective date for paragraphs (a)(19) through (a)(21), (c)(19) through (c)(25), and (c)(27) through (c)(33) of § 141.61 is January 17, 1994. The effective date of § 141.61(c)(26) is August 17, 1992.

(b) The effective dates for § 141.62 are as follows:

(1) The effective date of paragraph (b)(1) of § 141.62 is October 2, 1987.

(2) The effective date for paragraphs (b)(2) and (b)(4) through (b)(10) of § 141.62 is July 30, 1992.

(3) The effective date for paragraphs (b)(11) through (b)(15) of § 141.62 is January 17, 1994.

(4) The effective date for § 141.62(b)(16) is January 23, 2006.

[56 FR 3593, Jan. 30, 1991, as amended at 57 FR 31846, July 17, 1992; 59 FR 34324, July 1, 1994; 66FR 7063, Jan. 22, 2001]

§ 141.61 Maximum contaminant levels for organic contaminants.

(a) The following maximum contaminant levels for organic contaminants apply to community and non-transient, non-community water systems.

CAS No.	Contaminant	MCL (mg/l)
(1) 75–01–4	Vinyl chloride	0.002
(2) 71–43–2	Benzene	0.005
(3) 56–23–5	Carbon tetrachloride	0.005
(4) 107–06–2	1,2-Dichloroethane	0.005
(5) 79–01–6	Trichloroethylene	0.005
(6) 106–46–7	para-Dichlorobenzene	0.075
(7) 75–35–4	1,1-Dichloroethylene	0.007
(8) 71–55–6	1,1,1-Trichloroethane	0.2
(9) 156–59–2	cis-1,2-Dichloroethylene	0.07
(10) 78–87–5	1,2-Dichloropropane	0.005
(11) 100–41–4	Ethylbenzene	0.7
(12) 108–90–7	Monochlorobenzene	0.1
(13) 95–50–1	o-Dichlorobenzene	0.6
(14) 100–42–5	Styrene	0.1
(15) 127–18–4	Tetrachloroethylene	0.005
(16) 108–88–3	Toluene	1
(17) 156–60–5	trans-1,2-Dichloroethylene	0.1
(18) 1330–20–7	Xylenes (total)	10
(19) 75–09–2	Dichloromethane	0.005
(20) 120–82–1	1,2,4-Trichloro- benzene	.07
(21) 79–00–5	1,1,2-Trichloro- ethane	.005

(b) The Administrator, pursuant to section 1412 of the Act, hereby identifies as indicated in the Table below granular activated carbon (GAC), packed tower aeration (PTA), or oxidation (OX) as the best technology treatment technique, or other means available for achieving compliance with the maximum contaminant level for organic contaminants identified in paragraphs (a) and (c) of this section:

BAT FOR ORGANIC CONTAMINANTS LISTED IN § 141.61 (a) AND (c)

CAS No.	Contaminant	GAC	PTA	OX
15972–60–8	Alachlor	X		
116–06–3	Aldicarb	X		
1646–88–4	Aldicarb sulfone	X		
1646–87–3	Aldicarb sulfoxide	X		
1912–24–9	Atrazine	X		
71–43–2	Benzene	X	X	
50–32–8	Benzo[a]pyrene	X		
1563–66–2	Carbofuran	X		
56–23–5	Carbon tetrachloride	X	X	
57–74–9	Chlordane	X		
75–99–0	Dalapon	X		
94–75–7	2,4-D	X		
103–23–1	Di (2-ethylhexyl) adipate	X	X	
117–81–7	Di (2-ethylhexyl) phthalate	X		
96–12–8	Dibromochloropropane (DBCP)	X	X	
95–50–1	o-Dichlorobenzene	X	X	
106–46–7	para-Dichlorobenzene	X	X	
107–06–2	1,2-Dichloroethane	X	X	
75–35–4	1,1-Dichloroethylene	X	X	
156–59–2	cis-1,2-Dichloroethylene	X	X	
156–60–5	trans-1,2-Dichloroethylene	X	X	
75–09–2	Dichloromethane		X	
78–87–5	1,2-Dichloropropane	X	X	
88–85–7	Dinoseb	X		
85–00–7	Diquat	X		
145–73–3	Endothall	X		
72–20–8	Endrin	X		
100–41–4	Ethylbenzene	X	X	
106–93–4	Ethylene Dibromide (EDB)	X	X	
1071–83–6	Gylphosate			X
76–44–8	Heptachlor	X		
1024–57–3	Heptachlor epoxide	X		
118–74–1	Hexachlorobenzene	X		
77–47–3	Hexachlorocyclopentadiene	X	X	
58–89–9	Lindane	X		
72–43–5	Methoxychlor	X		
108–90–7	Monochlorobenzene	X	X	
23135–22–0	Oxamyl (Vydate)	X		
87–86–5	Pentachlorophenol	X		
1918–02–1	Picloram	X		
1336–36–3	Polychlorinated biphenyls (PCB)	X		
122–34–9	Simazine	X		
100–42–5	Styrene	X	X	
1746–01–6	2,3,7,8-TCDD (Dioxin)	X		
127–18–4	Tetrachloroethylene	X	X	
108–88–3	Toluene	X	X	
8001–35–2	Toxaphene	X		
93–72–1	2,4,5-TP (Silvex)	X		
120–82–1	1,2,4-Trichlorobenzene	X	X	
71–55–6	1,1,1-Trichloroethane	X	X	
79–00–5	1,1,2-Trichloroethane	X	X	
79–01–6	Trichloroethylene	X	X	
75–01–4	Vinyl chloride		X	
1330–20–7	Xylene	X	X	

(c) The following maximum contaminant levels for synthetic organic contaminants apply to community water systems and non-transient, non-community water systems:

CAS No.	Contaminant	MCL (mg/l)
(1) 15972–60–8	Alachlor	0.002
(2) 116–06–3	Aldicarb	0.003
(3) 1646–87–3	Aldicarb sulfoxide	0.004
(4) 1646–87–4	Aldicarb sulfone	0.002
(5) 1912–24–9	Atrazine	0.003
(6) 1563–66–2	Carbofuran	0.04
(7) 57–74–9	Chlordane	0.002
(8) 96–12–8	Dibromochloropropane	0.0002
(9) 94–75–7	2,4-D	0.07
(10) 106–93–4	Ethylene dibromide	0.00005
(11) 76–44–8	Heptachlor	0.0004
(12) 1024–57–3	Heptachlor epoxide	0.0002
(13) 58–89–9	Lindane	0.0002
(14) 72–43–5	Methoxychlor	0.04
(15) 1336–36–3	Polychlorinated biphenyls	0.0005
(16) 87–86–5	Pentachlorophenol	0.001
(17) 8001–35–2	Toxaphene	0.003
(18) 93–72–1	2,4,5-TP	0.05
(19) 50–32–8	Benzo[a]pyrene	0.0002
(20) 75–99–0	Dalapon	0.2
(21) 103–23–1	Di(2-ethylhexyl) adipate	0.4
(22) 117–81–7	Di(2-ethylhexyl) phthalate	0.006
(23) 88–85–7	Dinoseb	0.007
(24) 85–00–7	Diquat	0.02
(25) 145–73–3	Endothall	0.1
(26) 72–20–8	Endrin	0.002
(27) 1071–53–6	Glyphosate	0.7
(28) 118–74–1	Hexacholorbenzene	0.001
(29) 77–47–4	Hexachlorocyclopentadiene	0.05
(30) 23135–22–0	Oxamyl (Vydate)	0.2
(31) 1918–02–1	Picloram	0.5
(32) 122–34–9	Simazine	0.004
(33) 1746–01–6	2,3,7,8-TCDD (Dioxin)	3×10^{-8}

[56 FR 3593, Jan. 30, 1991, as amended at 56 FR 30280, July 1, 1991; 57 FR 31846, July 17, 1992; 59 FR 34324, July 1, 1994]

§ 141.62 Maximum contaminant levels for inorganic contaminants.

(a) [Reserved]

(b) The maximum contaminant levels for inorganic contaminants specified in paragraphs (b) (2)–(6), (b)(10), and (b)(11)–(16) of this section apply to community water systems and non-transient, non-community water systems. The maximum contaminant level specified in paragraph (b)(1) of this section only applies to community water systems. The maximum contaminant levels specified in (b)(7), (b)(8), and (b)(9) of this section apply to community water systems; non-transient, non-community water systems; and transient non-community water systems.

Contaminant	MCL (mg/l)
(1) Fluoride	4.0
(2) Asbestos	7 Million Fibers/liter (longer than 10 μm).
(3) Barium	2
(4) Cadmium	0.005
(5) Chromium	0.1
(6) Mercury	0.002
(7) Nitrate	10 (as Nitrogen)
(8) Nitrite	1 (as Nitrogen)
(9) Total Nitrate and Nitrite	10 (as Nitrogen)
(10) Selenium	0.05
(11) Antimony	0.006
(12) Beryllium	0.004
(13) Cyanide (as free Cyanide).	0.2
(14) [Reserved]	
(15) Thallium	0.002
(16) Arsenic	0.010

(c) The Administrator, pursuant to section 1412 of the Act, hereby identifies the following as the best technology, treatment technique, or other means available for achieving compliance with the maximum contaminant levels for inorganic contaminants identified in paragraph (b) of this section, except fluoride:

BAT FOR INORGANIC COMPOUNDS LISTED IN SECTION 141.62(B)

Chemical Name	BAT(s)
Antimony	2,7
Arsenic[4]	1, 2, 5, 6, 7, 9, 12[5]

USEPA CONTRACT LABORATORY PROGRAM

STATEMENT OF WORK

FOR

VOLATILE ORGANICS ANALYSIS

IN AIR

SAV01.X

Draft

June 2008

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STATEMENT OF WORK

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EXHIBIT A

SUMMARY OF REQUIREMENTS

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Exhibit A - Summary of Requirements

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1.0 PURPOSE

The purpose of the volatile organics in air analytical service is to provide analytical data for use by the U.S. Environmental Protection Agency (USEPA) in support of its investigation and clean-up activities under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986 (SARA). Other USEPA Program Offices that have similar analytical data needs also use this service.

2.0 DESCRIPTION OF SERVICE

The organic analytical service provides a contractual framework for laboratories to apply USEPA Contract Laboratory Program (CLP) analytical methods for the isolation, detection, and quantitative measurement of 65 volatile target compounds in air samples. The analytical service provides the methods to be used, and the specific contractual requirements by which USEPA will evaluate the data. This service uses Gas Chromatograph/Mass Spectrometer (GC/MS) methods to analyze the target compounds.

3.0 DATA USES

This analytical service provides data that USEPA uses for a variety of purposes, such as determining the nature and extent of contamination at a hazardous waste site, assessing priorities for response based on risks to human health and the environment, determining appropriate cleanup actions, and determining when remedial actions are complete. The data may be used in all stages in the investigation of a hazardous waste site, including, but not limited to, site inspections; Hazard Ranking System (HRS) scoring; remedial investigation/feasibility studies; remedial design; treatability studies; and removal actions.

The data may also be used in litigation against Potentially Responsible Parties (PRPs) in the enforcement of Superfund legislation. As a result, the Contractor must be aware of the importance of maintaining the integrity of the data generated under the contract, since it is used to make major decisions regarding public health and environmental welfare. The Contractor may be required to appear and testify to the accuracy and/or validity of the data generated.

4.0 SUMMARY OF REQUIREMENTS

4.1 Introduction to the Statement of Work

This Statement of Work (SOW) is designed as part of the documentation for a contract between USEPA and a commercial laboratory performing analyses in support of USEPA Superfund programs. The SOW is comprised of eight exhibits and one appendix. Exhibit A provides an overview of the SOW and its general requirements. Exhibit B contains a description of the reporting and deliverables requirements, in addition to the data reporting forms and the form instructions. Exhibit C specifies the Target Compound List (TCL) for this SOW with the Contract Required Quantitation Limits (CRQLs) for the sample matrix. Exhibit D details the specific analytical procedures to be used with this SOW and resulting contracts. Exhibit E provides descriptions of required Quality Assurance/Quality Control (QA/QC), Standard Operating Procedures (SOPs), and procedures used for evaluating analytical methodologies, QA/QC performance, and the reporting of data. Exhibit F contains chain-of-custody and sample documentation requirements which the Contractor shall follow. To ensure proper understanding of the terms utilized in this SOW, a glossary can be found in Exhibit G (when a term is used in the text without explanation, the glossary meaning shall be applicable). Specifications for reporting electronic data appear in Exhibit H. Appendix A contains a listing of USEPA Registry Names, Synonyms, and Chemical Abstracts Service (CAS) Registry Numbers.

4.2 Overview of Major Task Areas

For each sample, the Contractor shall perform the tasks described in this section. Specific requirements for each task are detailed in the exhibits as referenced.

4.2.1 Task I: Sample Receiving, Storage, and Disposal

4.2.1.1 Chain-of-Custody

The Contractor shall receive and maintain samples under proper chain-of-custody procedures. All associated document control and inventory procedures shall be developed and followed. Documentation, as described herein, shall be required to show that all procedures are being strictly followed. This documentation shall be reported as the Complete Sample Delivery Group (SDG) File (CSF) (Exhibit B). The Contractor shall establish and use appropriate procedures to safeguard confidential information received from USEPA. See Exhibit F for specific requirements.

4.2.1.2 Sample Scheduling/Shipments

Sample shipments to the Contractor's facility will be scheduled and coordinated by the Task Order Project Officer (TOPO). The Contractor shall communicate with the TOPO by telephone, fax, and/or email, as necessary throughout the process of sample ordering, shipment of canisters from and to the Contractor, analysis, and data reporting, to ensure that samples are properly processed.

4.2.1.2.1

Samples will be shipped routinely to the Contractor through an overnight delivery service. However, as necessary, the Contractor shall be responsible for any handling or processing required for the receipt of sample shipments. This includes the pick-up of samples at the nearest servicing airport, bus station, or other carrier service within the Contractor's geographical area. The

Contractor shall be available to receive and process sample shipments at any time the delivery service is operating, including Saturdays.

4.2.1.2.2 If there are problems with the samples (e.g., containers leaking) or sample documentation/paperwork [e.g., Traffic Report/Chain of Custody Records (TR/COCs) not with shipment, sample and TR/COC numbers do not correspond], the Contractor shall immediately contact the TOPO for resolution. The Contractor shall immediately notify the TOPO regarding any problems and laboratory conditions that affect the timeliness of analyses and data reporting. In particular, the Contractor shall notify the TOPO in advance regarding sample data that will be delivered late and shall specify the estimated delivery date.

4.2.1.2.3 The Contractor shall accept all samples ordered, provided that the total number of samples received in any calendar month does not exceed the monthly limitation expressed in the contract. Should the Contractor elect to accept additional samples, the Contractor shall remain bound by all contract requirements for analysis of those samples accepted.

4.2.1.2.4 The Contractor is required to retain unused sample volume, and partially used sample volume in original sample container for a period of 60 days after data submission.

4.2.2 Task II: Sample Preparation and Analysis

4.2.2.1 Overview

The Contractor is advised that the samples received under the contract are usually from known or suspected hazardous waste sites and may contain high levels of organic and inorganic materials of a potentially hazardous nature. It is the Contractor’s responsibility to take all necessary measures to ensure laboratory safety.

4.2.2.2 If analysis by the Selected Ion Monitoring (SIM) technique is requested, analysis by the appropriate full scan method must be performed prior to the SIM analysis. If the full scan analysis detects all the SIM target compounds at or above the CRQLs, then the SIM analysis is not to be performed.

4.2.2.3 Sample analyses will be ordered by groups of samples. Each order will identify a Case number(s). A Case signifies a group of samples collected at one site or geographical area over a finite time period, and will include one or more field samples with associated blanks. Samples may be shipped to the Contractor in a single shipment or multiple shipments over a period of time, depending on the size of the Case.

4.2.2.3.1 A Case consists of one or more SDG(s). An SDG may be defined in individual task orders. An SDG may also be defined as the following, whichever is most frequent:

- Each Case of field samples received; or
- Each 20 field samples [excluding Performance Evaluation (PE) samples] within a Case; or
- Each 7 calendar day period (3 calendar day period for 7 day turnaround) during which field samples in a Case are received (said period beginning with receipt of the first sample in the SDG).

In addition, all samples assigned to an SDG must have been ordered under the same contractual turnaround time. Preliminary Results have **no impact** on defining the SDG.

4.2.2.3.2 PE samples received within a Case shall be assigned to an SDG containing field samples for that Case. Such assignment shall be made at the time the samples are received, and shall not be made retroactively.

4.2.2.3.3 Each sample received by the Contractor will be labeled with an EPA assigned Sample Number, and accompanied by a Traffic Report/Chain of Custody (TR/COC) bearing the Sample Number and descriptive information regarding the sample. The Contractor shall complete and sign the TR/COC recording the date of sample receipt and sample condition on receipt for each sample container.

4.2.2.3.4 The Contractor shall submit signed copies of TR/COCs for all samples in an SDG to the TOPO within **three working days** following receipt of the last sample in the SDG. TR/COCs shall be submitted in SDG sets (i.e., all TR/COCs for an SDG shall be clipped together) with an SDG Cover Sheet containing information regarding the SDG, as specified in Exhibit B.

4.2.2.3.5 USEPA Case Numbers, SDG Numbers, and EPA Sample Numbers shall be used by the Contractor in identifying samples received under the contract, both verbally and in reports/correspondence.

4.2.2.4 Preparation Techniques

The Contractor will prepare samples as described in Exhibit D.

4.2.2.5 Analytical Techniques

The target compounds listed in Exhibit C shall be identified as described in the methodologies given in Exhibit D. Automated computer programs may be used to facilitate the identification of compounds.

4.2.2.6 Qualitative Verification of Compounds

The volatile compounds identified by GC/MS techniques shall be verified by an analyst competent in the interpretation of mass spectra by comparison of the suspect mass spectrum to the mass spectrum of a standard of the suspected compound. This procedure requires the use of multiple internal standards.

4.2.2.6.1 If a compound initially identified by GC/MS techniques cannot be verified, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the Contractor shall report that identification and proceed with quantitation.

4.2.2.7 Quantitation of Verified Compounds

The Contractor shall quantitate components identified by GC/MS techniques by the internal standard method stipulated in Exhibit D. Where multiple internal standards are required by USEPA, the Contractor shall perform quantitation utilizing the internal standards specified in Exhibit D.

4.2.2.8 Tentative Identification of Non-Target Sample Components

For each analysis of a sample, the Contractor may be required to conduct mass spectral library searches to determine tentative compound identifications. The Contractor shall conduct a search to determine the possible identity of up to 30 organic compounds of greatest

concentration which are not internal standard compounds, or alkanes, and are not target compounds listed in Exhibit C. In performing searches, the NIST/EPA/NIH (2002 release or later) and/or Wiley (1991 release or later), or equivalent, mass spectral library shall be used.

NOTE: Specific recipient names and addresses are subject to change during the term of the contract. The Contracting Officer (CO) will notify the Contractor, in writing, of such changes when they occur.

4.2.2.9 Quality Assurance/Quality Control (QA/QC) Procedures

The Contractor shall strictly adhere to all specific QA/QC procedures prescribed in Exhibits D and E. Records documenting the use of the protocol shall be maintained in accordance with the document control procedures prescribed in Exhibit F, and shall be reported in accordance with Exhibit B and Exhibit H.

4.2.2.9.1 The Contractor shall maintain a Quality Assurance Plan (QAP) with the objective of providing sound analytical chemical measurements. This program shall incorporate the QC procedures, any necessary corrective action, and all documentation required during data collection, as well as the quality assessment measures performed by management to ensure acceptable data production.

4.2.2.9.2 Additional QC shall be conducted in the form of the analysis of PE samples submitted to the laboratory by USEPA. Unacceptable results of all such QC or PE samples may be used as the basis for an equitable adjustment to reflect the reduced value of the data to USEPA or rejection of data for specific compound(s) within an SDG or the entire SDG. Also, unacceptable results may be used as the basis for contract action. "Compliant performance" is defined as that which yields correct analyte identification and concentration values, as determined by USEPA, as well as meeting the contract requirements for analysis (Exhibit D), QA/QC (Exhibit E), data reporting and other deliverables (Exhibits B and H), and sample custody, sample documentation, and SOP documentation (Exhibit F). As an alternative to data rejection, USEPA may require reanalysis of non-compliant samples. Reanalysis will be performed by the Contractor at no additional cost to USEPA, unless it is determined that the PE sample(s) was defective.

4.2.2.10 Modified Analysis

The Contractor may be requested by USEPA to perform modified analyses. These modifications may include, but are not limited to: additional compounds and lower quantitation limits. These requests will be made by the TOPO in writing, prior to sample ordering. All contract requirements specified in the SOW/specifications will remain in effect.

4.2.3 Task III: Sample Reporting Requirements and Resubmission of Data

4.2.3.1 Required formats for the reporting of data are found in Exhibits B and H. The Contractor shall be responsible for completing and submitting analysis data sheets and electronic data in the format specified in this SOW and within the time specified in Exhibit B, Section 1.1 or as specified in individual task orders.

4.2.3.2 Use of formats other than those approved will be deemed as non-compliant. Such data are unacceptable. Resubmission in the specified format at no additional cost to USEPA shall be required.

4.2.3.3 Computer-generated forms may be submitted in the hardcopy Sample Data Package(s) provided that the forms provide equivalent information as the **USEPA format**. This means that the order of data elements is the same as on each USEPA-required form, including form numbers and titles, page numbers, and header information.

4.2.3.4 If the submitted data package does not conform to the specified contractual or technical criteria, the Contractor will be required to resubmit the data package and electronic data deliverable with all deficiencies corrected at its own expense. The Contractor will respond within 7 days to requests for additional information or explanations that result from the Government's inspection activities. If the Contractor is required to submit or resubmit data as a result of a Regional request, the data shall be clearly marked as ADDITIONAL DATA. The Contractor shall include a cover letter that describes which data are being delivered, to which EPA Case Number the data pertain, and who requested the data. Any and all resubmissions must be in accordance with the documentation requirements of this SOW.

4.2.3.5 The data reported by the Contractor on the hardcopy data forms and the associated electronic data submitted by the Contractor shall contain identical information. If discrepancies are found during Government inspection, the Contractor shall be required to resubmit either the corrected hardcopy forms or the corrected electronic data, or both sets of corrected data, at no additional cost to USEPA.

4.2.3.6 In addition, the Contractor must be aware of the importance of maintaining the integrity of the data generated under the contract, since it is used to make major decisions regarding public health and environmental welfare. The data may also be used in litigation against Potentially Responsible Parties (PRPs) in the enforcement of Superfund legislation.

EXHIBIT B

REPORTING AND DELIVERABLES REQUIREMENTS

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Exhibit B - Reporting and Deliverables Requirements

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1.0 CONTRACT REPORTS/DELIVERABLES DISTRIBUTION

1.1 Report Deliverable Schedule

The following table reiterates the contract reporting and deliverables requirements specified in the Contract Schedule (Performance/Delivery Schedule) and specifies the distribution that is required for each deliverable. The turnaround times for Items B through D listed below are 7, 14, and 21 days.

NOTE: Specific recipient names and addresses are subject to change during the term of the contract. The Contracting Officer (CO) will notify the Contractor, in writing, of such changes when they occur.

TABLE 1
Report Deliverable Schedule

Item		No. of Copies[A]	Delivery Schedule	Distribution	
				SMO	Region
A.[2]	Sample Traffic Reports/Chain of Custody Records	1	3 working days after receipt of last sample in an Sample Delivery Group (SDG).[1]	X	
B.[2]	Sample Data Package[B]	1	XX[C] days after receipt of last sample in an SDG.	X	
C.[2]	Electronic Data Deliverable	1	XX[C] days after receipt of last sample in an SDG.	X	
D.[2, 3]	Complete SDG File	1	XX[C] days after receipt of last sample in an SDG.		X
E.[2]	Hardcopy Data in PDF Format	1	XX[c] days after receipt of last sample in an SDG.		X
F.[4]	Preliminary Results	1	Within 48 hours after receipt of each sample in an SDG at laboratory, if requested.	X	X
G.[5]	Standard Operating Procedures--Technical and Evidentiary	1	Revise within 60 days after contract award. Submit within 7 days of receipt of written request to recipients as directed.	As directed	

TABLE 1
Report Deliverable Schedule (Cont.)

Item		No. of Copies[A]	Delivery Schedule	Distribution	
				SMO	Region
H.[5]	Quality Assurance Plan	1	Revise within 60 days after contract award. Submit within 7 days of receipt of written request to recipients as directed.	As directed	
I.	GC/MS Electronic Data	Lot	Retain for 3 years after data submission. Submit within 7 days after receipt of written request by CLP PO.	As directed	
K.	Method Detection Limit Study[6]		Submit to USEPA within 7 days after receipt of written request by CLP PO or SMO, at USEPA's direction.	As directed	

Laboratories:

[A] The number of copies specified are the number of copies required to be delivered to each recipient.

[B] Contractor-concurrent delivery to USEPA-designated recipient may be required upon request by the Project Officer (PO). Retain for 365 days after data submission, and submit as directed within 7 days after receipt of written request by the CO or PO.

[C] The number of days associated with these elements will be provided in the associated laboratory contract document, and will also be provided at the time of the sample ordering in the task order.

[1] The Sample Delivery Group (SDG) will be defined in the individual task orders.

[2] **DELIVERABLES ARE TO BE REPORTED TOTAL AND COMPLETE. Delivery shall be made such that all designated recipients receive the item on the same calendar day. The Data Receipt Data (DRD) of the SDG and any samples within the SDG is the date that the Electronic Data Deliverable (EDD) and the Hardcopy of the Deliverable have both been received. If one of these items is delivered at a later date, the date that the last item is delivered is the SDG DRD. If the deliverables are due on a Saturday, Sunday, or Federal holiday, then they shall be delivered on the next business day. Deliverables delivered after this time will be considered late.**

[3] Complete Sample Delivery Group File (CSF) will contain the original Sample Data Package plus all of the original documents described under Section 2.6.

[4] If requested at the time of sample scheduling, the Contractor shall provide Preliminary Results, consisting of Form I and Form I TIC analytical results if requested, by fraction, for field and Quality Control (QC) sample analyses via facsimile or email. The Contractor may submit Preliminary Results in electronic format after obtaining permission from USEPA. The Contractor will be notified of the fax number or email address at the time of sample ordering. Sample Traffic Report/Chain of Custody Records (TR/COCs) and SDG Cover Sheets shall be submitted with the Preliminary Results. The Contractor shall document all communication in a telephone contact log.

[5] See Exhibit E and Exhibit F for a more detailed description.

[6] Method Detection Limit (MDL) Study is to be performed annually, or for each new instrument, whichever is more frequent. The information should be available on file and provided to USEPA within 7 days after the receipt of a written request.

Preliminary Results Delivery Schedule:

If the sample arrives before 5 p.m., the Preliminary Results for that sample are due within the required turnaround time. If the sample is received after 5 p.m., the Preliminary Results for that sample are due within the required turnaround time beginning at 8 a.m. the following day. **DELIVERABLES ARE TO BE REPORTED TOTAL AND COMPLETE. Concurrent delivery is required. Delivery shall be made such that all designated recipients receive the item on the same calendar day. If the deliverables are due on a Saturday, Sunday, or Federal holiday, then they shall be delivered on the next business day. Deliverables delivered after this time will be considered late.**

1.2 Distribution

The following addresses correspond to the "Distribution" column in Table 1 of Section 1.1:

SMO:

USEPA Contract Laboratory Program
Sample Management Office (SMO)[1]
15000 Conference Center Drive
Chantilly, VA 20151-3808

Task Order Project Officer (TOPO):

As identified in individual task orders.

USEPA REGIONS:

SMO will provide the Contractor with the list of addresses for the 10 USEPA Regions. SMO will provide the Contractor with updated Regional address/name lists as necessary throughout the period of the contract and identify other client recipients on a case-by-case basis.

Program Manager/Project Officer Mailing Address:

USEPA OSRTI Analytical Services Branch
Ariel Rios Building (5203P)
1200 Pennsylvania Avenue, N.W.
Washington, D.C. 20460
Attn: Air Volatiles Program Manager/Project Officer

[1] SMO is a Contractor-operated facility operating under the SMO contract, awarded and administered by USEPA.

Fed-Ex/Overnight Delivery:

USEPA OSRTI Analytical Services Branch
One Potomac Yard (South Building)
2777 South Crystal Drive
4th Floor, S-4838
Arlington, VA 22202
Attn: Air Volatiles Program Manager/Project Officer

2.0 REPORTING REQUIREMENTS AND ORDER OF DATA DELIVERABLES

2.1 Introduction

The Contractor shall provide reports and other deliverables as specified in the Contract Schedule (Performance/Delivery Schedule). The required content and form of each deliverable is described in this Exhibit. All reports and documentation **must be**:

- Legible;
- Clearly labeled and completed in accordance with instructions in this exhibit;
- Arranged in the order specified in this section;
- Paginated consecutively in ascending order starting from the Sample Delivery Group (SDG) Narrative;
- Copies must be legible and double-sided; and
- Information reported on the forms listed in this Exhibit [excluding the Sample Log-In Sheet (DC-1), the Complete SDG File (CSF) Inventory Sheet (DC-2), and the Canister Sampling Field Test Data Sheet (DC-3)] must be either typewritten or computer-generated. Handwritten corrections of the information must be legible, signed, and dated.

NOTE: CSFs need not be double-sided. (The CSF is composed of original documents.) However, Sample Data Packages delivered to the Sample Management Office (SMO), and USEPA-designated recipients [e.g., Quality Assurance Technical Support (QATS)] upon written request, must be double-sided.

2.1.1 Requirements for each deliverable item cited in the Contract Schedule (Performance/Delivery Schedule) are specified in Sections 2.3 through 2.10. Prior to submission, the Contractor shall arrange items and the components of each item in the order listed in these sections.

2.1.2 The Contractor shall use EPA/assigned Case Numbers, SDG numbers, designated Sample Numbers, and task order numbers (if applicable) to identify samples received under the contract, both verbally and in reports/correspondence. The Contract Number and task order number, if applicable, shall be specified in all correspondence.

2.1.3 If Selected Ion Monitoring (SIM) analysis is performed, then all SIM data (Forms and raw data) must be arranged at the end of the subsection [i.e., Trace VOA-SIM must be at the end of the Trace-VOA section].

2.2 Resubmission of Data

If submitted documentation does not conform to the above criteria, the Contractor is required to resubmit such documentation with deficiency(ies) corrected within 6 business days, at no additional cost to USEPA. Only the

nonconforming documentation is required to be resubmitted (i.e., if only the hardcopy in Portable Document Format (PDF) is nonconforming, then a resubmittal of only the corrected hardcopy is required).

2.2.1 Whenever the Contractor is required to submit or resubmit data as a result of an on-site laboratory evaluation, or through a Project Officer (TOPO) action or request, the data shall be clearly marked as ADDITIONAL DATA and shall be sent to all contractual data recipients as well as designated recipients. The Contractor shall include a cover letter that describes which data are being delivered, to which project the data pertain, and **who requested the data**. A copy of the cover letter shall be submitted to the Contracting Officer (CO).

2.3 Quality Assurance Plan (QAP) and Standard Operating Procedures (SOPs)

The Contractor shall adhere to the requirements in Exhibits E and F.

2.4 Traffic Report/Chain of Custody Records (TR/COCs)

Each sample received by the Contractor will be labeled with an designated Sample Number. Designated Numbers are continuous (without spaces or hyphens). Each sample will be accompanied by a Sample TR/COC bearing the Sample Number and descriptive information regarding the sample. The Contractor shall complete the TR/COC, recording the date of sample receipt and shall sign the TR/COC. Information shall be recorded for each sample in the SDG.

2.4.1 The Contractor shall submit TR/COCs in SDG sets (i.e., TR/COCs for all samples in an SDG shall be clipped together), with an SDG Cover Sheet attached. The SDG Cover Sheet shall contain the following items:

- Laboratory name;
- Contract number;
- Task Order number;
- Modification number;
- Sample analysis price (full sample price from the contract);
- Case Number; and
- List of designated Sample Numbers of all samples in the SDG, identifying the **first** and **last** samples received, and the Laboratory Receipt Dates (LRDs).

NOTE: When more than one sample is received in the first or last SDG shipment, the "first" sample received would be the lowest Sample Number (considering both alpha and numeric designations); the "last" sample received would be the highest Sample Number (considering both alpha and numeric designations).

2.4.2 Designated Sample Numbers are continuous (without spaces or hyphens).

2.4.3 Each TR/COC shall be clearly marked with the SDG Number, entered below the LRD on the TR/COC. The TR/COC for the **last** sample received in the SDG shall be clearly marked "SDG–FINAL SAMPLE". The SDG Number is the designated Sample Number of the first sample received in the SDG. When several samples are received together in the first SDG shipment, the SDG Number shall be the lowest Sample Number (considering both alpha and numeric designations) in the first group of samples received under the SDG.

2.4.4 If samples are received at the laboratory with multi-sample TR/COCs, all the samples on one multi-sample TR/COC may not necessarily be in the same SDG. In this instance, the Contractor shall make the appropriate number of photocopies of the TR/COC, and submit one copy with each SDG Cover Sheet.

2.5 Sample Data Package

The Sample Data Package is divided into the three major units described in this section. If analysis by SIM is required, report all data for SIM analysis as a subsection at the end of the fraction. The Sample Data Package shall include data for the analyses of all samples in one SDG, including: field samples; dilutions; reanalyses; blanks; and Laboratory Control Samples (LCSs). The Contractor shall retain a copy of the Sample Data Package for 365 days after final acceptance of data. After this time, the Contractor may dispose of the package.

2.5.1 SDG Narrative

This document shall be clearly labeled "SDG Narrative" and shall contain: Laboratory Name; Case Number; designated Sample Numbers in the SDG, differentiating between initial analyses and reanalyses; SDG Number; Contract Number; Task Order number; and detailed documentation of any Quality Control (QC), sample, shipment, and/or analytical problems encountered in processing the samples reported in the data package.

The Contractor shall also provide, in the SDG Narrative, sufficient information, including equations or curves (at least one equation or curve per method), to allow the recalculation of sample results from raw instrument output. The Contractor shall also include a discussion of any flexibility Statement of Work (SOW) modifications. This includes attaching a copy of the USEPA-approved modification form to the SDG Narrative. Additionally, the Contractor shall also identify and explain any differences that exist between the Form Is and supporting documentation provided in the data package and those previously provided as Preliminary Results.

All Gas Chromatography (GC) columns used for analysis shall be documented here, by fraction. List the GC column identification--brand name, the internal diameter, in millimeters (mm), and the length, in meters (m), packing/coating material, and film thickness. The trap used for volatile analysis shall be described here. List trap name, when denoted by the manufacturer, its composition (packing material/brand name, amount of packing material, in length). The Contractor shall include any technical and administrative problems encountered, the corrective actions taken, the resolution, and an explanation for all flagged edits (e.g., manual edits) on quantitation lists. The Contractor shall document in the SDG Narrative all instances of manual integration.

The SDG Narrative shall contain the following statement, verbatim: "**I certify that this Sample Data Package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy Sample Data Package and in the electronic data deliverable has been authorized by the Laboratory Manager or the Manager's designee, as verified by the following signature.**" This statement shall be directly followed by an original signature of the Laboratory Manager or designee with typed lines below it containing the signer's name and title, and the date of signature.

2.5.1.1 Whenever data from sample reanalyses are submitted, the Contractor shall state in the SDG Narrative for **each** reanalysis whether the reanalysis is billable, and if so, why.

2.5.1.2 The Contractor shall submit in writing all email correspondences or telephone conversations with SMO or the Region.

2.5.2 Traffic Report/Chain of Custody Records (TR/COC)

The Contractor shall include a copy of the TR/COCs submitted in Section 2.4 for all of the samples in the SDG. The TR/COCs shall be arranged in increasing designated Sample Number order, considering both letters and numbers. Copies of the SDG Cover Sheet are to be included with the copies of the TR/COCs. (See Section 2.4 for more detail on reporting requirements for TR/COCs.) In the case of multi-sample TR/COCs, the Contractor shall make the appropriate number of photocopies of the TR/COC so that a copy is submitted with each applicable data package. In addition, in any instance where samples from more than one multi-sample TR/COC are in the same data package, the Contractor shall submit a copy of the SDG Cover Sheet with copies of the TR/COCs.

2.5.3 Volatile Organics Analysis Data

2.5.3.1 Volatiles Quality Control (QC) Summary

2.5.3.1.1 Air Volatile Organics Laboratory Control Sample Recovery and Precision (Form II VOA-1, VOA-2, VOA-SIM):

2.5.3.1.2 Method Blank Summary (Form III VOA): If more than a single form is necessary, forms shall be arranged in chronological order by date of analysis of the blank, by instrument.

2.5.3.1.3 Form III contains a field labeled “Page ____ of ____” in the bottom left-hand corner. If the number of entries required on any of these forms exceeds the available space, continue entries on another copy of the same fraction-specific form, duplicating all header information. If a second page is required, number the pages consecutively (i.e., "Page 1 of 2" and "Page 2 of 2"). If a second page is **not** required, number the page "Page 1 of 1".

2.5.3.1.4 Internal Standard Area and Retention Time Study (Form VII VOA-1, VOA-SIM): If more than a single form is necessary, forms shall be arranged in chronological order, by instrument.

2.5.3.2 Volatile Organics Analysis Sample Data

Sample data shall be arranged with the Volatile Organics Analysis Data Sheet (Form I VOA-1, VOA-2), followed by the raw data for volatile samples. The sample data shall be placed in order of increasing designated Sample Number, considering both letters and numbers. Volatile sample data for SIM analysis must be arranged together with the rest of the SIM Volatiles data at the end of the subsection.

2.5.3.2.1 Target Compound Results, Volatile Organics Analysis Data Sheet (Form I VOA-1, VOA-2). Tabulated results (identification and quantitation) of the specified target compounds (Exhibit C - Volatiles) shall be included. The validation and release of these results are authorized by a specific, signed statement in the SDG Narrative (see Section 2.5.1). In the event that the Laboratory Manager cannot verify all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the SDG Narrative.

2.5.3.2.2 Tentatively Identified Compounds (TICs) (Form I VOA-TIC). Form I VOA-TIC is the tabulated list of the highest probable match for up

to 30 organic compounds that are not target compounds, internal standard compounds, or alkanes (excluding target compound n-octane). An alkane is defined as any hydrocarbon with the generic formula C_nH_{2n+2} (straight-chain or branched) or C_nH_{2n} (cyclic) that contains only C-H and C-C single bonds. The tabulated list includes the Chemical Abstracts Service (CAS) Number (if applicable), tentative identification, and estimated concentration. This form shall be included only if requested.

NOTE: This form is not required when submitting data for the optional analysis using the SIM technique.

2.5.3.2.3 Reconstructed Total Ion Chromatograms (for each sample including dilutions and reanalyses). Reconstructed ion chromatograms shall be normalized to the largest nonsolvent component and shall contain the following header information:

- Designated Sample Number;
- Date and time of analysis;
- GC/MS instrument identifier;
- Laboratory File Identifier; and
- Analyst ID.

NOTE: Each Selected Ion Current Profile (SICP) for samples taken through the optional analysis using the SIM technique shall be labeled as in this section.

2.5.3.2.3.1 Internal standards shall be labeled with the names of compounds, either directly out from the peak or on a printout of Retention Times (RTs) if RTs are printed over the peak. Labeling of other compounds is not required and should not detract from the legibility of the required labels.

2.5.3.2.3.2 If automated data system procedures are used for preliminary identification and/or quantitation of the target compounds, the complete data system report shall be included in all Sample Data Packages, in addition to the reconstructed ion chromatogram. The complete data system report shall include all of the information listed below.

- Designated Sample Number;
- Date and time of analysis;
- RT or scan number of identified target compounds;
- Ion used for quantitation with measured area;
- Copy of area table from data system;
- On column concentration/amount, including units;
- GC/MS instrument identifier;
- Laboratory File Identifier; and
- Analyst ID.

2.5.3.2.3.3 In all instances where the data system report has been edited, or where manual integration or manual quantitation has been performed, the GC/MS Operator shall identify such edits or manual procedures by initialing and dating the changes made to

the report, and shall include the integration scan range. The GC/MS Operator shall also mark each integrated area with the letter "m" on the quantitation report. In addition, a hardcopy printout of the Extracted Ion Current Profile (EICP) of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all compounds listed in Exhibit C, and internal standards.

2.5.3.2.4 Other Required Information. For each sample, by each compound identified, the following items shall be included in the data package:

- Copies of raw spectra and copies of background-subtracted mass spectra of target compounds listed in Exhibit C that are identified in the sample and corresponding background-subtracted target compound standard mass spectra. This includes target compounds that are identified during the optional analysis using the SIM technique. Spectra shall be labeled with designated Sample Number, Laboratory File Identifier, date and time of analysis, and GC/MS instrument identifier. Compound names shall be clearly marked on all spectra; and
- If TICs are requested, copies of mass spectra of organic compounds not listed in Exhibit C with associated best-match spectra (maximum of three best matches). Spectra shall be labeled with designated Sample Number, Laboratory File Identifier, date and time of analysis, and GC/MS instrument identifier. Compound names shall be clearly marked on all spectra.

2.5.3.3 Volatiles Standards Data

2.5.3.3.1 Initial Calibration Data (Form V VOA-1, VOA-2, VOA-SIM): If more than a single form is necessary, forms shall be arranged in chronological order, by instrument.

- Volatile standard(s) reconstructed ion chromatograms and quantitation reports for the initial (five-point) calibration, labeled as in Section 2.5.3.2.3. Spectra are not required.
- All initial calibration data that pertain to samples in the data package shall be included, regardless of when it was performed and for which Case. When more than one initial calibration is performed, the data shall be in chronological order, by instrument.
- Labels for standards shall reflect the concentrations of the analytes in ppbv.
- EICPs displaying each manual integration.

NOTE: Form V VOA-SIM is not required for the optional analysis when submitting data using the SIM technique.

2.5.3.3.2 Continuing Calibration Verification Data (Form VI VOA-1, VOA-2, VOA-SIM) shall be included in order by instrument, if more than one instrument is used.

- Volatile standard(s) reconstructed ion chromatograms and quantitation reports for all continuing (24-hour) calibration verifications, labeled as in Section 2.5.3.2.3. Spectra are not required.

- When more than one Continuing Calibration Verification (CCV) is performed, forms shall be in chronological order, by instrument.
- EICPs displaying each manual integration.

2.5.3.3.3 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS Operator shall identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the integration scan range. The GC/MS Operator shall also mark each integrated area with the letter "m" on the quantitation report. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all compounds listed in Exhibit C – Volatiles and internal standards.

2.5.3.4 Volatiles Raw QC Data

2.5.3.4.1 Instrument Performance Check Bromofluorobenzene (BFB) (Form IV VOA) shall be arranged in chronological order by instrument for each 24-hour period, for each GC/MS system utilized.

- Bar graph spectrum, labeled as in Section 2.5.3.2.3.
- Mass listing, labeled as in Section 2.5.3.2.3.
- Reconstructed total ion chromatogram, labeled as in Section 2.5.3.2.3.

2.5.3.4.2 Blank data shall be arranged in chronological order, by instrument.

NOTE: This order is different from that used for samples.

- Tabulated results (Form I VOA-1, VOA-2, VOA-SIM).
- Tentatively Identified Compounds (Form I VOA-TIC) required only if TICs have been requested.
- Reconstructed ion chromatogram(s) and quantitation report(s), labeled as in Section 2.5.3.2.3.
- Target compound spectra with laboratory-generated standard, labeled as in Section 2.5.3.2.4. Data systems that are incapable of dual display shall provide spectra in the following order:

  -- Raw target compound spectra.

  -- Enhanced or background-subtracted spectra.

  -- Laboratory-generated standard spectra.

- GC/MS library search spectra for TICs if requested, labeled as in Section 2.5.3.2.4.
- Quantitation/calculation of TIC concentrations if requested.

2.5.3.4.3 Volatiles LCS Data

- Tabulated results (Form I VOA-1, VOA-2, VOA-SIM) of target compounds. Form I VOA-TIC is not required.
- Reconstructed ion chromatogram(s) and quantitation report(s), labeled as in Section 2.5.3.2.3. Spectra are not required.

2.6 Complete SDG File (CSF)

As specified in Section 1, the Contractor shall deliver one CSF (including the original Sample Data Package) to the TOPO concurrently with delivery of the Sample Data Package to SMO. Delivery to USEPA's designated recipients is only required upon written request.

2.6.1 The CSF will contain all original documents specified in Sections 3 and 4 and on Form DC-2 (Section 3.13). No photocopies of original documents will be placed in the CSF unless the original data was initially written in a bound notebook, maintained by the Contractor, or the originals were previously submitted to USEPA with another Case/SDG in accordance with the requirements described in Exhibit F. The contents of the CSF shall be numbered according to the specifications described in Section 3.13.

2.6.2 The CSF will consist of the following original documents in addition to the documents in the Sample Data Package.

NOTE: All SDG-related documentation may be used or admitted as evidence in subsequent legal proceedings. Any other SDG-specific documents generated after the CSF is sent to the TOPO, as well as copies that are altered in any fashion are also deliverables. Deliver the original to the TOPO and a copy to SMO. Delivery to USEPA's designated recipients is only upon written request.

2.6.2.1 Original Sample Data Package

2.6.2.2 A completed and signed Organics CSF Inventory Sheet (Form DC-2).

2.6.2.3 All original shipping documents including, but not limited to, the following documents:

- Airbills (if an airbill is not received, include a hardcopy receipt requested from the shipping company or a printout of the shipping company's electronic tracking information);
- USEPA Sample TR/COCs; and
- Sample tags (if present) sealed in plastic bags.

2.6.2.4 All original receiving documents including, but not limited to, the following documents:

- Form DC-1;
- Other receiving forms or copies of receiving logbooks; and
- SDG Cover Sheet.

2.6.2.5 All original laboratory records, not already submitted in the Sample Data Package, of sample transfer, preparation, and analysis including, but not limited to, the following documents:

- Log book preparation entries documenting the steps and calculations of diluted and working standards and/or receipt of stock standards showing the lot number and date of receipt or date of preparation for all standards and spiking solutions;
- Original preparation and analysis forms or copies of preparation and analysis logbook pages;
- Internal sample transfer chain-of-custody records;
- Screening records; and
- All instrument output, including strip charts from screening activities.

2.6.2.6 All other original SDG-specific documents in the possession of the Contractor including, but not limited to, the following documents:

- Telephone contact logs;
- Copies of personal logbook pages;
- All handwritten SDG-specific notes; and
- Any other SDG-specific documents not covered by the above.

2.6.3 If the Contractor does submit SDG-specific documents to the TOPO after submission of the CSF, the documents should be identified with unique accountable numbers, a revised Form DC-2 should be submitted, and the unique accountable numbers and locations of the documents in the CSF should be recorded in the "Other Records" section on the revised Form DC-2. Alternatively, the Contractor may number the newly submitted SDG-specific documents to the TOPO as a new CSF and submit a new Form DC-2. The revised Form DC-2 or new Form DC-2 should be submitted to the TOPO only.

2.7 Electronic Data Deliverable

The Contractor shall provide an electronic data deliverable on analytical data for all samples in the SDG, as specified in Exhibit H, and delivered as specified in the Contract Schedule (Performance/Delivery Schedule).

2.8 Delivery of Hardcopy Data in PDF Format

In addition to all required deliverables identified in the laboratory’s contract and the SAVM01.0 SOW, the laboratory shall provide a complete copy of the hardcopy deliverable in PDF on a Compact Disc (CD) if requested by the Region.

2.8.1 The PDF file should be organized in accordance to directions provided in Exhibit B, "Reporting Requirements and Order of Data Deliverables" of the SAV01.0 SOW. The PDF file shall be bookmarked as described below for ease of data retrieval and navigation.

2.8.2 Organic data shall be bookmarked using a hierarchal bookmark structure (i.e., an overview or "parent" bookmark, and a subordinate or "child" bookmark nested underneath the "parent" bookmark). The required hierarchal bookmark structure is shown in Table 2.

TABLE 2
Hierarchal Bookmark Structure

Group Bookmark	Parent Bookmark	Child Bookmarks
Sample TR/COCs, TR/COC Cover Sheet, and SDG Narrative		
		Laboratory Control Sample (LCS) Summary
		Method Blank
		GC/MS Instrument Performance Check
		Internal Standard Area and RT Summary
	Sample Data	Samples in increasing alphanumeric designated Sample Number order (with supporting raw data)
	Standards Data	Initial Calibration Data
		CCV Data, including closing CCV
	Raw QC Data	BFB Data
		Blank Data
		LCS Data

2.9 Preliminary Results

The Form Is data results shall be submitted for all samples in one SDG of a Case. The Contractor shall clearly identify the Preliminary Results by labeling each Form I and Form I TIC as "Preliminary Results" under each form title.

2.10 GC/MS Electronic Deliverables

The Contractor shall adhere to the requirements in Exhibit H.

3.0 FORMS INSTRUCTIONS

3.1 Introduction

This section includes specific instructions for completing the data reporting forms required under the contract. Each of the forms are specific to a given fraction The Contractor shall submit only those forms pertaining to the fractions analyzed for a given sample(s).

3.2 General Information

The Contractor shall report values on the hardcopy forms according to the individual form instructions in this section. For example, results for concentrations of volatile target compounds shall be reported to two significant figures if the value is greater than or equal to 0.5. Values that exceed the maximum length allowed shall be reported to the maximum possible, maintaining the specified decimal place. Unless otherwise specified, all values must be reported to at least two significant figures.

3.2.1 The data reporting forms presented in Section 4 have been designed in conjunction with the computer-readable data format specified in Exhibit H. Information entered on these forms shall **not** exceed the size of the field given on the form, including such laboratory-generated items as "Lab Name" and "Lab Sample ID".

3.2.2 When submitting data, the Contractor shall reproduce **all** characters that appear on the data reporting forms in Section 4. The format of the forms submitted shall provide exactly the same information as that shown in the contract. No information may be added, deleted, or moved from its specified position without prior written approval from the Task Order Project Officer (TOPO). The names of the various fields and compounds (i.e., "Lab Code", "Chloromethane") shall appear as they do on the forms in the contract, including the options specified in the form.

3.2.3 If an entry does not fill the entire blank space provided on the form, null characters shall be used to remove the remaining underscores that comprise the blank line. However, the Contractor shall not remove the underscores or vertical bars that delineate "boxes" on the forms. The only exception would be those underscores at the bottom of a "box" that are intended as a data entry line.

3.3 Header Information

Seven pieces of information are common to the header section of each data reporting form: Laboratory Name (Lab Name); Contract; Laboratory Code (Lab Code); Case Number; Modification Reference Number (Mod. Ref. No.); Task Order Number (TO No.); and Sample Delivery Group (SDG) Number (SDG No.). Except as noted for Mod. Ref. No. and TO No., this information shall be entered on every form and shall match on every form.

3.3.1 Laboratory Name

The "Lab Name" shall be the name chosen by the Contractor to identify the laboratory. It shall not exceed 25 characters.

3.3.2 Contract

The "Contract" refers to the number of the USEPA contract under which the analyses were performed.

3.3.3 Laboratory Code

The "Lab Code" is an alphabetical abbreviation of up to six letters, as assigned by USEPA, to identify the laboratory and aid in data processing. This Laboratory Code will be assigned by USEPA at the time a contract is awarded, and shall not be modified by the Contractor, except at the direction of USEPA. If a change of name or ownership occurs at the laboratory, the Laboratory Code will remain the same until the Contractor is directed by USEPA to use another Laboratory Code.

3.3.4 Case Number

The "Case No." is the Sample Management Office (SMO)-assigned Case Number (to five characters) associated with the sample. This number is reported on the Traffic Report/Chain of Custody Record (TR/COC).

3.3.5 Modification Reference Number

The "Mod. Ref. No." is the USEPA-assigned number for analyses performed under the modified analysis clause in Exhibit A, Section 4.2.2.11. If sample analyses are performed under the modified analysis clause, the Contractor shall list both the Case Number and the Modification Reference Number on all forms. If there are no modified analysis requirements, leave the "Mod. Ref. No." field blank.

3.3.6 SDG Number

The "SDG No." field is for the SDG Number. It is the designated Sample Number of a field sample assigned to the SDG and shall be unique for each SDG within a Case. When several samples are received together in the first SDG shipment, the SDG Number shall be the lowest Sample Number (considering both alpha and numeric designations) in the first group of samples received under the SDG.

3.3.7 Task Order Number

The "TO No." field is for the Task Order Number. It is the number assigned to the Task Order under which the samples were ordered.

3.3.8 Sample Number

The "Designated Sample No." appears either in the header information of the form, or as the left column of a table summarizing data from a number of samples. When the Designated Sample Number is entered in the box in the upper right-hand corner of Form I, Form III, Form IV, or Form V, it should be centered.

3.3.8.1 The Contractor shall identify **all** samples, including: dilutions; re-analyses; Laboratory Control Samples (LCSs); blanks; instrument performance check; and standards with an EPA Sample Number. For field samples, the designated Sample Number is the unique identifying number given on the TR/COC that accompanied that sample. In order to facilitate data assessment, the Contractor shall use the following sample suffixes:

XXXXX = Designated Sample Number

XXXXXRE = Reanalyzed (re-injected) sample.

XXXXXDL = The suffix DL is appended to the designated Sample Number to indicate that the analytical results are a result of a dilution of the original analysis (reported as EPA Sample XXXXX). See Exhibit D for dilution requirements.

XXXXXDL2 = Samples analyzed at a secondary dilution.

XXXXXDL3 = Samples analyzed at a third dilution.

3.3.8.2 For blanks, the Contractor shall use the following identification scheme for the designated Sample Number:

- Volatile method blanks shall be identified as VBLK##. The designated Sample Number shall be unique for each blank within an SDG. Within a fraction, the Contractor shall achieve this by replacing the two-character suffix (##) of the identifier with one or two characters or numbers, or a combination of both. For example, possible identifiers for blanks would be VBLK1, VBLK2, VBLKA1, VBLKB2, VBLK10, VBLKAB, etc.

3.3.8.3 The designated Sample Number shall be unique for each LCS within the SDG. The LCSs shall be identified as: Volatiles LCS - VLCS##

3.3.8.4 Volatile instrument performance checks shall be identified as BFB##

BFB = Bromofluorobenzene (instrument performance check compound for Volatiles analysis).

= One or two characters, numbers, or combinations of both to create a unique EPA Sample Number within an SDG.

3.3.8.5 Volatile standards shall be identified as VSTD***##, where:

STD = Standard.

*** = Concentration of volatile standards in ppbv.

= One or two characters, numbers, or combinations of both to create a unique EPA Sample Number within an SDG.

3.3.9 Other Common Fields

Several other pieces of information are common to many of the data reporting forms. These include sample volume, Laboratory Sample Identifier, and Laboratory File Identifier.

3.3.9.1 The "Sample Volume" field is used for volatile samples and associated calibration standards to describe the total volume of sample or calibration standard that is pulled through the trap. Enter the volume in mL or L to three significant figures.

3.3.9.2 The Laboratory Sample Identifier is a unique laboratory-generated internal identifier pertaining to a particular analysis. The Contractor must enter the Laboratory Sample Identifier using alpha-numeric characters in the "Lab Sample ID" field. The Contractor may use the designated Sample Number as the Laboratory Sample Identifier.

3.3.9.3 The Laboratory File Identifier is the unique laboratory-generated name of the GC/MS data system file containing information pertaining to a particular analysis. The Contractor must enter the Laboratory File Identifier using alpha-numeric characters in the "Lab File ID" field.

3.3.9.4 The "Instrument ID" field is common to the forms containing calibration data. The identifier used by the Contractor shall include some indication of the manufacturer and/or model of the instrument, and shall contain additional characters that differentiate between all instruments of the same type in the laboratory.

3.3.9.5 Forms IV, V, and VIII contain a field labeled “Page ___ of __” in the bottom left-hand corner. If the number of entries required on any of these forms exceeds the available space, continue entries on another copy of the same fraction-specific form, duplicating all header information. If a second page is required, number the pages consecutively (i.e., "Page 1 of 2" and "Page 2 of 2"). If a second page is **not** required, number the page "Page 1 of 1".

3.3.10 Rounding Rule

For rounding off numbers to the appropriate level of precision, the Contractor shall follow these rules. If the figure following those to be retained is less than 5, drop it (round down). If the figure is greater than or equal to 5, drop it and increase the last digit to be retained by 1 (round up).

3.4 Volatile Organics Analysis Data Sheet (Form I)

3.4.1 Purpose

This form is used for tabulating and reporting sample analysis, including dilutions, reanalysis, blanks, and LCS results for target compounds and TICs. If all analyses are not required for analysis, only the pages for the fractions required shall be submitted. For example if only volatiles SCAN analysis is requested with no TICs, only Forms VOA-1 and VOA-2 would be needed for sample results. Additional Form I's would be needed for reporting the LCS, method blanks, etc. in the appropriate section of the data package.

3.4.2 Instructions

Complete the header information according to the instructions in Section 3.3. Complete the remainder of the form using the following instructions.

3.4.2.1 Enter the GC Column Identifier in the "GC Column" field on Forms I VOA-1, VOA-2, VOA-SIM, VOA-TIC, VOA-Canister-1, VOA-Canister-2, VOA-Canister-SIM, and VOA-Canister-TIC and the internal diameter in mm, to two decimal places, in the "ID" field.

3.4.2.2 Enter the date of sample receipt at the laboratory, as noted on the TR/Chain of Custody Record [i.e., the Validated Time of Sample Receipt (VTSR)], in the "Date Received" field. The date shall be entered as MM/DD/YYYY.

3.4.2.3 Complete the "Date Analyzed" fields in the same format (MM/DD/YYYY). The date of sample receipt will be compared with the extraction and analysis dates of each fraction to ensure that contract holding times were not exceeded.

3.4.2.4 If a sample has been diluted for analysis, enter the DF value to one decimal place in the "Dilution Factor" field (i.e., a DF of 1 will be reported as 1.0; DF of 10 will be reported as 10.0).

3.4.2.5 For positively identified target compounds, the Contractor shall report the concentrations as **uncorrected** for blank contaminants.

3.4.2.6 Report all analytical results to two significant figures (i.e., if the value is 9.7, report 9.7; if the value is 10.3, report 10).

3.4.2.7 Enter the concentration in the "ppbv" and "ug/m^3" fields.

3.4.2.8 Under the column labeled "Q" for qualifier, flag each result with the specific data reporting qualifiers listed below. When reporting results to USEPA, the Contractor shall use these contract-specific qualifiers. The Contractor shall not modify the qualifiers. Up to five qualifiers may be reported on Form I for each compound. The Contractor is encouraged to use additional flags or footnotes (see the X qualifier).

The USEPA-defined qualifiers to be used are:

U: This flag indicates the compound was analyzed for but not detected. The Contract Required Quantitation Limit (CRQL) shall be adjusted according to the equation listed in Exhibit D. CRQLs are listed in Exhibit C.

J: This flag indicates an estimated value. This flag is used when: (1) estimating a concentration for Tentatively Identified Compounds (TICs) where a 1:1 response is assumed; and (2) the mass spectral and Retention Time (RT) data indicate the presence of a compound that meets the GC/MS identification criteria, and the result is less than the adjusted CRQL but greater than zero; and For example, if the sample's adjusted CRQL is 5.0 µg/L, but a concentration of 3.0 µg/L is calculated, report it as 3.0J.

N: This flag indicates presumptive evidence of a compound. This flag is only used for TICs, where the identification is based on a mass spectral library search and must be used in combination with the J flag. It is applied to all TIC results. For generic characterization of a TIC, such as chlorinated hydrocarbon, or for an "unknown" (no matches ≥ 85%), the "N" flag is not used.

B: This flag is used when the analyte is found in the associated method blank as well as in the sample. It indicates probable blank contamination and warns the data user to take appropriate action. This flag shall be used for a TIC as well as for a positively identified target compound.

The combination of flags "BU" or "UB" is expressly prohibited. Blank contaminants are flagged "B" only when they are detected in the sample.

E: This flag identifies compounds whose response exceeds the response of the highest standard in the initial calibration range of the instrument for that specific analysis. If one or more compounds have a response greater than the response of the highest standard in the initial calibration, the sample or extract shall be diluted and reanalyzed according to the specifications in Exhibit D. Exceptions are also noted in Exhibit D. All such compounds with responses greater than the response of the highest standard in the initial calibration shall have the result flagged with an "E" on Form I for the original analysis. The results of both analyses shall be reported on separate copies of Form I. The Form I for the diluted sample shall have "DL" suffix appended to the Sample Number.

D: If a sample or extract is reanalyzed at a DF greater than 1 (e.g., when the response of an analyte exceeds the response of the highest standard in the initial calibration), the DL suffix is appended to the Sample Number on Form I for the more diluted sample, and **all** reported concentrations on that Form I are flagged with the "D" flag. This flag alerts data users that any discrepancies between the reported concentrations may be due to dilution of the sample or extract.

NOTE 1: The "D" flag is not applied to compounds which are not detected in the sample analysis (i.e., compounds reported with the adjusted CRQL and the "U" flag).

NOTE 2: Separate Form Is are required for reporting the original analysis (designated Sample No. XXXXX) and the more diluted sample analysis (designated Sample No. XXXXXDL). The results from both analyses cannot be combined on a single Form I.

X: Other specific flags may be required to properly define the results. If used, the flags shall be fully described in the SDG Narrative. Begin by using "X". If more than one flag is required, use "Y" and "Z" as needed. If more than five qualifiers are required for a sample result, use the "X" flag to represent a combination of several flags. The laboratory-defined flags **are limited to** "X", "Y", and "Z".

3.5 Volatile Organics Analysis Data Sheet: Tentatively Identified Compounds (Form I VOA-TIC)

3.5.1 Purpose

This form is used to report analysis results for non-target compounds (e.g., compounds not listed in Exhibit C), excluding internal standards. See Exhibit D for instructions on identification and quantitation. If TICs are requested, the Contractor shall submit Form I VOA-TIC for every analysis, including required dilutions, reanalyses, and blanks, even if no TICs are found.

3.5.2 Instructions

Complete the header information according to the instructions in Section 3.3. Complete the remainder of the form using the following instructions in addition to the instructions in Section 3.4.

3.5.2.1 Report all TICs including Chemical Abstracts Service (CAS) Number (if applicable), compound name, RT, and the estimated concentration as uncorrected for blank contaminants. TICs shall be reported in chronological order for blank contaminants. TICs shall be reported in chronological order with respect to RTs. Report to two significant figures (criteria for reporting TICs are given in Exhibit D, Section 11) in ppbv units only. RT shall be reported in minutes and decimal minutes, **not** seconds or minutes:seconds.

3.5.2.2 Peaks that are suspected to be straight-chained, branched, or cyclic alkanes, and are alone or part of an alkane series, shall be library searched. Documentation for the tentative identification must be supplied. Alkane concentrations will be summed and reported as "total alkanes" on Form I VOA-TIC. This is not to include the target compound n-octane. Other target alkanes need to be listed - hexane, heptane, cyclohexane, cumene, etc.

3.5.2.3 If the name of a compound exceeds the 28 spaces in the TIC column, truncate the name to 28 characters. If the compound is an unknown, restrict the description to no more than 28 characters (e.g., unknown hydrocarbon).

3.6 Laboratory Control Sample (LCS) Recovery (Form II)

3.6.1 Air Volatile Organics LCS Recovery and Precision (Form II VOA-1, VOA-2, VOA-SIM)

3.6.1.1 Purpose

This form is used to report the results of the analyses of LCSs.

3.6.1.2 Instructions

Complete the header information according to the instructions in Section 3.3. Complete the remainder of the form using the following instructions.

3.6.1.2.1 If the LCS mixture is purchased by the Contractor from a third party, report the identification number used by the third party to identify the LCS lot, if available, in the "LCS Lot No." field. If the LCS mixture was prepared in-house, leave this entry blank.

3.6.1.2.2 Enter the date analyzed, and Instrument ID. All dates should be entered in MM/DD/YYYY format.

3.6.1.2.3 Under the "True LCS conc." column enter the certified LCS concentration in ppbv. Under the "LCS % rec." column, enter the percent recovery of each compound as calculated according to Exhibit D. Under the "True Cont. Calib conc." column enter the true concentration of the compound in the continuing calibration check standard. Under the "Cont Calib % rec." column, enter the percent recovery of each compound as calculated according to Exhibit D. Calculate the relative percent difference (RPD) according to Exhibit D and enter in the "RPD" column. Flag all Percent Recoveries and RPDs outside the QC limits with an asterisk ("*"). The asterisk must be placed in the last space of the Percent Recovery column or RPD column as appropriate.

3.7 Volatile Organics Method Blank Summary (Form III VOA)

3.7.1 Purpose

This form summarizes the samples associated with each method blank analysis. The Contractor shall submit the appropriate Form III for each blank.

3.7.2 Instructions

Complete the header information according to the instructions in Section 3.3. The designated Sample Number entered in the upper right-hand corner shall be the same number entered on Form I for the blank. Complete the remainder of the form using the following instructions.

3.7.2.1 Complete the following fields: "Instrument ID", "Calibration Date(s)", and "Calibration Time(s)". Dates shall be entered as MM/DD/YYYY. The time shall be reported using military time.

3.7.2.2 Identify the purge volume, GC column, internal diameter and length in the appropriate fields.

3.7.2.3 Summarize the samples, including LCSs, associated with a given method blank in the table, entering the designated Sample Number and Laboratory Sample Identifier. Enter the Laboratory File Identifier, Canister Number, and the date and time of analysis of each sample.

3.7.2.5 Number all pages as described in Section 3.3.

3.8 Volatile Organics Instrument Performance Check (Form IV VOA)

3.8.1 Purpose

This form is used to report the results of the instrument performance check for the volatile fraction and to summarize the date and time of analyses of samples, including dilutions, re-analyses, standards, blanks, and LCSs associated with each analysis of the Instrument Performance Check solution.

3.8.2 Instructions

Complete the header information according to the instructions in Section 3.3. Complete the remainder of the form using the following instructions.

3.8.2.1 Enter the date and time of injection of the instrument performance check solution [4-Bromofluorobenzene (BFB) for volatiles--CAS Number 460-00-4]. The date shall be entered as MM/DD/YYYY. The time shall be reported using military time.

3.8.2.2 Identify the GC column and internal diameter.

3.8.2.3 For each ion listed on the form, enter the percent relative abundance in the right-hand column of the first table. Report relative abundances to the number of significant figures given for each ion in the ion abundance criteria column.

NOTE: One or more of the high mass ions may exceed the abundance of the ion listed on the form as the nominal base peak [mass-to-charge ratio (m/z) 95 for BFB]. Despite this possibility, all ion abundances shall be normalized to the nominal base peak, m/z 95.

3.8.2.4 All relative abundances shall be reported as a number. If the relative abundance is zero, enter "0", not a dash or other non-numeric character. Where parentheses appear, compute the percentage of the ion abundance of the mass given in the appropriate footnote, and enter that value in the parentheses.

3.8.2.5 In the lower table, list all samples, including dilutions and re-analyses, standards, blanks, and LCSs analyzed under that instrument performance check in chronological order, by time of analysis (using military time). Refer to Section 3.3.7 for specific instructions for identifying standards and blanks.

3.8.2.6 Complete the following fields for all standards, samples, including dilutions and reanalyses, blanks, and LCSs: "EPA SAMPLE NO.", "LAB SAMPLE ID", "LAB FILE ID", "DATE ANALYZED", and "TIME ANALYZED".

3.8.2.7 All Form Vs listing samples, including dilutions and reanalyses, standards, blanks, and LCSs must contain an opening and closing Continuing Calibration Verification (CCV) in Form VI VOA. If samples are run after an initial calibration sequence, the initial calibration may be substituted for an opening CCV.

3.8.2.8 Number all pages as described in Section 3.3.

3.9 Volatile Organics Initial Calibration Data (Form V VOA-1, VOA-2, VOA-SIM)

3.9.1 Purpose

After a GC/MS system has undergone an initial five-point calibration at the specific concentration levels described in Exhibit D, and after all initial calibration criteria have been met, the Contractor shall complete and submit these forms for each volatile target compound initial calibration performed that is relevant to the samples, including dilutions and reanalyses, blanks, and LCSs in the SDG, regardless of when that calibration was performed. A calibration containing more than five points may be performed but only five points are to be reported on the Forms. The points that can be excluded are at the extreme concentration levels (below CRQL or above the required high concentration level).

3.9.2 Instructions

Complete the header information according to the instructions in Section 3.3. Enter the Case Number and SDG Number for the current data package, regardless of the original Case for which the initial calibration was performed. Complete the remainder of the form using the following instructions.

3.9.2.1 Enter the date(s) of the calibration. If the calendar date changes during the calibration procedure, the inclusive dates shall be recorded. Dates shall be entered as MM/DD/YYYY.

3.9.2.2 Enter the injection times of the first and last of the standards analyzed in the "Calibration Times" field. Times shall be reported using military time.

3.9.2.3 Complete the "Sample volume", "Instrument ID", "GC Column" and "ID" fields.

3.9.2.4 Enter the concentration of each of the five standards after "RRF" in the space provided. Then enter the Laboratory File Identifier for the standards after the "=" in the space provided.

3.9.2.5 Complete the RRF data for the five calibration points, and then calculate and report the Mean Relative Response Factor ($\overline{RRF}$) for all target compounds.

3.9.2.6 The Contractor shall report the Percent Relative Standard Deviation (%RSD) for **all** compounds. See Exhibit D for equations.

3.10 Volatile Organics Continuing Calibration Data (Form VI VOA-1, VOA-2, VOA-SIM)

3.10.1 Purpose

This form is used to report the calibration verification of the GC/MS system by the analysis of specific calibration verification standards. Form VII is required for opening and closing CCVs for each 24-hour time period for target compound analyses. If analysis of volatiles using the SIM technique is requested, then an additional Form VII VOA shall be submitted for opening and closing CCVs for each 24-hour time period that samples are analyzed

3.10.2 Instructions

Complete the header information according to the instructions in Section 3.3. Complete the remainder of the form using the following instructions.

3.10.2.1 Enter the date (Calibration Date:) and time (Time:) of the CCV and the date(s) (Init. Calib. Dates:) and time(s) (Init. Calib. Times:) of the initial calibration (give inclusive dates if the initial calibration is performed over more than one date). Dates shall be entered as MM/DD/YYYY. Times shall be reported using military time.

3.10.2.2 Enter Instrument ID, sample volume, units, GC column identifier, internal diameter, and column length. Also enter the Sample Number for the CCV standard on Form VII.

3.10.2.3. Using the appropriate initial calibration, enter the Mean Relative Response Factor ($\overline{RRF}$) for each target compound.

3.10.2.4 Report the concentration of the CCV standard in the space provided, after "RRF".

3.10.2.5 Report the RRF for each target from the CCV standard analysis.

3.10.2.6 Under "MIN RRF" enter the appropriate value from Exhibit D. For an opening CCV or a closing CCV that is also used as an opening CCV for the next "12-hour period", the appropriate values can be found in Exhibit D. For a closing CCV enter "0.010" for all compounds. For a CCV that is both an opening and closing CCV, enter the values for an opening CCV.

This SOW does not have a closing CCV requirement.

3.10.2.7 Calculate the Percent Difference (%D) for all compounds. See Exhibit D for equations.

3.10.2.8 Under MAX %D enter the appropriate value from Exhibit D. For an opening CCV and a closing CCV that is also an opening CCV for the next 12-hour period, the appropriate values can be found in Exhibit D. For a closing CCV enter "50" for all target compounds.

This SOW does not have a closing CCV requirement.

3.11 Internal Standard Area and Retention Time (RT) Summary (Form VII VOA, VOA-SIM)

3.11.1 Purpose

This form is used to summarize the peak areas and RTs of the internal standards added to all calibration standards and samples, including: dilutions, re-analyses, blanks, and LCSs. The data are used to determine when changes in internal standard responses will adversely affect quantitation of target compounds. This form shall be completed each time a CCV is performed, or when samples are analyzed under the same GC/MS instrument performance check as an initial calibration.

3.11.2 Instructions

Complete the header information according to Section 3.3. Complete the remainder of the form using the following instructions. If samples are analyzed immediately following an initial calibration, before another instrument performance check and a CCV, Form VII shall be completed on the basis of the internal standard areas of the midpoint initial calibration standard. Use the date and time of analysis of this standard and the Laboratory File Identifier and areas in place of those of a CCV standard.

3.11.2.1 Enter the date and time of analysis of the continuing calibration standard. The date shall be entered as MM/DD/YYYY. The time shall be reported using military time.

3.11.2.2 Enter the Instrument ID, GC column identifier, internal diameter, and column length.

3.11.2.3 From the results of the analysis of the CCV standard, enter the area measured for each internal standard and its RT (in decimal minutes) under the appropriate column in the "24 HOUR STD" row.

3.11.2.4 For each internal standard, calculate the upper and lower limits of the area of the particular standard. Report these values in the "UPPER LIMIT" and "LOWER LIMIT" rows, respectively. Calculate the upper limit of the RT as the retention of the internal standard, and the lower limit of the RT as the RT in the standard minus 0.50 minutes (30 seconds).

3.11.2.5 For each sample, including dilutions, re-analyses, blanks, and LCSs, analyzed under a given CCV, enter the designated Sample Number and the area measured for each internal standard and its RT. If the internal standard area is outside the upper or lower limits calculated in Section 3.11.2.4, flag that area with an asterisk ("*"). The asterisk shall be placed in the far right-hand space of the box for each internal standard area, directly under the "#" symbol. Similarly, flag the RT of any internal standard that is outside the limits with an asterisk.

3.11.2.6 Number all pages as described in Section 3.3.

TABLE
Volatile Internal Standards

	Volatile Internal Standards	CAS Number
IS1	Bromochloromethane (BCM)	74-97-5
IS2	Chlorobenzene-d_5 (CBZ)	3114-55-4
IS3	1,4-Difluorobenzene (DFB)	540-36-3

3.12 Sample Log-In Sheet (Form DC-1)

3.12.1 Purpose

This form is used to document the receipt and inspection of sample containers and samples. One original Form DC-1 is required for each sample shipping container (only the hardcopy form is required). If the samples in a single sample shipping container are assigned to more than one SDG, the original Form DC-1 shall be placed with the deliverables for the SDG of the lowest alphanumeric number, and a copy of Form DC-1 shall be placed with the deliverables for the other SDGs. The copies shall be identified as "copy(ies)", and the location of the original shall be noted on the copies.

3.12.2 Instructions

3.12.2.1 Sign and date the airbill. If an airbill is not received, include a hardcopy receipt requested from the shipping company or a printout of the shipping company’s electronic tracking information.

3.12.2.2 Complete the header information on the form, including the log-in date.

3.12.2.3 Examine the shipping container and record the presence/absence of custody seals and their condition (e.g., intact, broken) in Item 1.

3.12.2.4 Record the Custody Seal Numbers in Item 2.

3.12.2.5 Open the container, remove the enclosed sample documentation, and record the presence/absence of USEPA forms, SMO forms (i.e., TR/Chain of Custody Records, Packing Lists), and airbills or airbill stickers in Items 3 and 4. Specify if there is an airbill present or an airbill sticker in Item 4. Record the airbill or sticker number in Item 5.

3.12.2.6 Remove the samples from the shipping container(s), examine the samples and the sample tags (if present), and record the condition of the sample canisters (e.g., intact, leaking) and presence or absence of sample tags in Items 6 and 7.

3.12.2.7 Review the sample shipping documents and compare the information recorded on all the documents and samples and circle the appropriate answer in Item 10.

3.12.2.8 The log-in date should be recorded at the top of Form DC-1; record the date and time of container receipt at the laboratory in Items 11 and 12.

3.12.2.9 If there are no problems observed during receipt, sign and date (include the time) Form DC-1 and the TR/COC, and record the Sample Numbers on Form DC-1 in the "EPA Sample #" column.

3.12.2.10 Record the appropriate Sample Tag Numbers and assigned laboratory numbers, if applicable.

3.12.2.11 Any comments should be made in the "Remarks" column.

3.12.2.12 Record the fraction designation (if appropriate) and the specific area designation in the "Sample Transfer" block located in the bottom left corner of Form DC-1. Sign and date the "Sample Transfer" block.

3.12.2.13 Cross out unused columns and spaces.

3.12.2.14 If there are problems observed during receipt or an answer marked with an asterisk (e.g., "absent*") was circled, contact the TOPO and document the contact as well as resolution of the problem on a Communication Log. Following resolution, sign and date the forms and note, where appropriate, the resolution of the problem.

3.13 Complete SDG File (CSF) Inventory Sheet (Form DC-2)

3.13.1 Purpose. Form DC-2 is used to record the inventory of documents in the original Sample Data Package sent to the USEPA Region.

3.13.2 Instructions

3.13.2.1 Organize all USEPA CSF documents as described in Section 2.6. Assemble the documents in the order specified on Form DC-2 and Section 2.6, and stamp each page with a consecutive number; however, do not number Form DC-2. Inventory the CSF by reviewing the document numbers and recording page number ranges in the columns provided on Form DC-2. The Contractor shall verify and record, in the "Comments" section on Form DC-2, all intentional gaps in the page numbering sequence (e.g., "page numbers not used, XXXX - XXXX, YYYY - YYYY"). If there are no documents for a specific document type, enter "NA" in the empty space.

3.13.2.2 Certain laboratory-specific documents related to the CSF may not fit into a clearly-defined category. The Contractor shall review Form DC-2 to determine if it is most appropriate to place them under categories 8, 9, 10, or 11. Category 11 should be used if there is no appropriate previous category. These types of documents should be described or listed in the blanks under each appropriate category on Form DC-2.

3.13.2.3 If it is necessary to insert new or inadvertently omitted documents, the Contractor shall identify the documents with unique accountable numbers and record the unique accountable numbers and the locations of the documents in the CSF (in the "Other Records" section on Form DC-2).

3.14 Canister Sampling Field Test Data Sheet (Form DC-3)

3.14.1 Purpose

Form DC-3 is used to record the inventory of canister sampling from field test data. This form is a routine deliverable and used by both the laboratory and the field samplers to document the conditions during the collection of the sample. These conditions will be used by the lab to calculate the concentration of VOC in the air samples.

3.14.2 Instructions

3.14.2.1 Complete all the header information in the General Information fields.

3.14.2.2 Record the temperature, pressure, sampling time and flow rates at the start and finish. Times shall be reported using military time.

3.14.2.3 Record the sampling system certification and quarterly recertification dates. Dates shall be entered as MM/DD/YYYY.

3.14.2.4 Record the laboratory information.

4.0 DATA REPORTING FORMS

The data reporting forms are shown on the following pages.

EPA SAMPLE NO.

1A - FORM I VOA-1
VOLATILE ORGANICS ANALYSIS DATA SHEET

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Lab Sample ID: _____ T.O. No._____Canister No.: _____

Sample vol: _____ (L/mL)_____ Date Received: _____

Lab File ID: _____ Instr ID:_____Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CAS NO.	COMPOUND	ppbv	ug/m^3	Q
115-07-1	Propylene			
75-71-8	Dichlorodifluoromethane (Freon 12)			
76-14-2	Dichlorotetrafluoroethane (Freon 114)			
74-87-3	Chloromethane			
75-01-4	Vinyl chloride			
106-99-0	1,3-Butadiene			
74-83-9	Bromomethane			
75-00-3	Chloroethane			
64-17-5	Ethanol			
75-69-4	Trichlorofluoromethane (Freon 11)			
75-35-4	1,1-Dichloroethene			
76-13-1	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)			
67-64-1	Acetone			
67-63-0	2-Propanol (Isopropanol)			
75-15-0	Carbon disulfide			
75-09-2	Methylene chloride			
156-60-5	trans-1,2-Dichloroethene			
110-54-3	n-Hexane			
1634-04-4	Methyl tert-butyl ether			
75-34-3	1,1-Dichloroethane			
156-59-2	cis-1,2-Dichloroethene			
126-99-8	2-Chloro-1,3-butadiene (Chloroprene)			
78-93-3	2-Butanone			
109-99-9	Tetrahydrofuran			
67-66-3	Chloroform			
71-55-6	1,1,1-Trichloroethane			
110-82-7	Cyclohexane			
56-23-5	Carbon tetrachloride			
141-78-6	Ethyl Acetate			
108-05-4	Vinyl Acetate			
71-43-2	Benzene			
107-06-2	1,2-Dichloroethane			
142-82-5	n-Heptane			
123-91-1	1,4-Dioxane			
79-01-6	Trichloroethene			

EPA SAMPLE NO.

1B - FORM I VOA-2
VOLATILE ORGANICS ANALYSIS DATA SHEET

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Lab Sample ID: _____ T.O. No._____Canister No.: _____

Sample vol: _____ (L/mL)_____ Date Received: _____

Lab File ID: _____ Instr ID:_____Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CAS NO.	COMPOUND	ppbv	ug/m^3	Q
78-87-5	1,2-Dichloropropane			
75-27-4	Bromodichloromethane			
10061-01-5	cis-1,3-Dichloropropene			
108-10-1	4-Methyl-2-pentanone			
108-88-3	Toluene			
10061-02-6	trans-1,3-Dichloropropene			
79-00-5	1,1,2-Trichloroethane			
127-18-4	Tetrachloroethene			
591-78-6	2-Hexanone			
124-48-1	Dibromochloromethane			
106-93-4	1,2-Dibromoethane			
111-65-9	n-Octane			
108-90-7	Chlorobenzene			
100-41-4	Ethylbenzene			
95-47-6	o-Xylene			
179601-23-1	m,p-Xylene			
100-42-5	Styrene			
75-25-2	Bromoform			
98-82-8	Cumene			
79-34-5	1,1,2,2-Tetrachloroethane			
103-65-1	Propylbenzene			
622-96-8	4-Ethyltoluene			
108-67-8	1,3,5-Trimethylbenzene			
95-63-6	1,2,4-trimethylbenzene			
100-44-7	Benzyl Chloride			
541-73-1	1,3-Dichlorobenzene			
106-46-7	1,4-Dichlorobenzene			
95-50-1	1,2-Dichlorobenzene			
87-68-3	Hexachlorobutadiene			
120-82-1	1,2,4-Trichlorobenzene			

EPA SAMPLE NO.

1C – FORM I VOA-SIM
TRACE VOLATILE ORGANICS SIM ANALYSIS DATA SHEET

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Lab Sample ID: _____ T.O. No._____Canister No.: _____

Sample vol: _____ (L/mL)_____ Date Received: _____

Lab File ID: _____ Instr ID:_____Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CAS NO.	COMPOUND	ppbv	ug/m^3	Q
75-01-4	Vinyl chloride			
75-35-4	1,1-Dichloroethene			
156-60-5	trans-1,2-Dichloroethene			
1634-04-4	Methyl-tert-butyl ether			
75-34-3	1,1-Dichloroethane			
156-59-2	cis-1,2-Dichloroethene			
71-55-6	1,1,1-Trichloroethane			
71-43-2	Benzene			
107-06-2	1,2-Dichloroethane			
79-01-6	Trichloroethene			
108-88-3	Toluene			
79-00-5	1,1,2-Trichloroethane			
127-18-4	Tetrachloroethene			
100-41-4	Ethylbenzene			
95-47-6	o-Xylene			
179601-23-1	m,p-Xylene			
79-34-5	1,1,2,2-Tetrachloroethane			

EPA SAMPLE NO.

1D – FORM I VOA-TIC
VOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Lab Sample ID: _____ T.O. No._____Canister No.: _____

Sample vol: _____ (L/mL)_____ Date Received: _____

Lab File ID: _____ Instr ID:_____Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

	CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					
25					
26					
27					
28					
29					
30					
	E966796[1]	Total Alkanes	N/A		

[1]EPA-designated Registry Number.

EPA SAMPLE NO.

1E – FORM I VOA-CANISTER1
VOLATILE ORGANICS SUMMA CANISTER
CERTIFICATION DATA SHEET

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Lab Sample ID: _____ T.O. No._____Canister No.: _____

Sample vol: _____ (L/mL)_____Date Canister Cleaned: _____

Lab File ID: _____ Instr ID:_____Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CAS NO.	COMPOUND	ppbv	ug/m^3	Q
115-07-1	Propylene			
75-71-8	Dichlorodifluoromethane (Freon 12)			
76-14-2	Dichlorotetrafluoroethane (Freon 114)			
74-87-3	Chloromethane			
75-01-4	Vinyl chloride			
106-99-0	1,3-Butadiene			
74-83-9	Bromomethane			
75-00-3	Chloroethane			
64-17-5	Ethanol			
75-69-4	Trichlorofluoromethane (Freon 11)			
75-35-4	1,1-Dichloroethene			
76-13-1	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)			
67-64-1	Acetone			
67-63-0	2-Propanol (Isopropanol)			
75-15-0	Carbon disulfide			
75-09-2	Methylene chloride			
156-60-5	trans-1,2-Dichloroethene			
110-54-3	n-Hexane			
1634-04-4	Methyl tert-butyl ether			
75-34-3	1,1-Dichloroethane			
156-59-2	cis-1,2-Dichloroethene			
126-99-8	2-Chloro-1,3-butadiene (Chloroprene)			
78-93-3	2-Butanone			
109-99-9	Tetrahydrofuran			
67-66-3	Chloroform			
71-55-6	1,1,1-Trichloroethane			
110-82-7	Cyclohexane			
56-23-5	Carbon tetrachloride			
141-78-6	Ethyl Acetate			
108-05-4	Vinyl Acetate			
71-43-2	Benzene			
107-06-2	1,2-Dichloroethane			
142-82-5	n-Heptane			
123-91-1	1,4-Dioxane			
79-01-6	Trichloroethene			

EPA SAMPLE NO.

1F – FORM I VOA-CANISTER2
VOLATILE ORGANICS SUMMA CANISTER
CERTIFICATION DATA SHEET

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Lab Sample ID: _____ T.O. No._____Canister No.: _____

Sample vol: _____ (L/mL)_____Date Canister Cleaned: _____

Lab File ID: _____ Instr ID:_____Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CAS NO.	COMPOUND	ppbv	ug/m^3	Q
78-87-5	1,2-Dichloropropane			
75-27-4	Bromodichloromethane			
10061-01-5	cis-1,3-Dichloropropene			
108-10-1	4-Methyl-2-pentanone			
108-88-3	Toluene			
10061-02-6	trans-1,3-Dichloropropene			
79-00-5	1,1,2-Trichloroethane			
127-18-4	Tetrachloroethene			
591-78-6	2-Hexanone			
124-48-1	Dibromochloromethane			
106-93-4	1,2-Dibromoethane			
111-65-9	n-Octane			
108-90-7	Chlorobenzene			
100-41-4	Ethylbenzene			
95-47-6	o-Xylene			
179601-23-1	m,p-Xylene			
100-42-5	Styrene			
75-25-2	Bromoform			
98-82-8	Cumene			
79-34-5	1,1,2,2-Tetrachloroethane			
103-65-1	Propylbenzene			
622-96-8	4-Ethyltoluene			
108-67-8	1,3,5-Trimethylbenzene			
95-63-6	1,2,4-trimethylbenzene			
100-44-7	Benzyl Chloride			
541-73-1	1,3-Dichlorobenzene			
106-46-7	1,4-Dichlorobenzene			
95-50-1	1,2-Dichlorobenzene			
87-68-3	Hexachlorobutadiene			
120-82-1	1,2,4-Trichlorobenzene			

EPA SAMPLE NO.

1G – FORM I VOA-CANISTER3
VOLATILE ORGANICS SIM SUMMA CANISTER
CERTIFICATION DATA SHEET

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Lab Sample ID: _____ T.O. No._____Canister No.: _____

Sample vol: _____ (L/mL)_____Date Canister Cleaned: _____

Lab File ID: _____ Instr ID:_____Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

CAS NO.	COMPOUND	ppbv	ug/m^3	Q
75-01-4	Vinyl chloride			
75-35-4	1,1-Dichloroethene			
156-60-5	trans-1,2-Dichloroethene			
1634-04-4	Methyl-tert-butyl ether			
75-34-3	1,1-Dichloroethane			
156-59-2	cis-1,2-Dichloroethene			
71-55-6	1,1,1-Trichloroethane			
71-43-2	Benzene			
107-06-2	1,2-Dichloroethane			
79-01-6	Trichloroethene			
108-88-3	Toluene			
79-00-5	1,1,2-Trichloroethane			
127-18-4	Tetrachloroethene			
100-41-4	Ethylbenzene			
95-47-6	o-Xylene			
179601-23-1	m,p-Xylene			
79-34-5	1,1,2,2-Tetrachloroethane			

EPA SAMPLE NO.

1H – FORM I VOA-CANISTER4
VOLATILE ORGANICS TENTATIVELY IDENTIFIED COMPOUNDS
SUMMA CANISTER CERTIFICATION DATA SHEET

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Lab Sample ID: _____ T.O. No._____Canister No.: _____

Sample vol: _____ (L/mL)_____Date Canister Cleaned: _____

Lab File ID: _____ Instr ID:_____Date Analyzed: _____

GC Column: _____ ID: _____(mm) Dilution Factor: _____

	CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					
25					
26					
27					
28					
29					
30					
	E966796[1]	Total Alkanes	N/A		

2A – FORM II VOA-1
AIR VOLATILE ORGANICS LCS RECOVERY AND PRECISION

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Lab Sample ID: _____ T.O. No._____Canister No.: _____

Sample vol: _____ (L/mL)_____ Cont Calib Date:_____

Lab File ID: _____ Instr ID:_____ Cont Calib Time:_____

Date Analyzed: _____ LCS Lot No._____

CAS NO.	COMPOUND	True LCS conc. ppbv	LCS % Rec.	True Cont Calib conc. ppbv	Cont Calib % Rec	RPD
115-07-1	Propylene					
75-71-8	Dichlorodifluoromethane (Freon 12)					
76-14-2	Dichlorotetrafluoroethane (Freon 114)					
74-87-3	Chloromethane					
75-01-4	Vinyl chloride					
106-99-0	1,3-Butadiene					
74-83-9	Bromomethane					
75-00-3	Chloroethane					
64-17-5	Ethanol					
75-69-4	Trichlorofluoromethane (Freon 11)					
75-35-4	1,1-Dichloroethene					
76-13-1	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)					
67-64-1	Acetone					
67-63-0	2-Propanol (Isopropanol)					
75-15-0	Carbon disulfide					
75-09-2	Methylene chloride					
156-60-5	trans-1,2-Dichloroethene					
110-54-3	n-Hexane					
1634-04-4	Methyl tert-butyl ether					
75-34-3	1,1-Dichloroethane					
156-59-2	cis-1,2-Dichloroethene					
126-99-8	2-Chloro-1,3-butadiene (Chloroprene)					
78-93-3	2-Butanone					
109-99-9	Tetrahydrofuran					
67-66-3	Chloroform					
71-55-6	1,1,1-Trichloroethane					
110-82-7	Cyclohexane					
56-23-5	Carbon tetrachloride					
141-78-6	Ethyl Acetate					
108-05-4	Vinyl Acetate					
71-43-2	Benzene					
107-06-2	1,2-Dichloroethane					
142-82-5	n-Heptane					
123-91-1	1,4-Dioxane					
79-01-6	Trichloroethene					

2B – FORM II VOA-2
AIR VOLATILE ORGANICS LCS RECOVERY AND PRECISION

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Lab Sample ID: _____ T.O. No._____Canister No.: _____

Sample vol: _____ (L/mL)_____ Cont Calib Date:_____

Lab File ID: _____ Instr ID:_____ Cont Calib Time:_____

Date Analyzed: _____ LCS Lot No._____

CAS NO.	COMPOUND	True LCS conc. ppbv	LCS % Rec.	True Cont Calib conc. ppbv	Cont Calib % Rec	RPD
78-87-5	1,2-Dichloropropane					
75-27-4	Bromodichloromethane					
10061-01-5	cis-1,3-Dichloropropene					
108-10-1	4-Methyl-2-pentanone					
108-88-3	Toluene					
10061-02-6	trans-1,3-Dichloropropene					
79-00-5	1,1,2-Trichloroethane					
127-18-4	Tetrachloroethene					
591-78-6	2-Hexanone					
124-48-1	Dibromochloromethane					
106-93-4	1,2-Dibromoethane					
111-65-9	n-Octane					
108-90-7	Chlorobenzene					
100-41-4	Ethylbenzene					
95-47-6	o-Xylene					
179601-23-1	m,p-Xylene					
100-42-5	Styrene					
75-25-2	Bromoform					
98-82-8	Cumene					
79-34-5	1,1,2,2-Tetrachloroethane					
103-65-1	Propylbenzene					
622-96-8	4-Ethyltoluene					
108-67-8	1,3,5-Trimethylbenzene					
95-63-6	1,2,4-trimethylbenzene					
100-44-7	Benzyl Chloride					
541-73-1	1,3-Dichlorobenzene					
106-46-7	1,4-Dichlorobenzene					
95-50-1	1,2-Dichlorobenzene					
87-68-3	Hexachlorobutadiene					
120-82-1	1,2,4-Trichlorobenzene					

2C – FORM II VOA-SIM
AIR VOLATILE ORGANICS SIM LCS RECOVERY AND PRECISION

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Lab Sample ID: _____ T.O. No._____Canister No.: _____

Sample vol: _____ (L/mL)_____ Cont Calib Date:_____

Lab File ID: _____ Instr ID:_____ Cont Calib Time:_____

Date Analyzed: _____ LCS Lot No._____

CAS NO.	COMPOUND	True LCS conc. ppbv	LCS % Rec.	True Cont Calib conc. ppbv	Cont Calib % Rec	RPD
75-01-4	Vinyl chloride					
75-35-4	1,1-Dichloroethene					
156-60-5	trans-1,2-Dichloroethene					
1634-04-4	Methyl-tert-butyl ether					
75-34-3	1,1-Dichloroethane					
156-59-2	cis-1,2-Dichloroethene					
71-55-6	1,1,1-Trichloroethane					
71-43-2	Benzene					
107-06-2	1,2-Dichloroethane					
79-01-6	Trichloroethene					
108-88-3	Toluene					
79-00-5	1,1,2-Trichloroethane					
127-18-4	Tetrachloroethene					
100-41-4	Ethylbenzene					
95-47-6	o-Xylene					
179601-23-1	m,p-Xylene					
79-34-5	1,1,2,2-Tetrachloroethane					

EPA SAMPLE NO.

3A – FORM III VOA
VOLATILE ORGANICS METHOD BLANK SUMMARY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Dates(s): _____

Purge Volume: _____(mL) Calibration Times(s): _____

GC Column: _____ ID: _____(mm) Length: _____(m)

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	CANISTER NUMBER	DATE ANALYZED	TIME ANALYZED
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						

COMMENTS: _____

EPA SAMPLE NO.

4A – FORM IV VOA
VOLATILE ORGANICS INSTRUMENT PERFORMANCE CHECK
BROMOFLUOROBENZENE (BFB)

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Lab File ID: _____ BFB Injection Date: _____

Instrument ID: _____ BFB Injection Time: _____

GC Column: _____ ID: _____(mm)

m/e	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE
50	15.0 - 40.0% of mass 95	
75	30.0 - 80.0% of mass 95	
95	Base peak, 100% relative abundance	
96	5.0 - 9.0% of mass 95	
173	Less than 2.0% of mass 174	( )1
174	50.0 - 120% of mass 95	
175	5.0 - 9.0% of mass 174	( )1
176	93.0 - 101% of mass 174	( )1
177	5.0 - 9.0% of mass 176	( )2

1 - Value is %mass 174 2 - Value is %mass 176

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED	TIME ANALYZED
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					

EPA SAMPLE NO.

5A – FORM V VOA-1
VOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Dates(s): _____

Purge Volume: _____(mL) Calibration Times(s): _____

GC Column: _____ ID: _____(mm) Length: _____(m)

LAB FILE ID: _____	RRF ____ =	_____	RRF ____ =	_____
RRF _____ = _____	RRF ____ =	_____	RRF ____ =	_____

COMPOUND	RRF___	RRF___	RRF___	RRF___	RRF___	$\overline{RRF}$	%RSD
Propylene							
Dichlorodifluoromethane (Freon 12)							
Dichlorotetrafluoroethane (Freon 114)							
Chloromethane							
Vinyl chloride							
1,3-Butadiene							
Bromomethane							
Chloroethane							
Ethanol							
Trichlorofluoromethane (Freon 11)							
1,1-Dichloroethene							
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)							
Acetone							
2-Propanol (Isopropanol)							
Carbon disulfide							
Methylene chloride							
trans-1,2-Dichloroethene							
n-Hexane							
Methyl tert-butyl ether							
1,1-Dichloroethane							
cis-1,2-Dichloroethene							
2-Chloro-1,3-butadiene (Chloroprene)							
2-Butanone							
Tetrahydrofuran							
Chloroform							
1,1,1-Trichloroethane							
Cyclohexane							
Carbon tetrachloride							
Ethyl Acetate							
Vinyl Acetate							
Benzene							
1,2-Dichloroethane							
n-Heptane							
1,4-Dioxane							
Trichloroethene							

5B – FORM V VOA-2
VOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Dates(s): _____ _____

Heated Purge: (Y/N) _____ Calibration Times(s): _____ _____

Purge Volume: _____(mL)

GC Column: _____ ID: _____(mm) Length: _____(m)

LAB FILE ID: _____	RRF ____ =	_____	RRF ____ =	_____
RRF _____ = _____	RRF ____ =	_____	RRF ____ =	_____

COMPOUND	RRF___	RRF___	RRF___	RRF___	RRF___	$\overline{RRF}$	%RSD
1,2-Dichloropropane							
Bromodichloromethane							
cis-1,3-Dichloropropene							
4-Methyl-2-pentanone							
Toluene							
trans-1,3-Dichloropropene							
1,1,2-Trichloroethane							
Tetrachloroethene							
2-Hexanone							
Dibromochloromethane							
1,2-Dibromoethane							
n-Octane							
Chlorobenzene							
Ethylbenzene							
o-Xylene							
m,p-Xylene							
Styrene							
Bromoform							
Cumene							
1,1,2,2-Tetrachloroethane							
Propylbenzene							
4-Ethyltoluene							
1,3,5-Trimethylbenzene							
1,2,4-trimethylbenzene							
Benzyl Chloride							
1,3-Dichlorobenzene							
1,4-Dichlorobenzene							
1,2-Dichlorobenzene							
Hexachlorobutadiene							
1,2,4-Trichlorobenzene							

5C – FORM V VOA-SIM
VOLATILE ORGANICS SIM INITIAL CALIBRATION DATA

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Date: _____ Time: _____

Lab File ID: _____ Init. Calib. Date(s): _____

EPA Sample No. (VSTD#####): _____ Init. Calib. Time(s): _____

GC Column: _____ ID: _____(mm) Length: _____(m)

Purge Volume: _____(mL)

COMPOUND	$\overline{RRF}$	RRF	MIN RRF	%D	MAX %D
Vinyl chloride					
1,1-Dichloroethene					
trans-1,2-Dichloroethene					
Methyl-tert-butyl ether					
1,1-Dichloroethane					
cis-1,2-Dichloroethene					
1,1,1-Trichloroethane					
Benzene					
1,2-Dichloroethane					
Trichloroethene					
Toluene					
1,1,2-Trichloroethane					
Tetrachloroethene					
Ethylbenzene					
o-Xylene					
m,p-Xylene					
1,1,2,2-Tetrachloroethane					

EPA SAMPLE NO.

6A – FORM VI VOA-1
VOLATILE ORGANICS CONTINUING CALIBRATION DATA

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Dates(s): _____

Purge Volume: _____(mL) Calibration Times(s): _____

GC Column: _____ ID: _____(mm) Length: _____(m)

LAB FILE ID: _____	RRF ____ =	_____	RRF ____ =	_____
RRF _____ = _____	RRF ____ =	_____	RRF ____ =	_____

COMPOUND	RRF___	RRF___	RRF___	RRF___	RRF___	$\overline{RRF}$	%RSD
Propylene							
Dichlorodifluoromethane (Freon 12)							
Dichlorotetrafluoroethane (Freon 114)							
Chloromethane							
Vinyl chloride							
1,3-Butadiene							
Bromomethane							
Chloroethane							
Ethanol							
Trichlorofluoromethane (Freon 11)							
1,1-Dichloroethene							
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)							
Acetone							
2-Propanol (Isopropanol)							
Carbon disulfide							
Methylene chloride							
trans-1,2-Dichloroethene							
n-Hexane							
Methyl tert-butyl ether							
1,1-Dichloroethane							
cis-1,2-Dichloroethene							
2-Chloro-1,3-butadiene (Chloroprene)							
2-Butanone							
Tetrahydrofuran							
Chloroform							
1,1,1-Trichloroethane							
Cyclohexane							
Carbon tetrachloride							
Ethyl Acetate							
Vinyl Acetate							
Benzene							
1,2-Dichloroethane							
n-Heptane							
1,4-Dioxane							
Trichloroethene							

6B – FORM VI VOA-2
VOLATILE ORGANICS CONTINUING CALIBRATION DATA

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Date: _____ Time: _____

Lab File ID: _____ Init. Calib. Date(s): _____ _____

EPA Sample No. (VSTD#####): _____ Init. Calib. Time(s): _____ _____

Heated Purge: (Y/N): _____ GC Column: _____ ID: _____(mm) Length: _____(m)

Purge Volume: _____(mL)

COMPOUND	$\overline{RRF}$	RRF	MIN RRF	%D	MAX %D
1,2-Dichloropropane					
Bromodichloromethane					
cis-1,3-Dichloropropene					
4-Methyl-2-pentanone					
Toluene					
trans-1,3-Dichloropropene					
1,1,2-Trichloroethane					
Tetrachloroethene					
2-Hexanone					
Dibromochloromethane					
1,2-Dibromoethane					
n-Octane					
Chlorobenzene					
Ethylbenzene					
o-Xylene					
m,p-Xylene					
Styrene					
Bromoform					
Cumene					
1,1,2,2-Tetrachloroethane					
Propylbenzene					
4-Ethyltoluene					
1,3,5-Trimethylbenzene					
1,2,4-trimethylbenzene					
Benzyl Chloride					
1,3-Dichlorobenzene					
1,4-Dichlorobenzene					
1,2-Dichlorobenzene					
Hexachlorobutadiene					
1,2,4-Trichlorobenzene					

6C – FORM VI VOA-SIM
TRACE VOLATILE ORGANICS SIM CONTINUING CALIBRATION DATA

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Date: _____ Time: _____

Lab File ID: _____ Init. Calib. Date(s): _____

EPA Sample No. (VSTD#####): _____ Init. Calib. Time(s): _____

GC Column: _____ ID: _____(mm) Length: _____(m)

Purge Volume: _____(mL)

COMPOUND	$\overline{RRF}$	RRF	MIN RRF	%D	MAX %D
Vinyl chloride					
1,1-Dichloroethene					
trans-1,2-Dichloroethene					
Methyl-tert-butyl ether					
1,1-Dichloroethane					
cis-1,2-Dichloroethene					
1,1,1-Trichloroethane					
Benzene					
1,2-Dichloroethane					
Trichloroethene					
Toluene					
1,1,2-Trichloroethane					
Tetrachloroethene					
Ethylbenzene					
o-Xylene					
m,p-Xylene					
1,1,2,2-Tetrachloroethane					

7A – FORM VII VOA-1
VOLATILE ORGANICS ANALYSIS
INTERNAL STANDARD AREA AND RETENTION TIME STUDY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Init. Calib. Date(s): _____ _____

EPA Sample No. (VSTD#####): _____ Date Analyzed: _____

Lab File ID (Standard): _____ Time Analyzed: _____

Instrument ID: _____

		IS1 (BCM) AREA #	RT #	IS2 (CBZ) AREA #	RT #	IS3 (DFB) AREA #	RT #
	24 HOUR STD						
	UPPER LIMIT						
	LOWER LIMIT						
	EPA SAMPLE NO.						
01							
02							
03							
04							
05							
06							
07							
08							
09							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							

IS1 (BCM) = Bromochloromethane
IS2 (CBZ) = Chlorobenzene-d5
IS3 (DFB) = 1,4-Difluorobenzene

AREA UPPER LIMIT = 140% of Internal standard area
AREA LOWER LIMIT = 60% of internal standard area
RT UPPER LIMIT = + 0.50 minutes of internal standard RT
RT LOWER LIMIT = - 0.50 minutes of internal standard RT

Column used to flag values outside QC limits with an asterisk

7B – FORM VII VOA-SIM
TRACE VOLATILE ORGANICS SIM
INTERNAL STANDARD AREA AND RETENTION TIME STUDY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ Mod. Ref No.: _____ SDG No.: _____

GC Column: _____ ID: _____(mm) Init. Calib. Date(s): _____ _____

EPA Sample No. (VSTD0.5##): _____ Date Analyzed: _____

Lab File ID (Standard): _____ Time Analyzed: _____

Instrument ID: _____

		IS1 (BCM) AREA #	RT #	IS2 (CBZ) AREA #	RT #	IS3 (DFB) AREA #	RT #
	24 HOUR STD						
	UPPER LIMIT						
	LOWER LIMIT						
	EPA SAMPLE NO.						
01							
02							
03							
04							
05							
06							
07							
08							
09							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							

IS1 (BCM) = Bromochloromethane
IS2 (CBZ) = Chlorobenzene-d5
IS3 (DFB) = 1,4-Difluorobenzene

AREA UPPER LIMIT = 140% of internal standard area
AREA LOWER LIMIT = 60% of internal standard area
RT UPPER LIMIT = + 0.50 minutes of internal standard RT
RT LOWER LIMIT = - 0.50 minutes of internal standard RT

Column used to flag values outside QC limits with an asterisk.

VOLATILE ORGANICS ANALYSIS
SAMPLE LOG-IN SHEET
FORM DC-1

Lab Name						Page ___ of ___
Received By (Print Name)						Log-in Date
Received By (Signature)						
Contract Number			Task Order No.			
Case Number		Sample Delivery Group No.				Mod. Ref. No.
Remarks:			Corresponding			
		EPA Sample #	Sample Tag Number	Canister Number	Assigned Lab Number	Remarks: Condition of Sample Shipment, etc.
1. Custody Seal(s)	Present/Absent* Intact/Broken					
2. Custody Seal Nos.	_____ _____					
3. Traffic Reports/ Chain of Custody Records (TR/COCs) or Packing Lists	Present/Absent*					
4. Airbill	Airbill/Sticker Present/Absent*					
5. Airbill No.	_____ _____					
6. Sample Tags	Present/Absent*					
Sample Tag Numbers	Listed/Not Listed on Chain-of-Custody					
7. Sample Condition	Intact/Broken*/ Leaking					
8. Cooler Temperature Indicator Bottle	Present/Absent*					
9. Cooler Temperature	_____					
10. Does information on TR/COCs and sample tags agree?	Yes/No*					
11. Date Received at Laboratory	_____					
12. Time Received	_____					
Sample Transfer						
Area #	Area #					
By	By					
On	On					

* Contact SMO and attach record of resolution

Reviewed By	Logbook No.
Date	Logbook Page No.

VOLATILE ORGANICS ANALYSIS
COMPLETE SDG FILE (CSF) INVENTORY SHEET
FORM DC-2

LABORATORY NAME _____
CITY/STATE _____
CASE NO. _____ SDG NO. _____
SDG NOs. TO FOLLOW _____ _____ _____
MOD. REF. NO. _____
TASK ORDER NO. _____
CONTRACT NO. _____
SOW NO. _____

All documents delivered in the Complete SDG File (CSF) must be original documents where possible.

	PAGE NOs.		CHECK	
	FROM	TO	LAB	USEPA
1. **Inventory Sheet** (DC-2) (Do not number)				
2. **SDG Case Narrative**				
3. **SDG Cover Sheet/Traffic Report**				
4. **Volatile Organics Analysis Data**				
a. QC Summary				
Method Blank Summary (Form III VOA)				
Instrument Performance Check (Form IV VOA-1)				
Summa Canister Certification Data Sheet (Form I VOA-CANISTER1, VOA-CANISTER2, VOA-CANISTER3)				
Internal Standard Area and RT Summary (Form VII VOA-1)				
LCS Recovery and Precision (Form II VOA-1)				
b. Sample Data				
TCL Results – Organics Analysis Data Sheet (Form I VOA-1 and VOA-2)				
Tentatively Identified Compounds (Form I VOA-TIC)				
For each sample:				
Raw Spectra and background-subtracted mass spectra of target compounds identified				
Quantitation reports				
Mass Spectra of all reported TICs with three best library matches				

VOLATILE ORGANICS ANALYSIS
COMPLETE SDG FILE (CSF) INVENTORY SHEET
FORM DC-2 (CONT.)

CASE NO. _____ SDG NO. _____ SDG NOs. TO FOLLOW _____
_____ _____ MOD. REF. NO. _____

	PAGE NOs.		CHECK	
	FROM	TO	LAB	USEPA
c. Volatile Organics Standards Data (All Instruments)				
Initial Calibration Data (Form V VOA-1, VOA-2, VOA-3)				
SIM Initial Calibration Data (Form V VOA-SIM)				
Continuing Calibration Data (Form VI VOA-1, VOA-2)				
Instrument Performance Check BFB (Form IV VOA)				
d. Raw/Quality Control (QC) Data				
BFB				
Blank Data				
5. **Trace SIM Volatile Organics Analysis Data**				
a. QC Summary				
Trace Volatile Organics SIM Internal Standard Area and RT Summary (Form VII VOA-SIM)				
b. Trace Volatile Organics SIM Analysis Data (Place at the end of the Trace Volatiles Section)				
[Form I VOA-SIM; Form II VOA-SIM; Form VI VOA-SIM; Form VII VOA-SIM; and all raw data for QC, Samples, and Standards.]				
8. **Miscellaneous Data**				
Original preparation and analysis forms or copies of preparation and analysis logbook pages				
Internal sample and sample extract transfer chain-of-custody records				
Screening records				
All instrument output, including strip charts from screening activities (describe or list)				
9. **EPA Shipping/Receiving Documents**				
Airbills (No. of shipments _____)				
Chain of Custody Records				
Sample Tags				
Sample Log-in Sheet (Lab & Form DC-1)				
Canister Sampling Field Test Data Sheet (Form DC-3)				
Miscellaneous Shipping/Receiving Records (describe or list)				
_____				
_____				

VOLATILE ORGANICS ANALYSIS
COMPLETE SDG FILE (CSF) INVENTORY SHEET
FORM DC-2 (CONT.)

CASE NO. _____ SDG NO. _____ SDG NOs. TO FOLLOW _____
_____ _____ MOD. REF. NO. _____

	PAGE NOs. FROM	PAGE NOs. TO	CHECK LAB	CHECK REGION
10. **Internal Lab Sample Transfer Records and Tracking Sheets** (describe or list)				
_____				
_____				
12. **Other Records** (describe or list)				
Telephone Communication Log				
_____				
_____				

13. Comments

_____
_____
_____

Completed by: _____ _____ _____
(CLP Lab) (Signature) (Printed Name/Title) (Date)

Verified by: _____ _____ _____
(CLP Lab) (Signature) (Printed Name/Title) (Date)

Audited by: _____ _____ _____
(USEPA) (Signature) (Printed Name/Title) (Date)

CANISTER SAMPLING FIELD TEST DATA SHEET
FORM DC – 3

A. GENERAL INFORMATION

SITE LOCATION: _____
SITE ADDRESS: _____
_____
SAMPLING DATE: _____

SHIPPING DATE: _____
CANISTER SERIAL NO.: _____
SAMPLER ID: _____
OPERATOR: _____
CANISTER LEAK CHECK DATE: _____

B. SAMPLING INFORMATION

TEMPERATURE

	INTERIOR	AMBIENT	MAXIMUM	MINIMUM
START				
STOP				

PRESSURE

CANISTER PRESSURE	

SAMPLING TIMES

	LOCAL TIME	ELAPSED TIME METER READING
START		
STOP		

FLOW RATES

MANIFOLD FLOW RATE	CANISTER FLOW RATE	FLOW CONTROLLER READOUT

SAMPLING SYSTEM CERTIFICATION DATE: _____
QUARTERLY RECERTIFICATION DATE: _____

C. LABORATORY INFORMATION

DATA RECEIVED: _____
RECEIVED BY: _____
INITIAL PRESSURE: _____
FINAL PRESSURE: _____
DILUTION FACTOR: _____
ANALYSIS
GC-MSD-SCAN DATE: _____
GC-MSD-SIM DATE: _____
RESULTS: _____
_____
GC-MSD-SCAN: _____
GC-MSD-SIM: _____

_____
SIGNATURE/TITLE

EXHIBIT C

TARGET COMPOUND LIST (TCL)
AND CONTRACT REQUIRED QUANTITATION LIMITS (CRQL)
FOR VOLATILE ORGANICS ANALYSIS

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Table of Contents

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1.0 VOLATILES TARGET COMPOUND LIST AND CONTRACT REQUIRED QUANTITATION LIMITS

	COMPOUND	CAS NO.	Quantitation Limits SCAN ppbv	Quantitation Limits SIM ppbv
1	Propylene	115-07-1	0.5	
2	Dichlorodifluoromethane (Freon 12)	75-71-8	0.5	
3	Dichlorotetrafluoroethane (Freon 114)	76-14-2	0.5	
4	Chloromethane	74-87-3	0.5	
5	Vinyl chloride	75-01-4	0.5	0.05
6	1,3-Butadiene	106-99-0	0.5	
7	Bromomethane	74-83-9	0.5	
8	Chloroethane	75-00-3	0.5	
9	Ethanol	64-17-5	0.5	
10	Trichlorofluoromethane (Freon 11)	75-69-4	0.5	
11	1,1-Dichloroethene	75-35-4	0.5	0.05
12	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	76-13-1	0.5	
13	Acetone	67-64-1	0.5	
14	2-Propanol (Isopropanol)	67-63-0	0.5	
15	Carbon disulfide	75-15-0	0.5	
16	Methylene chloride	75-09-2	0.5	
17	trans-1,2-Dichloroethene	156-60-5	0.5	0.05
18	n-Hexane	110-54-3	0.5	
19	Methyl tert-butyl ether	1634-04-4	0.5	0.05
20	1,1-Dichloroethane	75-34-3	0.5	0.05
21	cis-1,2-Dichloroethene	156-59-2	0.5	0.05
22	2-Chloro-1,3-butadiene (Chloroprene)	126-99-8	0.5	
23	2-Butanone	78-93-3	0.5	
24	Tetrahydrofuran	109-99-9	0.5	
25	Chloroform	67-66-3	0.5	
26	1,1,1-Trichloroethane	71-55-6	0.5	0.05
27	Cyclohexane	110-82-7	0.5	
28	Carbon tetrachloride	56-23-5	0.5	
29	Ethyl Acetate	141-78-6	0.5	
30	Vinyl Acetate	108-05-4	0.5	
31	Benzene	71-43-2	0.5	0.05
32	1,2-Dichloroethane	107-06-2	0.5	0.05
33	n-Heptane	142-82-5	0.5	
34	1,4-Dioxane	123-91-1	0.5	
35	Trichloroethene	79-01-6	0.5	0.05

			Quantitation Limits	
	COMPOUND	CAS NO.	SCAN ppbv	SIM ppbv
36	1,2-Dichloropropane	78-87-5	0.5	
37	Bromodichloromethane	75-27-4	0.5	
38	cis-1,3-Dichloropropene	10061-01-5	0.5	
39	4-Methyl-2-pentanone	108-10-1	0.5	
40	Toluene	108-88-3	0.5	0.05
41	trans-1,3-Dichloropropene	10061-02-6	0.5	
42	1,1,2-Trichloroethane	79-00-5	0.5	0.05
43	Tetrachloroethene	127-18-4	0.5	0.05
44	2-Hexanone	591-78-6	0.5	
45	Dibromochloromethane	124-48-1	0.5	
46	1,2-Dibromoethane	106-93-4	0.5	
47	n-Octane	111-65-9	0.5	
48	Chlorobenzene	108-90-7	0.5	
49	Ethylbenzene	100-41-4	0.5	0.05
50	o-Xylene	95-47-6	0.5	0.05
51	m,p-Xylene	179601-23-1	0.5	0.05
52	Styrene	100-42-5	0.5	
53	Bromoform	75-25-2	0.5	
54	Cumene	98-82-8	0.5	
55	1,1,2,2-Tetrachloroethane	79-34-5	0.5	0.05
56	Propylbenzene	103-65-1	0.5	
57	4-Ethyltoluene	622-96-8	0.5	
58	1,3,5-Trimethylbenzene	108-67-8	0.5	
59	1,2,4-Trimethylbenzene	95-63-6	0.5	
60	Benzyl Chloride	100-44-7	0.5	
61	1,3-Dichlorobenzene	541-73-1	0.5	
62	1,4-Dichlorobenzene	106-46-7	0.5	
63	1,2-Dichlorobenzene	95-50-1	0.5	
64	Hexachlorobutadiene	87-68-3	0.5	
65	1,2,4-Trichlorobenzene	120-82-1	0.5	

EXHIBIT D

ANALYTICAL METHOD FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS (VOC) IN AIR COLLECTED IN SPECIALLY-PREPARED CANISTERS AND ANALYZED BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

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Exhibit D – Analytical Method for the Analysis of VOCs in Air

Table of Contents

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1.0 SCOPE AND APPLICATION

1.1 This method is based on more than 30 years of USEPA's experience in determination of air toxics. Measurement of organic pollutants in ambient air is often difficult, in part because of the variety of organic substances of potential concern, the variety of potential techniques for sampling and analysis, and the lack of standardized and documented methods. As a result, the National Risk Management Research Laboratory (NRMRL) developed a Second Edition of the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* to assist Federal, State, and local regulatory personnel in developing and maintaining necessary expertise and up-to-date monitoring technology for characterizing organic pollutants in the ambient air. This method is based upon Method TO-15 as published in the January 1999 edition.

1.2 The analytical method that follows is designed to analyze air samples for volatile organic compounds on the Target Compound List (TCL) in Exhibit C. The method includes specifications for canister cleaning, sample collection, sample preconcentration and analysis to determine the approximate concentration of volatile organic constituents in the sample. The actual analysis is based on a preconcentration Gas Chromatograph/Mass Spectrometer (GC/MS) method for air samples. In addition, if required, samples will be analyzed for a select group of compounds using Selected Ion Monitoring (SIM) technique. If a SIM analysis is required, a full scan GC/MS analysis should be performed first. All sample results at or below the Contract Required Quantitation Limit (CRQL) shall be re-analyzed using SIM mode. If all required analytes are detected during full scan GC/MS analysis, then a SIM analysis is not to be performed and this should be documented in the SDG narrative. Laboratories which possess instruments that can perform SCAN and SIM analyses concurrently need not perform separate analyses as long as all requirements are met for both analyses.

1.3 This method also allows for the optional determination of tentatively identified compounds (TICs). If TICs are needed, the data user should notify the laboratory prior to sampling and specify the number of unknowns to be reported. Note the target compounds are reported in both ppbv and $\mu g/m^3$. Since conversion from ppbv to $\mu g/m^3$ requires knowledge of the molecular weight, TICs can only be reported in ppbv.

1.4 This method documents sampling and analytical procedures for the measurement of 66 volatile organic compounds (VOCs) that are a subset of the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. VOCs are defined here as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25°C and 760 mm Hg. Table 1 contains the list of the target VOCs along with their CAS number, boiling point, vapor pressure and molecular weight.

1.5 This method applies to ambient concentrations of VOCs and typically requires VOC enrichment by concentrating up to one liter of a sample volume to achieve a Contract Required Quantitation Limit (CRQL) of 0.5 ppbv using SCAN GC/MS. The use of Selected Ion Monitoring (SIM) GC/MS can lower the CRQL to 0.05 ppbv.

1.6 This method applies under most conditions encountered in sampling of ambient air into canisters. However, the composition of a gas mixture in a canister, under unique or unusual conditions, will change so that the sample is known not to be a true representation of the ambient air from which it was taken. For example, low humidity conditions in the sample may lead to

losses of certain VOCs on the canister walls, losses that would not happen if the humidity were higher. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water-soluble compounds. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence absolute storage stability cannot be assigned to a specific gas. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs can be recovered from canisters near their original concentrations within the 30-day specified holding time (see Section 8).

1.7 This method uses the GC/MS technique as the only means to identify and quantitate target compounds. The GC/MS approach provides a more scientifically-defensible detection scheme which is generally more desirable than the use of single or even multiple specific detectors. In addition, this method establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent sampling and analytical equipment. This method includes enhanced provisions for inherent quality control. The method uses internal analytical standards and frequent verification of analytical system performance to assure control of the analytical system. This more formal and better documented approach to quality control guarantees a higher percentage of good data.

2.0 SUMMARY OF METHOD

2.1 The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister. Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

2.2 After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to the laboratory for analysis.

2.3 Upon receipt at the laboratory, the canister tag data is recorded and the canister is stored until analysis. Samples must be analyzed within 30 days from collection.

2.4 To analyze the sample, a known volume of sample is directed from the canister through a solid multisorbent concentrator. A portion of the water vapor in the sample breaks through the concentrator during sampling, to a degree depending on the multisorbent composition, duration of sampling, and other factors. Water content of the sample can be further reduced by dry purging the concentrator with helium while retaining target compounds. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The sample is then released by thermal desorption and carried onto a gas chromatographic column for separation.

2.5 As a simple alternative to the multisorbent/dry purge water management technique, the amount of water vapor in the sample can be reduced below any threshold for affecting the proper operation of the analytical system by reducing the sample size. For example, a small sample can be concentrated on a cold trap and released directly to the gas chromatographic column. The reduction in sample volume may require an enhancement of detector sensitivity.

2.6 Other water management approaches including commercially available water management systems are also acceptable as long as their use does not compromise the attainment of the performance criteria listed in Sections 11 and 12. One of the alternative ways to dry the sample is to separate VOCs from condensate on a low temperature trap by heating and purging the trap.

2.7 The analytical strategy for this method involves using a high resolution gas chromatograph (GC) coupled to a mass spectrometer. If the mass spectrometer is a linear quadrupole system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN mode) or by monitoring a select number of ions [Selected Ion Monitoring (SIM) mode] based on a subset of compounds on the target list. If the mass spectrometer is based on a standard ion trap design, only a scanning mode is used (note however, that the Selected Ion Storage (SIS) mode for the ion trap has features of the SIM mode). Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound. For any given compound, the intensity of the quantitation ion is compared with the system response to the quantitation ion for known amounts of the compound. This establishes the compound concentration that exists in the sample.

2.8 Results for target compounds are reported in both ppbv and $\mu g/m^3$. If TICs are requested, they are reported in ppbv only. The laboratory must document any analytical or technical problems encountered in the SDG Narrative. Laboratories are encouraged to be very detailed in the Narrative.

3.0 DEFINITIONS

3.1 Gauge Pressure — Pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or psi. Zero gauge pressure is equal to atmospheric (barometric) pressure.

3.2 Absolute Pressure — Pressure measured with reference to absolute zero pressure, usually expressed in units of kPa, or psi.

3.3 Cryogen — A refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Typical cryogens are liquid nitrogen (bp: -195.8°C), liquid argon (bp: -185.7°C), and liquid carbon dioxide (bp: -79.5°C).

3.4 Dynamic Calibration — Calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system from a manifold through which the gas standards are flowing.

3.5 Dynamic Dilution — Means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with humidified zero air in a manifold so that a flowing stream of calibration mixture is available at the inlet of the analytical system.

3.6 MS-SCAN — Mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

3.7 MS-SIM — Mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

3.8 Qualitative Accuracy — The degree of measurement accuracy required to correctly identify compounds with an analytical system.

3.9 Quantitative Accuracy — The degree of measurement accuracy required to correctly measure the concentration of an identified compound with an analytical system with known uncertainty.

3.10 Replicate Precision — Precision determined from two canisters filled from the same air mass over the same time period and determined as the absolute value of the difference between the analyses of canisters divided by their average value and expressed as a percentage (see Section 12 for performance criteria for replicate precision).

3.11 Laboratory Control Sample – For the purpose of this SOW, a replicate of the Continuing Calibration Verification standard that is analyzed immediately after the method blank in the analytical sequence.

3.12 Duplicate Precision — precision determined from the analysis of the Continuing Calibration Verification standard and the Laboratory Control Sample taken from the same standard canister. The duplicate precision is determined as the absolute value of the difference between the canister analyses divided by their average value and expressed as a percentage.

3.13 Laboratory Control Sample Accuracy — the concentration determined by analysis of a laboratory control sample divided by the nominal value expressed as a percentage (see Section 12 for performance criteria for laboratory control sample).

4.0 INTERFERENCES

4.1 Very volatile compounds, such as chloromethane and vinyl chloride can display peak broadening and co-elution with other species if the compounds are not delivered to the GC column in a small volume of carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing trap or at the head of the gas chromatographic column, mitigates this problem.

4.2 Interferences in canister samples may result from improper use or from contamination of:

- canisters due to poor manufacturing practices,
- canister cleaning apparatus,
- sampling or analytical system.

Attention to the following details will help to minimize the possibility of contamination of canisters.

4.2.1 Canisters should be manufactured using high quality welding and cleaning techniques, and new canisters should be filled with humidified zero air and then analyzed, after “aging” for 24 hours, to determine cleanliness. The cleaning apparatus, sampling system, and analytical system should be assembled of clean, high quality components and each system should be shown to be free of contamination.

4.2.2 Canisters should be stored in a contaminant-free location and should be capped tightly during shipment to prevent leakage and minimize any compromise of the sample.

4.2.3 Impurities in the calibration dilution gas (if applicable) and carrier gas, organic compounds out-gassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by analyzing humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with Buna-N rubber components must be avoided.

4.2.4 Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses. Whenever a high concentration (>25 ppbv of a trace species) sample is encountered, it should be followed by an analysis of humid zero air to check for carry-over contamination. The trap and other parts of the system are also subjected to contamination; therefore, frequent bake-out and purging of the entire system may be required.

4.3 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to eliminate the presence of methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all Gas Chromatography (GC) carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however each chemical compound should be treated as a potential health hazard, Exposure to these chemicals must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should be made available to all personnel involved in the chemical analyses.

5.2 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, vinyl chloride, and 1,4-dioxane. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance maybe achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this analytical method is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Analytical Apparatus

6.1.1 Sampling/Concentrator System

6.1.1.1 Electronic Mass Flow Controllers

Used to maintain constant flow (for purge gas, carrier gas and sample gas) and to provide an analog output to monitor flow anomalies.

6.1.1.2 Vacuum Pump

General purpose laboratory pump, capable of reducing the downstream pressure of the flow controller to provide the pressure differential necessary to maintain controlled flow rates of sample air.

6.1.1.3 Stainless Steel Tubing and Stainless Steel Fittings

Coated with fused silica to minimize active adsorption sites.

6.1.1.4 Stainless Steel Cylinder Pressure Regulators. Standard, two-stage cylinder regulators with pressure gauges.

6.1.1.5 Gas Purifiers

Used to remove organic impurities and moisture from gas streams.

6.1.1.6 Six-port Gas Chromatographic Valve

For routing sample and carrier gas flows.

6.1.1.7 Multisorbent Concentrator

[Note: Guidance on the performance and selection of sorbents used in systems containing a solid sorbent preconcentrator with a cryofocusing trap are described in EPA Compendium Methods TO-15 and TO-17.]

Solid adsorbent packing with various retentive properties for adsorbing trace gases are commercially available from several sources. The packing contains more than one type of adsorbent packed in series. The following solid multisorbent concentrators or equivalent may be used.

6.1.1.7.1 A pre-packed solid adsorbent trap (Supelco 2-0321 or equivalent) containing 200 mg Carbopack B (60/80 mesh) and 50 mg Carbosieve S-III (60/80 mesh) retains VOCs and allows some water vapor to pass through.

6.1.1.7.2 A multisorbent containing Tenax/Ambersorb 340/Charcoal or equivalent trap approximately 20% of the initial water content in the sample after sampling 500 mL of air. Additional water reduction by a factor of 8 can be attained at temperatures of 45°C or higher (determined by using atomic emission detection of hydrogen atoms plotted versus purge gas volume.) Still further water reduction is possible using a two-stage concentration/dryer system.

6.1.1.8 Cryogenic Concentrator. Complete units are commercially available from several vendor sources. The characteristics of the latest concentrators include a rapid, "ballistic" heating of the concentrator to release any trapped VOCs into a small carrier gas volume. This facilitates the separation of compounds on the gas chromatographic column.

6.1.2 Gas Chromatographic/Mass Spectrometric (GC/MS) System

6.1.2.1 Gas Chromatograph. The gas chromatographic (GC) system must be capable of temperature programming. The column oven can be cooled to subambient temperature (e.g., -50°C) at the start of the gas chromatographic run to effect a resolution of the very volatile organic compounds. In other designs, the rate of release of compounds from the focusing trap in a two stage system obviates the need for retrapping of compounds on the column. The system must include or be interfaced to a concentrator and have all required accessories including analytical columns and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with Buna-N rubber components must not be used.

6.1.2.2 Chromatographic Columns. 100% methyl silicone or 5% phenyl, 95% methyl silicone fused silica capillary columns of 0.25- to 0.53-mm I.D. of varying lengths are recommended for separation of many of the possible subsets of target compounds involving nonpolar compounds. However, considering the diversity of the target list, the choice is left to the operator subject to the performance standards given in the Technical Acceptance criteria in Sections 9, 11 and 12.

6.1.2.3 Mass Spectrometer. Either a linear quadrupole or ion trap mass spectrometer can be used as long as it is capable of scanning from 35 to 300 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 50 ng or less of p-bromofluorobenzene (BFB) is analyzed. The system must be capable of SIM or equivalent. The instrument must be vented to the outside of the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.1.2.3.1 Linear Quadrupole Technology. The quadrupole consists of a parallel set of four rod electrodes mounted in a square configuration. The field within the analyzer is created by coupling opposite pairs of rods together and applying radio frequency (RF) and direct current (DC) potentials between the pairs of rods. Ions created in the ion source from the reaction of column eluates with electrons from the electron source are moved through the parallel array of rods under the influence of the generated field. Ions which are successfully transmitted through the quadrapole are said to possess stable trajectories and are subsequently recorded with the detection system. When the DC potential is zero, a wide band of m/z values is transmitted through the quadrupole are said to possess stable trajectories and are subsequently recorded with the detection system. This "RF only" mode is referred to as the "total-ion" mode. In this mode, the quadrupole acts as a strong focusing lens analogous to a high pass filter. The amplitude of the RF determines the low mass cutoff. A mass spectrum is generated by scanning the DC and RF voltages using a fixed DC/RF ratio and a constant drive frequency or by scanning the frequency and holding the DC and RF constant. With the quadrupole system only 0.1 to 0.2 percent of the ions formed in the ion source actually reach the detector.

6.1.2.3.2 Ion Trap Technology. An ion-trap mass spectrometer consists of a chamber formed between two metal surfaces in the shape of a hyperboloid of one shet (ring electrode) and a hyperboloid of two shets (the two end-cap electrodes). Ions are created within the chamber by electron impact from an electron beam admitted through a small aperture in one of the end caps. Radio frequency (RF) (and sometimes direct current voltage offsets) is applied between the ring electrode and the two end-cap electrodes establishing a quadrupole electric field. This field is uncoupled in three directions so that ion motion can be considered independently in each direction; the force acting upon an ion increases with the displacement of the ion from the center of the field but the direction of the force depends on the instantaneous voltage applied to the ring electrode. A restoring force along one coordinate (such as the distance, r, from the ion-trap's axis of radial symmetry) will exist concurrently with a repelling force along another coordinate (such as the distance, z, along the ion traps axis), and if the field were static the ions would eventually strike an electrode.

However, in an RF field, the force along each coordinate alternates direction so that a stable trajectory may be possible in which the ions do not strike a surface. In practice, ions of appropriate mass-to-charge ratios may be trapped within the device for periods of milliseconds to hours. Analysis of stored ions is performed by increasing the RF voltage, which makes the ions successively unstable.

The effect of the RF voltage on the ring electrode is to "squeeze" the ions in the xy plane so that they move along the z axis. Half the ions are lost to the top cap (held at ground potential); the remaining ions exit the lower end cap to be detected by the electron multiplier. As the energy applied to the ring electrode is increased, the ions are collected in order of increasing mass to produce a conventional mass spectrum. With the ion trap, approximately 50 percent of the generated ions are detected. As a result, a significant increase in sensitivity can be achieved when compared to a full scan linear quadrupole system.

6.1.2.4 GC/MS Interface. Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points for each of the analytes of interest and can be used to achieve all acceptable performance criteria may be used. Gas chromatograph to mass spectrometer interfaces constructed of all-glass, glass-lined, or fused silica-lined materials are recommended. Glass and fused silica should be deactivated.

6.1.2.5 Data System. The computer system that is interfaced to the mass spectrometer must allow the continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as a Selected Ion Current Profile (SICP). Software must also be available that allows integrating the abundance in any SICP between specified time or scan number limits. Also, software must be available that allows for the comparison of sample spectra against reference library spectra. The NIST (2002 release or later), Wiley (1991 release or later), or

equivalent mass spectral library shall be used as the reference library. The operational data system must be capable of flagging all data files that have been edited manually by laboratory personnel.

6.1.2.6 Off-line Data Storage Device. Device must be capable of rapid recording and retrieval of data and must be suitable for long-term, off-line data storage.

6.2 Calibration System and Manifold Apparatus

6.2.1 Calibration Manifold. Stainless steel, glass, or high purity quartz manifold, (e.g., 1.25-cm I.D. x 66-cm) with sampling ports and internal baffles for flow disturbance to ensure proper mixing. The manifold should be heated to ~50°C.

6.2.2 Humidifier. 500-mL impinger flask containing HPLC grade deionized water.

6.2.3 Electronic Mass Flow Controllers. One 0 to 5 L/min unit and one or more 0 to 100 mL/min units for air, depending on number of cylinders in use for calibration.

6.2.4 PTFE Filter(s). 47-mm PTFE filter for particulate collection.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Neat Materials or Manufacturer-Certified Solutions/Mixtures. Best source (see Section 7.2).

7.1.2 Helium and Air. Ultra-high purity grade in gas cylinders. He is used as carrier gas in the GC.

7.1.3 Liquid Nitrogen, Liquid Argon, or Liquid Carbon Dioxide. Used to cool secondary trap.

7.1.4 Deionized Water. High performance liquid chromatography (HPLC) grade, ultra-high purity (for humidifier).

7.2 Standards

7.2.1 Introduction

7.2.1.1 When available, standard mixtures of target gases in high pressure cylinders must be certified traceable to a NIST Standard Reference Material (SRM) or to a NIST/EPA approved Certified Reference Material (CRM). Manufacturer’s certificates of analysis must be retained to track the expiration date.

7.2.1.2 The neat standards that are used for making trace gas standards must be of high purity; generally a purity of 98 percent or better is commercially available.

7.2.1.3 Cylinder(s) containing approximately 10 ppmv of each of the target compounds are typically used as primary stock standards. The components may be purchased in one cylinder or in separate cylinders depending on compatibility of the compounds and the pressure of the mixture in the cylinder. Refer to manufacturer's specifications for guidance on purchasing and mixing VOCs in gas cylinders.

7.2.2 Preparing Working Standards

7.2.2.1 Instrument Performance Check Standard

Prepare a standard solution of BFB in humidified zero air at a concentration which will allow collection of 50 ng of BFB or less under the optimized concentration parameters.

7.2.2.2 Calibration Standards Scan Mode

Prepare five working initial calibration standards in humidified zero air at a concentration which will allow collection at the 0.5, 2, 5, 10, and 25 ppbv level for each component under the optimized concentration parameters. Continuing Calibration Verification working standard for Scan Mode shall be prepared containing all the target compounds at the 10 ppbv calibration level.

7.2.2.3 Calibration Standards SIM Mode

Prepare initial calibration standards at a minimum of five concentration levels that are applicable to the sensitivity of the instrument. For most operations, the calibration concentrations are to be prepared at 0.05, 0.1, 0.2, 0.4 and 0.8 ppbv for each target compound of interest. Continuing Calibration Verification working standards for SIM Mode shall be prepared containing each target compounds of interest at the 0.4 ppbv calibration level.

7.2.2.4 Internal Standard Spiking Mixture Scan Mode

Prepare an internal standard spiking mixture containing bromochloromethane, chlorobenzene-d5, and 1,4-difluorobenzene at 10 ppmv each in humidified zero air to be added to the sample or calibration standard. 500 µL of this mixture spiked into 500 mL of sample will result in a concentration of 10 ppbv. The internal standard is introduced into the trap during the collection time for all calibration, blank, and sample analyses using the apparatus or by equivalent means. The volume of internal standard spiking mixture added for each analysis must be the same from run to run.

7.2.2.5 Internal Standard Spiking Mixture SIM Mode

Prepare an internal standard spiking mixture containing the compounds listed in Section 7.2.2.4 at 0.4 ppmv each in humidified zero air to be added to the sample or calibration standard. Just prior to SIM analysis, a sufficient volume of the internal standard spiking mixture shall be added into 500 mL of sample to result in a concentration of 0.4 ppbv in each sample. Laboratories using instruments that allow for simultaneous SCAN and SIM analysis may use alternate internal standards for the SIM analysis. Alternate internal standards must be approved by EPA and noted in the SDG narrative. All technical acceptance criteria for internal standards response and retention time must be met for the alternate internal standards.

7.2.3 Standard Preparation by Dynamic Dilution Technique

7.2.3.1 Standards may be prepared by dynamic dilution of the gaseous contents of a cylinder(s) containing the gas calibration stock standards with humidified zero air using mass flow controllers and a calibration manifold. The working standard may be delivered from the manifold to a clean, evacuated canister using a pump and mass flow controller.

7.2.3.2 Alternatively, the analytical system may be calibrated by sampling directly from the manifold if the flow rates are optimized to provide the desired amount of calibration standards. However, the use of the canister as a reservoir prior to introduction into the concentration system resembles the procedure normally used to collect samples and is preferred. Flow rates of the dilution air and cylinder standards (all expressed in the same units) are measured using a bubble meter or calibrated electronic flow measuring device, and the concentrations of target compounds in the manifold are then calculated using the dilution ratio and the original concentration of each compound.

EQ. 1 Concentrations of Target Compounds in the Manifold

$$\text{Manifold Conc.} = \frac{(\text{Original Conc.})(\text{Std . Gas Flow rate})}{(\text{Air Flow rate}) + (\text{Std. Gas Flow rate})}$$

7.2.3.3 Consider the example of 1 mL/min flow of 10 ppmv standard diluted with 1,000 mL/min of humid air provides a nominal 10 ppbv mixture, as calculated below:

$$\text{Manifold Conc.} = \frac{(10\ \text{ppm})(1\ \text{mL/min})(10\ 00\ \text{ppb/1 ppm})}{(1000\ \text{mL/min}) + (1\ \text{mL/min})} = 10\ \text{ppb}$$

7.2.4 Standard Preparation by Static Dilution Bottle Technique

NOTE: Standards may be prepared in canisters by spiking the canister with a mixture of components prepared in a static dilution bottle. This technique is used specifically for liquid standards.

7.2.4.1 The volume of a clean 2-liter round-bottom flask, modified with a threaded glass neck to accept a Mininert septum cap, is determined by weighing the amount of water required to completely fill up the flask. Assuming a density for the water of 1 g/mL, the weight of the water in grams is taken as the volume of the flask in milliliters.

7.2.4.2 The flask is flushed with helium by attaching tubing into the glass neck to deliver the helium. After a few minutes, the tubing is removed and the glass neck is immediately closed with a Mininert septum cap.

7.2.4.3 The flask is placed in a 60°C oven and allowed to equilibrate at that temperature for about 15 minutes. Predetermined aliquots of liquid standards are injected into the flask making sure to keep the flask temperature constant at 60°C.

7.2.4.4 The contents are allowed to equilibrate in the oven for at least 30 minutes. To avoid condensation, syringes must be preheated in the oven at the same temperature prior to withdrawal of aliquots to avoid condensation.

7.2.4.5 Sample aliquots may then be taken for introduction into the analytical system or for further dilution. An aliquot or aliquots totaling greater than 1 percent of the flask volume should be avoided.

7.2.4.6 Standards prepared by this method are stable for one week. The septum must be replaced with each freshly prepared standard.

7.2.4.7 The concentration of each component in the flask is calculated using the following equation:

EQ. 2 Component Concentration Injected into the Flask

$$\text{Concentration, mg/L} = \frac{(Va)(d)}{Vf}$$

Where:

Va = Volume of liquid neat standard injected into the flask, µL.
d = Density of the liquid neat standard, mg/µL.
Vf = Volume of the flask, L.

7.2.4.8 To obtain concentrations in ppbv, Equation 4 in Section 7.2.5.7 can be used.

NOTE: In the preparation of standards by this technique, the analyst should make sure that the volume of neat standard injected into the flask does not result in an overpressure due to the higher partial pressure produced by the standard compared to the vapor pressure in the flask. Precautions should also be taken to avoid a significant decrease in pressure inside the flask after withdrawal of aliquot(s).

7.2.5 Standard Preparation Procedure in High Pressure Cylinders

NOTE: Standards may be prepared in high pressure cylinders. A modified summary of the procedure is provided below.

7.2.5.1 The standard compounds are obtained as gases or neat liquids (greater than 98 percent purity).

7.2.5.2 An aluminum cylinder is flushed with high-purity nitrogen gas and then evacuated to better than 25 in. Hg.

7.2.5.3 Predetermined amounts of each neat standard compound are measured using a microliter or gastight syringe and injected into the cylinder. The cylinder is equipped with a heated injection port and nitrogen flow to facilitate sample transfer.

7.2.5.4 The cylinder is pressurized to 1000 psig with zero nitrogen.

NOTE: User should read all SOPs associated with generating standards in high pressure cylinders. Follow all safety requirements to minimize danger from high pressure cylinders.

7.2.5.5 The contents of the cylinder are allowed to equilibrate (~24 hrs) prior to withdrawal of aliquots into the GC system.

7.2.5.6 If the neat standard is a gas, the cylinder concentration is determined using the following equation:

EQ. 3 Cylinder Concentration

$$\text{Concentration, ppbv} = (\text{Vol. standard})/\text{Vol. dil gas}) \times 10^9$$

NOTE: Both values must be expressed in the same units.

7.2.5.7 If the neat standard is a liquid, the gaseous concentration can be determined using the following equation:

EQ. 4 Gaseous Volume of Inject Compound

$$V = \frac{nRT}{P} \qquad n = \frac{(m1)(d)}{MW}$$

Where:

V = Gaseous volume of injected compound at EPA standard temperature (25°C) and pressure (760 mm Hg), L.

n = Moles.

R = Gas constant, 0.08206 L-atm/mole °K.

T = 298°K (standard temperature).

P = 1 standard pressure, 760 mm Hg (1 atm).

mL = Volume of liquid injected, mL.

d = Density of the neat standard, g/mL.

MW = Molecular weight of the neat standard expressed, g/g-mole.

The gaseous volume of the injected compound is divided by the cylinder volume at STP and then multiplied by 10^9 to obtain the component concentration in ppbvg units.

7.2.6 Standard Preparation by Water Methods

NOTE: Standards may be prepared by a water purge and trap method and summarized as follows.

7.2.6.1 A previously cleaned and evacuated canister is pressurized to 760 mm Hg absolute (1 atm) with zero grade air.

7.2.6.2 The air gauge is removed from the canister and the sparging vessel is connected to the canister with the short length of 1/16 in. stainless steel tubing.

NOTE: Extra effort should be made to minimize possible areas of dead volume to maximize transfer of analytes from the water to the canister.

7.2.6.3 A measured amount of the stock standard solution and the internal standard solution is spiked into 5 mL of water.

7.2.6.4 This water is transferred into the sparge vessel and purged with nitrogen for 10 mins at 100 mL/min. The sparging vessel is maintained at 40°C.

7.2.6.5 At the end of 10 mins, the sparge vessel is removed and the air gauge is re-installed, to further pressurize the canister with pure nitrogen to 1500 mm Hg absolute pressure (approximately 29 psia).

7.2.6.6 The canister is allowed to equilibrate overnight before use.

7.2.7 Preparation of Standards by Permeation Tubes

7.2.7.1 Permeation tubes can be used to provide standard concentration of a trace gas or gases. The permeation of the gas can occur from inside a permeation tube containing the trace species of interest to an air stream outside. Permeation can also occur from outside a permeable membrane tube to an air stream passing through the tube (e.g., a tube of permeable material immersed in a liquid).

7.2.7.2 The permeation system is usually held at a constant temperature to generate a constant concentration of trace gas. Commercial suppliers provide systems for generation and dilution of more than 250 compounds.

7.3 Storage of Standards

7.3.1 Working standards prepared in canisters may be stored for thirty days in an atmosphere free of potential contaminants.

7.3.2 It is required that a storage logbook be kept to document storage time.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE AND HOLDING TIMES

8.1 Collection and Storage of Samples in Canisters

8.1.1 Samples are collected in leak-free stainless steel pressure vessels of desired volume (e.g., 6 L), with valve and specially prepared interior surfaces. All canisters must be certified as free from contaminants prior to sampling.

8.1.2 Each canister shall have a unique identification number and the laboratory must keep records of each canister's use for the life of the contract.

8.1.3 Canisters shall be stored at room temperature [22° (± 3°C)] in a contaminant free area. The temperature of the storage area must be recorded on a daily basis.

8.1.4 Samples must be analyzed within 30 days of collection.

8.2 Canister Cleaning Procedures

The canister cleaning procedures given in this section require that canister pressure be reduced to <0.05mm Hg before the cleaning process is complete. Depending on the vacuum system design (diameter of connecting tubing, valve restrictions, etc.) and the placement of the vacuum gauge, the achievement of this value may take several hours. In any case, the pressure gauge should be placed near the canisters to determine pressure. The objective of requiring a low pressure evacuation during canister cleaning is to reduce contaminants. If canisters can be routinely certified (< 0.2 ppbv for target compounds) while using a higher vacuum, then this criteria can be relaxed. However, the ultimate vacuum achieved during cleaning should always be <0.2mm Hg. Canister cleaning as described in this section requires components with special features. The vacuum gauge must be capable of measuring 0.05mm Hg with less than a 20% error. The vacuum pump used for evacuating the canister must be noncontaminating while being capable of achieving the 0.05 mm Hg vacuum as monitored near the canisters. Thermoelectric vacuum gauges and turbomolecular drag pumps are typically being used for these two components. An alternate to achieving the canister certification requirement of <0.2 ppbv for all target compounds is the criteria used in Compendium Method TO-12 that the total carbon count be <10ppbC. This check is less expensive and typically more exacting than the current certification requirement and can be used if proven to be equivalent to the original requirement. This equivalency must be established by comparing the total nonmethane organic carbon (TNMOC) expressed in ppbC to the requirement that individual target compounds be <0.2 ppbv for a series of analytical runs.

8.2.1 Canister Cleaning and Certification

8.2.1.1 All canisters must be clean and free of any contaminants before sample collection.

8.2.1.2 All canisters are leak tested by pressurizing them to approximately 206 kPa (30 psig) with zero air.

NOTE: The canister cleaning system can be used for this task.

The initial pressure is measured, the canister valve is closed, and the final pressure is checked after 24 hours. If acceptable, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period.

8.2.1.3 A canister cleaning system should be assembled. Cryogen is added to both the vacuum pump and zero air supply traps. The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The vacuum pump is started and the vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) are evacuated to < 0.05 mm Hg for at least 1 hour.

NOTE: On a daily basis or more often if necessary, the cryogenic traps should be purged with zero air to remove any trapped water from previous canister cleaning cycles.

Air released/evacuated from canisters should be diverted to a fume hood.

8.2.1.4 The vacuum and vacuum/pressure gauge shut-off valves are closed and the zero air shut-off valve is opened to pressurize the canister(s) with humid zero air to approximately 206 kPa (30 psig). If a zero gas generator system is used, the flow rate may need to be limited to maintain the zero air quality.

8.2.1.5 The zero air shut-off valve is closed and the canister(s) is allowed to vent down to atmospheric pressure through the vent shut-off valve. The vent shut-off valve is closed. Repeat Sections 8.2.1.3 through 8.2.1.5 two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

8.2.1.6 At the end of the evacuation/pressurization cycle, the canister is pressurized to 206 kPa (30 psig) with humid zero air. The canister is then analyzed by a GC/MS analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.2 ppbv of targeted VOCs) should not be used. As a "blank" check of the canister(s) and cleanup procedure, the final humid zero air fill of 100% of the canisters is analyzed until the cleanup system and canisters are proven reliable (less than 0.2 ppbv of any target VOCs). The check can then be reduced to a lower percentage of canisters.

8.2.1.7 The canister is reattached to the cleaning manifold and is then reevacuated to <0.05 mm Hg (Section 8.2) and remains in this condition until used. The canister valve is closed. The canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting. The canister is now ready for collection of an air sample. An identification tag is attached to the inlet of each canister for field notes and chain-of-custody purposes. An alternative to evacuating the canister at this point is to store the canisters and reevacuate them just prior to the next use.

NOTE: The Contractor must supply documentation (Form I VOA-Canister) with the canisters and in the data packages, showing that all canisters have been cleaned and certified down to the requested detection limits. The GC/MS documentation for clean canister certification is also to be included in the Data Package.

8.2.1.8 As an option to the humid zero air cleaning procedures, the canisters are heated in an isothermal oven not to exceed 100°C during evacuation of the canister to ensure that higher molecular weight compounds are not retained on the walls of the canister.

NOTE: For sampling more complex VOC mixtures the canisters should be heated to higher temperatures during the cleaning procedure although a special high temperature valve would be needed.

Once heated, the canisters are evacuated to <0.05 mm Hg (see Section 8.2) and maintained there for 1 hour. At the end of the heated/evacuated cycle, the canisters are pressurized with humid zero air and analyzed by a GC/MS system after a minimum of 12 hrs of "aging." Any canister that has not tested clean (less than 0.2 ppbv each of targeted compounds) should not be used. Once tested clean, the canisters are re-evacuated to <0.05 mm Hg and remain in the evacuated state until used. As noted in Section 8.2.1.7, re-evacuation can occur just prior to the next use.

8.2.2 Cleaning Sampling System Components

8.2.2.1 Sample components are disassembled and cleaned before the sampler is assembled. Nonmetallic parts are rinsed with HPLC grade deionized water and dried in a vacuum oven at 50°C. Typically, stainless steel parts and fittings are cleaned by placing them in a beaker of methanol in an ultrasonic bath for 15 minutes. This procedure is repeated with hexane as the solvent.

8.2.2.2 The parts are then rinsed with HPLC grade deionized water and dried in a vacuum oven at 100°C for 12 to 24 hours.

8.2.2.3 Once the sampler is assembled, the entire system is purged with humid zero air for 24 hours.

8.2.3 Zero Air Certification

NOTE: In the following sections, "certification" is defined as evaluating the sampling system with humid zero air and humid calibration gases that pass through all active components of the sampling system. The system is "certified" if no significant additions or deletions (less than 0.2 ppbv each of target compounds) have occurred when challenged with the test gas stream.

8.2.3.1 The cleanliness of the sampling system is determined by testing the sampler with humid zero air without an evacuated gas sampling canister, as follows.

8.2.3.2 The calibration system and manifold are assembled. The sampler (without an evacuated gas canister) is connected to the manifold and the zero air cylinder is activated to generate a humid gas stream (2 L/min) to the calibration manifold.

8.2.3.3 The humid zero gas stream passes through the calibration manifold, through the sampling system (without an evacuated canister) to the water management system/VOC preconcentrator of an analytical system.

NOTE: The exit of the sampling system (without the canister) replaces the canister.

After the sample volume (e.g., 500 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed and refocussed on a cold trap. This trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. The VOCs are refocussed prior to gas chromatographic separation. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC/MS (see Section 9) system. The analytical system should not detect greater than 0.2 ppbv of any targeted VOCs in order for the sampling system to pass the humid zero air certification test. If the sampler passes the humid zero air test, it is then tested with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling (e.g., 0.5 to 2 ppbv) as outlined in Section 8.2.4.

8.2.4 Sampler System Certification with Humid Calibration Gas Standards from a Dynamic Calibration System

8.2.4.1 Assemble the dynamic calibration system and manifold.

8.2.4.2 Verify that the calibration system is clean (less than 0.2 ppbv of any target compounds) by sampling a humidified gas stream, *without* gas calibration standards, with a previously certified clean canister (see Section 8.1).

8.2.4.3 The assembled dynamic calibration system is certified clean if less than 0.2 ppbv of any targeted compounds is found.

8.2.4.4 For generating the humidified calibration standards, the calibration gas cylinder(s) containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs is attached to the calibration system. The gas cylinders are opened and the gas mixtures are passed through 0 to 10 mL/min certified mass flow controllers to generate ppb levels of calibration standards.

8.2.4.5 After the appropriate equilibrium period, attach the sampling system (containing a certified evacuated canister) to the manifold.

8.2.4.6 Sample the dynamic calibration gas stream with the sampling system.

8.2.4.7 Concurrent with the sampling system operation, real-time monitoring of the calibration gas stream is accomplished by the on-line GC/MS analytical system to provide reference concentrations of generated VOCs.

8.2.4.8 At the end of the sampling period (normally the same time period used for experiments), the sampling system canister is analyzed and compared to the reference GC/MS analytical system to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system.

8.2.4.9 A recovery of between 90% and 110% is expected for all targeted VOCs.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

9.1.1 Preconcentrator

The following are typical cryogenic and adsorbent preconcentrator analytical conditions which, however, depend on the specific combination of solid sorbent and must be selected carefully by the operator. An example of a system using a solid adsorbent preconcentrator with a cryofocusing trap is discussed in the literature.

Oven temperature programming starts above ambient.

9.1.1.1 Sample Collection Conditions

Cryogenic Trap	Adsorbent Trap
Set point: -150°C	Set point: 27°C
Sample volume - up to 100 mL	Sample volume - up to 1,000 mL
Carrier gas purge flow - none	Carrier gas purge flow-selectable
	Dry purge (optimum) 1300 mL N

NOTE: The analyst should optimize the flow rate, duration of sampling, and absolute sample volume to be used. The addition of a dry purging step allows for further water removal from the adsorbent trap. Other sample collection conditions may be used to pre-concentrate the sample provided technical criteria for all standards, samples and quality control samples are met.

9.1.1.2 Desorption Conditions

Cryogenic Trap	Adsorbent Trap
Desorb Temperature: 120°C	Desorb Temperature 220°C
Desorb Flow Rate - 3 mL/min He	Desorb Flow Rate - 3 mL/min He
Desorb Time < 60 sec	Desorb Time < 60 sec

The adsorbent trap conditions may depend on the specific solid adsorbents chosen (see manufacturers' specifications).

9.1.1.3 Trap Reconditioning Conditions

Cryogenic Trap	Adsorbent Trap
Initial bake out: 120°C (24 hrs)	Initial bake out Variable (24 hrs)
After each run: 120°C (5 min)	A trap bake-out at 260°C for 5

9.1.2 Gas Chromatograph (GC)

9.1.2.1 Optimize GC conditions for compound separation and sensitivity. Baseline separation of benzene and carbon tetrachloride on a 100% methyl polysiloxane stationary phase is an indication of acceptable chromatographic performance.

9.1.2.2 The following are the recommended gas chromatographic analytical conditions when using a 50-meter by 0.3-mm I.D., 1 µm film thickness fused silica column with refocusing on the column:

Item	Condition
Carrier Gas	Helium
Flow Rate	Generally 1-3 mL/min as recommended by manufacturer
Temperature Program	
Initial Temperature	-50°C
Initial Hold Time	2 min
Ramp Rate	8°C/min
Final Temperature	200°C
Final Hold Time	Until all target compounds elute

9.1.3 Mass Spectrometer (MS)

The following are the recommended mass spectrometer conditions:

Item	Condition
Electron Energy	70 Volts (nominal)
Mass Range	35-300 amu
Scan Time	To give at least 10 scans per peak, not to exceed 1 second per scan

NOTE: For SIM analyses, the laboratory is to use the appropriate primary ion and secondary ion listed in Table 2.

9.2 GC/MS Calibration (Tuning) and Ion Abundance

9.2.1 Summary of GC/MS Performance Check

9.2.1.1 The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibrant such as perfluoro-tri-N-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.2.1).

9.2.1.2 It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. The GC/MS system is set up according to the manufacturer's specifications, and the mass calibration and resolution of the GC/MS system are then verified by the analysis of the instrument performance check standard, bromofluorobenzene (BFB).

9.2.2 Frequency of GC/MS Performance Check

9.2.2.1 Prior to the analyses of any samples, blanks, or laboratory control samples or calibration standards, the laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard containing BFB. The instrument performance check solution must be analyzed initially and once per 24-hour time period of operation. The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or daily calibration check criteria) begins at the injection of the BFB which the laboratory records as documentation of a compliance tune.

NOTE: BFB may not be added to any calibration standard or continuing calibration verification standard to create a single injection of a calibration standard and a tune solution.

9.2.3 Procedure for GC/MS Performance Check

9.2.3.1 The analysis of the instrument performance check standard is performed as follows:

- By trapping 50 ng of BFB under the optimized preconcentration parameters.
- The BFB is introduced from a cylinder into the GC/MS via a sample loop valve injection system.

9.2.3.2 The mass spectrum of BFB must be acquired in the following manner:

- Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.
- Background subtraction is conducted using a single scan prior to the elution of BFB.

9.2.3.3 Results of the BFB tuning are to be recorded and maintained as part of the instrumentation log.

9.2.4 Technical Acceptance Criteria for GC/MS Performance Check

9.2.4.1 The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not background subtract part of the BFB peak.

NOTE: All subsequent standards, samples, LCS, and blanks associated with a BFB analysis must be run under identical GC/MS instrument run conditions.

9.2.4.2 Prior to the analysis of any samples, blanks, or calibration standards, the analyst must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard as specified in Table 3.

9.2.5 Corrective Action for GC/MS Performance Check

9.2.5.1 If the BFB acceptance criteria are not met, the MS must be retuned. It may be necessary to clean the ion source, or quadrupoles, or take other corrective actions to achieve the technical acceptance criteria.

9.2.5.2 BFB technical acceptance criteria must be met before any standards, samples, including LCS or required blanks, are analyzed. Any samples or required blanks analyzed when tuning technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

Prior to the analysis of samples and required blanks but after the instrument performance check standard criteria have been met, each GC/MS system must be calibrated at five concentrations that span the range of the initial calibration sequence to determine instrument sensitivity and the linearity of GC/MS response for the target compounds. The initial calibration range is 0.5 to 20 ppbv, in which the five concentrations are 0.5, 2.0, 5.0, 10 and 25 ppbv. One of the calibration points from the initial calibration curve must be at the same concentration as the daily calibration standard (e.g., 10 ppbv).

NOTE: For analysis using SIM technique, the GC/MS system must be calibrated at a minimum of five concentrations (Section 7.2.2.3), prior to the analysis of samples and required blanks, to determine instrument sensitivity and linearity. The calibration standards contain all target compounds and internal standards requiring analysis.

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be recalibrated following corrective action (e.g., ion source cleaning or repair, column replacement, etc.) which may change or affect the initial calibration criteria or if the daily calibration acceptance criteria have not been met.

9.3.2.2 If time remains in the 24-hour time period after meeting the acceptance criteria for the initial calibration, samples may be analyzed. If time does not remain in the 24-hour period after meeting the acceptance criteria for the initial calibration, a new analytical sequence shall commence with the analysis of the instrument performance check standard followed by analysis of a daily calibration standard

9.3.3 Procedure for Initial Calibration

9.3.3.1 Verify that the GC/MS system meets the instrument performance criteria in Section 9.2.4. The GC must be operated using temperature and flow rate parameters equivalent to those in Section 9.2.2 or with GC operating conditions such that all associated performance criteria are met, including the separation criteria in Section 9.1.2.1.

9.3.3.2 Calibrate the preconcentration-GC/MS system by drawing the standard into the system. Use one of the standards preparation techniques described under Section 7.2 or equivalent.

9.3.3.3 A minimum of five concentration levels are needed to determine the instrument sensitivity and linearity. One of the calibration levels should be equal to the CRQL for the each Target Compounds.

9.3.3.4 Add sufficient amount of the internal standard solution (Section 7.2.2.4) to each of the five aqueous calibration standard solutions (Section 7.2) for a concentration of 10.0 ppbv at the time of purge. Analyze each calibration standard according to Section 10.

9.3.3.5 The calibration range should be chosen so that linear results are obtained as defined in Sections 9.3.1 and 9.3.5.

9.3.4 Calculations for Initial Calibration

9.3.4.1 Calculate the Relative Retention Times (RRT) for each target compound over the initial calibration range using Equation 5.

EQ. 5 Relative Retention Time

$$RRT = \frac{RT_c}{RT_{is}}$$

Where:

RT_c = Retention time of the target compound, seconds

RT_{is} = Retention time of the internal standard, seconds.

9.3.4.2 Mean of the Relative Retention Times ($\overline{\overline{RRT}}$). Calculate the mean of the relative retention times ($\overline{RRT}$) for each analyte target compound over the initial calibration range using Equation 6:

EQ. 6 Mean Relative Retention Time

$$\overline{\overline{RR}} = \sum_{i=1}^{n} \frac{RRT}{n}$$

Where:

$\overline{\overline{RRT}}$ = Mean relative retention time for the target compound for each initial calibration standard.

RRT = Relative retention time for the target compound at each calibration level.

9.3.4.3 Tabulate Primary Ion Area Response (Y) for Internal Standard. Tabulate the area response (Y) of the primary ions (see Table 2) and the corresponding concentration for each compound and internal standard.

9.3.4.4 Mean Area Response ($\bar{Y}$) for Internal Standard. Calculate the mean area response ($\bar{Y}$) for each internal standard compound over the initial calibration range using the following equation:

EQ. 7 Mean Area Response

$$\bar{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$

Where:

$\bar{Y}$ = Mean area response.

Y = Area response for the primary quantitation ion for the internal standard for each initial calibration standard.

9.3.4.5 Mean Retention Times ($\overline{\overline{RT}}$). Calculate the mean of the retention times for each internal standard over the initial calibration range using the following equation:

EQ. 8 Mean Retention Time

$$\overline{\overline{RT}} = \sum_{i=1}^{n} \frac{RT_i}{n}$$

Where:

$\overline{\overline{RT}}$ = Mean retention time, seconds

RT = Retention time for the internal standard for each initial calibration standard, seconds.

9.3.4.6 Calculate the Relative Response Factor (RRF) for each target compound relative to the appropriate internal standard (i.e., standard with the nearest retention time) using Equation 9.

NOTE: In the following calculations, an internal standard approach is used to calculate response factors. The area response used is that of the primary quantitation ion unless otherwise stated.

EQ. 9 Relative Response Factor

$$RRF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

RRF = Relative response factor

A_x = Area of the primary ion for the compound to be measured, counts.

A_{is} = Area of the primary ion for the internal standard, counts.

C_{is} = Concentration of internal standard spiking mixture, ppbv.

C_x = Concentration of the compound in the calibration standard, ppbv

Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion. The primary characteristic ions used for quantitation are listed in Table 2. If an interference prevents the use of a primary ion for a given internal standard, use a secondary ion listed in the same table. Assign the target compounds to an internal standard according to Table 3.

NOTE: In the following calculations, an internal standard approach is used to calculate response factors. The area response used is that of the primary quantitation ion unless otherwise stated.

9.3.4.7 Mean Relative Response Factor. Calculate the mean RRF for each compound by averaging the values obtained at the five concentrations using the following equation:

EQ. 10 Mean Relative Response Factor

$$\overline{RRF} = \sum_{i=1}^{n} \frac{X_i}{n}$$

Where:

$\overline{RRF}$ = Mean relative response factor

x_i = RRF of the compound at concentration.

n = Number of concentration values, in this case, 5

9.3.4.8 Percent Relative Standard Deviation (%RSD). Using the RRFs from the initial calibration, calculate the %RSD for all target compounds using the following equations:

EQ. 11 Percent Relative Standard Deviation

$$\%RSD = \frac{SD_{RRF}}{\overline{RRF}} \times 100$$

and

EQ. 12 Standard Deviation of Initial Response Factors

$$SD_{RRF} = \sqrt{\sum_{i=1}^{N} \frac{(RRF_i - \overline{RRF})^2}{N - 1}}$$

Where:

SD_{RRF} = Standard deviation of initial response factors (per compound).

RRF = Relative response factor at a concentration level i.

$\overline{RRF}$ = Mean of initial relative response factors (per compound).

9.3.5 Technical Acceptance Criteria for the Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.2, and at the frequency described in Section 9.3.2 on a GC/MS system meeting the GC/MS Performance Check technical acceptance criteria.

9.3.5.2 The RRF at each calibration concentration for each target compound must be greater than or equal to the compound's minimum acceptable RRF listed in Table 5.

9.3.5.3 The calculated %RSD for the RRF for each compound in the calibration table must be less than 30% with at most two exceptions.

NOTE: This exception may not be acceptable for all projects. Many projects may have a specific target list of compounds which would require the lower limit for all compounds.

Up to two compounds may fail the criteria listed in Section 9.5.5.1 and up to two compounds may fail the criteria listed in Section 9.3.5.3 and still meet the minimum RRF and %RSD requirements. However, these compounds must have a minimum RRF greater than or equal to 0.01, and the %RSD must be less than or equal to 40%.

9.3.5.4 The RRT for each target compound at each calibration level must be within 0.06 RRT units of the mean RRT for the compound.

9.3.5.5 The area response Y of at each calibration level must be within 40% of the mean area response $\overline{Y}$ over the initial calibration range for each internal standard.

9.3.5.6 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer’s instrument operating manual to determine how saturation is indicated for your instrument.

9.3.5.7 The retention time shift for each of the internal standards at each calibration level must be within 30 seconds of the mean retention time over the initial calibration range for each internal standard.

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, service the preconcentrator or take other corrective actions to meet the initial calibration technical acceptance criteria.

9.3.6.2 Initial calibration technical acceptance criteria *must* be met before any samples, including Laboratory Control Samples or required blanks are analyzed. Any samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require re-analysis at no additional cost to USEPA.

9.4 Initial Calibration Verification

9.4.1 The initial calibration verification standard (ICV) must be analyzed to verify the initial calibration standards and to demonstrate equivalency between the second source standard and the initial calibration response. The ICV must be made from standard obtained from a certified second source that is traceable to a different lot or manufacturer than the source of the calibration standards.

9.4.2 Prior to the analysis of samples and required blanks and immediately after the Instrument Performance Check and initial calibration standard sequence, the initial calibration must be verified by analyzing the ICV containing all the target compounds at the 10 ppbv calibration level and internal standards to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the analytical method.

NOTE: For the analysis using SIM technique the initial calibration of the GC/MS system must be verified by analyzing an ICV standard, prior to the analysis of samples and required blanks. The ICV standard for SIM technique must include the required target analytes and internal standards.

9.4.3 Frequency of Internal Standard Verification Standard

9.4.3.1 The initial calibration curve must be verified by the ICV. After the laboratory has determined the initial calibration has met the technical acceptance criteria specified in Section 9.3.5, and prior to any sample analysis, the ICV standard must be analyzed. It is recommended an instrument blank be analyzed between the last initial calibration standard and the ICV standard. The ICV standard must be analyzed under a compliant BFB instrument performance check standard.

NOTE: For Selected Ion Monitoring technique (SIM), a BFB standard must be analyzed using the SCAN mode prior the SIM analysis. The instrument settings, other that those needed to be adjusted for the SIM analysis, would be required to remain the same. A 24-hour BFB clock would be required for all SIM analyses. The 24 hour time period begins at the moment of injection of the BFB standard prior to the first initial calibration standard.

9.4.3.2 If time remains in the 24-hour time period after meeting the technical acceptance criteria for the initial calibration and ICV, samples may be analyzed following the analysis of a method blank. Quantitate all sample and blank results using the mean RRF obtained from the initial calibration standard.

9.4.3 Procedure for Initial Calibration Verification

9.4.3.1 The ICV must be prepared at the mid-level calibration standard concentration (10 ppbv) and analyzed in a GC/MS system that has met the tuning and mass calibration criteria following the same procedure in Section 9.5. For SIM, the ICV should be at 0.4 ppbv.

9.4.4 Calculations for Initial Calibration Verification

9.4.4.1 Calculate an RRF for each target compound according to Section 9.3.4.6.

Perform the following calculations.

NOTE: As indicated earlier, the area response of the primary quantitation ion is used unless otherwise stated.

9.4.4.2 Calculate the Percent Difference (%D) between the ICV RRF_c and the most recent initial calibration $\overline{RRF_i}$ for each target analyte using the following equation.

EQ. 13 Percent Difference

$$\%D = \frac{RRF_c - \overline{RRF_i}}{RRF_i} \times 100$$

Where:

RRF_c = RRF of the compound in the initial calibration standard.

$\overline{RRF}$ = Mean RRF of the compound in the most recent initial calibration.

9.4.5 Technical Acceptance Criteria for Initial Calibration Verification (ICV)

9.4.5.1 The initial calibration verification standard must be analyzed at the concentration level and frequency described in Section 9.4.3 and on a GC/MS system meeting the BFB instrument performance check criteria (See Section 9.2). The %D for each target compound in an ICV standard must be within ±20 percent in order to proceed with the analysis of samples and blanks.

9.4.5.2 For an ICV, up to ten percent of compounds may fail the ICV requirements for the minimum RRF criteria and Percent Difference criteria. However, these compounds must have a minimum RRF greater than or equal to 0.010 and the Percent Difference must be within the inclusive range of ±40.0%.

NOTE: The ICV criteria in Section 9.4.5.1 and 9.4.5.2 also apply to analysis using SIM technique.

9.4.6 Corrective Action for Initial Calibration Verification (ICV)

9.4.6.1 If the initial calibration verification technical acceptance criteria are not met, the ICV standard and the initial calibration standard may not be equivalent. It may be necessary to prepare a new aliquot of the second source standard or calibration standard and recalibrate the instrument or take other corrective actions to meet the ICV technical acceptance criteria. Initial calibration verification acceptance criteria *must* be met before any samples, including Laboratory Control Samples or required blanks are analyzed.

9.5 Continuing Calibration Verification

9.5.1 Summary of Opening Continuing Calibration Verification (CCV)

Prior to the analysis of samples and required blanks and after the Instrument Performance Check and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing an opening CCV containing all the target compounds at the 10 ppbv calibration level and internal standards to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the analytical method.

NOTE: For the analysis using SIM technique the calibration of the GC/MS system must be routinely checked by analyzing a CCV standard, prior to the analysis of samples and required blanks, and after initial calibration technical acceptance criteria have been met. The continuing calibration standard for SIM technique must include the required target analytes and internal standards.

9.5.2 Frequency of Continuing Calibration Verification

9.5.2.1 A check of the calibration curve must be performed once every 24 hours on a GC/MS system that has met tuning criteria. The daily calibration sequence starts with the injection of the BFB. If the BFB analysis meets the ion abundance criteria for BFB, then a daily calibration standard may be analyzed. The 24-hour time period begins with the injection of BFB, followed by the injection of the opening CCV solution. BFB may NOT be added to any calibration standard or calibration verification solution to create a single injection of a calibration standard and a tune solution.

NOTE: For analysis by Selected Ion Monitoring technique (SIM), the 24 hour time period begins at the moment of injection of the BFB instrument performance check in SCAN mode. Following the analysis of the BFB, the instrument is adjusted to SIM mode for the analysis of the first initial calibration standard or the CCV standard, if initial calibration has already been analyzed.

9.5.2.2 If time remains in the 24-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. A method blank is required prior to sample analysis.

9.5.2.3 Quantitate all sample and blank results using the mean RRF obtained from the initial calibration standard.

9.5.3 Procedure for Continuing Calibration Verification (CCV)

9.5.3.1 The mid-level calibration standard (10 ppbv) is analyzed in a GC/MS system that has met the tuning and mass calibration criteria following the same procedure in Section 9.3.

9.5.4 Calculations for Continuing Calibration Verification

9.5.4.1 Calculate an RRF for each target compound according to Section 9.3.4.6.

Perform the following calculations.

NOTE: As indicated earlier, the area response of the primary quantitation ion is used unless otherwise stated.

9.5.4.2 Calculate the Percent Difference (%D) between the CCV RRF_c and the most recent initial calibration $\overline{RRF_i}$ for each target analyte using the following equation.

EQ. 14 Percent Difference

$$\%D = \frac{RRF_c - \overline{RRF_i}}{RRF_i} \times 100$$

Where:

RRF_c = RRF of the compound in the continuing calibration standard

$\overline{RRF}$ = Mean RRF of the compound in the most recent initial calibration

9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.5.5.1 The daily calibration standard must be analyzed at the concentration level and frequency described in Section 9.5 and on a GC/MS system meeting the BFB instrument performance check criteria (see Section 9.2). The %D for each target compound in a daily calibration sequence must be within ±30 percent in order to proceed with the analysis of samples and blanks.

9.5.5.2 For an opening CCV, up to ten percent of compounds may fail the CCV requirements for the minimum RRF criteria and Percent Difference criteria. However, these compounds must have a minimum RRF greater than or equal to 0.010 and the Percent Difference must be within the inclusive range of ±40.0%.

NOTE: For analysis using SIM technique, the criteria in Section 9.5.5. 1 and 9.5.5.2 apply.

9.5.6 Corrective Action for Continuing Calibration Verification

9.5.6.1 If the daily calibration technical acceptance criteria are not met, inspect the system for problems. If it is necessary to clean the ion source, change the column, take other corrective actions to meet the daily calibration technical acceptance criteria, a new initial calibration must be prepared and verified before samples may be analyzed. Daily calibration acceptance criteria *must* be met before any samples, including Laboratory Control Samples or required blanks, are analyzed. It will be necessary to rerun the ICV and all affected samples following the new initial calibration.

10.0 PROCEDURE

10.1 Air Sample Analysis

10.1.1 An aliquot of the air sample from a canister (e.g., 500 mL) is preconcentrated and analyzed by GC/MS under conditions stated in Sections 9.1 and 9.2. If using the multisorbent/dry purge approach, adjust the dry purge volume to reduce water effects in the analytical system to manageable levels.

NOTE: The analyst should be aware that pressurized samples of high humidity samples will contain condensed water. As a result, the humidity of the sample released from the canister during analysis will vary, being lower at the higher canister pressures and increasing in humidity as the canister pressures decreases. Storage integrity of water soluble compounds may also be affected.

10.1.2 If time remains in the 24-hour period in which an initial calibration is performed, samples may be analyzed without analysis of a daily calibration verification standard. If time does not remain in the 24-hour period since the injection of the instrument performance check standard in which an initial calibration is performed, both the instrument performance check standard and the daily calibration standard should be analyzed before sample analysis may begin.

10.1.3 Procedure for Instrumental Analysis

Perform the following procedure for analysis.

10.1.3.1 All canister samples should be at temperature equilibrium with the laboratory.

10.1.3.2 Check and adjust the mass flow controllers to provide correct flow rates for the system.

10.1.3.3 Connect the sample canister to the inlet of the GC/MS analytical system. The desired sample flow is established through the six-port chromatographic valve and the preconcentrator to the downstream flow controller. The absolute volume of sample being pulled through the trap must be consistent from run to run.

10.1.3.4 Heat/cool the GC oven and cryogenic or adsorbent trap to their set points. Assuming a six-port value is being used, as soon as the trap reaches its lower set point, the six-port chromatographic valve is cycled to the trap position to begin sample collection. Utilize the sample collection time which has been optimized by the analyst.

10.1.3.5 Use the arrangement (i.e., a gastight syringe or some alternate method) to introduce an internal standard during the sample collection period. Add sufficient internal standard equivalent to 10 ppbv in the sample. For example, a 0.5 mL volume of a mixture of internal standard compounds, each at 10 ppmv concentration, added to a sample volume of 500 mL, will result in 10 ppbv of each internal standard in the sample.

10.1.3.6 For SIM technique add sufficient internal standard equivalent to 0.4 ppbv in the samples and blanks (Section 7.2.2.5).

10.1.3.7 After the sample and internal standards are preconcentrated on the trap, the GC sampling valve is cycled to the inject position and the trap is swept with helium and heated. Assuming a focusing trap is being used, the trapped analytes are thermally desorbed onto a focusing trap and then onto the head of the capillary column and are separated on the column using the GC oven temperature program. The canister valve is closed and the canister is disconnected from the mass flow controller and capped. The trap is maintained at elevated temperature until the beginning of the next analysis.

10.1.3.8 Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak should be acquired. Scanning also allows identification of unknown compounds in the sample through searching of library spectra.

10.1.3.9 Each analytical run must be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound.

10.1.3.10 Secondary ion quantitation is allowed only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the laboratory record book and in the SDG narrative.

10.1.3.11 Samples must be diluted if the compound concentrations are outside of the calibration range of the instrument.

10.1.3.12 Add the air source to the sample for the dilution as that used for the preparation of the method blanks, that being humidified, ultra-pure zero air.

10.1.3.13 The laboratory must report data for both the undiluted sample and the diluted sample. The laboratory may not submit more than two sets of diluted sample data.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

11.1.1.1 The compounds listed in the Target Compound List (TCL) in Exhibit C shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of the standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

- Elution of the sample component at the same Gas Chromatograph (GC) Relative Retention Time (RRT) as the standard component
- Correspondence of the sample component and standard component mass spectra

11.1.1.2 For establishing correspondence of the GC RRT, the sample component RRT must compare within ±0.06 RRT units of the RRT of the corresponding continuing calibration standard component. For reference, the standard must be run in the same 24-hour time period as the sample. If samples are analyzed during the same 24-hour time period as the initial calibration standards, use the RRT values from the 10 ppbv standard. Otherwise, use the corresponding opening Continuing Calibration Verification (CCV) standard. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, then the RRT should be assigned by using Extracted Ion Current Profiles (EICP) or ions unique to the component of interest.

11.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/Mass Spectrometer (MS) are required. Once obtained, these standard spectra may be used for identification purposes, **only** if the Contractor's GC/MS meets the daily instrument performance requirements for 4-bromofluorobenzene (BFB). These standard spectra may be obtained from the run used to obtain reference retention times (RRTs).

11.1.1.4 The guidelines for qualitative verification by comparison of mass spectra are as follows:

All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

The relative intensities of ions specified in the above paragraph must agree within ±20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70%).

Ions greater than 10% in the sample spectrum but not presenting the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the Contract Required Quantitation Limit (CRQL), report the actual value followed by a "J" (e.g., "3J").

11.1.1.5 If a compound cannot be verified by all of the spectral identification criteria listed in Section 11.1.1.4, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification and proceed with quantitation.

11.1.2 Qualitative Identification of Non-Target Compounds (Optional)

11.1.2.1 A library search shall be executed for non-target sample components for the purpose of tentative identification. The NIST (2002 release or later), Wiley (1991 release or later), or equivalent mass spectral library, shall be used as the reference library.

11.1.2.2 All organic compounds that are not either internal standards or positively identified target compounds shall be tentatively identified using the procedures detailed in Section 11.1, shall be tentatively identified via a forward search of the NIST, Wiley, or equivalent mass spectral library. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer-generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

11.1.2.3 Up to 30 non-alkane Tentatively Identified Compounds (TICs) of greatest apparent concentration shall be reported on Form I VOA-TIC. Peaks that are tentatively identified as straight-chain, branched, or cyclic alkanes, and are alone or part of an alkane series, shall be reported as "total alkanes" on Form I VOA-TIC. An alkane is defined as any hydrocarbon with the generic formula CnH2n+2 (straight-chain or branched) or CnH2n (cyclic) that contains only C-H and C-C single bonds. The concentrations of each of the alkanes are to be summed and reported as a single result for the "total alkanes". Documentation for the tentative identification of each alkane shall be supplied in the hard copy deliverable packages. The alkanes are not to be counted as part of the 30 compounds individually reported as tentative identified compounds on Form I VOA-TIC. Carbon dioxide and compounds with responses less than 10% of the internal standard in which they are to be qualified (as determined by inspection of the peak areas or height) are not to be reported (nor are they to be counted as part of the 30 compounds that are to be reported).

11.1.2.4 Rules for Making Tentative Identification

11.1.2.4.1 For compounds to be reported, as per the instructions in Section 11.1.2.3., identification (as generated by the library search program) of those receiving a library search match of 85% or higher should be considered a "probable match". The compound should be reported with the identification generated by the search program unless the mass spectral interpretation specialist feels there is just evidence not to report the compound as identified by the library search program.

11.1.2.4.2 If the library search produces more than one compound at or above 85%, report the compound with the highest percent match (report first compound if the percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels there is just evidence not to report the compound with the highest match. Do not report internal standards, or analytes that are on the volatile target analyte list, unless the library search produces only one compound having a match of greater than 85%, and that compound is identified as an internal standard, or volatile target analyte.

11.1.2.4.3 If the library search produces a series of obvious isomer compounds with library search matches greater that 85% (e.g. halo-carbons), the compound with the highest library search percent match should be reported (or first compound if library search matches are the same).

11.1.2.4.4 If the mass spectral interpretation specialist has just evidence to support reporting a compound with a tentative identification of something other than that generated by the library search program (with a library search result of 85% or greater), the laboratory shall include in the Sample Delivery Group (SDG) Narrative the justification for not reporting a compound as listed by the search program. This narrative shall detail explicitly why a library search generated identification for a compound was rejected. If a TIC has obvious isomer analogs, the laboratory shall include in the SDG narrative a statement indicating that the exact isomer configuration, as reported, may not be absolutely accurate.

11.1.2.4.5 If the library search produces no matches at or above 85%, the mass spectral interpretation specialist is encouraged to make a valid tentative identification of the compound. If no valid tentative identification can be made, the compound should be reported as "unknown". The mass spectral interpretation specialist should give additional classification of the unknown, if possible (e.g., "unknown aromatic compound", "unknown chlorinated compound", etc.).

11.2 Calculations

11.2.1 Target Compounds

11.2.1.1 Identified target compounds shall be quantified by the internal standard method using Equation 15. The Mean Relative Response Factor (Mean $\overline{RRF}$) from the initial calibration standard is used to calculate the concentration in the sample.

11.2.1.2 Concentration

EQ. 15 Air Concentration Calculation

$$C_x = \frac{A_x C_{is} DF}{A_{is} \overline{RRF}}$$

Where:

C = Compound concentration, ppbv.

A_x = Area of the characteristic ion for the compound to be measured, counts.

A_{is} = Area of the characteristic ion for the specific internal standard, counts.

C_{is} = Concentration of the internal standard spiking mixture, ppbv

$\overline{RRF}$ = Mean relative response factor from the initial calibration.

DF = Dilution factor calculated as described in section 2. If no dilution is performed, DF = 1.

NOTE: The equation above is valid under the condition that the volume (~500 µL) of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume (~500 mL) of field and QC sample introduced into the trap is the same for each analysis.

Conversion of concentration ppbv to concentration µg/m3:

$$\text{Concentration (ppbv)} = \text{Concentration (ug/m}^3\text{)} \times 24.46/\text{MW @ 25°C}$$

For the reverse conversion:

$$\text{Concentration (ug/m}^3\text{)} = \text{Concentration (ppbv)} \times \text{MW}/24.46 \text{ @ 25°C}$$

Where:

MW = molecular weight (Table 1)

[Assumes standard temperature.]

These conversion equations depend on the ambient air temperature at time of collection conversion (usually about 20 to 25 degrees Centigrade).

At an ambient air pressure of 1 atmosphere, the equation is:

$$\text{ppbv} = (\mu g/m^3)(^\circ K)(0.08205)/MW$$

and for the reverse conversion:

$$\mu g/m^3 = (\text{ppbv})(MW)/[(0.08205)\ (K)]$$

Where:

ppbv = Air pollutant concentration, in parts per billion by volume.

$\mu g/m^3$ = Micrograms of pollutant per cubic meter of air.

K = Atmospheric temperature in degrees Kelvin = 273.15 + °C.

0.08205 = Universal gas law constant in (atm·liter)/(gmol·°K).

MW = Molecular weight of the air pollutant (dimensionless).

atm = absolute atmospheric pressure in atmospheres.

gmol = the amount of a compound equal in grams to its molecular weight (mole).

11.2.2 Quantitation of Non-Target Compounds (Optional)

11.2.2.1 An estimated concentration for non-target TICs shall be determined by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

11.2.2.2 The formula for calculating non-target compound concentrations is the same as in Section 11.2.1.2.Total area counts (or peak heights) from the total Reconstructed Ion Chromatograms (RICs) are to be used for both the non-target compound to be measured (A_x) and the internal standard (A_{is}). An RRF of 1.0 is to be assumed. The value from this quantitation shall be qualified as "J" (estimated due to the lack of a compound-specific RRF), and "N" (presumptive evidence of presence when a TIC is tentatively identified as a specific compound), indicating the quantitative and qualitative uncertainties associated with this non-target compound. An estimated concentration must be calculated for all TICs, as well as those identified as unknowns.

11.2.3 Internal Standard Responses and Retention Times (RTs)

Internal standard responses and RTs in all samples must be evaluated during, or immediately after, data acquisition. Compare the sample/blank internal standard responses and RTs to the opening CCV internal standard responses and RTs. For samples and blanks analyzed during the same 24-hour time period as the initial calibration standards, compare the internal standard responses and RTs against the 10 ppbv calibration standard.

The EICP of the internal standards must be monitored and evaluated for each sample including LCS/LCSD and blanks.

11.3 Technical Acceptance Criteria for Sample Analysis

NOTE: If sample analysis is performed in the time remaining from a instrument performance check standard (BFB) associated with an initial calibration (ICAL), the internal area responses and the RTs in the 10 ppbv standard from the ICAL shall be used for to evaluate the samples.

11.3.1 The field sample must be analyzed on a GC/MS system meeting the BFB tuning criteria in Section 9.2, the initial calibration criteria in Section 9.3, and continuing calibration criteria in Section 9.5 at the frequency described in each section.

11.3.2 The sample and any required dilution must be analyzed within the contract holding time.

11.3.3 The field samples must be analyzed along with a laboratory method blank that met the blank technical acceptance criteria.

11.3.4 All of the target analyte peaks should be within the initial calibration range. If a sample requires dilution, compounds reported in the original analysis may be reported above the initial calibration range but at least one of the two sample analyses must meet this criteria.

11.3.5 The EICP area for each of the internal standards in the sample must be within the range of ±40 percent of its response in the most recent opening CCV standard analysis.

11.3.6 The retention time for each internal standard must be within 0.5 minutes of the retention time of the internal standard in the most recent valid calibration.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample technical acceptance criteria must be met before data are reported. Samples contaminated from laboratory sources or any samples not meeting the sample technical acceptance criteria will require reanalysis at no additional cost to USEPA.

11.4.2 Corrective actions for failure to meet instrument performance checks, initial calibration, CCV, and method blanks must be completed before the analysis of samples.

11.4.3 If the on-column concentration of any compound in any sample exceeds the initial calibration range, an aliquot of the original sample must be diluted and reanalyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

- Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.
- The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

NOTE: Analysis involving dilution should be reported with a dilution factor and nature of the dilution gas.

11.4.4 Internal standard responses and retention times must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 0.5 minutes from the latest daily (24-hour) calibration standard (or mean retention time over the initial calibration range), the GC/MS system must be inspected for malfunctions, and corrections made as required.

11.4.5 If the area response for any internal standard changes by more than ±40 percent between the sample and the most recent valid calibration, the GC/MS system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

11.4.6 The laboratory must report data for both the initial analysis and the reanalysis. The laboratory may not submit more than two sets of diluted sample data.

12.0 QUALITY CONTROL (QC)

12.1 Blank Analyses

12.1.1 Summary

There are two types of blanks required by this method:

12.1.1.1 Method Blank - The purpose of the method blank is to determine the levels of contamination associated with processing and analysis of samples. To monitor for possible laboratory contamination, laboratory method blanks are analyzed at least once in a 24-hour analytical sequence. All steps in the analytical procedure are performed on the blank using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis. A laboratory method blank (LMB) is an unused, certified canister that has not left the laboratory. The blank canister is pressurized with humidified, ultra-pure zero air and carried through the same analytical procedure as a field sample. The injected aliquot of the blank must contain the same amount of internal standards that are added to each sample.

12.1.1.2 Instrument Blank – is analyzed after a sample/dilution that contains a target compound exceeding the initial calibration range. The results from the instrument blank analysis indicate whether there is contamination from a previous sample.

NOTE: If the Contractor during the analytical sequence determines that an instrument blank needs to be analyzed for any reason within an analytical sequence, the instrument blank is to meet the requirements in Section 12.1.5 to be acceptable. The samples must be labeled as an instrument blank and the reason for analyzing the blank documented in the case narrative.

12.1.2 Frequency of Blank Analyses

12.1.2.1 The laboratory method blank must be analyzed at least once during every 24-hour time period on each Gas Chromatograph/Mass Spectrometer (GC/MS) system used for volatile analysis.

12.1.2.2 The method blank **must** be analyzed after the Continuing Calibration Verification (CCV) and before any samples, including Laboratory Control Samples or dilutions, are analyzed. The method blank must be analyzed after the initial calibration sequence (including the ICV)and prior to sample analysis, if samples are to be analyzed before the 24-hour period expires.

12.1.2.3 If the Contractor is using an autosampler, and a subsequent sample analysis demonstrates the system is not contaminated (e.g. the sample analysis meets the technical acceptance criteria for the method blank), this may be used as proof the system is not contaminated in lieu of an instrument blank. If the instrument blank or sample analysis does not meet the criteria, the system is considered contaminated, and must be decontaminated. Until an instrument blank meets the method blank technical acceptance criteria, any samples analyzed since the original contaminated sample will require reanalysis at no additional cost to USEPA. This criteria apply to both SCAN and SIM analyses.

NOTE: Only the instrument blank that demonstrates that the system is clean shall be reported. Instrument blanks analyzed during the instrument decontamination process that exceed the requirements listed in Section 11.3 should not need to be reported.

12.1.3 Procedure for Blank Analysis

12.1.3.1 Fill a cleaned and evacuated canister with humidified zero air (RH > 20 percent, at 25°C). Pressurize the contents to 2 atm. The blank sample should be analyzed using the same procedure outlined under Section 10.1.

12.1.3.2 For SIM technique add sufficient internal standard equivalent to 0.4 ppbv in the samples and blanks (Section 7.2.2.5).

12.1.4 Calculations for Blank Concentration

12.1.4.1 Method blanks are analyzed using the same procedure as field samples. Analyte concentrations are calculated using Equation 15. If TICs are requested, labs are required to report TIC in associated blanks.

12.1.5 Technical Acceptance Criteria for Blank Analyses

12.1.5.1 A blank canister should be analyzed daily.

12.1.5.2 A method blank should be analyzed daily after the calibration verification standard and prior to sample analysis or; after the initial calibration sequence (including the ICV) and prior to sample analysis, if samples are to be analyzed before the 24-hour period expires for an ICAL.

12.1.5.3 The retention time for each of the internal standards must be within ±0.5 minutes between the blank and the most recent valid calibration.

12.1.5.4 The blank should not contain any target analyte at a concentration greater than half of the CRQL and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte. There should be no Tentatively Identified Compound (TIC) present with areas greater than the closest eluting internal standard.

12.1.6 Corrective Action for Blank Analyses

12.1.6.1 If the blanks do not meet the technical acceptance criteria, the analyst should consider the analytical system to be out of control. It is the responsibility of the analyst to ensure that contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures need to be taken and documented before further sample analysis proceeds. If an analyte in the blank is found to be out of control (i.e., contaminated) and the analyte is also found in associated samples, those sample results should be "flagged" as possibly contaminated.

12.1.6.2 Any method blank that has target compounds detected at levels above the CRQL or has failed to meet the technical acceptance criteria described in Section 12.1.5.3 must be reanalyzed. Further, all samples following a failed method blank or instrument blank in an analytical sequence must be re-analyzed in a verified calibration sequence and following an acceptable blank.

12.2 Laboratory Control Sample

12.2.1 The Laboratory Control Sample (LCS) is a replicate of the Continuing Calibration Verification standard that is analyzed immediately after the method blank in the analytical sequence.

12.2.2 The LCS must be prepared from the same standard and at the same concentration as the CCV (10 ppbv midpoint of calibration curve). All compounds in the target compound list must be present in the LCS. The LCS is prepared using the same procedures used in Section 7.2 to prepare the calibration standards (e.g. dynamic dilution, static dilution bottle technique, etc.)

12.2.2.1 For SIM technique the LCS must be prepared with a concentration at the (0.4 ppbv) of the calibration curve. All compounds in the SIM target compound list must be present in the LCS.

12.2.3 Laboratory Control Sample Analyses

12.2.3.1 The LCS is designed to assess the analytical precision by measuring the Relative Percent Difference (RPD) between the LCS and CCV. There are several factors which may affect the precision of the measurement (See Section 12.4.2).

12.2.4 Frequency of Laboratory Control Sample Analysis

12.2.4.1 LCS is analyzed immediately following the method blank and prior to sample analysis within every 24-hour analytical sequence.

12.2.5 Calculations for LCS

12.2.5.1 Calculate the concentrations of the LCS compounds using the same equations as used for target compounds (Equation 15 from Section 11.2.1). Calculate the recovery of each LCS compound as follows:

EQ. 16 LCS Spike Recovery Calculation

$$\%\ \text{LCS Recovery} = \frac{\text{Found Conc.}}{\text{True Conc.}} \times 100$$

12.2.5.2 Duplicate Precision

The Relative Percent Difference (RPD) shall be calculated for each analyte for the LCS and CCV using the following equation:

EQ. 17 Relative Percent Difference

$$RPD = \frac{\left|X_{LCS} - X_{CCV}\right|}{((X_{LCS} + X_{CCV})/2)} \times 100$$

Where:

x_{LCS} and x_{CCV} = The results for the analyte in the LCS and CCV respectively.

12.2.6 Technical Acceptance Criteria for LCS

12.2.6.1 The LCS must be analyzed on a GC/MS system meeting the BFB, initial calibration and continuing calibration verification technical acceptance criteria, blank technical acceptance criteria, and at the frequency described in Section 12.2.4.

12.2.6.2 The area response for each internal standard (IS) in the LCS must be within ±40 percent of the mean area response of the IS in the most recent valid calibration.

12.2.6.3 The retention time for each of the internal standards must be within ±0.5 minutes between the LCS and the most recent valid calibration.

12.2.6.4 The limits for LCS compound are ±30% (eg. 70 – 130% recovery). Ten percent of the LCS compounds may be outside of this limit as long as their recovery is ± 40%.

12.2.6.5 The precision between the recovery of compounds in the LCS and the CCV must be less than or equal to 25% RPD.

12.2.7 Corrective Action for LCS

12.2.7.1 If the LCS recovery and precision recovery are not met, the laboratory must perform maintenance as needed. If the criteria are still not met, the analytical system must be recalibrated and associated samples must be re-analyzed at no additional cost to the USEPA.

12.3 Method Detection Limit (MDL) Determination

12.3.1 The procedure chosen to define the method detection limit is that given in the *Code of Federal Regulations* (40 CFR 136 Appendix B).

12.3.2 The method detection limit is defined for each system in the SCAN mode by making seven replicate measurements of the compound of interest at a concentration near (within a factor of five) the expected detection limit by SCAN mode, computing the standard deviation for the seven replicate concentrations, and multiplying this value by 3.14 (i.e., the Student's t value for 99 percent confidence for seven values).

12.3.3 Before any field samples are analyzed under the contract, the MDL for each volatile target compound shall be determined on each instrument used for analysis. The MDLs must be verified annually thereafter (see Section 12.3.4 for MDL verification procedures), until the contract expires or is terminated, or after major instrument maintenance. Major instrument maintenance includes, but is not limited to, cleaning or replacement of the mass spectrometer or source, mass filters (e.g., quadrupole, ion trap, etc.), electron multiplier (or similar device), GC column, and replacement or overhaul of preconcentrator.

12.3.4 To determine the MDLs, the Contractor shall run an MDL study following the procedures specified in 40 CFR Part 136. The Contractor shall analyze the MDL samples on each instrument used for field sample analyses. MDL verification for air samples is achieved by analyzing a single ultra zero air blank (see method blank in Section 12.1) spiked with each volatile target compound at a concentration equal to 1-4 times the analytically determined MDL. Each target compound must produce a response and meet the criteria less than or equal to the clean canister certification criteria specified in Method TO-15. The resulting mass spectra of each target compound must meet the qualitative identification criteria outlined in Section 11.1.1.4.

12.3.5 The determined concentration of the MDL must be less than or equal to the 0.2 ppbv using SCAN mode of analysis.

12.4 Replicate Sample Precision

12.4.1 Relative Percent Difference (RPD)

The measure of precision between replicate samples from two different canisters expressed as the absolute value of the difference between sample replicate measurements divided by the average value and expressed as a percentage as follows:

EQ. 18 Relative Percent Difference

$$RPD = \frac{|X_1 - X_2|}{((X_1 + X_2)/2)} \times 100$$

Where:

x_1 = First measurement value

x_2 = Second measurement value

12.4.2 There are several factors which may affect the precision of the measurement. The nature of the compound of interest itself such as molecular weight, water solubility, polarizability, etc., each have some effect on the precision, for a given sampling and analytical system. For example, styrene, which is classified as a polar VOC, generally shows slightly poorer precision than the bulk of nonpolar VOCs. A primary influence on precision is the concentration level of the compound of interest in the sample, i.e., the precision degrades as the concentration approaches the detection limit. A conservative measure was obtained from replicate analysis of "real world" canister samples from the TAMS and UATMP networks. These data suggest that a replicate precision value of 25 percent can be achieved for each of the target compounds.

13.0 METHOD PERFORMANCE

13.1 Requirements for Demonstrating Method Acceptability for VOC Analysis from Canisters

13.1.1 The performance criteria for a system to qualify under this method are as follows:

- All technical criteria for the analysis of samples, standards and quality control samples
- Establish the CRQL ≤0.5 ppbv for SCAN analysis, CRQL ≤ 0.05 ppbv for selected SIM analysis

- MDL concentration determined must be less than or equal to the 0.2 ppbv using SCAN mode of analysis.
- Routinely meet the clean canister criteria for all SUMMA Canisters.
- Mass spectra of each target compound must meet the qualitative identification criteria.
- Audit accuracy ≤ 30% for all target compounds (Requirements for an Audit Samples will be specified in the Task Order Agreement.)

13.1.2 Either SIM or SCAN modes of operation can be used to achieve these criteria and the choice of mode will depend on the number of target compounds, the decision of whether or not to determine tentatively identified compounds along with other VOCs on the target list, as well as on the analytical system characteristics.

13.1.3 Specific criteria for each compound on the target compound list must be met by the analytical system. These criteria were established by examining summary data from EPA's Toxics Air Monitoring System Network and the Urban Air Toxics Monitoring Program network. Details for the determination of each of the criteria follow.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When waste cannot be feasibly reduced at the source, USEPA recommends recycling as the best option.

14.2 Information about pollution prevention that may be applicable to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, N.W. Washington D.C., 20036 (202) 872-4386.

15.0 WASTE MANAGEMENT

USEPA requires that laboratory waste management practices be consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all release from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

National Risk Management Research Laboratory (NRMRL). *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. Method TO-15. 2nd edition. January 1999.

US Environmental Protection Agency. *Volatile Organic Compountds by Gas Chromatography/Mass Spectrometry (GC/MS)*. Method 8260B. Revision 2. December 1996.

American Chemical Society. *Less is Better. Laboratory Chemical Management for Waste Reduction*. 1985.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

Target Compound Physical Properties

No	Compound	CAS No.	BP °C	Vapor Pressure, mm Hg	Molecular Weight
1	Propylene	115-07-1	-48	8664	42.1
2	Dichlorodifluoromethane (Freon 12)	75-71-8	-29.8	4390	120.9
3	Dichlorotetrafluoroethane (Freon 114)	76-14-2	4.1	1430	170.9
4	Chloromethane	74-87-3	-23.7	4310	50.5
5	Vinyl chloride	75-01-4	-14.0	2600	62.5
6	1,3-Butadiene	106-99-0	-4.5	2100	54
7	Bromomethane	74-83-9	3.6	1420	94.9
8	Chloroethane	75-00-3	12.5	1010	64.5
9	Ethanol	64-17-5	78.5	47	46.1
10	Trichlorofluoromethane (Freon 11)	75-69-4	23.7	690	137.4
11	1,1-Dichloroethene	75-35-4	31.7	500	97
12	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	76-13-1	48	284	187.4
13	Acetone	67-64-1	56.5	185	58.1
14	2-Propanol (Isopropanol)	67-63-0	82.5	42.7	60.1
15	Carbon disulfide	75-15-0	46.5	260	76
16	Methylene chloride	75-09-2	40.0	349	84.9
17	trans-1,2-Dichloroethene	156-60-5	48.0	395	96.9
18	n-Hexane	110-54-3	69.0	120	86.2
19	Methyl tert-butyl ether	1634-04-4	55.2	249	86
20	1,1-Dichloroethane	75-34-3	57.0	230	99
21	cis-1,2-Dichloroethene	156-59-2	60.3	273	96.9
22	2-Chloro-1,3-butadiene (Chloroprene)	126-99-8	59.4	226	88.5
23	2-Butanone	78-93-3	79.6	77.5	72
24	Tetrahydrofuran	109-99-9	66.0	129	72.1
25	Chloroform	67-66-3	61.2	160	119
26	1,1,1-Trichloroethane	71-55-6	74.1	100	133.4
27	Cyclohexane	110-82-7	80.7	98	84.2
28	Carbon tetrachloride	56-23-5	76.7	90.0	153.8
29	Ethyl Acetate	141-78-6	77.0	95	88.1
30	Vinyl Acetate	108-05-4	72.2	83.0	86
31	Benzene	71-43-2	80.1	76.0	78
32	1,2-Dichloroethane	107-06-2	83.5	61.5	99
33	n-Heptane	142-82-5	98.4	45.7	100.2
34	1,4-Dioxane	123-91-1	101	37.3	88
35	Trichloroethene	79-01-6	87.0	20.2	131.4
36	1,2-Dichloropropane	78-87-5	97.0	42.0	113
37	Bromodichloromethane	75-27-4	90.6	50	163.8
38	cis-1,3-Dichloropropene	10061-01-5	112	27.8	111
39	4-Methyl-2-pentanone	108-10-1	117.5	15.7	100.2
40	Toluene	108-88-3	111	22.0	92
41	trans-1,3-Dichloropropene	10061-02-6	112	23	111
42	1,1,2-Trichloroethane	79-00-5	114	19.0	113.4
43	Tetrachloroethene	127-18-4	121	14.0	165.8
44	2-Hexanone	591-78-6	117	6.0	100.2
45	Dibromochloromethane	124-48-1	119	5	208.2
46	1,2-Dibromoethane	106-93-4	132	11.0	187.9
47	n-Octane	111-65-9	125.6	14	114.2
48	Chlorobenzene	108-90-7	132	8.8	112.6
49	Ethylbenzene	100-41-4	136	7.0	106.2
50	o-Xylene	95-47-6	144	5.0	106.2

No	Compound	CAS No.	BP °C	Vapor Pressure, mm Hg	Molecular Weight
51	m,p-Xylene	179601-23-1	142	6.7	106.2
52	Styrene	100-42-5	145	6.6	104
53	Bromoform	75-25-2	149	5.6	252.8
54	Cumene	98-82-8	153	3.2	120
55	1,1,2,2-Tetrachloroethane	79-34-5	146	5.0	167.9
56	Propylbenzene	103-65-1	159	3.4	120.2
57	4-Ethyltoluene	622-96-8	162	3	120.2
58	1,3,5-Trimethylbenzene	108-67-8	165	1.9	120.2
59	1,2,4-Trimethylbenzene	95-63-6	169	2.0	120.2
60	Benzyl Chloride	100-44-7	179	1.0	126.6
61	1,3-Dichlorobenzene	541-73-1	173	2.2	147
62	1,4-Dichlorobenzene	106-46-7	173	0.60	147
63	1,2-Dichlorobenzene	95-50-1	180.5	1.2	147
64	Hexachlorobutadiene	87-68-3	215	0.40	260.8
65	1,2,4-Trichlorobenzene	120-82-1	213	0.18	181.5

Table 2

Characteristic Masses (Ions) Used for Quantifying Target Compounds

No	Compound	CAS No.	Primary Ion	Secondary Ion(s)
1	Propylene	115-07-1	41	39, 42
2	Dichlorodifluoromethane (Freon 12)	75-71-8	85	87
3	Dichlorotetrafluoroethane (Freon 114)	76-14-2	85	135, 87, 137
4	Chloromethane	74-87-3	50	52
5	Vinyl chloride	75-01-4	62	64
6	1,3-Butadiene	106-99-0	39	54
7	Bromomethane	74-83-9	94	96
8	Chloroethane	75-00-3	64	66
9	Ethanol	64-17-5	45	46
10	Trichlorofluoromethane (Freon 11)	75-69-4	101	103
11	1,1-Dichloroethene	75-35-4	96	61, 98
12	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	76-13-1	101	85, 151
13	Acetone	67-64-1	43	58
14	2-Propanol (Isopropanol)	67-63-0	45	43
15	Carbon disulfide	75-15-0	76	78
16	Methylene chloride	75-09-2	84	49, 51, 86
17	trans-1,2-Dichloroethene	156-60-5	96	61, 98
18	n-Hexane	110-54-3	57	41, 43
19	Methyl tert-butyl ether	1634-04-4	73	43, 57
20	1,1-Dichloroethane	75-34-3	63	65, 83, 85, 98, 100
21	cis-1,2-Dichloroethene	156-59-2	96	61, 98
22	2-Chloro-1,3-butadiene (Chloroprene)	126-99-8	88	53, 90
23	2-Butanone	78-93-3	43	57, 72*
24	Tetrahydrofuran	109-99-9	42	41, 72, 71
25	Chloroform	67-66-3	83	85
26	1,1,1-Trichloroethane	71-55-6	97	99, 117, 119
27	Cyclohexane	110-82-7	56	69, 84
28	Carbon tetrachloride	56-23-5	117	119, 121
29	Ethyl Acetate	141-78-6	43	61
30	Vinyl Acetate	108-05-4	43	86
31	Benzene	71-43-2	78	- - -
32	1,2-Dichloroethane	107-06-2	62	64, 100, 98
33	n-Heptane	142-82-5	57	41, 43, 71
34	1,4-Dioxane	123-91-1	88	58
35	Trichloroethene	79-01-6	130	95, 97, 132
36	1,2-Dichloropropane	78-87-5	63	65, 114
37	Bromodichloromethane	75-27-4	83	85
38	cis-1,3-Dichloropropene	10061-01-5	75	77
39	4-Methyl-2-pentanone	108-10-1	43	58, 100
40	Toluene	108-88-3	91	92
41	trans-1,3-Dichloropropene	10061-02-6	75	77
42	1,1,2-Trichloroethane	79-00-5	97	83, 85, 99, 132, 134
43	Tetrachloroethene	127-18-4	164	129, 131, 166
44	2-Hexanone	591-78-6	43	58, 57, 100
45	Dibromochloromethane	124-48-1	129	208, 206
46	1,2-Dibromoethane	106-93-4	107	109
47	n-Octane	111-65-9	57	41, 43, 85
48	Chlorobenzene	108-90-7	112	114
49	Ethylbenzene	100-41-4	106	91
50	o-Xylene	95-47-6	106	91
51	m,p-Xylene	179601-23-1	106	91
52	Styrene	100-42-5	104	78, 103
53	Bromoform	75-25-2	173	171, 175, 250, 252, 254
54	Cumene	98-82-8	105	120
55	1,1,2,2-Tetrachloroethane	79-34-5	83	131, 133, 166

No	Compound	CAS No.	Primary Ion	Secondary Ion(s)
56	Propylbenzene	103-65-1	91	120
57	4-Ethyltoluene	622-96-8	105	120
58	1,3,5-Trimethylbenzene	108-67-8	105	120
59	1,2,4-Trimethylbenzene	95-63-6	105	120
60	Benzyl Chloride	100-44-7	91	126
61	1,3-Dichlorobenzene	541-73-1	146	111, 75
62	1,4-Dichlorobenzene	106-46-7	146	111, 75
63	1,2-Dichlorobenzene	95-50-1	146	111, 75
64	Hexachlorobutadiene	87-68-3	225	227, 223
65	1,2,4-Trichlorobenzene	120-82-1	180	182, 145
	INTERNAL STANDARDS			
	Bromochloromethane	74-97-5	128	49, 130, 51
	1,4-Difluorobenzene	540-36-3	114	63, 88
	Chlorobenzene-d5	3114-55-4	117	82, 119

*mass 43 is used for quantitation of 2-Butanone, but mass 72 must be present for positive identification.

Table 3

Required BFB Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria1
50	15.0 to 40.0 % of mass 95
75	30.0 to 80.0 % of mass 95
95	Base Peak, 100 % Relative Abundance
96	5.0 to 9.0 % of mass 95 (see NOTE)
173	Less than 2.0 % of mass174
174	50.0 to 120.0 % of mass 95
175	5.0 to 9.0 % of mass 174
176	93.0 to 101.0 % of mass 174
177	5.0 to 9.0 % of mass 176

NOTE: All ion abundances must be normalized to mass 95, the nominal base peak, even though the ion abundance of mass 174 may be up to 120% that of mass.

Table 4

Volatile Target Compounds with Corresponding Internal Standards for Quantitation

Bromochloromethane	1,4-Difluorobenzene (IS)	Chlorobenzene-d5 (IS)
Propylene	Chloroform	n-Octane
Dichlorodifluoromethane	1,1,1-Trichloroethane	Chlorobenzene
Dichlorotetrafluoroethane	Cyclohexane	Ethylbenzene
Chloromethane	Carbon tetrachloride	o-Xylene
Vinyl chloride	Ethyl Acetate	m- and p-Xylenes
1,3-Butadiene	Vinyl Acetate	Styrene
Bromomethane	Benzene	Bromoform
Chloroethane	1,2-Dichloroethane	Cumene
Ethanol	n-Heptane	1,1,2,2-Tetrachloroethane
Trichlorofluoromethane	1,4-Dioxane	Propylbenzene
1,1-Dichloroethene	Trichloroethene	4-Ethyltoluene
1,1,2-Trichloro-1,2,2-trifluoroethane	1,2-Dichloropropane	1,3,5-Trimethylbenzene
Acetone	Bromodichloromethane	1.2.4-Trimethylbenzene
2-Propanol (Isopropanol)	cis-1,3-Dichloropropene	Benzyl Chloride
Carbon disulfide	4-Methyl-2-pentanone	1,3-Dichlorobenzene
Methylene chloride	Toluene	1,4-Dichlorobenzene
trans-1,2-Dichloroethene	trans-1,3-Dichloropropene	1,2-Dichlorobenzene
n-Hexane	1,1,2-Trichloroethane	Hexachlorobutadiene
Methyl tert-butyl ether	Tetrachloroethene	1,2,4-Trichlorobenzene
1,1-Dichloroethane	2-Hexanone	
cis-1,2-Dichloroethene	Dibromochloromethane	
2-Chloro-1,3-butadiene (Chloroprene)	1,2-Dibromoethane	
2-Butanone		
Tetrahydrofuran		

Table 5

Relative Response Factor, Initial Calibration, and Initial Calibration Verification Criteria for Volatile Organic Compounds

Volatile Compound	Minimum RRF [1]	Maximum %RSD [1]	ICV Maximum Difference [2]
Propylene	0.010	30.0	± 20.0
Dichlorodifluoromethane	0.010	30.0	± 20.0
Dichlorotetrafluoroethane	0.010	30.0	± 20.0
Chloromethane	0.010	30.0	± 20.0
Vinyl chloride	0.100	30.0	± 20.0
1,3-Butadiene	0.100	30.0	± 20.0
Bromomethane	0.100	30.0	± 20.0
Chloroethane	0.010	30.0	± 20.0
Ethanol	0.010	30.0	± 20.0
Trichlorofluoromethane	0.010	30.0	± 20.0
1,1-Dichloroethene	0.100	30.0	± 20.0
1,1,2-Trichloro-1,2,2-trifluoroethane	0.010	30.0	± 20.0
Acetone	0.010	30.0	± 20.0
2-Propanol (Isopropanol)	0.010	30.0	± 20.0
Carbon disulfide	0.010	30.0	± 20.0
Methylene chloride	0.010	30.0	± 20.0
trans-1,2-Dichloroethene	0.010	30.0	± 20.0
n-Hexane	0.100	30.0	± 20.0
Methyl tert-butyl ether	0.010	30.0	± 20.0
1,1-Dichloroethane	0.200	30.0	± 20.0
cis-1,2-Dichloroethene	0.010	30.0	± 20.0
2-Chloro-1,3-butadiene (Chloroprene)	0.010	30.0	± 20.0
2-Butanone	0.010	30.0	± 20.0
Tetrahydrofuran	0.100	30.0	± 20.0
Chloroform	0.200	30.0	± 20.0
1,1,1-Trichloroethane	0.100	30.0	± 20.0
Cyclohexane	0.010	30.0	± 20.0
Carbon tetrachloride	0.100	30.0	± 20.0
Ethyl Acetate	0.010	30.0	± 20.0
Vinyl Acetate	0.010	30.0	± 20.0
Benzene	0.400	30.0	± 20.0
1,2-Dichloroethane	0.100	30.0	± 20.0
n-Heptane	0.100	30.0	± 20.0
1,4-Dioxane	0.005	30.0	± 20.0
Trichloroethene	0.300	30.0	± 20.0
1,2-Dichloropropane	0.010	30.0	± 20.0
Bromodichloromethane	0.200	30.0	± 20.0
cis-1,3-Dichloropropene	0.200	30.0	± 20.0
4-Methyl-2-pentanone	0.010	30.0	± 20.0
Toluene	0.400	30.0	± 20.0
trans-1,3-Dichloropropene	0.100	30.0	± 20.0
1,1,2-Trichloroethane	0.100	30.0	± 20.0
Tetrachloroethene	0.100	30.0	± 20.0
2-Hexanone	0.010	30.0	± 20.0
Dibromochloromethane	0.100	30.0	± 20.0
1,2-Dibromoethane	0.010	30.0	± 20.0
n-Octane	0.100	30.0	± 20.0
Chlorobenzene	0.500	30.0	± 20.0
Ethylbenzene	0.100	30.0	± 20.0
o-Xylene	0.300	30.0	± 20.0
m,p-Xylene	0.300	30.0	± 20.0
Styrene	0.300	30.0	± 20.0
Bromoform	0.050	30.0	± 20.0
Cumene	0.050	30.0	± 20.0

Volatile Compound	Minimum RRF [1]	Maximum %RSD [1]	ICV Maximum Difference[2]
1,1,2,2-Tetrachloroethane	0.300	30.0	± 20.0
Propylbenzene	0.010	30.0	± 20.0
4-Ethyltoluene	0.100	30.0	± 20.0
1,3,5-Trimethylbenzene	0.100	30.0	± 20.0
1,2,4-trimethylbenzene	0.100	30.0	± 20.0
Benzyl Chloride	0.050	30.0	± 20.0
1,3-Dichlorobenzene	0.600	30.0	± 20.0
1,4-Dichlorobenzene	0.500	30.0	± 20.0
1,2-Dichlorobenzene	0.400	30.0	± 20.0
Hexachlorobutadiene	0.050	30.0	± 20.0
1,2,4-Trichlorobenzene	0.200	30.0	± 20.0

[1] Up to two compounds in the initial calibration may fail the criteria and still meet the minimum RRF and %RSD requirements. However, these compounds must have a minimum RRF greater than or equal to 0.01, and the %RSD must be less than equal than or equal to 40%.

[2] Up to ten percent of compounds may fail the ICV requirements for the minimum RRF criteria and Percent Difference criteria. However, these compounds in the ICV must have a minimum RRF greater than or equal to 0.010 and the Percent Difference must be within the inclusive range of ±40.0%.

Table 6

Percent Difference and Relative Percent Difference Criteria for Volatile Organic Compounds in the Continuing Calibration Verification Standard and Laboratory Control Sample

Volatile Organic Compound Standards	Maximum Difference[1]	LCS/CCV RPD[2]
Continuing Calibration Standard	± 30.0	≤ 25.0
Laboratory Control Sample	± 30.0	≤ 25.0

[1] Up to ten percent of compounds may fail the CCV and LCS requirement for the minimum RRF criteria and Percent Difference criteria. However, these compounds in the CCV must have a minimum RRF greater than or equal to 0.010 and the Percent Difference must be within the inclusive range of ±40.0%.

[2] Ten percent of the compounds may fail the CCV and LCS requirement for the maximum RPD criteria. However, these compounds in the LCS and CCV must have an RPD less than 40%.

EXHIBIT E

QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES AND REQUIREMENTS

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Exhibit E – Quality Assurance/Quality Control Procedures and Requirements

Table of Contents

Table of Contents (Cont.)

1.0 OVERVIEW

The QA process consists of management review and oversight at the planning, implementation, and completion stages of the environmental data collection activity, and ensures that data provided are of the quality required. The QC process includes those activities required during data collection to produce the data quality desired and to document the quality of the collected data.

1.1 Quality Assurance/Quality Control (QA/QC) Activities

During the planning of an environmental data collection program, QA activities focus on defining data quality criteria and designing a QC system to measure the quality of data being generated. During the implementation of the data collection effort, QA activities ensure that the QC system is functioning effectively, and that the deficiencies uncovered by the QC system are corrected. After environmental data are collected, QA activities focus on assessing the quality of data obtained to determine its suitability to support enforcement or remedial decisions.

1.1.1

This exhibit describes the overall QA/QC operations and the processes by which the QA/QC objectives defined above are met. This contract requires a variety of QA/QC activities. These contract requirements are the minimum QC operations necessary to satisfy the analytical requirements associated with the determination of the different compounds. These QC operations are designed to facilitate laboratory comparison by providing USEPA with comparable data from all Contractors. These requirements do not release the analytical Contractor from maintaining their own QC checks on method and instrument performance.

2.0 INTRODUCTION

Appropriate use of data generated under the large range of analytical conditions encountered in environmental analyses requires reliance on the Quality Control (QC) procedures and criteria incorporated into the analytical methods. Inaccuracies can also result from causes other than unanticipated matrix effects, such as sampling artifacts, equipment malfunctions, contamination, and operator error. Therefore, the QC component of each method is indispensable.

The data acquired from QC procedures are used to estimate and evaluate the information content of analytical results and to determine the necessity for, or the effect of, corrective action procedures. The parameters used to estimate information content include precision, accuracy, detection limit, and other quantitative and qualitative indicators. In addition, QC procedures give an overview of the activities required in an integrated program to generate data of known and documented quality required to meet defined objectives.

2.1 Quality Assurance/Quality Control (QA/QC) Program Components

2.1.1 The necessary components of a complete QA/QC program include internal QC criteria that demonstrate acceptable levels of performance, as determined by QA review. External review of data and procedures is accomplished by the monitoring activities of the USEPA through various reviews. These reviews are described in specific sections of this exhibit. Laboratory evaluation samples, electronic data audits, and data packages provide an external QA reference for the program. A Contractor on-site evaluation system is also part of the external QA monitoring. A feedback loop provides the results of the various review functions to the Contractors through direct communication with the Project Officer (PO).

2.1.2 This exhibit does not provide specific instructions for constructing QA Plans (QAPs), QC systems, or a QA organization. It is, however, an explanation of the QA/QC requirements of the Statement of Work (SOW). It outlines some minimum standards for QA/QC programs. It also includes specific items that are required in a QAP and by the QA/QC documentation detailed in the contract. Delivery of this documentation provides the Government with a complete data package which will stand alone, and limits the need for contact with the Contractor or with an analyst, at a later date, if some aspect of the analysis is questioned.

2.1.3 To assure the product delivered by the Contractor meets the requirements of the contract, and to improve inter-laboratory data comparison, the Contractor shall:

- Prepare and adhere to a written QAP, the elements of which are defined in Section 5;
- Prepare and adhere to QA/QC Standard Operating Procedures (SOPs), as described in Section 6;
- Adhere to the analytical methods in Exhibit D and associated QC requirements specified within Exhibit E;
- Verify and document analytical standards and retain documentation of the purity of neat materials, as well as the purity and accuracy of solutions obtained from private chemical supply houses;
- Submit all raw data and required documentation for Regional review;

- Submit results of all analyzed laboratory evaluation samples, including adherence to corrective action procedures;
- Submit, upon request, instrument data tapes and applicable documentation for tape audits, including a copy of the Sample Data Package;
- Participate in on-site laboratory evaluations, and adhere to corrective action procedures; and
- Submit all original documentation generated during sample analyses for Government review.

3.0 GENERAL QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) REQUIREMENTS

The Contractor shall adhere to USEPA's Good Laboratory Practices for laboratory cleanliness with regard to glassware and apparatus. The Contractor shall also adhere to good laboratory practices with regard to reagents, solvents, and gases.

4.0 SPECIFIC QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) PROCEDURES

4.1 Purpose

4.1.1 The purpose of this document is to provide a uniform set of procedures for the analysis of volatile organic constituents of air samples, documentation of methods and their performance, and verification of the sample data generated. Although it is impossible to address all analytical situations in one document, this exhibit defines the minimum requirements for all major steps relevant to any organic analysis.

4.1.2 The QA/QC procedures defined herein shall be used by the Contractor when performing the methods specified in Exhibit D. When additional QA/QC procedures are specified in Exhibit D, the Contractor shall follow those procedures, in addition to the procedures specified in this Exhibit.

4.2 Laboratory Audit and Intercomparison Study Program

As required by the Task Order agreement, the Contractor may be required to participate in the Laboratory Audit and Intercomparison Study Program run by USEPA.

4.3 Annual Verification of Method Detection Limits (MDLs)

The Contractor shall perform annual verification of MDLs by the method specified in Exhibit D for each instrument used on the contract. All the MDLs shall meet the requirements specified in Exhibit C and Exhibit D. The MDLs shall be available during on-site laboratory evaluations and shall be submitted within seven days of written request by the Project Officer (PO).

4.4 Quality Assurance/Quality Control (QA/QC) Measurements

4.4.1 In this Exhibit, as well as other places within this Statement of Work (SOW), the term "analytical sample" discusses the required frequency or placement of certain QA/QC measurements. The term "analytical sample" includes all field samples, including PE samples, received from an external source. It also includes all required QA/QC samples except those directly related to instrument calibration or calibration verification (calibration standards, Initial Calibration, Continuing Calibration, and tunes).

4.4.2 In order for the QA/QC information to reflect the status of the samples analyzed all samples and their associated QA/QC analysis shall be analyzed under the same analytical operating and procedural conditions.

4.4.3 If any QC measurement fails to meet contract criteria, the analytical measurement must not be repeated prior to taking the appropriate corrective action, as specified in Exhibit D.

4.4.4 The Contractor shall report all QC data in the exact format specified in Exhibits B and H.

4.4.5 In addition, the Contractor shall establish a QA program with the objective of providing sound analytical chemical measurements. This program shall incorporate the QC procedures, any necessary corrective action, and all documentation required during data collection, as well as the quality assessment measures performed by management to ensure acceptable data production.

5.0 QUALITY ASSURANCE PLAN (QAP)

5.1 Introduction

The Contractor shall establish a Quality Assurance (QA) program with the objective of providing sound analytical chemical measurements. This program shall incorporate the Quality Control (QC) procedures, any necessary corrective action, and all documentation required during data collection as well as the quality assessment measures performed by management to ensure acceptable data production. The Contractor shall follow the requirements for QA and QC procedures in the Task Order agreement if they are specified otherwise the contractor shall follow the USEPA EPA Requirements for Quality Management Plans (QA/R-2). An electronic version can be found at: http://www.epa.gov/QUALITY/qs-docs/r2-final.pdf.

5.1.1 The Contractor shall prepare a written QAP that describes the procedures that are implemented to achieve the following:

- Maintain data integrity, validity, and usability. Ensure that analytical measurement systems are maintained in an acceptable state of stability and reproducibility;
- Detect problems through data assessment and establish corrective action procedures that keep the analytical process reliable; and
- Document all aspects of the measurement process to provide data that are technically sound and legally defensible.

5.1.2 The QAP shall present, in specific terms, the policies, organization, objectives, functional guidelines, and specific QA/QC activities designed to achieve the data quality requirements in the contract. Where applicable, Standard Operating Procedures (SOPs) pertaining to each element shall be included or referenced as part of the QAP. The QAP shall be paginated consecutively in ascending order. The QAP shall be available during on-site laboratory evaluations and shall be submitted within 7 days of written request by the Project Officer (PO). Additional information relevant to the preparation of a QAP can be found in USEPA and American Society for Testing and Materials (ASTM) publications.

5.2 Required Elements of a Quality Assurance Plan (QAP)

The required elements of a laboratory's QAP are outlined in this section. This outline should be used as a framework for developing the QAP.

A. Organization and Personnel

1. QA Policy and Objectives (the mission and quality policy of the organization)
2. QA Management (the specific roles, authorities, and responsibilities of management and staff with respect to QA and QC activities)
    a. Organization
    b. Assignment of QA/QC Responsibilities
    c. Reporting Relationships (the means by which effective communications with personnel actually performing the work are assured)
    d. QA Document Control Procedures
    e. QA Program Assessment Procedures (the process used to plan, implement, and assess the work performed)
3. Key Personnel (Laboratory Personnel Involved in QA and QC Activities)
    a. Résumés
    b. Education and Experience Pertinent to the contract
    c. Training Records and Progress

B. Facilities and Equipment

1. Instrumentation and Backup Alternatives
2. Maintenance Activities and Schedules

C. Document Control

1. Laboratory Notebook Policy
2. Sample Tracking/Custody Procedures
3. Logbook Maintenance and Archiving Procedures
4. Sample Delivery Group (SDG) File Organization, Preparation, and Review Procedures
5. Procedures for Preparation, Approval, Review, Revision, and Distribution of SOPs
6. Process for Revision of Technical or Documentation Procedures

D. Analytical Methodology

1. Calibration Procedures and Frequency
2. Sample Analysis Procedures
3. Standards Preparation Procedures
4. Decision Processes, Procedures, and Responsibility for Initiation of Corrective Action

E. Data Generation

1. Data Collection Procedures
2. Data Reduction Procedures
3. Data Validation Procedures
4. Data Reporting and Authorization Procedures

F. Quality Control (QC)

1. Solvent, Reagent, and Adsorbent Check Analysis
2. Reference Material Analysis
3. Internal QC Checks
4. Corrective Action and Determination of QC Limit Procedures
5. Responsibility Designation

G. Quality Assurance (QA) (the process which measures the effectiveness of QA will be established and how frequently effectiveness will be measured)

1. Data QA
2. Systems/Internal Audits
3. Performance/External Audits
4. Corrective Action Procedures (the continual improvement based on lessons learned from previous experience)
5. QA Reporting Procedures
6. Responsibility Designation

5.3 Updating and Submitting the Quality Assurance Plan (QAP)

5.3.1 Initial Submission. During the contract solicitation process, the Contractor is required to submit their QAP to the USEPA Contracting Officer (CO). Within 60 days after contract award, the Contractor shall maintain, on file at their facility, a revised QAP that is fully compliant with the requirements of the contract. The Contractor shall maintain the QAP on file at the Contractor's facility for the term of the contract. The revised QAP will become the official QAP under the contract and may be used during legal proceedings. Both the initial QAP submission and the revised QAP shall be paginated consecutively in ascending order. The revised QAP shall include:

- Changes resulting from (1) the Contractor's internal review of their organization, personnel, facility, equipment, policy, and procedures and, (2) the Contractor's implementation of the requirements of the contract, and
- Changes resulting from USEPA review of the laboratory evaluation sample data, contractor-supplied documentation, and recommendations made during the pre-award on-site laboratory evaluation.

5.3.1.1 The Contractor shall send a copy of the latest version of the QAP within 7 days of a request from the PO or CO. The PO or CO will designate the recipients.

5.3.2 Subsequent Updates and Submissions. During the term of the contract, the Contractor shall amend the QAP when the following circumstances occur:

- USEPA modifies the contract or the requirements of the Task Order agreement;
- USEPA notifies the Contractor of deficiencies in the QAP documentation;
- USEPA notifies the Contractor of deficiencies resulting from USEPA's review of the Contractor's performance;

- The Contractor identifies deficiencies resulting from their internal review of the QAP documentation;
- The Contractor's organization, personnel, facility, equipment, policy, or procedures change; or
- The Contractor identifies deficiencies resulting from the internal review of changes in their organization, personnel, facility, equipment, policy, or procedures.

5.3.2.1 The Contractor shall amend the QAP within 14 days of when the circumstances listed in Section 5.3 result in a discrepancy between what was previously described in the QAP and what is presently occurring at the Contractor's facility. When the QAP is amended, all changes in the QAP shall be clearly marked (e.g., a bar in the margin indicating where the change is found in the document, highlighting the change by underlining the change, bold printing the change, or using a different print font). The amended pages shall have the date on which the changes were implemented and refer to the specific Task Order agreements that required the amendments. The Contractor shall incorporate all amendments and identify the changes specific to Task Order requirements in the latest version of the QAP document. The Contractor shall archive all amendments to the QAP document for future reference by USEPA.

5.3.2.2 The Contractor shall send a copy of the latest version of the QAP document within 7 days of a written request by the Contracting Officer (CO). The CO requestor will designate the recipients.

6.0 STANDARD OPERATING PROCEDURES (SOP)

6.1 Introduction

To obtain reliable results, adherence to prescribed analytical methodology is imperative. In any operation that is performed on a repetitive basis, reproducibility is best accomplished through the use of SOPs. As defined by USEPA, an SOP is a written document that provides directions for the step-by-step execution of an operation, analysis, or action which is commonly accepted as the method for performing certain routine or repetitive tasks. The Contractor shall follow the USEPA Guideline for Preparing Standard Operating Procedures (SOPs) (QA/G-6). An electronic version can be found at: http://www.epa.gov/quality1/qa_docs.html.

6.1.1 SOPs prepared by the Contractor shall be functional (i.e., clear, comprehensive, up-to-date, and sufficiently detailed to permit duplication of results by qualified analysts). The SOPs shall be paginated consecutively, in ascending order.

6.1.2 All SOPs shall reflect activities as they are currently performed by the Contractor. In addition, all SOPs shall be:

- Consistent with current USEPA regulations, guidelines, and the contract's requirements.
- Consistent with instrument manufacturers' specific instruction manuals.
- Available to USEPA during an on-site laboratory evaluation. A complete set of SOPs shall be bound together and available for inspection at such evaluations. During on-site laboratory evaluations, laboratory personnel may be asked to demonstrate the application of the SOPs;
- Available to the designated recipients within 7 days, upon request by the Contracting Officer (CO).
- Capable of providing for the development of documentation that is sufficiently complete to record the performance of all tasks required by the protocol.
- Capable of demonstrating the validity of data reported by the Contractor and explaining the cause of missing or inconsistent results.
- Capable of describing the corrective measures and feedback mechanism utilized when analytical results do not meet protocol requirements.
- Reviewed regularly and updated as necessary when contract, facility, or Contractor procedural modifications are made.
- Archived for future reference in usability or evidentiary situations.
- Available at specific work stations as appropriate.
- Subject to a document control procedure that precludes the use of outdated or inappropriate SOPs.
- Reviewed and signed by all Contractor personnel performing action identified in the SOP.

6.2 Format

The format for SOPs may vary depending upon the type of activity for which they are prepared; however, at a minimum, the following sections shall be included:

- Title page;
- Document Control;
- Scope and Applicability;
- Summary of Method;
- Definitions (acronyms, abbreviations, and specialized forms used in the SOP);
- Health and Safety;
- Personnel Qualifications;
- Interferences;
- Apparatus and Materials (list or specify, also note designated locations where found);
- Handling and Preservation;
- Instrument or Method Calibration;
- Sample Preparation and Analysis;
- Data Calculations;
- Procedures;
- Quality Control (QC) limits;
- Corrective action procedures, including procedures for secondary review of information being generated;
- Documentation description and example forms;
- Data Management and Records Management;
- Miscellaneous notes and precautions; and
- References.

6.3 Required SOPs

In addition to SOPs specified by the Task Order agreement, the Contractor shall maintain the following SOPs:

6.3.1 Evidentiary SOPs for required chain-of-custody and document control, as discussed in Exhibit F.

6.3.2 Sample receipt and storage

- Sample receipt and identification logbooks;
- Security precautions.

6.3.3 Glassware Cleaning

6.3.4 Calibration (Balances, etc.)

- Procedures;
- Frequency requirements;
- Preventative maintenance schedule and procedures;
- Acceptance criteria and corrective actions; and
- Logbook maintenance authorization.

6.3.5 Analytical Procedures for each analytical system

- Instrument performance specifications;
- Instrumental operating procedures;
- Data acquisition system operation;
- Procedures when automatic quantitation algorithms are overridden;
- QC required parameters;
- Analytical run/injection logbooks; and
- Instrumental error and editing flag descriptions and resulting corrective actions.

6.3.6 Maintenance Activities for each analytical system

- Preventative maintenance schedule and procedures;
- Corrective maintenance determinants and procedures; and
- Maintenance authorization.

6.3.7 Analytical Standards

- Standard coding/identification and inventory system;
- Standards preparation logbook(s);
- Standards preparation procedures;
- Procedures for equivalency/traceability analyses and documentation;
- Purity logbook (primary standards and solvents);
- Storage, replacement, and labeling requirements; and
- QC and corrective action measures.

6.3.8 Data Reduction Procedures

- Data processing systems operation;
- Outlier identification methods;
- Identification of data requiring corrective action; and
- Procedures for format and/or forms for each operation.

6.3.9 Documentation Policy/Procedures

- Contractor/analysts' notebook policy, including review policy;
- Complete Sample Delivery Group (SDG) File (CSF) contents;
- CSF organization and assembly procedures, including review policy; and

- Document inventory procedures, including review policy.

6.3.10 Data Validation/Self-Inspection Procedures

- Data flow and chain-of-command for data review;
- Procedures for measuring precision and accuracy;
- Evaluation parameters for identifying systematic errors;
- Procedures to ensure that hardcopy and electronic deliverables are complete and compliant with the requirements in Exhibits B and H;
- Procedures to ensure that hardcopy deliverables are in agreement with their comparable electronic deliverables;
- Demonstration of internal Quality Assurance (QA) inspection procedure [demonstrated by supervisory sign-off on personal notebooks, internal Performance Evaluation (PE) samples, etc.];
- Frequency and type of internal audits (e.g., random, quarterly, spot checks, perceived trouble areas);
- Demonstration of problem identification, corrective actions, and resumption of analytical processing; sequence resulting from internal audit (i.e., QA feedback); and
- Documentation of audit reports (internal and external), audit response, corrective action, etc.

6.3.11 Data Management and Handling

- Procedures for controlling and estimating data entry errors;
- Procedures for reviewing changes to data and deliverables and ensuring traceability of updates;
- Life Cycle Management (LCM) procedures for testing, modifying, and implementing changes to existing computing systems including hardware, software, and documentation or installing new systems;
- Database security, backup, and archival procedures including recovery from system failures;
- System maintenance procedures and response time;
- Individual(s) responsible for system operation, maintenance, data integrity, and security;
- Specifications for staff training procedures;
- Storage, retrieval, and verification of the completeness and readability of Gas Chromatograph/Mass Spectrometer (GC/MS) files transferred to electronic media; and
- Virus protection procedures for software and electronic deliverables.

6.4 Updating and Submitting SOPs

6.4.1 Initial Submission. During the contract solicitation process, the Contractor is required to submit their SOPs to the USEPA Contracting Officer (CO). Within 60 days after contract award, the Contractor shall prepare and maintain on file, at their facility, a complete, revised set of SOPs that are fully compliant with the requirements of the contract.

The revised SOPs will become the official SOPs under the contract and may be used during legal proceedings. The Contractor shall maintain the complete set of SOPs on file at the Contractor's facility for the term of the contract. Both the initial submission of SOPs and the revised SOPs shall be dated and paginated consecutively in ascending order. The revised SOPs shall include:

- Changes resulting from (1) the Contractor's internal review of their procedures, and (2) the Contractor's implementation of the requirements of the contract, and
- Changes resulting from USEPA's review of the laboratory evaluation sample data, bidder-supplied documentation, and recommendations made during the pre-award on-site laboratory evaluation.

6.4.1.1 The Contractor shall send a complete set of the latest version of SOPs or individual SOPs required by the Task Order agreement within 7 days of a request from the CO. The CO will designate the recipients.

6.4.2 Subsequent Updates and Submissions. During the term of the contract, the Contractor shall amend the SOPs when the following circumstances occur:

- USEPA modifies the technical requirements of the contract or Task Order agreement;
- USEPA notifies the Contractor of deficiencies in their SOP documentation;
- USEPA notifies the Contractor of deficiencies resulting from USEPA's review of the Contractor's performance;
- The Contractor's procedures change;
- The Contractor identifies deficiencies resulting from internal review of the SOPs documentation; or
- The Contractor identifies deficiencies resulting from internal review of the procedures.

6.4.2.1 Existing SOPs shall be amended or new SOPs shall be written within 14 days of when the circumstances listed in Section 6.4 result in a discrepancy between what was previously described in the SOPs and what is presently occurring at the Contractor's facility. All changes in the SOPs shall be clearly marked (e.g., a bar in the margin indicating where the change is found in the document, highlighting the change by underlining the change, bold printing the change, or using a different print font). The amended/new SOPs shall have the date on which the changes were implemented. Amended/new SOPs written for specific Task Order requirements shall identify the Task Order number.

6.4.2.2 When existing SOPs are amended or new SOPs are written, the Contractor shall document the reason(s) for the change, and maintain the amended SOPs or new SOPs on-file at the laboratory facility. Amended/new SOPs written for specific Task Order requirements shall identify the Task Order number. Documentation of the reason(s) for the change shall be maintained on file with the amended SOPs or new SOPs.

6.4.2.3 The Contractor shall send a complete set of the latest version of SOPs or individually requested SOPs within 7 days of a request from the CO. The CO will designate the recipients.

7.0 ANALYTICAL STANDARDS REQUIREMENTS

7.1 Overview

USEPA will not supply analytical reference standards either for direct analytical measurements or for the purpose of traceability. All Contractors shall be required to prepare from neat materials or purchase from private chemical supply houses those standards necessary to successfully and accurately perform the analyses required in this protocol.

7.2 Preparation of Chemical Standards from the Neat High Purity Bulk Material

7.2.1 If a Contractor cannot obtain analytical reference standards, the Contractor may prepare their own standards. Contractors shall obtain the highest purity possible when purchasing neat chemical standards. When standards are purchased at less than 98% purity, the Contractor shall document the reason why a higher purity could not be obtained.

7.2.2 If required by the manufacturer, the chemical standards shall be kept sealed when not being used in the preparation of standard solutions. Proper storage of standards is essential to safeguard them from decomposition.

7.2.3 The purity of a compound can sometimes be misrepresented by a chemical supply house. Since knowledge of purity is needed to calculate the concentration in a standard, it is the Contractor's responsibility to have analytical documentation proving the purity of each compound is correctly stated. Purity confirmation, when performed, should use appropriate techniques. Use of two or more independent methods is recommended.

7.2.4 Mis-identification of compounds occasionally occurs and it is possible that a mis-labeled compound may be received from a chemical supply house. It is the Contractor's responsibility to have analytical documentation ascertaining that all compounds used in the preparation of standards are correctly identified. Identification confirmation, when performed, shall use Gas Chromatography/Mass Spectrometry (GC/MS) analysis on at least two different analytical columns, or other appropriate techniques.

7.2.5 Log notebooks shall be kept for all dilutions. All subsequent dilutions from the primary standard and the calculations for determining their concentrations shall be recorded and verified by a second person. All standards shall be clearly labeled as to the identity of the compound or compounds, the standard ID number of the mixture, concentration, date prepared, expiration date, special storage requirements (if any), and initials of the preparer.

7.3 Purchase of Mixed Chemical Standards

Analytical reference standards can be purchased by Contractors provided the mixtures meet the following criteria.

7.3.1 Contractors shall maintain the following documentation to verify the integrity of the standard mixtures:

- Mass spectral identification confirmation;
- Purity confirmation; and
- Chromatographic and quantitative documentation that the standard was Quality Control (QC) checked according to the following section.

7.3.2 The Contractor is responsible for the quality of the standards employed for analyses under the contract.

7.4 Documentation of the Verification and Preparation of Chemical Standards

It is the responsibility of each Contractor to maintain the necessary documentation to show that the chemical standards they have used in the performance of analysis conform to the requirements previously listed in Section 7.3.1.

7.4.1 Logbooks, calculations, chromatograms, mass spectra, etc., whether produced by the Contractor or purchased from chemical supply houses, shall be maintained by the Contractor and may be subject to review during on-site laboratory evaluations. In those cases where the documentation is supportive of the analytical results of data packages sent to USEPA, such documentation is to be kept on file by the Contractor for a period of one year.

7.4.2 Upon request by the Project Officer (PO), the Contractor shall submit their most recent previous year's (12 months) documentation for the verification and preparation of stock or working chemical standards within 14 days of receipt of the request.

7.4.3 USEPA may periodically generate a report discussing deficiencies in the Contractor's documentation for the verification and preparation of chemical standards or may discuss the deficiencies during an on-site laboratory evaluation. In a detailed letter to the PO, the Contractor shall address the deficiencies and the subsequent corrective action implemented by the Contractor to correct the deficiencies within 14 days of receipt of the report or the on-site laboratory evaluation.

7.4.4 If new Standard Operating Procedures (SOPs) are required to be written or if existing SOPs are required to be rewritten or amended because of deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section 6.

8.0 REGIONAL DATA REVIEW

Contractor data are generated to meet the specific needs of the USEPA Regions as defined in the Task Order agreement. In order to verify the usability of data for the intended purpose, each Region may review data from the perspective of the end user, based upon functional guidelines for data review that have been developed jointly by the Regions and the USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB). Each Region may use these guidelines as the basis for data evaluation. Individual Regions may augment the basic guideline review process with additional review based on Region-specific or site-specific concerns. Regional reviews, like the sites under investigation, vary based on the nature of the problems under investigation and the Regional response appropriate to the specific circumstances.

9.0 PROFICIENCY TESTING

As a means of measuring and evaluating both the Contractor's and the method's analytical performance, the Contractor may be required to participate in USEPA's Proficiency Testing Program as defined in the Task Order agreement. If required under the Task Order agreement, the USEPA's Proficiency Testing Program may involve the analysis of Case-specific Performance Evaluation (PE) samples and blind audits. The Contractor's analytical PE samples and audit results maybe used by USEPA to assess and verify the Contractor's continuing ability to produce acceptable analytical data in accordance with the contractual requirements of the Task Order agreement. The Contractor must receive a passing score as specified by the Task Order agreement to be in compliance with the contract.

9.1 Performance Evaluation (PE) Samples

9.1.1 If specified by the Task Order agreement, the PE sample(s) may be scheduled with the Contractor as frequently as on a Sample Delivery Group (SDG)-by-SDG basis. The PE samples will be sent by the Regional Client. PE samples will assist USEPA in monitoring Contractor performance.

9.1.2 PE samples will be provided as either single-blinds (recognizable as a PE sample but of unknown composition), or as double-blinds (not recognizable as a PE sample and of unknown composition). The Contractor will not be informed of either the compounds or the concentrations in the PE samples.

9.1.3 If required under the Task Order agreement the Contractor may receive the PE samples as either pressurized gas cylinders or full volume air samples in SUMMA Canisters from USEPA or a designated USEPA Contractor. The PE samples shall come with instructions concerning the unique preparation procedures, if any, required to reconstitute the PE samples (i.e., the required dilution of the PE sample concentrate). **PE samples are to be analyzed with the rest of the routine samples in the SDG.** The Contractor shall prepare and analyze the PE sample using the procedure described in the sample preparation and method analysis sections of Exhibit D. All contract required Quality Control (QC) shall also be met. The PE sample results are to be submitted in the SDG deliverable package per normal reporting procedures detailed in Exhibit B.

9.1.4 In addition to PE sample preparation and analysis, the Contractor shall be responsible for correctly identifying and quantitating the analytes included in each PE sample. When PE sample results are received by USEPA, the PE sample results will be evaluated for correct analytical identification and quantitation. The results of the PE sample evaluation will be provided to the Contractor via coded evaluation sheets by analyte. USEPA will notify the Contractor of unacceptable performance. USEPA reserves the right to adjust the PE sample acceptance windows to compensate for any unanticipated difficulties with a particular PE sample.

9.2 Audits

9.2.1 An audit is a unique analytical Case containing only PE samples. The audit samples will be ordered by the CO. Audit samples assist USEPA in monitoring Contractor performance.

9.2.2 Audit samples will be provided as single-blinds (recognizable as a PE sample but of unknown composition). The Contractor will not be informed of either the compounds or the concentrations in the PE samples.

9.2.3 The Contractor may receive the audit samples as either full volume samples or concentrates from USEPA or a designated USEPA Contractor. The audit samples shall come with instructions concerning the unique preparation procedures, if any, required to reconstitute the samples (i.e., the required dilution of the sample concentrate). The Contractor shall prepare and analyze the samples using the procedure described in the sample preparation and method analysis sections of Exhibit D. All contract required QC shall also be met. The sample results are to be submitted in the SDG deliverable package per normal reporting procedures detailed in Exhibit B.

9.2.4 In addition to audit sample preparation and analysis, the Contractor shall be responsible for correctly identifying and quantitating the compounds included in each audit sample. When audit sample results are received by USEPA, the sample results will be scored for correct analytical identification and quantitation. The audit sample scoring will be provided to the Contractor via coded evaluation sheets, by compound. USEPA will notify the Contractor of unacceptable performance.

9.2.5 In the case of unacceptable performance, the Contractor shall describe the deficiency(ies) and the action(s) taken to correct the deficiency(ies) in a corrective action letter to the PO within 14 days of receipt of notification from USEPA.

9.2.6 In the case of unacceptable performance, if new Standard Operating Procedures (SOPs) are required to be written, or if existing SOPs are required to be rewritten or amended because of deficiencies and subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section 6.

10.0 ELECTRONIC DATA QUALITY ASSURANCE (QA) MONITORING AUDITS

10.1 Overview

Periodically, USEPA requests the instrument electronic data from Contractors for a specific Case to perform electronic data audits. Generally, electronic data submissions and audits are requested for the following reasons.

- Program overview;
- Indication of data quality problems;
- Support for on-site audits; and
- Specific Regional requests.

10.1.1 Depending upon the reason for an audit, the instrument electronic data from a recent Case, a specific Case, or a Performance Evaluation (PE) sample may be requested. Electronic data audits provide a mechanism to assess adherence to contractual requirements and to ensure the consistency of data reported on the hardcopy/electronic deliverables with that generated on analytical instruments. This function provides external monitoring of Program Quality Control (QC) requirements and checks adherence of the Contractor to internal QA procedures. In addition, electronic data audits enable USEPA to evaluate the utility, precision, and accuracy of the analytical methods.

10.1.2 The Contractor shall store all raw and processed electronic analytical data in appropriate instrument manufacturer's format, uncompressed, and with no security codes. The data shall include all necessary data files

for a complete reconstruction of the previously submitted hardcopy and electronic deliverable data package. All associated raw data files in the instrument manufacturer proprietary software format must be submitted if those files contain data or instrumental parameters regarding any analysis and/or correction applied to an instrument or analytical result. This instrument electronic data shall include data for all samples and all QC samples, including but not limited to: blanks; Laboratory Control Samples (LCSs); initial calibrations; initial and continuing calibration verification standards; and instrument performance check solutions [4-Bromofluorobenzene (BFB) as well as all Contractor-generated spectral libraries and quantitation reports required to generate the data package. In addition, the Contractor shall supply raw data for the Method Detection Limit (MDL) studies and values for the year in which the Sample Delivery Group (SDG) was analyzed. The Contractor shall maintain a written reference logbook of data files of the EPA Sample Number, calibration data, standards, and blanks. The logbook shall include EPA Sample Numbers, and standard and blank IDs, identified by Case and SDG.

10.1.3 The Contractor is required to retain the instrument electronic data for 3 years after submission of the reconciled Complete SDG File (CSF). Electronic media shipped to the USEPA designated recipient must be fully usable by the recipient. Diskettes must be MS-DOS formatted, 3.5-inch, high density, 1.44 MB and tapes must be either 4 mm or 8 mm. Alternative means for delivery of electronic data, including compact disks (CDs), may be utilized by the Contractor upon prior written approval from USEPA. When submitting electronic instrument data to USEPA, the following materials shall be delivered in response to the request.

10.1.3.1 All associated raw data files for all analytical samples, all QC samples, blanks, LCSs, initial calibrations, initial and continuing calibration verification standards, and instrument performance check solutions (BFB).

10.1.3.2 All processed data files and quantitation output files associated with the raw data files described in Section 10.1.3.1.

10.1.3.3 All associated identifications and calculation files (method files) used to generate the data submitted in the data package. This includes, but is not limited to, results files, acquisition files, calibration files, and method files.

10.1.3.4 All Contractor-generated Mass Spectral library files (NIST/EPA/NIH and/or Wiley, or equivalent, library not required).

10.1.3.5 A copy of the Contractor's reference logbook relating data files to EPA Sample Number, BFB, calibration data, standards, and blanks. The logbook shall include EPA Sample Numbers and laboratory file identifiers for all samples, blanks, and standards, identified by Case and SDG.

10.1.3.6 A printout of the directory of all files in each directory, including all subdirectories and the files contained therein.

10.1.3.7 A copy (hardcopy) of the completed Sample Data Package.

10.1.3.8 A statement attesting to the completeness of the electronic instrument data submission signed and dated by the Contractor's Laboratory Manager. The Contractor shall also provide a statement attesting that the data reported have not been altered in any way. These statements shall be part of a cover sheet that includes the following information relevant to the data tape submission:

- Contractor name;

- Date of submission;
- Case Number;
- SDG Number;
- Instrument make and model number;
- Instrument operating software name and version;
- Data software name and version used for acquisition, re-quantitation, and hardcopy/report generation;
- Data system computer;
- System operating software;
- Data system network;
- Data backup software;
- Data backup hardware;
- Data analysis software;
- Media type and volume of data (in MB) backed up; and
- Names and telephone numbers of two Contractor contacts for further information regarding the submission.

10.2 Submission of the Instrument Electronic Data

Upon request of the Contracting Officer (CO), the Contractor shall send the required instrument electronic data and all necessary documentation to the designated recipient within 7 days of notification.

10.3 Responding to the Electronic Data Audit Report

After completion of the electronic data audit, USEPA may send a copy of the electronic data audit report to the Contractor or may discuss the electronic data audit report at an on-site laboratory evaluation. In a detailed letter to the CO, the Contractor shall discuss the corrective actions implemented to resolve the deficiencies listed in the electronic data audit report within 14 days of receipt of the report or on-site laboratory evaluation.

10.3.1 If new Standard Operating Procedures (SOPs) are required to be written or if existing SOPs are required to be rewritten or amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section 6.

11.0 DATA PACKAGE AUDITS

11.1 Overview

Data package audits are performed by USEPA for program overview and specific Regional concerns. Standardized procedures have been established to assure uniformity of the auditing process. Data packages are periodically selected from recently received Cases. They are evaluated for the technical quality of hardcopy raw data, Quality Assurance (QA), and adherence to contractual requirements. This function provides external monitoring of program Quality Control (QC) requirements. Data package audits are used to assess the technical quality of the data and evaluate overall Contractor performance. Audits provide USEPA with an in-depth inspection and evaluation of the Sample Data Package with regard to achieving QA/QC acceptability. A thorough review of the raw data is completed, including: all instrument readouts used for the sample results; instrument printouts; quantitation reports; chromatograms; spectra; library searches and other documentation for deviations from the contractual requirements; a check for transcription and calculation errors; a review of the qualifications of the Contractor personnel involved with the Case; and a review of the latest version of all Standard Operating Procedures (SOPs) on file.

11.2 Responding to the Data Package Audit Report

11.2.1 After completing the data package audit, USEPA will send a copy of the data package audit report to the Contractor or discuss the data package audit report on an on-site laboratory evaluation. In a detailed letter to the Contracting Officer (CO), the Contractor shall discuss the corrective actions implemented to resolve the deficiencies listed in the data package audit report within 14 days of receipt of the report.

11.2.2 An alternate delivery schedule may be proposed by the Contractor, but it is the sole decision of USEPA, represented either by the CO, to approve or disapprove the alternate delivery schedule. If an alternate delivery schedule is proposed, the Contractor shall describe, in a letter to the PO, why the Contractor is unable to meet the delivery schedule listed in this section. The CO will not grant an extension for greater than 14 days for the Contractor's response letter to the Sample Data Package report. The Contractor shall proceed and not assume that an extension will be granted until so notified by the CO.

11.2.3 If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section 6.

12.0 ON-SITE LABORATORY EVALUATIONS

12.1 Overview

At a frequency dictated by a Contractor's performance, the Contracting Officer (CO) or an authorized representative will conduct an on-site laboratory evaluation. On-site laboratory evaluations are carried out to monitor the Contractor's ability to meet selected terms and conditions specified in the contract. The evaluation process incorporates two separate categories: Quality Assurance (QA) On-Site Evaluation and Evidentiary Audit.

12.2 Quality Assurance On-Site Evaluation

Quality Assurance Evaluators inspect the Contractor's facilities to verify the adequacy and maintenance of instrumentation, the continuity, experience and education of personnel, and the acceptable performance of analytical and Quality Control (QC) procedures for adherence to the contract requirements.

12.2.1 The Contractor shall expect that items to be monitored will include, but are not limited to, the following items:

- Size, cleanliness, and organization of the facility;
- Quantity, age, availability, scheduled maintenance, and performance of instrumentation;
- Availability, appropriateness, and utilization of the Quality Assurance Plan (QAP) and Standard Operating Procedures (SOPs);
- Staff qualifications and experience, and personnel training programs;
- Analysis of Performance Evaluation (PE) sample(s);
- Reagents, standards, and sample storage facilities;
- Standard preparation logbooks and raw data;
- Bench sheets and analytical logbook maintenance and review; and
- Review of the Contractor's sample analysis/data package inspection/data management procedures.

12.2.2 Prior to an on-site evaluation, various documentation pertaining to performance of the specific Contractor is integrated into a profile package for discussion during the evaluation. Items that may be included are: previous on-site reports; audit and/or Performance Evaluation (PE) sample score results; Regional review of data; Contractor performance information provided by the Region; Regional QA materials; data audit reports; and data trend reports.

12.3 Evidentiary Audit

Evidence auditors conduct an on-site laboratory evaluation to determine if Contractor policies and procedures are in place to satisfy evidence handling requirements as stated in Exhibit F. The evidence audit is comprised of a procedural audit, an audit of written SOPs, and an audit of analytical project file documentation.

12.3.1 Procedural Audit. The Contractor shall perform analysis of PE sample(s) in the presence of the USEPA-designated team during the procedural audit. The procedural audit will be comprised of everything from sample receipt to data package assembly and completion. This includes the review and

examination of actual SOPs and accompanying documentation for the following Contractor operations: sample receiving; sample storage; sample identification; sample security; sample tracking (from receipt to completion of analysis); analytical project file organization and assembly; and proper disposal of samples and co-generated wastes.

12.3.2 Written SOPs Audit. The written SOPs audit consists of review and examination of the written SOPs to determine if they are accurate and complete for the following Contractor operations: sample receiving; sample storage; sample identification; sample security; sample tracking (from receipt to completion of analysis); and analytical project file organization and assembly.

12.3.3 Analytical Project File Evidence Audit. The analytical project file evidence audit consists of review and examination of the analytical project file documentation. The auditors review the files to determine:

- The accuracy of the document inventory;
- The completeness of the file;
- The adequacy and accuracy of the document numbering system;
- Traceability of sample activity;
- Identification of activity recorded on the documents; and
- Error correction methods.

12.4 Discussion of the On-Site Team's Findings

The QA and evidentiary auditors discuss their findings with the PO and/or authorized representatives prior to debriefing the Contractor. During the debriefing, the auditors present their findings and recommendations for corrective actions necessary to the Contractor personnel. A report which discusses deficiencies found during the on-site audit will be sent to the Contractor to provide further clarification of findings. In a detailed letter to the PO, the Contractor shall discuss the deficiencies and the subsequent corrective actions implemented by the Contractor to resolve the deficiencies within 14 days of receipt of report or the on-site laboratory evaluation.

12.4.1 If new SOPs are required to be written or if existing SOPs are required to be rewritten or amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section 6.

13.0 DATA MANAGEMENT

13.1 Overview

Data management procedures are defined as procedures specifying the acquisition or entry, update, correction, deletion, storage, and security of computer-readable data and files. These procedures shall be in written form and contain a clear definition for all databases and files used to generate or resubmit deliverables. Key areas of concern include: system organization (including personnel and security); documentation operations; traceability; and Quality Control (QC).

13.1.2 Data manually entered from hardcopy shall be subject to QC checks and the error rates estimated. Systems shall prevent entry of incorrect or out-of-range data and alert data entry personnel of errors. In addition, data entry error rates shall be estimated and recorded on a monthly basis by re-entering a statistical sample of the data entered and calculating discrepancy rates by data element.

13.2 Documenting Data Changes

The record of changes in the form of corrections and updates to data originally generated, submitted, and/or resubmitted shall be documented to allow traceability of updates. Documentation shall include the following for each change.

- Justification or rationale for the change.
- Initials of the person making the change(s). Data changes shall be implemented and reviewed by a person or group independent of the source generating the deliverable.
- Documentation of changes shall be retained according to the schedule of the original deliverable.
- Resubmitted deliverables shall be re-inspected as a part of the Contractor's internal inspection process prior to resubmission. The entire deliverable, not just the changes, shall be inspected.
- The Laboratory Manager shall approve changes to originally submitted deliverables.
- Documentation of data changes may be requested by Contractor auditors.

13.3 Life Cycle Management (LCM) Procedures

LCM procedures shall be applied to computer software systems developed by the Contractor to be used to generate and edit contract deliverables. Such systems shall be thoroughly tested and documented prior to utilization.

13.3.1 A software test and acceptance plan including test requirements, test results, and acceptance criteria shall be developed, followed, and available in written form.

13.3.2 System changes shall not be made directly to production systems generating deliverables. Changes shall be made first to a development system and tested prior to implementation.

13.3.3 Each version of the production system will be given an identification number, date of installation, date of last operation, and will be archived.

13.3.4 System and operations documentation shall be developed and maintained for each system. Documentation shall include a user's manual and an operations and maintenance manual.

13.3.5 This documentation shall be available for on-site review and/or upon written request by the Project Officer (PO).

13.4 Personnel Responsibilities

Individual(s) responsible for the following functions shall be identified.

- System operation and maintenance, including documentation and training;
- Database integrity, including data entry, data updating and QC; and
- Data and system security, backup, and archiving.

EXHIBIT F

CHAIN-OF-CUSTODY, DOCUMENT CONTROL, AND WRITTEN STANDARD OPERATING PROCEDURES

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Exhibit F – Chain-of-Custody, Document Control,
and Written Standard Operating Procedures

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1.0 INTRODUCTION

1.1 A sample is physical evidence collected from a facility or from the environment. Controlling evidence is an essential part of the hazardous waste investigation effort. To ensure that the US Environmental Protection Agency's (USEPA) sample data and records supporting sample-related activities are admissible and have weight as evidence in future litigation, Contractors are required to maintain USEPA samples under chain-of-custody and to account for all samples and supporting records of sample handling, preparation, and analysis. Contractors shall maintain sample identity, sample custody, and all sample-related records according to the requirements in this exhibit.

1.2 Purpose of the Evidence Requirements

The purpose of the evidence requirements include:

- Ensuring traceability of samples while in the possession of the Contractor;
- Ensuring custody of samples while in the possession of the Contractor;
- Ensuring the integrity of sample identity while in the possession of the Contractor;
- Ensuring sample-related activities are recorded on documents or in other formats for USEPA sample receipt, storage, preparation, analysis, and disposal;
- Ensuring all laboratory records for each specified Sample Delivery Group (SDG) will be accounted for when the project is completed; and
- Ensuring that all laboratory records directly related to USEPA samples are assembled and delivered to USEPA or, prior to delivery, are available upon USEPA's request.

2.0 STANDARD OPERATING PROCEDURES (SOP)

The Contractor shall implement the following SOPs for sample receiving; sample identification; sample security; sample storage; sample tracking and document control; computer-resident sample data control; and Complete Sample Delivery Group (SDG) File (CSF) and Portable Document Format (PDF) file organization and assembly to ensure accountability of USEPA sample chain-of-custody, as well as control of all USEPA sample-related records.

2.1 Sample Receiving

2.1.1 The Contractor shall designate a Sample Custodian responsible for receiving USEPA samples.

2.1.2 The Contractor shall designate a representative to receive USEPA samples in the event that the Sample Custodian is not available.

2.1.3 Upon receipt, the condition of shipping containers and sample containers shall be inspected and recorded on Form DC-1 by the Sample Custodian or a designated representative.

2.1.4 Upon receipt, the condition of the custody seals (intact/broken) shall be inspected and recorded on Form DC-1 by the Sample Custodian or a designated representative.

2.1.5 The Sample Custodian or a designated representative shall verify and record on Form DC-1 the agreement or disagreement of information recorded on all documents received with samples and information recorded on sample containers.

2.1.6 The Sample Custodian or a designated representative shall verify and record the following information on Form DC-1 as samples are received and inspected:

- Presence or absence and condition of custody seals on shipping and/or sample containers;
- Custody seal numbers when present;
- Condition of the sample canisters;
- Presence or absence of airbills or airbill stickers;
- Airbill or airbill sticker numbers;
- Presence or absence of Traffic Report/Chain of Custody Records (TR/COCs) or Packing Lists;
- Sample tags listed/not listed on TR/COCs;
- Date of receipt;
- Time of receipt;
- Designated Sample Numbers;
- Canister ID;
- Presence or absence of sample tags;
- Sample tag numbers;
- Assigned laboratory numbers;
- Remarks regarding condition of sample shipment, etc.;

- Samples delivered by hand; and
- Problems and discrepancies.

2.1.7 The Sample Custodian or a designated representative shall sign, date, and record the time on all accompanying forms, when applicable, at the time of sample receipt (e.g., TR/COCs or packing lists, and airbills).

NOTE: Initials are not acceptable.

2.1.8 The Contractor shall contact the Contracting Officer (CO) to resolve problems and discrepancies including, but not limited to: absent documents, conflicting information, absent or broken custody seals; and unsatisfactory sample condition (e.g., leaking sample container).

2.1.9 The Contractor shall record the resolution of all problems and discrepancies communicated through the TOPO.

2.2 Sample Identification

2.2.1 The Contractor shall maintain the identity of USEPA samples throughout the laboratory.

2.2.2 Each sample shall be labeled with the EPA Sample Number or a unique laboratory sample identification number.

2.3 Sample Security

2.3.1 The Contractor shall demonstrate that USEPA sample custody is maintained from receiving through retention or disposal. A sample is in custody if:

- It is in your possession; or
- It is in your view after being in your possession; or
- It is locked in a secure area after being in your possession; or
- It is in a designated secure area (secure areas shall be accessible only to authorized personnel).

2.3.2 The Contractor shall demonstrate security of designated secure areas.

2.4 Sample Storage

The Contractor shall designate storage areas for USEPA samples and prepared samples.

2.5 Sample Tracking and Document Control

2.5.1 The Contractor shall record all activities performed on USEPA samples.

2.5.2 Titles that identify the recorded activities shall be printed on each page of all laboratory documents. Activities include, but are not limited to: sample receipt, sample storage, sample preparation, and sample analysis. When a document is a record of analysis, the instrument type and parameter group shall be included in the title.

2.5.3 When columns are used to organize information recorded on laboratory documents, the information recorded in the columns shall be identified in a column heading.

2.5.4 Reviewers' signatures shall be identified on laboratory documents when reviews are conducted.

NOTE: Individuals recording review comments on computer-generated raw data are not required to be identified unless the written comments address data validity.

2.5.5 The laboratory name shall be identified on preprinted laboratory documents.

2.5.6 Each laboratory document entry shall be dated as MM/DD/YYYY (e.g., 01/01/2007) and signed by the individual(s) responsible for performing the recorded activity at the time the activity is recorded.

2.5.7 Notations on laboratory documents shall be recorded in ink.

2.5.8 Corrections to laboratory data reporting forms and raw data shall be made by drawing single lines through the errors and entering the correct information. Information shall not be obliterated or rendered unreadable. Corrections and additions to information shall be signed (or initialed) and dated.

2.5.9 Unused portions of laboratory documents shall be lined-out.

2.5.10 Pages in bound and unbound logbooks shall be sequentially numbered.

2.5.11 Instrument-specific run logs shall be maintained to enable the reconstruction of run sequences.

2.5.12 Logbook entries shall be in chronological order.

2.5.13 Logbook entries shall include only one SDG per page, except in the event where the SDGs “share” Quality Control (QC) samples (e.g., instrument run logs and extraction logs).

2.5.14 Information inserted into laboratory documents shall be affixed permanently in place. The individual responsible for inserting information shall sign and date across the insert and logbook page at the time information is inserted.

2.5.15 The Contractor shall document disposal or retention of USEPA samples, remaining portions of samples, and prepared samples.

2.5.16 Each page in bound and unbound logbooks shall be dated (MM/DD/YYYY) and signed (no initials) at the bottom by the individual recording the activity (if a single entry is made on a page) or by the last individual recording information on the page (if multiple entries are on the same page).

2.6 Computer-Resident Sample Data Control

2.6.1 Contractor personnel responsible for original data entry shall be identified at the time of data input.

2.6.2 The Contractor shall make changes to electronic data in a manner that ensures that the original data entry is preserved, the editor is identified, and the revision date is recorded.

2.6.3 The Contractor shall routinely verify the accuracy of manually entered data, electronically entered data, and data acquired from instruments.

2.6.4 The Contractor shall routinely verify documents produced by the electronic data collection system to ensure accuracy of the information reported.

2.6.5 The Contractor shall ensure that the electronic data collection system is secure.

2.6.5.1 The electronic data collection system shall be maintained in a secure location.

2.6.5.2 Access to the electronic data collection system functions shall be limited to authorized personnel through utilization of software security techniques (e.g., log-ons or restricted passwords).

2.6.5.3 Electronic data collection systems shall be protected from the introduction of external programs or software (e.g., viruses).

2.6.6 The Contractor shall designate archive storage areas for electronic data and the software required to access the data.

2.6.7 The Contractor shall designate an individual responsible for maintaining archives of electronic data, including the software.

2.6.8 The Contractor shall maintain the archives of electronic data and necessary software in a secure location (secure areas shall be accessible only to authorized personnel).

2.7 Complete Sample Delivery Group File (CSF) Organization and Assembly

2.7.1 The Contractor shall designate a Document Control Officer responsible for the organization and assembly of the CSF.

2.7.2 The Contractor shall designate a representative responsible for the organization and assembly of the CSF in the event that the Document Control Officer is not available.

2.7.3 The Contractor shall maintain documents relating to the CSF in a secure location.

2.7.4 All original laboratory forms and copies of SDG-related logbook pages shall be included in the CSF.

2.7.5 Copies of laboratory documents in the CSF shall be photocopied in a manner to provide complete and legible replicates.

2.7.6 Documents relevant to each SDG including, but not limited to, the following shall be included in the CSF:

- Logbook pages;
- Bench sheets;
- Mass spectra;
- Chromatograms;
- Screening records;
- Analytical records;
- Reanalysis records;
- Records of failed or attempted analysis;
- Custody records;
- Sample tracking records;
- Raw data summaries;
- Computer printouts;
- Correspondence;
- FAX originals;
- Library search results; and
- Other.

2.7.7 The Document Control Officer or a designated representative shall ensure that sample tags are encased in clear plastic bags before placing them in the CSF.

2.7.8 CSF documents shall be organized and assembled on an SDG-specific basis.

2.7.9 Original documents which include information relating to more than one SDG (e.g., TR/COCs, calibration logs) shall be filed in the CSF of the lowest SDG number, and copies of these originals shall be placed in the other CSF(s). The Document Control Officer or a designated representative shall record the following statement on the copies in (indelible) dark ink:

COPY
ORIGINAL DOCUMENTS ARE INCLUDED IN CSF _____

_____
Signature

_____
Date

2.7.10 All CSFs shall be submitted with a completed Form DC-2. All resubmitted CSFs shall be submitted with a new or revised Form DC-2.

2.7.11 Each item in the CSF and resubmitted CSFs shall be inventoried and assembled in the order specified on Form DC-2. Each page of the CSF shall be stamped with a sequential number. Page number ranges shall be recorded in the columns provided on Form DC-2. Intentional gaps in the page numbering sequence shall be recorded in the "Comments" section on Form DC-2. When inserting new or inadvertently omitted documents, the Contractor shall identify them with unique accountable numbers. The unique accountable numbers and the locations of the documents shall be recorded in the "Other Records" section on Form DC-2.

2.7.12 Before shipping each CSF, the Document Control Officer or a designated representative shall verify the agreement of information recorded on all documentation and ensure that the information is consistent and the CSF is complete.

2.7.13 The Document Control Officer or a designated representative shall document the shipment of deliverable packages including what was sent, to whom the package was sent, the date, and the carrier used.

2.7.14 Shipments of deliverable packages, including resubmittals, shall be sealed with custody seals by the Document Control Officer or a designated representative in a manner such that opening the packages would break the seals.

2.7.15 Custody seals shall be signed and dated by the Document Control Officer or a designated representative when sealing deliverable packages.

2.8 Data in PDF Organization and Assembly

2.8.1 The Contractor shall designate a Document Control Officer responsible for the organization and assembly of the PDF file.

2.8.2 The Contractor shall designate a representative responsible for the organization and assembly of the PDF file in the event that the Document Control Officer is not available.

2.8.3 The Contractor shall maintain documents relating to the PDF file in a secure location.

2.8.4 In addition to all required deliverables identified in the laboratory’s contract and the Statement of Work (SOW), the laboratory shall provide a complete copy of the hardcopy deliverable in PDF on a Compact Disc (CD).

2.8.5 The PDF file should be organized in accordance to directions provided in Exhibit B, "Reporting Requirements and Order of Data Deliverables" of the SOW. The PDF file shall be bookmarked for ease of data retrieval and navigation.

2.8.6 Organic data shall be bookmarked using a hierarchal bookmark structure (i.e., an overview or "parent" bookmark, and a subordinate or "child" bookmark nested underneath the "parent" bookmark). Refer to Exhibit B, Section 2.8, Table 2 for the specific hierarchal bookmark structure.

2.8.7 Before shipping each PDF file, the Document Control Officer or a designated representative shall verify the agreement of information recorded in the PDF file and ensure that the information is consistent and the PDF file is complete.

2.8.8 The Document Control Officer or a designated representative shall document the shipment of deliverable packages including what was sent, to whom the package was sent, the date, and the carrier used.

2.8.9 Shipments of deliverable packages, including resubmittals, shall be sealed with custody seals by the Document Control Officer or a designated representative in a manner such that opening the packages would break the seals.

2.8.10 Custody seals shall be signed and dated by the Document Control Officer or a designated representative when sealing deliverable packages.

3.0 WRITTEN STANDARD OPERATING PROCEDURES (SOP)

The Contractor shall develop and implement the following written SOPs for sample receiving, sample identification, sample security, sample storage, sample tracking and document control, computer-resident sample data control, and Complete Sample Delivery Group (SDG) File (CSF) and Portable Document Format (PDF) file organization and assembly to ensure accountability for USEPA sample chain-of-custody and control of all USEPA sample-related records.

3.1 Sample Receiving

3.1.1 The Contractor shall have written SOPs for sample receiving that accurately reflect the procedures used by the laboratory.

3.1.2 The written SOPs for sample receiving shall ensure that the procedures listed below are in use at the laboratory.

3.1.2.1 The condition of shipping containers and sample containers are inspected and recorded on Form DC-1 upon receipt by the Sample Custodian or a designated representative.

3.1.2.2 The condition of custody seals are inspected and recorded on Form DC-1 upon receipt by the Sample Custodian or a designated representative.

3.1.2.3 The agreement or disagreement of information recorded on shipping documents with information recorded on sample containers is verified and recorded on Form DC-1 by the Sample Custodian or a designated representative.

3.1.2.4 The following information is recorded on Form DC-1 by the Sample Custodian or a designated representative as samples are received and inspected:

- Presence or absence and condition of custody seals on shipping and/or sample containers;
- Custody seal numbers, when present;
- Condition of the sample canisters;
- Presence or absence of airbill or airbill stickers;
- Airbill or airbill sticker numbers;
- Presence or absence of Traffic Report/Chain of Custody Records (TR/COCs) or Packing Lists;

- Sample tag numbers listed/not listed on TR/COCs;
- Date of receipt;
- Time of receipt;
- Designated Sample Numbers;
- Canister ID;
- Presence or absence of sample tags;
- Sample tag numbers;
- Assigned laboratory numbers;
- Samples delivered by hand; and
- Problems and discrepancies.

3.1.2.5 The Sample Custodian or a designated representative shall sign, date, and record the time on all accompanying forms (e.g., TR/COCs or packing lists, and airbills), when applicable, at the time of sample receipt.

NOTE: Initials are not acceptable.

3.1.2.6 The Contractor shall contact the Task Order Project Officer (TOPO) to resolve problems and discrepancies including, but not limited to: absent documents; conflicting information; absent or broken custody seals; and unsatisfactory sample condition (e.g., leaking sample container).

3.1.2.7 The Contractor shall record resolution of problems and discrepancies communicated through the TOPO.

3.2 Sample Identification

3.2.1 The Contractor shall have written SOPs for sample identification that accurately reflect the procedures used by the laboratory.

3.2.2 The written SOPs for sample identification shall ensure that the procedures listed below are in use at the laboratory.

3.2.2.1 The identity of USEPA samples and prepared samples is maintained throughout the laboratory when:

- The Contractor assigns unique laboratory sample identification numbers, the written SOPs shall include a description of the procedure used to assign these numbers;
- The Contractor uses prefixes or suffixes in addition to laboratory sample identification numbers, the written SOPs shall include the definitions; and
- The Contractor uses methods to uniquely identify fractions/parameter groups and matrix type, the written SOPs shall include a description of these methods.

3.2.2.2 Each sample and sample preparation container is labeled with the EPA sample number or a unique laboratory sample identification number.

3.3 Sample Security

3.3.1 The Contractor shall have written SOPs for sample security that accurately reflects the procedures used by the laboratory.

3.3.2 The written SOPs for sample security shall include the items listed below.

3.3.2.1 Procedures that ensure the following:

- Sample custody is maintained; and
- The security of designated secure areas is maintained.

3.3.2.2 A list of authorized personnel who have access to locked storage areas.

3.4 Sample Storage

3.4.1 The Contractor shall have written SOPs for sample storage that accurately reflect the procedures used by the laboratory.

3.4.2 The written SOPs for sample storage shall describe locations, contents, and identities of all storage areas for USEPA samples and prepared samples in the laboratory.

3.5 Sample Tracking and Document Control

3.5.1 The Contractor shall have written SOPs for sample tracking and document control that accurately reflect the procedures used by the laboratory.

3.5.2 The written SOPs for sample tracking and document control shall include the items listed below.

3.5.2.1 Examples of all laboratory documents used during sample receiving, sample storage, sample transfer, sample analyses, CSF organization and assembly, and sample retention or disposal.

3.5.2.2 Procedures that ensure the following:

- All activities performed on USEPA samples are recorded;
- Titles that identify the activities recorded are printed on each page of all laboratory documents;
- Information recorded in columns is identified with column headings;
- Reviewers' signatures are identified on laboratory documents;
- The laboratory name is included on preprinted laboratory documents;
- Laboratory document entries are signed and dated as MM/DD/YYYY (e.g., 01/01/2007);
- Entries on all laboratory documents are recorded in ink;
- Corrections and additions to laboratory documents are made by drawing single lines through the errors, entering the correct information, and initialing and dating the new information;
- Unused portions of laboratory documents are lined-out;
- Pages in bound and unbound logbooks are sequentially numbered;
- Instrument-specific run logs are maintained to enable the reconstruction of run sequences;
- Logbook entries are recorded in chronological order;
- Entries are recorded for only one SDG on a page, except in the events where SDGs "share" Quality Control (QC) samples (e.g., instrument run logs and extraction logs);

- Each page in bound and unbound logbooks shall be dated as (MM/DD/YYYY) and signed (no initials) at the bottom by the individual recording the activity (if a single entry is made on a page) or by the last individual recording information on the page (if multiple entries are on the same page);
- Information inserted in laboratory documents is affixed permanently, signed, and dated across the insert; and
- The retention or disposal of USEPA samples, remaining portions of samples, and prepared samples is documented.

3.6 Computer-Resident Sample Data Control

3.6.1 The Contractor shall have written SOPs for computer-resident sample data control that accurately reflects the procedures used by the laboratory.

3.6.2 The written SOPs for computer-resident sample data control shall include the items listed below.

3.6.2.1 Procedures which ensure the following:

- Contractor personnel responsible for original data entry are identified;
- Changes to electronic data are made such that the original data entry is preserved, the editor is identified, and the revision date is recorded;
- The accuracy of manually entered data, electronically entered data, and data acquired from instruments is verified;
- Report documents produced by the electronic data collection system are routinely verified to ensure the accuracy of the information reported;
- Off-site backup and storage of electronic data is maintained;
- Electronic data collection system security is maintained; and
- Archives of electronic data and accompanying software are maintained in a secure location.

3.6.2.2 Descriptions of archive storage areas for the electronic data and the software required to access data archives.

3.6.2.3 A list of authorized personnel who have access to electronic data collection system functions and to archived data.

3.7 CSF Organization and Assembly

3.7.1 The Contractor shall have written SOPs for CSF organization and assembly that accurately reflect the procedures used by the laboratory.

3.7.2 The written SOPs for CSF organization and assembly shall ensure that the procedures listed below are in use at the laboratory.

- Documents relating to the CSF are maintained in a secure location.
- All original laboratory forms and copies of SDG-related logbook pages are included in the CSF.
- Laboratory documents are photocopied in a manner to provide complete and legible replicates.

- All documents relevant to each SDG are included in the CSF.
- Sample tags are encased in clear plastic bags by the Document Control Officer or a designated representative before placing them in the CSF.
- The CSF is organized and assembled on an SDG-specific basis.
- In the event that an original document contains information relating to more than one SDG, the original documents are filed in the CSF of the lowest SDG number and copies are referenced to the originals.
- Each CSF is submitted with a completed Form DC-2, and resubmitted CSFs are submitted with a new or revised Form DC-2.
- Each page of the CSF is stamped with a sequential number and the page number ranges are recorded in the columns provided on Form DC-2. Intentional gaps in the page numbering sequence are recorded in the "Comments" section of Form DC-2. Inserted documents are recorded in the "Other Record" section of Form DC-2.
- Consistency and completeness of the CSF is verified by the Document Control Officer or a designated representative.
- Shipments of deliverable packages are documented by the Document Control Officer or a designated representative.
- Deliverable packages are shipped by the Document Control Officer or a designated representative using custody seals in a manner such that opening the packages would break the seals.
- Custody seals are signed and dated by the Document Control Officer or a designated representative before placing them on deliverable packages.

3.8 PDF File Organization and Assembly

3.8.1 The Contractor shall have written SOPs for PDF file organization and assembly that accurately reflect the procedures used by the laboratory.

3.8.2 The written SOPs for PDF file organization and assembly shall ensure that the procedures listed below are in use at the laboratory.

- PDF files are maintained in a secure location.
- The PDF file is organized and assembled as specified in Exhibit B, Section 2.8 and Exhibit F, Section 2.8.
- Completeness and compliance of the PDF file is verified by the Document Control Officer or a designated representative.
- Shipments of deliverable packages are documented by the Document Control Officer or a designated representative.
- Deliverable packages are shipped by the Document Control Officer or a designated representative using custody seals in a manner such that opening the packages would break the seals.
- Custody seals are signed and dated by the Document Control Officer or a designated representative before placing them on deliverable packages.

EXHIBIT G

GLOSSARY OF TERMS

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ABSOLUTE PRESSURE – Pressure measured with reference to absolute zero pressure, usually expressed in units of kPa or psi.

ALKANE - Any hydrocarbon with the generic formula C_nH_{2n+2} (straight-chain or branched) or C_nH_{2n} (cyclic) that contains only C-H and C-C single bonds.

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) - A developer and provider of voluntary consensus standards.

ANALYSIS DATE/TIME - The date and military time (24-hour clock) of the injection of the sample, standard, or blank into the Gas Chromatograph/Mass Spectrometer (GC/MS) or GC system.

ANALYTE - The element or ion an analysis seeks to determine; the element of interest.

ANALYTICAL METHOD - Specifies the procedures for sample preparation, instrument calibration, sample analysis, and result calculations.

ANALYTICAL REFERENCE STANDARD - Standards purchased from private chemical supply houses used to prepare calibration standards, Contract Required Quantitation Limit (CRQL) Check Standards (CRI), and Continuing Calibration Verification (CCV) standards.

ANALYTICAL SAMPLE - Any solution or media introduced into an instrument on which an analysis is performed, excluding instrument calibration, Initial Calibration Verification (ICV), Initial Calibration Blank (ICB), Continuing Calibration Verification (CCV), Continuing Calibration Blank (CCB), and tunes. Note the following are all defined as analytical samples: undiluted and diluted samples (USEPA and non-USEPA), matrix spike samples, duplicate samples, serial dilution samples, analytical spike samples, post-digestion spike samples, Interference Check Samples (ICSs), Contract Required Quantitation Limit (CRQL) Check Standards (CRIs), Laboratory Control Samples (LCSs), Performance Evaluation (PE) samples, Preparation Blanks (PBs), and cyanide MIDRANGE samples.

ANALYTICAL SEQUENCE - The actual instrumental analysis of the samples from the time of instrument calibration through the analysis of the final Continuing Calibration Verification (CCV) or Continuing Calibration Blank (CCB). All sample analyses during the analytical sequence are subject to the QC protocols set forth in Exhibits D and E of this contract unless otherwise specified in the individual methods.

ANALYTICAL SERVICES BRANCH (ASB) - The division of United States Environmental Protection Agency’s (USEPA) Office of Superfund Remediation and Technology Innovation (OSRTI) responsible for the overall management of the Contract Laboratory Program (CLP).

ANALYTICAL SPIKE - A spike that is fortified just prior to analysis by adding a known quantity of the analyte to an aliquot of the prepared sample.

AUTOZERO - Zeroing the instrument at the proper wavelength. It is equivalent to running a standard blank with the absorbance set at zero.

BACKGROUND CORRECTION - A technique to compensate for variable background contribution to the instrument signal in the determination of trace elements.

BAR GRAPH SPECTRUM - A plot of the mass-to-charge ratio (m/e) versus relative intensity of the ion current.

BASELINE - Analysis used to reset the baseline during mercury or cyanide runs.

BATCH - A group of samples prepared at the same time in the same location using the same method.

BLANK - An analytical sample designed to assess specific sources of contamination. See the individual definitions for types of blanks.

BREAKDOWN - A measure of the decomposition of certain analytes (DDT and Endrin) into by-products.

4-BROMOFLUOROBENZENE (BFB) - The compound chosen to establish mass spectral instrument performance check for volatile (VOA) analyses.

CALIBRATION - The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type of reagents or concentration of acids as used in the sample preparation.

CALIBRATION BLANK - A blank solution containing all of the reagents and in the same concentration as those used in the analytical sample preparation. This blank is not subjected to the preparation method.

CALIBRATION FACTOR (CF) - A measure of the Gas Chromatographic response of a target analyte to the mass injected.

CALIBRATION STANDARDS - A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). The solutions may or may not be subjected to the preparation method but contain the same matrix (i.e., the same amount of reagents and/or preservatives) as the sample preparations to be analyzed.

CASE - A finite, usually predetermined number of samples collected over a given time period from a particular site. Case numbers are assigned by the Sample Management Office (SMO). A Case consists of one or more Sample Delivery Groups (SDGs).

CHARACTERIZATION - A determination of the approximate concentration range of compounds of interest used to choose the appropriate analytical protocol.

CAS – Chemical Abstracts Service.

CLOSING CONTINUING CALIBRATION VERIFICATION - Last analytical standard run every 12 hours to verify the initial calibration accuracy of the system.

CO – Contracting Officer.

CONCENTRATION LEVEL (trace, low, or medium) - Characterization of sample fractions as trace concentration, low concentration, or medium concentration is made on the basis of the laboratory's preliminary screen, not on the basis of information entered on the Traffic Report/Chain of Custody Record (TR/COC)by the sampler.

CONTAMINATION - A component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents laboratory environment, or analytical instruments.

CONTRACT COMPLIANCE SCREENING (CCS) - A screening of electronic and hardcopy data deliverables for completeness and compliance with the contract. This screening is done under USEPA direction by the Sample Management Office (SMO) contractor.

CONTRACT LABORATORY PROGRAM (CLP) - Supports the USEPA's Superfund effort by providing a range of state-of-the-art chemical analytical services of known quality. This program is directed by the Analytical Services Branch (ASB) of the Office of Superfund Remediation and Technology Innovation (OSRTI) of USEPA.

CONTINUING CALIBRATION VERIFICATION (CCV) - A single parameter or multi-parameter standard solution prepared by the analyst and used to verify the stability of the instrument calibration with time, and the instrument performance during the analysis of samples. The CCV can be one of the calibration standards. However, all parameters being measured by the particular system must be represented in this standard and the standard must have the same matrix (i.e., the same amount of reagents and/or preservatives) as the samples. The CCV should have a concentration in the middle of the calibration range and shall be run at the beginning of the day prior to the analysis of samples, and for every 10 analytical samples or every 2 hours, whichever is more frequent.

CONTRACT COMPLIANCE SCREENING (CCS) - A screening of electronic and hardcopy data deliverables for completeness and compliance with the contract. This screening is done under USEPA direction by the SMO Contractor.

CONTRACT REQUIRED QUANTITATION LIMIT (CRQL) - Minimum level of quantitation acceptable under the contract Statement of Work (SOW).

CONTRACT REQUIRED QUANTITATION LIMIT (CRQL) CHECK STANDARD (CRI) - A single parameter or multi-parameter standard solution prepared at the CRQL and used to verify the instrument calibration at low levels.

CONTROL LIMITS - A range within which specified measurement results must fall to be compliant. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that noncompliant data be flagged.

CRITICAL LEVEL (L_c) - An estimate of the smallest amount or concentration of analyte that can be distinguished from a blank at 99% confidence. Values above this level should not represent false positives.

CRYOGEN — A refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Typical cryogens are liquid nitrogen (bp: -195.8°C), liquid argon (bp: -185.7°C), and liquid carbon dioxide (bp: -79.5°C).CYANIDE (Total) - Cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

DATE - MM/DD/YYYY - Where MM = 01 for January, 02 for February, 12 for December; DD = 01 to 31; YYYY = 2005, 2006, 2007, etc.

DAY - Unless otherwise specified, day shall mean calendar day.

DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP) - Compound chosen to establish mass spectral instrument performance check for semivolatile analysis.

DEUTERATED MONITORING COMPOUNDS (DMCs) - Compounds added to every calibration standard, blank, and sample used to evaluate the efficiency of the extraction/purge-and-trap procedures, and the performance of the Gas Chromatograph/Mass Spectrometer (GC/MS) systems. DMCs are isotopically labeled (deuterated) analogs of native target compounds. DMCs are not expected to be naturally detected in the environmental media.

DIGESTION LOG - An official record of the sample preparation (digestion).

DIRECT ANALYSIS - Analysis of a sample, standard, or blank that has not been taken through a preparation procedure (digestion or distillation).

DISSOLVED METALS - Analyte elements in a water/aqueous sample which will pass through a 0.45 micrometer (μm) filter.

DRD – Data Receipt Date.

DUPLICATE - A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

DUPLICATE PRECISION — precision determined from the analysis of the Continuing Calibration Verification standard and the Laboratory Control Sample taken from the same standard canister. The duplicate precision is determined as the absolute value of the difference between the canister analyses divided by their average value and expressed as a percentage.

DYNAMIC CALIBRATION — Calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system from a manifold through which the gas standards are flowing.

DYNAMIC DILUTION — Means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with humidified zero air in a manifold so that a flowing stream of calibration mixture is available at the inlet of the analytical system.

EDD – Electronic Data Deliverable.

EXTRACTABLE - A compound that can be partitioned into an organic solvent from the sample matrix and is amenable to Gas Chromatography.

EXTRACTED ION CURRENT PROFILE (EICP) - A plot of ion abundance versus time (or scan number) for ion(s) of specified mass(es).

FIELD BLANK - Any sample that is submitted from the field and is identified as a blank. This includes trip blanks, rinsates, equipment blanks, etc.

FIELD QC - Any Quality Control (QC) samples submitted from the field to the laboratory. Examples include, but are not limited to: field blanks, field duplicates, and field spikes.

FIELD SAMPLE - A portion of material obtained from an assigned site to be analyzed that is contained in single or multiple containers and identified by a unique EPA Sample Number.

GAS CHROMATOGRAPH (GC) - The instrument used to separate analytes on a stationary phase within a chromatographic column. The analytes are volatized directly from the sample (VOA water and low-soil), volatized from the sample extract (VOA medium soil), or injected as extracts (SVOA, PEST, and ARO). In VOA and SVOA analysis, the compounds are detected by a Mass Spectrometer (MS).In Pesticide and Aroclor analysis, the compounds are detected by an Electron Capture Detector (ECD).

GAS CHROMATOGRAPH/MASS SPECTROMETER - A specialized form of Gas Chromatography(GC) used in conjunction with Mass Spectrometry (MS). GC/MS is considered the method of choice for the unequivocal identification of many volatile and semivolatile organic compounds.

GAUGE PRESSURE – Pressure marked with reference to the surrounding atmospheric pressure, usually expressed in unt of kPa or psi. Zero gauge pressure is equal to atmospheric (barometric) pressure.

HAP – Hazardous air pollutant.

HOLDING TIME - The elapsed time expressed in days from the date of receipt of the sample by the Contractor until the date of its analysis.

INDEPENDENT STANDARD - A Contractor-prepared standard solution that is composed of analytes from a different source than those used in the standards for the calibration.

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY (ICP-AES) – A technique for the simultaneous or sequential multi-element determination of elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Characteristic atomic line emission spectra are produced by excitation of the sample in a radio frequency inductively coupled plasma.

INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (ICP-MS) - A technique for the multi-element determination of elements in solution. The basis of the technique is the detection of atomic ions produced by an ICP and sorted by mass-to-charge (m/z) ratio.

IN-HOUSE - At the Contractor's facility.

INITIAL CALIBRATION - Analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity, and dynamic range of the response of the Mass Spectrometer (MS) or Electron Capture Detector (ECD) to the target compounds.

INITIAL CALIBRATION - Analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity, and dynamic range of the instrument to target analytes.

INITIAL CALIBRATION VERIFICATION (ICV) - Solution(s) prepared from stock standard solutions, metals, or salts obtained from a source separate from that utilized to prepare the calibration standards. The ICV is used to verify the concentration of the calibration standards and the adequacy of the instrument calibration. The ICV should be traceable to NIST or other certified standard sources when USEPA ICV solutions are not available.

INJECTION - Introduction of the analytical sample into the instrument excitation system to measure absorbance, emission, or concentration of an analyte. May also be referred to as exposure.

INSTRUMENT BLANK - A blank designed to determine the level of contamination associated with the analytical instruments.

INSUFFICIENT QUANTITY - When there is not enough volume (water sample) or weight (soil/sediment) to perform any of the required operations: sample analysis or extraction, Percent Moisture (%Moisture), Matrix Spike and Matrix Spike Duplicate (MS/MSD), etc. Exhibit D provides guidance for addressing this situation.

INSUFFICIENT QUANTITY - When there is not enough volume (water/aqueous sample) or weight (soil/sediment) to perform any of the required operations: sample analysis, percent solids, etc. Exhibit D provides guidance for addressing this problem.

INTEGRATION SCAN RANGE - The scan number of the scan at the beginning of thearea of integration to the scan number at the end of the area of integration.Performed in accordance with Exhibit D Trace and Low/Medium VOA and SVOA.

INTEGRATION TIME RANGE - The Retention Time (RT) at the beginning of the are aof integration to the RT at the end of the area of integration.

INTERFERANTS - Substances which affect the analysis for the element of interest.

INTERFERENCE CHECK SAMPLE (ICS) - A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors.

INTERFERENTS - Substances which affect the analysis for the element of interest.

INTERNAL STANDARD - A non-target element added to a sample at a known concentration after preparation but prior to analysis. Instrument responses to internal standards are monitored as a means of assessing overall instrument performance.

INTERNAL STANDARDS - Compounds added to every standard, blank, Matrix Spike and Matrix Spike Duplicate (MS/MSD), sample (for volatiles), and sample extract (for semivolatiles) at a known concentration, prior to analysis. Instrument responses to internal standards are used as the basis for quantitation of the target compounds.

LABORATORY - Synonymous with Contractor, as used herein.

LABORATORY CONTROL SAMPLE (LCS) - A control sample of known composition. LCSs are analyzed using the same sample preparation, reagents, and analytical methods employed for the USEPA samples received. An internal laboratory Quality Control (QC) sample used to monitor the capability of the Contractor to perform the analytical method. For the purpose of this SOW, a replicate of the Continuing Calibration Verification standard that is analyzed immediately after the method blank in the analytical sequence.

LABORATORY CONTROL SAMPLE ACCURACY — the concentration determined by analysis of a laboratory control sample divided by the nominal value expressed as a percentage.

LABORATORY RECEIPT DATE (LRD) - The date on which a sample is received at the Contractor’s facility, as recorded on the shipper’s delivery receipt and Sample Traffic Report/Chain of Custody Record. Also referred to as VTSR (Validated Time of Sample Receipt).

LIMIT OF DETECTION (L_d) - An estimate of the smallest value that protects against false negatives; the smallest value that must be present to be detected. The lowest possible value for the confident reporting of a non-detect.

LIMIT OF QUANTITATION (L_q) - An estimate of the lowest concentration that produces quantitatively reliable results. For the purposes of this contract, this is defined as two times the Limit of Detection.

m/z - Mass to charge ratio; synonymous with "m/e".

MS-SCAN — Mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

MS-SIM — Mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

MATRIX - The predominant material of which the sample to be analyzed is composed. For the purpose of this Statement of Work (SOW), a sample matrix is either water/aqueous, soil/sediment, wipe, or small (e.g., 37 mm) air filter. Matrix is not synonymous with phase (liquid or solid).

MATRIX EFFECT - In general, the effect of a particular matrix (water or soil/sediment) on the constituents with which it contacts. Matrix effects may prevent efficient purging/extraction of target analytes, and may affect Deuterated Monitoring Compound (DMC) and surrogate recoveries. In addition, non-target analytes may be extracted from the matrix causing interferences.

MATRIX SPIKE - Aliquot of a sample (water/aqueous or soil) taken from one of the field samples to be analyzed within an SDG, fortified (spiked) with known quantities of specific compounds, and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - A second aliquot of the same sample as the Matrix Spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - An analytical control consisting of all reagents, internal standards, and surrogate standards [or Deuterated Monitoring Compounds (DMCs) for Trace VOA, Low/Medium VOA, and SVOA], that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

METHOD DETECTION LIMIT (MDL) - The concentration of a target parameter that, when a sample is processed through the complete method, produces a signal with99 percent probability that it is different from the blank. For 7 replicates of the sample, the mean value must be 3.14s above the blank, where "s" is the standard deviation of the 7 replicates.

MIDRANGE - A distilled standard at a concentration approximately equivalent to the midpoint of the calibration curve used to verify the reliability of the distillation procedure.

NARRATIVE (SDG Narrative) - Portion of the data package which includes laboratory, contract, Case, and Sample Number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution. Complete Sample Delivery Group (SDG) Narrative specifications are included in Exhibit B.

OPENING CONTINUING CALIBRATION VERIFICATION - First analytical standard run every 12 hours to verify the initial calibration of the system.

PERCENT DIFFERENCE (%D) - As used in this Statement of Work (SOW) and elsewhere to compare two values, the difference between the two values divided by one of the values.

PERCENT DIFFERENCE (%Difference) - As used in this analytical method and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison [i.e., the Percent Difference (%Difference) may be either negative, positive, or zero].

PERCENT MOISTURE (%Moisture) - An approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The Percent Moisture (%Moisture) determined in this manner also includes contributions from all compounds that may volatilize at or below 105°C, including water. Percent Moisture may be determined from decanted samples and from samples that are not decanted.

PERFORMANCE EVALUATION MIXTURE (PEM) - A calibration solution of specific analytes used to evaluate both recovery and Percent Breakdown (%Breakdown) as a measure of performance.

PERFORMANCE EVALUATION (PE) SAMPLE - A sample of known composition provided by USEPA for Contractor analysis. Used by USEPA to evaluate Contractor performance.

PREPARATION BLANK - An analytical control that contains reagent water and reagents, which is carried through the entire preparation and analytical procedure.

PREPARATION LOG - An official record of the sample preparation (digestion or distillation).

PRIMARY QUANTITATION ION - A contract specified ion used to quantitate a target analyte.

PROTOCOL - Describes the exact procedures to be followed with respect to sample receipt and handling, analytical methods, data reporting and deliverables, and document control. Used synonymously with analytical method.

PURGE-AND-TRAP (DEVICE) - Analytical technique (device) used to isolatevolatile (purgeable) organics by stripping the compounds from water or soil by a stream of inert gas, trapping the compounds on an adsorbent such as a porouspolymer trap, and thermally desorbing the trapped compounds onto the gaschromatographic column.

PURGEABLES - Volatile compounds.

QA/QC – Quality Assurance/Quality Control.

QAP – Quality Assurance Plan.

QUALITY ASSURANCE TECHNICAL SUPPORT (QATS) Laboratory - A Contractor-operated facility operated under the QATS contract, awarded and administered by USEPA.

QUALITATIVE ACCURACY — The degree of measurement accuracy required to correctly identify compounds with an analytical system.

QUANTITATIVE ACCURACY — The degree of measurement accuracy required to correctly measure the concentration of an identified compound with an analytical system with known uncertainty.

REAGENT WATER - Water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest. The purity of this water must be equivalent to ASTM Type II reagent water of specification D119377, "Standard Specification for Reagent Water".

REAGENT WATER - The purity of this water must be equivalent to ASTM Type II reagent water of Specification D1193-99e1, "Standard Specification for Reagent Water".

RECONSTRUCTED ION CHROMATOGRAM (RIC) - A mass spectral graphical representation of the separation achieved by a Gas Chromatograph (GC); a plot of total ion current versus Retention Time (RT).

REFERENCE MATERIAL - Standards, typically provided by USEPA, used to verify method and instrument performance. Examples include Initial Calibration Verification (ICV) standards, Interference Check Solution (ICS) standards, and Laboratory Control Samples (LCS).

RELATIVE PERCENT DIFFERENCE (RPD) - As used in this Statement of Work (SOW) and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value (i.e., always expressed as a positive number or zero).

RELATIVE RESPONSE FACTOR (RRF) - A measure of the relative mass spectral response of an analyte compared to its internal standard. RRFs are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RELATIVE RETENTION TIME (RRT) - The ratio of the Retention Time (RT) of a compound to that of a standard (such as an internal standard).

REPLICATE PRECISION — Precision determined from two canisters filled from the same air mass over the same time period and determined as the absolute value of the difference between the analyses of canisters divided by their average value and expressed as a percentage (see Section 12 for performance criteria for replicate precision).

REPRESENTATIVE - Alternate or designee who has the knowledge and authority to perform a specific task.

REPRESENTATIVE - Alternate or designee who has the knowledge and authority to perform a specific task.

RESLOPE - An analysis used to re-align the calibration curve during mercury or cyanide runs.

RESOLUTION - Also termed Separation or Percent Resolution, the separation between peaks on a chromatogram, calculated by dividing the depth of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.

RESOLUTION CHECK MIXTURE - A solution of specific analytes used to determine resolution of adjacent peaks; used to assess instrumental performance.

RESPONSE (Instrumental Response) - A measurement of the output of the Gas Chromatograph (GC) detector [Mass Spectrometer (MS), Electron Capture Detector (ECD), or Flame Ionization Detector (FID)] in which the intensity of the signal is proportionate to the amount (or concentration) detected. Measured by peak area or peak height.

RETENTION TIME (RT) - The time a target analyte is retained on a GC column before elution. The identification of a target analyte is dependent on a target compound's RT falling within the specified RT window established for that compound. The RT is dependent on the nature of the column's stationary phase, column diameter, temperature, flow rate, and other parameters.

ROUNDING RULES - If the figure is greater than or equal to 5, round up, otherwise round down. As an example, 11.443 is rounded down to 11.44 and 11.455 is rounded up to 11.46. If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures. See forms instructions (Exhibit B) for exceptions.

RUN - A continuous analytical sequence consisting of prepared samples and all associated Quality Assurance (QA) measurements as required by the contract Statement of Work (SOW). A run begins with the instrument calibration or tune.

SAMPLE - A portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

SAMPLE DELIVERY GROUP (SDG) - A unit within a sample Case that is used to identify a group of samples for delivery. An SDG is defined by the following, whichever occurs first:

- Each Case of field samples received, or
- Each 20 field samples [excluding Performance Evaluation (PE) samples] within a Case, or
- Each 7 calendar day period (3 calendar day period for 7 day turnaround) during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).
- In addition, all samples and/or sample fractions assigned to an SDG must have been scheduled under the same contractual turnaround time. Preliminary Results have **no impact** on defining the SDG.

Samples may be assigned to SDGs by matrix (i.e., all soil samples in one SDG, all water samples in another) at the discretion of the laboratory.

SAMPLE MANAGEMENT OFFICE (SMO) - A Contractor-operated facility operated under the SMO contract, awarded and administered by USEPA.

SAMPLE NUMBER (EPA SAMPLE NUMBER) - A unique identification number designated by USEPA for each sample. The EPA sample number appears on the Sample Traffic Report/Chain of Custody Record which documents information on that sample.

SDG NARRATIVE - Portion of the data package which includes laboratory, contract, Case, sample number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution. Complete SDG Narrative specifications are included in Exhibit B.

SECONDARY QUANTITATION ION - Contract specified ion(s) to be used in quantitation of target analytes when interferences prevent the use of the primary quantitation ion.

SICP – Selected Ion Current Profile.

SEMIVOLATILE COMPOUNDS - Compounds amenable to analysis by extraction of the sample with an organic solvent. Used synonymously with Base/Neutral and Acid(BNA) compounds.

SENSITIVITY - The slope of the analytical curve (i.e., functional relationship between instrument response and concentration).

SERIAL DILUTION - The dilution of a sample by a factor of five. When corrected by the dilution factor, the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents.

SIM – Selected Ion Monitoring.

SOP - Standard Operating Procedure.

SOW - Statement of Work.

STANDARD ANALYSIS - An analytical determination made with known quantities of target compounds; used to determine response factors.

STANDARD ANALYSIS - An analytical determination made with known quantities of target analytes.

STOCK SOLUTION - A standard solution which can be diluted to derive other standards.

STORAGE BLANK - Reagent water (two 40.0 mL aliquots) stored with volatile samples in an SDG. It is analyzed after all samples have been analyzed in the SDG and is used to determine the level of contamination acquired during storage.

SULFUR BLANK - A modified method blank that is prepared only when some of the samples in a batch are subjected to sulfur cleanup. It is used to determine the level of contamination associated with the sulfur cleanup procedure. When all of the samples are subjected to sulfur cleanup, then the method blank serves this purpose. When none of the samples are subjected to sulfur cleanup, no sulfur blank is required.

SURROGATES (Surrogate Standard) - For pesticides and Aroclors, compounds added to every blank, sample, Matrix Spike and Matrix Spike Duplicates (MS/MSDs), and standard. Surrogates are used to evaluate analytical efficiency by measuring recovery. Surrogates are not expected to be detected in environmental media.

TARGET ANALYTE LIST (TAL) - A list of Inorganic Analytes (metals and cyanide) as designated in Exhibit C.

TARGET COMPOUND LIST (TCL) - A list of compounds as designated in Exhibit C for analysis.

TOPO – Task Order Project Officer.

TENTATIVELY IDENTIFIED COMPOUNDS (TIC) - Compounds detected in samples that are not target compounds, internal standards, Deuterated Monitoring Compounds (DMCs), or surrogates. Up to 30 peaks, not including those identified as alkanes (those greater than 10% of the peak area or height of the nearest internal standard) are subjected to mass spectral library searches for tentative identification.

TIME - When required to record time on any deliverable item, time shall be expressed as Military Time [i.e., a 24-hour clock (0000-2359)].

TRAFFIC REPORT/CHAIN OF CUSTODY RECORD (TR/COC) - An USEPA sample identification form filled out by the sampler, which accompanies the sample during shipment to the laboratory and is used for documenting sample identity, sample chain-of-custody, and sample receipt by the laboratory.

TWELVE-HOUR TIME PERIOD - The 12-hour time period for Gas Chromatograph/Mass Spectrometer (GC/MS) system instrument performance check, standards calibration (initial or continuing calibration), and method blank analysis begins at the moment of injection of the Decafluorotriphenylphosphine (DFTPP)or 4-Bromofluorobenzene (BFB) analysis that the laboratory submits as documentation of instrument performance. The time period ends after 12 hours have elapsed according to the system clock. For pesticide and Arocloranalyses performed by Gas Chromatography/Electron Capture Detection (GC/ECD), the 12-hour time period in the analytical sequence begins at the moment of injection of the instrument blank that precedes sample analyses, and ends after 12 hours have elapsed according to the system clock.

TUNE - Analysis of a solution containing a range of isotope masses to establish ICP-MS accuracy, resolution, and precision prior to calibration.

USEPA OSRTI ASB PROGRAM MANAGER (ASB PM) - The USEPA OSRTI ASB Official who manages the CLP.

USEPA REGIONAL CLP PROJECT OFFICER (CLP PO) - The Regional USEPA official responsible for monitoring laboratory performance and/or requesting analytical data or services from a CLP laboratory.

VALIDATED TIME OF SAMPLE RECEIPT (VTSR) - The date on which a sample is received at the Contractor’s facility, as recorded on the shipper’s delivery receipt and Traffic Report/Chain of Custody Record.

VOLATILE ORGANIC COMPOUNDS (VOCs) - Compounds amenable to analysis by the purge-and-trap technique. Used synonymously with purgeable compounds.

EXHIBIT H

FORMAT FOR ELECTRONIC DATA DELIVERABLES

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Table of Contents

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1.0 FORMAT CHARACTERISTICS

1.1 This constitutes an implementation of the Staged Electronic Data Deliverable (SEDD) based on analytical results and ancillary information required by the contract. Because this implementation is specific to the contract, not all data elements listed in the cross-program Document Type Definition (DTD) are required. This implementation is based on SEDD Specifications 5.2 and 5.0 that can be found at:

http://www.epa.gov/superfund/programs/clp/sedd-docs.htm

1.1.1 The SEDD deliverable consists of an eXtensible Markup Language (XML) file(s) compliant with the XML specification 1.0 of the World Wide Web Consortium (W3C). The deliverable must be well-formed based on the W3C XML specification and must be valid based on the DTD.

1.1.2 The Contractor shall create the deliverable using the UTF-8 (Unicode Transformation Format - 8 bit) character set.

1.1.3 The initial line of the deliverable shall be: <?xml version="1.0" encoding="UTF-8"?>.

1.1.4 The second line of the deliverable shall be a DOCTYPE line that contains the filename of the DTD. The DOCTYPE line shall be <!DOCTYPE Header SYSTEM "SEDD_5-2_GENERAL_2a_1.dtd"> or <!DOCTYPE Header SYSTEM "GENERAL_2a_1.dtd"> where "Header" denotes the name of the root element, and "SEDD_5-2_GENERAL_2a_1.dtd" (for a Specification 5.2 deliverable) or "GENERAL_2a_1.dtd" (for a Specification 5.0 deliverable) denotes the filename of the DTD.

1.1.5 The use of XML comment lines is permitted at any position in the file after the first two lines.

1.2 This implementation includes detailed specifications for the required format of the content of each data element for each fraction. The content of each data element is specified as either literal (contained in quotes) which must appear exactly as shown (without quotes), or as a variable for which descriptions and formats are listed. Exhibit H, Section 2.0 describes requirements for each data element.

1.2.1 For this implementation, numeric data elements may contain numeric digits, a decimal place, and a leading minus sign. Values without a leading minus sign are assumed to be positive. Values must be reported to the specified precision or significance.

1.2.2 The values reported by the Contractor are used for data assessment. The Contractor shall not use rounded intermediate values in calculating the final result, and no rounding shall be performed until reaching the final result.

1.2.3 The completeness of analytical data provided in the EDD will be verified against the analytical data requested on the Traffic Report/Chain of Custody (TR/COC). The laboratory code, case number, contract number, SDG number, sample number, and fraction shall be identical in the EDD and the TR/COC and the SDG coversheet submitted by the Contractor for the SDG.

1.2.4 The following variables must be present where required and correct: QC Type; instrument ID; analysis date and time; method ID; collected date; matrix; client analysis ID; client analyte ID; preparation batch; percent recovery.

2.0 DATA ELEMENTS

2.1 The Staged Electronic Data Deliverable (SEDD) consists of data elements arranged hierarchically by data nodes (parent elements). Figure 1 depicts the data node hierarchy. Each data element consists of a start tag, content, and an end tag. An element may contain other elements (child elements).

NOTE: There shall be no more than one occurrence of each child element within a node, unless the child element also behaves as a parent element. For example, in each SamplePlusMethod node, there may be only one occurrence of the element ClientSampleID, but there may be more than one occurrence of the element Analysis.

The tags, nodes, and hierarchy are specified in the Document Type Definition (DTD) against which the deliverable will be validated (see Exhibit H, Section 5.0). The frequency requirements for each of the data nodes applicable to this implementation are described below.

2.1.1 Header Node

One Header node must be reported for each fraction.

2.1.2 SamplePlusMethod Node

Each Header node must contain one SamplePlusMethod node for each field sample, field blank (including equipment and trip blanks), Performance Evaluation (PE) sample, method blank, Laboratory Control Sample (LCS), any diluted analysis of the preceding samples, any re-analyses of the preceding samples, and non-client sample analyzed.

2.1.3 ReportedResult Node

Each SamplePlusMethod node must contain a ReportedResult node for each target compound.

2.1.4 ContactInformation Node (Required for Specification 5.2 deliverables)

Each Header node must contain one ContactInformation node.

2.1.5 Analysis Node

Each SamplePlusMethod node must contain one Analysis node.

2.1.6 Analyte Node

Each Analysis node under a SamplePlusMethod node must contain one Analyte node for each target compound, Tentatively Identified Compound (TIC), and internal standard.

2.1.7 PreparationPlusCleanup Node

Each Analysis node under a SamplePlusMethod node must contain one PreparationPlusCleanup node to link the Method Blank and the LCS to the appropriate field samples.

2.1.8 Characteristic Node (Required for Specification 5.2 deliverables)

Each SamplePlusMethod and PreparationPlusCleanup node may contain one or more Characteristic nodes, one for each sample characteristic that must be reported for a sample at time of receipt, or after preparation.

2.1.9 AnalyteGroup Node (For Specification 5.2 deliverables)

Not required.

2.2 Detailed instructions for the content of each data element are provided in Tables 1 and 2. The following is an explanation of the data fields contained in each table.

2.2.1 Node and Data Elements

This field reports each node in bold text, followed by its data elements. If an entire node is not required, then none of its data elements are listed.

2.2.2 Applicability

This field reports the samples, blanks, and standards for which each node and data element is required. An "X" in a column indicates that the node or element is required. Sample refers to field samples, field blanks, PE samples and their dilutions and re-analyses unless otherwise noted. Abbreviations used in this field are defined in Table 3.

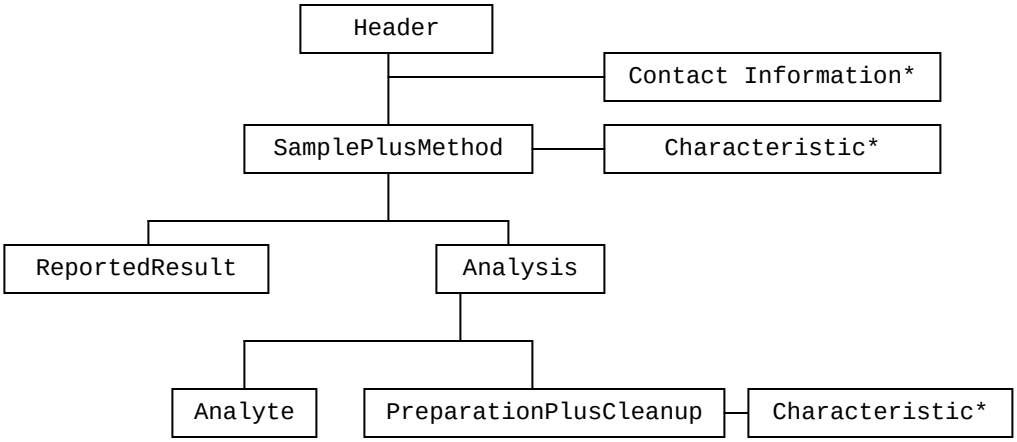

Figure 1: Data Node Hierarchy for
Level 2a Deliverable

NOTE: Data Nodes marked with "*" are required only for SEDD Version 5.2.

2.2.3 Instructions

This field describes the required format and content of each data element. The content of each data element is specified as either literal (contained in quotes), or as a variable for which description and format is listed. Abbreviations used in this field are defined in Table 3.

3.0 BATCHES

3.1 This implementation requires the use of the following batches from the Staged Electronic Data Deliverable (SEDD) Specification: "LabReportingBatch"; "PreparationBatch".

3.1.1 The "LabReportingBatch" links all samples reported in the same Sample Delivery Group (SDG). Report the SDG Number.

3.1.2 The "PreparationBatch" links samples prepared together. All samples analyzed, including method blanks and Laboratory Control Samples (LCS) that are prepared together must have the same content for the "PreparationBatch" element.

4.0 DELIVERABLE

4.1 Each Sample Delivery Group (SDG) shall be submitted as a separate compressed (zipped) file

4.2 The Contractor will utilize a designated website (provided in its Laboratory Welcome Package) to electronically submit their Electronic Data Deliverable (EDD) to the Sample Management Office (SMO). USEPA may approve alternative electronic means of file delivery. Written permission must be obtained from the USEPA Analytical Services Branch (ASB) prior to the use of any alternative means.

4.3 The Contractor must follow the delivery instructions in Exhibit B of this Statement of Work (SOW) and deliver their hardcopy and EDD to SMO concurrently. If one of these items is delivered on a later date, the Data Receipt Date (DRD) for the SDG will be the later of the two dates.

4.4 Information in the electronic deliverable must correspond to information submitted in the hardcopy raw data package and on Quality Control (QC) summary forms. If information in the raw data or on the forms is changed, the information in the electronic deliverable shall be changed accordingly. An electronic deliverable containing the changed information for the SDG shall be resubmitted along with the hardcopy at no additional cost to the USEPA.

4.5 The format for the file name shall be Case number_SDG number_contract number_submission number_DTD used_.zip. For example, the first submission of SDG number ABC12, Case number 12345, contract 68-W-0000 would be named 12345_ABC12_68-W-0000_1_SEDD_5-2_GENERAL_2a_1.zip.

5.0 DOCUMENT TYPE DEFINITION (DTD)

5.1 Introduction

The deliverable will be validated against DTD SEDD_5-2_GENERAL_2a_1 or DTD GENERAL_2a_1. The deliverable must not contain any tags not included in the DTD, and must conform to the hierarchical structure modeled in the DTD.

5.2 SEDD Specification 5.2 General Stage 2a DTD

```
<?xml version="1.0" encoding="UTF-8"?>
<!—SEDD_5-2_GENERAL_2a_1.dtd 02/01/2008 Based on SEDD Specification 5.2 -->
<!-- Acronym Description -->
<!-- EDD   - Electronic Data Deliverable -->
<!-- ID    - Identity -->
<!-- Lab   - Laboratory -->
<!-- QC    - Quality Control -->
<!-- RPD   - Relative Percent Difference -->
<!ELEMENT Header (
          ClientID|
          ClientName|
          Comment|
          DateFormat|
          EDDID|
          EDDImplementationID|
          EDDImplementationVersion|
          EDDVersion|
          GeneratingSystemID|
          GeneratingSystemVersion|
          LabContract|
          LabContractModificationDescription|
          LabContractModificationID|
          LabDataPackageID|
          LabDataPackageName|
          LabDataPackageVersion|
          LabID|
          LabName|
          LabNarrative|
          LabQualifiersDefinition|
          LabReportedDate|
          ProjectID|
          ProjectName|
          SiteID|
          SiteName|
          ContactInformation|
          SamplePlusMethod
                   )*>
<!ELEMENT Analysis (
          AliquotAmount|
          AliquotAmountUnits|
          AnalysisDuration|
          AnalysisDurationUnits|
          AnalysisGroupID|
          AnalysisType|
          Analyst|
          AnalyzedAmount|
          AnalyzedAmountUnits|
          AnalyzedDate|
```

```
                ClientAnalysisID|
                ClientMethodCode|
                ClientMethodID|
                ClientMethodModificationDescription|
                ClientMethodModificationID|
                ClientMethodName|
                ClientMethodSource|
                ClientMethodVersion|
                Column|
                ColumnInternalDiameter|
                ColumnInternalDiameterUnits|
                ColumnLength|
                ColumnLengthUnits|
                Comment|
                ConfirmationAnalysisID|
                DetectorID|
                DetectorType|
                DilutionFactor|
                Efficiency|
                HeatedPurge|
                Inclusion|
                InjectionVolume|
                InjectionVolumeUnits|
                InstrumentID|
                LabAnalysisID|
                LabFileID|
                LabID|
                LabMethodID|
                LabMethodName|
                LabName|
                MethodCode|
                MethodID|
                MethodModificationDescription|
                MethodModificationID|
                MethodName|
                MethodSource|
                MethodVersion|
                PreparationBatch|
                ProcedureID|
                ProcedureName|
                ReferenceDate|
                ResultBasis|
                Temperature|
                TemperatureUnits|
                Wavelength|
                WavelengthUnits|
                Yield|
                PreparationPlusCleanup|
                Analyte|
                AnalyteGroup
                          )*>
      <!ELEMENT AnalysisGroup (
                AnalysisGroupID|
                AnalysisType|
                Comment|
                Analyte|
                AnalyteGroup
                          )*>
```

```
<!ELEMENT Analyte (
          AnalyteGroupID|
          AnalyteName|
          AnalyteNameContext|
          AnalyteType|
          CASRegistryNumber|
          ClientAnalyteID|
          ClientAnalyteName|
          Comment|
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          DetectionLimitType|
          DetectionLimitUnits|
          DifferenceErrorRatio|
          Efficiency|
          ExpectedResult|
          ExpectedResultUnits|
          Inclusion|
          LabAnalyteID|
          LabQualifiers|
          LotNumber|
          PeakID|
          PercentRecovery|
          PercentRecoveryLimitHigh|
          PercentRecoveryLimitLow|
          PercentRecoveryLimitType|
          PercentRecoveryType|
          QuantitationLimit|
          QuantitationLimitType|
          QuantitationLimitUnits|
          ReportingLimit|
          ReportingLimitType|
          ReportingLimitUnits|
          Result|
          ResultLimitHigh|
          ResultLimitLow|
          ResultLimitType|
          ResultType|
          ResultUncertainty|
          ResultUnits|
          StandardSource|
          Wavelength|
          WavelengthUnits
                    )*>
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          AnalyteName|
          AnalyteNameContext|
          AnalyteType|
          CASRegistryNumber|
          ClientAnalyteID|
          ClientAnalyteName|
          Comment|
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          LabQualifiers|
          Result|
          ResultType|
          ResultUncertainty|
```

```
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                        )*>
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                CharacteristicUnits|
                Comment
                       )*>
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                LabAddress1|
                LabAddress2|
                LabCity|
                LabCountry|
                LabID|
                LabName|
                LabPointOfContact|
                LabPointOfContactElectronicAddress|
                LabPointOfContactTitle|
                LabPointOfContactType|
                LabState|
                LabTelephoneNumber|
                LabZipCode
                        )*>
      <!ELEMENT Handling (
                Analyst|
                ClientMethodCode|
                ClientMethodID|
                ClientMethodModificationDescription|
                ClientMethodModificationID|
                ClientMethodName|
                ClientMethodSource|
                ClientMethodVersion|
                Comment|
                HandledDate|
                HandlingBatch|
                HandlingType|
                InitialAmount|
                InitialAmountUnits|
                LabID|
                LabMethodID|
                LabMethodName|
                LabName|
                MethodCode|
                MethodID|
                MethodModificationDescription|
                MethodModificationID|
                MethodName|
                MethodSource|
                MethodVersion|
                ProcedureID|
                ProcedureName|
                SampleAmount|
                SampleAmountUnits|
                Characteristic
                        )*>
      <!ELEMENT PreparationPlusCleanup (
                AliquotAmount|
```

```
          AliquotAmountUnits|
          Analyst|
          CleanedUpDate|
          CleanupBatch|
          CleanupType|
          ClientMethodCode|
          ClientMethodID|
          ClientmethodModificationDescription|
          ClientMethodModificationID|
          ClientMethodName|
          ClientMethodSource|
          ClientMethodVersion|
          Comment|
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          FinalAmountUnits|
          InitialAmount|
          InitialAmountUnits|
          LabID|
          LabMethodID|
          LabMethodName|
          LabName|
          LotNumber|
          MethodCode|
          MethodID|
          MethodModificationDescription|
          MethodModificationID|
          MethodName|
          MethodSource|
          MethodVersion|
          PreparationBatch|
          PreparationPlusCleanupType|
          PreparationType|
          PreparedDate|
          ProcedureID|
          ProcedureName|
          Solvent|
          Characteristic
                    )*>
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          AnalyteName|
          AnalyteNameContext|
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          CASRegistryNumber|
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          ClientAnalyteName|
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          ClientDetectionLimitUnits|
          ClientQuantitationLimit|
          ClientQuantitationLimitUnits|
          Comment|
          DetectionLimit|
          DetectionLimitType|
          DetectionLimitUnits|
          DifferenceErrorRatio|
          ExpectedResult|
```

```
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                LabAnalyteID|
                LabQualifiers|
                LabResultStatus|
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                PercentDifferenceLimitLow|
                PercentDifferenceLimitType|
                PercentRecovery|
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                PercentRecoveryLimitLow|
                PercentRecoveryLimitType|
                PercentRecoveryType|
                QuantitationLimit|
                QuantitationLimitType|
                QuantitationLimitUnits|
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                ReportingLimitType|
                ReportingLimitUnits|
                Result|
                ResultLimitHigh|
                ResultLimitLow|
                ResultLimitType|
                ResultType|
                ResultUncertainty|
                ResultUnits|
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                RPD|
                RPDLimitHigh|
                RPDLimitType|
                RPDType
                            )*>
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                ClientMethodCode|
                ClientMethodID|
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                ClientMethodModificationID|
                ClientMethodName|
                ClientMethodSource|
                ClientMethodType|
                ClientMethodVersion|
                ClientName|
                ClientSampleID|
                CollectedDate|
                CollectedEndDate|
                Comment|
                Composite|
                CoolerID|
                CustodyID|
                EquipmentBatch|
                Filtered|
                LabContract|
```

```
            LabContractModificationDescription|
            LabContractModificationID|
            LabID|
            LabMethodID|
            LabMethodName|
            LabName|
            LabReceiptDate|
            LabReportingBatch|
            LabSampleID|
            LocationID|
            LocationName|
            MatrixID|
            MatrixMedium|
            MethodBatch|
            MethodCategory|
            MethodCode|
            MethodID|
            MethodLevel|
            MethodModificationDescription|
            MethodModificationID|
            MethodName|
            MethodSource|
            MethodType|
            MethodVersion|
            OriginalClientSampleID|
            OriginalLabSampleID|
            Preservative|
            ProjectID|
            ProjectName|
            QCCategory|
            QCLinkage|
            QCType|
            Quarantine|
            SamplingBatch|
            ShippingBatch|
            SiteID|
            SiteName|
            StorageBatch|
            Analysis|
            Characteristic|
            ReportedResult|
            Handling|
            AnalysisGroup
                      )*>

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<!ELEMENT AnalyteNameContext (#PCDATA)>
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```

```
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```

```
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<!ELEMENT HandlingType (#PCDATA)>
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<!ELEMENT LabDataPackageVersion (#PCDATA)>
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<!ELEMENT MethodCategory (#PCDATA)>
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<!ELEMENT MethodID (#PCDATA)>
<!ELEMENT MethodLevel (#PCDATA)>
<!ELEMENT MethodModificationDescription (#PCDATA)>
```

```
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      <!ELEMENT MethodSource (#PCDATA)>
      <!ELEMENT MethodType (#PCDATA)>
      <!ELEMENT MethodVersion (#PCDATA)>
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      <!ELEMENT OriginalLabSampleID (#PCDATA)>
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      <!ELEMENT PercentDifferenceLimitLow (#PCDATA)>
      <!ELEMENT PercentDifferenceLimitType (#PCDATA)>
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      <!ELEMENT PercentRecoveryLimitHigh (#PCDATA)>
      <!ELEMENT PercentRecoveryLimitLow (#PCDATA)>
      <!ELEMENT PercentRecoveryLimitType (#PCDATA)>
      <!ELEMENT PercentRecoveryType (#PCDATA)>
      <!ELEMENT PreparationBatch (#PCDATA)>
      <!ELEMENT PreparationPlusCleanupType (#PCDATA)>
      <!ELEMENT PreparationType (#PCDATA)>
      <!ELEMENT PreparedDate (#PCDATA)>
      <!ELEMENT Preservative (#PCDATA)>
      <!ELEMENT ProcedureID (#PCDATA)>
      <!ELEMENT ProcedureName (#PCDATA)>
      <!ELEMENT ProjectID (#PCDATA)>
      <!ELEMENT ProjectName (#PCDATA)>
      <!ELEMENT QCCategory (#PCDATA)>
      <!ELEMENT QCLinkage (#PCDATA)>
      <!ELEMENT QCType (#PCDATA)>
      <!ELEMENT QuantitationLimit (#PCDATA)>
      <!ELEMENT QuantitationLimitType (#PCDATA)>
      <!ELEMENT QuantitationLimitUnits (#PCDATA)>
      <!ELEMENT Quarantine (#PCDATA)>
      <!ELEMENT ReferenceDate (#PCDATA)>
      <!ELEMENT ReportingLimit (#PCDATA)>
      <!ELEMENT ReportingLimitType (#PCDATA)>
      <!ELEMENT ReportingLimitUnits (#PCDATA)>
      <!ELEMENT Result (#PCDATA)>
      <!ELEMENT ResultBasis (#PCDATA)>
      <!ELEMENT ResultLimitHigh (#PCDATA)>
      <!ELEMENT ResultLimitLow (#PCDATA)>
      <!ELEMENT ResultLimitType (#PCDATA)>
      <!ELEMENT ResultType (#PCDATA)>
      <!ELEEMNT ResultUncertainty (#PCDATA)>
      <!ELEMENT ResultUnits (#PCDATA)>
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      <!ELEMENT RetentionTimeUnits (#PCDATA)>
      <!ELEMENT RPD (#PCDATA)>
      <!ELEMENT RPDLimitHigh (#PCDATA)>
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      <!ELEMENT RPDType (#PCDATA)>
      <!ELEMENT SampleAmount (#PCDATA)>
      <!ELEMENT SampleAmountUnits (#PCDATA)>
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      <!ELEMENT ShippingBatch (#PCDATA)>
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      <!ELEMENT SiteName (#PCDATA)>
```

```
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<!ELEMENT StandardSource (#PCDATA)>
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<!ELEMENT Wavelength (#PCDATA)>
<!ELEMENT WavelengthUnits (#PCDATA)>
<!ELEMENT Yield (#PCDATA)>
```

5.3 SEDD Specification 5.0 General Stage 2a DTD

```
<?xml version="1.0" encoding="UTF-8"?>
<!-- GENERAL_2a_1.dtd 08/15/2003 Based on SEDD Specification Draft 5.0 -->
<!-- Acronym Description -->
<!-- EDD   - Electronic Data Deliverable -->
<!-- ID    - Identity -->
<!-- Lab   - Laboratory -->
<!-- QC    - Quality Control -->
<!-- RPD   - Relative Percent Difference -->
<!ELEMENT Header (
          EDDID|
          EDDVersion|
          EDDImplementationID|
          EDDImplementationVersion|
          GeneratingSystemID|
          GeneratingSystemVersion|
          LabDataPackageID|
          LabDataPackageName|
          LabDataPackageVersion|
          LabReportedDate|
          DateFormat|
          Comment|
          SamplePlusMethod
                  )*>
<!ELEMENT Analysis (
          AnalysisGroupID|
          AnalysisType|
          Analyst|
          AnalyzedAmount|
          AnalyzedAmountUnits|
          AnalyzedDate|
          ClientAnalysisID|
          ClientMethodID|
          Comment|
          ConfirmationAnalysisID|
          DetectorID|
          DetectorType|
          DilutionFactor|
          HeatedPurge|
          InstrumentID|
          LabAnalysisID|
          LabFileID|
          ProcedureID|
          ProcedureName|
          ResultBasis|
          PreparationPlusCleanup|
          Analyte
                   )*>
```

```
      <!ELEMENT AnalysisGroup (
               AnalysisGroupID|
               AnalysisType|
               Comment|
               Analyte
                        )*>
      <!ELEMENT Analyte (
               AnalyteName|
               AnalyteType|
               CASRegistryNumber|
               ClientAnalyteID|
               Comment|
               ExpectedResult|
               ExpectedResultUnits|
               LabQualifiers|
               PeakID|
               PercentRecovery|
               PercentRecoveryLimitHigh|
               PercentRecoveryLimitLow|
               PercentRecoveryLimitType|
               Result|
               ResultLimitHigh|
               ResultLimitLow|
               ResultLimitType|
               ResultType|
               ResultUnits
                        )*>
      <!ELEMENT Handling (
               Analyst|
               ClientMethodID|
               Comment|
               HandledDate|
               HandlingBatch|
               HandlingType|
               InitialAmount|
               InitialAmountUnits|
               ProcedureID|
               ProcedureName|
               PercentMoisture|
               PercentSolids|
               SampleAmount|
               SampleAmountUnits
                        )*>
      <!ELEMENT PreparationPlusCleanup (
               AliquotAmount|
               AliquotAmountUnits|
               Analyst|
               CleanedUpDate|
               CleanupBatch|
               CleanupType|
               ClientMethodID|
               Comment|
               FinalAmount|
               FinalAmountUnits|
               InitialAmount|
               InitialAmountUnits|
               PreparationBatch|
```

```
          PreparationType|
          PreparedDate|
          ProcedureID|
          ProcedureName
                    )*>
<!ELEMENT ReportedResult (
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          AnalyteName|
          AnalyteType|
          CASRegistryNumber|
          ClientAnalyteID|
          Comment|
          DetectionLimit|
          DetectionLimitType|
          DetectionLimitUnits|
          ExpectedResult|
          ExpectedResultUnits|
          LabAnalysisID|
          LabQualifiers|
          PeakID|
          PercentDifference|
          PercentDifferenceLimitHigh|
          PercentDifferenceLimitLow|
          PercentDifferenceLimitType|
          PercentRecovery|
          PercentRecoveryLimitHigh|
          PercentRecoveryLimitLow|
          PercentRecoveryLimitType|
          QuantitationLimit|
          QuantitationLimitType|
          QuantitationLimitUnits|
          RPD|
          RPDLimitHigh|
          RPDLimitType|
          ReportingLimit|
          ReportingLimitType|
          ReportingLimitUnits|
          Result|
          ResultLimitHigh|
          ResultLimitLow|
          ResultLimitType|
          ResultType|
          ResultUnits|
          RetentionTime|
          RetentionTimeUnits
                    )*>
<!ELEMENT SamplePlusMethod (
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          ClientMethodType|
          ClientSampleID|
          CollectedDate|
          Comment|
          Composite|
          CoolerID|
          CustodyID|
          EquipmentBatch|
          LabContract|
          LabID|
```

```
                LabName|
                LabReceiptDate|
                LabReportingBatch|
                LabSampleID|
                MatrixID|
                MethodLevel|
                MethodBatch|
                OriginalClientSampleID|
                OriginalLabSampleID|
                PercentMoisture|
                PercentSolids|
                pH|
                Preservative|
                ProjectID|
                ProjectName|
                QCCategory|
                QCLinkage|
                QCType|
                SamplingBatch|
                ShippingBatch|
                SiteID|
                SiteName|
                StorageBatch|
                Temperature|
                TemperatureUnits|
                Analysis|
                ReportedResult|
                Handling|
                AnalysisGroup
                          )*>

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      <!ELEMENT AliquotAmountUnits (#PCDATA)>
      <!ELEMENT AnalysisGroupID (#PCDATA)>
      <!ELEMENT AnalysisType (#PCDATA)>
      <!ELEMENT Analyst (#PCDATA)>
      <!ELEMENT AnalyteName (#PCDATA)>
      <!ELEMENT AnalyteType (#PCDATA)>
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      <!ELEMENT AnalyzedAmountUnits (#PCDATA)>
      <!ELEMENT AnalyzedDate (#PCDATA)>
      <!ELEMENT CASRegistryNumber (#PCDATA)>
      <!ELEMENT CleanedUpDate (#PCDATA)>
      <!ELEMENT CleanupBatch (#PCDATA)>
      <!ELEMENT CleanupType (#PCDATA)>
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```

```
<!ELEMENT DetectionLimitType (#PCDATA)>
<!ELEMENT DetectionLimitUnits (#PCDATA)>
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<!ELEMENT GeneratingSystemVersion (#PCDATA)>
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<!ELEMENT HandlingBatch (#PCDATA)>
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```

```
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      <!ELEMENT RPDLimitType (#PCDATA)>
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      <!ELEMENT ReportingLimitType (#PCDATA)>
      <!ELEMENT ReportingLimitUnits (#PCDATA)>
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      <!ELEMENT ResultBasis (#PCDATA)>
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      <!ELEMENT ResultLimitLow (#PCDATA)>
      <!ELEMENT ResultLimitType (#PCDATA)>
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      <!ELEMENT TemperatureUnits (#PCDATA)>
```

6.0 DATA ELEMENT INSTRUCTION TABLES

6.1 Specification 5.2 Stage 2a

Table 1

Air Volatiles Data Element Instructions

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
Header	X	X	X	X	
ClientID	X	X	X	X	Report "1" for Region 1, "2" for Region 2, etc. For samples received from QATS, report "91".
ClientName					Not required.
Comment					Not required.
DateFormat	X	X	X	X	Report MMDDYYYYThh:mm:ss. All dates and times reported in the EDD must follow this format. If any part of the time is unknown, report "00" for the unknown hours, minutes, and seconds.
EDDID	X	X	X	X	Report "SEDD".
EDDImplementationID	X	X	X	X	Report "SEDD_5.2_GENERAL_2a" (This is the DTD used).
EDDImplementationVersion	X	X	X	X	Report "1" (This is the version of the DTD used).
EDDVersion	X	X	X	X	Report "5.2".
GeneratingSystemID	X	X	X	X	Report name of generating software or vendor.
GeneratingSystemVersion	X	X	X	X	Report software version number.
Lab Contract	X	X	X	X	Report the Task Order number.
LabContractModificationDescription					Not required.
LabContractModificationID					Not required.
LabDataPackageID	X	X	X	X	Report the Sample Delivery Group (SDG).
LabDataPackageName	X	X	X	X	Report "VOA" or "SIM_VOA" as appropriate.
LabDataPackageVersion	X	X	X	X	Report "1", then increment with each resubmission.
LabID					Report the Agency-assigned Lab Code.
Lab Name	X	X	X	X	Report the Lab Name.
LabNarrative	X	X	X	X	Report the text of the Lab Narrative.
LabQualifiersDefinition	X	X	X	X	Use the format 'Qualifier:Definition' to report each qualifier used. Use a ';' to separate the definitions of multiple qualifiers.
LabReportedDate	X	X	X	X	Report the date this data was reported to the client.
ProjectID	X	X	X	X	Report the Case Number.
ProjectName					Not required.
SiteID					Not required.
SiteName					Not required.
SamplePlusMethod	**X**	**X**	**X**	**X**	
ClientID	X				Report "1" for Region 1, "2" for Region 2, etc. For samples received from QATS, report "91".
ClientMethodCategory					Not required.
ClientMethodCode					Not required.

Table 1

Air Volatiles Data Element Instructions (Cont.)

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
ClientMethodID	X	X	X	X	Report "SAV01.X".
ClientMethodModificationDescription					Not required.
ClientMethodModificationID	X	X	X		Report the Task Order number.
ClientMethodName					Not required.
ClientMethodSource	X	X	X	X	Report "USEPA_CLP".
ClientMethodType	X	X	X	X	Report "GC/MS".
ClientMethodVersion	X	X	X	X	Report month and year the SOW was issued.
ClientName					Not required.
ClientSampleID	X	X	X	X	Report the Sample Number.
CollectedDate	X				Report the date and time the sample was collected.
CollectedEndDate					Not required.
Comment					Not required.
Composite					Not required.
CoolerID					Not required.
CustodyID	X				Report the Traffic Report/Chain of Custody Form number.
EquipmentBatch					Not required.
Filtered					Not required.
LabContract	X	X	X		Report the Contract number.
LabContractModificationDescription					Not required.
LabContractModificationID					Not required.
LabID	X	X	X	X	Report the Agency-assigned Lab Code.
LabMethodID					Not required.
LabMethodName					Not required.
LabName	X	X	X	X	Report the Lab Name.
LabReceiptDate	X				Report the date and time the sample was received.
LabReportingBatch	X	X	X	X	Links all samples analyzed to this deliverable. Report the SDG number.
LabSampleID	X	X	X	X	Report the Lab Sample ID as assigned by the lab.
LocationID					Not required.
LocationName					Not required.
MatrixID	X	X	X	X	Report "AIR".
MatrixMedium	X	X	X	X	Report "Air”.
MethodBatch					Not required.
MethodCategory					Not required.
MethodCode					Not required.
MethodID	X	X	X	X	Report "SAV01.X".

Table 1

Air Volatiles Data Element Instructions (Cont.)

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
MethodLevel					Not required.
MethodModificationDescription					Not required.
MethodModificationID					Not required.
MethodName					Not required.
MethodSource	X	X	X	X	Report "USEPA_CLP".
MethodType	X	X	X	X	Report "GC/MS".
MethodVersion	X	X	X	X	Report month and year the SOW was issued.
OriginalClientSampleID	X				For dilutions and re-analyses, report the Sample Number of the original sample this sample was derived from.
OriginalLabSampleID					Not required.
Preservative					Not required.
ProjectID	X	X	X		Report the Case Number.
ProjectName					Not required.
QCCategory		X	X		Report "Blank" for MB; "Blank_Spike" for LCS;
QCLinkage		X	X		Report "PreparationBatch" for MB and LCS.
QCType	X	X	X		Report "Field_Sample" for field samples; "Field_Blank" for field, or equipment blanks; "PT_Sample" for PE samples; "Method_Blank" for MB; "Laboratory_Control_Sample" for LCS.
Quarantine					Not required.
SamplingBatch					Not required.
ShippingBatch					Not required.
SiteID					Not required.
SiteName					Not required.
StorageBatch					Not required.
Characteristic	**X**	**X**	**X**		
CharacteristicType	X				Report “Temperature” for temperature at time of sampling; “Pressure” for canister pressure; “Flow_Rate” for canister flow rate.
CharacteristicValue	X				Report the temperature, pressure, and flow rate as provided by the samplers.
CharacteristicUnits	X				Report units as provided by the samplers.
Comment					Not required.
ContactInformation	**X**	**X**	**X**	**X**	
LabAddress1	X	X	X	X	Report the street address of the laboratory.

Table 1

Air Volatiles Data Element Instructions (Cont.)

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
LabAddress2	X	X	X	X	If applicable, report any additional address information (e.g., suite, maildrop). Otherwise leave blank.
LabCity	X	X	X	X	Report the city in which the laboratory is located.
LabCountry	X	X	X	X	Report the country in which the laboratory is located.
LabID	X	X	X	X	Report the Agency-assigned Lab Code.
LabName	X	X	X	X	Report the Lab Name.
LabPointOfContact	X	X	X	X	Report the name of the person at the laboratory serving as the point of contact.
LabPointOfContactElectronicAddress	X	X	X	X	Report the email address of the point of contact.
LabPointOfContactTitle	X	X	X	X	Report the title of the point of contact
LabPointOfContactType					Not required.
LabState	X	X	X	X	Report the state or province in which the laboratory is located.
LabTelephoneNumber	X	X	X	X	Report the 10-digit phone number for the laboratory.
LabZipCode	X	X	X	X	Report the ZIP or postal code.
Analysis	X	X	X	X	
AliquotAmount					Not required.
AliquotAmountUnits					Not required.
AnalysisDuration					Not required.
AnalysisDurationUnits					Not required.
AnalysisGroupID					Not required.
AnalysisType	X	X	X		Report "Initial", "Dilution-01", or "Reanalysis-01", then increment as necessary.
Analyst	X	X	X		Report the Analyst’s initials.
AnalyzedAmount					Not required.
AnalyzedAmountUnits					Not required.
AnalyzedDate	X	X	X	X	Report the date and time the sample was analyzed.
ClientAnalysisID					Not required.
ClientMethodCode					Not required.
ClientMethodID	X	X	X	X	Report "SAV01.X".
ClientMethodModificationDescription					Not required.
ClientMethodModificationID					Not required.
ClientMethodName					Not required.
ClientMethodSource	X	X	X	X	Report "USEPA_CLP".
ClientMethodVersion	X	X	X	X	Report month and year the SOW was issued.
Column	X	X	X		Report the column used.
ColumnInternalDiameter	X	X	X		Report the internal diameter in mm.
ColumnInternalDiameterUnits	X	X	X		Report “mm”.
ColumnLength	X	X	X		Report the length in meters .

Table 1

Air Volatiles Data Element Instructions (Cont.)

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
ColumnLengthUnits	X	X	X		Report “m”.
Comment					Not required.
ConfirmationAnalysisID					Not required.
DetectorID					Not required.
DetectorType					Not required.
DilutionFactor	X	X	X		Report the Dilution Factor used to the nearest tenth. Report "1.0" when no dilutions are used.
Efficiency					Not required.
HeatedPurge					Not required.
Inclusion					Not required.
InjectionVolume					Not required.
InjectionVolumeUnits					Not required.
InstrumentID	X	X	X	X	Report the laboratory identifier for the instrument used for this analysis.
LabAnalysisID	X	X	X	X	Report a unique identifier.
LabFileID	X	X	X	X	Report the lab file ID.
LabID					Not required.
LabMethodID					Not required.
LabMethodName					Not required.
LabName					Not required.
MethodCode					Not required.
MethodID	X	X	X	X	Report "SAV01.X".
MethodModificationDescription					Not required.
MethodModificationID					Not required.
MethodName					Not required.
MethodSource	X	X	X	X	Report "USEPA_CLP".
MethodVersion	X	X	X	X	Report month and year the SOW was issued.
PreparationBatch					Not required.
ProcedureID					Not required.
ProcedureName					Not required.
ReferenceDate					Not required.
ResultBasis					Not required.
Temperature					Not required.
TemperatureUnits					Not required.
WaveLength					Not required.
WaveLengthUnits					Not required.
Yield					Not required.
AnalysisGroup					**Not required.**

Table 1

Air Volatiles Data Element Instructions (Cont.)

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
Handling					Not required.
ReportedResult	X	X	X		
AnalysisGroupID					Not required.
AnalyteGroupID					Not required.
AnalyteName	X	X	X		Report analytes as they appear in the CAS Registry.
AnalyteNameContext	X	X	X		Report "CAS".
AnalyteType	X	X	X		Report "Target" for all target compounds.
CASRegistryNumber	X	X	X		Report CAS Numbers as they appear in the SOW.
ClientAnalyteID	X	X	X		Report CAS number.
ClientAnalyteName	X	X	X		Report analytes as they appear in the SOW.
ClientDetectionLimit					Not required.
ClientDetectionLimitUnits					Not required.
ClientQuantitationLimit	X	X	X		Report the CRQL.
ClientQuantitationLimitUnits	X	X	X		Report "ppbv”.
Comment					Not required.
DetectionLimit	X	X	X		Report the Method Detection Limit (MDL) adjusted for dilution to two significant figures.
DetectionLimitType	X	X	X		Report "MDL_sa ".
DetectionLimitUnits	X	X	X		Report "ppbv”.
DifferenceErrorRatio					Not required.
ExpectedResult		X			Report the true value for LCS.
ExpectedResultUnits		X			Report "ppbv”.
LabAnalysisID	X	X	X		Report the unique identifier from the analysis this reported result was derived from.
LabAnalyteID					Not required.
LabQualifiers	X	X	X		Report flags as specified in the SOW.
LabResultStatus					Not required.
PeakID					Not required.
PercentDifference					Not required.
PercentDifferenceLimitHigh					Not required.
PercentDifferenceLimitLow					Not required.
PercentDifferenceLimitType					Not required.
PercentRecovery		X			Report the Percent Recovery.
PercentRecoveryLimitHigh		X			Report the upper limit for the Percent Recovery.
PercentRecoveryLimitLow		X			Report the lower limit for the Percent Recovery.
PercentRecoveryLimitType		X			Report "Method".
PercentRecoveryType					Not required.

Table 1

Air Volatiles Data Element Instructions (Cont.)

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
QuantitationLimit	X	X	X		Report the CRQL adjusted for dilution to two significant figures.
QuantitationLimitType	X	X	X		Report "CRQL_sa".
QuantitationLimitUnits	X	X	X		Report "ppbv”.
ReportingLimit					Not required.
ReportingLimitType					Not required.
ReportingLimitUnits					Not required.
Result	X	X	X		Report the final calculated result for detects that meet all technical acceptance criteria.
ResultLimitHigh					Not required.
ResultLimitLow					Not required.
ResultLimitType					Not required.
ResultType	X	X	X		Report "=" for all detected analytes that meet technical acceptance criteria. Report "Not_Detected" for non-detects.
ResultUncertainty					Not required.
ResultUnits	X	X	X		Report "ppbv”.
RetentionTime	X	X	X		Report the retention time in decimal minutes for all detects that meet all technical acceptance criteria.
RetentionTimeUnits	X	X	X		Report "Minutes".
RPD					Not required.
RPDLimitHigh					Not required.
RPDLimitType					Not required.
RPDType					Not required.
PreparationPlusCleanup	X	X	X		
AliquotAmount	X	X	X		Report the amount pulled through the trap in liters or milliliters.
AliquotAmountUnits	X	X	X		Report "L” or “mL".
Analyst	X	X	X		Report the Analyst’s initials.
CleanedUpDate					Not required.
CleanUpBatch					Not required.
CleanUpType					Not required.
ClientMethodCode					Not required.
ClientMethodID					Not required.

Table 1

Air Volatiles Data Element Instructions (Cont.)

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
ClientMethodModificationDescription					Not required.
ClientMethodModificationID					Not required.
ClientMethodName					Not required.
ClientMethodSource	X	X	X		Report "USEPA_CLP".
ClientMethodVersion	X	X	X		Report month and year the SOW was issued.
Comment					Not required.
FinalAmount					Not required.
FinalAmountUnits					Not required.
InitialAmount					Not required.
InitialAmountUnits					Not required.
LabID					Not required.
LabMethodID					Not required.
LabMethodName					Not required.
LabName					Not required.
LotNumber					Not required.
MethodCode					Not required.
MethodID	X	X	X		Report "SAV01.X".
MethodModificationDescription					Not required.
MethodModificationID					Not required.
MethodName					Not required.
MethodSource	X	X	X		Report "USEPA_CLP".
MethodVersion	X	X	X		Report month and year the SOW was issued.
PreparationBatch	X	X	X		Links all samples to their MB and LCS. Report a unique identifier for each batch.
PreparationPlusCleanupType	X	X	X		Report "Preparation".
PreparationType					Not required.
PreparedDate	X	X	X		Report the date and time the sample was pulled through the trap.
ProcedureID					Not required.
ProcedureName					Not required.
Solvent					Not required.
Analyte	X	X	X		
AnalyteGroupID					Not required.
AnalyteName	X	X	X		Report analytes as they appear in the CAS registry.
AnalyteNameContext	X	X	X		Report "CAS".

Table 1

Air Volatiles Data Element Instructions (Cont.)

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
AnalyteType	X	X	X		Report "Target" for all target compounds, "Internal_Standard" for internal standards, and "TIC" for tentatively identified compounds.
CASRegistryNumber	X	X	X		Report the CAS Number as it appears in the SOW.
ClientAnalyteID	X	X	X		Report CAS number.
ClientAnalyteName	X	X	X		Report the analytes as they appear in the SOW.
Comment					Not required.
DetectionLimit	X	X	X		Report the Method Detection Limit (MDL).
DetectionLimitType	X	X	X		Report "MDL".
DetectionLimitUnits	X	X	X		Report "ppbv”.
DifferenceErrorRatio					Not required.
Efficiency					Not required.
ExpectedResult	X	X	X		Report the concentration of internal standards added.
ExpectedResultUnits	X	X	X		Report "ppbv”.
Inclusion					Not required.
LabAnalyteID					Not required.
LabQualifiers	X	X	X		Report qualifiers as specified in the SOW.
LotNumber	X	X	X		Report the vendor/manufacturer assigned lot number for this internal standard.
PeakID					Not required.
PercentRecovery					Not required.
PercentRecoveryLimitHigh					Not required.
PercentRecoveryLimitLow					Not required.
PercentRecoveryLimitType					Not required.
PercentRecoveryType					Not required.
QuantitationLimit	X	X	X		Report the CRQL.
QuantitationLimitType	X	X	X		Report "CRQL".
QuantitationLimitUnits	X	X	X		Report "ppbv”.
ReportingLimit					Not required.
ReportingLimitType					Not required.
ReportingLimitUnits					Not required.
Result	X	X	X		For targets and TICs, report the final calculated result.
ResultLimitHigh					Not required.
ResultLimitLow					Not required.
ResultLimitType					Not required.

Table 1

Air Volatiles Data Element Instructions (Cont.)

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
ResultType	X	X	X		Report "=" for all detected analytes that meet technical acceptance criteria, "Not_Detected" for non-detects.
ResultUncertainty					Not required.
ResultUnits	X	X	X		Report "ppbv”.
StandardSource	X	X	X		Report the vendor/manufacturer for this standard.
Wavelength					Not required.
WavelengthUnits					Not required.
AnalyteGroup					Not required

Table 2

Air Volatiles Data Element Instructions

6.2 SEDD Specification 5.0 Stage 2a

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
Header	**X**	**X**	**X**	**X**	
Comment					Not required.
DateFormat	X	X	X	X	Report MMDDYYYYThh:mm:ss. All dates and times reported in the EDD must follow this format. If any part of the time is unknown, report "00" for the unknown hours, minutes, and seconds.
EDDID	X	X	X	X	Report "SEDD".
EDDImplementationID	X	X	X	X	Report "GENERAL_2a" (This is the DTD used).
EDDImplementationVersion	X	X	X	X	Report "1" (This is the version of the DTD used).
EDDVersion	X	X	X	X	Report "5.0".
GeneratingSystemID	X	X	X	X	Report name of generating software or vendor.
GeneratingSystemVersion	X	X	X	X	Report software version number.
LabDataPackageID	X	X	X	X	Report the Sample Delivery Group (SDG).
LabDataPackageName	X	X	X	X	Report "VOA" or "VOA_SIM".
LabDataPackageVersion	X	X	X	X	Report "1", then increment with each resubmission.
LabReportedDate	X	X	X	X	Report the date this data was reported to the client.
SamplePlusMethod	**X**	**X**	**X**	**X**	
ClientMethodID	X	X	X	X	Report "SAV01.X".
ClientSampleID	X	X	X	X	Report the Sample Number.
CollectedDate	X				Report the date and time the sample was collected.
Comment					Not required.
Composite					Not required.
CoolerID					Not required.
CustodyID	X				Report the Traffic Report/Chain of Custody Form number.
EquipmentBatch					Not required.
LabContract	X	X	X		Report the Contract number.
LabID	X	X	X	X	Report the Agency-assigned Lab Code.
LabName	X	X	X	X	Report the Lab Name.
LabReceiptDate	X				Report the date and time the sample was received.
LabReportingBatch	X	X	X	X	Links all samples analyzed to this deliverable. Report the SDG number.
LabSampleID	X	X	X	X	Report the Lab Sample ID as assigned by the lab.
MatrixID	X	X	X	X	Report "AIR".
MethodBatch					Not required.
MethodLevel					Not required.
OriginalClientSampleID	X				For dilutions and re-analyses, report the Sample Number of the original sample this sample was derived from.
OriginalLabSampleID					Not required.
PercentMoisture					Not required.

Table 2

Air Volatiles Data Element Instructions (Cont.)

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
PercentSolids					Not required.
pH					Not required.
Preservative					Not required.
ProjectID	X	X	X		Report the Case Number.
ProjectName					Not required.
QCCategory		X	X		Report "Blank" for MB; "Blank_Spike" for LCS;
QCLinkage		X	X		Report "PreparationBatch" for MB and LCS.
QCType	X	X	X		Report "Field_Sample" for field samples; "Field_Blank" for field, equipment, or trip blanks; "PT_Sample" for Performance Evaluation Samples; "Method_Blank" for MB; "Laboratory_Control_Sample" for LCS.
SamplingBatch					Not required.
ShippingBatch					Not required.
SiteID					Not required.
SiteName					Not required.
StorageBatch					Not required.
Temperature	X				Report the temperature at the time of sample collection as provided by the sampler.
TemperatureUnits	X				Report as provided by sampler.
Analysis	X	X	X	X	
AnalysisGroupID					Not required.
AnalysisType	X	X	X		Report "Initial", "Dilution-01", or "Reanalysis-01", then increment as necessary.
Analyst	X	X	X		Report the Analyst’s initials.
AnalyzedAmount					Not required.
AnalyzedAmountUnits					Not required.
AnalyzedDate	X	X	X	X	Report the date and time the sample was analyzed.
ClientAnalysisID					Not required.
ClientMethodID	X	X	X	X	Report "SAV01.X".
Comment					Not required.
ConfirmationAnalysisID					Not required.
DetectorID					Not required.
DetectorType					Not required.
DilutionFactor	X	X	X		Report the Dilution Factor used to the nearest tenth. Report "1.0" when no dilutions are used.
HeatedPurge					Not required.
InstrumentID	X	X	X	X	Report the laboratory identifier for the instrument used for this analysis.
LabAnalysisID	X	X	X	X	Report a unique identifier.
LabFileID	X	X	X	X	Report the Lab File ID.
ProcedureID					Not required.

Table 2

Air Volatiles Data Element Instructions (Cont.)

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
ProcedureName					Not required.
ResultBasis					Not required.
AnalysisGroup					Not required.
Handling					Not required.
ReportedResult	X	X	X		
AnalysisGroupID					Not required.
AnalyteName	X	X	X		Report analytes as they appear in the CAS Registry.
AnalyteType	X	X	X		Report "Target" for all target compounds.
CASRegistryNumber	X	X	X		Report CAS Numbers as they appear in the SOW.
ClientAnalyteID	X	X	X		Report CAS number.
Comment					Not required.
DetectionLimit	X	X	X		Report the Method Detection Limit (MDL)adjusted for dilutiono to two significant figures.
DetectionLimitType	X	X	X		Report "MDL_sa".
DetectionLimitUnits	X	X	X		Report "ppbv.
ExpectedResult		X			Report the true value for LCS.
ExpectedResultUnits		X			Report "ppbv”.
LabAnalysisID	X	X	X		Report the unique identifier from the analysis this reported result was derived from.
LabQualifiers	X	X	X		Report flags as specified in the SOW.
PeakID					Not required.
PercentDifference					Not required.
PercentDifferenceLimitHigh					Not required.
PercentDifferenceLimitLow					Not required.
PercentDifferenceLimitType					Not required.
PercentRecovery		X			Report the Percent Recovery.
PercentRecoveryLimitHigh		X			Report the upper limit for the Percent Recovery.
PercentRecoveryLimitLow		X			Report the lower limit for the Percent Recovery.
PercentRecoveryLimitType		X			Report "Method".
QuantitationLimit	X	X	X		Report the CRQL adjusted for dilution to two significant figures.
QuantitationLimitType	X	X	X		Report "CRQL_sa".
QuantitationLimitUnits	X	X	X		Report "ppbv”.
ReportingLimit					Not required.
ReportingLimitType					Not required.
ReportingLimitUnits					Not required.

Table 2

Air Volatiles Data Element Instructions (Cont.)

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
Result	X	X	X		Report the final calculated result for detects that meet all technical acceptance criteria.
ResultLimitHigh					Not required.
ResultLimitLow					Not required.
ResultLimitType					Not required.
ResultType	X	X	X		Report "=" for all detected analytes that meet technical acceptance criteria. Report "Not_Detected" for non-detects.
ResultUnits	X	X	X		Report "ppbv”.
RetentionTime	X	X	X		Report the retention time in decimal minutes for all detects that meet all technical acceptance criteria.
RetentionTimeUnits	X	X	X		Report "Minutes".
RPD					Not required.
RPDLimitHigh					Not required.
RPDLimitType					Not required.
PreparationPlusCleanup	X	X	X		
AliquotAmount	X	X	X		Report the amount pulled throughthe trap in liters or milliliters.
AliquotAmountUnits	X	X	X		Report "L" or “mL”.
Analyst	X	X	X		Report the Analyst’s initials.
CleanedUpDate					Not required.
CleanUpBatch					Not required.
CleanUpType					Not required.
ClientMethodID					Not required.
Comment					Not required.
FinalAmount					Not required.
FinalAmountUnits					Not required.
InitialAmount					Not required.
InitialAmountUnits					Not required.
PreparationBatch	X	X	X		Links all samples to their MB and LCS. Report a unique identifier for each batch.
PreparationType					Not required.
PreparedDate	X	X	X		Report the date and time the sample was pulled throughthe trap.
ProcedureID					Not required.
ProcedureName					Not required.

Table 2

Air Volatiles Data Element Instructions (Cont.)

Node and Data Elements	Sample	LCS	MB	NCS	Instructions
Analyte	X	X	X		
AnalyteName	X	X	X		Report analytes as they appear in the SOW.
AnalyteType	X	X	X		Report "Target" for all target compounds, "Internal_Standard" for internal standards, and “TIC" for tentatively identified compounds.
CASRegistryNumber	X	X	X		Report the CAS Number as it appears in the SOW.
ClientAnalyteID	X	X	X		Report CAS number.
Comment					Not required.
ExpectedResult	X	X	X		Report the concentration of internal standards added.
ExpectedResultUnits	X	X	X		Report "ppbv".
LabQualifiers	X	X	X		Report qualifiers as specified in the SOW.
PeakID					Not required.
PercentRecovery					Not required.
PercentRecoveryLimitHigh					Not required.
PercentRecoveryLimitLow					Not required.
PercentRecoveryLimitType					Not required.
Result	X	X	X		For targets and TICs, report the final calculated result.
ResultLimitHigh					Not required.
ResultLimitLow					Not required.
ResultLimitType					Not required.
ResultType	X	X	X		Report "=" for all detected analytes that meet technical acceptance criteria, "Not_Detected" for non-detects.
ResultUnits	X	X	X		Report "ppbv".

Table 3

Abbreviations Used in the Instructions

Abbreviation	Definition
C	Celsius
CAS	Chemical Abstracts Service
CRQL	Contract Required Quantitation Limit
DTD	Document Type Definition
EDD	Electronic Data Deliverable
EDL	Estimated Detection Limit
EMPC	Estimated Maximum Possible Concentration
ID	Identifier
Lab	Laboratory
LCS	Laboratory Control Sample
MB	Method Blank
NCS	Non-Client (ZZZZZZ) Sample
PE	Performance Evaluation
QC	Quality Control

EXHIBIT E

QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES AND REQUIREMENTS

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Exhibit E - Quality Assurance/Quality Control Procedures and Requirements

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1.0 OVERVIEW

Quality Assurance (QA) and Quality Control (QC) are integral parts of the U.S. Environmental Protection Agency's (USEPA) Contract Laboratory Program (CLP). The QA process consists of management review and oversight at the planning, implementation, and completion stages of the environmental data collection activity, and ensures that data provided are of the quality required. The QC process includes those activities required during data collection to produce the data quality desired and to document the quality of the collected data.

1.1 Quality Assurance/Quality Control (QA/QC) Activities

During the planning of an environmental data collection program, QA activities focus on defining data quality criteria and designing a QC system to measure the quality of data being generated. During the implementation of the data collection effort, QA activities ensure that the QC system is functioning effectively, and that the deficiencies uncovered by the QC system are corrected. After environmental data are collected, QA activities focus on assessing the quality of data obtained to determine its suitability to support enforcement or remedial decisions.

1.1.1

This exhibit describes the overall QA/QC operations and the processes by which the CLP meets the QA/QC objectives defined above. The contract requires a variety of QA/QC activities. These contract requirements are the minimum QC operations necessary to satisfy the analytical requirements associated with the determination of the different compounds. These QC operations are designed to facilitate laboratory comparison by providing USEPA with comparable data from all Contractors. These requirements do not release the analytical Contractor from maintaining their own QC checks on method and instrument performance.

1.2 Incentives/Sanctions

The Contractor may anticipate incentives by <u>consistently</u> providing the following: (1) high quality, technically sound data, as stipulated by the contract; (2) on-time or early delivery of the Sample Delivery Group (SDG) Cover Sheet; (3) above average Quarterly Blind (QB) Performance Evaluation (PE) sample scores; (4) electronic deliverables that pass the initial Contract Compliance Screening (CCS) acceptance criteria; and (5) SDGs delivered on-time. Samples are distributed routinely to Contractors based on the quality of work performed, as measured by the Performance Scheduling Algorithm (PSA) (as stated in the contract). A Contractor that consistently meets the contract performance requirements as highlighted above, will earn a higher PSA score, thereby increasing the likelihood of receiving samples for analyses. If the Contractor fails to meet the requirements set forth in this Statement of Work (SOW) or elsewhere in the contract, USEPA may take, but is not limited to, the following actions (as stated in the contract): reduction in the number of samples sent under the contract; suspension of sample shipments; data package audit(s); electronic data audit(s); on-site laboratory evaluation(s); and/or remedial PE sample(s).

2.0 INTRODUCTION

Appropriate use of data generated under the large range of analytical conditions encountered in environmental analyses requires reliance on the Quality Control (QC) procedures and criteria incorporated into the analytical methods. The methods in the contract have been validated on samples typical of those received by the laboratories in the Contract Laboratory Program (CLP). However, the validation of these methods does not guarantee that they perform equally well for all sample matrices encountered. Inaccuracies can also result from causes other than unanticipated matrix effects, such as sampling artifacts, equipment malfunctions, contamination, and operator error. Therefore, the QC component of each method is indispensable.

The data acquired from QC procedures are used to estimate and evaluate the information content of analytical results and to determine the necessity for, or the effect of, corrective action procedures. The parameters used to estimate information content include precision, accuracy, detection limit, and other quantitative and qualitative indicators. In addition, QC procedures give an overview of the activities required in an integrated program to generate data of known and documented quality required to meet defined objectives.

2.1 Quality Assurance/Quality Control (QA/QC) Program Components

2.1.1 The necessary components of a complete QA/QC program include internal QC criteria that demonstrate acceptable levels of performance, as determined by QA review. External review of data and procedures is accomplished by the monitoring activities of the USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB), Regional data users, the Sample Management Office (SMO), and the Quality Assurance Technical Support (QATS) Laboratory. Each external review accomplishes a different purpose. These reviews are described in specific sections of this exhibit. Laboratory evaluation samples, electronic data audits, and data packages provide an external QA reference for the program. A Contractor on-site evaluation system is also part of the external QA monitoring. A feedback loop provides the results of the various review functions to the Contractors through direct communication with the USEPA Regional CLP Project Officer (CLP PO).

2.1.2 This exhibit does not provide specific instructions for constructing QA Plans (QAPs), QC systems, or a QA organization. It is, however, an explanation of the QA/QC requirements of the Statement of Work (SOW). It outlines some minimum standards for QA/QC programs. It also includes specific items that are required in a QAP and by the QA/QC documentation detailed in the contract. Delivery of this documentation provides USEPA with a complete data package which will stand alone, and limits the need for contact with the Contractor or with an analyst, at a later date, if some aspect of the analysis is questioned.

2.1.3 To assure the product delivered by the Contractor meets the requirements of the contract, and to improve interlaboratory data comparison, the Contractor shall:

- Prepare and adhere to a written QAP, the elements of which are defined in Section 5;
- Prepare and adhere to QA/QC Standard Operating Procedures (SOPs), as described in Section 6;

- Adhere to the analytical methods in Exhibit D and associated QC requirements specified within Exhibit E;

- Verify and document analytical standards and retain documentation of the purity of neat materials, as well as the purity and accuracy of solutions obtained from private chemical supply houses;

- Submit all raw data and required documentation for Regional review;

- Submit results of all analyzed laboratory evaluation samples, including adherence to corrective action procedures;

- Submit, upon request, instrument data tapes and applicable documentation for tape audits, including a copy of the Sample Data Package;

- Submit on-site laboratory evaluations, and adhere to corrective action procedures; and

- Submit all original documentation generated during sample analyses for USEPA review.

3.0 GENERAL QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) REQUIREMENTS

The Contractor shall adhere to USEPA's Good Laboratory Practices for laboratory cleanliness with regard to glassware and apparatus. The Contractor shall also adhere to good laboratory practices with regard to reagents, solvents, and gases. For additional guidelines regarding these general laboratory procedures, see the Handbook for Analytical Quality Control in Water and Wastewater Laboratories USEPA-600/4-79-019, USEPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, September 1982.

4.0 SPECIFIC QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) PROCEDURES

4.1 Purpose

4.1.1 The purpose of this document is to provide a uniform set of procedures for the analysis of organic constituents of samples, documentation of methods and their performance, and verification of the sample data generated. Although it is impossible to address all analytical situations in one document, this exhibit defines the minimum requirements for all major steps relevant to any organic analysis.

4.1.2 The primary function of the Contract Laboratory Program (CLP) QA/QC program is the definition of procedures for the evaluation and documentation of analytical methodologies, and the reduction and reporting of data. The objective is to provide a uniform basis for sample handling, instrument and methods maintenance, performance evaluation, and analytical data gathering and reporting. In many instances where methodologies are available, specific QC procedures are incorporated into the method documentation (Exhibit D).

4.1.3 The QA/QC procedures defined herein shall be used by the Contractor when performing the methods specified in Exhibit D. When additional QA/QC procedures are specified in Exhibit D, the Contractor shall follow those procedures, in addition to the procedures specified in this Exhibit.

4.2 Laboratory Audit and Intercomparison Study Program

The Contractor is required to participate in the Laboratory Audit and Intercomparison Study Program run by USEPA. The Contractor can expect to analyze at least two Performance Evaluation (PE) samples per calendar quarter during the contract period for organic analyses.

4.3 Annual Verification of Method Detection Limits (MDLs)

The Contractor shall perform and report annual verification of MDLs by the method specified in Exhibit D (by type, matrix, and model for each instrument used on the contract) to Sample Management Office (SMO), Quality Assurance Technical Support (QATS), and the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) as specified in Exhibit B. All the MDLs shall meet the requirements specified in Exhibit C and Exhibit D.

4.4 Quality Assurance/Quality Control (QA/QC) Measurements

4.4.1 In this Exhibit, as well as other places within this Statement of Work (SOW), the term "analytical sample" discusses the required frequency or placement of certain QA/QC measurements. The term "analytical sample" includes all field samples, including PE samples, received from an external source. It also includes all required QA/QC samples [requested Matrix Spike and Matrix Spike Duplicate(s) (MS/MSD)] except those directly related to instrument calibration or calibration verification (calibration standards, Initial Calibration, Continuing Calibration, and tunes).

4.4.2 In order for the QA/QC information to reflect the status of the samples analyzed, all samples and their associated QA/QC analysis shall be analyzed under the same analytical operating and procedural conditions.

4.4.3 If any QC measurement fails to meet contract criteria, the analytical measurement must not be repeated prior to taking the appropriate corrective action, as specified in Exhibit D.

4.4.4 The Contractor shall report all QC data in the exact format specified in Exhibits B and H.

4.4.5 In addition, the Contractor shall establish a QA program with the objective of providing sound analytical chemical measurements. This program shall incorporate the QC procedures, any necessary corrective action, and all documentation required during data collection, as well as the quality assessment measures performed by management to ensure acceptable data production.

5.0 QUALITY ASSURANCE PLAN (QAP)

5.1 Introduction

The Contractor shall establish a Quality Assurance (QA) program with the objective of providing sound analytical chemical measurements. This program shall incorporate the Quality Control (QC) procedures, any necessary corrective action, and all documentation required during data collection as well as the quality assessment measures performed by management to ensure acceptable data production. The Contractor shall follow the USEPA EPA Requirements for Quality Management Plans (QA/R-2). An electronic version can be found at: http://www.epa.gov/quality1/qa_docs.html.

5.1.1 The Contractor shall prepare a written QAP that describes the procedures that are implemented to achieve the following:

- Maintain data integrity, validity, and usability;
- Ensure that analytical measurement systems are maintained in an acceptable state of stability and reproducibility;
- Detect problems through data assessment and establish corrective action procedures that keep the analytical process reliable; and
- Document all aspects of the measurement process to provide data that are technically sound and legally defensible.

5.1.2 The QAP shall present, in specific terms, the policies, organization, objectives, functional guidelines, and specific QA/QC activities designed to achieve the data quality requirements in the contract. Where applicable, Standard Operating Procedures (SOPs) pertaining to each element shall be included or referenced as part of the QAP. The QAP shall be paginated consecutively in ascending order. The QAP shall be available during on-site laboratory evaluations and shall be submitted to the designee within 7 days of written request by the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) or USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB) Organic Program Manager (PM). Additional information relevant to the preparation of a QAP can be found in USEPA and American Society for Testing and Materials (ASTM) publications.

5.2 Required Elements of a Quality Assurance Plan (QAP)

The required elements of a laboratory's QAP are outlined in this section. This outline should be used as a framework for developing the QAP.

A. Organization and Personnel

1. QA Policy and Objectives (the mission and quality policy of the organization)

2. QA Management (the specific roles, authorities, and responsibilities of management and staff with respect to QA and QC activities)

   a. Organization

   b. Assignment of QA/QC Responsibilities

   c. Reporting Relationships (the means by which effective communications with personnel actually performing the work are assured)

   d. QA Document Control Procedures

   e. QA Program Assessment Procedures (the process used to plan, implement, and assess the work performed)

3. Key Personnel (Laboratory Personnel Involved in QA and QC Activities)

   a. Résumés

   b. Education and Experience Pertinent to the contract

   c. Training Records and Progress

B. Facilities and Equipment

1. Instrumentation and Backup Alternatives

2. Maintenance Activities and Schedules

C. Document Control

1. Laboratory Notebook Policy

2. Sample Tracking/Custody Procedures

3. Logbook Maintenance and Archiving Procedures

4. Sample Delivery Group (SDG) File Organization, Preparation, and Review Procedures

5. Procedures for Preparation, Approval, Review, Revision, and Distribution of SOPs

6. Process for Revision of Technical or Documentation Procedures

D. Analytical Methodology

1. Calibration Procedures and Frequency

2. Sample Preparation/Extraction Procedures

3. Sample Analysis Procedures

4. Standards Preparation Procedures

5. Decision Processes, Procedures, and Responsibility for Initiation of Corrective Action

E. Data Generation

1. Data Collection Procedures

2. Data Reduction Procedures

3. Data Validation Procedures

4. Data Reporting and Authorization Procedures

F. Quality Control (QC)

1. Solvent, Reagent, and Adsorbent Check Analysis

2. Reference Material Analysis

3. Internal QC Checks

4. Corrective Action and Determination of QC Limit Procedures

5. Responsibility Designation

G. Quality Assurance (QA) (the process which measures the effectiveness of QA will be established and how frequently effectiveness will be measured)

1. Data QA

2. Systems/Internal Audits

3. Performance/External Audits

4. Corrective Action Procedures (the continual improvement based on lessons learned from previous experience)

5. QA Reporting Procedures

6. Responsibility Designation

5.3 Updating and Submitting the Quality Assurance Plan (QAP)

5.3.1 Initial Submission. During the contract solicitation process, the Contractor is required to submit their QAP to the USEPA Contracting Officer (CO). Within 60 days after contract award, the Contractor shall maintain, on file at their facility, a revised QAP that is fully compliant with the requirements of the contract. The Contractor shall maintain the QAP on file at the Contractor's facility for the term of the contract. The revised QAP will become the official QAP under the contract and may be used during legal proceedings. Both the initial QAP submission and the revised QAP shall be paginated consecutively in ascending order. The revised QAP shall include:

- Changes resulting from (1) the Contractor's internal review of their organization, personnel, facility, equipment, policy, and procedures and, (2) the Contractor's implementation of the requirements of the contract, and

- Changes resulting from USEPA's review of the laboratory evaluation sample data, bidder-supplied documentation, and recommendations made during the pre-award on-site laboratory evaluation.

5.3.1.1 The Contractor shall send a copy of the latest version of the QAP within 7 days of a request from the USEPA Regional CLP PO or the USEPA OSRTI ASB PM. The USEPA requestor will designate the recipients.

5.3.2 Subsequent Updates and Submissions. During the term of the contract, the Contractor shall amend the QAP when the following circumstances occur:

- USEPA modifies the technical requirements of the Statement of Work (SOW) or the contract;
- USEPA notifies the Contractor of deficiencies in the QAP documentation;
- USEPA notifies the Contractor of deficiencies resulting from USEPA's review of the Contractor's performance;
- The Contractor identifies deficiencies resulting from their internal review of the QAP documentation;
- The Contractor's organization, personnel, facility, equipment, policy, or procedures change; or
- The Contractor identifies deficiencies resulting from the internal review of changes in their organization, personnel, facility, equipment, policy, or procedures.

5.3.2.1 The Contractor shall amend the QAP within 14 days of when the circumstances listed in Section 5.3, result in a discrepancy between what was previously described in the QAP and what is presently occurring at the Contractor's facility. When the QAP is amended, all changes in the QAP shall be clearly marked (e.g., a bar in the margin indicating where the change is found in the document, highlighting the change by underlining the change, bold printing the change, or using a different print font) and a copy is sent to the USEPA Regional CLP PO and Quality Assurance Technical Support (QATS). The amended pages shall have the date on which the changes were implemented. The Contractor shall incorporate all amendments to the latest version of the QAP document. The Contractor shall archive all amendments to the QAP document for future reference by USEPA.

5.3.2.2 The Contractor shall send a copy of the latest version of the QAP document within 7 days of a written request from USEPA Regional CLP PO or the USEPA OSRTI ASB Organic PM. The USEPA requestor will designate the recipients.

5.4 Incentives/Sanctions

The Contractor shall amend the QAP as specified within this section. The QAP describes the policies and procedures for ensuring that work processes, products, or services satisfy expectations or specifications in the contract. Failure to comply with the requirements of this section may result in sanctions, as described in the contract.

6.0 STANDARD OPERATING PROCEDURES (SOPs)

6.1 Introduction

To obtain reliable results, adherence to prescribed analytical methodology is imperative. In any operation that is performed on a repetitive basis, reproducibility is best accomplished through the use of SOPs. As defined by USEPA, an SOP is a written document that provides directions for the step-by-step execution of an operation, analysis, or action which is commonly accepted as the method for performing certain routine or repetitive tasks. The Contractor shall follow the USEPA Guideline for Preparing Standard Operating Procedures (SOPs) (QA/G-6). An electronic version can be found at: http://www.epa.gov/quality1/qa_docs.html.

6.1.1 SOPs prepared by the Contractor shall be functional (i.e., clear, comprehensive, up-to-date, and sufficiently detailed to permit duplication of results by qualified analysts). The SOPs shall be paginated consecutively, in ascending order.

6.1.2 All SOPs shall reflect activities as they are currently performed by the Contractor. In addition, all SOPs shall be:

- Consistent with current USEPA regulations, guidelines, and the Contract Laboratory Program (CLP) contract's requirements.
- Consistent with instrument manufacturers' specific instruction manuals.
- Available to USEPA during an on-site laboratory evaluation. A complete set of SOPs shall be bound together and available for inspection at such evaluations. During on-site laboratory evaluations, laboratory personnel shall demonstrate the application of the SOPs if requested.
- Available to the designated recipients within 7 days, upon request by the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) or USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB) Organic Program Manager (PM).
- Capable of providing for the development of documentation that is sufficiently complete to record the performance of all tasks required by the protocol.
- Capable of demonstrating the validity of data reported by the Contractor and explaining the cause of missing or inconsistent results.
- Capable of describing the corrective measures and feedback mechanism utilized when analytical results do not meet protocol requirements.
- Reviewed regularly and updated as necessary when contract, facility, or Contractor procedural modifications are made.
- Archived for future reference in usability or evidentiary situations.
- Available at specific work stations as appropriate.

- Subject to a document control procedure that precludes the use of outdated or inappropriate SOPs.

- Reviewed and signed by all Contractor personnel performing action identified in the SOP.

6.2 Format

The format for SOPs may vary depending upon the type of activity for which they are prepared; however, at a minimum, the following sections shall be included:

- Title page;
- Document Control;
- Scope and Applicability;
- Summary of Method;
- Definitions (acronyms, abbreviations, and specialized forms used in the SOP);
- Health and Safety;
- Personnel Qualifications;
- Interferences;
- Apparatus and Materials (list or specify, also note designated locations where found);
- Handling and Preservation;
- Instrument or Method Calibration;
- Sample Preparation and Analysis;
- Data Calculations;
- Procedures;
- Quality Control (QC) limits;
- Corrective action procedures, including procedures for secondary review of information being generated;
- Documentation description and example forms;
- Data Management and Records Management;
- Miscellaneous notes and precautions; and
- References.

6.3 Required SOPs

The Contractor shall maintain the following SOPs:

6.3.1 Evidentiary SOPs for required chain-of-custody and document control, as discussed in Exhibit F.

6.3.2 Sample receipt and storage

- Sample receipt and identification logbooks;
- Refrigerator temperature logbooks;
- Extract storage logbooks; and
- Security precautions.

6.3.3 Sample Preparation

- Reagent purity check procedures and documentation;
- Extraction procedures;
- Extraction bench sheets; and
- Extraction logbook maintenance.

6.3.4 Glassware Cleaning

6.3.5 Calibration (Balances, etc.)

- Procedures;
- Frequency requirements;
- Preventative maintenance schedule and procedures;
- Acceptance criteria and corrective actions; and
- Logbook maintenance authorization.

6.3.6 Analytical Procedures [for each analytical system, including Gel Permeation Chromatography (GPC)]

- Instrument performance specifications;
- Instrumental operating procedures;
- Data acquisition system operation;
- Procedures when automatic quantitation algorithms are overridden;
- QC required parameters;
- Analytical run/injection logbooks; and
- Instrumental error and editing flag descriptions and resulting corrective actions.

6.3.7 Maintenance Activities (for each analytical system, including GPC)

- Preventative maintenance schedule and procedures;
- Corrective maintenance determinants and procedures; and
- Maintenance authorization.

6.3.8 Analytical Standards

- Standard coding/identification and inventory system;
- Standards preparation logbook(s);
- Standards preparation procedures;
- Procedures for equivalency/traceability analyses and documentation;
- Purity logbook (primary standards and solvents);
- Storage, replacement, and labeling requirements; and
- QC and corrective action measures.

6.3.9 Data Reduction Procedures

- Data processing systems operation;
- Outlier identification methods;
- Identification of data requiring corrective action; and
- Procedures for format and/or forms for each operation.

6.3.10 Documentation Policy/Procedures

- Contractor/analysts' notebook policy, including review policy;
- Complete Sample Delivery Group (SDG) File (CSF) contents;
- CSF organization and assembly procedures, including review policy; and
- Document inventory procedures, including review policy.

6.3.11 Data Validation/Self-Inspection Procedures

- Data flow and chain-of-command for data review;
- Procedures for measuring precision and accuracy;
- Evaluation parameters for identifying systematic errors;
- Procedures to ensure that hardcopy and electronic deliverables are complete and compliant with the requirements in Exhibits B and H;
- Procedures to ensure that hardcopy deliverables are in agreement with their comparable electronic deliverables;
- Demonstration of internal Quality Assurance (QA) inspection procedure [demonstrated by supervisory sign-off on personal notebooks, internal Performance Evaluation (PE) samples, etc.];
- Frequency and type of internal audits (e.g., random, quarterly, spot checks, perceived trouble areas);

- Demonstration of problem identification, corrective actions, and resumption of analytical processing; sequence resulting from internal audit (i.e., QA feedback); and

- Documentation of audit reports (internal and external), audit response, corrective action, etc.

6.3.12 Data Management and Handling

- Procedures for controlling and estimating data entry errors;

- Procedures for reviewing changes to data and deliverables and ensuring traceability of updates;

- Life Cycle Management (LCM) procedures for testing, modifying, and implementing changes to existing computing systems including hardware, software, and documentation or installing new systems;

- Database security, backup, and archival procedures including recovery from system failures;

- System maintenance procedures and response time;

- Individual(s) responsible for system operation, maintenance, data integrity, and security;

- Specifications for staff training procedures;

- Storage, retrieval, and verification of the completeness and readability of Gas Chromatograph/Mass Spectrometer (GC/MS) and GC/ECD files transferred to electronic media; and

- Virus protection procedures for software and electronic deliverables.

6.4 Updating and Submitting SOPs

6.4.1 Initial Submission. During the contract solicitation process, the Contractor is required to submit their SOPs to the USEPA Contracting Officer (CO). Within 60 days after contract award, the Contractor shall prepare and maintain on file, at their facility, a complete, revised set of SOPs that are fully compliant with the requirements of the contract. The revised SOPs will become the official SOPs under the contract and may be used during legal proceedings. The Contractor shall maintain the complete set of SOPs on file at the Contractor's facility for the term of the contract. Both the initial submission of SOPs and the revised SOPs shall be dated and paginated consecutively in ascending order. The revised SOPs shall include:

- Changes resulting from (1) the Contractor's internal review of their procedures, and (2) the Contractor's implementation of the requirements of the contract, and

- Changes resulting from USEPA's review of the laboratory evaluation sample data, bidder-supplied documentation, and recommendations made during the pre-award on-site laboratory evaluation.

6.4.1.1 The Contractor shall send a complete set of the latest version of SOPs or individually requested SOPs within 7 days of a request from the USEPA Regional CLP PO or the USEPA OSRTI ASB Organic PM. The USEPA requestor will designate the recipients.

6.4.2 Subsequent Updates and Submissions. During the term of the contract, the Contractor shall amend the SOPs when the following circumstances occur:

- USEPA modifies the technical requirements of the Statement of Work (SOW) or the contract;
- USEPA notifies the Contractor of deficiencies in their SOP documentation;
- USEPA notifies the Contractor of deficiencies resulting from USEPA's review of the Contractor's performance;
- The Contractor's procedures change;
- The Contractor identifies deficiencies resulting from internal review of the SOPs documentation; or
- The Contractor identifies deficiencies resulting from internal review of the procedures.

6.4.2.1 Existing SOPs shall be amended or new SOPs shall be written within 14 days of when the circumstances listed in Section 6.4, result in a discrepancy between what was previously described in the SOPs and what is presently occurring at the Contractor's facility. All changes in the SOPs shall be clearly marked (e.g., a bar in the margin indicating where the change is found in the document, highlighting the change by underlining the change, bold printing the change, or using a different print font) and a copy is sent to the USEPA Regional CLP PO and Quality Assurance Technical Support (QATS). The amended/new SOPs shall have the date on which the changes were implemented.

6.4.2.2 When existing SOPs are amended or new SOPs are written, the Contractor shall document the reason(s) for the change, and maintain the amended SOPs or new SOPs on-file at the laboratory facility. Documentation of the reason(s) for the change shall be maintained on file with the amended SOPs or new SOPs.

6.4.2.3 The Contractor shall send a complete set of the latest version of SOPs or individually requested SOPs within 7 days of a request from the USEPA Regional CLP PO or the USEPA OSRTI ASB Organic PM. The USEPA requestor will designate the recipients.

6.5 Incentives/Sanctions

The Contractor shall amend SOPs as specified within this section. The SOPs specify analytical procedures in greater detail than appear in Exhibit D. Adherence to these requirements will ensure that the procedures are conducted in a standard, reliable, and reproducible process as described in this SOW. Failure to comply with the requirements specified herein may result in sanctions, as described in the contract.

7.0 ANALYTICAL STANDARDS REQUIREMENTS

7.1 Overview

USEPA will not supply analytical reference standards either for direct analytical measurements or for the purpose of traceability. All Contractors shall be required to prepare from neat materials or purchase from private chemical supply houses those standards necessary to successfully and accurately perform the analyses required in this protocol.

7.2 Preparation of Chemical Standards from the Neat High Purity Bulk Material

7.2.1 If a Contractor cannot obtain analytical reference standards, the Contractor may prepare their own chemical standards. Contractors shall obtain the highest purity possible when purchasing neat chemical standards. When standards are purchased at less than 97% purity, the Contractor shall document the reason why a higher purity could not be obtained.

7.2.2 If required by the manufacturer, the chemical standards shall be kept sealed and refrigerated when not being used in the preparation of standard solutions. Proper storage of chemicals is essential to safeguard them from decomposition.

7.2.3 The purity of a compound can sometimes be misrepresented by a chemical supply house. Since knowledge of purity is needed to calculate the concentration of solute in a solution standard, it is the Contractor's responsibility to have analytical documentation proving the purity of each compound is correctly stated. Purity confirmation, when performed, should use either differential scanning calorimetry, Gas Chromatography with Flame Ionization Detection (GC/FID), High Performance Liquid Chromatography (HPLC), Infrared (IR) spectrometry, or other appropriate techniques. Use of two or more independent methods is recommended. The correction factor for impurity when weighing neat materials in the preparation of solution standards is:

EQ. 1 Weight of Impure Compound

$$\text{weight of impure compound} = \frac{\text{weight of pure compound}}{(\text{percent purity} / 100)}$$

Where "weight of pure compound" is that required to prepare a specific volume of a standard solution at a specified concentration.

7.2.4 When compound purity is assayed to be 97% or greater, the weight may be used without correction to calculate the concentration of the stock standard. If the compound purity is assayed to be less than 97%, the weight shall be corrected when calculating the concentration of the stock solution.

7.2.5 Mis-identification of compounds occasionally occurs and it is possible that a mis-labeled compound may be received from a chemical supply house. It is the Contractor's responsibility to have analytical documentation ascertaining that all compounds used in the preparation of solution standards are correctly identified.

Identification confirmation, when performed, shall use Gas Chromatography/Mass Spectrometry (GC/MS) analysis on at least two different analytical columns, or other appropriate techniques.

7.2.6 Calculate the weight of material to be weighed out for a specified volume, taking into account the purity of the compound and the desired concentration. A second person shall verify the accuracy of the calculations. Check balances for accuracy with a set of standard weights every 12 hours. All weighing shall be performed on an analytical balance to the nearest 0.1 mg and verified by a second person. The solvent used to dissolve the solute shall be compatible with the protocol in which the standard is to be used; the solute shall be soluble, stable, and nonreactive with the solvent. In the case of a multicomponent solution, the components must not react with each other.

7.2.7 Transfer the solute to a volumetric flask and dilute to the specified solution volume with solvent after ensuring dissolution of the solute in the solvent. Sonication or warming may be performed to promote dissolution of the solute. This solution shall be called the primary standard and all subsequent dilutions shall be traceable back to the primary standard.

7.2.8 Log notebooks shall be kept for all weighing and dilutions. All subsequent dilutions from the primary standard and the calculations for determining their concentrations shall be recorded and verified by a second person. All solution standards shall be refrigerated, if required, when not in use. All solution standards shall be clearly labeled as to the identity of the compound or compounds, the standard ID number of the solution, concentration, date prepared, solvent, expiration date of the solution, special storage requirements (if any), and initials of the preparer.

7.3 Purchase of Chemical Standards Already in Solution

Solutions of analytical reference standards can be purchased by Contractors provided the solutions meet the following criteria.

7.3.1 Contractors shall maintain the following documentation to verify the integrity of the standard solutions:

- Mass spectral identification confirmation of the solution,
- Purity confirmation of the solution, and
- Chromatographic and quantitative documentation that the solution standard was Quality Control (QC) checked according to the following section.

7.3.2 The quality of reference standards purchased shall be demonstrated statistically and analytically by a method of the supplier's choice. One way this may be demonstrated is to prepare and analyze three solutions: a high standard, a low standard, and a standard at the target concentration (Sections 7.3.2.1 and 7.3.2.2). The Contractor shall have documentation to demonstrate that the analytical results for the high standard and low standard are consistent with the difference in theoretical concentrations. This is done by the Student's t-test in Section 7.3.2.4. If this is achieved, the Contractor shall then demonstrate that the concentration of the target standard lies midway between the concentrations of the low and high standards. This is done by the Student's t-test in Section 7.3.2.5. The standard is then certified to be within 10% of the

target concentration using the equations in Section 7.3.2.6. If this procedure is used, the Contractor shall document that the following have been achieved.

7.3.2.1 Two solutions of identical concentration shall be prepared independently from neat materials. An aliquot of the first solution shall be diluted to the intended concentration (the "target standard"). One aliquot is taken from the second solution and diluted to a concentration 10% greater than the target standard. This is called the "high standard". One further aliquot is taken from the second solution and diluted to a concentration 10% less that the target standard. This is called the "low standard".

7.3.2.2 Six replicate analyses of each standard (a total of 18 analyses) shall be performed in the following sequence: low standard; target standard; high standard; low standard; target standard; high standard; etc.

7.3.2.3 The mean and variance of the six results for each solution shall be calculated.

EQ. 2 Mean

$$\text{Mean} = \frac{\sum_{i=1}^{6} Y_i}{6}$$

EQ. 3 Variance

$$\frac{\sum_{i=0}^{6} Y_i^2 - 6(\text{MEAN})^2}{5}$$

The values Y_i represent the results of the six analyses of each standard. The means of the low, target, and high standards are designated M_1, M_2, and M_3, respectively. The variances of the low, target, and high standards are designated V_1, V_2, and V_3, respectively. Additionally, a pooled variance, V_p, is calculated.

EQ. 4 Pooled Variance

$$V_p = \frac{\frac{V_1}{0.81} + V_2 + \frac{V_3}{1.21}}{3}$$

If the square root of V_p is less than 1% of M_2, then $M_2^2/10{,}000$ shall be used as the value of V_p in all subsequent calculations.

7.3.2.4 The test statistic shall be calculated.

EQ. 5 Low and High Standard Test Statistic

$$\text{Test Statistic} = \frac{\left| \frac{M_3}{1.1} - \frac{M_1}{0.9} \right|}{\sqrt{\frac{V_p}{3}}}$$

If the test statistic exceeds 2.13, then the supplier has failed to demonstrate a 20% difference between the high and low standards. In such a case, the standards are not acceptable.

7.3.2.5 EQ. 6 Target Standard Test Statistic

$$\text{Test Statistic} = \frac{\left| M_2 - \frac{M_1}{1.8} - \frac{M_3}{2.2} \right|}{\sqrt{\frac{V_p}{4}}}$$

If the test statistic exceeds 2.13, then the target standard concentration has not been demonstrated to be midway between the high and low standards. In such a case, the standards are not acceptable.

7.3.2.6 The 95% confidence intervals for the mean result of each standard shall be calculated.

EQ. 7 Low Standard Interval

$$\text{Interval for Low Standard} = M_1 \pm 2.13\sqrt{\frac{V_p}{6}}$$

EQ. 8 Target Standard Interval

$$\text{Interval for Target Standard} = M_2 \pm 2.13\sqrt{\frac{V_p}{6}}$$

EQ. 9 High Standard Interval

$$\text{Interval for High Standard} = M_3 \pm 2.13\sqrt{\frac{V_p}{6}}$$

7.3.2.6.1 These intervals shall not overlap. If overlap is observed, the ability to discriminate the 10% difference in concentrations has not been demonstrated. In such a case, the standards are not acceptable.

7.3.2.6.2 In any event, the Contractor is responsible for the quality of the standards employed for analyses under the contract.

7.4 Documentation of the Verification and Preparation of Chemical Standards

It is the responsibility of each Contractor to maintain the necessary documentation to show that the chemical standards they have used in the performance of Contract Laboratory Program (CLP) analyses conform to the requirements previously listed.

7.4.1 Weighing logbooks, calculations, chromatograms, mass spectra, etc., whether produced by the Contractor or purchased from chemical supply houses, shall be maintained by the Contractor and may be subject to review during on-site laboratory evaluations. In those cases where the documentation is supportive of the analytical results of data packages sent to USEPA, such documentation is to be kept on file by the Contractor for a period of one year.

7.4.2 Upon request by the USEPA Regional CLP Project Officer (CLP PO), the Contractor shall submit, to the designated recipients, their most recent previous year's (12 months) documentation for the verification and preparation of chemical standards within 14 days of receipt of the request.

7.4.3 USEPA will periodically generate a report discussing deficiencies in the Contractor's documentation for the verification and preparation of chemical standards or may discuss the deficiencies during an on-site laboratory evaluation. In a detailed letter to the USEPA Regional CLP PO and CLP Quality Assurance (QA) Coordinator, the Contractor shall address the deficiencies and the subsequent corrective action implemented by the Contractor to correct the deficiencies within 14 days of receipt of the report or the on-site laboratory evaluation.

7.4.4 If new Standard Operating Procedures (SOPs) are required to be written or if existing SOPs are required to be rewritten or amended because of deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section 6.

7.5 Incentives/Sanctions

The Contractor shall obtain the highest purity possible when purchasing chemical standards specified within this section. The use of high purity standards will ensure a more accurate identification and quantitation of analytes described in the Statement of Work (SOW). Failure to meet the requirements set forth in this section may result in sanctions, as described in the contract.

8.0 CONTRACT COMPLIANCE SCREENING (CCS)

8.1 Overview

8.1.1 CCS is one aspect of the Government's contractual right of inspection of analytical data. CCS examines the Contractor's adherence to the contract requirements based on the Sample Data Package delivered to USEPA.

8.1.2 CCS is performed by the Sample Management Office (SMO) under the direction of USEPA. To assure a uniform review, a set of standardized procedures has been developed to evaluate the Sample Data Package submitted by a Contractor against the technical and completeness requirements of the contract. USEPA reserves the right to add and/or delete individual checks.

8.2 CCS Results

CCS results are distributed to the Contractor and all other data recipients. The Contractor has 6 business days to correct deficiencies. The Contractor shall send all corrections to the Regional client and SMO within 6 business days. CCS results are used in conjunction with other information to measure overall Contractor performance and to take appropriate actions to correct deficiencies in performance.

8.3 CCS Trend Report

USEPA will periodically generate a CCS trend report that summarizes CCS results over a given period of time. USEPA will send the CCS trend report or discuss the CCS trend report during an on-site laboratory evaluation. In a detailed letter to the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) and the USEPA Contracting Officer (CO), the Contractor shall address the deficiencies and the subsequent corrective action implemented by the Contractor to correct the deficiencies within 14 days of receipt of the report or the on-site laboratory evaluation.

8.4 Incentives/Sanctions

If new Standard Operating Procedures (SOPs) are required to be written, or if existing SOPs are required to be rewritten or amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section 6.

The Contractor shall correct deficiencies and resubmit the data within six business days, as specified within this section. Resubmission and correction of the data will ensure that the end user is reviewing contractually compliant data described in the Statement of Work (SOW). Correct resubmission of the data may also result in a reduction in overall sanctions. Specific details on incentives can be found in the contract. If the Contractor fails to adhere to the requirements listed in this section, the Contractor will be in noncompliance with the contract and may be subjected to sanctions, as described in the contract.

9.0 REGIONAL DATA REVIEW

9.1 Overview

Contractor data are generated to meet the specific needs of the USEPA Regions. In order to verify the usability of data for the intended purpose, each Region reviews data from the perspective of the end user, based upon functional guidelines for data review that have been developed jointly by the Regions and the USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB). Each Region uses these guidelines as the basis for data evaluation. Individual Regions may augment the basic guideline review process with additional review based on Region-specific or site-specific concerns. Regional reviews, like the sites under investigation, vary based on the nature of the problems under investigation and the Regional response appropriate to the specific circumstances.

9.1.1 Regional data reviews, relating usability of the data to a specific site, are part of the collective assessment process. They complement the review performed by the Sample Management Office (SMO), which is designed to identify contractual discrepancies, and the review performed by USEPA OSRTI ASB, which is designed to evaluate Contractor and method performance. These individual evaluations are integrated into a collective review that is necessary for Program and Contractor administration and management and may be used to take appropriate action to correct deficiencies in the Contractor's performance.

10.0 PROFICIENCY TESTING

As a means of measuring and evaluating both the Contractor’s and the method’s analytical performance, the Contractor must participate in USEPA’s Proficiency Testing Program. USEPA’s Proficiency Testing Program involves the analysis of Case-specific Performance Evaluation (PE) samples and Quarterly Blind (QB) Audits. The Contractor’s analytical PE samples and QB results will be used by USEPA to assess and verify the Contractor’s continuing ability to produce acceptable analytical data in accordance with the contractual requirements. The Contractor must receive a passing score of 75% to be in compliance with the contract.

10.1 Performance Evaluation (PE) Samples

10.1.1 The PE sample(s) may be scheduled with the Contractor as frequently as on an Sample Delivery Group (SDG)-by-SDG basis. The PE samples may be sent either by the Regional Client or the USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB). PE samples will assist USEPA in monitoring Contractor performance.

10.1.2 PE samples will be provided as either single-blinds (recognizable as a PE sample but of unknown composition), or as double-blinds (not recognizable as a PE sample and of unknown composition). The Contractor will not be informed of either the compounds or the concentrations in the PE samples.

10.1.3 The Contractor may receive the PE samples as either full volume samples or ampulated/bottled concentrates from USEPA or a designated USEPA Contractor. The PE samples shall come with instructions concerning the unique preparation procedures, if any, required to reconstitute the PE samples (i.e., the required dilution of the PE sample concentrate). **PE samples are to be extracted and/or analyzed**

with the rest of the routine samples in the SDG. The Contractor shall prepare and analyze the PE sample using the procedure described in the sample preparation and method analysis sections of Exhibit D. All contract required Quality Control (QC) shall also be met. The PE sample results are to be submitted in the SDG deliverable package per normal reporting procedures detailed in Exhibit B. If these requirements are not met, the Region may reject all the data associated with the SDG.

10.1.4 In addition to PE sample preparation and analysis, the Contractor shall be responsible for correctly identifying and quantitating the analytes included in each PE sample. When PE sample results are received by USEPA, the PE sample results will be evaluated for correct analytical identification and quantitation. The PE sample evaluation will be provided to the Contractor via coded evaluation sheets, by compound. USEPA will notify the Contractor of unacceptable performance. USEPA reserves the right to adjust the PE sample acceptance windows in order to compensate for any unanticipated difficulties with a particular PE sample.

10.2 Quarterly Blind (QB) Audits

10.2.1 A QB Audit is a unique analytical Case containing only PE samples (i.e., referred to as QB samples). The QB samples will be scheduled by USEPA OSRTI ASB through the Sample Management Office (SMO). QB samples assist USEPA in monitoring Contractor performance.

10.2.2 QB samples will be provided as single-blinds (recognizable as a PE sample but of unknown composition). The Contractor will not be informed of either the compounds or the concentrations in the PE samples.

10.2.3 The Contractor may receive the QB samples as either full volume samples or ampulated/bottled concentrates from USEPA or a designated USEPA Contractor. The QB samples shall come with instructions concerning the unique preparation procedures, if any, required to reconstitute the QB samples (i.e., the required dilution of the QB sample concentrate). The Contractor shall prepare and analyze the QB samples using the procedure described in the sample preparation and method analysis sections of Exhibit D. All contract required QC shall also be met. The QB sample results are to be submitted in the SDG deliverable package per normal reporting procedures detailed in Exhibit B.

10.2.4 In addition to QB sample preparation and analysis, the Contractor shall be responsible for correctly identifying and quantitating the compounds included in each QB sample. When QB sample results are received by USEPA, the QB sample results will be scored for correct analytical identification and quantitation. The QB sample scoring will be provided to the Contractor via coded evaluation sheets, by compound. USEPA will notify the Contractor of unacceptable performance. The Contractor's QB sample performance will be assessed into one of the following three categories:

10.2.4.1 **Acceptable, No Response Required**: Score greater than or equal to 90%. The data meets most or all of the scoring criteria. No response is required.

10.2.4.2 **Acceptable, Response Explaining Deficiencies Required**: Score greater than or equal to 75%, but less than 90%. Deficiencies exist in the Contractor's performance. Corrective action response required.

10.2.4.3 **Unacceptable Performance, Response Explaining Deficiencies Required:** Score less than 75%. Corrective action response required.

10.2.5 In the case of Section 10.2.4.2 or 10.2.4.3, the Contractor shall describe the deficiency(ies) and the action(s) taken to correct the deficiency(ies) in a corrective action letter to the USEPA Contracting Officer (CO), USEPA Regional Contract Laboratory Program Project Officer (CLP PO), and the CLP Quality Assurance (QA) Coordinator within 14 days of receipt of notification from USEPA.

10.2.6 In the case of Section 10.2.4.2 or 10.2.4.3, if new Standard Operating Procedures (SOPs) are required to be written, or if existing SOPs are required to be rewritten or amended because of deficiencies and subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section 6.

10.2.7 The Contractor shall be notified by the USEPA CO concerning agreement or disagreement with the proposed remedy for unacceptable performance.

10.2.8 A Remedial QB Audit is a unique analytical Case containing only QB samples. A Remedial QB Audit may be scheduled by USEPA OSRTI ASB with the Contractor(s) for any of the following reasons: unacceptable PE sample performance; unacceptable QB sample performance; and/or major change in the laboratory (e.g., relocation, new owner, or high turn-over of key personnel). Sections 10.2.2 through 10.2.7 apply to the Remedial QB Audit process.

10.3 Incentives/Sanctions

The Contractor shall analyze PE and QB samples and provide acceptable analytical results in accordance with the contractual requirements as described in this section. If the Contractor fails to adhere to the requirements listed in this section, the Contractor will be in noncompliance with the contract and may be subjected to sanctions, as described in the contract.

11.0 ELECTRONIC DATA QUALITY ASSURANCE (QA) MONITORING AUDITS

11.1 Overview

Periodically, USEPA requests the instrument electronic data from Contractors for a specific Case to perform electronic data audits. Generally, electronic data submissions and audits are requested for the following reasons.

- Program overview;
- Indication of data quality problems;
- Support for on-site audits; and
- Specific Regional requests.

11.1.1 Depending upon the reason for an audit, the instrument electronic data from a recent Case, a specific Case, or a Performance Evaluation (PE) sample may be requested. Electronic data audits provide a mechanism to assess adherence to contractual requirements and to ensure the consistency of data reported on the hardcopy/electronic deliverables with that generated on analytical instruments. This function provides external monitoring of Program Quality Control (QC) requirements and checks adherence of the Contractor to internal QA procedures. In addition, electronic data audits enable USEPA to evaluate the utility, precision, and accuracy of the analytical methods.

11.1.2 The Contractor shall store <u>all</u> raw and processed electronic analytical data in appropriate instrument manufacturer's format, uncompressed, and with no security codes. The data shall include all necessary data files for a complete reconstruction of the previously submitted hardcopy and electronic deliverable data package. All associated raw data files in the instrument manufacturer proprietary software format must be submitted if those files contain data or instrumental parameters regarding any analysis and/or correction applied to an instrument or analytical result. This instrument electronic data shall include data for all samples and all QC samples, including but not limited to: blanks; Matrix Spike and Matrix Spike Duplicates (MS/MSDs); Laboratory Control Samples (LCSs); initial calibrations; continuing calibrations; calibration verification standards, including resolution check samples and Performance Evaluation Mixtures (PEMs), Gel Permeation Chromatography (GPC), single component and multicomponent and Florisil cartridge check samples and associated calibrations; and instrument performance check solutions [4-Bromofluorobenzene (BFB) and decafluorotriphenylphosphine (DFTPP)] as well as all Contractor-generated spectral libraries and quantitation reports required to generate the data package. In addition, the Contractor shall supply raw data for the Method Detection Limit (MDL) studies and values for the year in which the Sample Delivery Group (SDG) was analyzed. The Contractor shall maintain a written reference logbook of data files of the EPA Sample Number, calibration data, standards, blanks, and MS/MSDs. The logbook shall include EPA Sample Numbers, and standard and blank IDs, identified by Case and SDG.

11.1.3 The Contractor is required to retain the instrument electronic data for 3 years after submission of the reconciled Complete SDG File (CSF). Electronic media shipped to the USEPA designated recipient must be fully usable by the recipient. Diskettes must be MS-DOS formatted, 3.5-inch, high density, 1.44 MB and tapes must be either 4

mm or 8 mm. Alternative means for delivery of electronic data may be utilized by the Contractor upon prior written approval from USEPA. When submitting electronic instrument data to USEPA, the following materials shall be delivered in response to the request.

11.1.3.1 All associated raw data files for all analytical samples, all QC samples, blanks, MS/MSDs, initial calibrations, continuing calibrations, calibration verification standards, including resolution check samples and PE mixtures, GPC single component and multicomponent Florisil cartridge check samples and associated calibrations, and instrument performance check solutions (BFB and DFTPP).

11.1.3.2 All processed data files and quantitation output files associated with the raw data files described in Section 11.1.3.1.

11.1.3.3 All associated identifications and calculation files (method files) used to generate the data submitted in the data package. This includes, but is not limited to, results files, acquisition files, calibration files, and method files.

11.1.3.4 All Contractor-generated Mass Spectral library files (NIST/EPA/NIH and/or Wiley, or equivalent, library <u>not</u> required).

11.1.3.5 A copy of the Contractor's reference logbook relating data files to EPA Sample Number, BFB or DFTPP, calibration data, standards, blanks, and MS/MSDs. The logbook shall include EPA Sample Numbers and laboratory file identifiers for all samples, blanks, and standards, identified by Case and SDG.

11.1.3.6 A printout of the directory of all files in each directory, including all subdirectories and the files contained therein.

11.1.3.7 A copy (hardcopy) of the completed Sample Data Package.

11.1.3.8 A statement attesting to the completeness of the electronic instrument data submission, signed and dated by the Contractor's Laboratory Manager. The Contractor shall also provide a statement attesting that the data reported have not been altered in any way. These statements shall be part of a cover sheet that includes the following information relevant to the data tape submission:

- Contractor name;
- Date of submission;
- Case Number;
- SDG Number;
- Instrument make and model number;
- Instrument operating software name and version;
- Data software name and version used for acquisition, re-quantitation, and hardcopy/report generation;
- Data system computer;
- System operating software;
- Data system network;

- Data backup software;
- Data backup hardware;
- Data analysis software;
- Media type and volume of data (in MB) backed up; and
- Names and telephone numbers of two Contractor contacts for further information regarding the submission.

11.2 Submission of the Instrument Electronic Data

Upon request of the USEPA Regional Contract Laboratory Program Project Officer (CLP PO), the Contractor shall send the required instrument electronic data and all necessary documentation to the USEPA designated recipient [e.g., Quality Assurance Technical Support (QATS)] within 7 days of notification.

11.3 Responding to the Electronic Data Audit Report

After completion of the electronic data audit, USEPA may send a copy of the electronic data audit report to the Contractor or may discuss the electronic data audit report at an on-site laboratory evaluation. In a detailed letter to the USEPA Regional CLP PO, the Contractor shall discuss the corrective actions implemented to resolve the deficiencies listed in the electronic data audit report within 14 days of receipt of the report or on-site laboratory evaluation.

11.3.1 If new Standard Operating Procedures (SOPs) are required to be written or if existing SOPs are required to be rewritten or amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section 6.

11.4 Incentives/Sanctions

The Contractor shall submit to electronic data audits and adhere to the requirements specified in this section. Resubmission and correction of electronic data will ensure that the end user is reviewing contractually compliant data described in the Statement of Work (SOW). If the Contractor fails to adhere to the requirements listed in this section, the Contractor will be in noncompliance with the contract and may be subjected to sanctions, as described in the contract.

12.0 DATA PACKAGE AUDITS

12.1 Overview

Data package audits are performed by USEPA for program overview and specific Regional concerns. Standardized procedures have been established to assure uniformity of the auditing process. Data packages are periodically selected from recently received Cases. They are evaluated for the technical quality of hardcopy raw data, Quality Assurance (QA), and adherence to contractual requirements. This function provides external monitoring of program Quality Control (QC) requirements. Data package audits are used to assess the technical quality of the data and evaluate overall Contractor performance. Audits provide USEPA with an in-depth inspection and evaluation of the Sample Data Package with regard to achieving QA/QC acceptability. A thorough review of the raw data is completed, including: all instrument readouts used for the sample results; instrument printouts; quantitation reports; chromatograms; spectra; library searches and other documentation for deviations from the contractual requirements; a check for transcription and calculation errors; a review of the qualifications of the Contractor personnel involved with the Case; and a review of the latest version of all Standard Operating Procedures (SOPs) on file.

12.2 Responding to the Data Package Audit Report

12.2.1 After completing the data package audit, USEPA will send a copy of the data package audit report to the Contractor or discuss the data package audit report on an on-site laboratory evaluation. In a detailed letter to the USEPA Regional Contract Laboratory Program Project Officer (CLP PO), the Contractor shall discuss the corrective actions implemented to resolve the deficiencies listed in the data package audit report within 14 days of receipt of the report.

12.2.2 An alternate delivery schedule may be proposed by the Contractor, but it is the sole decision of USEPA, represented either by the USEPA Regional CLP PO or the USEPA Contracting Officer (CO), to approve or disapprove the alternate delivery schedule. If an alternate delivery schedule is proposed, the Contractor shall describe, in a letter to the USEPA Regional CLP PO and the USEPA CO, why the Contractor is unable to meet the delivery schedule listed in this section. The USEPA Regional CLP PO will not grant an extension for greater than 14 days for the Contractor's response letter to the Sample Data Package report. The Contractor shall proceed and not assume that an extension will be granted until so notified by the USEPA Regional CLP PO or the USEPA CO.

12.2.3 If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section 6.

12.3 Incentives/Sanctions

The Contractor shall discuss the corrective actions implemented to resolve the deficiencies listed in the data package audit report within 14 days of receipt of the comments from USEPA, as specified within this section. The data package audits ensure that the policies and procedures identified in this Statement of Work (SOW) meet the requirements of the contract. If the Contractor fails to adhere to the requirements listed in this section, the Contractor will be in

noncompliance with the contract and may be subjected to sanctions, as described in the contract.

13.0 ON-SITE LABORATORY EVALUATIONS

13.1 Overview

At a frequency dictated by a Contractor's performance, the USEPA Regional Contract Laboratory Program Project Officer (CLP PO), or the USEPA Contracting Officer's (CO's) authorized representative will conduct an on-site laboratory evaluation. On-site laboratory evaluations are carried out to monitor the Contractor's ability to meet selected terms and conditions specified in the contract. The evaluation process incorporates two separate categories: Quality Assurance (QA) On-Site Evaluation and Evidentiary Audit.

13.2 Quality Assurance On-Site Evaluation

Quality Assurance Evaluators inspect the Contractor's facilities to verify the adequacy and maintenance of instrumentation, the continuity, experience and education of personnel, and the acceptable performance of analytical and Quality Control (QC) procedures for adherence to the contract requirements.

13.2.1 The Contractor shall expect that items to be monitored will include, but are not limited to, the following items:

- Size, cleanliness, and organization of the facility;
- Quantity, age, availability, scheduled maintenance, and performance of instrumentation;
- Availability, appropriateness, and utilization of the Quality Assurance Plan (QAP) and Standard Operating Procedures (SOPs);
- Staff qualifications and experience, and personnel training programs;
- Analysis of Performance Evaluation (PE) sample(s);
- Reagents, standards, and sample storage facilities;
- Standard preparation logbooks and raw data;
- Bench sheets and analytical logbook maintenance and review; and
- Review of the Contractor's sample analysis/data package inspection/data management procedures.

13.2.2 Prior to an on-site evaluation, various documentation pertaining to performance of the specific Contractor is integrated into a profile package for discussion during the evaluation. Items that may be included are: previous on-site reports; Quarterly Blind (QB) and/or Performance Evaluation (PE) sample score results; Regional review of data; Contractor performance information provided by the Region; Regional QA materials; data audit reports; results of Contract Compliance Screening (CCS); and data trend reports.

13.3 Evidentiary Audit

Evidence auditors conduct an on-site laboratory evaluation to determine if Contractor policies and procedures are in place to satisfy evidence

handling requirements as stated in Exhibit F. The evidence audit is comprised of a procedural audit, an audit of written SOPs, and an audit of analytical project file documentation.

13.3.1 Procedural Audit. The Contractor shall perform analysis of PE sample(s) in the presence of the USEPA-designated team during the procedural audit. The procedural audit will be comprised of everything from sample receipt to data package assembly and completion. This includes the review and examination of actual SOPs and accompanying documentation for the following Contractor operations: sample receiving; sample storage; sample identification; sample security; sample tracking (from receipt to completion of analysis); analytical project file organization and assembly; and proper disposal of samples and co-generated wastes.

13.3.2 Written SOPs Audit. The written SOPs audit consists of review and examination of the written SOPs to determine if they are accurate and complete for the following Contractor operations: sample receiving; sample storage; sample identification; sample security; sample tracking (from receipt to completion of analysis); and analytical project file organization and assembly.

13.3.3 Analytical Project File Evidence Audit. The analytical project file evidence audit consists of review and examination of the analytical project file documentation. The auditors review the files to determine:

- The accuracy of the document inventory;
- The completeness of the file;
- The adequacy and accuracy of the document numbering system;
- Traceability of sample activity;
- Identification of activity recorded on the documents; and
- Error correction methods.

13.4 Discussion of the On-Site Team's Findings

The QA and evidentiary auditors discuss their findings with the USEPA Regional CLP PO prior to debriefing the Contractor. During the debriefing, the auditors present their findings and recommendations for corrective actions necessary to the Contractor personnel. A report which discusses deficiencies found during the on-site audit will be sent to the Contractor to provide further clarification of findings. In a detailed letter to the USEPA Regional CLP PO and USEPA QA Coordinator, the Contractor shall discuss the deficiencies and the subsequent corrective actions implemented by the Contractor to resolve the deficiencies within 14 days of receipt of report or the on-site laboratory evaluation.

13.4.1 If new SOPs are required to be written or if existing SOPs are required to be rewritten or amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section 6.

13.5 Incentives/Sanctions

The contractor shall submit to on-site evaluations, as specified within this section. The on-site evaluations ensure that the policies and procedures identified in this Statement of Work (SOW) meet the requirements of the contract. If the Contractor fails to adhere to the requirements listed in the section, the Contractor will be in non-compliance with the contract and may be subjected to sanctions, as described in the contract.

14.0 DATA MANAGEMENT

14.1 Overview

Data management procedures are defined as procedures specifying the acquisition or entry, update, correction, deletion, storage, and security of computer-readable data and files. These procedures shall be in written form and contain a clear definition for all databases and files used to generate or resubmit deliverables. Key areas of concern include: system organization (including personnel and security); documentation operations; traceability; and Quality Control (QC).

14.1.2 Data manually entered from hardcopy shall be subject to QC checks and the error rates estimated. Systems shall prevent entry of incorrect or out-of-range data and alert data entry personnel of errors. In addition, data entry error rates shall be estimated and recorded on a monthly basis by re-entering a statistical sample of the data entered and calculating discrepancy rates by data element.

14.2 Documenting Data Changes

The record of changes in the form of corrections and updates to data originally generated, submitted, and/or resubmitted shall be documented to allow traceability of updates. Documentation shall include the following for each change.

- Justification or rationale for the change.
- Initials of the person making the change(s). Data changes shall be implemented and reviewed by a person or group independent of the source generating the deliverable.
- Documentation of changes shall be retained according to the schedule of the original deliverable.
- Resubmitted deliverables shall be reinspected as a part of the Contractor's internal inspection process prior to resubmission. The entire deliverable, not just the changes, shall be inspected.
- The Laboratory Manager shall approve changes to originally submitted deliverables.
- Documentation of data changes may be requested by Contractor auditors.

14.3 Life Cycle Management (LCM) Procedures

LCM procedures shall be applied to computer software systems developed by the Contractor to be used to generate and edit contract deliverables. Such systems shall be thoroughly tested and documented prior to utilization.

14.3.1 A software test and acceptance plan including test requirements, test results, and acceptance criteria shall be developed, followed, and available in written form.

14.3.2 System changes shall not be made directly to production systems generating deliverables. Changes shall be made first to a development system and tested prior to implementation.

14.3.3 Each version of the production system will be given an identification number, date of installation, date of last operation, and will be archived.

14.3.4 System and operations documentation shall be developed and maintained for each system. Documentation shall include a user's manual and an operations and maintenance manual.

14.3.5 This documentation shall be available for on-site review and/or upon written request by the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) or USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB) Organic Program Manager (PM).

14.4 Personnel Responsibilities

Individual(s) responsible for the following functions shall be identified.

- System operation and maintenance, including documentation and training;
- Database integrity, including data entry, data updating and QC; and
- Data and system security, backup, and archiving.

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EXHIBIT F

CHAIN-OF-CUSTODY, DOCUMENT CONTROL,
AND WRITTEN STANDARD OPERATING PROCEDURES

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Exhibit F - Chain-of-Custody, Document Control, and
Written Standard Operating Procedures

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1.0 INTRODUCTION

1.1 A sample is physical evidence collected from a facility or from the environment. Controlling evidence is an essential part of the hazardous waste investigation effort. To ensure that the US Environmental Protection Agency's (USEPA's) sample data and records supporting sample-related activities are admissible and have weight as evidence in future litigation, Contractors are required to maintain USEPA samples under chain-of-custody and to account for all samples and supporting records of sample handling, preparation, and analysis. Contractors shall maintain sample identity, sample custody, and all sample-related records according to the requirements in this exhibit.

1.2 Purpose of the Evidence Requirements

The purpose of the evidence requirements include:

- Ensuring traceability of samples while in the possession of the Contractor;
- Ensuring custody of samples while in the possession of the Contractor;
- Ensuring the integrity of sample identity while in the possession of the Contractor;
- Ensuring sample-related activities are recorded on documents or in other formats for USEPA sample receipt, storage, preparation, analysis, and disposal;
- Ensuring all laboratory records for each specified Sample Delivery Group (SDG) will be accounted for when the project is completed; and
- Ensuring that all laboratory records directly related to USEPA samples are assembled and delivered to USEPA or, prior to delivery, are available upon USEPA's request.

2.0 STANDARD OPERATING PROCEDURES (SOPs)

The Contractor shall implement the following SOPs for sample receiving; sample identification; sample security; sample storage; sample tracking and document control; computer-resident sample data control; and Complete Sample Delivery Group (SDG) File (CSF) and Portable Document Format (PDF) file organization and assembly to ensure accountability of USEPA sample chain-of-custody, as well as control of all USEPA sample-related records.

2.1 Sample Receiving

2.1.1 The Contractor shall designate a Sample Custodian responsible for receiving USEPA samples.

2.1.2 The Contractor shall designate a representative to receive USEPA samples in the event that the Sample Custodian is not available.

2.1.3 Upon receipt, the condition of shipping containers and sample containers shall be inspected and recorded on Form DC-1 by the Sample Custodian or a designated representative.

2.1.4 Upon receipt, the condition of the custody seals (intact/broken) shall be inspected and recorded on Form DC-1 by the Sample Custodian or a designated representative.

2.1.5 The Sample Custodian or a designated representative shall verify and record on Form DC-1 the agreement or disagreement of information recorded on all documents received with samples and information recorded on sample containers.

2.1.6 The Sample Custodian or a designated representative shall verify and record the following information on Form DC-1 as samples are received and inspected:

- Presence or absence and condition of custody seals on shipping and/or sample containers;
- Custody seal numbers when present;
- Condition of the sample bottles;
- Presence or absence of airbills or airbill stickers;
- Airbill or airbill sticker numbers;
- Presence or absence of Traffic Report/Chain of Custody Records (TR/COCs) or Packing Lists;
- Sample tags listed/not listed on TR/COCs;
- Presence or absence of cooler temperature indicator bottle;
- Cooler temperature;
- Date of receipt;
- Time of receipt;
- EPA Sample Numbers;
- Presence or absence of sample tags;

- Sample tag numbers;
- Assigned laboratory numbers;
- Remarks regarding condition of sample shipment, etc.;
- Samples delivered by hand; and
- Problems and discrepancies.

2.1.7 The Sample Custodian or a designated representative shall sign, date, and record the time on all accompanying forms, when applicable, at the time of sample receipt (e.g., TR/COCs or packing lists, and airbills).

NOTE: Initials are not acceptable.

2.1.8 The Contractor shall contact the Sample Management Office (SMO) to resolve problems and discrepancies including, but not limited to: absent documents, conflicting information, absent or broken custody seals; insufficient sample volume; absent temperature indicator bottle, unsatisfactory sample condition (e.g., leaking sample container), and samples not preserved to the proper pH.

2.1.9 The Contractor shall record the resolution of all problems and discrepancies communicated through SMO.

2.2 Sample Identification

2.2.1 The Contractor shall maintain the identity of USEPA samples and prepared samples (including extracted samples, digested samples, and distilled samples) throughout the laboratory.

2.2.2 Each sample and sample preparation container shall be labeled with the EPA Sample Number or a unique laboratory sample identification number.

2.3 Sample Security

2.3.1 The Contractor shall demonstrate that USEPA sample custody is maintained from receiving through retention or disposal. A sample is in custody if:

- It is in your possession; or
- It is in your view after being in your possession; or
- It is locked in a secure area after being in your possession; or
- It is in a designated secure area (secure areas shall be accessible only to authorized personnel).

2.3.2 The Contractor shall demonstrate security of designated secure areas.

2.4 Sample Storage

The Contractor shall designate storage areas for USEPA samples and prepared samples.

2.5 Sample Tracking and Document Control

2.5.1 The Contractor shall record all activities performed on USEPA samples.

2.5.2 Titles that identify the recorded activities shall be printed on each page of all laboratory documents. Activities include, but are not limited to: sample receipt, sample storage, sample preparation, and sample analysis. When a document is a record of analysis, the instrument type and parameter group (e.g., GC/MS-VOA) shall be included in the title.

2.5.3 When columns are used to organize information recorded on laboratory documents, the information recorded in the columns shall be identified in a column heading.

2.5.4 Reviewers' signatures shall be identified on laboratory documents when reviews are conducted.

NOTE: Individuals recording review comments on computer-generated raw data are not required to be identified unless the written comments address data validity.

2.5.5 The laboratory name shall be identified on preprinted laboratory documents.

2.5.6 Each laboratory document entry shall be dated as MM/DD/YYYY (e.g., 01/01/2005) and signed (or initialed) by the individual(s) responsible for performing the recorded activity at the time the activity is recorded.

2.5.7 Notations on laboratory documents shall be recorded in ink.

2.5.8 Corrections to laboratory data reporting forms and raw data shall be made by drawing single lines through the errors and entering the correct information. Information shall not be obliterated or rendered unreadable. Corrections and additions to information shall be signed (or initialed) and dated.

2.5.9 Unused portions of laboratory documents shall be lined-out.

2.5.10 Pages in bound and unbound logbooks shall be sequentially numbered.

2.5.11 Instrument-specific run logs shall be maintained to enable the reconstruction of run sequences.

2.5.12 Logbook entries shall be in chronological order.

2.5.13 Logbook entries shall include only one SDG per page, except in the event where the SDGs "share" Quality Control (QC) samples (e.g., instrument run logs and extraction logs).

2.5.14 Information inserted into laboratory documents shall be affixed permanently in place. The individual responsible for inserting information shall sign and date across the insert and logbook page at the time information is inserted.

2.5.15 The Contractor shall document disposal or retention of USEPA samples, remaining portions of samples, and prepared samples.

2.5.16 Each page in bound and unbound logbooks shall be dated (MM/DD/YYYY) and signed (no initials) at the bottom by the individual recording

the activity (if a single entry is made on a page) or by the last individual recording information on the page (if multiple entries are on the same page).

2.6 Computer-Resident Sample Data Control

2.6.1 Contractor personnel responsible for original data entry shall be identified at the time of data input.

2.6.2 The Contractor shall make changes to electronic data in a manner that ensures that the original data entry is preserved, the editor is identified, and the revision date is recorded.

2.6.3 The Contractor shall routinely verify the accuracy of manually entered data, electronically entered data, and data acquired from instruments.

2.6.4 The Contractor shall routinely verify documents produced by the electronic data collection system to ensure accuracy of the information reported.

2.6.5 The Contractor shall ensure that the electronic data collection system is secure.

2.6.5.1 The electronic data collection system shall be maintained in a secure location.

2.6.5.2 Access to the electronic data collection system functions shall be limited to authorized personnel through utilization of software security techniques (e.g., log-ons or restricted passwords).

2.6.5.3 Electronic data collection systems shall be protected from the introduction of external programs or software (e.g., viruses).

2.6.6 The Contractor shall designate archive storage areas for electronic data and the software required to access the data.

2.6.7 The Contractor shall designate an individual responsible for maintaining archives of electronic data, including the software.

2.6.8 The Contractor shall maintain the archives of electronic data and necessary software in a secure location (secure areas shall be accessible only to authorized personnel).

2.7 Complete Sample Delivery Group File (CSF) Organization and Assembly

2.7.1 The Contractor shall designate a Document Control Officer responsible for the organization and assembly of the CSF.

2.7.2 The Contractor shall designate a representative responsible for the organization and assembly of the CSF in the event that the Document Control Officer is not available.

2.7.3 The Contractor shall maintain documents relating to the CSF in a secure location.

2.7.4 All original laboratory forms and copies of SDG-related logbook pages shall be included in the CSF.

2.7.5 Copies of laboratory documents in the CSF shall be photocopied in a manner to provide complete and legible replicates.

2.7.6 Documents relevant to each SDG including, but not limited to, the following shall be included in the CSF:

- Logbook pages;
- Bench sheets;
- Mass spectra;
- Chromatograms;
- Screening records;
- Preparation records;
- Repreparation records;
- Analytical records;
- Reanalysis/Reextraction records;
- Records of failed or attempted analysis;
- Custody records;
- Sample tracking records;
- Raw data summaries;
- Computer printouts;
- Correspondence;
- FAX originals;
- Library search results; and
- Other.

2.7.7 The Document Control Officer or a designated representative shall ensure that sample tags are encased in clear plastic bags before placing them in the CSF.

2.7.8 CSF documents shall be organized and assembled on an SDG-specific basis.

2.7.9 Original documents which include information relating to more than one SDG (e.g., TR/COCs, calibration logs) shall be filed in the CSF of the lowest SDG number, and copies of these originals shall be placed in the other CSF(s). The Document Control Officer or a designated representative shall record the following statement on the copies in (indelible) dark ink:

COPY
ORIGINAL DOCUMENTS ARE INCLUDED IN CSF _____

_____
Signature

_____
Date

2.7.10 All CSFs shall be submitted with a completed Form DC-2. All resubmitted CSFs shall be submitted with a new or revised Form DC-2.

2.7.11 Each item in the CSF and resubmitted CSFs shall be inventoried and assembled in the order specified on Form DC-2. Each page of the CSF shall be stamped with a sequential number. Page number ranges shall be recorded in the columns provided on Form DC-2. Intentional gaps in the page numbering sequence shall be recorded in the "Comments" section on Form DC-2. When inserting new or inadvertently omitted documents, the Contractor shall identify them with unique accountable numbers. The unique accountable numbers and the locations of the documents shall be recorded in the "Other Records" section on Form DC-2.

2.7.12 Before shipping each CSF, the Document Control Officer or a designated representative shall verify the agreement of information recorded on all documentation and ensure that the information is consistent and the CSF is complete.

2.7.13 The Document Control Officer or a designated representative shall document the shipment of deliverable packages including what was sent, to whom the package was sent, the date, and the carrier used.

2.7.14 Shipments of deliverable packages, including resubmittals, shall be sealed with custody seals by the Document Control Officer or a designated representative in a manner such that opening the packages would break the seals.

2.7.15 Custody seals shall be signed and dated by the Document Control Officer or a designated representative when sealing deliverable packages.

2.8 Data in PDF Organization and Assembly

2.8.1 The Contractor shall designate a Document Control Officer responsible for the organization and assembly of the PDF file.

2.8.2 The Contractor shall designate a representative responsible for the organization and assembly of the PDF file in the event that the Document Control Officer is not available.

2.8.3 The Contractor shall maintain documents relating to the PDF file in a secure location.

2.8.4 In addition to all required deliverables identified in the laboratory's contract and the SOM01.1 Statement of Work (SOW), the laboratory shall provide a complete copy of the hardcopy deliverable in PDF on a Compact Disc (CD).

2.8.5 The PDF file should be organized in accordance to directions provided in Exhibit B, "Reporting Requirements and Order of Data Deliverables" of the SOM01.1 SOW. The PDF file shall be bookmarked for ease of data retrieval and navigation.

2.8.6 Organic data shall be bookmarked using a hierarchal bookmark structure (i.e., an overview or "parent" bookmark, and a subordinate or "child" bookmark nested underneath the "parent" bookmark). Refer to Exhibit B, Section 2.8, Table 2 for the specific hierarchal bookmark structure.

2.8.7 Before shipping each PDF file, the Document Control Officer or a designated representative shall verify the agreement of information recorded in the PDF file and ensure that the information is consistent and the PDF file is complete.

2.8.8 The Document Control Officer or a designated representative shall document the shipment of deliverable packages including what was sent, to whom the package was sent, the date, and the carrier used.

2.8.9 Shipments of deliverable packages, including resubmittals, shall be sealed with custody seals by the Document Control Officer or a designated representative in a manner such that opening the packages would break the seals.

2.8.10 Custody seals shall be signed and dated by the Document Control Officer or a designated representative when sealing deliverable packages.

3.0 WRITTEN STANDARD OPERATING PROCEDURES (SOPs)

The Contractor shall develop and implement the following written SOPs for sample receiving, sample identification, sample security, sample storage, sample tracking and document control, computer-resident sample data control, and Complete Sample Delivery Group (SDG) File (CSF) and Portable Document Format (PDF) file organization and assembly to ensure accountability for USEPA sample chain-of-custody and control of all USEPA sample-related records.

3.1 Sample Receiving

3.1.1 The Contractor shall have written SOPs for sample receiving that accurately reflect the procedures used by the laboratory.

3.1.2 The written SOPs for sample receiving shall ensure that the procedures listed below are in use at the laboratory.

3.1.2.1 The condition of shipping containers and sample containers are inspected and recorded on Form DC-1 upon receipt by the Sample Custodian or a designated representative.

3.1.2.2 The condition of custody seals are inspected and recorded on Form DC-1 upon receipt by the Sample Custodian or a designated representative.

3.1.2.3 The agreement or disagreement of information recorded on shipping documents with information recorded on sample containers is verified and recorded on Form DC-1 by the Sample Custodian or a designated representative.

3.1.2.4 The following information is recorded on Form DC-1 by the Sample Custodian or a designated representative as samples are received and inspected:

- Presence or absence and condition of custody seals on shipping and/or sample containers;
- Custody seal numbers, when present;
- Condition of the sample bottles;
- Presence or absence of airbill or airbill stickers;
- Airbill or airbill sticker numbers;
- Presence or absence of Traffic Report/Chain of Custody Records (TR/COCs) or Packing Lists;
- Sample tag numbers listed/not listed on TR/COCs,
- Presence or absence of cooler temperature indicator bottle;
- Cooler temperature;
- Date of receipt;
- Time of receipt;
- EPA Sample Numbers;
- Presence or absence of sample tags;

- Sample tag numbers;
- Assigned laboratory numbers;
- Samples delivered by hand; and
- Problems and discrepancies.

3.1.2.5 The Sample Custodian or a designated representative shall sign, date, and record the time on all accompanying forms (e.g., TR/COCs or packing lists, and airbills), when applicable, at the time of sample receipt.

NOTE: Initials are not acceptable.

3.1.2.6 The Contractor shall contact the Sample Management Office (SMO) to resolve problems and discrepancies including, but not limited to: absent documents; conflicting information; absent or broken custody seals; insufficient sample volume; absent temperature indicator bottle; unsatisfactory sample condition (e.g., leaking sample container); and samples not preserved to the proper pH.

3.1.2.7 The Contractor shall record resolution of problems and discrepancies communicated through SMO.

3.2 Sample Identification

3.2.1 The Contractor shall have written SOPs for sample identification that accurately reflect the procedures used by the laboratory.

3.2.2 The written SOPs for sample identification shall ensure that the procedures listed below are in use at the laboratory.

3.2.2.1 The identity of USEPA samples and prepared samples is maintained throughout the laboratory when:

- The Contractor assigns unique laboratory sample identification numbers, the written SOPs shall include a description of the procedure used to assign these numbers;
- The Contractor uses prefixes or suffixes in addition to laboratory sample identification numbers, the written SOPs shall include the definitions; and
- The Contractor uses methods to uniquely identify fractions/parameter groups and matrix type, the written SOPs shall include a description of these methods.

3.2.2.2 Each sample and sample preparation container is labeled with the EPA Contract Laboratory Program (CLP) sample number or a unique laboratory sample identification number.

3.3 Sample Security

3.3.1 The Contractor shall have written SOPs for sample security that accurately reflect the procedures used by the laboratory.

3.3.2 The written SOPs for sample security shall include the items listed below.

3.3.2.1 Procedures that ensure the following:

- Sample custody is maintained; and
- The security of designated secure areas is maintained.

3.3.2.2 A list of authorized personnel who have access to locked storage areas.

3.4 Sample Storage

3.4.1 The Contractor shall have written SOPs for sample storage that accurately reflect the procedures used by the laboratory.

3.4.2 The written SOPs for sample storage shall describe locations, contents, and identities of all storage areas for USEPA samples and prepared samples in the laboratory.

3.5 Sample Tracking and Document Control

3.5.1 The Contractor shall have written SOPs for sample tracking and document control that accurately reflect the procedures used by the laboratory.

3.5.2 The written SOPs for sample tracking and document control shall include the items listed below.

3.5.2.1 Examples of all laboratory documents used during sample receiving, sample storage, sample transfer, sample analyses, CSF organization and assembly, and sample retention or disposal.

3.5.2.2 Procedures that ensure the following:

- All activities performed on USEPA samples are recorded;
- Titles that identify the activities recorded are printed on each page of all laboratory documents;
- Information recorded in columns is identified with column headings;
- Reviewers' signatures are identified on laboratory documents;
- The laboratory name is included on preprinted laboratory documents;
- Laboratory document entries are signed and dated as MM/DD/YYYY (e.g., 01/01/2005);
- Entries on all laboratory documents are recorded in ink;
- Corrections and additions to laboratory documents are made by drawing single lines through the errors, entering the correct information, and initialing and dating the new information;
- Unused portions of laboratory documents are lined-out;
- Pages in bound and unbound logbooks are sequentially numbered;
- Instrument-specific run logs are maintained to enable the reconstruction of run sequences;

- Logbook entries are recorded in chronological order;
- Entries are recorded for only one SDG on a page, except in the events where SDGs "share" Quality Control (QC) samples (e.g., instrument run logs and extraction logs);
- Each page in bound and unbound logbooks shall be dated as (MM/DD/YYYY) and signed (no initials) at the bottom by the individual recording the activity (if a single entry is made on a page) or by the last individual recording information on the page (if multiple entries are on the same page);
- Information inserted in laboratory documents is affixed permanently, signed, and dated across the insert; and
- The retention or disposal of USEPA samples, remaining portions of samples, and prepared samples is documented.

3.6 Computer-Resident Sample Data Control

3.6.1 The Contractor shall have written SOPs for computer-resident sample data control that accurately reflect the procedures used by the laboratory.

3.6.2 The written SOPs for computer-resident sample data control shall include the items listed below.

3.6.2.1 Procedures which ensure the following:

- Contractor personnel responsible for original data entry are identified;
- Changes to electronic data are made such that the original data entry is preserved, the editor is identified, and the revision date is recorded;
- The accuracy of manually entered data, electronically entered data, and data acquired from instruments is verified;
- Report documents produced by the electronic data collection system are routinely verified to ensure the accuracy of the information reported;
- Off-site backup and storage of electronic data is maintained;
- Electronic data collection system security is maintained; and
- Archives of electronic data and accompanying software are maintained in a secure location.

3.6.2.2 Descriptions of archive storage areas for the electronic data and the software required to access data archives.

3.6.2.3 A list of authorized personnel who have access to electronic data collection system functions and to archived data.

3.7 CSF Organization and Assembly

3.7.1 The Contractor shall have written SOPs for CSF organization and assembly that accurately reflect the procedures used by the laboratory.

3.7.2 The written SOPs for CSF organization and assembly shall ensure that the procedures listed below are in use at the laboratory.

- Documents relating to the CSF are maintained in a secure location.
- All original laboratory forms and copies of SDG-related logbook pages are included in the CSF.
- Laboratory documents are photocopied in a manner to provide complete and legible replicates.
- All documents relevant to each SDG are included in the CSF.
- Sample tags are encased in clear plastic bags by the Document Control Officer or a designated representative before placing them in the CSF.
- The CSF is organized and assembled on an SDG-specific basis.
- In the event that an original document contains information relating to more than one SDG, the original documents are filed in the CSF of the lowest SDG number and copies are referenced to the originals.
- Each CSF is submitted with a completed Form DC-2, and resubmitted CSFs are submitted with a new or revised Form DC-2.
- Each page of the CSF is stamped with a sequential number and the page number ranges are recorded in the columns provided on Form DC-2. Intentional gaps in the page numbering sequence are recorded in the "Comments" section of Form DC-2. Inserted documents are recorded in the "Other Record" section of Form DC-2.
- Consistency and completeness of the CSF is verified by the Document Control Officer or a designated representative.
- Shipments of deliverable packages are documented by the Document Control Officer or a designated representative.
- Deliverable packages are shipped by the Document Control Officer or a designated representative using custody seals in a manner such that opening the packages would break the seals.
- Custody seals are signed and dated by the Document Control Officer or a designated representative before placing them on deliverable packages.

3.8 PDF File Organization and Assembly

3.8.1 The Contractor shall have written SOPs for PDF file organization and assembly that accurately reflect the procedures used by the laboratory.

3.8.2 The written SOPs for PDF file organization and assembly shall ensure that the procedures listed below are in use at the laboratory.

- PDF files are maintained in a secure location.
- The PDF file is organized and assembled as specified in Exhibit B, Section 2.8 and Exhibit F, Section 2.8.

- Completeness and compliance of the PDF file is verified by the Document Control Officer or a designated representative.

- Shipments of deliverable packages are documented by the Document Control Officer or a designated representative.

- Deliverable packages are shipped by the Document Control Officer or a designated representative using custody seals in a manner such that opening the packages would break the seals.

- Custody seals are signed and dated by the Document Control Officer or a designated representative before placing them on deliverable packages.

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EXHIBIT G

GLOSSARY OF TERMS

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ALIQUOT - A measured portion of a field sample, standard, or solution taken for sample preparation and/or analysis.

ALKANE - Any hydrocarbon with the generic formula C_nH_{2n+2} (straight-chain or branched) or C_nH_{2n} (cyclic) that contains only C-H and C-C single bonds.

ANALYSIS DATE/TIME - The date and military time (24-hour clock) of the injection of the sample, standard, or blank into the Gas Chromatograph/Mass Spectrometer (GC/MS) or GC system.

ANALYTICAL METHOD - Specifies the procedures for sample preparation, instrument calibration, sample analysis, and result calculations.

ANALYTICAL SEQUENCE - The actual instrumental analysis of the samples from the time of instrument calibration through the analysis of the final Continuing Calibration Verification (CCV). All sample analyses during the analytical sequence are subject to the Quality Control (QC) protocols set forth in Exhibits D and E of the contract unless otherwise specified in the individual methods.

ANALYTICAL SERVICES BRANCH (ASB) - The division of United States Environmental Protection Agency's (USEPA) Office of Superfund Remediation and Technology Innovation (OSRTI) responsible for the overall management of the Contract Laboratory Program (CLP).

ASTM - American Society for Testing and Materials. A developer and provider of voluntary consensus standards.

BAR GRAPH SPECTRUM - A plot of the mass-to-charge ratio (m/e) versus relative intensity of the ion current.

BATCH - A group of samples prepared at the same time in the same location using the same method.

BLANK - An analytical sample designed to assess specific sources of laboratory contamination. See individual definitions for the following types of blanks: Method Blank; Instrument Blank; Storage Blank; and Sulfur Blank.

BREAKDOWN - A measure of the decomposition of certain analytes (DDT and Endrin) into by-products.

4-BROMOFLUOROBENZENE (BFB) - The compound chosen to establish mass spectral instrument performance check for volatile (VOA) analyses.

CALIBRATION FACTOR (CF) - A measure of the Gas Chromatographic response of a target analyte to the mass injected.

CALIBRATION STANDARDS - A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). The solutions may or may not be subjected to the preparation method but contain the same matrix (i.e., the same amount of reagents and/or preservatives) as the sample preparations to be analyzed.

CASE - A finite, usually predetermined number of samples collected over a given time period from a particular site. Case Numbers are assigned by the Sample Management Office (SMO). A Case consists of one or more Sample Delivery Groups (SDGs).

CHARACTERIZATION - A determination of the approximate concentration range of compounds of interest used to choose the appropriate analytical protocol.

CLASS A GLASSWARE - Defined by American Society for Testing and Materials (ASTM) standards as glassware used in measurement with the smallest degree of

uncertainty or tolerance associated with the measurement of volume. For example, a Class A 5 mL volumetric flask will have ±0.02 mL tolerance. Class A volumetric glassware usually has a large "A" prominent near the label.

CLOSING CONTINUING CALIBRATION VERIFICATION - Last analytical standard run every 12 hours to verify the initial calibration accuracy of the system.

CONCENTRATION LEVEL (trace, low, or medium) - Characterization of sample fractions as trace concentration, low concentration, or medium concentration is made on the basis of the laboratory's preliminary screen, not on the basis of information entered on the Traffic Report/Chain of Custody Record (TR/COC) by the sampler.

CONTAMINATION - A component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

CONTINUOUS LIQUID-LIQUID EXTRACTION (CLLE) - Used herein synonymously with the terms continuous extraction, continuous liquid extraction, and liquid extraction. This extraction technique involves boiling the extraction solvent in a flask and condensing the solvent above the aqueous sample. The condensed solvent drips through the sample, extracting the compounds of interest from the aqueous phase.

CONTRACT COMPLIANCE SCREENING (CCS) - A screening of electronic and hardcopy data deliverables for completeness and compliance with the contract. This screening is done under USEPA direction by the Sample Management Office (SMO) contractor.

CONTRACT LABORATORY PROGRAM (CLP) - Supports USEPA's Superfund effort by providing a range of state-of-the-art chemical analytical services of known quality. This program is directed by the Analytical Services Branch (ASB) of the USEPA Office of Superfund Remediation and Technology Innovation (OSRTI).

CONTRACT REQUIRED QUANTITATION LIMIT (CRQL) - Minimum level of quantitation acceptable under the contract Statement of Work (SOW).

DATE - MM/DD/YYYY - Where MM = 01 for January, 02 for February...,12 for December; DD = 01 to 31; YYYY = 1998, 1999, 2000, 2001, etc.

DAY - Unless otherwise specified, day shall mean calendar day.

DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP) - Compound chosen to establish mass spectral instrument performance check for semivolatile analysis.

DEUTERATED MONITORING COMPOUNDS (DMCs) - Compounds added to every calibration standard, blank, and sample used to evaluate the efficiency of the extraction/purge-and-trap procedures, and the performance of the Gas Chromatograph/Mass Spectrometer (GC/MS) systems. DMCs are isotopically labeled (deuterated) analogs of native target compounds. DMCs are not expected to be naturally detected in the environmental media.

EXTRACTABLE - A compound that can be partitioned into an organic solvent from the sample matrix and is amenable to Gas Chromatography. Extractables include semivolatile (SVOA), pesticide (PEST), and Aroclor (ARO) compounds.

EXTRACTED ION CURRENT PROFILE (EICP) - A plot of ion abundance versus time (or scan number) for ion(s) of specified mass(es).

FIELD BLANK - Any sample that is submitted from the field and is identified as a blank. This includes trip blanks, rinsates, equipment blanks, etc.

FIELD QC - Any Quality Control (QC) samples submitted from the field to the laboratory. Examples include, but are not limited to: field blanks, field duplicates, and field spikes.

FIELD SAMPLE - A portion of material obtained from an assigned site to be analyzed that is contained in single or multiple containers and identified by a unique EPA Sample Number.

GAS CHROMATOGRAPH (GC) - The instrument used to separate analytes on a stationary phase within a chromatographic column. The analytes are volatized directly from the sample (VOA water and low-soil), volatized from the sample extract (VOA medium soil), or injected as extracts (SVOA, PEST, and ARO). In VOA and SVOA analysis, the compounds are detected by a Mass Spectrometer (MS). In Pesticide and Aroclor analysis, the compounds are detected by an Electron Capture Detector (ECD).

GAS CHROMATOGRAPH/ELECTRON CAPTURE DETECTOR - A Gas Chromatograph (GC) equipped with an Electron Capture Detector (ECD). This is one of the most sensitive gas chromatographic detectors for halogen-containing compounds such as organochlorine pesticides and polychlorinated biphenyls.

GAS CHROMATOGRAPH/MASS SPECTROMETER - A specialized form of Gas Chromatography (GC) used in conjunction with Mass Spectrometry (MS). GC/MS is considered the method of choice for the unequivocal identification of many volatile and semivolatile organic compounds.

GEL PERMEATION CHROMATOGRAPHY (GPC) - A size-exclusion chromatographic technique that is used as a cleanup procedure for removing large organic molecules, particularly naturally occurring macro-molecules such as lipids, polymers, viruses, etc.

HOLDING TIME - The elapsed time expressed in days from the date of receipt of the sample by the Contractor until the date of its analysis.

Holding time = (sample analysis date - sample receipt date)

HYDROMATRIX™ - Diatomaceous earth-based material that is capable of adsorbing and retaining up to twice its weight of an aqueous media.

IN-HOUSE - At the Contractor's facility.

INITIAL CALIBRATION - Analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity, and dynamic range of the response of the Mass Spectrometer (MS) or Electron Capture Detector (ECD) to the target compounds.

INSTRUMENT BLANK - A blank designed to determine the level of contamination associated with the analytical instruments.

INSUFFICIENT QUANTITY - When there is not enough volume (water sample) or weight (soil/sediment) to perform any of the required operations: sample analysis or extraction, Percent Moisture (%Moisture), Matrix Spike and Matrix Spike Duplicate (MS/MSD), etc. Exhibit D provides guidance for addressing this situation.

INTEGRATION SCAN RANGE - The scan number of the scan at the beginning of the area of integration to the scan number at the end of the area of integration. Performed in accordance with Exhibit D Trace and Low/Medium VOA and SVOA.

INTEGRATION TIME RANGE - The Retention Time (RT) at the beginning of the area of integration to the RT at the end of the area of integration.

INTERFERANTS - Substances which affect the analysis for the element of interest.

INTERNAL STANDARDS - Compounds added to every standard, blank, Matrix Spike and Matrix Spike Duplicate (MS/MSD), sample (for volatiles), and sample extract (for semivolatiles) at a known concentration, prior to analysis. Instrument responses to internal standards are used as the basis for quantitation of the target compounds.

LABORATORY - Synonymous with Contractor, as used herein.

LABORATORY CONTROL SAMPLE (LCS) - An internal laboratory Quality Control (QC) sample used to monitor the capability of the Contractor to perform the analytical method.

LABORATORY RECEIPT DATE - The date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and Sample Traffic Report/Chain of Custody Record (TR/COC). Also referred to as Validated Time of Sample Receipt (VTSR).

m/z - Mass to charge ratio; synonymous with "m/e".

MATRIX - The predominant material of which the sample to be analyzed is composed. For the purpose of this analytical method, a sample matrix is either water or soil/sediment. Matrix is <u>not</u> synonymous with phase (liquid or solid).

MATRIX EFFECT - In general, the effect of a particular matrix (water or soil/sediment) on the constituents with which it contacts. Matrix effects may prevent efficient purging/extraction of target analytes, and may affect Deuterated Monitoring Compound (DMC) and surrogate recoveries. In addition, non-target analytes may be extracted from the matrix causing interferences.

MATRIX SPIKE - Aliquot of a sample (water or soil) taken from one of the field samples to be analyzed within an SDG, fortified (spiked) with known quantities of specific compounds, and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - A second aliquot of the same sample as the Matrix Spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - An analytical control consisting of all reagents, internal standards, and surrogate standards [or Deuterated Monitoring Compounds (DMCs) for Trace VOA, Low/Medium VOA, and SVOA], that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

METHOD DETECTION LIMIT (MDL) - The concentration of a target parameter that, when a sample is processed through the complete method, produces a signal with 99 percent probability that it is different from the blank. For 7 replicates of the sample, the mean value must be 3.14s above the blank, where "s" is the standard deviation of the 7 replicates.

NARRATIVE (SDG Narrative) - Portion of the data package which includes laboratory, contract, Case, and Sample Number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution. Complete Sample Delivery Group (SDG) Narrative specifications are included in Exhibit B.

OPENING CONTINUING CALIBRATION VERIFICATION - First analytical standard run every 12 hours to verify the initial calibration of the system.

PERCENT DIFFERENCE (%Difference) - As used in this analytical method and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison [i.e., the Percent Difference (%Difference) may be either negative, positive, or zero].

PERCENT MOISTURE (%Moisture) - An approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The Percent Moisture (%Moisture) determined in this manner also includes contributions from all compounds that may volatilize at or below 105°C, including water. Percent Moisture may be determined from decanted samples and from samples that are not decanted.

PERFORMANCE EVALUATION MIXTURE (PEM) - A calibration solution of specific analytes used to evaluate both recovery and Percent Breakdown (%Breakdown) as a measure of performance.

PERFORMANCE EVALUATION (PE) SAMPLE - A sample of known composition provided by USEPA for Contractor analysis. Used by USEPA to evaluate Contractor performance.

PREPARATION BLANK - An analytical control that contains reagent water and reagents, which is carried through the entire preparation and analytical procedure.

PREPARATION LOG - An official record of the sample preparation (digestion or distillation).

PRIMARY QUANTITATION ION - A contract specified ion used to quantitate a target analyte.

PROTOCOL - Describes the exact procedures to be followed with respect to sample receipt and handling, analytical methods, data reporting and deliverables, and document control. Used synonymously with analytical method.

PURGE-AND-TRAP (DEVICE) - Analytical technique (device) used to isolate volatile (purgeable) organics by stripping the compounds from water or soil by a stream of inert gas, trapping the compounds on an adsorbent such as a porous polymer trap, and thermally desorbing the trapped compounds onto the gas chromatographic column.

PURGEABLES - Volatile compounds.

QUALITY ASSURANCE TECHNICAL SUPPORT (QATS) Laboratory - A Contractor-operated facility operated under the QATS contract, awarded and administered by USEPA.

REAGENT WATER - Water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest. The purity of this water must be equivalent to ASTM Type II reagent water of specification D1193-77, "Standard Specification for Reagent Water".

RECONSTRUCTED ION CHROMATOGRAM (RIC) - A mass spectral graphical representation of the separation achieved by a Gas Chromatograph (GC); a plot of total ion current versus Retention Time (RT).

RELATIVE PERCENT DIFFERENCE (RPD) - As used in this analytical method and elsewhere to compare two values, the RPD is based on the mean of the two values, and is reported as an absolute value (i.e., always expressed as a positive number or zero).

RELATIVE RESPONSE FACTOR (RRF) - A measure of the relative mass spectral response of an analyte compared to its internal standard. RRFs are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RELATIVE RETENTION TIME (RRT) - The ratio of the Retention Time (RT) of a compound to that of a standard (such as an internal standard).

REPRESENTATIVE - Alternate or designee who has the knowledge and authority to perform a specific task.

RESOLUTION - Also termed Separation or Percent Resolution, the separation between peaks on a chromatogram, calculated by dividing the depth of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.

RESOLUTION CHECK MIXTURE - A solution of specific analytes used to determine resolution of adjacent peaks; used to assess instrumental performance.

RESPONSE (Instrumental Response) - A measurement of the output of the Gas Chromatograph (GC) detector [Mass Spectrometer (MS), Electron Capture Detector (ECD), or Flame Ionization Detector (FID)] in which the intensity of the signal is proportionate to the amount (or concentration) detected. Measured by peak area or peak height.

RETENTION TIME (RT) - The time a target analyte is retained on a GC column before elution. The identification of a target analyte is dependent on a target compound's RT falling within the specified RT window established for that compound. The RT is dependent on the nature of the column's stationary phase, column diameter, temperature, flow rate, and other parameters.

ROUNDING RULES - If the figure is greater than or equal to 5, round up, otherwise round down. As an example, 11.443 is rounded down to 11.44 and 11.455 is rounded up to 11.46. If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures. See Forms instructions (Exhibit B) for exceptions.

SAMPLE - A portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

SAMPLE DELIVERY GROUP (SDG) - A unit within a sample Case that is used to identify a group of samples for delivery. An SDG is defined by one of the following, whichever occurs first:

- Each Case of field samples received ; or
- Each 20 field samples [excluding Performance Evaluation (PE) samples] within a Case; or
- Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples in a Case are received (said period beginning with receipt of the first sample in the SDG).

In addition, all samples and/or sample fractions assigned to an SDG must have been scheduled under the same contractual turnaround time. Preliminary Results have **no impact** on defining the SDG.

Samples may be assigned to SDGs by matrix (i.e., all soil samples in one SDG, all water samples in another), at the discretion of the laboratory.

SAMPLE MANAGEMENT OFFICE (SMO) - A Contractor-operated facility operated under the SMO contract, awarded and administered by USEPA.

SAMPLE NUMBER (EPA Sample Number) - A unique identification number designated by USEPA for each sample. The EPA Sample Number appears on the sample Traffic Report/Chain of Custody Record (TR/COC) which documents information on that sample.

SECONDARY QUANTITATION ION - Contract specified ion(s) to be used in quantitation of target analytes when interferences prevent the use of the primary quantitation ion.

SEMIVOLATILE COMPOUNDS - Compounds amenable to analysis by extraction of the sample with an organic solvent. Used synonymously with Base/Neutral and Acid (BNA) compounds.

SOIL - Used herein synonymously with soil/sediment.

SOP - Standard Operating Procedure.

SOW - Statement of Work.

STANDARD ANALYSIS - An analytical determination made with known quantities of target compounds; used to determine response factors.

STOCK SOLUTION - A standard solution which can be diluted to derive other standards.

STORAGE BLANK - Reagent water (two 40.0 mL aliquots) stored with volatile samples in an SDG. It is analyzed after all samples have been analyzed in the SDG and is used to determine the level of contamination acquired during storage.

SULFUR BLANK - A modified method blank that is prepared only when some of the samples in a batch are subjected to sulfur cleanup. It is used to determine the level of contamination associated with the sulfur cleanup procedure. When all of the samples are subjected to sulfur cleanup, then the method blank serves this purpose. When none of the samples are subjected to sulfur cleanup, no sulfur blank is required.

SURROGATES (Surrogate Standard) - For pesticides and Aroclors, compounds added to every blank, sample, Matrix Spike and Matrix Spike Duplicates (MS/MSDs), and standard. Surrogates are used to evaluate analytical efficiency by measuring recovery. Surrogates are not expected to be detected in environmental media.

TARGET COMPOUND LIST (TCL) - A list of compounds as designated in Exhibit C for analysis.

TENTATIVELY IDENTIFIED COMPOUNDS (TIC) - Compounds detected in samples that are not target compounds, internal standards, Deuterated Monitoring Compounds (DMCs), or surrogates. Up to 30 peaks, not including those identified as alkanes (those greater than 10% of the peak area or height of the nearest internal standard) are subjected to mass spectral library searches for tentative identification.

TIME - When required to record time on any deliverable item, time shall be expressed as Military Time [i.e., a 24-hour clock (0000 - 2359)].

TRAFFIC REPORT/CHAIN OF CUSTODY RECORD (TR/COC) - A USEPA sample identification form completed by the sampler, which accompanies the sample during shipment to the laboratory and is used to document sample identity, sample chain-of-custody, sample condition, and sample receipt by the laboratory.

TWELVE-HOUR TIME PERIOD - The 12-hour time period for Gas Chromatograph/Mass Spectrometer (GC/MS) system instrument performance check, standards calibration (initial or continuing calibration), and method blank analysis begins at the moment of injection of the Decafluorotriphenylphosphine (DFTPP) or 4-Bromofluorobenzene (BFB) analysis that the laboratory submits as documentation of instrument performance. The time period ends after 12 hours

have elapsed according to the system clock. For pesticide and Aroclor analyses performed by Gas Chromatography/Electron Capture Detection (GC/ECD), the 12-hour time period in the analytical sequence begins at the moment of injection of the instrument blank that precedes sample analyses, and ends after 12 hours have elapsed according to the system clock.

ULTRASONIC CELL DISRUPTOR (SONICATOR) - A device that uses the energy from controlled ultrasound applications to mix, disperse, and dissolve organic materials from a given matrix.

USEPA ASB ORGANIC PROGRAM MANAGER - The USEPA Analytical Services Branch (ASB) official who manages the Contract Laboratory Program (CLP) Organic program.

USEPA REGIONAL CLP PROJECT OFFICER - The Regional USEPA official responsible for monitoring laboratory performance and/or requesting analytical data or services from a Contract Laboratory Program (CLP) laboratory.

VALIDATED TIME OF SAMPLE RECEIPT (VTSR) - The date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and sample Traffic Report/Chain of Custody Record.

VOLATILE COMPOUNDS - Compounds amenable to analysis by the purge-and-trap technique. Used synonymously with purgeable compounds.

WET WEIGHT - The weight of a sample aliquot including moisture (undried).

WIDE BORE CAPILLARY COLUMN - A Gas Chromatographic column with an Internal Diameter (ID) that is greater than or equal to 0.53 mm. Columns with lesser diameters are classified as narrow bore capillary columns.

EXHIBIT H

FORMAT FOR ELECTRONIC DATA DELIVERABLES

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Exhibit H - Format for Electronic Data Deliverables

Table of Contents

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1.0 FORMAT CHARACTERISTICS

1.1 This constitutes an implementation of the Staged Electronic Data Deliverable (SEDD) based on analytical results and ancillary information required by the contract. Because this implementation is specific to the contract, not all data elements listed in the cross-program Document Type Definition (DTD) are required. This implementation is based on SEDD Specification Draft 5.1 that can be found at:

http://www.epa.gov/superfund/programs/clp/sedd.htm.

1.1.1 The SEDD deliverable consists of an Extensible Markup Language (XML) file(s) compliant with the XML specification 1.0 of the World Wide Web Consortium (W3C). The deliverable must be well-formed based on the W3C XML specification and must be valid based on the DTD.

1.1.2 The Contractor shall create the deliverable using the UTF-8 (Unicode Transformation Format - 8 bit) character set.

1.1.3 The initial line of the deliverable shall be: <?xml version="1.0" encoding="UTF-8"?>.

1.1.4 The second line of the deliverable shall be a DOCTYPE line that contains the filename of the DTD. For example, the DOCTYPE line might look like <!DOCTYPE Header SYSTEM "ORGANICGENERAL_3_2.dtd"> where "Header" denotes the name of the root element, and "ORGANICGENERAL_3_2.dtd" denotes the filename of the DTD.

1.1.5 The use of XML comment lines is permitted at any position in the file after the first two lines.

1.2 This implementation includes detailed specifications for the required format of the content of each data element for each fraction. The content of each data element is specified as either literal (contained in quotes) which must appear exactly as shown (without quotes), or as a variable for which descriptions and formats are listed. Exhibit H, Section 2.0 describes requirements for each data element.

1.2.1 For this implementation, numeric data elements may contain numeric digits, a decimal place, and a leading minus sign. Values without a leading minus sign are assumed to be positive. Values must be reported to the specified precision or significance.

1.2.2 The values reported by the Contractor are used for Contract Compliance Screening (CCS) and data assessment. All calculated values, including final results and Contract Required Quantitation Limits (CRQLs) reported in the deliverable (rounded according to the rounding rules in Exhibit B) must match final values calculated by CCS from the raw data, sample data, and factors reported in the deliverable. The Contractor shall not use rounded intermediate values in calculating the final result, and no rounding shall be performed until reaching the final result.

2.0 DATA ELEMENTS

2.1 The Staged Electronic Data Deliverable (SEDD) consists of data elements arranged hierarchically by data nodes (parent elements). Figure 1 depicts the data node hierarchy. Each data element consists of a start tag, content, and an end tag. An element may contain other elements (child elements).

NOTE: There shall be no more than one occurrence of each child element within a node, unless the child element also behaves as a parent element. For example, in each SamplePlusMethod node, there may be only one occurrence of the element ClientSampleID, but there may be more than one occurrence of the element Analysis.

The tags, nodes, and hierarchy are specified in the Document Type Definition against which the deliverable will be validated (see Exhibit H, Section 5.0). The frequency requirements for each of the eleven data nodes applicable to this implementation are described below.

2.1.1 Header Node

One Header node must be reported for each fraction. Selected Ion Monitoring (SIM) analyses for Trace Volatiles and Semivolatiles are separate fractions and must be reported with a separate header node.

2.1.2 SamplePlusMethod Node

Each Header node must contain one SamplePlusMethod node for each field sample, field blank, dilution, reanalysis, Performance Evaluation sample, required Matrix Spike/Matrix Spike Duplicate samples, method blank, storage blank (Volatiles only), instrument blank (Volatiles, Pesticides, and Aroclors only), cleanup blank (Pesticides and Aroclors only), Laboratory Control Sample (Pesticides and Aroclors only), and non-client sample (Pesticides and Aroclors only) analyzed.

2.1.3 InstrumentQC Node

Each Header node must contain one InstrumentQC node for each initial calibration sequence, instrument performance check (tune), Continuing Calibration Verification (CCV), Florisil Cartridge Check (Pesticides only), and GPC Calibration Check (Pesticides only) analyzed.

NOTE: Tunes may be reported as separate InstrumentQC nodes or may be included in InstrumentQC nodes for initial calibration or CCV. This will depend on whether the tune is analyzed as a separate injection or is combined with a calibration standard.

2.1.4 ReportedResult Node

Each SamplePlusMethod node must contain a ReportedResult node for each target compound. For Volatiles and Semivolatiles, each SamplePlusMethod node must also contain a ReportedResult node for each Tentatively Identified Compound (TIC).

2.1.5 Handling Node

Each SamplePlusMethod node must contain one Handling node for Semivolatiles, Pesticides, and Aroclors containing information for each handling procedure (e.g., decanting) performed on the sample.

2.1.6 AnalysisGroup Node

Each initial calibration InstrumentQC node for multi-point calibration must contain one AnalysisGroup node containing summary data for the initial calibration.

2.1.7 Analysis Node

Each SamplePlusMethod node and InstrumentQC node must contain one Analysis node for Volatiles and Semivolatiles, and two Analysis nodes for Pesticides and Aroclors (one for each gas chromatography column).

2.1.8 Analyte Node

Each Analysis node under a SamplePlusMethod node must contain one Analyte node for each target compound, TIC, Deuterated Monitoring Compound (DMC) (Volatiles and Semivolatiles only), surrogate (Pesticides and Aroclors only), and internal standard (Volatiles and Semivolatiles only). Each Analysis node under an InstrumentQC node must contain one Analyte node for each target compound, DMC (Volatiles and Semivolatiles only), surrogate (Pesticides and Aroclors only), and internal standard (Volatiles and Semivolatiles only). Each Analysis node under an InstrumentQC node for tune must contain one Analyte node for each tune compound. Each AnalysisGroup node must contain one Analyte node for each target compound, DMC (Volatiles and Semivolatiles only), and surrogate (Pesticides and Aroclors only).

2.1.9 PreparationPlusCleanup Node

Each Analysis node under a SamplePlusMethod node must contain one PreparationPlusCleanup node with a PreparationPlusCleanupType equal to "Preparation", and one PreparationPlusCleanup node with a PreparationPlusCleanupType equal to "Cleanup" for each applicable cleanup technique performed. Each Analysis node under an InstrumentQC node with a QCType equal to "Florisil_Cartridge_Check" or "GPC_Calibration_Check" must contain one PreparationPlusCleanup node.

NOTE: For each analysis, no more than one PreparationPlusCleanup Node with PreparationPlusCleanupType equal to "Preparation" shall be present.

2.1.10 Peak Node

Each Analyte node must contain one Peak node for Volatiles, Semivolatiles, and Pesticides (except Toxaphene), and at least three Peak nodes for Toxaphene and each Aroclor. Within a RunBatch, a peak must be consistently identified.

2.1.11 PeakComparison Node

Each Peak node for Volatiles and Semivolatiles must contain at least one PeakComparison node.

2.2 Detailed instructions for the content of each data element are provided in Tables 1 through 4. Table 1 provides instructions for the Volatiles and Trace Volatiles fractions, Table 2 for the Semivolatiles fraction, Table 3 for the Pesticides fraction, and Table 4 for the Aroclors fraction. The following is an explanation of the data fields contained in each table.

2.2.1 Node and Data Elements

This field reports each node in bold text, followed by its data elements. If an entire node is not required, then none of its data elements are listed.

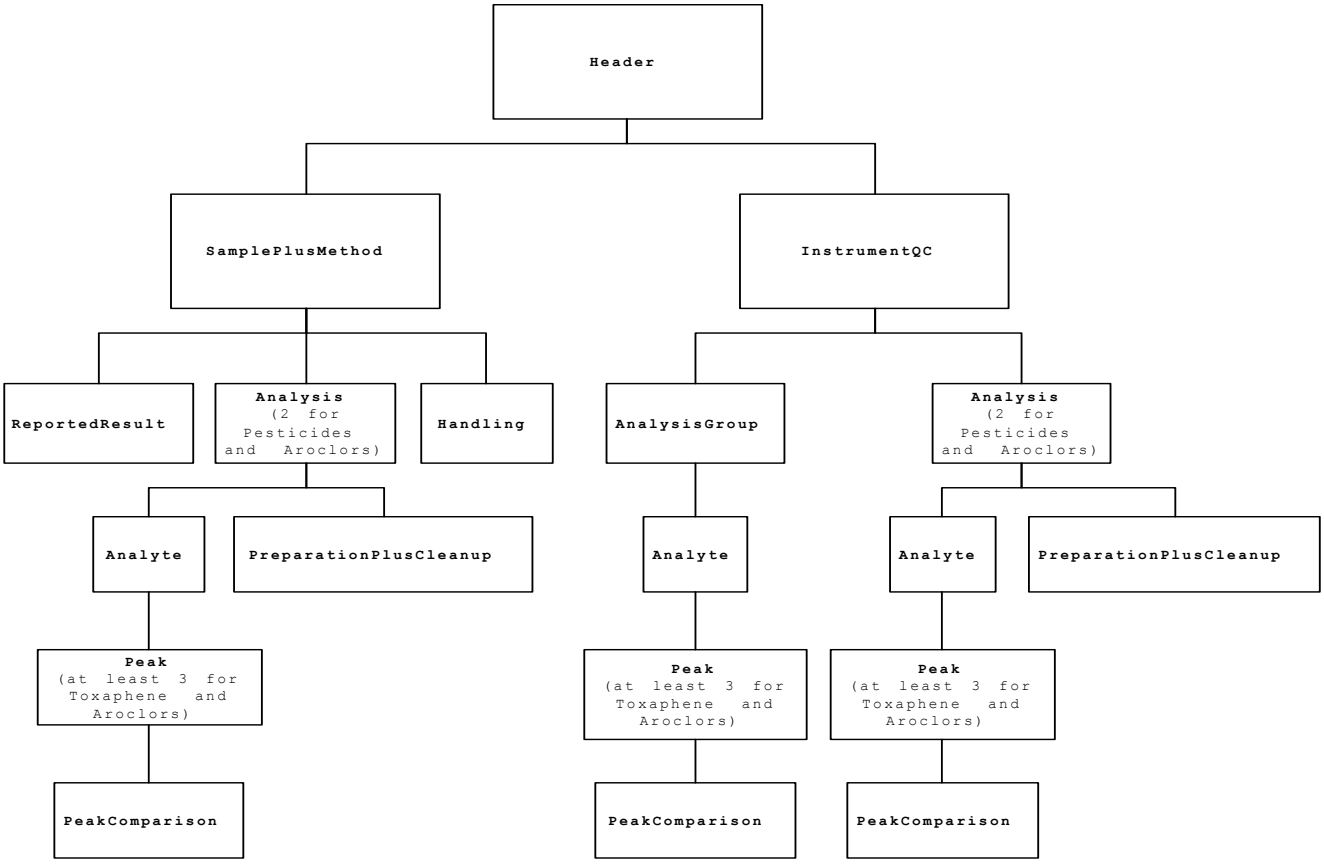
2.2.2 Applicability

This field reports the samples, blanks, and standards for which each node and data element is required. An "X" in a column indicates that the node or element is required. Sample refers to field samples, field blanks, and performance evaluation samples unless otherwise noted. Abbreviations used in this field are defined in Table 5.

2.2.3 Instructions

This field describes the required format and content of each data element. The content of each data element is specified as either literal (contained in quotes), or as a variable for which description and format is listed. Abbreviations used in this field are defined in Table 5.

Figure 1: Data Node Hierarchy



3.0 BATCHES

3.1 This implementation requires the use of the following batches from the Staged Electronic Data Deliverable (SEDD) Specification: "LabReportingBatch"; "RunBatch"; "AnalysisBatch"; "PreparationBatch"; "CleanupBatch"; "StorageBatch".

3.1.1 The "LabReportingBatch" links all samples reported in the same Sample Delivery Group (SDG). Report the SDG Number.

3.1.2 The "RunBatch" links all analyses performed under the same initial calibration. All analyses performed under an initial calibration must have the same content for the "RunBatch" element as the initial calibration from which their results are calculated.

3.1.3 The "AnalysisBatch" and "AnalysisBatchEnd" link all analyses performed within the same analytical sequence (12-hour period). All analyses performed within the same analytical sequence must have the same content for the "AnalysisBatch" element as the tune or standard that began the analytical sequence, and the same content for the "AnalysisBatchEnd" as the calibration standard that ends the analytical sequence.

3.1.4 The "PreparationBatch" links all samples of the same matrix prepared at the same time by the same preparation method. All samples analyzed, including method blanks, storage and instrument blank (volatiles only), Matrix Spike and Matrix Spike Duplicate (MS/MSD),

and Laboratory Control Sample (LCS) (pesticide and Aroclor fractions only) that are prepared together must have the same content for the "PreparationBatch" element.

3.1.5 The "CleanupBatch" links all samples processed through a cleanup procedure at the same time [or between calibration checks for the Gel Permeation Chromatography (GPC) procedure]. Samples of the same matrix in a fraction are not required to have identical Cleanup batches [i.e., need not all be subjected to the same cleanup procedure(s)]. All samples analyzed, including method blanks, MS/MSD, and LCS (pesticide and Aroclor fractions only) that are cleaned up together must have the same content for the "CleanupBatch" element.

3.1.6 The "StorageBatch" links all samples stored together with a storage blank. All samples that are stored together must have the same content for the "StorageBatch" element as the storage blank sample.

4.0 DELIVERABLE

4.1 Each fraction in a Sample Delivery Group (SDG) shall be submitted as a separate compressed (zipped) file. For reporting requirements, the fractions are "VOA_Trace"; "VOA_Low_Med"; "VOA_SIM"; "BNA"; "BNA_SIM"; "Pest"; and "Aroclor". For example, if Selected Ion Monitoring (SIM) analysis is requested for Base/Neutral Acid (BNA), then two separate files must be submitted and labeled as "BNA" and "BNA_SIM". All fractions within an SDG shall be submitted at the same time [i.e., the file for the second fraction in an SDG shall be submitted immediately after the file for the first fraction has been transmitted, etc.].

4.2 The laboratory will utilize a designated website (provided in their laboratory welcome package) to electronically submit their Electronic Data Deliverable (EDD) to the Sample Management Office (SMO). USEPA may approve alternative electronic means of file delivery. Written permission must be obtained from the USEPA Analytical Services Branch (ASB) prior to the use of any alternative means.

4.3 The laboratory must follow the delivery instructions in Exhibit B of this Statement of Work (SOW) and deliver their hardcopy and EDD to SMO concurrently. If one of these items are delivered on a later date, the Data Receipt Date (DRD) for the SDG will be the later of the two dates.

4.4 Information in the electronic deliverable must correspond to information submitted in the hardcopy raw data package and on Quality Control (QC) summary forms, provided that any "raw" values reported (e.g., IS areas on Form VIIIs)are neither rounded on the Form or EDD. If information in the raw data or on the forms is changed, the information in the electronic deliverable shall be changed accordingly. An electronic deliverable containing the changed information for the SDG shall be resubmitted along with the hardcopy at no additional cost to the USEPA.

4.5 The format for the file name shall be Case number_SDG number_contract number_submission number_DTD used_Fraction.zip. For example, the first submission of the Trace VOA fraction from SDG number ABC12, Case number 12345, contract 68-W-0000 would be named 12345_ABC12_68-W-0000_1_ORGANICGENERAL_3_2_VOA_Trace.zip.

5.0 DOCUMENT TYPE DEFINITION (DTD)

5.1 Introduction

The deliverable will be validated against DTD ORGANICGENERAL_3_2. The deliverable must not contain any tags not included in the DTD and must conform to the hierarchical structure modeled in the DTD.

5.2 Organic General DTD

```
<?xml version="1.0" encoding="UTF-8"?>
<!-- ORGANICGENERAL_3_2.dtd 9/17/2004 Based on SEDD Specification Draft 5.1 -->
<!-- Acronym Description -->
<!-- Coeff - Coefficient -->
<!-- EDD - Electronic Data Deliverable -->
<!-- ID - Identity -->
<!-- Lab - Laboratory -->
<!-- QC - Quality Control -->
<!-- RPD - Relative Percent Difference -->
<!-- RRF - Relative Response Factor -->
<!-- RSD - Relative Standard Deviation -->
<!ELEMENT Header (
                ClientDataPackageID|
                ClientDataPackageName|
                ClientDataPackageVersion|
                EDDID|
                EDDVersion|
                EDDImplementationID|
                EDDImplementationVersion|
                GeneratingSystemID|
                GeneratingSystemVersion|
                LabDataPackageID|
                LabDataPackageName|
                LabDataPackageVersion|
                LabReportedDate|
                DateFormat|
                Comment|
                SamplePlusMethod|
                InstrumentQC
                        )*>
<!ELEMENT Analysis (
                AliquotAmount|
                AliquotAmountUnits|
                AnalysisBatch|
                AnalysisBatchEnd|
                AnalysisGroupID|
                AnalysisType|
                Analyst|
                AnalyzedAmount|
                AnalyzedAmountUnits|
                AnalyzedDate|
                BottleID|
                ClientAnalysisID|
                ClientMethodID|
                ClientMethodName|
                ClientMethodSource|
                Column|
                ColumnInternalDiameter|
                ColumnInternalDiameterUnits|
                ColumnLength|
                ColumnLengthUnits|
                Comment|
```

```
                ConfirmationAnalysisID|
                DetectorID|
                DetectorType|
                DilutionFactor|
                HeatedPurge|
                InjectionVolume|
                InjectionVolumeUnits|
                InstrumentID|
                LabAnalysisID|
                LabFileID|
                LabMethodID|
                LabMethodName|
                OriginalLabAnalysisID|
                ProcedureID|
                ProcedureName|
                ResultBasis|
                RunBatch|
                PreparationPlusCleanup|
                Analyte
                        )*>
<!ELEMENT AnalysisGroup (
                AnalysisGroupID|
                AnalysisType|
                Comment|
                Analyte
                        )*>
<!ELEMENT Analyte (
                AmountAdded|
                AmountAddedUnits|
                AnalyteName|
                AnalyteNameContext|
                AnalyteType|
                CASRegistryNumber|
                ClientAnalyteID|
                Comment|
                ExpectedResult|
                ExpectedResultUnits|
                IntermediateResult|
                IntermediateResultUnits|
                LabAnalyteID|
                LabQualifiers|
                LotNumber|
                PeakID|
                PercentBreakdown|
                PercentBreakdownLimitHigh|
                PercentBreakdownLimitType|
                PercentDifference|
                PercentDifferenceLimitHigh|
                PercentDifferenceLimitLow|
                PercentDifferenceLimitType|
                PercentMatch|
                PercentRecovery|
                PercentRecoveryLimitHigh|
                PercentRecoveryLimitLow|
                PercentRecoveryLimitType|
                Result|
                ResultLimitHigh|
                ResultLimitLow|
                ResultLimitType|
                ResultType|
                ResultUnits|
                RPD|
```

```
                RPDLimitHigh|
                RPDLimitType|
                StandardConcentration|
                StandardConcentrationUnits|
                StandardID|
                StandardSource|
                TailingFactor|
                TailingFactorLimitHigh|
                TailingFactorLimitType|
                Peak
                        )*>
<!ELEMENT Handling (
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                BottleID|
                ClientMethodID|
                ClientMethodName|
                ClientMethodSource|
                Comment|
                HandledDate|
                HandlingBatch|
                HandlingType|
                InitialAmount|
                InitialAmountUnits|
                LabMethodID|
                LabMethodName|
                ProcedureID|
                ProcedureName|
                PercentMoisture|
                PercentSolids|
                SampleAmount|
                SampleAmountUnits
                        )*>
<!ELEMENT InstrumentQC (
                ClientInstrumentQCType|
                ClientMethodID|
                ClientMethodName|
                ClientMethodSource|
                Comment|
                LabInstrumentQCID|
                LabID|
                LabName|
                QCLinkage|
                QCType|
                AnalysisGroup|
                Analysis
                        )*>
<!ELEMENT Peak (
                CalibrationFactor|
                CalibrationFactorUnits|
                CalibrationType|
                Coeffa0|
                Coeffa1|
                Coeffa2|
                Coeffa3|
                CoeffOfDetermination|
                CoeffOfDeterminationLimitLow|
                CoeffOfDeterminationLimitType|
                Comment|
                CorrelationCoeff|
                CorrelationCoeffLimitLow|
                CorrelationCoeffLimitType|
                IntermediateResult|
```

```
                IntermediateResultUnits|
                LabQualifiers|
                ManualIntegration|
                MeanCalibrationFactor|
                MeanCalibrationFactorUnits|
                MeanRetentionTime|
                MeanRetentionTimeLimitHigh|
                MeanRetentionTimeLimitLow|
                MeanRetentionTimeLimitType|
                MeanRetentionTimeUnits|
                MeanRRF|
                MeanRRFLimitLow|
                MeanRRFLimitType|
                PeakID|
                PercentDifference|
                PercentDifferenceLimitHigh|
                PercentDifferenceLimitLow|
                PercentDifferenceLimitType|
                PercentRecovery|
                PercentRecoveryLimitHigh|
                PercentRecoveryLimitLow|
                PercentRecoveryLimitType|
                PercentRSD|
                PercentRSDLimitHigh|
                PercentRSDLimitLow|
                PercentRSDLimitType|
                Resolution|
                ResolutionLimitLow|
                ResolutionLimitType|
                ResolutionUnits|
                Response|
                ResponseLimitHigh|
                ResponseLimitLow|
                ResponseLimitType|
                ResponseUnits|
                Result|
                ResultLimitHigh|
                ResultLimitLow|
                ResultLimitType|
                ResultType|
                ResultUnits|
                RetentionTime|
                RetentionTimeLimitHigh|
                RetentionTimeLimitLow|
                RetentionTimeLimitType|
                RetentionTimeUnits|
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                ClientMethodSource|
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                PercentRecoveryLimitType|
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```
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                CustodyID|
                EquipmentBatch|
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                MatrixName|
                MethodBatch|
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                QCType|
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                ServicesID|
                ShippingBatch|
                SiteID|
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6.0 DATA ELEMENT INSTRUCTIONS TABLES

Table 1

Volatiles and Trace Volatiles Data Element Instructions

Node and Data Elements	Applicability Sample	MB	SB	IB	MS	MSD	Instructions
Header	X		X		X		
ClientDataPackageID	X		X		X		Report the Case Number.
ClientDataPackageName	X		X		X		Report the Contract Number.
ClientDataPackageVersion	X		X		X		Report "1", then increment with each resubmission.
EDDID	X		X		X		Report "SEDD".
EDDVersion	X		X		X		Report "Draft 5.1".
EDDImplementationID	X		X		X		Report "ORGANICGENERAL_3" (This is the DTD used).
EDDImplementationVersion	X		X		X		Report "2" (This is the version of the DTD used).
GeneratingSystemID	X		X		X		Report name of generating software or vendor.
GeneratingSystemVersion	X		X		X		Report software version number.
LabDataPackageID	X		X		X		Report the Sample Delivery Group (SDG).
LabDataPackageName	X		X		X		Report "VOA_Trace", "VOA_Low_Med", "VOA_SIM" as applicable.
LabDataPackageVersion	X		X		X		Report "1", then increment with each resubmission.
LabReportedDate	X		X		X		Report the date this data was reported to the client.
DateFormat	X		X		X		Report "MMDDYYYY HH:mm:SS". All dates and times reported in the EDD must follow this format. If any part of the time is unknown, report "00" for the unknown hours, minutes, and seconds.
Comment							Not required.
SamplePlusMethod	X		X		X		
Bottles							Not required.
BottleType							Not required.
ClientID	X				X		Report "1" for Region 1, "2" for Region 2, etc. For samples received from QATS, report "91".
ClientMethodID	X		X		X		Report "SOM01.1".
ClientMethodName							Not required.
ClientMethodSource	X		X		X		Report "USEPA_CLP".
ClientMethodType	X		X		X		Report "GCMS_Internal_Standard".
ClientSampleID	X		X		X		Report the EPA Sample Number.
CollectedDate	X				X		Report the date and time the sample was collected.
Comment							Not required.
Composite							Not required.
CoolerID							Not required.
CustodyID	X				X		Report the Traffic Report/Chain of Custody Form number.
EquipmentBatch							Not required.
LabContract	X		X		X		Report the Contract Number.
LabID	X		X		X		Report the Agency-assigned Lab Code.
LabName	X		X		X		Report the Lab Name.
LabReceiptDate	X				X		Report the date and time the sample was received.

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability					Instructions
	Sample	MB	SB	IB	MS MSD	
LabReportingBatch	X		X		X	Links all samples analyzed to this deliverable. Report the SDG Number.
LabSampleID	X		X		X	Report the Lab Sample ID as assigned by the lab.
MatrixID	X		X		X	Report "Water", "Soil", or "Sediment".
MatrixName						Not required.
MethodLevel	X		X		X	Report "Trace", "Low", or "Medium".
MethodBatch						Not required.
OriginalClientSampleID					X	Report the EPA Sample Number of the original sample this sample was derived from.
OriginalLabSampleID						Not required.
PercentMoisture	X		X		X	For Soil/Sediment samples only, report the percent moisture to at least two significant figures.
PercentSolids						Not required.
pH	X				X	For water samples only, report the pH as measured by the laboratory to the nearest whole pH unit.
Preservative	X				X	Report any chemical preservative used. For unpreserved soils stored in a freezer, report "Freeze".
ProjectID	X		X		X	Report the Case Number.
ProjectName						Not required.
QCCategory			X		X	Report "Blank" for MB, SB, and IB; "Spike" for MS; "Spike_Duplicate" for MSD.
QCLinkage			X		X	Report "LabReportingBatch" for MS/MSD; "AnalysisBatch" for MB; or "StorageBatch" for SB.
QCType	X		X		X	Report "Method_Blank" for MB; "Storage_Blank" for SB; "Method_Instrument_Blank" for IB; "Matrix_Spike" for MS; "Matrix_Spike_Duplicate" for MSD; "Field_Sample" for field samples; "Field_Blank" for field, equipment, rinse, trip, or other blanks; or "PT_Sample" for Performance Evaluation samples.
SamplingBatch						Not required.
ServicesID	X				X	Report the Modification Reference Number, if applicable.
ShippingBatch						Not required.
SiteID						Not required.
SiteName						Not required.
StorageBatch	X		X		X	Links all samples stored together with the Storage Blank. Report the Lab File ID of the Storage Blank. Not required for MB or IB.
Temperature	X				X	Report the temperature as measured by the laboratory upon receipt to the nearest whole °C.
TemperatureUnits	X				X	Report "C".

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Sample	MB	SB	IB	MS	MSD	Instructions
InstrumentQC							Not required.
Analysis	X		X		X		
AliquotAmount							Not required.
AliquotAmountUnits							Not required.
AnalysisBatch	X		X		X		Links this analysis to the beginning of a 12-hour period. Report the Lab File ID of the standard (Tune or CCV) that starts this sequence.
AnalysisBatchEnd	X		X		X		Links this analysis to the end of a 12-hour period. Report the Lab File ID of the CCV that ends this sequence.
AnalysisGroupID							Not required.
AnalysisType	X		X		X		Report "Initial", "Dilution-01", "Reanalysis-01", or "Reinjection-01". Then increment as necessary.
Analyst	X		X		X		Report Analyst's initials.
AnalyzedAmount	X		X		X		Report the Soil Aliquot Volume (for Medium Soils) in microliters to at least two significant figures.
AnalyzedAmountUnits	X		X		X		Report "uL".
AnalyzedDate	X		X		X		Report the date and time the sample was analyzed.
BottleID							Not required.
ClientAnalysisID	X		X		X		Report the EPA Sample Number.
ClientMethodID	X		X		X		Report "SOM01.1".
ClientMethodName							Not required.
ClientMethodSource	X		X		X		Report "USEPA_CLP".
Column	X		X		X		Report the GC Column used.
ColumnInternalDiameter	X		X		X		Report the GC Column Internal Diameter in millimeters.
ColumnInternalDiameterUnits	X		X		X		Report "mm".
ColumnLength	X		X		X		Report the Column Length in meters.
ColumnLengthUnits	X		X		X		Report "m".
Comment							Not required.
ConfirmationAnalysisID							Not required.
DetectorID							Not required.
DetectorType							Not required.
DilutionFactor	X		X		X		Report the Dilution Factor used to the nearest tenth.
HeatedPurge	X		X		X		Report "Yes" if a heated purge was used; otherwise report "No".
InjectionVolume	X		X		X		Report the Purge Volume used in milliliters to at least two significant figures.
InjectionVolumeUnits	X		X		X		Report "mL".
InstrumentID	X		X		X		Report the laboratory identifier for the instrument used for this analysis.
LabAnalysisID	X		X		X		Report the Lab File ID.
LabFileID	X		X		X		Report the Lab File ID.
LabMethodID							Not required.
LabMethodName							Not required.
OriginalLabAnalysisID							Not required.

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability: Sample	MB	SB	IB	MS	MSD	Instructions
ProcedureID							Not required.
ProcedureName							Not required.
ResultBasis	X		X		X		Report "Dry" for Soil/Sediment samples. Report "Total" or "Filtered" for water samples, as applicable.
RunBatch	X		X		X		Links this analysis to an initial calibration. Report the Lab File ID of the standard (Tune or calibration standard) that started the ICAL sequence.
AnalysisGroup							Not required.
Handling							Not required.
ReportedResult	X		X		X		
AnalysisGroupID							Not required.
AnalyteName	X		X		X		Report analytes as they appear in the SOW, or as identified for TICs. Report unknown TICs as "Unknown-01", then increment with each TIC.
AnalyteNameContext							Not required.
AnalyteType	X		X		X		Report "Target" for all target compounds, "Spike" for all target compounds designated as spike compounds for MS/MSD analysis, and "TIC" for all TICs.
CASRegistryNumber	X		X		X		Report CAS Numbers for targets as they appear in the SOW, and for TICs if known.
ClientAnalyteID	X		X		X		Report CAS Number. For TICs with no CAS Number, report the TIC name or as "Unknown-01", then increment with each TIC.
Comment							Not required.
DetectionLimit	X		X		X		For target compounds, report the adjusted current Method Detection Limit determined by the laboratory to at least two significant figures.
DetectionLimitType	X		X		X		Report "MDL".
DetectionLimitUnits	X		X		X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
ExpectedResult					X		Report the theoretical final calculated concentration for the spiked analytes.
ExpectedResultUnits					X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
LabAnalysisID	X		X		X		Report the Lab File ID from the analysis this reported result was derived from.
LabAnalyteID							Not required.
LabQualifiers	X		X		X		Report up to five flags as specified in the SOW ("U", "J", "N", "B", "E", "D", "X", "Y", "Z").
PeakID							Not required.
PercentDifference							Not required.
PercentDifferenceLimitHigh							Not required.

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability: Sample	MB	SB	IB	MS	MSD	Instructions
PercentDifferenceLimitLow							Not required.
PercentDifferenceLimitType							Not required.
PercentRecovery					X		Report the Percent Recovery to the nearest whole percent.
PercentRecoveryLimitHigh					X		Report the upper limit for the Percent Recovery to the nearest whole percent.
PercentRecoveryLimitLow					X		Report the lower limit for the Percent Recovery to the nearest whole percent.
PercentRecoveryLimitType					X		Report "Method".
QuantitationLimit	X		X		X		For target compounds, report the adjusted CRQL to at least two significant figures.
QuantitationLimitType	X		X		X		Report "CRQL".
QuantitationLimitUnits	X		X		X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
ReportingLimit	X		X		X		For target compounds, report the adjusted CRQL.
ReportingLimitType	X		X		X		Report "CRQL".
ReportingLimitUnits	X		X		X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
Result	X		X		X		Report the final calculated concentration to at least two significant figures. Leave blank if analyte is not detected.
ResultLimitHigh							Not required.
ResultLimitLow							Not required.
ResultLimitType							Not required.
ResultType	X		X		X		Report "=" for all reported Result values.
ResultUnits	X		X		X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
RetentionTime	X		X				Report Retention Times in decimal minutes for all TICs.
RetentionTimeUnits	X		X				Report "Minutes".
RPD					X		Report the RPD to the nearest whole percent.
RPDLimitHigh					X		Report the upper limit for the RPD to the nearest whole percent.
RPDLimitType					X		Report "Method".
PreparationPlusCleanup	X		X		X		
AliquotAmount	X		X		X		Report the sample amount in grams to at least three significant figures for Soil/Sediment.
AliquotAmountUnits	X		X		X		Report "g".
Analyst							Not required.
BottleID							Not required.
CleanedUpDate							Not required.
CleanupBatch							Not required.
CleanupType							Not required.
ClientMethodID	X		X		X		Report "SOM01.1".
ClientMethodName							Not required.
ClientMethodSource	X		X		X		Report "USEPA_CLP".
Comment							Not required.

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Sample	MB	SB	IB	MS	MSD	Instructions
FinalAmount							Not required.
FinalAmountUnits							Not required.
InitialAmount	X		X		X		Report the Soil Extract Volume in microliters to at least two significant figures (for Medium Soils).
InitialAmountUnits	X		X		X		Report "uL".
LabMethodID							Not required.
LabMethodName							Not required.
LotNumber							Not required.
PreparationBatch	X		X		X		Links all samples that were prepared together. Report the Lab File ID of the associated Method Blank.
PreparationPlusCleanupType	X		X		X		Report "Preparation" or "Cleanup" as applicable.
PreparationType							Not required.
PreparedDate	X		X		X		Report the date and time the sample was extracted (medium soils).
ProcedureID							Not required.
ProcedureName							Not required.
Analyte	X		X		X		
AmountAdded	X		X		X		Report the volume of internal standard, DMC, or MS/MSD spiking solution added to the sample in uL.
AmountAddedUnits	X		X		X		Report "uL".
AnalyteName	X		X		X		Report analytes as they appear in the SOW or as identified for TICs. Report unknown TICs as "Unknown-01", then increment with each TIC.
AnalyteNameContext							Not required.
AnalyteType	X		X		X		Report "Surrogate" for DMCs; "Internal_Standard" for internal standards; "Target" for all target compounds; "Spike" for all target compounds designated as spike compounds for MS/MSD analysis; or "TIC" for all TICs.
CASRegistryNumber	X		X		X		Report CAS Numbers as they appear in the SOW, and for TICs if known.
ClientAnalyteID	X		X		X		Report CAS Number. For TICs with no CAS Number, report TIC name or as "Unknown-01", then increment with each TIC.
Comment							Not required.
ExpectedResult	X		X		X		Report the final amount added in nanograms for DMCs and internal standards.
ExpectedResultUnits	X		X		X		Report "ng".
IntermediateResult	X		X		X		Report the on-column amount in nanograms from the raw data. Leave blank if not detected.
IntermediateResultUnits	X		X		X		Report "ng".
LabAnalyteID							Not required.
LabQualifiers	X		X		X		Report up to five flags as specified in the SOW ("U", "J', 'N", "B", "E", "D", "X", "Y", "Z").

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability: Sample	MB	SB	IB	MS	MSD	Instructions
LotNumber	X		X		X		Report the vendor/manufacturer assigned lot number for this standard (DMCs, internal standards, and MS/MSD spiking compounds only).
PeakID							Not required.
PercentBreakdown							Not required.
PercentBreakdownLimitHigh							Not required.
PercentBreakdownLimitType							Not required.
PercentDifference							Not required.
PercentDifferenceLimitHigh							Not required.
PercentDifferenceLimitLow							Not required.
PercentDifferenceLimitType							Not required.
PercentMatch	X		X				Report the percent match for TICs only.
PercentRecovery	X		X		X		Report the final calculated Percent Recovery of the DMCs to the nearest whole percent.
PercentRecoveryLimitHigh	X		X		X		Report the upper limit for the Percent Recovery of the DMCs to the nearest whole percent.
PercentRecoveryLimitLow	X		X		X		Report the lower limit for the Percent Recovery of the DMCs to the nearest whole percent.
PercentRecoveryLimitType	X		X		X		Report "Method".
Result	X		X		X		Report the final calculated concentration or amount to at least two significant figures. Leave blank if compound is not detected.
ResultLimitHigh							Not required.
ResultLimitLow							Not required.
ResultLimitType							Not required.
ResultType	X		X		X		Report "=" for all reported Result values.
ResultUnits	X		X		X		For targets, TICs, DMCs and spikes, report "ug/kg" for Soil/Sediment or "ug/L" for Water.
RPD							Not required.
RPDLimitHigh							Not required.
RPDLimitType							Not required.
StandardConcentration	X		X		X		Report the concentration of the internal standard, DMC, or MS/MSD spiking solution added to the sample in ug/L.
StandardConcentrationUnits	X		X		X		Report "ug/L".
StandardID	X		X		X		Report the laboratory assigned identifier for this standard.
StandardSource	X		X		X		Report the vendor/manufacturer for this standard.
TailingFactor							Not required.
TailingFactorLimitHigh							Not required.
TailingFactorLimitType							Not required.
Peak	X		X		X		
CalibrationFactor							Not required.
CalibrationFactorUnits							Not required.
CalibrationType							Not required.

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability					Instructions
	Sample	MB	SB	IB	MS MSD	
Coeffa0						Not required.
Coeffa1						Not required.
Coeffa2						Not required.
Coeffa3						Not required.
CoeffOfDetermination						Not required.
CoeffOfDeterminationLimitLow						Not required.
CoeffOfDeterminationLimitType						Not required.
Comment						Not required.
CorrelationCoeff						Not required.
CorrelationCoeffLimitLow						Not required.
CorrelationCoeffLimitType						Not required.
IntermediateResult	X		X		X	Report the on-column amount in nanograms from the raw data. Leave blank if compound is not detected.
IntermediateResultUnits	X		X		X	Report "ng".
LabQualifiers						Not required.
ManualIntegration	X		X		X	Report "Yes" if this peak was manually integrated, otherwise report "No".
MeanCalibrationFactor						Not required.
MeanCalibrationFactorUnits						Not required.
MeanRetentionTime						Not required.
MeanRetentionTimeLimitHigh						Not required.
MeanRetentionTimeLimitLow						Not required.
MeanRetentionTimeLimitType						Not required.
MeanRetentionTimeUnits						Not required.
MeanRRF						Not required.
MeanRRFLimitLow						Not required.
MeanRRFLimitType						Not required.
PeakID	X		X		X	Report the primary quantitation ion used or "Total" if all ions were used.
PercentDifference						Not required.
PercentDifferenceLimitHigh						Not required.
PercentDifferenceLimitLow						Not required.
PercentDifferenceLimitType						Not required.
PercentRecovery						Not required.
PercentRecoveryLimitHigh						Not required.
PercentRecoveryLimitLow						Not required.
PercentRecoveryLimitType						Not required.
PercentRSD						Not required.
PercentRSDLimitHigh						Not required.
PercentRSDLimitLow						Not required.
PercentRSDLimitType						Not required.
Resolution						Not required.
ResolutionLimitLow						Not required.
ResolutionLimitType						Not required.
ResolutionUnits						Not required.
Response	X		X		X	Report the actual Peak Area from the raw data.
ResponseLimitHigh	X		X		X	Report the upper limit for this response for the internal standards only.

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability: Sample	MB	SB	IB	MS	MSD	Instructions
ResponseLimitLow	X		X		X		Report the lower limit for this response for the internal standards only.
ResponseLimitType	X		X		X		Report "Method".
ResponseUnits	X		X		X		Report "Peak_Area".
Result							Not required.
ResultLimitHigh							Not required.
ResultLimitLow							Not required.
ResultLimitType							Not required.
ResultType							Not required.
ResultUnits							Not required.
RetentionTime	X		X		X		Report the actual Retention Time in decimal minutes from the raw data for this peak.
RetentionTimeLimitHigh	X		X		X		Report the upper limit for this retention time in decimal minutes for the internal standards.
RetentionTimeLimitLow	X		X		X		Report the lower limit for this retention time in decimal minutes for the internal standards.
RetentionTimeLimitType	X		X		X		Report "Method".
RetentionTimeUnits	X		X		X		Report "Minutes".
RRF							Not required.
RRFLimitLow							Not required.
RRFLimitType							Not required.
WeightingFactor							Not required.
PeakComparison	X		X		X		
AnalyteName	X		X		X		Report the name of the associated internal standard as it appears in the SOW.
AnalyteNameContext							Not required.
CASRegistryNumber	X		X		X		Report the CAS Number of the associated internal standard.
ClientAnalyteID	X		X		X		Report the CAS Number of the associated internal standard.
Comment							Not required.
LabAnalyteID							Not required.
PeakID	X		X		X		Report the primary quantitation ion used for the internal standard.
PercentRatio							Not required.
PercentRatioLimitHigh							Not required.
PercentRatioLimitLow							Not required.
PercentRatioLimitType							Not required.

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Tune	ICAL	CCV	Instructions
Header	X	X	X	
ClientDataPackageID	X	X	X	Report the Case Number.
ClientDataPackageName	X	X	X	Report the Contract Number.
ClientDataPackageVersion	X	X	X	Report "1", then increment with each resubmission.
EDDID	X	X	X	Report "SEDD".
EDDVersion	X	X	X	Report "Draft 5.1".
EDDImplementationID	X	X	X	Report "ORGANICGENERAL_3" (This is the DTD used).
EDDImplementationVersion	X	X	X	Report "2" (This is the version of the DTD used).
GeneratingSystemID	X	X	X	Report name of generating software or vendor.
GeneratingSystemVersion	X	X	X	Report software version number.
LabDataPackageID	X	X	X	Report the Sample Delivery Group (SDG).
LabDataPackageName	X	X	X	Report "VOA_Trace", "VOA_Low_Med", or "VOA_SIM" as appropriate.
LabDataPackageVersion	X	X	X	Report "1", then increment with each resubmission.
LabReportedDate	X	X	X	Report the date this data was reported to the client.
DateFormat	X	X	X	Report "MMDDYYYY HH:mm:SS". All dates and times reported in this EDD must follow this format. If any part of the time is unknown, report "00" for the unknown hours, minutes, and seconds.
Comment				Not required.
SamplePlusMethod				Not required.
InstrumentQC	X	X	X	
ClientInstrumentQCType				Not required.
ClientMethodID	X	X	X	Report "SOM01.1".
ClientMethodName				Not required.
ClientMethodSource	X	X	X	Report "USEPA_CLP".
Comment				Not required.
LabInstrumentQCID	X	X	X	Report the EPA Sample Number. For ICAL, report the EPA Sample Number of the first standard.
LabID	X	X	X	Report the Agency-assigned Lab Code.
LabName	X	X	X	Report the Lab Name.
QCLinkage	X	X	X	Report "AnalysisBatch" for Tune and CCV, "RunBatch" for ICAL.
QCType	X	X	X	Report "Instrument_Performance_Check", "Initial_Calibration", or "Continuing_Calibration_Verification".
Analysis	X	X	X	
AliquotAmount				Not required.
AliquotAmountUnits				Not required.

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Tune	ICAL	CCV	Instructions
AnalysisBatch	X	X	X	Links this analysis to the beginning of a 12-hour period. Report the Lab File ID of the standard (Tune or CCV) that starts this sequence. For the standard that starts the 12-hour period, enter the Lab File ID of the standard itself.
AnalysisBatchEnd			X	Links this analysis to the end of a 12-hour period. Report the Lab File ID of the CCV that ends this sequence. For the closing CCV, report the Lab File ID of the CCV itself.
AnalysisGroupID		X		This links a group of analyses together that are used for the initial calibration. Report the Lab File ID of the standard (Tune or calibration standard) that starts the ICAL sequence.
AnalysisType	X	X	X	For Tune, report "Initial". For ICAL/CCV report the calibration level used (e.g., "RRF-20").
Analyst	X	X	X	Report the Analyst's initials.
AnalyzedAmount		X	X	Report the volume of sample in microliters that internal standards are added to.
AnalyzedAmountUnits		X	X	Report "uL".
AnalyzedDate	X	X	X	Report the date and time the sample was analyzed.
BottleID				Not required.
ClientAnalysisID	X	X	X	Report the EPA Sample Number.
ClientMethodID	X	X	X	Report "SOM01.1".
ClientMethodName				Not required.
ClientMethodSource	X	X	X	Report "USEPA_CLP".
Column	X	X	X	Report the GC Column used.
ColumnInternalDiameter	X	X	X	Report the GC Column Internal Diameter in millimeters.
ColumnInternalDiameterUnits	X	X	X	Report "mm".
ColumnLength	X	X	X	Report the GC Column Length in meters.
ColumnLengthUnits	X	X	X	Report "m".
Comment				Not required.
ConfirmationAnalysisID				Not required.
DetectorID				Not required.
DetectorType				Not required.
DilutionFactor				Not required.
HeatedPurge	X	X	X	Report "Yes" if a heated purge was used; otherwise report "No".
InjectionVolume	X	X	X	Report the Purge Volume in milliliters.
InjectionVolumeUnits	X	X	X	Report "mL".
InstrumentID	X	X	X	Report the laboratory identifier for the instrument used for this analysis.
LabAnalysisID	X	X	X	Report the Lab File ID.
LabFileID	X	X	X	Report the Lab File ID.
LabMethodID				Not required.
LabMethodName				Not required.
OriginalLabAnalysisID				Not required.
ProcedureID				Not required.
ProcedureName				Not required.
ResultBasis				Not required.

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Tune	ICAL	CCV	Instructions
RunBatch	X	X	X	Links this analysis to an initial calibration. Report the Lab File ID of the standard (Tune or calibration standard) that started the ICAL sequence.
AnalysisGroup		X		
AnalysisGroupID		X		This links a group of analyses together that are used for the initial calibration. Report the Lab File ID of the standard that starts this ICAL sequence.
AnalysisType		X		Report "Initial_Calibration".
Comment				Not required.
Handling				Not required.
ReportedResult				Not required.
PreparationPlusCleanup				Not required.
Analyte	X	X	X	
AmountAdded	X	X	X	Report the volume of the standard used in microliters.
AmountAddedUnits	X	X	X	Report "uL".
AnalyteName	X	X	X	Report analytes as they appear in the SOW.
AnalyteNameContext				Not required.
AnalyteType	X	X	X	Report "Target" for all target compounds; "Surrogate" for DMCs; "Internal_Standard"; or "Instrument_Performance" for Tunes as appropriate.
CASRegistryNumber	X	X	X	Report CAS Number as they appear in the SOW.
ClientAnalyteID	X	X	X	Report CAS Number.
Comment				Not required.
ExpectedResult		X	X	For internal standards, report the final amount added in nanograms.
ExpectedResultUnits		X	X	For internal standards, report "ng".
IntermediateResult		X	X	Report the on-column in nanograms amount from the raw data.
IntermediateResultUnits		X	X	Report "ng".
LabAnalyteID				Not required.
LabQualifiers				Not required.
LotNumber	X	X	X	Report the vendor/manufacturer assigned lot number for this standard.
PeakID				Not required.
PercentBreakdown				Not required.
PercentBreakdownLimitHigh				Not required.
PercentBreakdownLimitType				Not required.
PercentDifference				Not required.
PercentDifferenceLimitHigh				Not required.
PercentDifferenceLimitLow				Not required.
PercentDifferenceLimitType				Not required.
PercentMatch				Not required.
PercentRecovery				Not required.
PercentRecoveryLimitHigh				Not required.
PercentRecoveryLimitLow				Not required.

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Tune	ICAL	CCV	Instructions
PercentRecoveryLimitType				Not required.
Result				Not required.
ResultLimitHigh				Not required.
ResultLimitLow				Not required.
ResultLimitType				Not required.
ResultType				Not required.
ResultUnits				Not required.
RPD				Not required.
RPDLimitHigh				Not required.
RPDLimitType				Not required.
StandardConcentration	X	X	X	Report the concentration of the standard used in micrograms per liter.
StandardConcentrationUnits	X	X	X	Report "ug/L".
StandardID	X	X	X	Report the laboratory assigned identifier for this standard.
StandardSource	X	X	X	Report the vendor/manufacturer for this standard.
TailingFactor				Not required.
TailingFactorLimitHigh				Not required.
TailingFactorLimitType				Not required.
Peak	X	X	X	
CalibrationFactor				Not required.
CalibrationFactorUnits				Not required.
CalibrationType		X		Report "Average_Response_Factor".
Coeffa0				Not required.
Coeffa1				Not required.
Coeffa2				Not required.
Coeffa3				Not required.
CoeffOfDetermination				Not required.
CoeffOfDeterminationLimitLow				Not required.
CoeffOfDeterminationLimitType				Not required.
Comment				Not required.
CorrelationCoeff				Not required.
CorrelationCoeffLimitLow				Not required.
CorrelationCoeffLimitType				Not required.
IntermediateResult		X	X	Report the on-column amount in nanograms from the raw data.
IntermediateResultUnits		X	X	Report "ng".
LabQualifiers				Not required.
ManualIntegration	X	X	X	Report "Yes" if this peak was manually integrated, otherwise report "No".
MeanCalibrationFactor				Not required.
MeanCalibrationFactorUnits				Not required.
MeanRetentionTime				Not required.
MeanRetentionTimeLimitHigh				Not required.
MeanRetentionTimeLimitLow				Not required.
MeanRetentionTimeLimitType				Not required.
MeanRetentionTimeUnits				Not required.
MeanRRF		X		Report the calculated mean RRF to the nearest thousandth under the AnalysisGroup node only.

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Tune	ICAL	CCV	Instructions
MeanRRFLimitLow				Not required.
MeanRRFLimitType				Not required.
PeakID	X	X	X	Report the primary quantitation ion used or "Total" if all ions were used. For tunes, report the mass of each ion monitored in the spectrum.
PercentDifference			X	Report the calculated Percent Difference for this peak to the nearest tenth of a percent.
PercentDifferenceLimitHigh			X	Report the upper limit for the Percent Difference to the nearest tenth of a percent.
PercentDifferenceLimitLow			X	Report the lower limit for the Percent Difference to the nearest tenth of a percent.
PercentDifferenceLimitType			X	Report "Method".
PercentRecovery				Not required.
PercentRecoveryLimitHigh				Not required.
PercentRecoveryLimitLow				Not required.
PercentRecoveryLimitType				Not required.
PercentRSD		X		Report the calculated Percent Relative Standard Deviation to the nearest tenth of a percent under the AnalysisGroup node only.
PercentRSDLimitHigh		X		Report the upper limit for the %RSD to the nearest tenth of a percent.
PercentRSDLimitLow				Not required.
PercentRSDLimitType		X		Report "Method".
Resolution				Not required.
ResolutionLimitLow				Not required.
ResolutionLimitType				Not required.
ResolutionUnits				Not required.
Response	X	X	X	Report the actual Peak Area from the raw data. For tunes, report the abundance for the ion.
ResponseLimitHigh		X	X	Report the upper limit for this response for the internal standards only.
ResponseLimitLow		X	X	Report the lower limit for this response for the internal standards only.
ResponseLimitType		X	X	Report "Method".
ResponseUnits	X	X	X	Report "Peak_Area" or "Abundance".
Result				Not required.
ResultLimitHigh				Not required.
ResultLimitLow				Not required.
ResultLimitType				Not required.
ResultType				Not required.
ResultUnits				Not required.
RetentionTime	X	X	X	Report the actual Retention Time in decimal minutes from the raw data for this peak.
RetentionTimeLimitHigh		X	X	Report the upper limit for this retention time in decimal minutes for the internal standards.
RetentionTimeLimitLow		X	X	Report the lower limit for this retention time in decimal minutes for the internal standards.
RetentionTimeLimitType		X	X	Report "Method".
RetentionTimeUnits	X	X	X	Report "Minutes".

Table 1

Volatiles and Trace Volatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Tune	ICAL	CCV	Instructions
RRF		X	X	Report the calculated RRF to the nearest thousandth. Leave blank if this analyte is not to be included in the initial calibration curve.
RRFLimitLow		X	X	Report the lower limit for the RRF to the nearest thousandth.
RRFLimitType		X	X	Report "Method".
WeightingFactor				Not required.
PeakComparison	X	X	X	
AnalyteName	X	X	X	Report tune compound or the associated internal standard as they appear in the SOW.
AnalyteNameContext				Not required.
CASRegistryNumber	X	X	X	Report the CAS Number of the tune compound or associated internal standard.
ClientAnalyteID	X	X	X	Report the CAS Number of the tune compound or associated internal standard.
Comment				Not required.
LabAnalyteID				Not required.
PeakID	X	X	X	For tunes, report the mass being compared to the monitored mass. For internal standards, report the primary quantitation ion.
PercentRatio	X			Report the Percent Ratio (%Relative Abundance or %Mass) to the nearest hundredth.
PercentRatioLimitHigh	X			Report the upper limit for the Percent Ratio to the nearest hundredth.
PercentRatioLimitLow	X			Report the lower limit for the Percent Ratio to the nearest hundredth.
PercentRatioLimitType	X			Report "Method".

Table 2

Semivolatiles Data Element Instructions

Node and Data Elements	Applicability Sample	MB	MS	MSD	Instructions
Header	X	X	X		
ClientDataPackageID	X	X	X		Report the Case Number.
ClientDataPackageName	X	X	X		Report the Contract Number.
ClientDataPackageVersion	X	X	X		Report "1", then increment with each resubmission.
EDDID	X	X	X		Report "SEDD".
EDDVersion	X	X	X		Report "Draft 5.1".
EDDImplementationID	X	X	X		Report "ORGANICGENERAL_3" (This is the DTD used).
EDDImplementationVersion	X	X	X		Report "2" (This is the version of the DTD used).
GeneratingSystemID	X	X	X		Report name of generating software or vendor.
GeneratingSystemVersion	X	X	X		Report software version number.
LabDataPackageID	X	X	X		Report the Sample Delivery Group (SDG).
LabDataPackageName	X	X	X		Report "BNA" or "BNA_SIM".
LabDataPackageVersion	X	X	X		Report "1", then increment with each resubmission.
LabReportedDate	X	X	X		Report the date this data was reported to the client.
DateFormat	X	X	X		Report "MMDDYYYY HH:mm:SS". All dates and times reported in the EDD must follow this format. If any part of the time is unknown, report "00" for the unknown hours, minutes, and seconds.
Comment					Not required.
SamplePlusMethod	X	X	X		
Bottles					Not required.
BottleType					Not required.
ClientID	X		X		Report "1" for Region 1, "2" for Region 2, etc. For samples received from QATS, report "91".
ClientMethodID	X	X	X		Report "SOM01.1".
ClientMethodName					Not required.
ClientMethodSource	X	X	X		Report "USEPA_CLP".
ClientMethodType	X	X	X		Report "GCMS_Internal_Standard".
ClientSampleID	X	X	X		Report the EPA Sample Number.
CollectedDate	X		X		Report the date and time the sample was collected.
Comment					Not required.
Composite					Not required.
CoolerID					Not required.
CustodyID	X		X		Report the Traffic Report/Chain of Custody Form Number.
EquipmentBatch					Not required.
LabContract	X	X	X		Report the Contract Number.
LabID	X	X	X		Report the Agency-assigned Lab Code.
LabName	X	X	X		Report the Lab Name.
LabReceiptDate	X		X		Report the date and time the sample was received.
LabReportingBatch	X	X	X		Links all samples analyzed to this deliverable. Report the SDG Number.
LabSampleID	X	X	X		Report the Lab Sample ID as assigned by the lab.

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Sample	MB	MS MSD	Instructions
MatrixID	X	X	X	Report "Water", "Soil", or "Sediment".
MatrixName				Not required.
MethodLevel	X	X	X	Report "Low" or "Medium".
MethodBatch				Not required.
OriginalClientSampleID			X	Report the EPA Sample Number of the original sample this sample was derived from.
OriginalLabSampleID				Not required.
PercentMoisture	X	X	X	For Soil/Sediment samples only, report the percent moisture to at least two significant figures.
PercentSolids				Not required.
pH	X		X	Report the pH as measured by the laboratory upon receipt to the nearest tenth of a pH unit.
Preservative	X		X	Report any chemical preservative used.
ProjectID	X	X	X	Report the Case Number.
ProjectName				Not required.
QCCategory		X	X	Report "Blank" for MB, "Spike" for MS, and "Spike_Duplicate" for MSD.
QCLinkage		X	X	Report "LabReportingBatch" for MS/MSD; or "PreparationBatch" for MB.
QCType	X	X	X	Report "Method_Blank" for MB; "Matrix_Spike" for MS; "Matrix_Spike_Duplicate" for MSD; "Field_Sample" for field samples; "Field_Blank" for field, equipment, rinse, trip, or other blanks; or "PT_Sample" for Performance Evaluation samples.
SamplingBatch				Not required.
ServicesID	X		X	Report the Modification Reference Number, if applicable.
ShippingBatch				Not required.
SiteID				Not required.
SiteName				Not required.
StorageBatch				Not required.
Temperature	X		X	Report the temperature as measured by the laboratory upon receipt to the nearest whole °C.
TemperatureUnits	X		X	Report "C".
InstrumentQC				Not required.
Analysis	X	X	X	
AliquotAmount				Not required.
AliquotAmountUnits				Not required.
AnalysisBatch	X	X	X	Links this analysis to the beginning of a 12-hour period. Report the Lab File ID of the standard (Tune or CCV) that starts this sequence.
AnalysisBatchEnd	X	X	X	Links this analysis to the end of a 12-hour period. Report the Lab File ID of the CCV that ends this sequence.
AnalysisGroupID				Not required.

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Sample	MB	MS	MSD	Instructions
AnalysisType	X	X	X		Report "Initial", "Dilution-01", "Reanalysis-01", or "Reinjection-01". Then increment as necessary.
Analyst	X	X	X		Report Analyst's initials.
AnalyzedAmount	X	X	X		Report the volume of sample in microliters that internal standards are added to.
AnalyzedAmountUnits	X	X	X		Report "uL".
AnalyzedDate	X	X	X		Report the date and time the sample was analyzed.
BottleID					Not required.
ClientAnalysisID	X	X	X		Report the EPA Sample Number.
ClientMethodID	X	X	X		Report "SOM01.1".
ClientMethodName					Not required.
ClientMethodSource	X	X	X		Report "USEPA_CLP".
Column	X	X	X		Report the GC Column used.
ColumnInternalDiameter	X	X	X		Report the GC Column Internal Diameter in millimeters.
ColumnInternalDiameterUnits	X	X	X		Report "mm".
ColumnLength	X	X	X		Report the GC Column Length in meters.
ColumnLengthUnits	X	X	X		Report "m".
Comment					Not required.
ConfirmationAnalysisID					Not required.
DetectorID					Not required.
DetectorType					Not required.
DilutionFactor	X	X	X		Report the Dilution Factor used to the nearest tenth.
HeatedPurge					Not required.
InjectionVolume	X	X	X		Report the Injection Volume used in microliters to at least two significant figures.
InjectionVolumeUnits	X	X	X		Report "uL".
InstrumentID	X	X	X		Report the laboratory identifier for the instrument used for this analysis.
LabAnalysisID	X	X	X		Report the Lab File ID.
LabFileID	X	X	X		Report the Lab File ID.
LabMethodID					Not required.
LabMethodName					Not required.
OriginalLabAnalysisID	X				If a dilution or reinjection is prepared from a sample to which internal standards have been added, report the Lab Analysis ID of the original sample that the dilution or reinjection is prepared from.
ProcedureID					Not required.
ProcedureName					Not required.
ResultBasis	X	X	X		Report "Dry" for Soil/Sediment samples. Report "Total" or "Filtered" for water samples, as applicable.
RunBatch	X	X	X		Links this analysis to an initial calibration. Report the Lab File ID of the standard (Tune or calibration standard) that started the ICAL sequence.
AnalysisGroup					Not required.

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Sample	MB	MS	MSD	Instructions
Handling	X	X	X		
Analyst					Not required.
BottleID					Not required.
ClientMethodID	X	X	X		Report "SOM01.1".
ClientMethodName					Not required.
ClientMethodSource	X	X	X		Report "USEPA_CLP".
Comment					Not required.
HandledDate	X	X	X		Report the date and time the sample was handled.
HandlingBatch					Not required.
HandlingType	X		X		Report "Decanted" if water was decanted from Soil samples, otherwise report "Not_Decanted".
InitialAmount					Not required.
InitialAmountUnits					Not required.
LabMethodID					Not required.
LabMethodName					Not required.
ProcedureID					Not required.
ProcedureName					Not required.
PercentMoisture					Not required.
PercentSolids					Not required.
SampleAmount					Not required.
SampleAmountUnits					Not required.
ReportedResult	X	X	X		
AnalysisGroupID					Not required.
AnalyteName	X	X	X		Report analytes as they appear in the SOW, or as identified for TICs. Report unknown TICs as "Unknown-01", then increment with each TIC.
AnalyteNameContext					Not required.
AnalyteType	X	X	X		Report "Target" for all target compounds, "Spike" for all target compounds designated as spike compounds for MS/MSD analysis, and "TIC" for all TICs.
CASRegistryNumber	X	X	X		Report CAS Numbers as they appear in the SOW, and for TICs if known.
ClientAnalyteID	X	X	X		Report CAS Number. For TICs with no CAS Number, report TIC name or as "Unknown-01", then increment with each TIC.
Comment					Not required.
DetectionLimit	X	X	X		For target compounds, report the adjusted Method Detection Limit determined by the laboratory to at least two significant figures.
DetectionLimitType	X	X	X		Report "MDL".
DetectionLimitUnits	X	X	X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
ExpectedResult			X		Report the theoretical final calculated concentration for the spiked analytes.
ExpectedResultUnits			X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
LabAnalysisID	X	X	X		Report the Lab File ID from the analysis this reported result was derived from.
LabAnalyteID					Not required.

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Sample	MB	MS	MSD	Instructions
LabQualifiers	X	X	X		Report up to five flags as specified in the SOW ("U", "J", "N", "B", "E", "D", "A", "X", "Y", "Z").
PeakID					Not required.
PercentDifference					Not required.
PercentDifferenceLimitHigh					Not required.
PercentDifferenceLimitLow					Not required.
PercentDifferenceLimitType					Not required.
PercentRecovery			X		Report the Percent Recovery to the nearest whole percent.
PercentRecoveryLimitHigh			X		Report the upper limit for the Percent Recovery to the nearest whole percent.
PercentRecoveryLimitLow			X		Report the lower limit for the Percent Recovery to the nearest whole percent.
PercentRecoveryLimitType			X		Report "Method".
QuantitationLimit	X	X	X		For target compounds, report the adjusted CRQL to at least two significant figures.
QuantitationLimitType	X	X	X		Report "CRQL".
QuantitationLimitUnits	X	X	X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
ReportingLimit	X	X	X		For target compounds, report the adjusted CRQL.
ReportingLimitType	X	X	X		Report "CRQL".
ReportingLimitUnits	X	X	X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
Result	X	X	X		Report the final calculated concentration to at least two significant figures. Leave blank if compound is not detected.
ResultLimitHigh					Not required.
ResultLimitLow					Not required.
ResultLimitType					Not required.
ResultType	X	X	X		Report "=" for all reported Result values.
ResultUnits	X	X	X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
RetentionTime	X	X			Report Retention Times in decimal minutes for all TICs.
RetentionTimeUnits	X	X			Report "Minutes".
RPD			X		Report the RPD to the nearest whole percent.
RPDLimitHigh			X		Report the upper limit for the RPD to the nearest whole percent.
RPDLimitType			X		Report "Method".
PreparationPlusCleanup	X	X	X		
AliquotAmount	X	X	X		Report the sample amount used for this analysis to at least three significant figures.
AliquotAmountUnits	X	X	X		Report "g" for Soil/Sediment and "mL" for Water.
Analyst					Not required.
BottleID					Not required.
CleanedUpDate	X	X	X		Report the date and time the sample was cleaned up.

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Sample	MB	MS	MSD	Instructions
CleanupBatch	X	X	X		Links all samples that were cleaned up together. Report the Lab File ID of the associated blank or other unique identifier.
CleanupType	X	X	X		Report "GPC", "Silica_Gel", or "Alumina" as applicable.
ClientMethodID	X	X	X		Report "SOM01.1".
ClientMethodName					Not required.
ClientMethodSource	X	X	X		Report "USEPA_CLP".
Comment					Not required.
FinalAmount	X	X	X		Report the Final Amount of material produced upon completion of this Prep or Cleanup in microliters.
FinalAmountUnits	X	X	X		Report "uL".
InitialAmount	X	X	X		Report the initial amount of extracted sample used for this cleanup method in microliters.
InitialAmountUnits	X	X	X		Report "uL".
LabMethodID					Not required.
LabMethodName					Not required.
LotNumber					Not required.
PreparationBatch	X	X	X		Links all samples that were extracted together. Report the Lab File ID of the associated Method Blank.
PreparationPlusCleanupType	X	X	X		Report "Preparation" or "Cleanup" as applicable.
PreparationType	X	X	X		Report "Sonication", "Soxhlet", or "Pressurized_Fluid" for Soil/Sediment. Report "Liq_Liq" or "Liq_Membrane" for Water.
PreparedDate	X	X	X		Report the date and time the sample was extracted.
ProcedureID					Not required.
ProcedureName					Not required.
Analyte	X	X	X		
AmountAdded	X	X	X		Report the volume of internal standard, DMC, or MS/MSD spiking solution added to the sample in uL.
AmountAddedUnits	X	X	X		Report "uL".
AnalyteName	X	X	X		Report analytes as they appear in the SOW or as identified for TICs. Report unknown TICs as "Unknown-01", then increment with each TIC.
AnalyteNameContext					Not required.
AnalyteType	X	X	X		Report "Surrogate" for DMCs; "Internal_Standard" for internal standards; "Target" for all target compounds; "Spike" for all target compounds designated as spike compounds for MS/MSD analysis; or "TIC" for all TICs.
CASRegistryNumber	X	X	X		Report CAS Numbers as they appear in the SOW, and for TICs if known.
ClientAnalyteID	X	X	X		Report CAS Number. For TICs with no CAS Number, report TIC name or as "Unknown-01", then increment with each TIC.
Comment					Not required.

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Sample	MB	MS	MSD	Instructions
ExpectedResult	X	X	X		For DMCs and internal standards, report the final amount added in nanograms.
ExpectedResultUnits	X	X	X		Report "ng".
IntermediateResult	X	X	X		Report the on-column amount in nanograms from the raw data. Leave blank if not detected.
IntermediateResultUnits	X	X	X		Report "ng".
LabAnalyteID					Not required.
LabQualifiers	X	X	X		Report up to five flags as specified in the SOW ("U", "J", "N", "B", "E", "D", "A", "X", "Y", "Z").
LotNumber	X	X	X		Report the vendor/manufacturer assigned lot number for this standard (DMCs, internal standards, and MS/MSD spiking compounds only).
PeakID					Not required.
PercentBreakdown					Not required.
PercentBreakdownLimitHigh					Not required.
PercentBreakdownLimitType					Not required.
PercentDifference					Not required.
PercentDifferenceLimitHigh					Not required.
PercentDifferenceLimitLow					Not required.
PercentDifferenceLimitType					Not required.
PercentMatch	X	X			Report the percent match for TICs only.
PercentRecovery	X	X	X		Report the final calculated Percent Recovery of the DMCs to the nearest whole percent.
PercentRecoveryLimitHigh	X	X	X		Report the upper limit for the Percent Recovery of the DMCs to the nearest whole percent.
PercentRecoveryLimitLow	X	X	X		Report the lower limit for the Percent Recovery of the DMCs to the nearest whole percent.
PercentRecoveryLimitType	X	X	X		Report "Method".
Result	X	X	X		Report the final calculated concentration or amount to at least two significant figures. Leave blank if compound is not detected.
ResultLimitHigh					Not required.
ResultLimitLow					Not required.
ResultLimitType					Not required.
ResultType	X	X	X		Report "=" for all reported Result values.
ResultUnits	X	X	X		For Targets, TICs, DMCs, and spikes, report "ug/kg" for Soil/Sediment or "ug/L" for Water.
RPD					Not required.
RPDLimitHigh					Not required.
RPDLimitType					Not required.
StandardConcentration	X	X	X		Report the concentration of the internal standard, DMC, or MS/MSD spiking solution added to the sample in ug/L.
StandardConcentrationUnits	X	X	X		Report "ug/L".
StandardID	X	X	X		Report the laboratory assigned identifier for this standard.
StandardSource	X	X	X		Report the vendor/manufacturer for this standard.

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Sample	MB	MS	MSD	Instructions
TailingFactor					Not required.
TailingFactorLimitHigh					Not required.
TailingFactorLimitType					Not required.
Peak	X	X	X		
CalibrationFactor					Not required.
CalibrationFactorUnits					Not required.
CalibrationType					Not required.
Coeffa0					Not required.
Coeffa1					Not required.
Coeffa2					Not required.
Coeffa3					Not required.
CoeffOfDetermination					Not required.
CoeffOfDeterminationLimitLow					Not required.
CoeffOfDeterminationLimitType					Not required.
Comment					Not required.
CorrelationCoeff					Not required.
CorrelationCoeffLimitLow					Not required.
CorrelationCoeffLimitType					Not required.
IntermediateResult	X	X	X		Report the on-column amount in nanograms from the raw data. Leave blank if compound is not detected.
IntermediateResultUnits	X	X	X		Report "ng".
LabQualifiers					Not required.
ManualIntegration	X	X	X		Report "Yes" if this peak was manually integrated, otherwise report "No".
MeanCalibrationFactor					Not required.
MeanCalibrationFactorUnits					Not required.
MeanRetentionTime					Not required.
MeanRetentionTimeLimitHigh					Not required.
MeanRetentionTimeLimitLow					Not required.
MeanRetentionTimeLimitType					Not required.
MeanRetentionTimeUnits					Not required.
MeanRRF					Not required.
MeanRRFLimitLow					Not required.
MeanRRFLimitType					Not required.
PeakID	X	X	X		Report the primary quantitation ion used or "Total" if all ions were used.
PercentDifference					Not required.
PercentDifferenceLimitHigh					Not required.
PercentDifferenceLimitLow					Not required.
PercentDifferenceLimitType					Not required.
PercentRecovery					Not required.
PercentRecoveryLimitHigh					Not required.
PercentRecoveryLimitLow					Not required.
PercentRecoveryLimitType					Not required.
PercentRSD					Not required.
PercentRSDLimitHigh					Not required.
PercentRSDLimitLow					Not required.
PercentRSDLimitType					Not required.
Resolution					Not required.
ResolutionLimitLow					Not required.

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Sample	MB	MS MSD	Instructions
ResolutionLimitType				Not required.
ResolutionUnits				Not required.
Response	X	X	X	Report the actual Peak Area from the raw data.
ResponseLimitHigh	X	X	X	Report the upper limit for this response for the internal standards only.
ResponseLimitLow	X	X	X	Report the lower limit for this response for the internal standards only.
ResponseLimitType	X	X	X	Report "Method".
ResponseUnits	X	X	X	Report "Peak_Area".
Result				Not required.
ResultLimitHigh				Not required.
ResultLimitLow				Not required.
ResultLimitType				Not required.
ResultType				Not required.
ResultUnits				Not required.
RetentionTime	X	X	X	Report the actual Retention Time in decimal minutes from the raw data for this peak.
RetentionTimeLimitHigh	X	X	X	Report the upper limit for this retention time in decimal minutes for the internal standards.
RetentionTimeLimitLow	X	X	X	Report the lower limit for this retention time in decimal minutes for the internal standards.
RetentionTimeLimitType	X	X	X	Report "Method".
RetentionTimeUnits	X	X	X	Report "Minutes".
RRF				Not required.
RRFLimitLow				Not required.
RRFLimitType				Not required.
WeightingFactor				Not required.
PeakComparison	X	X	X	
AnalyteName	X	X	X	Report the name of the associated internal standard as it appears in the SOW.
AnalyteNameContext				Not required.
CASRegistryNumber	X	X	X	Report the CAS Number of the associated internal standard.
ClientAnalyteID	X	X	X	Report the CAS Number of the associated internal standard.
Comment				Not required.
LabAnalyteID				Not required.
PeakID	X	X	X	Report the primary quantitation ion used for the internal standard.
PercentRatio				Not required.
PercentRatioLimitHigh				Not required.
PercentRatioLimitLow				Not required.
PercentRatioLimitType				Not required.

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Tune	ICAL	CCV	Instructions
Header	X	X	X	
ClientDataPackageID	X	X	X	Report the Case Number.
ClientDataPackageName	X	X	X	Report the Contract Number.
ClientDataPackageVersion	X	X	X	Report "1", then increment with each resubmission.
EDDID	X	X	X	Report "SEDD".
EDDVersion	X	X	X	Report "Draft 5.1".
EDDImplementationID	X	X	X	Report "ORGANICGENERAL_3" (This is the DTD used).
EDDImplementationVersion	X	X	X	Report "2" (This is the version of the DTD used).
GeneratingSystemID	X	X	X	Report name of generating software or vendor.
GeneratingSystemVersion	X	X	X	Report software version number.
LabDataPackageID	X	X	X	Report the Sample Delivery Group (SDG).
LabDataPackageName	X	X	X	Report "BNA" or "BNA_SIM".
LabDataPackageVersion	X	X	X	Report "1", then increment with each resubmission.
LabReportedDate	X	X	X	Report the date this data was reported to the client.
DateFormat	X	X	X	Report "MMDDYYYY HH:mm:SS". All dates and times reported in the EDD must follow this format. If any part of the time is unknown, report "00" for the unknown hours, minutes, and seconds.
Comment				Not required.
SamplePlusMethod				Not required.
InstrumentQC	X	X	X	
ClientInstrumentQCType				Not required.
ClientMethodID	X	X	X	Report "SOM01.1".
ClientMethodName				Not required.
ClientMethodSource	X	X	X	Report "USEPA_CLP".
Comment				Not required.
LabInstrumentQCID	X	X	X	Report the EPA Sample Number. For ICAL, report the EPA Sample Number of the first standard.
LabID	X	X	X	Report the Agency-assigned Lab Code.
LabName	X	X	X	Report the Lab Name.
QCLinkage	X	X	X	Report "AnalysisBatch" for Tune and CCV, "RunBatch" for ICAL.
QCType	X	X	X	Report "Instrument_Performance_Check", "Initial_Calibration", or "Continuing_Calibration_Verification".
Analysis	X	X	X	
AliquotAmount				Not required.
AliquotAmountUnits				Not required.
AnalysisBatch	X	X	X	Links this analysis to the beginning of a 12-hour period. Report the Lab File ID of the standard (Tune or CCV) that starts this sequence. For the standard that starts the 12-hour period, enter the Lab File ID of the standard itself.

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Tune	ICAL	CCV	Instructions
AnalysisBatchEnd			X	Links this analysis to the end of a 12-hour period. Report the Lab File ID of the CCV that ends this sequence. For the closing CCV that closes the 12-hour period, report the Lab File ID of the standard itself.
AnalysisGroupID		X		This links a group of analyses together that are used for the initial calibration. Report the Lab File ID of the standard (Tune or calibration standard) that starts this ICAL sequence.
AnalysisType	X	X	X	For Tune, report "Initial". For ICAL/CCV, report the calibration level used (e.g., "RRF-20").
Analyst	X	X	X	Report Analyst's initials.
AnalyzedAmount		X	X	Report the volume of sample in microliters that internal standards are added to.
AnalyzedAmountUnits		X	X	Report "uL".
AnalyzedDate	X	X	X	Report the date and time the sample was analyzed.
BottleID				Not required.
ClientAnalysisID	X	X	X	Report the EPA Sample Number.
ClientMethodID	X	X	X	Report "SOM01.1".
ClientMethodName				Not required.
ClientMethodSource	X	X	X	Report "USEPA_CLP".
Column	X	X	X	Report the GC Column used.
ColumnInternalDiameter	X	X	X	Report the GC Column Internal Diameter in millimeters.
ColumnInternalDiameterUnits	X	X	X	Report "mm".
ColumnLength	X	X	X	Report the GC Column Length in meters.
ColumnLengthUnits	X	X	X	Report "m".
Comment				Not required.
ConfirmationAnalysisID				Not required.
DetectorID				Not required.
DetectorType				Not required.
DilutionFactor				Not required.
HeatedPurge				Not required.
InjectionVolume	X	X	X	Report the Injection Volume used in microliters to at least two significant figures.
InjectionVolumeUnits	X	X	X	Report "uL".
InstrumentID	X	X	X	Report the laboratory identifier for the instrument used for this analysis.
LabAnalysisID	X	X	X	Report the Lab File ID.
LabFileID	X	X	X	Report the Lab File ID.
LabMethodID				Not required.
LabMethodName				Not required.
OriginalLabAnalysisID				Not required.
ProcedureID				Not required.
ProcedureName				Not required.
ResultBasis				Not required.
RunBatch	X	X	X	Links this analysis to an initial calibration. Report the Lab File ID of the standard (Tune or calibration standard) that started the ICAL sequence.

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Tune	ICAL	CCV	Instructions
AnalysisGroup		X		
AnalysisGroupID		X		This links a group of analyses together that are used for the initial calibration. Report the Lab File ID of the standard that starts this ICAL sequence.
AnalysisType		X		Report "Initial_Calibration".
Comment				Not required.
Handling				Not required.
ReportedResult				Not required.
PreparationPlusCleanup				Not required.
Analyte	X	X	X	
AmountAdded	X	X	X	Report the volume of the standard used in microliters.
AmountAddedUnits	X	X	X	Report "uL".
AnalyteName	X	X	X	Report analytes as they appear in the SOW.
AnalyteNameContext				Not required.
AnalyteType	X	X	X	Report "Target" for target compounds; "Surrogate" for DMCs; "Internal_Standard" for internal standards; or "Instrument_Performance" for Tunes as appropriate.
CASRegistryNumber	X	X	X	Report CAS Numbers as they appear in the SOW.
ClientAnalyteID	X	X	X	Report CAS Number.
Comment				Not required.
ExpectedResult		X	X	For internal standards, report the final amount added in nanograms.
ExpectedResultUnits		X	X	For internal standards, report "ng".
IntermediateResult			X	Report the on-column amount in nanograms from the raw data.
IntermediateResultUnits			X	Report "ng".
LabAnalyteID				Not required.
LabQualifiers				Not required.
LotNumber	X	X	X	Report the vendor/manufacturer assigned lot number for this standard.
PeakID				Not required.
PercentBreakdown				Not required.
PercentBreakdownLimitHigh				Not required.
PercentBreakdownLimitType				Not required.
PercentDifference				Not required.
PercentDifferenceLimitHigh				Not required.
PercentDifferenceLimitLow				Not required.
PercentDifferenceLimitType				Not required.
PercentMatch				Not required.
PercentRecovery				Not required.
PercentRecoveryLimitHigh				Not required.
PercentRecoveryLimitLow				Not required.
PercentRecoveryLimitType				Not required.
Result				Not required.
ResultLimitHigh				Not required.

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Tune	ICAL	CCV	Instructions
ResultLimitLow				Not required.
ResultLimitType				Not required.
ResultType				Not required.
ResultUnits				Not required.
RPD				Not required.
RPDLimitHigh				Not required.
RPDLimitType				Not required.
StandardConcentration	X	X	X	Report the concentration of the standard used in micrograms per liter.
StandardConcentrationUnits	X	X	X	Report "ug/L".
StandardID	X	X	X	Report the laboratory assigned identifier for this standard.
StandardSource	X	X	X	Report the vendor/manufacturer for this standard.
TailingFactor				Not required.
TailingFactorLimitHigh				Not required.
TailingFactorLimitType				Not required.
Peak	X	X	X	
CalibrationFactor				Not required.
CalibrationFactorUnits				Not required.
CalibrationType		X		Report "Average_Response_Factor".
Coeffa0				Not required.
Coeffa1				Not required.
Coeffa2				Not required.
Coeffa3				Not required.
CoeffiOfDetermination				Not required.
CoeffOfDeterminationLimitLow				Not required.
CoeffOfDeterminationLimitType				Not required.
Comment				Not required.
CorrelationCoeff				Not required.
CorrelationCoeffLimitLow				Not required.
CorrelationCoeffLimitType				Not required.
IntermediateResult		X	X	Report the on-column amount in nanograms from the raw data.
IntermediateResultUnits		X	X	Report "ng".
LabQualifiers				Not required.
ManualIntegration	X	X	X	Report "Yes" if this peak was manually integrated, otherwise report "No".
MeanCalibrationFactor				Not required.
MeanCalibrationFactorUnits				Not required.
MeanRetentionTime				Not required.
MeanRetentionTimeLimitHigh				Not required.
MeanRetentionTimeLimitLow				Not required.
MeanRetentionTimeLimitType				Not required.
MeanRetentionTimeUnits				Not required.
MeanRRF		X		Report the calculated mean RRF to the nearest thousandth under the AnalysisGroup node only.
MeanRRFLimitLow				Not required.
MeanRRFLimitType				Not required.

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Tune	ICAL	CCV	Instructions
PeakID	X	X	X	Report the primary quantitation ion used or "Total" if all ions were used. For tunes, report the mass of each ion monitored in the spectrum.
PercentDifference			X	Report the calculated Percent Difference for this peak to the nearest tenth of a percent.
PercentDifferenceLimitHigh			X	Report the upper limit for the Percent Difference to the nearest tenth of a percent.
PercentDifferenceLimitLow			X	Report the lower limit for the Percent Difference to the nearest tenth of a percent.
PercentDifferenceLimitType			X	Report "Method".
PercentRecovery				Not required.
PercentRecoveryLimitHigh				Not required.
PercentRecoveryLimitLow				Not required.
PercentRecoveryLimitType				Not required.
PercentRSD		X		Report the calculated Percent Relative Standard Deviation to the nearest tenth of a percent under the AnalysisGroup node only.
PercentRSDLimitHigh		X		Report the upper limit for the Percent Relative Standard Deviation to the nearest tenth of a percent under the Analysis Group node only.
PercentRSDLimitLow				Not required.
PercentRSDLimitType		X		Report "Method".
Resolution				Not required.
ResolutionLimitLow				Not required.
ResolutionLimitType				Not required.
ResolutionUnits				Not required.
Response	X	X	X	Report the actual Peak Area from the raw data. For tunes, report the abundance for the ion.
ResponseLimitHigh		X	X	Report the upper limit for this response for the internal standards only.
ResponseLimitLow		X	X	Report the lower limit for this response for the internal standards only.
ResponseLimitType		X	X	Report "Method".
ResponseUnits	X	X	X	Report "Peak_Area" or "Abundance".
Result				Not required.
ResultLimitHigh				Not required.
ResultLimitLow				Not required.
ResultLimitType				Not required.
ResultType				Not required.
ResultUnits				Not required.
RetentionTime	X	X	X	Report the actual Retention Time in decimal minutes from the raw data for this peak.
RetentionTimeLimitHigh		X	X	Report the upper limit for this retention time in decimal minutes for the internal standards.
RetentionTimeLimitLow		X	X	Report the lower limit for this retention time in decimal minutes for the internal standards.
RetentionTimeLimitType		X	X	Report "Method".

Table 2

Semivolatiles Data Element Instructions (Con't)

Node and Data Elements	Applicability Tune	ICAL	CCV	Instructions
RetentionTimeUnits	X	X	X	Report "Minutes".
RRF		X	X	Report the calculated RRF to the nearest thousandth. Leave blank if this analyte is not to be included in the initial calibration curve.
RRFLimitLow		X	X	Report the lower limit for the RRF to the nearest thousandth.
RRFLimitType		X	X	Report "Method".
WeightingFactor				Not required.
PeakComparison	X	X	X	
AnalyteName	X	X	X	Report tune compound or the associated internal standard as they appear in the SOW.
AnalyteNameContext				Not required.
CASRegistryNumber	X	X	X	Report the CAS Number of the tune compound or associated internal standard.
ClientAnalyteID	X	X	X	Report the CAS Number of the tune compound or associated internal standard.
Comment				Not required.
LabAnalyteID				Not required.
PeakID	X	X	X	For tunes, report the mass being compared to the monitored mass. For internal standards, report the primary quantitation ion.
PercentRatio	X			Report the Percent Ratio (%Relative Abundance or %Mass) to the nearest hundredth.
PercentRatioLimitHigh	X			Report the upper limit for the Percent Ratio to the nearest hundredth.
PercentRatioLimitLow	X			Report the lower limit for the Percent Ratio to the nearest hundredth.
PercentRatioLimitType	X			Report "Method".

Table 3

Pesticides Data Element Instructions

Node and Data Elements	Applicability: Sample	MB CB IB	MS MSD	LCS	NCS	Instructions
Header	X	X	X	X	X	
ClientDataPackageID	X	X	X	X	X	Report the Case Number.
ClientDataPackageName	X	X	X	X		Report the Contract Number.
ClientDataPackageVersion	X	X	X	X	X	Report "1", then increment with each resubmission.
EDDID	X	X	X	X	X	Report "SEDD".
EDDVersion	X	X	X	X	X	Report "Draft 5.1".
EDDImplementationID	X	X	X	X	X	Report "ORGANICGENERAL_3" (This is the DTD used).
EDDImplementationVersion	X	X	X	X	X	Report "2" (This is the version of the DTD used).
GeneratingSystemID	X	X	X	X	X	Report name of generating software or vendor.
GeneratingSystemVersion	X	X	X	X	X	Report software version number.
LabDataPackageID	X	X	X	X	X	Report the Sample Delivery Group (SDG).
LabDataPackageName	X	X	X	X	X	Report "Pest".
LabDataPackageVersion	X	X	X	X	X	Report "1", then increment with each resubmission.
LabReportedDate	X	X	X	X	X	Report the date this data was reported to the client.
DateFormat	X	X	X	X	X	Report "MMDDYYYY HH:mm:SS". All dates and times reported in the EDD must follow this format. If any part of the time is unknown, report "00" for the unknown hours, minutes, and seconds.
Comment						Not required.
SamplePlusMethod	X	X	X	X	X	
Bottles						Not required.
BottleType						Not required.
ClientID	X		X			Report "1" for Region 1, "2" for Region 2, etc. For samples received from QATS, report "91".
ClientMethodID	X	X	X	X	X	Report "SOM01.1".
ClientMethodName						Not required.
ClientMethodSource	X	X	X	X	X	Report "USEPA_CLP".
ClientMethodType	X	X	X	X	X	Report "GC_External_Standard".
ClientSampleID	X	X	X	X	X	Report the EPA Sample Number.
CollectedDate	X		X			Report the date and time the sample was collected.
Comment						Not required.
Composite						Not required.
CoolerID						Not required.
CustodyID	X		X			Report the Traffic Report/Chain of Custody Form number.
EquipmentBatch						Not required.
LabContract	X	X	X	X		Report the Contract Number.
LabID	X	X	X	X	X	Report the Agency-assigned Lab Code.
LabName	X	X	X	X	X	Report the Lab Name.

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
LabReceiptDate	X				X				Report the date and time the sample was received.
LabReportingBatch	X	X			X	X	X	X	Links all samples analyzed to this SDG. Report the SDG Number.
LabSampleID	X	X			X	X			Report the Lab Sample ID as assigned by the laboratory.
MatrixID	X	X			X	X			Report "Water", "Soil", or "Sediment".
MatrixName									Not required.
MethodLevel									Not required.
MethodBatch									Not required.
OriginalClientSampleID					X				Report the EPA Sample Number of the original sample from which this sample was derived.
OriginalLabSampleID									Not required.
PercentMoisture	X	X			X	X			For Soil/Sediment samples only, report the percent moisture to at least two significant figures.
PercentSolids									Not required.
pH	X				X				Report the pH as measured by the laboratory upon receipt to the nearest tenth of a pH unit.
Preservative	X				X				Report any chemical preservative used.
ProjectID	X	X			X	X			Report the Case Number.
ProjectName									Not required.
QCCategory		X			X	X	X	X	Report "Blank" for MB, CB and IB; "Spike" for MS; "Spike_Duplicate" for MSD; and "Blank_Spike" for LCS.
QCLinkage		X			X	X	X	X	Report "LabReportingBatch" for MS/MSD; "PreparationBatch" for MB and LCS; "CleanupBatch" for CB; or "AnalysisBatch" for IB and non-client samples.
QCType	X	X			X	X	X	X	Report "Method_Blank" for MB; "Cleanup_Blank" for CB; "Instrument_Blank" for IB; "Matrix_Spike" for MS; "Matrix_Spike_Duplicate" for MSD; "Laboratory_Control_Sample" for LCS; "Field_Sample" for field samples; "Field_Blank" for field, equipment rinse, trip, or other blanks; "PT_Sample" for Performance Evaluation samples; or "Non_Client_Sample" for NCS.
SamplingBatch									Not required.
ServicesID	X				X				Report the Modification Reference Number, if applicable.
ShippingBatch									Not required.
SiteID									Not required.
SiteName									Not required.
StorageBatch									Not required.

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
Temperature	X				X				Report the temperature as measured by the laboratory upon receipt to the nearest whole °C.
TemperatureUnits	X				X				Report "C".
InstrumentQC									Not required.
Analysis	X				X		X	X	
AliquotAmount									Not required.
AliquotAmountUnits									Not required.
AnalysisBatch	X		X		X		X	X	Links this analysis to the beginning of a 12-hour period. Report the Lab File ID of the PIBLK (for CCV) or RESC (for initial calibration) that starts this sequence. For the PIBLK or RESC at the beginning of a 12-hour period, report the Lab File ID of the PIBLK or RESC itself.
AnalysisBatchEnd	X		X		X		X	X	Links this analysis to the QC immediately following a 12-hour period. Report the Lab File ID of the last CCV standard used to close out the 12-hour period.
AnalysisGroupID									Not required.
AnalysisType	X		X		X		X		Report "Initial", "Dilution-01", "Reanalysis-01", or "Reinjection-01". Then increment as necessary.
Analyst	X		X		X		X		Report Analyst's initials.
AnalyzedAmount	X		X		X		X		Report the volume of final extract added to the sample vial in microliters.
AnalyzedAmountUnits	X		X		X		X		Report "uL".
AnalyzedDate	X		X		X		X	X	Report the date and time the sample was analyzed.
BottleID									Not required.
ClientAnalysisID	X		X		X		X	X	Report the EPA Sample Number.
ClientMethodID	X		X		X		X	X	Report "SOM01.1".
ClientMethodName									Not required.
ClientMethodSource	X		X		X		X	X	Report "USEPA_CLP".
Column	X		X		X		X	X	Report the GC Column used.
ColumnInternalDiameter	X		X		X		X	X	Report the GC Column Internal Diameter in millimeters.
ColumnInternalDiameterUnits	X		X		X		X	X	Report "mm".
ColumnLength	X		X		X		X	X	Report the GC Column Length in meters.
ColumnLengthUnits	X		X		X		X	X	Report "m".
Comment									Not required.
ConfirmationAnalysisID	X		X		X		X		Links an analysis to a confirmation analysis. Report the Lab File ID of the confirmation analysis.
DetectorID									Not required.
DetectorType	X		X		X		X	X	Report "ECD".

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability						Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
DilutionFactor	X		X		X		X		Report the Dilution Factor used to the nearest tenth.
HeatedPurge									Not required.
InjectionVolume	X		X		X		X		Report the column specific Injection Volume used in microliters to at least two significant figures.
InjectionVolumeUnits	X		X		X		X		Report "uL".
InstrumentID	X		X		X		X	X	Report the laboratory identifier for the instrument used for this analysis.
LabAnalysisID	X		X		X		X	X	Report the Lab File ID.
LabFileID	X		X		X		X	X	Report the Lab File ID.
LabMethodID									Not required.
LabMethodName									Not required.
OriginalLabAnalysisID	X								If a dilution or reinjection is prepared from a previously analyzed sample, report the Lab Analysis ID of the original sample that the dilution or the reinjection is prepared from.
ProcedureID									Not required.
ProcedureName									Not required.
ResultBasis	X		X		X		X		Report "Dry" for Soil/Sediment samples. Report "Total" or "Filtered" for water samples, as applicable.
RunBatch	X		X		X		X	X	Links this analysis to an initial calibration. Report the Lab File ID of the RESC standard that started the ICAL sequence.
AnalysisGroup									Not required.
Handling	X		X		X		X		
Analyst									Not required.
BottleID									Not required.
ClientMethodID	X		X		X		X		Report "SOM01.1".
ClientMethodName									Not required.
ClientMethodSource	X				X				Report "USEPA_CLP".
Comment									Not required.
HandledDate	X		X		X		X		Report the date and time the sample was handled.
HandlingBatch									Not required.
HandlingType	X				X				Report "Decanted" if water was decanted from Soil samples, otherwise report "Not_Decanted".
InitialAmount									Not required.
InitialAmountUnits									Not required.
LabMethodID									Not required.
LabMethodName									Not required.
ProcedureID									Not required.
ProcedureName									Not required.
PercentMoisture									Not required.

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability: Sample	MB CB IB	MS MSD	LCS	NCS	Instructions
PercentSolids						Not required.
SampleAmount						Not required.
SampleAmountUnits						Not required.
ReportedResult	X	X	X	X		
AnalysisGroupID						Not required.
AnalyteName	X	X	X	X		Report analytes as they appear in the SOW.
AnalyteNameContext						Not required.
AnalyteType	X	X	X	X		Report "Target" for all target compounds and "Spike" for all target compounds designated as spike compounds for MS/MSD and LCS analysis.
CASRegistryNumber	X	X	X	X		Report CAS Numbers as they appear in the SOW.
ClientAnalyteID	X	X	X	X		Report CAS Number.
Comment						Not required.
DetectionLimit	X	X	X	X		For target compounds, report the adjusted Method Detection Limit as determined by the laboratory to at least two significant figures.
DetectionLimitType	X	X	X	X		Report "MDL".
DetectionLimitUnits	X	X	X	X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
ExpectedResult						Not required.
ExpectedResultUnits						Not required.
LabAnalysisID	X	X	X	X		Report the Lab File ID from the analysis this reported result was derived from.
LabAnalyteID						Not required.
LabQualifiers	X	X	X	X		Report up to five flags as specified in the SOW ("U", "J", "P", "C", "B", "E", "D", "X", "Y", "Z").
PeakID						Not required.
PercentDifference	X	X	X	X		Report the percent difference between the reported result and the confirmation result to the nearest whole percent (excluding IB).
PercentDifferenceLimitHigh	X	X	X	X		Report the upper limit for the percent difference to the nearest whole percent (excluding IB).
PercentDifferenceLimitLow						Not required.
PercentDifferenceLimitType	X	X	X	X		Report "Method" (excluding IB).
PercentRecovery						Not required.
PercentRecoveryLimitHigh						Not required.
PercentRecoveryLimitLow						Not required.
PercentRecoveryLimitType						Not required.
QuantitationLimit	X	X	X	X		For target compounds, report the adjusted CRQL to at least two significant figures.
QuantitationLimitType	X	X	X	X		Report "CRQL".

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
QuantitationLimitUnits	X		X		X		X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
ReportingLimit	X		X		X		X		For target compounds, report the adjusted CRQL.
ReportingLimitType	X		X		X		X		Report "CRQL".
ReportingLimitUnits	X		X		X		X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
Result	X		X		X		X		Report the final calculated concentration to at least two significant figures. Leave blank if analyte is not detected.
ResultLimitHigh									Not required.
ResultLimitLow									Not required.
ResultLimitType									Not required.
ResultType	X		X		X		X		Report "=" for all reported Result values.
ResultUnits	X		X		X		X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
RetentionTime									Not required.
RetentionTimeUnits									Not required.
RPD									Not required.
RPDLimitHigh									Not required.
RPDLimitType									Not required.
PreparationPlusCleanup	X		X		X		X		
AliquotAmount	X		X		X		X		Report the sample amount used for this analysis to at least three significant figures.
AliquotAmountUnits	X		X		X		X		Report "g" for Soil/Sediment and "mL" for Water.
Analyst									Not required.
BottleID									Not required.
CleanedUpDate	X		X		X		X		Report the date and time the sample was cleaned up.
CleanupBatch	X		X		X		X		Links all samples that were cleaned up together. Report the Lab File ID of the associated blank or other unique identifier.
CleanupType	X		X		X		X		Report "GPC", "Florisil", "Sulfur", "Silica_Gel", "Alumina", or "Acid_Base_Partition" as applicable.
ClientMethodID	X		X		X		X		Report "SOM01.1".
ClientMethodName									Not required.
ClientMethodSource	X		X		X		X		Report "USEPA_CLP".
Comment									Not required.
FinalAmount	X		X		X		X		Report the Final Amount of material produced upon completion of this Prep or Cleanup in microliters.
FinalAmountUnits	X		X		X		X		Report "uL".

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability: Sample	MB	CB	IB	MS	MSD	LCS	NCS	Instructions
InitialAmount	X	X			X		X		Report the initial amount of extracted sample used for this cleanup method in microliters.
InitialAmountUnits	X	X			X		X		Report "uL".
LabMethodID									Not required.
LabMethodName									Not required.
LotNumber	X	X			X		X		Report the manufacturer's lot number for the Florisil cartridges used.
PreparationBatch	X	X			X		X		Links all samples that were extracted together. Report the Lab File ID of the associated Method Blank.
PreparationPlusCleanupType	X	X			X		X		Report "Preparation" or "Cleanup" as applicable.
PreparationType	X	X			X		X		Report "Sonication", "Soxhlet", or "Pressurized_Fluid" for Soil/Sediment. Report "Sep_Funnel", "Liq_Liq", or "Liq_Membrane" for Water.
PreparedDate	X	X			X		X		Report the date and time the sample was extracted.
ProcedureID									Not required.
ProcedureName									Not required.
Analyte	X	X			X		X		
AmountAdded	X	X			X		X		Report the volume of surrogate standard or spiking solution added to the sample in uL.
AmountAddedUnits	X	X			X		X		Report "uL".
AnalyteName	X	X			X		X		Report analytes as they appear in the SOW.
AnalyteNameContext									Not required.
AnalyteType	X	X			X		X		Report "Target" for all target compounds, "Surrogate" for surrogate compounds, or "Spike" for target compounds designated as spike compounds for MS/MSD or LCS analysis.
CASRegistryNumber	X	X			X		X		Report CAS Numbers as they appear in the SOW.
ClientAnalyteID	X	X			X		X		Report CAS Number.
Comment									Not required.
ExpectedResult	X	X			X		X		Report the theoretical final calculated concentration for spikes and LCS compounds. Report the amount of surrogate in ng.
ExpectedResult_Units	X	X			X		X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water spikes and LCS. Report "ng" for surrogates.
IntermediateResult	X	X			X		X		Report the on-column amount in nanograms from the raw data. Leave blank if not detected.
IntermediateResultUnits	X	X			X		X		Report "ng".
LabAnalyteID									Not required.

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
LabQualifiers	X		X		X		X		Report up to five flags as specified in the SOW ("U", "J", "P", "C", "B", "E", "D", "X", "Y", "Z").
LotNumber	X		X		X		X		Report the vendor/manufacturer assigned lot number for this standard.
PeakID									Not required.
PercentBreakdown									Not required.
PercentBreakdownLimitHigh									Not required.
PercentBreakdownLimitType									Not required.
PercentDifference									Not required.
PercentDifferenceLimitHigh									Not required.
PercentDifferenceLimitLow									Not required.
PercentDifferenceLimitType									Not required.
PercentMatch									Not required.
PercentRecovery	X		X		X		X		Report the final calculated Percent Recovery of the spikes and surrogates to the nearest whole percent.
PercentRecoveryLimitHigh	X		X		X		X		Report the upper limit for the Percent Recovery of the spikes and surrogates to the nearest whole percent.
PercentRecoveryLimitLow	X		X		X		X		Report the lower limit for the Percent Recovery of the spikes and surrogates to the nearest whole percent.
PercentRecoveryLimitType	X		X		X		X		Report "Method".
Result	X		X		X		X		Report the calculated concentration or amount to at least two significant figures. Leave blank if compound is not detected.
ResultLimitHigh									Not required.
ResultLimitLow									Not required.
ResultLimitType									Not required.
ResultType	X		X		X		X		Report "=" for all reported Result values.
ResultUnits	X		X		X		X		Report "ug/kg" for Soil/Sediment or "ug/L" for Water.
RPD					X				Report the RPD to the nearest whole percent.
RPDLimitHigh					X				Report the upper limit for the RPD to the nearest whole percent.
RPDLimitType					X				Report "Method".
StandardConcentration	X		X		X		X		Report the concentration of the surrogate standard or spiking solution used in ug/L.
StandardConcentrationUnits	X		X		X		X		Report "ug/L".
StandardID	X		X		X		X		Report the laboratory assigned identifier for this standard.
StandardSource	X		X		X		X		Report the vendor/manufacturer for this standard.
TailingFactor									Not required.
TailingFactorLimitHigh									Not required.

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
TailingFactorLimitType									Not required.
Peak	X		X		X		X		
CalibrationFactor									Not required.
CalibrationFactorUnits									Not required.
CalibrationType									Not required.
Coeffa0									Not required.
Coeffa1									Not required.
Coeffa2									Not required.
Coeffa3									Not required.
CoeffOfDetermination									Not required.
CoeffOfDeterminationLimitLow									Not required.
CoeffOfDeterminationLimitType									Not required.
Comment									Not required.
CorrelationCoeff									Not required.
CorrelationCoeffLimitLow									Not required.
CorrelationCoeffLimitType									Not required.
IntermediateResult	X		X		X		X		Report the on-column amount in nanograms from the raw data for this peak. Leave blank if compound is not detected.
IntermediateResultUnits	X		X		X		X		Report "ng".
LabQualifiers									Not required.
ManualIntegration	X		X		X		X		Report "Yes" if this peak was manually integrated, otherwise report "No".
MeanCalibrationFactor									Not required.
MeanCalibrationFactorUnits									Not required.
MeanRetentionTime									Not required.
MeanRetentionTimeLimitHigh									Not required.
MeanRetentionTimeLimitLow									Not required.
MeanRetentionTimeLimitType									Not required.
MeanRetentionTimeUnits									Not required.
MeanRRF									Not required.
MeanRRFLimitLow									Not required.
MeanRRFLimitType									Not required.
PeakID	X		X		X		X		Report the peak identifier as used by the laboratory to uniquely identify this peak.
PercentDifference									Not required.
PercentDifferenceLimitHigh									Not required.
PercentDifferenceLimitLow									Not required.
PercentDifferenceLimitType									Not required.
PercentRecovery									Not required.
PercentRecoveryLimitHigh									Not required.
PercentRecoveryLimitLow									Not required.
PercentRecoveryLimitType									Not required.
PercentRSD									Not required.
PercentRSDLimitHigh									Not required.
PercentRSDLimitLow									Not required.
PercentRSDLimitType									Not required.
Resolution									Not required.
ResolutionLimitLow									Not required.

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
ResolutionLimitType									Not required.
ResolutionUnits									Not required.
Response	X		X		X		X		Report the actual Peak Area (or Peak Height) from the raw data.
ResponseLimitHigh									Not required.
ResponseLimitLow									Not required.
ResponseLimitType									Not required.
ResponseUnits	X		X		X		X		Report "Peak_Area" or "Peak_Height".
Result									Not required.
ResultLimitHigh									Not required.
ResultLimitLow									Not required.
ResultLimitType									Not required.
ResultType									Not required.
ResultUnits									Not required.
RetentionTime	X		X		X		X		Report the actual Retention Time in decimal minutes from the raw data for this peak.
RetentionTimeLimitHigh	X		X		X		X		Report the upper limit for this Retention Time in decimal minutes.
RetentionTimeLimitLow	X		X		X		X		Report the lower limit for this Retention Time in decimal minutes.
RetentionTimeLimitType	X		X		X		X		Report "Method".
RetentionTimeUnits	X		X		X		X		Report "Minutes".
RRF									Not required.
RRFLimitLow									Not required.
RRFLimitType									Not required.
WeightingFactor									Not required.
PeakComparison									Not required.

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability IPC	ICAL	CCV	FLO	GPC	Instructions
Header	X	X	X	X		
ClientDataPackageID	X	X	X	X		Report the Case Number.
ClientDataPackageName	X	X	X	X		Report the Contract Number.
ClientDataPackageVersion	X	X	X	X		Report "1", then increment with each resubmission.
EDDID	X	X	X	X		Report "SEDD".
EDDVersion	X	X	X	X		Report "Draft 5.1".
EDDImplementationID	X	X	X	X		Report "ORGANICGENERAL_3" (This is the DTD used).
EDDImplementationVersion	X	X	X	X		Report "2" (This is the version of the DTD used).
GeneratingSystemID	X	X	X	X		Report name of generating software or vendor.
GeneratingSystemVersion						Report software version number
LabDataPackageID	X	X	X	X		Report the Sample Delivery Group (SDG).
LabDataPackageName	X	X	X	X		Report "Pest".
LabDataPackageVersion	X	X	X	X		Report "1", then increment with each resubmission.
LabReportedDate	X	X	X	X		Report the date this data was reported to the client.
DateFormat	X	X	X	X		Report "MMDDYYYY HH:mm:SS". All dates and times reported in the EDD must follow this format. If any part of the time is unknown, report "00" for the unknown hours, minutes, and seconds.
Comment						Not required.
SamplePlusMethod						Not required.
InstrumentQC	X	X	X	X		
ClientInstrumentQCType	X	X				For the RESC and standards, report "1" if using a single mixture to calibrate instrument. Report "2" if using two mixtures to calibrate instrument.
ClientMethodID	X	X	X	X		Report "SOM01.1".
ClientMethodName						Not required.
ClientMethodSource	X	X	X	X		Report "USEPA_CLP".
Comment						Not required.
LabInstrumentQCID	X	X	X	X		Report the EPA Sample Number. For ICAL, report the EPA Sample Number of the first standard.
LabID	X	X	X	X		Report the Agency-assigned Lab Code.
LabName	X	X	X	X		Report the Lab Name.
QCLinkage	X	X	X	X		Report "AnalysisBatch" for CCV, "RunBatch" for ICAL and IPC, and "CleanupBatch" for FLO and GPC.
QCType	X	X	X	X		Report "Instrument_Performance_Check" for the RESC standard; "Instrument_Performance_Check_PEM" for the PEM standards that are part of the ICAL; "Initial_Calibration" for the initial calibration; "Continuing_Calibration_Verification" for the CCV; "Florisil_Cartridge_Check" for the Florisil cartridge check; and "GPC_Calibration_Check" for the GPC calibration check.

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability IPC	ICAL	CCV	FLO	GPC	Instructions
Analysis	X	X	X	X		
AliquotAmount						Not required.
AliquotAmountUnits						Not required.
AnalysisBatch	X	X	X	X		Links this analysis to the beginning of a 12-hour period. Report the Lab File ID of the PIBLK (for CCV) or RESC (for initial calibration) that starts this sequence. For the PIBLK or RESC at the beginning of a 12-hour period, report the Lab File ID of the PIBLK or RESC itself.
AnalysisBatchEnd			X	X		Links this analysis to the QC immediately following the end of a 12-hour period. Report the Lab File ID of the last CCV used to close out the 12-hour period. For the last CCV, report the Lab File ID of the CCV itself.
AnalysisGroupID		X				Links a group of analyses together that are used for the multipoint initial calibration. Report the Lab File ID of the standard that starts this sequence.
AnalysisType	X	X	X	X		For IPC, FLO, and GPC, report "Initial". For ICAL/CCV report the calibration level used (e.g., "CF-4").
Analyst	X	X	X	X		Report Analyst's initials.
AnalyzedAmount	X	X	X	X		Report the volume of the standard placed on instrument for analysis in microliters.
AnalyzedAmountUnits	X	X	X	X		Report "uL".
AnalyzedDate	X	X	X	X		Report the date and time the sample was analyzed.
BottleID						Not required.
ClientAnalysisID	X	X	X	X		Report the EPA Sample Number.
ClientMethodID	X	X	X	X		Report "SOM01.1".
ClientMethodName						Not required.
ClientMethodSource	X	X	X	X		Report "USEPA_CLP".
Column	X	X	X	X		Report the GC Column used.
ColumnInternalDiameter	X	X	X	X		Report the GC Column Internal Diameter in millimeters.
ColumnInternalDiameterUnits	X	X	X	X		Report "mm".
ColumnLength	X	X	X	X		Report the GC Column Length in meters.
ColumnLengthUnits	X	X	X	X		Report "m".
Comment						Not required.
ConfirmationAnalysisID						Not required.
DetectorID						Not required.
DetectorType	X	X	X	X		Report "ECD".
DilutionFactor						Not required.
HeatedPurge						Not required.
InjectionVolume	X	X	X	X		Report the column specific Injection Volume used in microliters to at least two significant figures.
InjectionVolumeUnits	X	X	X	X		Report "uL".
InstrumentID	X	X	X	X		Report the laboratory identifier for the instrument used for this analysis.
LabAnalysisID	X	X	X	X		Report the Lab File ID.
LabFileID	X	X	X	X		Report the Lab File ID.
LabMethodID						Not required.
LabMethodName						Not required.
OriginalLabAnalysisID						Not required.

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability IPC	ICAL	CCV	FLO	GPC	Instructions
ProcedureID						Not required.
ProcedureName						Not required.
ResultBasis						Not required.
RunBatch	X	X	X		X	Links this analysis to an initial calibration. Report the Lab File ID of the RESC standard that started this ICAL sequence.
AnalysisGroup		X				
AnalysisGroupID		X				Links a group of analyses together that are used for the initial calibration. Report the Lab File ID of the standard that starts this sequence.
AnalysisType		X				Report "Initial_Calibration".
Comment						Not required.
Handling						Not required.
ReportedResult						Not required.
PreparationPlusCleanup					X	
AliquotAmount						Not required.
AliquotAmountUnits						Not required.
Analyst						Not required.
BottleID						Not required.
CleanedUpDate					X	Report the date and time the sample was cleaned up.
CleanupBatch					X	Links all samples that were cleaned up together. Report the Lab File ID of the associated cleanup blank.
CleanupType					X	Report "GPC" or "Florisil" as applicable.
ClientMethodID					X	Report "SOM01.1".
ClientMethodName						Not required.
ClientMethodSource					X	Report "USEPA_CLP".
Comment						Not required.
FinalAmount					X	Report the Final Amount of material produced upon completion of this Prep or Cleanup in microliters.
FinalAmountUnits					X	Report "uL".
InitialAmount					X	Report the initial amount of extracted sample used for this cleanup method in microliters.
InitialAmountUnits					X	Report "uL".
LabMethodID						Not required.
LabMethodName						Not required.
LotNumber					X	Report the manufacturer's lot number for the Florisil cartridges used.
PreparationBatch						Not required.
PreparationPlusCleanupType					X	Report "Cleanup".
PreparationType						Not required.
PreparedDate						Not required.
ProcedureID						Not required.
ProcedureName						Not required.

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability IPC	ICAL	CCV	FLO	GPC	Instructions
Analyte	X	X	X	X		
AmountAdded	X	X	X	X		Report the volume of the standard used in microliters.
AmountAddedUnits	X	X	X	X		Report "uL".
AnalyteName	X	X	X	X		Report analytes as they appear in the SOW.
AnalyteNameContext						Not required.
AnalyteType	X	X	X	X		Report "Target" for target compounds or "Surrogate" for surrogates.
CASRegistryNumber	X	X	X	X		Report CAS Numbers as they appear in the SOW.
ClientAnalyteID	X	X	X	X		Report CAS Number.
Comment						Not required.
ExpectedResult	X	X	X	X		Report the final amount added in nanograms.
ExpectedResultUnits	X	X	X	X		Report "ng".
IntermediateResult	X	X	X	X		Report the on-column amount in nanograms from the raw data.
IntermediateResultUnits	X	X	X	X		Report "ng".
LabAnalyteID						Not required.
LabQualifiers						Not required.
LotNumber	X	X	X	X		Report the vendor/manufacturer assigned lot number for this standard.
PeakID						Not required.
PercentBreakdown	X					Report the calculated Percent Breakdown for 4,4'-DDT and Endrin to the nearest whole percent.
PercentBreakdownLimitHigh	X					Report the upper limit for the Percent_Breakdown to the nearest whole percent.
PercentBreakdownLimitType	X					Report "Method".
PercentDifference						Not required.
PercentDifferenceLimitHigh						Not required.
PercentDifferenceLimitLow						Not required.
PercentDifferenceLimitType						Not required.
PercentMatch						Not required.
PercentRecovery				X		Report the final calculated Percent Recovery to the nearest whole percent.
PercentRecoveryLimitHigh				X		Report the upper limit for the Percent Recovery to the nearest whole percent.
PercentRecoveryLimitLow				X		Report the lower limit for the Percent Recovery to the nearest whole percent.
PercentRecoveryLimitType				X		Report "Method".
Result						Not required.
ResultLimitHigh						Not required.
ResultLimitLow						Not required.
ResultLimitType						Not required.
ResultType						Not required.
ResultUnits						Not required.
RPD						Not required.
RPDLimitHigh						Not required.
RPDLimitType						Not required.
StandardConcentration	X	X	X	X		Report the concentration of the standard used in micrograms per liter.
StandardConcentrationUnits	X	X	X	X		Report "ug/L".

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability IPC	ICAL	CCV	FLO	GPC	Instructions
StandardID	X	X	X	X		Report the laboratory assigned identifier for this standard.
StandardSource	X	X	X	X		Report the vendor/manufacturer for this standard.
TailingFactor						Not required.
TailingFactorLimitHigh						Not required.
TailingFactorLimitType						Not required.
Peak	X	X	X	X		
CalibrationFactor		X	X			Report the calculated Calibration Factor. Leave blank if this compound is not to be included in the initial calibration curve.
CalibrationFactorUnits		X	X			Report the units for the Calibration Factor.
CalibrationType		X				Report "Average_Calibration_Factor".
Coeffa0						Not required.
Coeffa1						Not required.
Coeffa2						Not required.
Coeffa3						Not required.
CoeffOfDetermination						Not required.
CoeffOfDeterminationLimitLow						Not required.
CoeffOfDeterminationLimitType						Not required.
Comment						Not required.
CorrelationCoeff						Not required.
CorrelationCoeffLimitLow						Not required.
CorrelationCoeffLimitType						Not required.
IntermediateResult	X	X	X	X		Report the on-column amount in nanograms from the raw data for this peak. Leave blank if compound is not detected.
IntermediateResultUnits	X	X	X	X		Report "ng".
LabQualifiers						Not required.
ManualIntegration	X	X	X	X		Report "Yes" if this peak was manually integrated, otherwise report "No".
MeanCalibrationFactor		X				Report the calculated Mean Calibration Factor under the AnalysisGroup node only.
MeanCalibrationFactorUnits		X				Report the units for the Mean Calibration Factor under the AnalysisGroup node only.
MeanRetentionTime		X				Report the mean retention time in decimal minutes under AnalysisGroup only.
MeanRetentionTimeLimitHigh		X				Report the upper limit for the mean retention time in decimal minutes from the ICAL.
MeanRetentionTimeLimitLow		X				Report the lower limit for the mean retention time in decimal minutes from the ICAL.
MeanRetentionTimeLimitType		X				Report "Method".
MeanRetentionTimeUnits		X				Report "Minutes".
MeanRRF						Not required.
MeanRRFLimitLow						Not required.
MeanRRFLimitType						Not required.
PeakID	X	X	X	X		Report the peak identifier as used by the laboratory to uniquely identify this peak.
PercentDifference	X		X			Report the calculated Percent Difference for this peak to the nearest tenth of a percent.

Table 3

Pesticides Data Element Instructions (Con't)

Node and Data Elements	Applicability IPC	ICAL	CCV	FLO	GPC	Instructions
PercentDifferenceLimitHigh	X		X			Report the upper limit for the Percent Difference for this peak to the nearest tenth of a percent.
PercentDifferenceLimitLow	X		X			Report the lower limit for the Percent Difference for this peak to the nearest tenth of a percent.
PercentDifferenceLimitType	X		X			Report "Method".
PercentRecovery						Not required.
PercentRecoveryLimitHigh						Not required.
PercentRecoveryLimitLow						Not required.
PercentRecoveryLimitType						Not required.
PercentRSD		X				Report the calculated Percent Relative Standard Deviation to the nearest tenth of a percent under the AnalysisGroup node only.
PercentRSDLimitHigh		X				Report the upper limit for the Percent Relative Standard Deviation to the nearest tenth of a percent under the AnalysisGroup node only.
PercentRSDLimitLow						Not required.
PercentRSDLimitType		X				Report "Method".
Resolution	X	X	X			Report percent resolutions for midpoint INDA, INDB, or INDC initial calibration standards only; report resolutions for all PEMs used in the initial and calibration verification standards.
ResolutionLimitLow	X	X	X			Report the lower limit for the percent resolution.
ResolutionLimitType	X	X	X			Report "Method".
ResolutionUnits	X	X	X			Report "Percent".
Response	X	X	X		X	Report the actual Peak Area (or Peak Height) from the raw data.
ResponseLimitHigh						Not required.
ResponseLimitLow						Not required.
ResponseLimitType						Not required.
ResponseUnits	X	X	X		X	Report "Peak_Area" or "Peak_Height".
Result						Not required.
ResultLimitHigh						Not required.
ResultLimitLow						Not required.
ResultLimitType						Not required.
ResultType						Not required.
ResultUnits						Not required.
RetentionTime	X	X	X		X	Report the actual Retention Time in decimal minutes from the raw data for this peak.
RetentionTimeLimitHigh	X	X	X		X	Report the upper limit for this Retention Time in decimal minutes.
RetentionTimeLimitLow	X	X	X		X	Report the lower limit for this Retention Time in decimal minutes.
RetentionTimeLimitType	X	X	X		X	Report "Method".
RetentionTimeUnits	X	X	X		X	Report "Minutes".
RRF						Not required.
RRFLimitLow						Not required.
RRFLimitType						Not required.
WeightingFactor						Not required.
PeakComparison						Not required.

Table 4

Aroclors Data Element Instructions

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
Header	X		X		X		X	X	
ClientDataPackageID	X		X		X		X	X	Report the Case Number.
ClientDataPackageName	X		X		X		X	X	Report the Contract Number.
ClientDataPackageVersion	X		X		X		X	X	Report "1", then increment with each resubmission.
EDDID	X		X		X		X	X	Report "SEDD".
EDDVersion	X		X		X		X	X	Report "Draft 5.1".
EDDImplementationID	X		X		X		X	X	Report "ORGANICGENERAL_3" (This is the DTD used).
EDDImplementationVersion	X		X		X		X	X	Report "2" (This is the version of the DTD used).
GeneratingSystemID	X		X		X		X	X	Report name of generating software or vendor.
GeneratingSystemVersion	X		X		X		X	X	Report software version number.
LabDataPackageID	X		X		X		X	X	Report the Sample Delivery Group (SDG).
LabDataPackageName	X		X		X		X	X	Report "Aroclor".
LabDataPackageVersion	X		X		X		X	X	Report "1", then increment with each resubmission.
LabReportedDate	X		X		X		X	X	Report the date this data was reported to the client.
DateFormat	X		X		X		X	X	Report "MMDDYYYY HH:mm:SS". All dates and times reported in the EDD must follow this format. If any part of the time is unknown, report "00" for the unknown hours, minutes, and seconds.
Comment									Not required.
SamplePlusMethod	X		X		X		X	X	
Bottles									Not required.
BottleType									Not required.
ClientID	X				X				Report "1" for Region 1, "2" for Region 2, etc. For samples received from QATS, report "91".
ClientMethodID	X		X		X		X	X	Report "SOM01.1".
ClientMethodName									Not required.
ClientMethodSource	X		X		X		X	X	Report "USEPA_CLP".
ClientMethodType	X		X		X		X	X	Report "GCECD_External_Standard".
ClientSampleID	X		X		X		X	X	Report the EPA Sample Number.
CollectedDate	X				X				Report the date and time the sample was collected.
Comment									Not required.
Composite									Not required.
CoolerID									Not required.
CustodyID	X				X				Report the Traffic Report/Chain of Custody Form Number.
EquipmentBatch									Not required.
LabContract	X		X		X		X		Report the Contract Number.
LabID	X		X		X		X	X	Report the Agency-assigned Lab Code.

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability						Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
LabName	X		X		X		X	X	Report the Lab Name.
LabReceiptDate	X				X				Report the date and time the sample was received.
LabReportingBatch	X		X		X		X	X	Links all samples analyzed to this SDG. Report the SDG Number.
LabSampleID	X		X		X		X		Report the Lab Sample ID as assigned by the laboratory.
MatrixID	X		X		X		X		Report "Water", "Soil", or "Sediment".
MatrixName									Not required.
MethodLevel									Not required.
MethodBatch									Not required.
OriginalClientSampleID					X				Report the EPA Sample Number of the original sample from which this sample was derived.
OriginalLabSampleID									Not required.
PercentMoisture	X		X		X		X		For Soil/Sediment samples only, report the percent moisture to at least two significant figures.
PercentSolids									Not required.
pH	X				X				Report the pH as measured by the laboratory upon receipt to the nearest tenth of a pH unit.
Preservative	X				X				Report any chemical preservative used.
ProjectID	X		X		X		X		Report the Case Number.
ProjectName									Not required.
QCCategory			X		X		X		Report "Blank" for MB, CB and IB; "Spike" for MS; "Spike_Duplicate" for MSD; and "Blank_Spike" for LCS.
QCLinkage			X		X		X	X	Report "LabReportingBatch" for MS and MSD; "PreparationBatch" for MB, CB and LCS; or "AnalysisBatch" for IB and non-client samples.
QCType	X		X		X		X	X	Report "Method_Blank" for MB; "Cleanup_Blank" for CB; "Instrument_Blank" for IB; "Matrix_Spike" for MS; "Matrix_Spike_Duplicate" for MSD; "Laboratory_Control_Sample" for LCS; "Field_Sample" for field samples; "Field_Blank" for field, equipment, rinse, trip, or other blanks; "PT_Sample" for Performance Evaluation samples; or "Non_Client_Sample" for non-client samples.
SamplingBatch									Not required.
ServicesID	X				X				Report the Modification Reference Number, if applicable.
ShippingBatch									Not required.
SiteID									Not required.

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability: Sample	MB	CB	IB	MS	MSD	LCS	NCS	Instructions
SiteName									Not required.
StorageBatch									Not required.
Temperature	X				X				Report the temperature as measured by the laboratory upon receipt to the nearest whole °C.
TemperatureUnits	X				X				Report "C".
InstrumentQC									Not required.
Analysis	X		X		X		X	X	
AliquotAmount									Not required.
AliquotAmountUnits									Not required.
AnalysisBatch	X		X		X		X	X	Links this analysis to the beginning of a 12-hour period. Report the Lab File ID of the instrument blank that starts this sequence. For the instrument blank that starts this sequence, report the Lab File ID of the instrument blank itself.
AnalysisBatchEnd	X		X		X		X	X	Links this analysis to the QC immediately following a 12-hour period. Report the Lab File ID of the last CCV standard used to close out the 12-hour period.
AnalysisGroupID									Not required.
AnalysisType	X		X		X		X		Report "Initial", "Dilution-01", "Reanalysis-01" or "Reinjection-01". Then increment as necessary.
Analyst	X		X		X		X		Report Analyst's initials.
AnalyzedAmount	X		X		X		X		Report the volume of the final extract added to the sample vial in microliters.
AnalyzedAmountUnits	X		X		X		X		Report "uL".
AnalyzedDate	X		X		X		X	X	Report the date and time the sample was analyzed.
BottleID									Not required.
ClientAnalysisID	X		X		X		X	X	Report the EPA Sample Number.
ClientMethodID	X		X		X		X	X	Report "SOM01.1".
ClientMethodName									Not required.
ClientMethodType	X		X		X		X	X	Report "USEPA_CLP".
Column	X		X		X		X	X	Report the GC Column used.
ColumnInternalDiameter	X		X		X		X	X	Report the GC Column Internal Diameter in millimeters.
ColumnInternalDiameterUnits	X		X		X		X	X	Report "mm".
ColumnLength	X		X		X		X	X	Report the GC Column Length in meters.
ColumnLengthUnits	X		X		X		X	X	Report "m".
Comment									Not required.
ConfirmationAnalysisID	X		X		X		X		Links an analysis to a confirmation analysis. Report the Lab File ID of the confirmation analysis.
DetectorID									Not required.

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
DetectorType	X		X		X		X	X	Report "ECD".
DilutionFactor	X		X		X		X		Report the Dilution Factor used to the nearest tenth.
HeatedPurge									Not required.
InjectionVolume	X		X		X		X		Report the column specific Injection Volume used in microliters to at least two significant figures.
InjectionVolumeUnits	X		X		X		X		Report "uL".
InstrumentID	X		X		X		X	X	Report the laboratory identifier for the instrument used for this analysis.
LabAnalysisID	X		X		X		X	X	Report the Lab File ID.
LabFileID	X		X		X		X	X	Report the Lab File ID.
LabMethodID									Not required.
LabMethodName									Not required.
OriginalLabAnalysisID									If a dilution or reinjection is prepared from a previously analyzed sample, report the Lab Analysis ID of the original sample that the dilution or reinjection is prepared from.
ProcedureID									Not required.
ProcedureName									Not required.
ResultBasis	X		X		X		X		Report "Dry" for Soil/Sediment samples. Report "Total" or "Filtered" for water samples, as applicable.
RunBatch	X		X		X		X	X	Links this analysis to an initial calibration. Report the Lab File ID of the standard that started the ICAL sequence.
AnalysisGroup									Not required.
Handling	X		X		X		X		
Analyst									Not required.
BottleID									Not required.
ClientMethodID	X		X		X		X		Report "SOM01.1".
ClientMethodName									Not required.
ClientMethodSource	X		X		X		X		Report "USEPA_CLP".
Comment									Not required.
HandledDate	X		X		X		X		Report the date and time the sample was handled.
HandlingBatch									Not required.
HandlingType	X				X				Report "Decanted" if water was decanted from Soil samples, otherwise report "Not_Decanted".
InitialAmount									Not required.
InitialAmountUnits									Not required.
LabMethodID									Not required.
LabMethodName									Not required.
ProcedureID									Not required.
ProcedureName									Not required.

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
PercentMoisture									Not required.
PercentSolids									Not required.
SampleAmount									Not required.
SampleAmountUnits									Not required.
ReportedResult	X		X		X		X		
AnalysisGroupID									Not required.
AnalyteName	X		X		X		X		Report analytes as they appear in the SOW.
AnalyteNameContext									Not required.
AnalyteType	X		X		X		X		Report "Target" for all target compounds and "Spike" for all target compounds designated as spike compounds for MS/MSD and LCS analysis.
CASRegistryNumber	X		X		X		X		Report CAS Numbers as they appear in the SOW.
ClientAnalyteID	X		X		X		X		Report CAS Number.
Comment									Not required.
DetectionLimit	X		X		X		X		For target compounds, report the adjusted Method Detection Limit as determined by the laboratory to at least two significant figures.
DetectionLimitType	X		X		X		X		Report "MDL".
DetectionLimitUnits	X		X		X		X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
ExpectedResult									Not required.
ExpectedResultUnits									Not required.
LabAnalysisID	X		X		X		X		Report the Lab File ID of the analysis for which this reported result was derived from.
LabAnalyteID									Not required.
LabQualifiers	X		X		X		X		Report up to five flags as specified in the SOW ("U", "J", "P", "C", "B", "E", "D", "S", "X", "Y", "Z").
PeakID									Not required.
PercentDifference	X		X		X		X		Report the percent difference between the reported result and the confirmation result to the nearest whole percent (excluding IB).
PercentDifferenceLimitHigh	X		X		X		X		Report the upper limit for the percent difference to the nearest whole percent (excluding IB).
PercentDifferenceLimitLow									Not required.
PercentDifferenceLimitType	X		X		X		X		Report "Method" (excluding IB).
PercentRecovery									Not required.
PercentRecoveryLimitHigh									Not required.
PercentRecoveryLimitLow									Not required.
PercentRecoveryLimitType									Not required.

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS
QuantitationLimit	X		X		X		X	For target compounds, report the adjusted CRQL to at least two significant figures.
QuantitationLimitType	X		X		X		X	Report "CRQL".
QuantitationLimitUnits	X		X		X		X	Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
ReportingLimit	X		X		X		X	For target compounds, report the adjusted CRQL.
ReportingLimitType	X		X		X		X	Report "CRQL".
ReportingLimitUnits	X		X		X		X	Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
Result	X		X		X		X	Report the final calculated concentration to at least two significant figures. Leave blank if analyte is not detected.
ResultLimitHigh								Not required.
ResultLimitLow								Not required.
ResultLimitType								Not required.
ResultType	X		X		X		X	Report "=" for all reported Result values.
ResultUnits	X		X		X		X	Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
RetentionTime								Not required.
RetentionTimeUnits								Not required.
RPD								Not required.
RPDLimitHigh								Not required.
RPDLimitType								Not required.
PreparationPlusCleanup	X		X		X		X	
AliquotAmount	X		X		X		X	Report the sample amount used for this analysis to at least three significant figures.
AliquotAmountUnits	X		X		X		X	Report "g" for Soil/Sediment and "mL" for Water.
Analyst								Not required.
BottleID								Not required.
CleanedUpDate	X		X		X		X	Report the date and time the sample was cleaned up.
CleanupBatch	X		X		X		X	Links all samples that were cleaned up together. Report the Lab File ID of the associated blank or other unique identifier.
CleanupType	X		X		X		X	Report "GPC", "Florisil", "Sulfuric_Acid", "Silica_Gel", "Alumina", or "Acid_Base_Partition" as applicable.
ClientMethodID	X		X		X		X	Report "SOM01.1".
ClientMethodName								Not required.
ClientMethodSource	X		X		X		X	Report "USEPA_CLP".
Comment								Not required.

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
FinalAmount	X		X		X		X		Report the Final Amount of material produced upon completion of this Prep or Cleanup in microliters.
FinalAmountUnits	X		X		X		X		Report "uL".
InitialAmount	X		X		X		X		Report the initial amount of extracted sample used for this cleanup method in microliters.
InitialAmountUnits	X		X		X		X		Report "uL".
LabMethodID									Not required.
LabMethodName									Not required.
LotNumber	X		X		X		X		Report the manufacturer's lot number for the Florisil cartridges used.
PreparationBatch	X		X		X		X		Links all samples that were extracted together. Report the Lab File ID of the associated Method Blank.
PreparationPlusCleanupType	X		X		X		X		Report "Preparation" or "Cleanup" as applicable.
PreparationType	X		X		X		X		Report "Sonication", "Soxhlet", or "Pressurized_Fluid" for Soil/Sediment. Report "Sep_Funnel", "Liq_Liq", or "Liq_Membrane" for Water.
PreparedDate	X		X		X		X		Report the date and time the sample was extracted.
ProcedureID									Not required.
ProcedureName									Not required.
Analyte	X		X		X		X		
AmountAdded	X		X		X		X		Report the volume of the surrogate standard or spiking solution added to the sample in uL.
AmountAddedUnits	X		X		X		X		Report "uL".
AnalyteName	X		X		X		X		Report analytes as they appear in the SOW.
AnalyteNameContext									Not required.
AnalyteType	X		X		X		X		Report "Target for all target compounds; "Surrogate" for surrogate compounds; or "Spike" for target compounds designated as spike compounds for MS/MSD or LCS analysis.
CASRegistryNumber	X		X		X		X		Report CAS Numbers as they appear in the SOW.
ClientAnalyteID	X		X		X		X		Report CAS Number.
Comment									Not required.
ExpectedResult	X		X		X		X		Report the amount in ng for the surrogates. For spikes and LCS, report the theoretical final calculated concentration for the compounds.
ExpectedResultUnits	X		X		X		X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water. Report "ng" for surrogates.

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
IntermediateResult	X		X		X		X		Report the on-column amount in nanograms from the raw data. Leave blank if not detected.
IntermediateResultUnits	X		X		X		X		Report "ng".
LabAnalyteID									Not required.
LabQualifiers	X		X		X		X		Report up to five flags as specified in the SOW ("U", "J", "P", "C", "B", "E", "D", "S", "X", "Y", "Z").
LotNumber	X		X		X		X		Report the vendor/manufacturer assigned lot number for this standard.
PeakID									Not required.
PercentBreakdown									Not required.
PercentBreakdownLimitHigh									Not required.
PercentBreakdownLimitType									Not required.
PercentDifference									Not required.
PercentDifferenceLimitHigh									Not required.
PercentDifferenceLimitLow									Not required.
PercentDifferenceLimitType									Not required.
PercentMatch									Not required.
PercentRecovery	X		X		X		X		Report the final calculated Percent Recovery of the spikes and surrogates to the nearest whole percent.
PercentRecoveryLimitHigh	X		X		X		X		Report the upper limit for the Percent Recovery of the spikes and surrogates to the nearest whole percent.
PercentRecoveryLimitLow	X		X		X		X		Report the lower limit for the Percent Recovery of the spikes and surrogates to the nearest whole percent.
PercentRecoveryLimitType	X		X		X		X		Report "Method".
Result	X		X		X		X		Report the calculated concentration or amount to at least two significant figures. Leave blank if compound is not detected.
ResultLimitHigh									Not required.
ResultLimitLow									Not required.
ResultLimitType									Not required.
ResultType	X		X		X		X		Report "=" for all reported Result values.
ResultUnits	X		X		X		X		Report "ug/kg" for Soil/Sediment and "ug/L" for Water.
RPD					X				Report the RPD to the nearest whole percent.
RPDLimitHigh					X				Report the upper limit for the RPD to the nearest whole percent.
RPDLimitType					X				Report "Method".
StandardConcentration	X		X		X		X		Report the concentration of the surrogate standard or spiking solution used in ug/L.
StandardConcentrationUnits	X		X		X		X		Report "ug/L".

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS
StandardID	X		X		X		X	Report the laboratory assigned identifier for this standard.
StandardSource	X		X		X		X	Report the vendor/manufacturer for this standard.
TailingFactor								Not required.
TailingFactorLimitHigh								Not required.
TailingFactorLimitType								Not required.
Peak	X		X		X		X	
CalibrationFactor								Not required.
CalibrationFactorUnits								Not required.
CalibrationType								Not required.
Coeffa0								Not required.
Coeffa1								Not required.
Coeffa2								Not required.
Coeffa3								Not required.
CoeffOfDetermination								Not required.
CoeffOfDeterminationLimitLow								Not required.
CoeffOfDeterminationLimitType								Not required.
Comment								Not required.
CorrelationCoeff								Not required.
CorrelationCoeffLimitLow								Not required.
CorrelationCoeffLimitType								Not required.
IntermediateResult	X		X		X		X	Report the on-column amount in nanograms from the raw data for this peak. Leave blank if compound is not detected.
IntermediateResultUnits	X		X		X		X	Report "ng".
LabQualifiers								Not required.
ManualIntegration	X		X		X		X	Report "Yes" if this peak was manually integrated, otherwise report "No".
MeanCalibrationFactor								Not required.
MeanCalibrationFactorUnits								Not required.
MeanRetentionTime								Not required.
MeanRetentionTimeLimitHigh								Not required.
MeanRetentionTimeLimitLow								Not required.
MeanRetentionTimeLimitType								Not required.
MeanRetentionTimeUnits								Not required.
MeanRRF								Not required.
MeanRRFLimitLow								Not required.
MeanRRFLimitType								Not required.
PeakID	X		X		X		X	Report the peak identifier as used by the laboratory to uniquely identify this peak.
PercentDifference								Not required.
PercentDifferenceLimitHigh								Not required.
PercentDifferenceLimitLow								Not required.
PercentDifferenceLimitType								Not required.
PercentRecovery								Not required.
PercentRecoveryLimitHigh								Not required.
PercentRecoveryLimitLow								Not required.
PercentRecoveryLimitType								Not required.

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability							Instructions
	Sample	MB	CB	IB	MS	MSD	LCS	NCS	
PercentRSD									Not required.
PercentRSDLimitHigh									Not required.
PercentRSDLimitLow									Not required.
PercentRSDLimitType									Not required.
Resolution									Not required.
ResolutionLimitLow									Not required.
ResolutionLimitType									Not required.
ResolutionUnits									Not required.
Response	X		X		X		X		Report the actual Peak Area (or Peak Height) from the raw data.
ResponseLimitHigh									Not required.
ResponseLimitLow									Not required.
ResponseLimitType									Not required.
ResponseUnits	X		X		X		X		Report "Peak_Area" or "Peak_Height".
Result									Not required.
ResultLimitHigh									Not required.
ResultLimitLow									Not required.
ResultLimitType									Not required.
ResultType									Not required.
ResultUnits									Not required.
RetentionTime	X		X		X		X		Report the actual Retention Time in decimal minutes from the raw data for this peak.
RetentionTimeLimitHigh	X		X		X		X		Report the upper limit for this Retention Time in decimal minutes.
RetentionTimeLimitLow	X		X		X		X		Report the lower limit for this Retention Time in decimal minutes.
RetentionTimeLimitType	X		X		X		X		Report "Method".
RetentionTimeUnits	X		X		X		X		Report "Minutes".
RRF									Not required.
RRFLimitLow									Not required.
RRFLimitType									Not required.
WeightingFactor									Not required.
PeakComparison									Not required.

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability ICAL	Applicability CCV	Instructions
Header	X	X	
ClientDataPackageID	X	X	Report the Case Number.
ClientDataPackageName	X	X	Report the Contract Number.
ClientDataPackageVersion	X	X	Report "1", then increment with each resubmission.
EDDID	X	X	Report "SEDD".
EDDVersion	X	X	Report "Draft 5.1".
EDDImplementationID	X	X	Report "ORGANICGENERAL_3" (This is the DTD used).
EDDImplementationVersion	X	X	Report "2" (This is the version of the DTD used).
GeneratingSystemID	X	X	Report name of generating software or vendor.
GeneratingSystemVersion	X	X	Report software version number.
LabDataPackageID	X	X	Report the Sample Delivery Group (SDG).
LabDataPackageName	X	X	Report "Aroclor".
LabDataPackageVersion	X	X	Report "1", then increment with each resubmission.
LabReportedDate	X	X	Report the date this data was reported to the client.
DateFormat	X	X	Report "MMDDYYYY HH:mm:SS". All dates and times reported in the EDD must follow this format. If any part of the time is unknown, report "00" for the unknown hours, minutes, and seconds.
Comment			Not required.
SamplePlusMethod			Not required.
InstrumentQC	X	X	
ClientInstrumentQCType			Not required.
ClientMethodID	X	X	Report "SOM01.1".
ClientMethodName			Not required.
ClientMethodSource	X	X	Report "USEPA_CLP".
Comment			Not required.
LabInstrumentQCID	X	X	Report the EPA Sample Number. For ICAL, report the EPA Sample Number of the first standard.
LabID	X	X	Report the Agency-assigned Lab Code.
LabName	X	X	Report the Lab Name.
QCLinkage	X	X	Report "AnalysisBatch" for CCV and "RunBatch" for ICAL.
QCType	X	X	Report "Initial_Calibration" or "Continuing_Calibration_Verification".
Analysis	X	X	
AliquotAmount			Not required.
AliquotAmountUnits			Not required.
AnalysisBatch	X	X	Links this analysis to the beginning of a 12-hour period. Report the Lab File ID of the instrument blank that starts this sequence.
AnalysisBatchEnd		X	Links this analysis to the QC immediately following the end of a 12-hour period. Report the Lab File ID of the last CCV used to close out the 12-hour period. For the last CCV, report the Lab File ID of the CCV itself.
AnalysisGroupID	X		Links a group of analyses together that are used for multipoint initial calibration. Report the Lab File ID of the standard that starts this sequence.

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability ICAL	CCV	Instructions
AnalysisType	X	X	For ICAL/CCV report the calibration level used (e.g., "CF-10").
Analyst	X	X	Report Analyst's initials.
AnalyzedAmount	X	X	Report the volume of the standard placed on instrument for analysis in microliters.
AnalyzedAmountUnits	X	X	Report "uL".
AnalyzedDate	X	X	Report the date and time the sample was analyzed.
BottleID			Not required.
ClientAnalysisID	X	X	Report the EPA Sample Number.
ClientMethodID	X	X	Report "SOM01.1".
ClientMethodName			Not required.
ClientMethodSource	X	X	Report "USEPA_CLP".
Column	X	X	Report the GC Column used.
ColumnInternalDiameter	X	X	Report the GC Column Internal Diameter in millimeters.
ColumnInternalDiameterUnits	X	X	Report "mm".
ColumnLength	X	X	Report the GC Column Length in meters.
ColumnLengthUnits	X	X	Report "m".
Comment			Not required.
ConfirmationAnalysisID			Not required.
DetectorID			Not required.
DetectorType	X	X	Report "ECD".
DilutionFactor			Not required.
HeatedPurge			Not required.
InjectionVolume	X	X	Report the column specific Injection Volume used in microliters to at least two significant figures.
InjectionVolumeUnits	X	X	Report "uL".
InstrumentID	X	X	Report the laboratory identifier for the instrument used for this analysis.
LabAnalysisID	X	X	Report the Lab File ID.
LabFileID	X	X	Report the Lab File ID.
LabMethodID			Not required.
LabMethodName			Not required.
OriginalLabAnalysisID			Not required.
ProcedureID			Not required.
ProcedureName			Not required.
ResultBasis			Not required.
RunBatch	X	X	Links this analysis to an initial calibration. Report the Lab File ID of the standard that started the ICAL sequence.
AnalysisGroup	X		
AnalysisGroupID	X		Links a group of analyses together that are used for multipoint initial calibration. Report the Lab File ID of the standard that starts this sequence.
AnalysisType	X		Report "Initial_Calibration".
Comment			Not required.
Handling			Not required.
ReportedResult			Not required.

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability ICAL	Applicability CCV	Instructions
PreparationPlusCleanup			Not required.
Analyte	X	X	
AmountAdded	X	X	Report the volume of the standard used in microliters.
AmountAddedUnits	X	X	Report "uL".
AnalyteName	X	X	Report analytes as they appear in the SOW.
AnalyteNameContext			Not required.
AnalyteType	X	X	Report "Target" for target compounds or "Surrogate" for surrogates.
CASRegistryNumber	X	X	Report CAS Numbers as they appear in the SOW.
ClientAnalyteID	X	X	Report CAS Number.
Comment			Not required.
ExpectedResult	X	X	Report the final amount added in nanograms.
ExpectedResultUnits	X	X	Report "ng".
IntermediateResult	X	X	Report the on-column amount in nanograms from the raw data.
IntermediateResultUnits	X	X	Report "ng".
LabAnalyteID			Not required.
LabQualifiers			Not required.
LotNumber	X	X	Report the vendor/manufacturer assigned lot number for this standard.
PeakID			Not required.
PercentBreakdown			Not required.
PercentBreakdownLimitHigh			Not required.
PercentBreakdownLimitType			Not required.
PercentDifference			Not required.
PercentDifferenceLimitHigh			Not required.
PercentDifferenceLimitLow			Not required.
PercentDifferenceLimitType			Not required.
PercentMatch			Not required.
PercentRecovery			Not required.
PercentRecoveryLimitHigh			Not required.
PercentRecoveryLimitLow			Not required.
PercentRecoveryLimitType			Not required.
Result			Not required.
ResultLimitHigh			Not required.
ResultLimitLow			Not required.
ResultLimitType			Not required.
ResultType			Not required.
ResultUnits			Not required.
RPD			Not required.
RPDLimitHigh			Not required.
RPDLimitType			Not required.
StandardConcentration	X	X	Report the concentration of the standard used in micrograms per liter.
StandardConcentrationUnits	X	X	Report "ug/L".
StandardID	X	X	Report the laboratory assigned identifier for this standard.
StandardSource	X	X	Report the vendor/manufacturer for this standard.
TailingFactor			Not required.
TailingFactorLimitHigh			Not required.
TailingFactorLimitType			Not required.

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability ICAL	Applicability CCV	Instructions
Peak	X	X	
CalibrationFactor	X	X	Report the calculated Calibration Factor. Leave blank if this compound is not to be included in the initial calibration curve.
CalibrationFactorUnits	X	X	Report the units for the Calibration Factor.
CalibrationType	X		Report "Average_Calibration_Factor".
Coeffa0			Not required.
Coeffa1			Not required.
Coeffa2			Not required.
Coeffa3			Not required.
CoeffOfDetermination			Not required.
CoeffOfDeterminationLimitLow			Not required.
CoeffOfDeterminationLimitType			Not required.
Comment			Not required.
CorrelationCoeff			Not required.
CorrelationCoeffLimitLow			Not required.
CorrelationCoeffLimitType			Not required.
IntermediateResult	X	X	Report the on-column amount in nanograms from the raw data for this peak. Leave blank if compound is not detected.
IntermediateResultUnits	X	X	Report "ng".
LabQualifiers			Not required.
ManualIntegration	X	X	Report "Yes" if this peak was manually integrated, otherwise report "No".
MeanCalibrationFactor	X		Report the calculated Mean Calibration Factor under the AnalysisGroup node only.
MeanCalibrationFactorUnits	X		Report the units for the Mean Calibration Factor under the AnalysisGroup node only.
MeanRetentionTime	X		Report the mean retention time in decimal minutes under AnalysisGroup only.
MeanRetentionTimeLimitHigh	X		Report the upper limit for the mean retention time in decimal minutes from the ICAL.
MeanRetentionTimeLimitLow	X		Report the lower limit for the mean retention time in decimal minutes from the ICAL.
MeanRetentionTimeLimitType	X		Report "Method".
MeanRetentionTimeUnits	X		Report "Minutes".
MeanRRF			Not required.
MeanRRFLimitLow			Not required.
MeanRRFLimitType			Not required.
PeakID	X	X	Report the peak identifier as used by the laboratory to uniquely identify this peak.
PercentDifference		X	Report the calculated Percent Difference for this peak to the nearest tenth of a percent.
PercentDifferenceLimitHigh		X	Report the upper limit for the Percent Difference for this peak to the nearest tenth of a percent.
PercentDifferenceLimitLow		X	Report the lower limit for the Percent Difference for this peak to the nearest tenth of a percent.
PercentDifferenceLimitType		X	Report "Method".
PercentRecovery			Not required.
PercentRecoveryLimitHigh			Not required.
PercentRecoveryLimitLow			Not required.
PercentRecoveryLimitType			Not required.

Table 4

Aroclors Data Element Instructions (Con't)

Node and Data Elements	Applicability ICAL	Applicability CCV	Instructions
PercentRSD	X		Report the calculated Percent Relative Standard Deviation to the nearest tenth of a percent under the AnalysisGroup node only.
PercentRSDLimitHigh	X		Report the calculated Percent Relative Standard Deviation to the nearest tenth of a percent under the AnalysisGroup node only.
PercentRSDLimitLow			Not required.
PercentRSDLimitType	X		Report "Method".
Resolution			Not required.
ResolutionLimitLow			Not required.
ResolutionLimitType			Not required.
ResolutionUnits			Not required.
Response	X	X	Report the actual Peak Area (or Peak Height) from the raw data.
ResponseLimitHigh			Not required.
ResponseLimitLow			Not required.
ResponseLimitType			Not required.
ResponseUnits	X	X	Report "Peak_Area" or "Peak_Height".
Result			Not required.
ResultLimitHigh			Not required.
ResultLimitLow			Not required.
ResultLimitType			Not required.
ResultType			Not required.
ResultUnits			Not required.
RetentionTime	X	X	Report the actual Retention Time in decimal minutes from the raw data for this peak.
RetentionTimeLimitHigh	X	X	Report the upper limit for this Retention Time in decimal minutes.
RetentionTimeLimitLow	X	X	Report the lower limit for this Retention Time in decimal minutes.
RetentionTimeLimitType	X	X	Report "Method".
RetentionTimeUnits	X	X	Report "Minutes".
RRF			Not required.
RRFLimitLow			Not required.
RRFLimitType			Not required.
WeightingFactor			Not required.
PeakComparison			Not required.

Table 5

Abbreviations Used in the Instructions

Abbreviation	Definition
%D	Percent Difference
%RSD	Percent Relative Standard Deviation
C	Celsius
CB	Cleanup Blank
CCV	Continuing Calibration Verification
CRQL	Contract-Required Quantitation Limit
DMC	Deuterated Monitoring Compounds
DTD	Document Type Definition
EDD	Electronic Data Deliverable
FLO	Florisil Cartridge Check
GC	Gas Chromatography
GPC	Gel Permeation Chromatography Calibration Verification
IB	Instrument Blank
ICAL	Initial Calibration
ID	Identifier
IPC	Instrument Performance Check
LCS	Laboratory Control Sample
MB	Method Blank
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NCS	Non-Client Sample
PIBLK	Pesticides Instrument Blank
PEM	Performance Evaluation Mixture
RESC	Resolution Check Mixture
RRF	Relative Response Factor
SB	Storage Blank
TIC	Tentatively Identified Compounds

APPENDIX A

USEPA REGISTRY NAMES, SYNONYMS, AND CAS REGISTRY NUMBERS

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Appendix A - USEPA Registry Names, Synonyms, and CAS Registry Numbers

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1.0 VOLATILE COMPOUNDS

Systematic Name	EPA Registry Name	Synonyms	CAS #
Methane, dichlorodifluoro-	CFC-12	Dichlorodifluoromethane	75-71-8
Methane, chloro-		Methyl chloride	74-87-3
Ethene, chloro-		Vinyl chloride	75-01-4
Methane, bromo-		Methyl bromide	74-83-9
Ethane, chloro-		Ethyl chloride	75-00-3
Methane, trichlorofluoro-	CFC-11	Fluorotrichloromethane	75-69-4
Ethene, 1,1-dichloro-		Vinylidene chloride	75-35-4
Ethane, 1,1,2-trichloro-1,2,2-trifluoro-	CFC-113	Freon 113	76-13-1
2-Propanone		Acetone	67-64-1
Carbon disulfide	Carbon disulfide	Dithiocarbonic anhydride	75-15-0
Acetic acid, methyl ester		Methyl acetate	79-20-9
Methane, dichloro		Methylene chloride	75-09-2
Ethene, 1,2-dichloro-, (1E)-		trans-1,2-Dichloroethylene	156-60-5
Propane, 2-methoxy-2-methyl-		Methyl tert-butyl ether	1634-04-4
Ethane, 1,1-dichloro-		Ethylidene dichloride	75-34-3
cis-1,2-Dichloroethene (1Z)	cis-1,2-Dichloroethylene		156-59-2
2-Butanone		Methyl ethyl ketone	78-93-3
Methane, trichloro-		Chloroform	67-66-3
Ethane, 1,1,1-trichloro-		1,1,1-Trichloroethane	71-55-6
Cyclohexane	Cyclohexane	Hexahydrobenzene	110-82-7
Methane, tetrachloro-		Carbon tetrachloride	56-23-5
Benzene	Benzene	Benzol	71-43-2
Ethane, 1,2-dichloro-		Ethylene dichloride	107-06-2
Ethene, trichloro-		Trichloroethylene	79-01-6
Cyclohexane, methyl-		Methylcyclohexane	108-87-2
Propane, 1,2-dichloro-		1,2-Dichloropropane	78-87-5
Methane, bromodichloro-		Bromodichloromethane	75-27-4
1-Propene, 1,3-dichloro-, (Z)-		cis-1,3-Dichloropropene	10061-01-5
2-Pentanone, 4-methyl-		4-Methyl-2-pentanone	108-10-1
Benzene, methyl-		Toluene	108-88-3
1-Propene, 1,3-dichloro-, (1E)-		trans-1,3-Dichloropropene	10061-02-6
Ethane, 1,1,2-trichloro-	1,1,2-Trichloroethane	1,1,2-TCA	79-00-5

Systematic Name	EPA Registry Name	Synonyms	CAS #
Ethene, tetrachloro-		Tetrachloroethene	127-18-4
2-Hexanone		Methyl n-butyl ketone (MNBK)	591-78-6
Methane, dibromochloro-		Dibromochloromethane	124-48-1
Ethane, 1,2-dibromo-		1,2-Dibromoethane	106-93-4
Benzene, chloro	Chlorobenzene	Phenyl chloride	108-90-7
Benzene, ethyl-	Ethylbenzene	Phenylethane	100-41-4
Benzene, 1,2-dimethyl	o-Xylene	1,2-Dimethyl benzene	95-47-6
Benzene, (1,3 and 1,4)-dimethyl	m,p-Xylene	(1,3 and 1,4)-Dimethyl benzene	179601-23-1
Benzene, ethenyl-		Styrene	100-42-5
Methane, tribromo-	Tribromomethane	Bromoform	75-25-2
Benzene, (1-methylethyl)-		Cumene	98-82-8
Ethane, 1,1,2,2-tetrachloro-	1,1,2,2-Tetrachloroethane	1,1,2,2-PCA	79-34-5
Benzene, 1,3-dichloro-		m-Dichlorobenzene	541-73-1
Benzene, 1,4-dichloro-		p-Dichlorobenzene	106-46-7
Benzene, 1,2-dichloro-		o-Dichlorobenzene	95-50-1
Propane, 1,2-dibromo-3-chloro-		1,2-Dibromo-3-chloropropane	96-12-8
Benzene, 1,2,4-trichloro-	1,2,4-Trichlorobenzene	Pseudocumene	120-82-1
Methane, bromochloro-	Halon 1011	Chlorobromomethane	74-97-5
Benzene, 1,2,3-trichloro-		1,2,3-Trichlorobenzene	87-61-6
1,4-Dioxane		1,4-Diethyleneoxide	123-91-1

2.0 SEMIVOLATILE COMPOUNDS

Systematic Name	EPA Registry Name	Synonym	CAS #
Benzaldehyde		Benzoic aldehyde	100-52-7
Phenol	Phenol	Hydroxybenzene	108-95-2
Ethane, 1,1'-oxybis[2-chloro-		Bis(2-chloroethyl)ether	111-44-4
Phenol, 2-chloro-		o-Chlorophenol	95-57-8
Phenol, 2-methyl-		o-Cresol	95-48-7
Propane, 2,2'-oxybis[1-chloro-	Bis(2-chloro-1-methylethyl)ether	2,2'-Dichloroisopropyl ether	108-60-1
Ethanone, 1-phenyl-	Acetophenone	Acetylbenzene	98-86-2
Phenol, 4-methyl-		p-Cresol	106-44-5
1-Propanamine, N-nitroso-N-propyl-		N-Nitroso-di-n-propylamine	621-64-7
Ethane, hexachloro-	Hexachloroethane	Perchloroethane	67-72-1
Benzene, nitro-	Nitrobenzene	Nitrobenzol	98-95-3
2-Cyclohexen-1-one, 3,5,5-trimethyl-		Isophorone	78-59-1
Phenol, 2-nitro-		o-Nitrophenol	88-75-5
Phenol, 2,4-dimethyl-		Xylenol	105-67-9
Ethane, 1,1'-[methylenebis(oxy)]bis[2-chloro-		Bis(2-chloroethoxy)methane	111-91-1
Phenol, 2,4-dichloro-	2,4-Dichlorophenol	o,p-Dichlorophenol	120-83-2
Naphthalene	Naphthalene	Naphthalin	91-20-3
Benzenamine, 4-chloro-		4-Chloroaniline	106-47-8
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-		Hexachlorobutadiene	87-68-3
2H-Azepin-2-one, hexahydro-		Caprolactam	105-60-2
Phenol, 4-chloro-3-methyl-		p-Chloro-m-cresol	59-50-7
Naphthalene, 2-methyl-		2-Methylnaphthalene	91-57-6
1,3-Cyclopentadiene, 1,2,3,4,5,5-hexachloro-		Hexachlorocyclopentadiene	77-47-4
Phenol, 2,4,6-trichloro-	2,4,6-Trichlorophenol	Dowicide 2S	88-06-2
Phenol, 2,4,5-trichloro-	2,4,5-Trichlorophenol	Collunosol	95-95-4
1,1'-Biphenyl		Biphenyl	92-52-4
Naphthalene, 2-chloro-		beta-Chloronaphthalene	91-58-7
Benzenamine, 2-nitro-		2-Nitroaniline	88-74-4
1,2-Benzenedicarboxylic acid, dimethyl ester	Dimethyl phthalate	Dimethylphthalate	131-11-3

Systematic Name	EPA Registry Name	Synonym	CAS #
Benzene, 2-methyl-1,3-dinitro-		2,6-Dinitrotoluene	606-20-2
Acenaphthylene			208-96-8
Benzenamine, 3-nitro-		3-Nitroaniline	99-09-2
Acenaphthylene, 1,2-dihydro-		Acenaphthene	83-32-9
Phenol, 2,4-dinitro-	2,4-Dinitrophenol	Aldifen	51-28-5
Phenol, 4-nitro-		p-Nitrophenol	100-02-7
Dibenzofuran	Dibenzofuran		132-64-9
Benzene, 1-methyl-2,4-dinitro-	2,4-Dinitrotoluene	Toluene, 2,4-dinitro-	121-14-2
1,2-Benzenedicarboxylic acid, diethyl ester	Diethyl phthalate	Phthalic acid, diethyl ester	84-66-2
9H-Fluorene		Fluorene	86-73-7
Benzene, 1-chloro-4-phenoxy-		4-Chlorophenyl-phenyl ether	7005-72-3
Benzenamine, 4-nitro-		4-Nitroaniline	100-01-6
Phenol, 2-methyl-4,6-dinitro-		4,6-Dinitro-2-methylphenol	534-52-1
Benzenamine, N-nitroso-N-phenyl-		N-Nitrosodiphenylamine	86-30-6
Benzene, 1,2,4,5-tetrachloro-		1,2,4,5-Tetrachlorobenzene	95-94-3
Benzene, 1-bromo-4-phenoxy-		4-Bromophenyl-phenylether	101-55-3
Benzene, hexachloro-	Hexachlorobenzene	Amatin	118-74-1
1,3,5-Triazine-2,4-diamine, 6-chloro-N-ethyl-N'-(1-methylethyl)-	Atrazine	Fenatrol	1912-24-9
Phenol, pentachloro-	Pentachlorophenol	PCP	87-86-5
Phenanthrene	Phenanthrene		85-01-8
Anthracene	Anthracene	Paranaphthalene	120-12-7
9H-Carbazole		Carbazole	86-74-8
1,2-Benzenedicarboxylic acid, dibutyl ester	Dibutyl phthalate	Di-n-butylphthalate	84-74-2
Fluoranthene		Benzo[j,k]fluorene	206-44-0
Pyrene		Benzo[d,e,f]phenanthrene	129-00-0
1,2-Benzenedicarboxylic acid, butyl phenylmethyl ester	Butyl benzyl phthalate	Phthalic acid, benzyl butyl ester	85-68-7
[1,1'-Biphenyl]-4,4'-diamine, 3,3'-dichloro-		3,3'-Dichlorobenzidine	91-94-1
Benz[a]anthracene		Benzo[a]anthracene	56-55-3
Chrysene		Benzo[a]phenanthrene	218-01-9

Systematic Name	EPA Registry Name	Synonym	CAS #
1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	Di(2-ethylhexyl) phthalate	Bis(2-ethylhexyl)phthalate	117-81-7
1,2-Benzenedicarboxylic acid, dioctyl ester	Di-n-octyl phthalate	N-Dioctyl phthalate	117-84-0
Benz[e]acephenanthrylene		Benzo[b]fluoranthene	205-99-2
Benzo[k]fluoranthene		11,12-Benzofluoranthene	207-08-9
Benzo[a]pyrene		3,4-Benzopyrene	50-32-8
Indeno[1,2,3-cd]pyrene		1,10-(1,2-Phenylene)pyrene	193-39-5
Dibenzo[a,h]-anthracene		1,2,5,6-Dibenzanthracene	53-70-3
Benzo[g,h,i]perylene		1,12-Benzoperylene	191-24-2
Phenol,2,3,4,6-tetrachloro	2,3,4,6-Tetrachlorophenol		58-90-2

3.0 PESTICIDE COMPOUNDS

Systematic Name	Synonym	CAS #
Cyclohexane, 1,2,3,4,5,6-hexachloro-, (1.alpha.,2.alpha.,3.beta.,4.alpha.,5.beta.,6.beta.)-	.alpha.-BHC	319-84-6
Cyclohexane, 1,2,3,4,5,6-hexachloro-, (1.alpha.,2.beta.,3.alpha.,4.beta.,5.alpha.,6.beta.)-	.beta.-BHC	319-85-7
Cyclohexane, 1,2,3,4,5,6-hexachloro-, (1.alpha.,2.alpha.,3.alpha.,4.beta.,5.alpha.,6.beta.)-	.delta.-BHC	319-86-8
Cyclohexane, 1,2,3,4,5,6-hexachloro-, (1.alpha.,2.alpha.,3.beta.,4.alpha.,5.alpha.,6.beta.)-	.gamma.-BHC (Lindane)	58-89-9
4,7-Methano-1H-indene, 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-	Heptachlor	76-44-8
1,4:5,8-Dimethanonaphthalene, 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-, (1.alpha.,4.alpha.,4a.beta.,5.alpha.,8.alpha.,8a.beta.)-	Aldrin	309-00-2
2,5-Methano-2H-indeno[1,2-b]oxirene, 2,3,4,5,6,7,7-heptachloro-1a,1b,5,5a,6,6a-hexahydro-, (1aR,1bS,2R,5S,5aR,6S,6aR)-rel-	Heptachlor epoxide	1024-57-3
6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3-oxide, (3.alpha.,5a.beta.,6.alpha.,9.alpha.,9a.beta.)-	Endosulfan I	959-98-8
2,7:3,6-Dimethanonaphth(2,3-b)oxirene, 3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-, (1a.alpha.,2.beta.,2a.alpha.,3.beta.,6.beta.,6a.alpha.,7.beta.,7a.alpha.)-	Dieldrin	60-57-1
Benzene, 1,1'-(dichloroethenylidene)bis[4-chloro-	4,4'-DDE	72-55-9
2,7:3,6-Dimethanonaphth(2,3-b)oxirene, 3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-, (1a.alpha.,2.beta.,2a.beta.,3.alpha.,6.alpha.,6a.beta.,7.beta.,7a.alpha.)-	Endrin	72-20-8
6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3-oxide, (3.alpha.,5a.alpha.,6.beta.,9.beta.,9a.alpha.)-	Endosulfan II	33213-65-9
Benzene, 1,1'-(2,2-dichloroethylidene)bis[4-chloro-	4,4'-DDD	72-54-8
6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3,3-dioxide	Endosulfan sulfate	1031-07-8
Benzene, 1,1'-(2,2,2-trichloroethylidene)bis[4-chloro-	4,4'-DDT	50-29-3
Benzene, 1,1'-(2,2,2-trichloroethylidene)bis[4-methoxy-	Methoxychlor	72-43-5

Systematic Name	Synonym	CAS #
2,5,7-Metheno-3H-cyclopenta[a]pentalen-3-one, 3b,4,5,6,6,6a-hexachlorodecahydro-, (2.alpha.,3a.beta., 3b.beta., 4.beta., 5.beta.,6a.beta.,7.alpha.,7a.beta.,8R*)	Endrin ketone	53494-70-5
1,2,4-Methenocyclopenta[cd]pentalene-5-carboxaldehyde, 2,2a,3,3,4,7-hexachlorodecahydro-, (1.alpha.,2.beta.,2a.beta.,4.beta.,4a.beta.,5.beta.,6a.beta.,6b.beta.,7R*)-	Endrin aldehyde	7421-93-4
4,7-Methano-1H-indene, 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-, (1.alpha.,2.alpha.,3a.alpha.,4.beta.,7.beta.,7a.alpha.)	alpha-Chlordane	5103-71-9
4,7-Methano-1H-indene, 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-, (1.alpha.,2.beta.,3a.alpha.,4.beta.,7.beta.,7a.alpha.)-	gamma-Chlordane	5103-74-2
Toxaphene	Chlorinated camphene	8001-35-2

4.0 AROCLOR COMPOUNDS

Systematic Name	Synonym	CAS #
Aroclor 1016	PCB-1016	12674-11-2
Aroclor 1221	PCB-1221	11104-28-2
Aroclor 1232	PCB-1232	11141-16-5
Aroclor 1242	PCB-1242	53469-21-9
Aroclor 1248	PCB-1248	12672-29-6
Aroclor 1254	PCB-1254	11097-69-1
Aroclor 1260	PCB-1260	11096-82-5
Aroclor 1262	PCB-1262	37324-23-5
Aroclor 1268	PCB-1268	11100-14-4

EXHIBIT D

ANALYTICAL METHOD FOR THE ANALYSIS OF AROCLORS

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Exhibit D - Analytical Methods for Aroclors

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1.0 SCOPE AND APPLICATION

1.1 In 1978, US Environmental Protection Agency (USEPA) Headquarters and Regional representatives designed analytical methods for the analysis of chlorinated pesticides and Aroclors in hazardous waste samples. These methods were based on USEPA Method 608, Organochlorine Pesticides, and Polychlorinated Biphenyls (PCBs). In 1980, these methods were adopted for use in the Contract Laboratory Program (CLP). As the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) evolved, the CLP methods, as well as their precedent USEPA 600 Series methods, established the basis of other USEPA methods to perform the analysis of Aroclors contained in hazardous waste samples (i.e., SW-846). The following CLP method has continuously improved to incorporate technological advancements promulgated by USEPA, and has continued to set the standard for the preparation, extraction, isolation, identification, and reporting of Aroclors [and pesticides in Exhibit D (Analytical Method for the Analysis of Pesticides)] at hazardous waste sites.

1.2 The analytical method that follows is designed to analyze water and soil/sediment samples from hazardous waste sites to determine the presence and concentration of the Aroclors found in the Target Compound List (TCL) in Exhibit C (Aroclors). The method can be used for determining concentrations in the range from the Contract Required Quantitation Limits (CRQLs) to one million times the CRQL in these matrices when appropriate dilutions are made. The method includes sample extraction, extract cleanup techniques, and Gas Chromatograph/Electron Capture Detector (GC/ECD) analytical methods for Aroclors.

2.0 SUMMARY OF METHOD

2.1 Water

Continuous Liquid-Liquid Extraction (CLLE) or Separatory Funnel Extraction (SFE) procedures are employed for aqueous samples. A 1 L volume of sample is spiked with the surrogate solution and extracted with methylene chloride using a separatory funnel or a continuous extractor. The methylene chloride extract is dried with anhydrous sodium sulfate, concentrated, and cleaned up by Gel Permeation Chromatography (GPC) (GPC cleanup is optional). The extract is then solvent exchanged into hexane, a 1.0 or 2.0 mL aliquot of the extract is subjected to a sulfuric acid cleanup, and the final volume adjusted to the same volume as the aliquot (1.0 mL or 2.0 mL). The extract is analyzed using a dual column wide-bore capillary Gas Chromatograph/Electron Capture Detector (GC/ECD) technique.

2.2 Soil/Sediment

A 30 g aliquot of sample is spiked with the surrogate and then mixed with anhydrous sodium sulfate or Hydromatrix™ and extracted with a 1:1 (v/v) acetone/methylene chloride solvent mixture by sonication, Soxhlet extraction, or pressurized fluid extraction. The extract is filtered, concentrated, and cleaned up by GPC (GPC cleanup is optional). The extract is then solvent exchanged into hexane, a 1.0 or 2.0 mL aliquot of the extract is subjected to a sulfuric acid cleanup, and the final volume adjusted to the same volume as the aliquot (1.0 mL or 2.0 mL). The extract is analyzed using a dual column wide-bore capillary GC/ECD technique.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. These contaminants lead to discrete artifacts or to elevated baselines in gas chromatograms. These materials must be routinely demonstrated to be free from interferences under the sample preparation and analysis conditions by analyzing method blanks. Interferences caused by phthalate esters can pose a major problem in Aroclor analysis. Because common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory.

4.2 Matrix Interferences

Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. The cleanup procedures must be used to remove such interferences in order to achieve the Contract Required Quantitation Limits (CRQLs).

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in the chemical analyses.

Specifically, concentrated sulfuric acid and the 10 N sodium hydroxide solution are moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

5.2 Aroclors covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this analytical method is the responsibility of the Contractor. The Contractor must document any use of alternative equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Glassware

6.1.1 Continuous Liquid-Liquid Extractors

Equipped with polytetrafluoroethylene (PTFE) or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf extractor) or hydrophobic membrane-based extractor.

6.1.2 Separatory Funnels - 2 L with PTFE stopcock.

6.1.3 Ultrasonic Preparation - A horn-type device equipped with a titanium tip, or a device that will give the equivalent performance.

6.1.3.1 Ultrasonic Cell Disruptor - Minimum power output of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturer's instructions for preparing the disruptor for extraction of samples with low and medium/high concentration.

6.1.3.2 Use a 1/4 inch horn for the low concentration method and a 1/8 inch tapered microtip attached to a ½ inch horn for the medium/high concentration method.

6.1.4 [Automated] Soxhlet Extraction System - With temperature-controlled oil bath. Tecator bath oil should be used with the Soxhlet extractor (Silicone oil may not be used because it destroys the rubber parts). Accessories and consumables for the automated Soxhlet system include:

6.1.4.1 Cellulose or Glass Extraction Thimbles - 26 mm ID x 60 mm, contamination free.

6.1.4.2 Glass Extraction Cups (80 mL) (set of six required for the HT-6).

6.1.4.3 Thimble Adapters (set of six required for the HT-6).

6.1.4.4 Viton Seals.

6.1.5 Pressurized Fluid Extraction Device

6.1.5.1 Dionex Accelerated Solvent Extractor (ACE-300) or equivalent with appropriately sized extraction cells. Currently, 100 mL cells are available that will accommodate greater than 30 g samples. Cells should be made of stainless steel or other material capable of withstanding the pressure requirements (2000+ psi) necessary for this procedure.

6.1.5.2 Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.1.6 Drying Column - 20 mm ID borosilicate chromatographic column with borosilicate glass wool at bottom and a PTFE stopcock.

6.1.7 Syringes - 5 mL, 100 µL, and 1000 µL.

6.1.8 Vials - 1, 2, 10, 40, 60 mL glass with PTFE-lined screw-caps or crimp tops.

6.1.9 Disposable Glass Pasteur Pipet and Bulb - 1 mL.

6.1.10 Class A Graduated Cylinder - 1 L capacity, 100 mL.

6.1.11 Erlenmeyer Flask - 250 mL.

6.1.12 Graduated, Conical-Bottom Glass Tubes - 15 mL or 10 mL Kuderna-Danish (K-D) concentrator tube.

6.1.13 Beakers - 400 mL.

6.1.14 Class A Volumetric Flasks - 10 mL to 1000 mL.

6.2 Kuderna-Danish (K-D) Apparatus

6.2.1 Concentrator Tubes - 10 mL, graduated.

6.2.2 Evaporation Flasks - 500 mL.

6.2.3 Snyder Column - Three-ball macro.

6.2.4 Snyder Column - Two-ball micro.

6.2.5 Springs - 1/2 inch.

6.3 pH Indicator Paper - pH range including the desired extraction pH.

6.4 Boiling Chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide, or equivalent).

6.5 Solvent Vapor Recovery System.

6.6 Water Bath - Heated, with concentric ring cover, capable of temperature control (±5°C).

NOTE: The water bath should be used in a hood.

6.7 Heating Mantle - Rheostat controlled.

6.8 Nitrogen Evaporation Device - Equipped with a heated bath that can be maintained at 35-40°C.

6.9 Apparatus for Determining Percent Dry Weight

6.9.1 Drying Oven - Capable of maintaining 105°C.

6.9.2 Desiccator.

6.9.3 Crucibles - Porcelain or disposable aluminum.

6.10 Apparatus for Grinding - Capable of reducing particle size to less than 1 mm.

6.11 Analytical Balance - Capable of weighing to 0.001/0.0001 g. The balances must be calibrated with Class S weights or known reference weights once per each 12-hour work shift. The balances must be

calibrated with Class S weights at a minimum of once per month. The balances must also be annually checked by a certified technician.

6.12 Aluminum Weighing Dish.

6.13 pH Meter - With a combination glass electrode. Calibrate according to the manufacturer's instructions. The pH meter must be calibrated prior to each use.

6.14 Vacuum or Pressure Filtration Apparatus

6.14.1 Buchner Funnel.

6.14.2 Filter Paper - Whatman No. 41, or equivalent.

6.15 Sonabox - Recommended with ultrasonic disruptor for decreasing cavitation sound.

6.16 Glass Scintillation Vials - 20 mL, with PTFE-lined screw-caps.

6.17 Spatula - Stainless steel or PTFE.

6.18 Filter Disk - 1.91 cm, Type D28 (Whatman 10289356, or equivalent).

6.19 Cell Cap Sealing Disk (Dionex 49454, 49455, or equivalent).

6.20 Gel Permeation Chromatography (GPC) Cleanup System

6.20.1 GPC System - Systems that perform satisfactorily have been assembled from the following components: a High Performance Liquid Chromatograph (HPLC) pump; an auto sampler or a valving system with sample loops; and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements of Section 10.3.1.

6.20.1.1 Chromatographic Column - 700 mm x 25 mm ID glass column. Flow is upward. To simplify switching from the ultraviolet (UV) detector during calibration to the GPC collection device during extract cleanup, an optional double 3-way valve may be attached so that the column exit flow can be shunted either to the UV flow-through cell or the GPC collection device.

6.20.1.2 Guard Column (optional) - 5 cm, with appropriate fittings to connect to the inlet side of the analytical column (Supelco 5-8319, or equivalent).

6.20.1.3 Bio Beads (SX-3) - 200-400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, or equivalent). An additional 5 g of Bio Beads is required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

6.20.1.4 UV Detector - Fixed wavelength (254 nm) with a semi-prep flow-through cell.

6.20.1.5 Strip Chart Recorder - Recording integrator or laboratory data system.

6.20.1.6 Syringe Filter Assembly, disposable, 5 micron.

NOTE: Some instrument manufacturers recommend a smaller micron filter disc. Consult your instrument operation manual to determine the proper size filter disc to use in your system. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

6.21 Sulfuric Acid Cleanup System

6.21.1 Syringe or Class A volumetric glass pipet; 1.0, 2.0, and 5.0 mL.

6.21.2 Vials - 1, 2, and 10 mL, glass with PTFE-lined screw-caps or crimp tops.

6.21.3 Vortex Mixer.

6.22 Gas Chromatograph (GC)

6.22.1 The GC must adequately regulate temperature in order to give a reproducible temperature program and have a flow controller that maintains a constant column flow rate throughout temperature program operations. The system must have all required accessories including syringes, analytical columns, and gases.

6.22.2 GC Columns - Two wide-bore (0.53 mm ID) fused silica GC columns are required. A separate detector is required for each column. The specified analytical columns are:

6.22.2.1 30 m x 0.53 mm ID, 0.5 µm or 0.83 µm film thickness, DB-608, SPB-608, Rtx-35, or equivalent.

6.22.2.2 30 m x 0.53 mm ID, 1.0 µm film thickness, DB-1701, Rtx-CLP I, Rtx-CLP II, or equivalent.

6.22.2.3 30 m x 0.53 mm ID, 1.5 µm film thickness, DB-5, SPB-5, Rtx-5, or equivalent.

NOTE: The column length stated above is the minimum requirement. Longer columns that meet resolution and calibration requirements may be used. A description of the GC columns used for analysis shall be provided in the SDG Narrative.

6.22.3 **PACKED COLUMNS CANNOT BE USED**.

6.22.4 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantitation of the compounds listed in Exhibit C (Aroclors).
- The analytical results generated using the column meet the initial calibration and calibration verification technical acceptance criteria listed in the analytical method and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Aroclors).
- The column pair chosen must have dissimilar phases [choose only one column from each list (i.e., one from 6.22.2.1, one from 6.22.2.2, etc.)].

6.22.5 Although the instructions included in the analytical method are for wide bore capillary columns, narrower bore capillary columns may be evaluated for use. Follow the manufacturer's instructions for use of

its product. Document in the SDG Narrative if other columns are used by specifying the column used.

6.22.6 The Contractor must maintain documentation verifying that the column met the criteria in Section 6.22.4. The minimum documentation is as follows:

6.22.6.1 Manufacturer-provided information concerning the performance characteristics of the column.

6.22.6.2 Chromatograms and data system reports for initial calibration, calibration verification standard, and blanks that are generated on the GC/Electron Capture Detector (ECD) and used for Contract Laboratory Program (CLP) analyses.

6.22.6.3 Based on the Contractor-generated data described in Section 6.22.6.2, the Contractor must complete a written review, signed by the Laboratory Manager, certifying that:

- The column performance is comparable to the required column performance in its ability to produce initial calibration and calibration verifications that meet the technical acceptance criteria in Sections 9.2.5 and 9.3.4.

- The instrument blanks demonstrate that the column does not introduce contaminants that interfere with the identification and quantitation of compounds listed in Exhibit C (Aroclors).

6.22.6.4 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request by the USEPA Regional CLP Project Officer (CLP PO).

6.22.7 Columns are mounted in a press-fit Y-shaped glass 3-way union splitter or a Y-shaped fused-silica connector from a variety of commercial sources. The two columns may be mounted in an 8 inch deactivated glass injection tee. The Contractor should follow the manufacturer's recommendations for mounting 0.53 mm capillary columns in injector ports.

6.22.8 The carrier gas for routine applications is helium. The Contractor may choose to use hydrogen as a carrier gas, but they must clearly identify its use in the SDG Narrative and on all divider pages preceding raw chromatographic data in submissions to USEPA. Use of a hydrogen leak detector is highly recommended when hydrogen is used as the carrier gas. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants or flow controllers with rubber components are not to be used.

6.23 Electron Capture Detector (ECD)

The linearity of the response of the ECD may be greatly dependent on the flow rate of the make-up gas. The make-up gas must be P-5, P-10 (argon/methane), or nitrogen according to the instrument specification. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector. The GC/ECD system must be in a room in which the atmosphere has been demonstrated to be free of all contaminants that may interfere with the analysis. The instrument must be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.24 Data System

A data system must be interfaced to the GC/ECD. The data system must allow the continuous acquisition of data throughout the duration of the chromatographic program and must permit, at a minimum, the output of time vs. intensity (peak height or peak area) data. Also, the data system must be able to rescale chromatographic data in order to report chromatograms meeting the requirements listed within this method.

6.25 Data Storage Device

Data storage devices must be suitable for long-term, off-line storage of data.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

7.1.1 Reagent Water - Reagent water is defined as water in which an interferant is not observed at or above the Contract Required Quantitation Limit (CRQL) for each compound of interest.

7.1.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g (1 lb) of activated carbon.

7.1.1.2 Reagent water may be generated using a water purification system.

7.1.2 Sodium Sulfate - Granular-anhydrous reagent grade, heated at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

CAUTION: An open container of sodium sulfate may become contaminated during storage in the laboratory.

OR

Hydromatrix - Diatomaceous earth-based material rinsed with methylene chloride and dried at 400°C for 4 hours in a shallow tray, cooled in a desiccator, and stored in a glass bottle. A method blank must be analyzed demonstrating that there is no interference from the Hydromatrix.

7.1.3 Sulfuric Acid Solution - Prepare a 1:1 (v/v) solution by slowly adding 50 mL of sulfuric acid (sp. gr. 1.84) to 50 mL of reagent water.

7.1.4 Sodium Hydroxide Solution (10 N) - Carefully dissolve 40 g of sodium hydroxide in reagent water and dilute the solution to 100 mL.

7.1.5 Phosphoric Acid Solution - Prepare a 1:1 (v/v) solution of 85% phosphoric acid in reagent water.

7.1.6 Tetrabutylammonium Sulfite.

7.1.7 Sodium Sulfite.

7.1.8 Acetone/hexane (1:1 v/v).

7.1.9 Acetone/methylene chloride (1:1 v/v).

7.1.10 Methylene chloride, hexane, acetone, toluene, iso-octane, 2-propanol, cyclohexane, acetonitrile, n-butyl chloride, and methanol (optional). It is recommended that each lot of solvent used be analyzed to demonstrate that it is free of interference before use. Methylene chloride must be certified as acid free or must be tested to demonstrate that it is free of hydrochloric acid. Acidic methylene chloride must be passed through basic alumina and then demonstrated to be free of hydrochloric acid.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit E. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor that are immediately ampulated in glass vials may be retained for 2 years from preparation date. The expiration date of the ampulated standards upon the breaking of the glass seal is 6 months or sooner if the standard has degraded or evaporated.

7.2.2 Stock Standard Solutions (1000 µg/mL)

7.2.2.1 Stock standard solutions are defined as standards that are to be used to produce working standards. They may be in the form of single compounds or mixtures. They may be purchased or prepared in methylene chloride or another suitable solvent.

7.2.3 Working Standards

7.2.3.1 Surrogate Standard Spiking Solution

The surrogates, tetrachloro-m-xylene and decachlorobiphenyl, are added to all standards, samples [including Laboratory Control Samples (LCSs)], Matrix Spike and Matrix Spike Duplicates (MS/MSDs), Performance Evaluation (PE) samples (if required), and blanks (method/sulfur cleanup) prior to extraction. Prepare a surrogate spiking solution of 0.20 µg/mL of tetrachloro-m-xylene and 0.40 µg/mL of decachlorobiphenyl in acetone. The solution should be checked frequently for stability. The solution must be replaced every 6 months, or sooner if the solution has degraded or concentrated.

NOTE: Other concentrations for surrogate standard spiking solutions may be used provided the appropriate amount of each surrogate is added to all standards, samples (including LCS), MS/MSD, PE samples, and blanks.

7.2.3.2 Matrix Spiking Solution

Prepare a matrix spiking solution of 4.0 µg/mL of Aroclor 1016 and Aroclor 1260 in acetone or methanol. The solution must be replaced every 6 months, or sooner if the solution has degraded or concentrated.

7.2.3.3 Laboratory Control Sample (LCS) Spiking Solution

Prepare an LCS spiking solution of 1.0 µg/mL of Aroclor 1016 and Aroclor 1260 in acetone or methanol. The LCS solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.3.4 Calibration Standards for Aroclors

Aroclor standards must be prepared individually, except for Aroclor 1260 and Aroclor 1016 which may be combined in one standard mixture. All Aroclor standards must be prepared hexane or iso-octane every 6 months, or sooner, if the solution has degraded or concentrated. See Table 3 for the concentration levels for the calibration standards.

7.2.3.4.1 Prepare five-point initial calibration standard solutions containing a mixture of Aroclors 1016 and 1260 at the following suggested levels: 100; 200; 400; 800; and 1600 ng/mL and surrogates at 5.0, 10, 20, 40 and 80 ng/mL for tetrachloro-m-xylene and 10, 20, 40, 80 and 160 ng/mL for decachlorobiphenyl. Also, prepare a single-point initial calibration standard solution containing Aroclors 1221, 1232, 1242, 1248, 1254, 1262, and 1268 at 400 ng/mL and surrogates at 20 ng/mL for tetrachloro-m-xylene and 40 ng/mL for decachlorobiphenyl. The solutions must be prepared every 6 months, or sooner if the solutions have degraded or concentrated.

7.2.3.4.2 Prepare a single-point calibration verification standard solution containing Aroclor 1260 and Aroclor 1016 at 400 ng/mL and surrogates at 20 ng/mL for tetrachloro-m-xylene and 40 ng/mL for decachlorobiphenyl. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.3.4.3 If Aroclor 1221, 1232, 1242, 1248, 1254, 1262, or 1268 are detected in a sample, then a five-point initial calibration solution for the detected Aroclor must be prepared at the following levels: 100, 200, 400, 800, and 1600 ng/mL and surrogates at 5.0, 10, 20, 40, and 80 ng/mL for tetrachloro-m-xylene and 10, 20, 40, 80, and 160 ng/mL for decachlorobiphenyl. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.3.4.4 The concentration levels in Sections 7.2.3.4.1 - 7.2.3.4.3 are based upon 10 mL final extract volume for samples not undergoing Gel Permeation Chromatography (GPC) cleanup, and 5.0 mL final extract volume for those samples undergoing GPC cleanup. Other concentration levels may be used for more sensitive instrumentation and final extract volume levels. For example, in the case of Aroclor 1016, a laboratory may use a final extract volume of 10 mL for samples undergoing GPC cleanup, and a low calibration standard of 50 ng/mL. The alternative calibration standards and final extract volumes may be used as long as the following requirements are met:

- The laboratory can demonstrate that the CRQL for each analyte listed in Exhibit C can be reached using the calibration and final extract volume scheme. This demonstration is made when there is formal documentation of laboratory Method Detection Limit (MDL) studies indicating that the calculated MDL for each target analyte is below the required CRQL for that analyte when using the laboratory's specific final extract volume and calibration level scheme.

- All five calibration levels are in the same ratio as shown in Sections 7.2.3.4.1 and 7.2.3.4.3 (e.g., if a laboratory were using a 50 ng/mL low standard, then the other calibration levels must be 100, 200, 400, and 800 ng/mL).

7.2.3.5 GPC Calibration Solution

Prepare a GPC calibration solution in methylene chloride that contains the following analytes at the minimum concentrations listed below. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

Analyte	Concentration (mg/mL)
Corn oil	25.0
Bis(2-ethylhexyl)phthalate	0.5
Methoxychlor	0.1
Perylene	0.02
Sulfur	0.08

NOTE: Sulfur is not very soluble in methylene chloride, but it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

7.3 Storage of Standard Solutions

7.3.1 Store the stock and secondary standard solutions at 4°C (±2°C) in polytetrafluoroethylene (PTFE)-lined, screw-cap, amber bottles/vials.

7.3.2 Store the working standard solutions at 4°C (±2°C) in PTFE-lined screw-cap, amber bottles/vials. The working standards must be checked frequently for signs of degradation or evaporation.

NOTE: Refrigeration may cause the corn oil in the GPC calibration solution to precipitate. Before use, allow the GPC calibration solution to stand at room temperature until the corn oil dissolves.

7.3.3 Protect all standards from light.

7.3.4 Samples, sample extracts, and standards must be stored separately.

7.3.5 The Contractor is responsible for maintaining and verifying the integrity of standard solutions prior to use.

NOTE: Storage of standard solutions in the freezer may cause some compounds to precipitate. This means that at a minimum, the standards must be brought to room temperature prior to use, checked for losses, and checked to verify that all components have remained in solution. Additional steps may be necessary to ensure that all components are in solution.

7.4 Temperature Records for Storage of Standards

7.4.1 The temperature of all standard storage refrigerators/freezers shall be recorded daily.

7.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

7.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators/freezers.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in 1 L (or 1 quart) amber glass containers, fitted with screw-caps lined with polytetrafluoroethylene (PTFE). If amber containers are not available, the samples should be protected from light. Soil samples may be collected in glass containers or closed end tubes (e.g., brass sleeves) in sufficient quantity to perform the analysis. The specific requirements for site sample collection are outlined by the USEPA Region.

8.1.2 All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until extraction.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3 Procedure for Sample Extract Storage

8.3.1 Sample extracts must be protected from light and stored at 4°C (±2°C) until 365 days after delivery of a complete, reconciled data package to USEPA.

8.3.2 Sample extracts must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3.3 Samples, sample extracts, and standards must be stored separately.

8.4 Records for Sample and Sample Extract Storage

8.4.1 The temperature of all sample and sample extract storage refrigerators shall be recorded daily.

8.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

8.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators.

8.5 Contract Required Holding Times

8.5.1 Extraction of water samples by separatory funnel procedures must be completed within 5 days of the Validated Time of Sample Receipt (VTSR). Extraction of water samples by Continuous Liquid-Liquid Extraction (CLLE) procedures must be started within 5 days of the VTSR. Extraction of soil/sediment samples must be completed within 10 days of the VTSR.

8.5.2 As part of USEPA's Quality Assurance (QA) program, USEPA may provide Performance Evaluation (PE) samples as standard extracts that the Contractor is required to prepare per instructions provided by USEPA. PE samples must be prepared and analyzed concurrently with the samples in the Sample Delivery Group (SDG). The extraction holding time (5 days after the VTSR for water, 10 days after the VTSR for soil/sediment) does not apply for PE samples received as standard extracts.

8.5.3 Analysis of sample extracts must be completed within 40 days following the start of extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Gas Chromatograph (GC) Operation Conditions

9.1.1 The following are the gas chromatographic analytical conditions for a wide-bore capillary column. The conditions are recommended unless otherwise noted.

Column Conditions	0.5/1.0 um film thickness	1.5 um film thickness
Carrier gas (He)	5-7 mL/min.	6 mL/min.
Make-up gas [argon/methane (P-5 or P-10) or N2]	30 mL/min.	30 mL/min.
Injector temperature	205°C	205°C
Detector temperature	290°C	290°C
Initial temperature	150°C, hold 0.5 min.	140°C, hold 2 min.
Temperature program	150°C to 270°C at 5°C/min.	140°C to 240°C at 10°C/min., hold 5 min. at 240°C, 240°C to 265°C at 5°C/min.
Final temperature	270°C, hold 10 min.	265°C, hold 18 min.

9.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, and samples including Laboratory Control Samples (LCSs) and Matrix Spike and Matrix Spike Duplicates (MS/MSDs). The linearity of the Electron Capture Detector (ECD) may be greatly dependent on the flow rate of the make-up gas. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector.

9.1.3 The same injection volume, 1.0 or 2.0 µL, must be used for all standards, required blanks (method/sulfur cleanup/instrument), and samples (including LCSs and MS/MSDs).

9.2 Initial Calibration

9.2.1 Summary of Initial Calibration

Prior to sample analysis (including LCSs and MS/MSDs) and required blanks (method/sulfur cleanup/instrument), each GC/ECD system must be initially calibrated to determine instrument sensitivity and the linearity of Aroclor response. An initial five-point calibration is performed using Aroclors 1016 and 1260 to demonstrate the linearity of the detector response. The other seven Aroclors are calibrated at a single mid-point for pattern recognition. The standards for these seven Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five levels of the Aroclor 1016/1260 standards.

9.2.2 Frequency of Initial Calibration

Each GC/ECD system must be initially calibrated upon award of the contract, whenever major instrument maintenance or modification is

performed (e.g., column replacement or repair, cleaning or replacement of the ECD, etc.), or if the calibration verification technical acceptance criteria have not been met. Also, for any sample in which an Aroclor, other than Aroclor 1016 or Aroclor 1260 is detected, results for the specific Aroclor(s) may only be reported if the Aroclor(s) have been calibrated using multipoint standards (five-point). If time remains in the 12-hour period after a valid five-point initial calibration for a detected Aroclor(s) has been performed, then samples containing the Aroclor(s) may be analyzed. If the previously-analyzed five-point initial calibration containing the Aroclor(s) detected in the sample(s) is not in the same 12-hour sequence, then the sample(s) must be analyzed after a Continuing Calibration Verification (CCV) analysis containing the Aroclor(s) detected in the sample(s) that meets the criteria for CCVs in Section 9.3.

9.2.3 Procedure for Initial Calibration

9.2.3.1 Set up the GC/ECD systems as described in Section 9.1. Optimize the instrumental conditions for resolution of the target compounds and sensitivity.

NOTE: Once the GC conditions have been established, the same operating conditions must be used for both calibrations and sample analyses.

9.2.3.2 Prepare the initial calibration standards using the analytes and the concentrations specified in Sections 7.2.3.4.1 and 7.2.3.4.2.

9.2.3.3 If Aroclors other than Aroclor 1016/1260 are detected in an analysis, a separate five-point calibration must be prepared (Section 7.2.3.4.3) and run for that particular Aroclor.

9.2.3.4 All standards, blanks, samples, LCSs, MS/MSDs, and extracts must be allowed to warm to ambient temperature before analysis.

9.2.3.5 Analyze the initial calibration sequence as given below.

NOTE: The single-point Aroclor standards may be analyzed after the analysis of the five levels of the Aroclor 1016/1260 standards. The steps pertaining to the instrument blank are used as part of the calibration verification as well.

Initial Calibration Sequence

1. Aroclor 1221 CS3 (400 ng/mL)
2. Aroclor 1232 CS3 (400 ng/mL)
3. Aroclor 1242 CS3 (400 ng/mL)
4. Aroclor 1248 CS3 (400 ng/mL)
5. Aroclor 1254 CS3 (400 ng/mL)
6. Aroclor 1262 CS3 (400 ng/mL)
7. Aroclor 1268 CS3 (400 ng/mL)
8. Aroclor 1016/1260 CS1 (100 ng/mL)
9. Aroclor 1016/1260 CS2 (200 ng/mL)

Initial Calibration Sequence (Con't)

10. Aroclor 1016/1260 CS3 (400 ng/mL)

11. Aroclor 1016/1260 CS4 (800 ng/mL)

12. Aroclor 1016/1260 CS5 (1600 ng/mL)

13. Instrument blank

9.2.4 Calculations for Initial Calibration

9.2.4.1 During the initial calibration sequence, absolute Retention Times (RTs) are determined for each surrogate and a minimum of 3 major peaks of each Aroclor.

9.2.4.2 For Aroclors 1016 and 1260, an RT is measured for a minimum of 3 peaks in each of the five calibration standards and the mean RT ($\overline{RT}$) is calculated for each of the peaks as the average of the five values obtained from the five calibration standards. For Aroclors 1221, 1232, 1242, 1248, 1254, 1262, and 1268 an RT is measured for each of the peaks for a single-point calibration standard. If a valid five-point calibration is present for a specific Aroclor then an RT is measured for each of the peaks in each of the five calibration standards and the $\overline{RT}$ is calculated as the average of the five values for each of the peaks obtained from the five calibration standards. An RT is measured for the surrogates in each of the five calibration standards and the $\overline{RT}$ is calculated as the average of the five values. Calculate the $\overline{RT}$ using Equation 1:

EQ. 1 Mean Retention Time

$$\overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n}$$

Where,

$\overline{RT}$ = Mean absolute Retention Time of analyte.

RT_i = Absolute Retention Time of analyte.

n = Number of measurements.

9.2.4.3 An RT window is calculated for the major peaks (a minimum of 3) of each Aroclor and for each surrogate using the RT window listed below. Analytes are identified when peaks are observed in the RT window for the compound on both GC columns.

Compounds	Retention Time Windows (minutes)
Aroclors	±0.07
Tetrachloro-m-xylene	±0.05
Decachlorobiphenyl	±0.10

9.2.4.4 The linearity of the instrument is determined by calculating a Percent Relative Standard Deviation (%RSD) of the Calibration Factors (CFs). Either peak area or peak height may be used to calculate CFs used in the %RSD equation.

Five sets of CFs will be generated for the Aroclor 1016/1260 mixture, each set consisting of the CFs for each of the five peaks chosen for this mixture. The single standard for each of the other Aroclors will generate at least three CFs, one for each selected peak, unless a valid five-point calibration is present for a specific Aroclor, in which case five sets of CFs will be generated for the specific Aroclor.

Calculate CFs, the Mean CF ($\overline{CF}$), and the %RSD of the CFs for each peak in a selected set of a minimum of 3 major peaks for each Aroclor using Equations 2, 3, and 4.

EQ. 2 Calibration Factor Calculation

$$CF = \frac{\text{Peak area (or Height) of the standard}}{\text{Mass Injected (ng)}}$$

EQ. 3 Mean Calibration Factor Calculation

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

EQ. 4 Percent Relative Standard Deviation Calculation

$$\%RSD = \frac{SD_{CF}}{\overline{CF}} \times 100$$

Where,

SD_{CF} = $$\sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n}}$$

%RSD = Percent Relative Standard Deviation.

SD_{CF} = Standard Deviation of Calibration Factors.

CF_i = Calibration Factor.

$\overline{CF}$ = Mean Calibration Factor.

n = Total number of values.

9.2.5 Technical Acceptance Criteria for Initial Calibration

All initial calibration technical acceptance criteria apply independently to each GC column.

9.2.5.1 The initial calibration sequence must be analyzed according to the procedure listed in Section 9.2.3, at the concentrations listed in Section 7.2.3.5, and at the frequency listed in Section 9.2.2. The GC/ECD operating conditions optimized in Section 9.1 must be followed.

9.2.5.2 The identification of Aroclors by GC methods is based primarily on recognition of patterns of RTs displayed on a chromatogram. Therefore, the following requirements apply to all data presented for Aroclors.

- The chromatograms of the standards for the Aroclors analyzed during the initial calibration sequence must display the peaks chosen for identification of each analyte at greater than 25% and less than 100% of full scale.
- If a chromatogram is replotted electronically to meet requirements, the scaling factor used must be displayed on the chromatogram.

9.2.5.3 The %RSD of the CFs for each Aroclor peak and surrogates must be less than or equal to 20%. The %RSD requirement applies to any other Aroclor analyzed at the five-point calibration (if required in Section 9.2.3.3).

9.2.5.4 All instrument blanks must meet the technical acceptance criteria in Section 12.1.4.5.

9.2.6 Corrective Action for Initial Calibration

9.2.6.1 If the technical acceptance criteria for the initial calibration are not met, inspect the system for problems. It may be necessary to change the column, bake-out the detector, clean the injection port, or take other corrective actions to achieve the acceptance criteria.

9.2.6.2 Contamination should be suspected as a cause if the detector cannot achieve acceptable linearity using this method. In the case of low-level contamination, baking out the detector at an elevated temperature (350°C) should be sufficient to achieve acceptable performance. In the case of heavy contamination, passing hydrogen through the detector for 1-2 hours at an elevated temperature may correct the problem. In the case of severe contamination, the detector may require servicing by the ECD manufacturer.

CAUTION: DO NOT OPEN THE DETECTOR. THE ECD CONTAINS RADIOCHEMICAL SOURCES.

9.2.6.3 If a laboratory cleans out a detector using an elevated temperature, the ECD electronics must be turned off during the bake-out procedure.

9.2.6.4 After bake-out or hydrogen reduction, the detector must be recalibrated using the initial calibration sequence.

9.2.6.5 Initial calibration technical acceptance criteria must be met before any sample, including MS/MSD, LCS, or required blanks, are analyzed. Any samples or required blanks analyzed before the initial calibration technical acceptance criteria have been met will require reanalysis at no additional cost to USEPA.

9.3 Continuing Calibration Verification

9.3.1 Summary of Continuing Calibration Verification (CCV)

The analyses of instrument blanks and the required Aroclor CS3 Standard Mixtures (see Section 9.3.2) constitute the calibration verification. Sample (including LCS and MS/MSD) and required blank (method/sulfur cleanup) data are not acceptable unless bracketed by acceptable analyses of instrument blanks and the Aroclor CS3 Standard Mixtures. In cases where a valid five-point initial calibration for the detected Aroclors is required, that initial calibration may be substituted for the opening CCV.

9.3.2 Frequency of Continuing Calibration Verification (CCV)

9.3.2.1 An instrument blank and Aroclor 1016/1260 CS3 Standard Mixture must bracket one end of a 12-hour period (opening CCV) during which sample and required blank data are collected, and a second instrument blank and the Aroclor 1016/1260 CS3 Standard Mixture must bracket the other end of the 12-hour period (closing CCV). If during any 12-hour period, an Aroclor other than 1016 or 1260 is detected and the 12-hour time period for the five-point initial calibration of the detected Aroclor(s) has elapsed, then an instrument blank and a CS3 standard of the detected Aroclor(s) must bracket both ends of the 12-hour period. If the opening CCV does not meet all technical acceptance criteria, then a new valid five-point initial calibration for the detected Aroclors must be performed before samples containing the detected Aroclors may be analyzed.

9.3.2.2 For the 12-hour period immediately following the initial calibration sequence, the instrument blank is the last step in the initial calibration sequence and brackets the front end of that 12-hour period. The injection of the instrument blank starts the beginning of the 12-hour period (Section 10.3.2.1.1), followed by the injection of the Aroclor 1016/1260 CS3 Standard. Samples (including LCSs and MS/MSDs) and required blanks (method/sulfur cleanup) may be injected for 12 hours from the injection of the instrument blank. The first injections immediately after that 12-hour period must be an instrument blank and the Aroclor 1016/1260 CS3 Standard Mixture. The instrument blank must be analyzed first, before the standard.

9.3.2.3 The analyses of the instrument blank and CS3 Standard Mixture (closing CCV) immediately following one 12-hour period may be used to begin the subsequent 12-hour period as an opening CCV, provided that they meet the technical acceptance criteria in Section 9.3.5. In that instance, the subsequent 12-hour period must be bracketed by the acceptable analyses of an instrument blank and a CS3 Standard Mixture (closing CCV), in that order. Those two analyses may in turn be used to bracket the front end of yet another 12-hour period (opening CCV). This progression may continue every 12 hours until such time as any of the instrument blanks or the CS3 Standard Mixture fails to meet the technical acceptance criteria in Section 9.3.4, or an Aroclor has been detected in a sample for which the corresponding CS3 standard was not performed

for the opening CCV. The 12-hour time period begins with the injection of the instrument blank.

9.3.2.4 If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an acceptable instrument blank and an Aroclor 1016/1260 CS3 standard must be analyzed in order to start a new sequence. This requirement applies even if no analyses were performed since that standard was injected.

9.3.2.5 The requirements for running the instrument blanks and CS3 Aroclor 1016/1260 Standard Mixture are waived when no samples (including LCSs and MS/MSDs), dilutions, reanalyses, or required blanks (method/sulfur cleanup) are analyzed during that 12-hour period. To resume analysis, using the existing initial calibration, the Contractor must first analyze an instrument blank and CS3 Aroclor 1016/1260 Standard that meet the technical acceptance criteria.

9.3.2.6 If the entire 12-hour period is not required for the analyses of all samples and blanks to be reported and all data collection is to be stopped, the sequence must be ended with the instrument blank/CS3 Aroclor Standard Mixture(s) (1016/1260 and all detected Aroclors) combination.

9.3.2.7 No more than 14 hours may elapse from the injection beginning the opening CCV (instrument blank) and the injection ending the closing CCV (Aroclor Standard).

9.3.3 Procedure for Continuing Calibration Verification (CCV)

9.3.3.1 All standards and blanks must warm to ambient temperature prior to analysis.

9.3.3.2 Analyze the instrument blank and the CS3 Aroclor Standard Mixture(s) at the required frequencies (Section 9.3.2).

9.3.4 Calculations for Calibration Verification

For each analysis of the CS3 Individual Standard Mixture(s) used to demonstrate calibration verification, calculate the Percent Difference between the CF of each Aroclor peak (including the surrogates) in the standard mixture and the $\overline{CF}$ from the initial calibration, using Equation 5.

EQ. 5 Percent Difference Between the Calibration Factor and the Mean Calibration Factor

$$\%Difference = \frac{CF - \overline{CF}}{\overline{CF}} \times 100$$

Where,

%Difference = Percent Difference.

CF = Calibration Factor for CS3 Standard used for Calibration Verification.

$\overline{CF}$ = Mean Calibration Factor.

9.3.5 Technical Acceptance Criteria for Continuing Calibration Verification (CCV)

All CCV technical acceptance criteria apply independently to each column, and must meet the chromatogram criteria specified in Section 9.2.5.2.

9.3.5.1 The Aroclor 1016/1260 standards and Aroclor standards of other detected Aroclors must be analyzed at the required frequency on a GC/ECD system that has met the initial calibration technical acceptance criteria.

9.3.5.2 The absolute RT of each of the Aroclor peaks and surrogates in the calibration verification standard must be within the RT window determined from the initial calibration standard in Section 9.2.4.3.

9.3.5.3 For the opening CCV, Percent Difference for each Aroclor peak and surrogates calculated from the CCV standard must not exceed ±15%. For the closing CCV, Percent Difference for each Aroclor peak and surrogates calculated from the CCV must not exceed ±50%. If the Percent Difference for the closing CCV is ±15% or less, then it can be used for the opening CCV of the next 12-hour period.

9.3.6 Corrective Action for Continuing Calibration Verification (CCV)

9.3.6.1 If the technical acceptance criteria for the CCV are not met, inspect the system for problems and take corrective action to achieve the acceptance criteria.

9.3.6.2 Major corrective actions such as replacing the GC column or baking out the detector will require that a new initial calibration be performed that meets the technical acceptance criteria in Section 9.2.5.

9.3.6.3 Minor corrective actions may not require performing a new initial calibration, provided that a new analysis of the standard that originally failed the criteria and an associated instrument blank immediately after the corrective action do meet all the acceptance criteria.

9.3.6.4 If the Aroclor 1016/1260 standard does not meet technical acceptance criteria listed in Sections 9.3.5.2 and 9.3.5.3, it must be re-injected immediately. If the second injection of the Aroclor 1016/1260 standard meets the criteria, sample analysis may continue. If the second injection does not meet the criteria, all data collection must be stopped. Appropriate corrective action must be taken, and a new initial calibration sequence must be run before more sample data are collected.

9.3.6.5 If an instrument blank does not meet the technical acceptance criteria listed in Section 12.1.4.5, all data collection must be stopped. Appropriate corrective action must be taken to clean out the system, and an acceptable instrument blank must be analyzed before more sample data are collected.

9.3.6.6 The Contractor is reminded that running an instrument blank and an Aroclor 1016/1260 standard once every 12 hours is the minimum contract requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable.

Therefore, it may be necessary to run standards more often to avoid discarding data.

9.3.6.7 If a successful instrument blank and Aroclor 1016/1260 standard cannot be run after an interruption in analysis (Section 9.3.2.6), an acceptable initial calibration must be run before sample data may be collected. All acceptable sample (including LCS and MS/MSDs) and required blank (method/sulfur cleanup) analyses must be preceded and followed by acceptable standards and instrument blanks, as described in Section 9.3.2.

9.3.6.8 Calibration verification technical acceptance criteria must be met before any sample, including MS/MSD and LCS is reported. Any samples, including MS/MSDs, LCSs, and required blanks associated with a calibration verification that do not meet the technical acceptance criteria will require reanalysis at no additional cost to USEPA.

10.0 PROCEDURE

The Contractor must have the capability to perform all of the sample cleanup procedures presented in this Exhibit, including those included by reference. The Contractor may use any of the procedures or combinations of procedures to cleanup the samples prior to analysis, unless the Contractor is specifically directed by the Region to use a particular cleanup procedure or combination of cleanup procedures.

The Contractor must demonstrate that each cleanup procedure is capable of producing data that meets the technical acceptance criteria for the method, including Method Detection Limits (MDLs) and any precision and recovery limits.

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to apprise them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 Multi-Phase Samples

If multi-phase samples (e.g., a two-phase liquid sample, oily, sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region.

10.1.2.1 If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample;
- Separate the phases of the sample and analyze each phase separately. SMO will provide EPA Sample Numbers for the additional phases, if required;

- Separate the phases and analyze one or more of the phases, but not all of the phases. SMO will provide EPA Sample Numbers for the additional phases, if required; or

- Do not analyze the sample.

10.1.2.2 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do any of the following:

- Separate the phase(s) and analyze the phase(s) that is(are) amenable to analysis. SMO will provide EPA Sample Numbers for the additional phases, if required.

- Do not analyze the sample.

10.1.2.3 No other change in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Extraction of Water Samples

Water samples may be extracted by either a separatory funnel procedure or a Continuous Liquid-Liquid Extraction (CLLE) procedure. If an emulsion prevents acceptable solvent recovery with the separatory funnel procedure, CLLE must be employed. Allow the samples to warm to ambient temperature.

10.1.3.1 Separatory Funnel Extraction (SFE)

10.1.3.1.1 Measure out each 1.0 L sample aliquot in a separate graduated cylinder. Measure and record the pH of the sample with wide range pH paper and adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring pH adjustment must be noted in the SDG Narrative. Place the sample aliquot into a 2 L separatory funnel.

10.1.3.1.2 Using a syringe or a volumetric pipet, add 3.0 mL of the surrogate solution (Section 7.2.3.1) to all water samples.

10.1.3.1.3 Rinse the graduated cylinder with 30 mL of methylene chloride and transfer the rinsate to the separatory funnel. If the sample container is empty, rinse the container with 30 mL of methylene chloride and add the rinsate to the separatory funnel. If the sample container is not rinsed, then add another 30 mL of methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 minutes, with periodic venting to release excess pressure.

NOTE: The total volume of solvent used for extraction is 60 mL. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration through glass wool, centrifugation, or other physical means. Drain the methylene chloride into a 250 mL Erlenmeyer flask.

10.1.3.1.4 Add a second 60 mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second

time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Proceed to Section 10.1.5.

10.1.3.2 Continuous Liquid-Liquid Extraction (CLLE)

10.1.3.2.1 CLLE without Hydrophobic Membrane

10.1.3.2.1.1 Follow manufacturer's instructions for set-up.

10.1.3.2.1.2 Add methylene chloride to the bottom of the extractor and fill it to a depth of at least one inch above the bottom sidearm.

10.1.3.2.1.3 Measure out each 1.0 L sample aliquot in a separate, clean graduated cylinder; transfer the aliquot to the continuous extractor. Measure the pH of the sample with wide range pH paper or a pH meter and record the pH. Adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring the pH adjustment must be noted in the SDG Narrative.

NOTE: With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and the water layer in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

10.1.3.2.1.4 Using a syringe or volumetric pipet, add 3.0 mL of the surrogate standard spiking solution (Section 7.2.3.1) into the sample and mix well.

10.1.3.2.1.5 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor. If the sample container is empty, rinse the container with 50 mL of methylene chloride and add the rinsate to the continuous extractor.

10.1.3.2.1.6 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 5-15 mL/minute (recommended); optimize the extraction drip rate. Extract for a <u>minimum</u> of 18 hours.

NOTE 1: When a minimum drip rate of 10-15 mL/minute is maintained throughout the extraction, the extraction time may be reduced to a minimum of 12 hours. Allow to cool, then detach the distillation flask. Proceed to Section 10.1.5.

NOTE 2: Some continuous extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor.

10.1.3.2.2 CLLE with Hydrophobic Membrane

10.1.3.2.2.1 Follow the procedure in Sections 10.1.3.2.1, but reduce the amount of methylene chloride used to 50 mL and extract for a <u>minimum</u> of 6 hours.

10.1.3.2.2.2 Due to the smaller volume of solvent used during the extraction process, some sample matrices (e.g., oily samples, samples containing a high concentration of surfactants) may create an emulsion that will consume the solvent volume, preventing the efficient extraction of the sample. When this occurs, add additional solvent to ensure efficient extraction of the sample, and extend the extraction time by a minimum of 6 hours. If the sample matrix prevents the free flow of solvent through the membrane, then the non-hydrophobic membrane continuous liquid-liquid type extractor must be used. Proceed to Section 10.1.5.

NOTE 1: It may not be necessary to dry the extract with sodium sulfate if the hydrophobic membrane type extractor is used.

NOTE 2: If low surrogate recoveries occur, assure that: 1) the apparatus was properly assembled to prevent leaks; 2) the drip rate/solvent cycling was optimized; and 3) there was proper cooling for condensation of solvent.

NOTE 3: Alternate continuous liquid-liquid extractor types that meet the requirements of the analytical method may also be used. If using alternate extractors or design types, follow the manufacturer's instructions for set-up.

10.1.4 Soil/Sediment Samples

Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Also, decant and discard any standing aqueous phase.

10.1.4.1 pH Determination

Transfer 50 g of soil/sediment to a 100 mL beaker. Add 50 mL of water and stir the solution with a magnetic stirrer for 1 hour. Determine the pH of the sample by using a combination glass electrode and pH meter while the sample is stirred. Report the pH value on the appropriate data sheet. If the pH of the soil/sediment is greater than 9 or less than 5, document any subsequent problems in the analysis related to pH in the SDG Narrative, but do not attempt to adjust the pH of the sample. Discard the portion of the sample used for pH determination.

NOTE: If insufficient volume of soil/sediment is received, use a smaller 1:1 ratio of grams of sample to milliliters of water for the pH determination, and note in the SDG Narrative.

10.1.4.2 Percent Moisture (%Moisture)

Weigh 5-10 g of the soil/sediment to the nearest 0.01 g into a tarred crucible or aluminum weighing pan. Determine the weight percent volatilized (hereafter referred to as Percent Moisture) by drying overnight at 105°C. After the sample is dry, remove the sample and pan and allow them to cool in a desiccator before weighing. Calculate the Percent Moisture according to Equation 6 below. Concentrations of individual analytes will be reported relative to the dry weight of soil/sediment.

CAUTION: Gases volatized from some soil/sediment samples may require that this drying procedure be carried out in a hood.

EQ. 6 Percent Moisture Calculation

$$\%\text{Moisture} = \frac{\text{grams of wet sample - grams of dry sample}}{\text{grams of wet sample}} \times 100$$

10.1.4.3 Extraction of Soil/Sediment Samples

10.1.4.3.1 Three procedures are provided for the extraction of Aroclor compounds from soil/sediment samples:

- Ultrasonic extraction;
- [Automated] Soxhlet extraction; and
- Pressurized fluid extraction.

The Contractor shall use one of the above procedures for the extraction of soil/sediment samples.

NOTE: All soil/sediment samples in a Case must be extracted by the same procedure.

10.1.4.3.2 For soil/sediment extractions, weigh approximately 30-50 g of sample, to the nearest 0.1 g, into a 400 mL beaker. 30 g is ideal, as more sample may be used to compensate for high moisture content. If a soil sample contains greater than 65% moisture, up to 50 g of sample may be used. SMO should be contacted if the laboratory wishes to use more than 50 g. Add 60 g of anhydrous powdered or granulated sodium sulfate or 30 g of Hydromatrix, and mix well. Proceed to Section 10.1.4.3.3 for ultrasonic extraction, Section 10.1.4.3.4 for automated Soxhlet extraction, or Section 10.1.4.3.5 for pressurized fluid extraction. As applicable, follow the manufacturer's instructions for use of all extraction equipment.

NOTE: For samples extracted by the Pressurized Fluid Extraction procedure (Section 10.1.4.3.5), the use of sodium sulfate is not recommended.

10.1.4.3.3 Ultrasonic Extraction

10.1.4.3.3.1 Add 3.0 mL of the surrogate standard spiking solution (Section 7.2.3.1) to the sample, then immediately add 100 mL of 1:1 (v/v) acetone/methylene chloride.

10.1.4.3.3.2 Place the bottom surface of the tip of the 3/4 inch tapered disruption horn about ½ inch below the surface of the solvent, but above the sediment layer. Do <u>not</u> use a microtip probe.

10.1.4.3.3.3 Sonicate for 3 minutes with the output control knob set at 10 (full power), mode switch on Pulse, and the percent duty cycle knob set at 50.0%.

10.1.4.3.3.4 Decant and filter extracts through Whatman No. 41 or equivalent filter paper using vacuum filtration or centrifuge, and decant extraction solvent.

10.1.4.3.3.5 Repeat the extraction two more times with two additional 100 mL portions of 1:1 (v/v) acetone/methylene chloride. Before each extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or, very carefully, with the tip of the unenergized probe. Decant the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 (v/v) acetone/methylene chloride. Proceed to Section 10.1.5.

10.1.4.3.4 [Automated] Soxhlet Extraction

Contractor may use either automated or non-automated Soxhlet extraction. The following procedure is based on the use of a Soxtec HT-6 automated Soxhlet extraction system. When using a different system, refer to the instructions provided by the manufacturer for the appropriate procedure.

10.1.4.3.4.1 Check the heating oil level in the automated Soxhlet unit and add oil if needed. Follow the manufacturer's instructions to set the temperature on the service unit. Press the "MAINS" button and observe that the switch lamp is now "ON". Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/minute to prevent solvent loss through the condensers.

10.1.4.3.4.2 Transfer the entire sample from the beaker (Section 10.1.4.3.2) to the thimble. Add 3.0 mL of the surrogate standard spiking solution (Section 7.2.3.1) to the sample.

10.1.4.3.4.3 Immediately transfer the thimbles containing the samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.

10.1.4.3.4.4 Insert the extraction cups containing boiling chips, and load each with an appropriate volume of extraction solvent 1:1 (v/v) acetone/methylene chloride. Using the cup holder, lower the locking handle, ensuring that the safety catch engages. The cups are now clamped into position.

NOTE: The seals must be pre-rinsed or preextracted with extraction solvent prior to initial use.

10.1.4.3.4.5 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 minutes. The condenser valves must be in the "OPEN" position. Extract for the preset time.

10.1.4.3.4.6 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set the timer for 60 minutes. Make certain that condenser valves are still open. Extract for the preset time. After the rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.

10.1.4.3.4.7 When all but 2-5 mL of solvent have been collected, open the system and remove the cups. Transfer the contents of the cups to graduated, conical-bottom glass tubes. Rinse the cups using methylene chloride and add the rinsates to the glass tubes. Proceed to Section 10.1.5.

10.1.4.3.5 Pressurized Fluid Extraction

10.1.4.3.5.1 Transfer the entire sample from the beaker (Section 10.1.4.3.2) to an extraction cell of the appropriate size for the aliquot. Add 3.0 mL of the surrogate standard spiking solution (Section 7.2.3.1) to the sample.

10.1.4.3.5.2 Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer.

10.1.4.3.5.3 Place a precleaned collection vessel in the instrument for each sample, as described by the instrument manufacturer. The total volume of the collected extract will depend on the specific instrumentation and the extraction procedure recommended by the manufacturer and may range from 0.5 - 1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract.

10.1.4.3.5.4 The following are recommended extraction conditions:

Oven temperature	100°C
Pressure	1500-2000 psi
Static time	5 min. (after 5 min. pre-heat equilibration)
Flush volume	60% of the cell volume
Nitrogen purge	60 sec. at 150 psi (purge time may be extended for larger cells)
Static cycles	1

10.1.4.3.5.5 Optimize the extraction conditions, as needed, according to the manufacturer's instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. Any pressure in the range of 1500-2000 psi should suffice. An appropriate amount of 1:1 (v/v) acetone/methylene chloride should be used to achieve the conditions in Section 10.1.4.3.5.4.

10.1.4.3.5.6 Once established, the same pressure should be used for all samples in the same SDG.

10.1.4.3.5.7 Begin the extraction according to the manufacturer's instructions. Collect each extract in a clean vial. Allow the extracts to cool after the extractions are complete. Proceed to Section 10.1.5.

10.1.5 Extract Concentration

10.1.5.1 Concentration by Kuderna-Danish (K-D)

Assemble a K-D concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if equivalency is demonstrated for all the Aroclors listed in Exhibit C (Aroclors).

10.1.5.1.1 For water samples, transfer the extract to a K-D concentrator by pouring the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate.

10.1.5.1.2 For soil/sediment samples, directly transfer the extract to the K-D concentrator.

10.1.5.1.3 Rinse the Erlenmeyer flask (for both water and soil/sediment samples) and the column (for water samples) with at least two 20-30 mL portions of methylene chloride to complete the quantitative transfer.

10.1.5.1.4 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60-70°C recommended) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-30 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 3-5 mL for water samples (and less than 10 mL for soil/sediment samples), remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

10.1.5.1.5 For both water and soil/sediment extracts that do not require Gel Permeation Chromatography (GPC) cleanup, proceed with the hexane exchange described in Section 10.1.5.2.

10.1.5.1.6 For water extracts that require GPC cleanup, remove the Snyder column, rinse the flask and its lower joint, collect the rinsate in the concentrator tube, and adjust the volume to 10 mL with methylene chloride. Proceed to Section 10.2.1 for GPC cleanup.

10.1.5.1.7 For soil/sediment extracts that require GPC cleanup, it is absolutely necessary to further reduce the volume of all soil/sediment extracts to 1 mL in order to remove most of the acetone. This is best accomplished using the nitrogen evaporation technique (Section 10.1.5.3.2). The presence of acetone will cause a dead volume to develop in the GPC column and thus will cause a loss of surrogates and analytes during the GPC cleanups. Adjust the soil/sediment extract volume to 10 mL with methylene chloride. Proceed to Section 10.2.1 for GPC cleanup.

10.1.5.2 Solvent Exchange into Hexane

This procedure applies to both extracts of water samples and extracts of soil/sediment samples.

10.1.5.2.1 With the extract in a K-D apparatus, remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as described in Section 10.1.5.1, but increase the temperature of the water bath (80-90°C recommended) to maintain proper distillation.

10.1.5.2.2 Remove the Snyder column; using 1-2 mL of hexane, rinse the flask and its lower joint into the concentrator tube. Complete quantitative transfer of the extract to a 10 mL vial by using hexane.

10.1.5.2.3 For samples that have <u>not</u> been subjected to GPC cleanup, adjust the volume of the hexane extract to 10 mL. For samples that <u>have</u> been subjected to GPC cleanup, concentrate the hexane extract to 5 mL using a Micro Snyder Column or nitrogen evaporation, as described in Section 10.1.5.3.1 or 10.1.5.3.2, then proceed to Section 10.2.2 for sulfuric acid cleanup.

10.1.5.3 Final Concentration of Extract

Two different techniques are permitted to concentrate the extract to volume before cleanup or instrumental analysis. They are the Micro Snyder Column and Nitrogen Evaporation Technique. If the Region requests lower Contract Required Quantitation Limits (CRQLs) than those listed in Exhibit C Aroclors, the extracts may be further concentrated (2.0 mL instead of 10 mL when GPC cleanup is required or 5.0 mL when GPC cleanup is not required), provided a proper MDL study (see Sections 7.2.3.4.4 and 12.4) is performed. The MDL study must demonstrate that the lower CRQLs can be achieved.

NOTE: If the Region requests CRQLs lower than those listed in Exhibit C Aroclors, sufficient surrogate spiking solution must be added to samples (including LCS and MS/MSD) and blanks such that the expected surrogate concentrations after final concentration of extract are 12 times the surrogate concentrations in the low standard (CS1) of the associated initial calibration.

10.1.5.3.1 Micro Snyder Column Concentration

Add another one or two clean boiling chips to the concentrator tube and attach a two-ball Micro Snyder Column. Pre-wet the Snyder column by adding about 0.5 mL of hexane to the top of the column. Place the K-D apparatus in a hot water bath (80-90°C recommended) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse its flask and lower joint into the concentrator tube with 0.2 mL of hexane. If GPC cleanup is needed and not yet performed, adjust the volume to 10 mL with methylene chloride and proceed to Section 10.2.1 for GPC cleanup. For samples that do not require GPC cleanup, adjust the volume to 10 mL with hexane and proceed to Section 10.2.2 for sulfuric acid

cleanup. For samples that have already undergone GPC cleanup adjust the volume with hexane to 5 mL and proceed to Section 10.2.2 for sulfuric acid cleanup. If no further cleanup is needed, adjust the volume with hexane to the same volume of the aliquot used for sulfuric acid and/or sulfur cleanup (1.0 or 2.0 mL) and proceed to Section 10.3 for Gas Chromatograph/Electron Capture Detector (GC/ECD) analysis.

10.1.5.3.2 Nitrogen Evaporation Technique (taken from ASTM Method D3086)

10.1.5.3.2.1 Place the Concentrator tube in a warm water bath (30-35°C recommended) and evaporate the solvent volume to the final volume by blowing a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon) onto the solvent. DO NOT ALLOW THE EXTRACT TO GO DRY. If GPC cleanup is needed and not yet performed, adjust the volume to 10 mL with methylene chloride and proceed to Section 10.2.1 for GPC cleanup. For samples that do not require GPC cleanup, adjust the volume to 10 mL with hexane and proceed to Section 10.2.2 for sulfuric acid cleanup. For samples that have already undergone GPC cleanup, adjust the volume with hexane to 5 mL and proceed to Section 10.2.2 for sulfuric acid cleanup. If no further cleanup is needed, adjust the volume with hexane to the same volume of the aliquot used for sulfuric acid cleanup and/or sulfur cleanup (1.0 or 2.0 mL) and proceed to Section 10.3 for GC/ECD analysis.

10.1.5.3.2.2 Gas lines from the gas source to the evaporation apparatus must be stainless steel, copper, or polytetrafluoroethylene (PTFE) tubing. Plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of new tubing must be rinsed several times with hexane and then dried prior to use.

10.1.5.3.2.3 During evaporation, the tube solvent level must be kept below the water level of the bath.

10.2 Cleanup Procedures

There are three cleanup procedures specified in the method: GPC cleanup, sulfuric acid cleanup, and sulfur cleanup. GPC cleanup is optional for water and soil/sediment extracts. Sulfuric acid cleanup is <u>mandatory</u> for all extracts. Method blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them. Sulfur cleanup must be performed for all sample extracts contaminated with sulfur. The following may be used in addition to those described here, so long as all technical acceptance criteria are met: SW-846 Methods 3610B (Alumina); 3630C (Silica Gel); and 3650B (Acid/Base Partition).

10.2.1 GPC Cleanup

10.2.1.1 Introduction

GPC is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of natural (and synthetic) macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated.

10.2.1.2 GPC Column Preparation

Prepare the GPC column using Bio Beads. Alternate column packings may be used if 1) the column packings have equivalent or better performance than the Bio Beads and meet the technical acceptance criteria for GPC calibration, and 2) the column packings do not introduce contaminants/artifacts into the sample that interfere with the analysis of the Aroclor compounds. Follow the manufacturer's instructions for preparation of the GPC column.

10.2.1.3 Calibration of GPC

10.2.1.3.1 Summary of GPC Calibration

10.2.1.3.1.1 The GPC calibration procedure is based on monitoring the elution of standards with an ultraviolet (UV) detector connected to the GPC column.

10.2.1.3.1.2 The UV detector calibration procedure described in Section 10.2.1.3.3 is needed for the analyses of Aroclors listed in Exhibit C (Aroclors). IT MUST NOT BE USED FOR THE ANALYSIS OF GAS CHROMATOGRAPH/MASS SPECTROMETER (GC/MS) EXTRACTABLES OR OTHER ANALYTES WITHOUT A RECOVERY STUDY.

10.2.1.3.2 Frequency of GPC Calibration

Each GPC system must be calibrated upon award of the contract, when the GPC calibration fails to meet acceptance criteria (Section 10.2.1.3.4), when the column is changed, when channeling occurs, and once every 7 days. Also, the Retention Time (RT) shift must be less than 5% when compared to RTs in the last calibration UV traces.

10.2.1.3.3 Procedure for GPC Calibration

Follow the manufacturer's instructions for operating the GPC system. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte RTs and must be monitored.

10.2.1.3.3.1 Using a 10 mL syringe, load the calibration solution (Section 7.2.3.5) onto the GPC. Determine the elution times for the phthalate, methoxychlor, and perylene. Phthalate will elute first; perylene will elute last.

Choose a "DUMP" time that removes greater than 85% of the phthalate. Choose a "COLLECT" time so that greater than 95% of the methoxychlor is collected, and continue to collect until just prior to the elution time of sulfur. Use a "WASH" time of 10 minutes.

NOTE: The "DUMP" and "COLLECT" times must be adjusted to compensate for the difference in volume of the lines between the detector and the collection flask.

10.2.1.3.3.2 Re-inject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

10.2.1.3.3.3 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for

each sample extract processed may be used to indicate problems with the system during sample processing.

10.2.1.3.3.4 Analyze a GPC blank of methylene chloride. Concentrate the methylene chloride that passed through the system during the collect cycle using a K-D evaporator. Exchange the solvent to hexane as in Section 10.1.5.2 and analyze the concentrate by GC/ECD according to the procedure in Section 10.3 (usual protocol). If the blank exceeds the estimated quantitation limit of the analytes, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping, if necessary.

10.2.1.3.4 Technical Acceptance Criteria for GPC Calibration

10.2.1.3.4.1 The GPC system must be calibrated at the frequency described in Section 10.2.1.3.2. The UV trace must meet the following requirements:

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution;
- Corn oil and phthalate peaks should exhibit greater than 85% resolution;
- Phthalate and methoxychlor peaks should exhibit greater than 85% resolution;
- Methoxychlor and perylene peaks should exhibit greater than 85% resolution; and
- Perylene and sulfur peaks must not be saturated and should exhibit greater than 90% baseline resolution.

10.2.1.3.4.2 The solvent flow rate and column pressure must be within the manufacturer's specified ranges.

10.2.1.3.4.3 The RTs for bis(2-ethylhexyl)phthalate and perylene must not vary more than ±5% between calibrations. Excessive RT shifts are caused by the following:

- Poor laboratory temperature control or system leaks;
- An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight; and/or
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

10.2.1.3.5 Corrective Action for GPC Calibration

10.2.1.3.5.1 If the flow rate and/or column pressure do not fall within the manufacturer's specified ranges, a new column should be prepared.

10.2.1.3.5.2 A UV trace that does not meet the criteria in Section 10.2.1.3.4 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

10.2.1.3.5.3 If the GPC blank is equal to or exceeds the Contract Required Quantitation Limit (CRQL) of any compound in Exhibit C (Aroclors), pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

10.2.1.4 Daily UV Calibration Check (Optional)

The calibration of the GPC may be monitored daily by use of the UV-GPC calibration solution (Section 7.2.3.5) and the UV detector calibration procedure (Section 10.2.1.3.3). The UV detector should be used to monitor the elution times for the phthalate, methoxychlor, and perylene, in that order. The precalibrated GPC program should "DUMP" greater than 85% of the phthalate and should "COLLECT" greater than 95% of the methoxychlor and perylene. Significant changes in elution times of the analytes (e.g., >0.5 minutes) indicate that the column is out of calibration and must be recalibrated or replaced.

10.2.1.5 Sample Cleanup by GPC

10.2.1.5.1 Introduction to Sample Cleanup by GPC

10.2.1.5.1.1 It is very important to have consistent laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not consistent, RTs will shift, and the dump and collect times determined by the calibration standard will no longer be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22°C.

10.2.1.5.1.2 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of 1:1 (v/v) glycerol/water solution must be diluted and loaded into several loops. Similarly, extracts containing more than 40 mg/mL of non-volatile residue must be diluted and loaded into several loops. The non-volatile residue may be determined by evaporating a 100 µL aliquot of the extract to dryness in a tarred aluminum weighing pan, or other suitable container. When multiple loops/runs are necessary for an individual sample, be sure to combine all of the sample eluates collected.

10.2.1.5.1.3 Systems using automated injection devices to load the sample on the column must be carefully monitored to assure that the required amount is injected onto the column. Viscous extracts, or extracts containing large amounts of non-volatile residue, will cause problems with injecting the proper amount of sample extract onto the column using automated injection systems. After the sample extract has been processed, the remaining sample extract in an injection vial must be checked to assure that the proper amount of extract was injected on the column before proceeding with the sample analysis. If the proper amount of extract was not injected, the sample must be reprepared and the sample extract must be either diluted and loaded into several loops or the sample extract must be injected manually.

10.2.1.5.2 Frequency of Sample Cleanup by GPC

GPC cleanup must be performed at least once for each soil/sediment and water extracts that contain high molecular weight contaminants that interfere with the analysis of the target analytes and all associated Quality Control (QC) [blanks, Laboratory Control Samples (LCSs), and Matrix Spike and Matrix Spike Duplicates (MS/MSDs)]. If the cleanup procedure is inadequate, contact SMO.

10.2.1.5.3 Procedure for Sample Cleanup by GPC

10.2.1.5.3.1 Particles greater than 5 microns may scratch the valve, which may result in a system leak and cross contamination of sample extracts in the sample loops. To avoid such problems, filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container (e.g., a 15 mL culture tube with a PTFE-lined screw-cap). Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. Draw a minimum of 8 mL of extract into a 10 mL syringe.

10.2.1.5.3.2 INTRODUCTION OF PARTICULATES OR GLASS WOOL INTO THE GPC SWITCHING VALVES MAY REQUIRE FACTORY REPAIR OF THE APPARATUS.

10.2.1.5.3.3 Follow the manufacturer's instructions for operation of the GPC system being utilized.

NOTE: These instructions were written for a 5 mL GPC injection loop. A 2 mL injection loop may be used in place of a 5 mL injection loop. If a 2 mL loop is used, concentrate the 10 mL extract to 4 mL, and then inject 2 mL from the 4 mL.

10.2.1.5.3.4 If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action following the manufacturer's recommendations. The problem must be resolved prior to loading sample extracts.

10.2.1.5.3.5 After loading each sample loop, wash the loading port with methylene chloride to minimize cross contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

10.2.1.5.3.6 Collect each sample in a 250 mL Erlenmeyer flask covered with aluminum foil to reduce solvent evaporation, or directly into a K-D evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems:

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure;
- Increase in column operating pressure due to the absorption of particles or gel fines onto either the

guard column or the analytical column gel, if a guard column is not used; and/or

- Leaks in the system or significant variances in room temperature.

10.2.1.5.3.7 After the appropriate GPC fraction has been collected for each sample, concentrate the extract as per Section 10.1.5.1 and proceed to solvent exchange into hexane as described in Section 10.1.5.2.

10.2.1.5.3.8 Any samples that were loaded into two or more loops must be recombined before proceeding with concentration.

10.2.2 Sulfuric Acid Cleanup

10.2.2.1 Sulfuric acid cleanup uses hexane solvent that will be treated with concentrated sulfuric acid. This method is used for rigorous cleanup of sample extracts prior to analysis of Aroclors. This method is used to provide accuracy in quantitation of Aroclors by eliminating elevated baselines or overly complex chromatograms.

10.2.2.2 Frequency of Sulfuric Acid Cleanup

Sulfuric acid cleanup is required for all water and soil/sediment extracts.

10.2.2.3 Procedure for Sulfuric Acid

10.2.2.3.1 Using a syringe or a volumetric pipet, transfer all of the hexane extract to a 10 mL vial and, in a fume hood, carefully add 5 mL of the 1:1 (v/v) sulfuric acid/water solution.

10.2.2.3.2 The volume of hexane extract used depends on the requirements of the Gas Chromatograph (GC) autosampler used by the laboratory. If the autosampler functions reliably with 1 mL of sample volume, 1.0 mL of extract should be used. If the autosampler requires more than 1 mL of sample volume, 2.0 mL of extract should be used.

NOTE: Make sure that there is no exothermic reaction or evolution of gas prior to proceeding.

10.2.2.3.3 Cap the vial tightly and vortex for 1 minute. A vortex must be visible in the vial.

NOTE: Stop the vortexing immediately if the vial leaks. AVOID SKIN CONTACT, AS SULFURIC ACID BURNS.

10.2.2.3.4 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer; it should not be highly colored, nor should it have a visible emulsion or cloudiness.

10.2.2.3.5 If a clean phase separation is achieved, proceed to Section 10.2.2.3.8.

10.2.2.3.6 If the hexane layer is colored or the emulsion persists for several minutes, remove the sulfuric acid layer from the vial and dispose of it properly. Add another 5 mL portion of the clean 1:1 (v/v) sulfuric acid/water solution and perform another acid cleanup, beginning at Section 10.2.2.3.7.

NOTE: Do not remove any hexane from the vial at this stage of the procedure.

If the extract is no longer colored, the analyst may proceed to Section 10.2.2.3.11.

10.2.2.3.7 Vortex the sample for 1 minute and allow the phases to separate.

10.2.2.3.8 Transfer the hexane layer to a clean 10 mL vial. Take care not to include any of the acid layer in this clean vial, as it can cause damage to the analytical instrumentation. Once the hexane layer is removed, perform a second "extraction" of the acid layer, as described in Section 10.2.2.3.9.

10.2.2.3.9 Add an additional 1 mL of hexane to the sulfuric acid layer, cap, and vortex. This second extraction is done to ensure quantitative transfer of the PCBs.

10.2.2.3.10 Remove the second hexane layer and combine with the hexane from Section 10.2.2.3.8.

10.2.2.3.11 Reduce the volume of the combined hexane layers to the original volume (1 mL or 2 mL) using an appropriate concentration technique. Analyze the extract immediately. If analysis of the extract is not performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract is stored longer than 2 days, it should be transferred to a vial with a PTFE-lined screw-cap top, and labeled appropriately.

10.2.3 Sulfur Cleanup

10.2.3.1 Sulfur contamination will cause a rise in the baseline of chromatogram and may interfere with the analyses of the later eluting pesticides. If crystals of sulfur are evident or if the presence of sulfur is suspected, sulfur removal must be performed. Interference which is due to sulfur is not acceptable. Sulfur can be removed by one of three methods, according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean centrifuge tube or clean concentrator tube before proceeding with further sulfur cleanup.

10.2.3.1.2 If only part of a set of samples require sulfur cleanup, then, a sulfur cleanup blank is required for that part of the set (Section 12.1.3).

10.2.3.2 Frequency of Sulfur Cleanup

Sulfur removal is required for all sample extracts that contain sulfur.

10.2.3.3 Procedure for Sulfur Cleanup

10.2.3.3.1 Removal of Sulfur using Tetrabutylammonium (TBA) Sulfite

10.2.3.3.1.1 The TBA procedure removes elemental sulfur by conversion to the thiosulfate ion, which is water-soluble. TBA sulfite causes the least amount of degradation to a broad range of

pesticides and organics compounds, while mercury may degrade organophosphorus and some organochlorine pesticides. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

10.2.3.3.1.2 Add 2.0 mL TBA Sulfite Reagent, 1.0 mL 2-propanol, and approximately 0.65 g of sodium sulfite crystals to extract and shake for at least 5 minutes on the wrist shaker and observe. An excess of sodium sulfite must remain in the sample extract during the procedure. If the sodium sulfite crystals are entirely consumed, add one or two more aliquots (approximately 0.65 g) to the extract and observe. Replace the samples on the wrist shaker for 45 minutes, observing at 15-minute intervals to make sure that the sodium sulfite is not consumed. Add 5 mL organic free water and shake for 10-15 minutes. Place the samples into the centrifuge and spin at a setting and duration appropriate to spin down the solids. Transfer the hexane layer to a clean 10 mL and cap. The extract transferred to the vial still represents the 1.0 or 2.0 mL final volume.

10.2.3.3.2 Copper Technique

Add approximately 2 g of cleaned copper powder to the extract in the centrifuge or concentrator tube (2 g will fill the tube to about the 0.5 mL mark). Mix the copper and extract for at least 1 minute on a mechanical shaker. Separate the extract from the copper powder by drawing off the extract with a disposable pipet, and transfer the extract to a clean vial. The extract transferred to the vial still represents the 1.0 or 2.0 mL final volume. If the separation of the extract from the copper appears bright, proceed to Section 10.3 and analyze the extracts. If the copper changes color, repeat the sulfur removal procedure as necessary.

10.3 GC/ECD Analysis

10.3.1 Introduction

10.3.1.1 Before samples (including LCSs and MS/MSDs) and required blanks (method, sulfur, and/or instrument) can be analyzed, the instrument must meet the initial calibration and calibration verification technical acceptance criteria. All sample extracts, required blanks, and calibration standards must be analyzed under the same instrumental conditions. All sample extracts, required blank extracts, and standard/spiking solutions must be allowed to warm to ambient temperature before preparation/analysis. Sample analysis on two different non-equivalent GC columns (see Section 6.21) is required for <u>all</u> samples and blanks.

10.3.1.2 Set up the GC/ECD system per the requirements in Section 9.1. Unless ambient temperature on-column injection is used (Section 9.1), the injector must be heated to at least 200°C. The optimized GC conditions from Section 9.1 must be used.

10.3.2 Procedure for Sample Analysis by GC/ECD

The injection must be made on-column by using either automatic or manual injection. 1.0 to 2.0 µL injection volumes may be used provided that all associated standards, samples, and blanks use the same injection volume. The same injection volume must be used for all standards, samples (including LCSs and MS/MSDs), and blanks

associated with the same initial calibration. If a single injection is used for two GC columns attached to a single injection port, it may be necessary to use an injection volume greater than 2.0 µL. However, the same injection volume must be used for all analyses.

10.3.2.1 Analytical Sequence

All acceptable samples must be analyzed within a valid analysis sequence as given below:

Time	Injection #	Material Injected
	1-12	First 12 steps of the initial calibration
0 hr.	13	Instrument blank
	14	Aroclor 1016/1260 Standard Sample
12 hr.		Last sample
	1st injection past 12 hr.	Instrument blank
	2nd injection past 12 hr.	Aroclor 1016/1260 standard subsequent samples
Another 12 hrs.		Last sample
	1st injection past 12 hr.	Instrument blank
	2nd injection past 12 hr.	Aroclor 1016/1260 standard
	3rd injection past 12 hr.	Sample

10.3.2.1.1 The first 12 hours are counted from injection #13, not from injection #1. Samples may be injected until 12:00 hours have elapsed. All subsequent 12-hour periods are timed from the injection of the instrument blank that brackets the front end of the samples. If more than 12 hours elapse between the injections of two instrument blanks that bracket a 12-hour period in which samples or required blanks are analyzed, then the time between the injection of the instrument blank and the preceding sample may not exceed the length of one chromatographic run. While the 12-hour period may not be exceeded, the laboratory may run instrument blanks and standards more frequently, for instance, to accommodate staff working on 8-hour shifts. No more than 14 hours may elapse from the injection beginning the opening CCV (instrument blank) and the injection ending the closing CCV (Aroclor Standard).

10.3.2.1.2 After the initial calibration, the analysis sequence may continue as long as acceptable calibration verification(s) are analyzed at the required frequency. This analysis sequence shows only the minimum required standards. More standards may be run at the discretion of the Contractor; however, the standards must also satisfy the criteria presented in Section 9 in order to continue the run sequence.

10.3.2.1.3 An analysis sequence must also include all samples and required blank analyses, but the Contractor may decide at what point in the sequence they are to be analyzed.

10.3.2.1.4 The requirements for the analysis sequence apply to both GC columns and for all instruments used for these analyses.

10.3.3 Sample Dilutions

10.3.3.1 All samples must be analyzed at the most concentrated level that is consistent with achieving satisfactory chromatography (defined in Section 11.3).

10.3.3.2 If the response of the largest peak for any Aroclor is greater than the response of the same peak in the high-point standard in the initial calibration for both columns, then the sample must be diluted to have the response of the largest peak of the lower of the two column analyses be between the low and high calibration standards.

10.3.3.3 If dilution is employed solely to bring a peak within the calibration range or to get an Aroclor pattern on scale, the results for both the more and the less concentrated extracts must be reported. The resulting changes in quantitation limits and surrogate recovery must be reported also for the diluted samples.

10.3.3.4 If the Contractor has reason to believe that diluting the final extracts will be necessary, a less diluted run may still be required. If an acceptable chromatogram (as defined in Section 11.3) is achieved with the diluted extract, then:

- If the Dilution Factor (DF) is greater than 10, an additional extract 10 times more concentrated than the diluted sample extract must be injected and reported with the sample data.

- If the DF is less than or equal to 10, then an undiluted sample extract must be injected and reported with the sample data.

If the analysis of the most concentrated extract does not meet the requirement for dilution in Section 10.3.3.2, then the analysis of the dilution is at no additional cost to USEPA.

10.3.3.5 When diluted, Aroclors must be able to be reported at greater than 25.0% of full scale but less than 100.0% of full scale.

10.3.3.6 Samples with analytes detected at a level greater than the high calibration point must be diluted until the concentration is within the linear range established during calibration or to a maximum of 1:100,000.

10.3.3.7 If the concentration is still above the high calibration standard after the dilution of 1:100,000, the Contractor shall contact SMO immediately.

10.3.3.8 Use the results of the original analysis to determine the approximate DF required to get the largest analyte peak (for the lower of the two column responses) within the initial calibration range.

10.3.3.9 Sample dilutions must be made quantitatively. Dilute the sample extract with hexane.

10.3.3.10 If more than two analyses (i.e., from the original sample extract and more than one dilution, or from the most concentrated dilution analyzed and further dilutions) are required to get all target compounds within the calibration range, contact SMO for guidance.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

11.1.1.1 The laboratory will identify and quantitate analyte peaks based on the Retention Time (RT) windows and the Calibration Factors (CFs) of each standard established during the initial calibration sequence.

11.1.1.2 Analytes are identified when peaks are observed in the RT window for the analyte on both Gas Chromatograph (GC) columns.

11.1.1.3 A set of a minimum of 3 major peaks is selected for each Aroclor. The RT window for each peak is determined from the initial calibration analysis. Identification of an Aroclor in the sample is based on pattern recognition in conjunction with the elution of a minimum of 3 sample peaks within the RT windows of the corresponding peaks of the standard on both GC columns.

11.1.1.4 When an Aroclor other than 1016 or 1260 is detected in a sample, a valid five-point calibration curve specific to that Aroclor must be run, followed by reanalysis of the sample or appropriately diluted sample with the detected Aroclor present. The Mean Calibration Factor ($\overline{CF}$) will be used to quantitate the analyte in the sample.

11.1.1.5 The choice of the peaks used for Aroclor identification and the recognition of those peaks may be complicated by the environmental alteration of the Aroclors, and by the presence of coeluting analytes or matrix interferences, or both. Because of the alteration of test materials in the environment, Aroclors in samples may give patterns similar to, but not identical with, those of the standards.

11.1.1.6 If more than one Aroclor is observed in a sample, the Contractor must choose different peaks to quantitate each Aroclor. A peak common to both analytes present in the sample must not be used to quantitate either compound.

11.1.2 Gas Chromatograph/Mass Spectrometer (GC/MS) Confirmation of Aroclors

11.1.2.1 Any Aroclor analyte listed in Exhibit C (Aroclors) for which a concentration is reported from a GC/Electron Capture Detection (GC/ECD) analysis may have the identification confirmed by GC/MS if the concentration is sufficient for that purpose. Before GC/MS confirmation is to be performed, the Region must be contacted for further guidance. The following paragraphs are to be used as guidance in performing GC/MS confirmation, as appropriate. USEPA may require reanalysis of any affected samples at no additional cost to USEPA.

11.1.2.2 The GC/MS confirmation may be accomplished by one of three general means:

- Examination of the semivolatile GC/MS library search results [i.e., Tentatively Identified Compound (TIC) data]; or
- A second analysis of the semivolatile extract; or
- Analysis of the Aroclor extract, following any solvent exchange and concentration steps that may be necessary.

11.1.2.3 If an individual peak concentration (on-column concentration) for an Aroclor is greater than or equal to 10 ng/µL for both columns the laboratory shall contact SMO to determine whether GC/MS confirmation is required. The on-column concentration is calculated using Equation 8 for water samples and Equation 10 for soil samples.

11.1.2.3.1 For water samples prepared according to the method in Section 10, the corresponding sample concentration is 100 µg/L.

11.1.2.3.2 For soil/sediment samples prepared according to the method described in Section 10, the corresponding sample concentration is 3,300 µg/kg.

11.1.2.4 In order to confirm the identification of the target Aroclor, the laboratory must also analyze a reference standard for the analyte. In order to demonstrate the ability of the GC/MS system to identify the analyte in question, the concentration of the standard should be 50 ng/µL for Aroclors.

11.1.2.5 The laboratory is advised that library search results from the NIST (2002 release or later) mass spectral library will not likely list the name of the Aroclor analyte as it appears in this analytical method, hence, the mass spectral interpretation specialist is advised to compare the Chemical Abstracts Service (CAS) Registry numbers for the Aroclors to those from the library search routine.

11.1.2.6 If the analyte cannot be confirmed from the semivolatile library search data for the original semivolatile GC/MS analysis, the laboratory may analyze another aliquot of the semivolatile sample extract after further concentration of the aliquot. This second aliquot must either be analyzed as part of a routine semivolatile GC/MS analysis, including instrument performance checks (DFTPP), or it must be analyzed along with separate reference standards for the analytes to be confirmed.

11.1.2.7 If the analyte cannot be confirmed by the procedure in Section 11.1.2.6, then an aliquot of the extract prepared for the GC/ECD analysis must be analyzed by GC/MS, following any necessary solvent exchange and concentration steps. As in Section 11.1.2.4, analysis of a reference standard is required if the GC/MS continuing calibration standard does not contain the analyte to be confirmed.

11.1.2.8 Regardless of which of the approaches above is used for GC/MS confirmation, the appropriate blank must also be analyzed by GC/MS to demonstrate that the presence of the analyte was not the result of laboratory contamination. If the confirmation is based on the analysis of the semivolatile extract, then the semivolatile method blank extracted with the sample must also be analyzed. If the confirmation is based on the analysis of the extract prepared for the GC/ECD analysis, then the method blank extracted with the sample must also be analyzed.

11.1.2.9 If the identification of the analyte cannot be confirmed by any of the GC/MS procedures above, and the concentration calculated from the GC/ECD analysis is greater than or equal to the concentration of the reference standard analyzed by GC/MS, then report the analyte as undetected, adjust the sample quantitation limit (the value associated with the "U" qualifier) to a sample concentration equivalent to the concentration of the GC/MS reference standard, and qualify the results on Form I with one of the laboratory-defined qualifiers ("X", "Y", or "Z"). In this instance, define the qualifier explicitly in the Sample Delivery Group (SDG) Narrative, and describe the steps taken to confirm the analyte in the SDG Narrative.

11.1.2.10 For GC/MS confirmation of Aroclors, spectra of three characteristic peaks are required for both the sample component and the reference standard.

11.1.2.11 The purpose of the GC/MS analysis for the Aroclors is to confirm the presence of chlorinated biphenyls in Aroclors. The GC/MS analytical results for the Aroclors shall not be used for quantitation and the GC/MS results shall not be reported on Form I and Form X. The exception noted in Section 11.1.2.9 applies only to analytes that cannot be confirmed above the reference standard concentration.

11.2 Calculations

11.2.1 Aroclor Concentrations

11.2.1.1 Water

11.2.1.1.1 EQ. 7 Concentration Calculation for Water Samples

$$\text{Concentration } \mu g/L = \frac{(A_x)\,(V_t)\,(DF)\,(GPC)}{(\overline{CF})\,(V_o)\,(V_i)}$$

Where,

A_x = Area or height of the peak for the compound to be measured.

$\overline{CF}$ = Mean Calibration Factor from the specific five-point calibration (area/ng).

V_o = Volume of water extracted in mL (Note: for instrument and sulfur blanks assume a volume of 1000 mL).

V_i = Volume of extract injected in µL. (If a single injection is made onto two columns, use one half the volume in the syringe as the volume injected onto each column).

V_t = Volume of the concentrated extract in µL. (If GPC is not performed, then V_t = 10000 µL. If GPC is performed, then $V_t = V_{out}$).

DF = Dilution Factor. The DF for analysis of water samples by this method is defined as follows:

$$\frac{\text{µL most concentrated extract used to make dilution + µL clean solvent}}{\text{µL most concentrated extract used to make dilution}}$$

If no dilution is performed, DF = 1.0.

$GPC = \frac{V_{in}}{V_{out}}$ = GPC factor. (If no GPC is performed, GPC = 1.0).

V_{in} = Volume of extract loaded onto GPC column.

V_{out} = Volume of extracted collected after GPC cleanup.

11.2.1.1.2 EQ. 8 On-Column Concentration of Water Sample Extract

$$\text{On-Column Concentration (ng/µL)} = \frac{(A_x)}{(\overline{CF})\,(V_i)}$$

Where,

A_x = Same as EQ. 7.

$\overline{CF}$ = Same as EQ. 7.

V_i = Volume of extract injected (µL). (If a single injection is made onto two columns, use ½ the volume in the syringe as the volume injected onto each column).

11.2.1.2 Soil/Sediment

11.2.1.2.1 EQ. 9 Concentration Calculation for Soil Samples

$$\text{Concentration µg/Kg (Dry weight basis)} = \frac{(A_x)\,(V_t)\,(DF)\,(GPC)}{(\overline{CF})\,(V_i)\,(W_s)\,(D)}$$

Where,

A_x, V_t, $\overline{CF}$, and GPC are as given for water in EQ 7.

V_i = Volume of extract injected in µL. (If a single injection is made onto two columns, use one half the volume in the syringe as the volume injected onto each column.)

$D = \frac{100 - \%Moisture}{100}$

W_s = Weight of sample extracted in g.

DF = Dilution Factor. The DF for analysis of soil/sediment samples by this method is defined as follows:

$$\frac{\mu L \text{ most concentrated extract used to make dilution} + \mu L \text{ clean solvent}}{\mu L \text{ most concentrated extract used to make dilution}}$$

If no dilution is performed, DF = 1.0.

11.2.1.2.2 EQ. 10 On-Column Concentration of Soil Sample Extract

$$\text{On-Column Concentration (ng/µL)} = \frac{(A_x)}{(\overline{CF})\,(V_i)}$$

Where,

A_x = Same as EQ. 7.

$\overline{CF}$ = Same as EQ. 7.

V_i = Volume of extract injected (µL). (If a single injection is made onto two columns, use ½ the volume in the syringe as the volume injected onto each column).

11.2.2 Target Compounds

The quantitation of Aroclors must be accomplished by comparing the heights or the areas of each of a minimum of 3 major peaks of the Aroclor in the sample with the $\overline{CF}$ for the same peaks established during the specific five-point calibration. The concentration of multi-component analytes is calculated by using Equations 7 and 9, where A_x is the area for each of the major peaks of the Aroclor. The concentration of each peak is determined and then a mean concentration for a minimum of 3 major peaks is determined on each column.

11.2.2.1 Note that the $\overline{CF}$s used for the quantitation of Aroclors are the $\overline{CF}$s from the concentration of the specific five-point calibration.

11.2.2.2 The lower mean concentration (from a minimum of 3 peaks) is reported on Form I, and the two mean concentrations reported on Form X. The two mean concentrations are compared by calculating the Percent Difference (%Difference) using Equation 11.

EQ. 11 Percent Difference Calculation

$$\%Difference = \frac{Conc_H - Conc_L}{Conc_L} \times 100$$

Where,

$Conc_H$ = The higher of the two concentrations for the target compound in question.

$Conc_L$ = The lower of the two concentrations for the target compound in question.

NOTE: Using this equation will result in Percent Difference values that are always positive.

11.2.3 Contract Required Quantitation Limit (CRQL) Calculation

11.2.3.1 Water Samples

EQ. 12 Adjusted CRQL Calculation for Water Samples

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{(V_x)\,(V_t)\,(DF)}{(V_o)\,(V_c)}$$

Where,

V_t, DF, and V_o = As given in Equation 7.

V_x = Contract sample volume (1000 mL).

V_c = Contract concentrated extract volume (10,000 µL if GPC was not performed and V_c=V_{out} if GPC was performed).

11.2.3.2 Soil/Sediment Samples

EQ. 13 Adjusted CRQL Calculation for Soil/Sediment Samples

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{(W_x)\,(V_t)\,(DF)}{(W_s)\,(V_c)\,(D)}$$

Where,

DF, W_s, and D = As given in Equation 9.

V_t = As given in Equation 7.

W_x = Contract sample weight (30 g).

V_c = Contract concentrated extract volume (10,000 µL if GPC was not performed).

11.2.4 Surrogate Recoveries

The concentrations for surrogate compounds can be calculated by using Equation 7 (for waters) and Equation 9 (for soils) and the $\overline{CF}$ from the most recent initial calibration.

11.2.4.1 Calculate surrogate recoveries for each GC column using Equation 14.

EQ. 14 Surrogate Recovery Calculation

$$\text{Percent Recovery} = \frac{(Q_d \times DF)}{Q_a} \times 100$$

Where,

Q_d = Quantity determined by analysis.

Q_a = Quantity added.

DF = Dilution Factor.

11.2.4.2 The recovery limits for the surrogates are 30-150% for both surrogate compounds.

11.2.4.3 Surrogate recovery data from both GC columns are reported (see Exhibit B).

11.3 Technical Acceptance Criteria for Sample Analysis

The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

11.3.1 Samples must be analyzed under the GC/ECD operating conditions in Section 9. The instrument must have met all initial calibration, calibration verification, and blank technical acceptance criteria. Sample data must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks and calibration verification standards described in Section 10.3.2.1.

11.3.2 The samples must be extracted and analyzed within the contract required holding times.

11.3.3 The LCS associated with the samples must meet the LCS technical acceptance criteria.

11.3.4 The samples must have an associated method blank meeting the technical acceptance criteria for method blanks. If a sulfur blank is associated with the samples, that blank must meet the sulfur cleanup blank technical acceptance criteria in Section 12.1.3.5.

11.3.5 The RT for each of the surrogates must be within the RT window (Section 9.2.4.3) for both GC columns.

11.3.6 The percent recoveries for the surrogates must be between 30 - 150% inclusive. Up to one surrogate may fail this criteria per column.

NOTE: The surrogate recovery requirements do not apply to a sample that has been diluted.

11.3.7 No target compound concentrations may exceed the upper limit of the initial calibration or else the extract must be diluted and reanalyzed.

11.3.8 If a valid initial calibration is not available, then a five-point calibration curve specific for any identified Aroclor must be analyzed during a valid analytical sequence on the same instrument and column upon its detection in a sample. Reanalysis of the sample or required diluted sample with the detected Aroclor is necessary and billable to USEPA.

11.3.9 The identification of Aroclors is based primarily on recognition of patterns of RTs displayed on a chromatogram. Therefore, the following requirements apply to all data presented for Aroclors.

11.3.9.1 A minimum of 3 peaks must be chosen for each Aroclor, and preferably 5 peaks, but more than 5 peaks may be chosen. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3-5 peaks should include at least one peak that is unique to that Aroclor.

11.3.9.2 Chromatograms must display the largest peak of any Aroclor detected in the sample at less than full scale.

11.3.9.3 If an extract must be diluted, chromatograms must display the peaks chosen for quantitation of Aroclors between 25 and 100% of full scale.

11.3.9.4 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample analysis technical acceptance criteria MUST be met before data are reported. Samples contaminated from laboratory sources or associated with a contaminated method blank or sulfur cleanup blank will require reextraction and reanalysis at no additional cost to USEPA. Any samples analyzed that do not meet the technical acceptance criteria will require reextraction and/or reanalysis at no additional cost to USEPA. In cases, where the conditions in Section 11.3.8 apply, the sample or required diluted sample with the detected Aroclor is necessary and billable to USEPA.

11.4.2 If the sample analysis technical acceptance criteria are not met, check calculations, surrogate solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the technical acceptance criteria, in which case, the affected samples must be reanalyzed at no additional cost to USEPA after the corrective action.

11.4.3 The extract from samples that were cleaned up by GPC using an automated injection system, and have both surrogate recoveries outside the lower surrogate acceptance limits, must be checked to assure that the proper amount was injected on the GPC column. If insufficient volume was injected, the sample must be reprepared and reanalyzed at no additional cost to USEPA.

11.4.4 If sample chromatograms have a high baseline or interfering peaks, inspect the system to determine the cause of the problem (e.g., carryover, column bleed, dirty ECD, contaminated gases, leaking septum, etc.). After correcting the problem, reanalyze the sample extracts. If the problem with the samples still exists, then those samples must be reextracted and reanalyzed. Samples that cannot be made to meet the given specifications after one reextraction and cleanup procedures (sulfuric acid and GPC cleanups) are reported in the SDG Narrative and do not require further analysis.

12.0 QUALITY CONTROL (QC)

12.1 Blank Analyses

12.1.1 Introduction

There are two types of blanks required by this method: the method blank and the instrument blank. A separate sulfur cleanup blank may also be required if some, but not all of the samples are subjected to sulfur cleanup. Samples that are associated with a sulfur cleanup blank are also associated with the method blank with which they were extracted. Both the method and sulfur cleanup blanks must meet the respective technical acceptance criteria for the sample analysis technical acceptance criteria to be met.

NOTE: Under no circumstances should blanks (method/instrument/sulfur cleanup) be analyzed at a dilution (i.e., blanks should always have a DF=1.0).

12.1.2 Method Blank

12.1.2.1 Summary of Method Blank

A method blank is a volume of a clean reference matrix (reagent water for aqueous samples, or purified sodium sulfate of Hydromatrix for soil/sediment samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

12.1.2.2 Frequency of Method Blank

A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples [excluding Matrix Spike and Matrix Spike Duplicates (MS/MSDs), Performance Evaluation (PE) samples, and Laboratory Control Samples (LCSs)]. In addition, a method blank shall:

- Be extracted by the same procedure used to extract samples; and
- Be analyzed on each Gas Chromatograph/Electron Capture Detector (GC/ECD) system used to analyze associated samples.

12.1.2.3 Procedure for Method Blank

For Aroclor analyses, a method blank for water samples consists of a 1 L volume of reagent water spiked with 3.0 mL of the surrogate spiking solution (Section 7.2.3.1). For soil/sediment samples,

the method blank consists of 30 g of sodium sulfate or Hydromatrix spiked with 3.0 mL of the surrogate spiking solution. Extract, concentrate, and analyze method blanks according to Section 10.

12.1.2.4 Calculations for Method Blank

Calculate method blank results according to Section 11.

12.1.2.5 Technical Acceptance Criteria for Method Blank

12.1.2.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.1.2.5.2 All method blanks must be prepared and analyzed at the frequency described in Section 12.1.2, using the procedure above and in Section 10 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria. Method blanks must undergo Gel Permeation Chromatography (GPC) cleanup, when required, on a GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration checks.

12.1.2.5.3 Method blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, and required Aroclor standards, as described in Section 10.3.2.1.

12.1.2.5.4 The concentration of the target compounds [Exhibit C (Aroclors)]in the method blank must be less than the Contract Required Quantitation Limit (CRQL) for each target compound.

12.1.2.5.5 The method blank must meet all sample technical acceptance criteria in Sections 11.3.5 and 11.3.7.

12.1.2.5.6 Surrogate recoveries must fall within the acceptance window of 30-150%. These limits are not advisory.

12.1.2.5.7 Method blanks must be analyzed at the original concentration (i.e., DF=1.0).

12.1.2.6 Corrective Action for Method Blank

12.1.2.6.1 If a method blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out of QC limits.

12.1.2.6.2 If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. Further, all samples (including LCSs, MS/MSDs, and PE samples) processed with a method blank that does not meet the method blank technical acceptance criteria (i.e.,contaminated) will require reextraction and reanalysis at no additional cost to USEPA. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.

12.1.2.6.3 If surrogate recoveries in the method blank do not meet the technical acceptance criteria listed in Section 12.1.2.5.6, first reanalyze the method blank. If the surrogate recoveries

do not meet the technical acceptance criteria after reanalysis, then the method blank and all samples (including LCSs, MS/MSDs, and PE samples) associated with that method blank must be reextracted and reanalyzed at no additional cost to USEPA.

12.1.2.6.4 If the method blank fails to meet a technical acceptance criteria other than what is listed in Sections 12.1.2.5.4 and 12.1.2.5.6, then the problem is an instrument problem. Correct the instrument problem, recalibrate the instrument (if necessary) and reanalyze the method blank.

12.1.3 Sulfur Cleanup Blank

12.1.3.1 Summary of Sulfur Cleanup Blank

The sulfur cleanup blank is a modified form of the method blank. The sulfur cleanup blank is hexane spiked with the surrogates and passed through the sulfur cleanup and analysis procedures. The purpose of the sulfur cleanup is to determine the levels of contamination associated with the separate sulfur cleanup steps.

12.1.3.2 Frequency of Sulfur Cleanup Blank

The sulfur cleanup blank is prepared when only part of a set of samples extracted together requires sulfur removal. A method blank is associated with the entire set of samples. The sulfur cleanup blank is associated with the part of the set that required sulfur cleanup. If all the samples associated with a given method blank are subjected to sulfur cleanup, then no separate sulfur cleanup blank is required.

12.1.3.3 Procedure for Sulfur Cleanup Blank

The concentrated volume of the blank must be the same as the final volume of the samples associated with the blank. The sulfur blank must also contain the surrogates at the same concentrations as the sample extracts (assuming 100.0% recovery). Therefore, add 0.6 mL of the surrogate spiking solution (Section 7.2.3) to 1.4 mL of hexane in a clean vial.

12.1.3.3.1 Proceed with the sulfur removal (Section 10.2.3.3) using the same technique (TBA sulfite or copper) as the samples associated with the blank.

12.1.3.3.2 Analyze the sulfur blank according to Section 10.3.2.

12.1.3.4 Calculations for Sulfur Cleanup Blank

12.1.3.4.1 Assuming that the material in the sulfur blank resulted from the extraction of a 1 L water sample, calculate the concentration of each analyte using Equation 7 in Section 11.2.1.1.1. Compare the results to the CRQL values in Exhibit C (Aroclors).

NOTE: See Section 11.2 for the equations for the other calculations.

12.1.3.5 Technical Acceptance Criteria for Sulfur Cleanup Blanks

12.1.3.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each column.

12.1.3.5.2 All sulfur cleanup blanks must be prepared and analyzed at the frequency described in Section 12.1.3.2 using the procedure in Section 12.1.3.3 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.1.3.5.3 Sulfur cleanup blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, and required Aroclor Standards, as described in Section 10.3.2.1.

12.1.3.5.4 The concentration of the target compounds [Exhibit C (Aroclors)] in the sulfur cleanup blank must be less than the CRQL for each target compound.

12.1.3.5.5 The sulfur cleanup blank must meet all sample technical acceptance criteria in Sections 11.3.5 and 11.3.7.

12.1.3.5.6 Surrogate recoveries must fall within the acceptance windows of 30-150%. These limits are <u>not</u> advisory.

12.1.3.5.7 Sulfur cleanup blanks must be analyzed at the original concentration only (i.e., DF=1.0).

12.1.3.6 Corrective Action for Sulfur Cleanup Blank

12.1.3.6.1 If a sulfur cleanup blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be outside of QC limits.

12.1.3.6.2 If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. Further, all samples processed with a sulfur cleanup blank that does not meet the sulfur cleanup blank technical acceptance criteria (i.e., contaminated) will require reextraction and reanalysis at no additional cost to USEPA. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.

12.1.3.6.3 If surrogate recoveries in the sulfur cleanup blank do not meet the technical acceptance criteria in Section 12.1.3.5.6, first reanalyze the sulfur cleanup blank. If the surrogate recoveries do not meet the technical acceptance criteria after reanalysis, then the sulfur cleanup blank and all samples associated with that sulfur cleanup blank must be reprepared/reextracted and reanalyzed at no additional cost to USEPA.

12.1.3.6.4 If the sulfur cleanup blank fails to meet a technical acceptance criteria other than what is listed in Sections 12.1.3.5.4 and 12.1.3.5.6, then the problem is an instrumen problem. Correct the instrument problem, recalibrate the instrument (if necessary), and reanalyze the sulfur cleanup blank.

12.1.4 Instrument Blank

12.1.4.1 Summary of Instrument Blank

An instrument blank is a volume of clean solvent spiked with the surrogates and analyzed on each GC column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis, particularly with regard to carryover of analytes from standards or highly contaminated samples into other analysis.

12.1.4.2 Frequency of Instrument Blank

The first analysis in a 12-hour analysis sequence (Section 9.3.2) must be an instrument blank. All groups of acceptable sample analyses are to be preceded and followed by acceptable instrument blanks (Section 10.3.2.1). If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an instrument blank must be analyzed to initiate a new 12-hour sequence (Section 9.3.2).

12.1.4.3 Procedure for Instrument Blank

12.1.4.3.1 Prepare the instrument blank by spiking the surrogates into hexane or iso-octane for a concentration of 20.0 ng/mL of tetrachloro-m-xylene and 40.0 ng/mL of decachlorobiphenyl.

12.1.4.3.2 Analyze the instrument blank according to Section 10.3.2, at the frequency listed in Section 12.1.4.2.

12.1.4.4 Calculations for Instrument Blank

12.1.4.4.1 Assuming that the material in the instrument blank resulted from the extraction of a 1 L water sample, calculate the concentration of each analyte using Equation 7 in Section 11.2.1.1.1. Compare the results to the CRQL values for water samples in Exhibit C (Aroclors).

NOTE: See Section 11.2 for the equations for the other calculations.

12.1.4.5 Technical Acceptance Criteria for Instrument Blanks

12.1.4.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed and reported independently on Form I ARO for each GC column.

12.1.4.5.2 All instrument blanks must be prepared and analyzed at the frequency described in Section 12.1.4.2, using the procedure in Section 10.3.2 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.1.4.5.3 The concentration of each target analyte [Exhibit C (Aroclors)] in the instrument blank must be less than the CRQL for that analyte.

12.1.4.5.4 The instrument blank must meet all sample technical acceptance criteria in Sections 11.3.5 and 11.3.7.

12.1.4.5.5 Instrument blanks must be analyzed at the original concentration (i.e., DF=1.0).

12.1.4.6 Corrective Action for Instrument Blank

12.1.4.6.1 If compounds are detected at concentrations greater than the CRQL, or the surrogate Retention Times (RTs) are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples that were run between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be run before additional data are collected. All samples (including LCSs, MS/MSDs, and PE samples) and required blanks that were run after the last acceptable instrument blank must be reinjected during a valid run sequence and must be reported at no additional cost to USEPA.

12.2 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the methods used for Aroclor analyses, USEPA has prescribed a mixture of Aroclor target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method.

12.2.2 Frequency of MS/MSD Analysis

12.2.2.1 An MS/MSD must be extracted and analyzed for every 20 field samples of a similar matrix in a Sample Delivery Group (SDG). MS/MSD samples shall be analyzed unless otherwise specified on the Traffic Report/Chain of Custody Record (TR/COC). If no MS/MSD samples are specified on the TR/COC, the Contractor shall contact the Sample Management Office (SMO) to confirm that MS/MSD analyses are not required.

12.2.2.2 As part of USEPA's Quality Assurance/Quality Control (QA/QC) program, water rinsate samples and/or field blanks may be delivered to a laboratory for analysis. Do not perform MS/MSD analysis on a water rinsate sample or field blank.

12.2.2.3 If a USEPA Region designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample volume remaining to perform an MS/MSD, then the Contractor shall choose another sample to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify SMO that insufficient sample was received and identify the USEPA sample selected for the MS/MSD analysis. SMO shall contact the Region for confirmation immediately after notification. The rationale for the choice of another sample other than the one designated by USEPA shall be documented in the SDG Narrative.

12.2.2.4 If there is insufficient sample volume remaining in any of the samples in an SDG to perform an MS/MSD, the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD be performed, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than required by the contract, the Contractor shall contact SMO. SMO will contact the Region to determine which

samples should have an MS/MSD performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If this procedure is not followed, the Contractor will not be paid for MS/MSD analysis performed at a greater frequency than required by the contract.

12.2.2.6 When a Contractor receives only PE samples, no MS/MSD shall be performed within that SDG.

12.2.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the MS/MSD when the Region did not designate samples to be used for this purpose. If the PE sample is received as an ampulated standard extract, the ampulated PE sample is not considered to be another matrix type.

12.2.3 Procedure for Preparing MS/MSD

12.2.3.1 Water Samples

For water samples, measure out two additional 1 L aliquots of the sample chosen for spiking. Adjust the pH of the samples (if required) and fortify each with 1 mL of matrix spiking solution (Section 7.2.3.2). Using a syringe or volumetric pipet, add 3.0 mL of surrogate spiking solution to each sample (Section 7.2.3.1). Extract, concentrate, cleanup, and analyze the MS/MSDs according to Section 10.

12.2.3.2 Soil/Sediment Samples

For soil/sediment samples, weigh out two additional 30 g (to the nearest 0.1 g) aliquots of the sample chosen for spiking. Add 1 mL of matrix spiking solution (Section 7.2.3.2) and 3.0 mL of surrogate solution (Section 7.2.3.1). Extract, concentrate, cleanup, and analyze the MS/MSDs according to Section 10.

12.2.3.3 Before any MS/MSD analysis, analyze the original sample, then analyze the MS/MSD at the same concentration as the most concentrated extract for which the original sample results will be reported. For example, if the original sample is to be reported at a 1:1 dilution and a 1:10 dilution, then analyze and report the MS/MSD at a 1:1 dilution only. However, if the original sample is to be reported at a 1:10 dilution and a 1:100 dilution, then the MS/MSD must be analyzed and reported at a 1:10 dilution only. Do not dilute MS/MSD samples further to get either spiked or nonspiked analytes within calibration range.

12.2.4 Calculations for MS/MSD

12.2.4.1 The Percent Recoveries (%Rs) and the Relative Percent Difference (RPD) between the recoveries of each of the compounds in the Matrix Spike samples will be calculated and reported by using the following equations:

EQ. 15 Percent Recovery of Spike Compounds in MS/MSD Samples

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike Sample Result.

SR = Original Sample Result.

SA = Spike Added.

EQ. 16 Relative Percent Difference Between MS/MSD Spike Recoveries

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where,

RPD = Relative Percent Difference.

MSR = Matrix Spike recovery.

MSDR = Matrix Spike Duplicate recovery.

12.2.5 Technical Acceptance Criteria for MS/MSD

12.2.5.1 The requirements below apply independently to <u>each</u> GC column and to all instruments used for these analyses. Quantitation must be performed on both GC columns.

12.2.5.2 All MS/MSDs must be prepared and analyzed at the frequency described in Section 12.2.2 using the procedure above, and in Section 10, on a GC/ECD system meeting the initial calibration, calibration verification, and blank technical acceptance criteria. MS/MSDs must be cleaned up when required. MS/MSDs must be bracketed at 12-hour intervals (or less) by acceptable calibration verification described in Section 10.3.2.1.

12.2.5.3 The samples must be extracted and analyzed within the contract required holding times.

12.2.5.4 The Retention Time (RT) for each of the surrogates must be within the RT window as calculated in Section 9.2.4.3 for both GC columns.

12.2.5.5 The limits for Matrix Spike compound recovery and RPD are given in Table 1. As these limits are only advisory, no further action by the laboratory is required. However, frequent failure to meet the limits for recovery or RPD warrants investigation by the laboratory, and may result in questions from USEPA.

12.2.6 Corrective Action for MS/MSD

Any MS/MSD that fails to meet the technical acceptance criteria in Sections 12.2.5.1, 12.2.5.2, and 12.2.5.4 for MS/MSD must be reanalyzed at no additional cost to USEPA.

12.3 Laboratory Control Sample (LCS)

12.3.1 Summary of LCS

The LCS is an internal laboratory QC sample designed to assess (on an SDG-by-SDG basis) the capability of the contractor to perform the analytical method listed in this Exhibit.

12.3.2 Frequency of LCS

The LCS must be prepared, extracted, analyzed, and reported once for every 20 field samples of a similar matrix per SDG. The LCS must be extracted and analyzed concurrently with the samples in the SDG using the same extraction protocol and cleanup procedures instrumentation as the samples in the SDG.

12.3.3 Procedure for Preparing LCS

12.3.3.1 Water Samples

For water samples, measure out 1 L of reagent water and spike with 1.0 mL of the LCS spiking solution (Section 7.2.3.3) and 3.0 mL of the surrogate spiking solution (Section 7.2.3.1). Extract, concentrate, and analyze the sample according to Section 10.

12.3.3.2 Soil/Sediment Samples

For soil samples, measure out 30 g of a clean reference matrix (e.g., sodium sulfate, Hydromatrix) and spike with 1.0 mL of the LCS spiking solution (Section 7.2.3.3) and 3.0 mL of surrogate spiking solution (Section 7.2.3.1). Extract, concentrate, and analyze the LCS according to Section 10.

12.3.4 Calculations for LCS

12.3.4.1 Calculate the results according to Section 11.

12.3.4.2 Calculate individual compound recoveries of the LCS using Equation 14.

12.3.5 Technical Acceptance Criteria for LCS

12.3.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.3.5.2 The LCS must be analyzed at the frequency described in Section 12.3.2 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.3.5.3 The LCS must be prepared as described in Section 12.3.3.

12.3.5.4 The LCS must meet all sample technical acceptance criteria in Sections 11.3.5 and 11.3.6.

12.3.5.5 The Percent Recovery (%R) for each of the compounds in the LCS must be within the recovery limits listed in Table 2.

12.3.5.6 Surrogate recoveries must fall within the acceptable windows of 30-150%. These limits are not advisory.

12.3.6 Corrective Action for LCS

12.3.6.1 If the LCS technical acceptance criteria for the surrogates or the LCS compound recovery are not met, check calculations, the surrogate and LCS solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the surrogate and LCS recovery criteria.

12.3.6.2 LCS technical acceptance criteria MUST be met before data are reported. LCS contamination from laboratory sources or any LCS analyzed not meeting the technical acceptance criteria will require reextraction and reanalysis of the LCS at no additional cost to USEPA.

12.3.6.3 All samples (including MS/MSDs and PE samples) and required blanks, prepared and analyzed in an SDG with an LCS that does not meet the technical acceptance criteria, will also require reextraction and reanalysis at no additional cost to USEPA.

12.4 Method Detection Limit (MDL) Determination

12.4.1 Before any field samples are analyzed under the contract, the MDL for each Aroclor target compound shall be determined on each instrument used for analysis. MDL determination is matrix and level specific (i.e., the MDL shall be determined for water and soil samples). The MDLs must be verified annually thereafter (see Section 12.4.2 for MDL verification procedures), until the contract expires or is terminated, or after major instrument maintenance. Major instrument maintenance includes, but is not limited to, cleaning or replacement of the detector and replacement of the GC column.

12.4.2 To determine the MDLs, the Contractor shall run an MDL study following the procedures specified in 40 CFR Part 136. The Contractor shall analyze the MDL samples on each instrument used for field sample analyses. MDL verification for water samples is achieved by analyzing a single reagent water blank (see method blank for water samples in Section 12.1) spiked with each Aroclor at a concentration equal to 2 times the analytically determined MDL. MDL verification for soil samples is achieved by analyzing a single purified solid matrix blank (see method blank for soil samples in Section 12.1) spiked with each Aroclor at a concentration equal to two times the analytically determined MDL. Each target compound must produce a response and meet the criteria in Section 11.1.1. Samples used for MDL determination and verification must be subjected to the same extraction and cleanup procedures used for field samples. The resulting chromatograms of each target compound must meet the qualitative identification criteria outlined in Section 11.1.1 for both columns.

12.4.3 The determined concentration of the MDL must be less than the CRQL.

12.4.4 All documentation for the MDL studies shall be maintained at the laboratory and provided to USEPA upon written request.

13.0 METHOD PERFORMANCE

Not Applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasiblely reduced at the source, USEPA recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036, (202) 872-4386.

15.0 WASTE MANAGEMENT

USEPA requires that laboratory waste management practices be consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Polychlorinated Biphenyls (PCBs) by Gas Chromatography. SW-846 Method 8082A, Revision 1. November 2000.

16.2 US Environmental Protection Agency. Separatory Funnel Liquid-Liquid Extraction. SW-846 Method 3510C, Revision 3. December 1996.

16.3 US Environmental Protection Agency. Continuous Liquid-Liquid Extraction. SW-846 Method 3520C, Revision 3. December 1996.

16.4 US Environmental Protection Agency. Automated Soxhlet Extraction. SW-846 Method 3541, Revision 0. September 1994.

16.5 US Environmental Protection Agency. Pressurized Fluid Extraction (PFE). SW-846 Method 3545A, Revision 1. January 1998.

16.6 US Environmental Protection Agency. Ultrasonic Extraction. SW-846 Method 3550C, Revision 3. November 2000.

16.7 US Environmental Protection Agency. Sulfuric Acid/Permanganate Cleanup. SW-846 Method 3665A, Revision 1. December 1996.

16.8 US Environmental Protection Agency. Gel-Permeation Cleanup. SW-846 Method 3640A, Revision 1. September 1994.

16.9 US Environmental Protection Agency. Silica Gel Cleanup. SW-846 Method 3630C, Revision 3. December 1996.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

Matrix Spike Recovery and Relative Percent Difference Limits - Water and Soil

Compound	Percent Recovery QC Limits	RPD
AR1016	29-135	0-15
AR1260	29-135	0-20

Table 2

Laboratory Control Sample Recovery - Water and Soil

Compound	Percent Recovery QC Limits
AR1016	50-150
AR1260	50-150

Table 3

Concentration Levels of Calibration Standards

Compound	Concentration (ng/mL)				
	CS1	CS2	CS3	CS4	CS5
Aroclor 1016	100	200	400	800	1600
Aroclor 1260	100	200	400	800	1600
Aroclor 1221	100	200	400	800	1600
Aroclor 1232	100	200	400	800	1600
Aroclor 1242	100	200	400	800	1600
Aroclor 1248	100	200	400	800	1600
Aroclor 1254	100	200	400	800	1600
Aroclor 1262	100	200	400	800	1600
Aroclor 1268	100	200	400	800	1600
*Tetrachloro-m-xylene	5.0	10	20	40	80
*Decachlorobiphenyl	10	20	40	80	160

*Surrogates are present in all calibration standards at the above concentrations.

NOTE: Aroclor 1016 and 1260 standards may be prepared together but the other Aroclor standards (1221 - 1268) must be prepared individually. For example, Aroclor 1016/1260 CS3 standard will contain both Aroclor 1016 and Aroclor 1260 at a concentration of 400 ng/mL, and the surrogates tetrachloro-m-xylene and decachlorobiphenyl, at concentrations of 20 and 40 ng/mL respectively. Aroclor 1242 CS3 Standard will contain only Aroclor 1242, tetrachloro-m-xylene, and decachlorobiphenyl at 400, 20 and 40 ng/mL respectively.

EXHIBIT D

ANALYTICAL METHOD FOR THE ANALYSIS OF PESTICIDES

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Exhibit D - Analytical Methods for Pesticides

Table of Contents

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1.0 SCOPE AND APPLICATION

1.1 In 1978, US Environmental Protection Agency (USEPA) Headquarters and Regional representatives designed analytical methods for the analysis of chlorinated pesticides in hazardous waste samples. These methods were based on USEPA Method 608, Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs). In 1980, these methods were adopted for use in the Contract Laboratory Program (CLP). As the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) evolved, the CLP methods, as well as their precedent USEPA 600 Series methods, established the basis for other USEPA methods to perform the analysis of chlorinated pesticides contained in hazardous waste samples (i.e., SW-846). The following CLP method has continuously improved to incorporate technological advancements promulgated by USEPA, and has continued to set the standard for the preparation, extraction, isolation, identification, and reporting of chlorinated pesticides [and Aroclors in Exhibit D (Analytical Method for the Analysis of Aroclors)] at hazardous waste sites.

1.2 The analytical method that follows is designed to analyze water and soil/sediment samples from hazardous waste sites to determine the presence and concentration of the chlorinated pesticides found in the Target Compound List (TCL) in Exhibit C (Pesticides). The method can be used for determining compound concentrations in the range from the Contract Required Quantitation Limits (CRQLs) to one million times the CRQL in these matrices, when appropriate dilutions are made. The method includes sample extraction, extract cleanup techniques, and Gas Chromatograph/Electron Capture Detector (GC/ECD) analytical methods for pesticides.

1.3 Resolution difficulties have been associated with the following pairs of compounds using this method:

- On a DB-608 or equivalent column, DDE and Dieldrin; Methoxychlor and Endrin ketone; and Endosulfan I and gamma-Chlordane; and
- On a DB-1701 or equivalent column, Endosulfan I and gamma-Chlordane, and Methoxychlor and Endosulfan sulfate.

1.4 There are two isomers of heptachlor epoxide, the endo epoxy isomer (Isomer A) and the exo epoxy isomer (Isomer B). The two isomers are separable using current GC capillary columns. Only the exo epoxy isomer (Isomer B) is of environmental significance. This is the isomer that must be used as an analytical standard, identified and quantitated in sample analysis, and reported on appropriate forms as heptachlor epoxide.

2.0 SUMMARY OF METHOD

2.1 Water

Continuous liquid-liquid or separatory funnel extraction procedures are employed for aqueous samples. A 1 L volume of sample is spiked with the surrogate solution and extracted with methylene chloride using a separatory funnel or a continuous extractor. The methylene chloride extract is dried with anhydrous sodium sulfate (or Hydromatrix™), concentrated, and cleaned up. Gel Permeation Chromatography (GPC) is required when higher molecular weight compounds are present that interfere with the analyses of target compounds; GPC is optional for all other circumstances. The extract is then solvent exchanged into hexane, cleaned up by Florisil cartridges or other methods as applicable, and analyzed using a dual column wide-bore capillary Gas Chromatograph/Electron Capture Detector (GC/ECD).

2.2 Soil/Sediment

A 30 g aliquot of sample is dried with anhydrous sodium sulfate (or Hydromatrix), spiked with the surrogates, and extracted with a 1:1 (v/v) acetone/methylene chloride solvent mixture by ultrasonic extraction, Soxhlet extraction, or pressurized fluid extraction. The extract is filtered (for ultrasonic extraction), concentrated, and solvent-exchanged into methylene chloride. The methylene chloride extract is then cleaned up by GPC (mandatory), solvent-exchanged into hexane, cleaned up by a Florisil cartridge or other methods as applicable, and analyzed using a dual column wide-bore capillary GC/ECD.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware, and sample processing hardware. These contaminants lead to discrete artifacts or to elevated baselines in Gas Chromatograms. These materials must be routinely demonstrated to be free from interferences under the sample preparation and analysis conditions by analyzing instrument and method blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Because common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory.

4.2 Matrix Interferences

Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. The cleanup procedures in this method must be used to remove such interferences in order to achieve the Contract Required Quantitation Limits (CRQLs).

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should be made available to all personnel involved in the chemical analyses.

5.2 Specifically, concentrated sulfuric acid and the 10 N sodium hydroxide solution are moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4'-DDT; 4,4'-DDD; and the 1,2,3,4,5,6-hexachlorocyclohexane (BHCs). Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this analytical method is the responsibility of the Contractor. The Contractor must document any use of alternative equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Glassware

6.1.1 Continuous Liquid-Liquid Extractors

Continuous Liquid-Liquid Extractors - Equipped with polytetrafluoroethylene (PTFE) or glass connecting joints and stopcocks requiring no lubrication or hydrophobic membrane-based extractor.

6.1.2 Separatory Funnels - 2 L with PTFE stopcock.

6.1.3 Beakers - 100 mL, 125 mL, 250 mL, and 400 mL.

6.1.4 Erlenmeyer Flasks - 250 mL.

6.1.5 Syringes - 10 mL with Luer-Lok fitting; l mL or 2 mL, 5 mL, 100 µL, and 1000 µL.

6.1.6 Vials and Caps - 10 mL (optional), 20 mL, 40 mL, and 60 mL with screw-cap and PTFE or aluminum foil liner, 2 mL capacity for Gas Chromatograph (GC) auto sampler.

6.1.7 Pipets - Glass volumetric l mL or 2 mL.

6.1.8 Centrifuge Tube - 12 to 15 mL with 19 mm ground glass joint (optional).

6.1.9 Class A Graduated Cylinder - 1 L and 100 mL capacity.

6.1.10 Drying Column - Chromatographic column approximately 400 mm long x 19 mm ID, with coarse frit. (Substitution of a small pad of disposable borosilicate glass wool for the frit will help prevent cross-contamination of sample extracts).

6.1.11 Class A Volumetric Flasks - 10 mL and l or 2 mL.

6.1.12 Bottle or Test Tube - 20 mL with PTFE-lined screw-cap for sulfur removal and a glass bottle - 1 L volume, for use in preparation of Bio Beads for packing into a column.

6.1.13 Powder Funnels - 10 cm diameter, for filtration/drying.

6.1.14 Buchner Funnels - 9 cm diameter, for filtration.

6.1.15 Kuderna-Danish (K-D) Apparatus.

6.1.15.1 Concentrator Tubes - 10 mL, graduated.

6.1.15.2 Evaporative Flasks - 500 mL.

6.1.15.3 Snyder Column - Three-ball macro.

6.1.15.4 Snyder Column - Two-ball micro.

6.2 [Automated] Soxhlet Extraction System

[Automated] Soxhlet Extraction System - With temperature-controlled oil bath. Silicone oil must not be used because it destroys the rubber parts. The apparatus must be used in a hood.

6.2.1 Cellulose or Glass Extraction Thimbles - 26 mm ID x 60 mm, contaminant-free.

6.2.2 Glass Extraction Cups (80 mL) - (set of six required for the HT-6).

6.2.3 Thimble Adapters - (set of six required for the HT-6).

6.2.4 Viton Seals.

6.3 Pressurized Fluid Extraction System

Pressurized Fluid Extraction System - Dionex Accelerated Solvent Extractor (ASE-300) or equivalent with appropriately-sized extraction cells. Currently, 100 mL cells are available that will accommodate greater than 30 g samples. Cells should be made of stainless steel or other material capable of withstanding the pressure requirements [2000+ pounds per square inch (psi)] necessary for this procedure. Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.4 Florisil Cleanup Equipment

6.4.1 Florisil - 500 mg or 1 g cartridges with stainless steel or PTFE frits.

6.4.2 Vacuum System for Eluting Multiple Cleanup Cartridges.

6.4.3 Vacuum Trap - Made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.

6.4.4 Vacuum Pressure Gauge.

6.5 Gel Permeation Chromatography (GPC) Equipment

6.5.1 GPC System - Systems that perform satisfactorily have been assembled from the following components: a High Performance Liquid Chromatography (HPLC) pump; an auto sampler or a valving system with sample loops; and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements in Section 10.3.1.3.

NOTE: GPC cleanup is required for extracts for <u>all</u> soils/sediments and for water extracts containing higher molecular weight contaminants that interfere with the analyses of the target compounds.

6.5.2 Chromatographic column - 700 mm x 25 mm ID glass column. Flow is upward. To simplify switching from the ultraviolet (UV) detector during calibration to the GPC collection device during extract cleanup, an optional double 3-way valve may be attached to that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

6.5.3 Guard Column (optional) - 5 cm, with appropriate fittings to connect to the inlet side of the analytical column.

6.5.4 Bio Beads (SX-3) - 200 to 400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, or equivalent). An additional 5 g of Bio Beads is required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

6.5.5 UV Detector - Fixed wavelength (254 nm) with a semi-prep flow-through cell.

6.5.6 Strip Chart Recorder - Recording integrator or laboratory data system.

6.5.7 Syringe Filter Assembly, disposable.

NOTE: Consult your instrument operation manual to determine the proper size filter disc to use in your system. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

6.6 pH Paper - Wide range.

6.7 Spatula - Stainless steel or PTFE.

6.8 Centrifuge - Table top (optional).

6.9 Balances - Top loading, capable of weighing accurately to ±0.01 g, analytical, capable of weighing accurately to ±0.0001 g. The balances must be calibrated with Class S weights or known reference weights once per each 12-hour work shift. The balances must be calibrated with Class S weights at a minimum of once per month. The balances must also be annually checked by a certified technician.

6.10 Ultrasonic Cell Disruptor - Minimum 300 watt output capability.

NOTE: To ensure that sufficient energy is transferred to the sample during extraction, the horn must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

6.11 Sonabox Acoustic Enclosure (or equivalent) - For use with disruptor to decrease noise level.

6.12 Filter Paper - Whatman No. 41, 9 cm circles, or equivalent.

6.13 Filter Disks - 1.91 cm Type D28.

6.14 Cell Cap Sealing Disks.

6.15 Borosilicate Glass Wool - Rinsed with methylene chloride and dried before use.

6.16 Boiling Chips

6.16.1 Silicon carbide boiling chips - Approximately 10 to 40 mesh. Heat the chips to 400°C for 30 minutes or solvent rinse before use.

6.16.2 PTFE Boiling Chips (optional) - Solvent rinse the chips before use.

6.17 Water Bath - Heated, with concentric ring cover, capable of temperature control.

6.18 Nitrogen Evaporation Device - Equipped with a heated bath that can be maintained at 35-40°C.

6.19 Oven - Drying.

6.20 Desiccator

6.21 Crucibles - Porcelain crucibles or aluminum weighing pans.

6.22 Aluminum Weighing Dish

6.23 pH Meter - With a combination glass electrode. Calibrate according to manufacturer's instructions. The pH meter must be calibrated prior to each use.

6.24 Magnetic Stirrer Motor

6.25 Magnetic Stirrer Bar - PTFE coated, at least 4 cm long.

6.26 Gas Chromatograph/Electron Capture Detector (GC/ECD) System

6.26.1 Gas Chromatograph (GC)

6.26.1.1 The GC must adequately regulate temperature in order to give a reproducible temperature program and have a flow controller that maintains a constant column flow rate throughout temperature program operations. The system must have all required accessories including syringes, analytical columns, and gases.

6.26.1.2 GCs that are available from some manufacturers may have difficulty in meeting certain method QC requirements because of Endrin and DDT breakdown in the injector. This problem can be minimized by operating the injector at 200-205°C, using a <u>borosilicate glass</u> (not quartz) methyl silicone deactivated injector liner, and deactivating the metal parts in the injector with dichlorodimethyl silane. In some cases, using a 0.25 inch packed column injector converted for use with 0.53 mm capillary columns works better than a Grob-type injector. If a Grob-type injector is used, a 4 mm liner may be required to meet breakdown criteria.

6.26.1.3 GC Columns - Wide-bore (0.53mm ID) fused silica GC columns may be used provided that the resolution requirements are met (see Section 9.2.5.2); if two wide-bore (0.53 mm ID) fused silica GC columns are used, then a separate detector is required for each column. The specified analytical columns are a 30 m x 0.53 mm ID, 1.0 µm film thickness DB-1701 (J&W Scientific); SPB 1701 (Supelco); AT 1701 (Alltech); RTX-1701, RTX CLP I, RTX CLP II (Restek); CP-Sil 19CB (Chrompack); 007-1701 (Quadrex); BP-10 (SGE); or equivalent, and a 30 m x 0.53 mm ID, 0.5 to 1.0 µm film thickness DB-608 (J&W Scientific); HP-608 (Agilent); SPB-608 (Supelco); 007-608 (Quadrex); BP-608 (SGE); CP-Sil 8CB (Chrompack); or equivalent.

NOTE: The column length stated above is the minimum requirement. Longer columns that meet resolution and calibration requirements may be used. A description of the GC columns used for analysis shall be provided in the SDG Narrative.

6.26.1.3.1 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantitation of the compounds listed in Exhibit C (Pesticides);
- The analytical results generated using the column meet the initial calibration and calibration verification technical acceptance criteria listed in the analytical method and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Pesticides);
- The column can accept at least 16 times the low-point concentration level as listed in Section 7.2.2.5 for each compound listed in Exhibit C (Pesticides) without becoming overloaded; and
- The column pair chosen must have dissimilar phases/chemical properties in order to separate the compounds of interest in different Retention Time (RT) order.

6.26.1.3.2 Although the instructions included in the analytical method are for wide bore capillary columns, narrower bore capillary columns may be evaluated for use. Follow manufacturer's instructions for use of its product. Document in the SDG Narrative if other columns are used by specifying the column used.

6.26.1.3.3 As applicable, follow the manufacturer's instructions for use of its product.

6.26.1.3.4 The Contractor must maintain documentation verifying that the alternate column met the criteria in Sections 9.2.5 and 9.3.5. The minimum documentation is as follows:

6.26.1.3.4.1 Manufacturer provided information concerning the performance characteristics of the column.

6.26.1.3.4.2 GC chromatograms and data system reports generated on the GC/ECD and used for Contract Laboratory Program (CLP) analyses:

- From instrument blanks which demonstrate that there are no contaminants that interfere with the pesticide analysis when using the alternate column;
- For initial calibration standards analyzed using the alternate column; and
- For calibration verification standards analyzed using the alternate column.

6.26.1.3.5 Based on the Contractor-generated data described in Section 6.26.1.3.4.2, the Contractor must complete a written comparison and review, signed by the Laboratory Manager, certifying that:

- The alternate column performance is comparable to the required column performance in its ability to produce initial calibrations and calibration verifications that meet the technical acceptance criteria in Sections 9.2.5 and 9.3.5;

- The low-point initial calibration standard analyses have adequate sensitivity to meet the pesticide CRQLs;
- The high-point initial calibration standard analyses were not overloaded; and
- The alternate column does not introduce contaminants which interfere with the identification and quantitation of compounds listed in Exhibit C (Pesticides).

6.26.1.3.6 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request of the USEPA Regional CLP Project Officer (CLP PO).

6.26.1.3.7 **PACKED COLUMNS CANNOT BE USED.**

6.26.1.4 Columns are mounted in a press-fit Y-shaped glass 3-way union splitter or a Y-shaped fused-silica connector from a variety of commercial sources. The two columns may be mounted in an 8 inch deactivated glass injection tee. The Contractor should follow the manufacturer's recommendations for mounting 0.53 mm capillary columns in injector ports.

6.26.1.5 The carrier gas for routine applications is helium. Laboratories may choose to use hydrogen as a carrier gas, but they must clearly identify its use in the SDG Narrative and on all divider pages preceding raw chromatographic data in submissions to USEPA. Laboratories that choose to use hydrogen are advised to exercise caution in its use. Use of a hydrogen leak detector is highly recommended when hydrogen is used as the carrier gas. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants or flow controllers with rubber components are not to be used.

6.26.2 Electron Capture Detector (ECD)

The linearity of the response of the ECD may be greatly dependent on the flow rate of the make-up gas. The make-up gas must be P-5, P-10 (argon/methane) or nitrogen according to the instrument specification. Care must be taken to maintain stable and an appropriate flow of make-up gas to the detector. The GC/ECD system must be in a room in which the atmosphere has been demonstrated to be free of all contaminants that may interfere with the analysis. The instrument must be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.26.3 Data System

A data system must be interfaced to the GC/ECD. The data system must allow the continuous acquisition of data throughout the duration of the chromatographic program and must permit, at a minimum, the output of time vs. intensity (peak height or peak area) data. Also, the data system must be able to rescale chromatographic data in order to report chromatograms meeting the requirements listed within this method.

6.26.4 Data Storage Device

Data storage devices must be suitable for long-term, off-line storage of data.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

7.1.1 Reagent Water - Reagent water is defined as water in which an interferant is not observed at or above the Contract Required Quantitation Limit (CRQL) for each compound of interest.

7.1.1.1 Reagent water may also be generated by passing tap water through a carbon filter bed containing about 453 g (1 lb) of activated carbon.

7.1.1.2 Reagent water may be generated using a water purification system.

7.1.2 Sodium sulfate - Granular anhydrous reagent grade, heated at 400°C for 4 hours, or at 120°C for 16 hours, cooled in a desiccator, and stored in a glass bottle. Each lot must be extracted with hexane and analyzed by a Gas Chromatograph/Electron Capture Detector (GC/ECD) to demonstrate that it is free of interference before use.

OR

Hydromatrix - Diatomaceous earth-based material rinsed with methylene chloride and dried at 400°C for 4 hours in a shallow tray, cooled in a desiccator, and stored in a glass bottle.

7.1.3 Methylene chloride, hexane, acetone, toluene, iso-octane, and methanol (optional) - pesticide quality or equivalent. It is recommended that each lot of solvent be analyzed to demonstrate that it is free of interference before use. Methylene chloride must be certified as acid free or must be tested to demonstrate that it is free of hydrochloric acid. Acidic methylene chloride must be passed through basic alumina and then demonstrated to be free of hydrochloric acid.

7.1.4 Copper powder (optional) - Fine, granular. Copper may be used instead of mercury for sulfur cleanup. Remove oxides by treating with dilute nitric acid, rinse with distilled water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.

7.1.5 Sodium hydroxide solution (10 N). Carefully dissolve 40 g of NaOH in reagent water and dilute the solution to 100 mL.

7.1.6 Tetrabutylammonium **S**ulfite

7.1.7 Sodium **S**ulfite

7.1.8 Concentrated sulfuric acid (18 N).

7.1.9 Nitric acid - Dilute, for sulfur removal with copper.

7.1.10 10% acetone in hexane (v/v). Prepare by adding 10.0 mL of acetone to 90.0 mL of hexane.

7.2 Standards

Introduction

The Contractor must provide all standards to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit E. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor that are immediately ampulated in glass vials may be retained for 2 years from the preparation date. The expiration date of the ampulated standards upon the breaking of the glass seal is 6 months (or sooner if the standard has degraded or evaporated).

7.2.1 Stock Standard Solutions

7.2.1.1 Stock standard solutions are defined as standards that are to be used to produce working standards. They may be in the form of single compounds or mixtures. They may be purchased or prepared in methylene chloride or another suitable solvent.

7.2.2 Working Standards

7.2.2.1 Surrogate Standard Spiking Solution

The surrogates, tetrachloro-m-xylene and decachlorobiphenyl, are added to all standards, samples [including Laboratory Control Samples (LCSs)], Matrix Spikes and Matrix Spike Duplicates (MS/MSDs), Performance Evaluation (PE) samples (if required), and required blanks (method/sulfur cleanup/instrument). Prepare a surrogate spiking solution of 0.20 µg/mL for tetrachloro-m-xylene and 0.40 µg/mL for decachlorobiphenyl in acetone. The solution should be checked frequently for stability. The solution must be replaced every 6 months, or sooner if the solution has degraded or concentrated.

NOTE: Other concentrations for surrogate standard spiking solutions may be used, provided that the appropriate amount of surrogates are added to all standards, samples (including LCSs), MS/MSDs, PE samples, and blanks.

7.2.2.2 Matrix Spiking Solution

Prepare a matrix spiking solution in acetone or methanol that contains the following pesticides at the concentrations specified. The solution must be replaced every 6 months, or sooner if the solution has degraded or concentrated.

Pesticide	Concentration (µg/mL)
gamma-BHC (Lindane)	0.50
Heptachlor	0.50
Aldrin	0.50
Dieldrin	1.0
Endrin	1.0
4,4'-DDT	1.0

7.2.2.3 Resolution Check Mixture

The Resolution Check Mixture is composed of all the pesticides listed in Exhibit C and surrogates at the concentrations listed below in hexane or iso-octane. The mixture must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

Compounds	Concentration (ng/mL)
alpha-BHC	10.0
beta-BHC	10.0
delta-BHC	10.0
gamma-BHC	10.0
Aldrin	10.0
Heptachlor	10.0
Heptachlor-epoxide	10.0
alpha-Chlordane	10.0
gamma-Chlordane	10.0
Endosulfan I	10.0
Endosulfan II	20.0
4,4'-DDD	20.0
4,4'-DDE	20.0
4,4'-DDT	20.0
Dieldrin	20.0
Endrin	20.0
Endosulfan sulfate	20.0
Endrin ketone	20.0
Endrin aldehyde	20.0
Methoxychlor	100.0
Tetrachloro-m-xylene	10.0
Decachlorobiphenyl	20.0

7.2.2.4 Performance Evaluation Mixture (PEM)

The PEM is prepared in hexane or iso-octane, as listed below. The PEM must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

Compounds	Concentration (ng/mL)
alpha-BHC	10.0
beta-BHC	10.0
gamma-BHC	10.0
Endrin	50.0

Compounds	Concentration (ng/mL)
4,4'-DDT	100.0
Methoxychlor	250.0
Tetrachloro-m-xylene	20.0
Decachlorobiphenyl	20.0

7.2.2.5 Individual Standard Mixtures

The suggested compositions of Individual Standard Mixture A and Mixture B are listed in this section with the concentrations of each target compound and surrogate given for the CS1 Standard A and CS1 Standard B. The CS1 Standard C for Individual Standard Mixture C will contain all target compounds and surrogates for both Mixture A and Mixture B at the same concentrations as the CS1 Standard for Mixture A and Mixture B. The Calibration Standard Mixture solutions must be prepared in either hexane or iso-octane. The analysis of the Resolution Check Mixture will determine whether one or two sets of Individual Standard Mixture solutions will be needed. Prepare calibration standards at a minimum of five concentration levels. The concentrations of the pesticides in the low-point standard mixtures (CS1) correspond to the low-point concentration (see Table in this section) or lower for each analyte. The concentration for each analyte in the high-point standard must be at least 16 times the concentration of the low-point standard, but a higher concentration may be chosen by the Contractor provided that the higher concentration standards meets the technical acceptance criteria in Sections 9.2.5 and 9.3.5. The concentration levels of each target compound for each calibration standard are listed in Table 4. These levels are based upon 10 mL final volume extracts for samples not undergoing Gel Permeation Chromatography (GPC) cleanup, and 5.0 mL final volume extracts for those samples undergoing GPC cleanup. Other concentration levels may be used for more sensitive instrumentation and final extract levels. For example in the case of alpha-BHC, a laboratory may use a final extract volume of 10 mL for samples undergoing GPC cleanup, and a low calibration standard of 2.5 ng/mL. The alternate calibration standards and final volumes may be used as long as the following requirements are met:

- The laboratory can demonstrate that the CRQL for each analyte listed in Exhibit C can be reached using the calibration and final volume scheme. This demonstration is made when there is formal documentation of laboratory Method Detection Limit (MDL) studies indicating that the calculated MDL for each target analyte is below the required CRQL for that analyte when using the laboratory's specific final volume and calibration level scheme.

- All five calibration levels are in the same ratio as that shown in Table 4 (e.g., if a laboratory were using a 2.5 ng/mL low standard, then the other calibration levels must be 5.0, 10, 20, and 40 ng/mL).

The standards must be prepared every 6 months, or sooner if the solutions have degraded or concentrated.

Individual Standard Mix A	Low-Point (CS1) Concentration (ng/mL)	Individual Standard Mix B	Low-Point (CS1) Concentration (ng/mL)
alpha-BHC	5.0	beta-BHC	5.0
gamma-BHC	5.0	delta-BHC	5.0
Heptachlor	5.0	Aldrin	5.0
Endosulfan I	5.0	Heptachlor-epoxide (exo-epoxy isomer)	5.0
Dieldrin	10	4,4'-DDE	10
Endrin	10	Endosulfan II	10
4,4'-DDD	10	Endosulfan sulfate	10
4,4'-DDT	10	Endrin ketone	10
Methoxychlor	50	Endrin aldehyde	10
Tetrachloro-m-xylene	5.0	alpha-Chlordane	5.0
Decachlorobiphenyl	10	gamma-Chlordane	5.0
		Tetrachloro-m-xylene	5.0
		Decachloro-biphenyl	10

NOTE: Only the exo-epoxy isomer (Isomer B) of heptachlor epoxide is used as an analytical standard.

7.2.2.6 Toxaphene Standards

Prepare Toxaphene standard solutions at a minimum of five concentration levels. The Toxaphene standards must be prepared in hexane or iso-octane and contain the surrogates at the appropriate concentrations (for CS1, the concentrations of tetrachloro-m-xylene and decachlorobiphenyl should be 5.0 and 10 ng/mL respectively). The concentration of Toxaphene in the low-point standard (CS1) should be 500 ng/mL or lower. The concentration in the high-point standard (CS5) must be at least 16 times the low-point standard for Toxaphene but a higher concentration may be chosen by the Contractor. For most operations, the calibrations standards are to be prepared at 500, 1000, 2000, 4000 and 8000 ng/mL (see discussion on alternate calibration standards and final volumes in Section 7.2.3.5). The standard must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.7 Florisil Cartridge Check Solution

Prepare a 0.10 µg/mL solution of 2,4,5-trichlorophenol in acetone. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.8 Gel Permeation Chromatography (GPC) Calibration and Calibration Verification Solutions

7.2.2.8.1 GPC Calibration Solution

Prepare a GPC calibration solution in methylene chloride that contains the following analytes at the minimum concentrations

listed below. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

Analyte	Concentration (mg/mL)
Corn oil	25.0
Bis(2-ethylhexyl)phthalate	0.5
Methoxyclor	0.1
Perylene (CAS # 198-55-0)	0.02
Sulfur (CAS # 7704-34-9)	0.08

7.2.2.8.2 GPC Calibration Verification Solution

Prepare a GPC calibration verification solution in methylene chloride that contains the following compounds. The concentrations listed below are for a 5 mL GPC injection loop. See Section 10.3.1.4.3.1 for compound concentrations if a smaller size loop is being used. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

Compound	Concentration (ng/mL)
gamma-BHC (Lindane)	20.0
Heptachlor	20.0
Aldrin	20.0
4,4'-DDT	40.0
Endrin	40.0
Dieldrin	40.0

NOTE: Sulfur is not very soluble in methylene chloride, but it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

7.2.2.9 Laboratory Control Sample (LCS) Spiking Solution

Prepare an LCS spiking solution that contains each of the analytes at the concentrations listed below in methanol or acetone. The LCS solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

Compounds	Concentration (µg/mL)
gamma-BHC	0.050
gamma-Chlordane	0.050
Heptachlor epoxide	0.050
Dieldrin	0.10
4,4'-DDE	0.10
Endrin	0.10
Endosulfan sulfate	0.10

7.2.3 Storage of Standards

7.2.3.1 Store the stock standard solutions at 4°C (±2°C) in polytetrafluoroethylene (PTFE)-lined, screw-cap, amber bottles/vials.

7.2.3.2 Store the working standard solutions at 4°C (±2°C) in PTFE-lined screw-cap, amber bottles/vials. The working standards must be checked frequently for signs of degradation or evaporation.

NOTE: Refrigeration may cause the corn oil in the GPC calibration solution to precipitate. Before use, allow the GPC calibration solution to stand at room temperature until the corn oil dissolves.

7.2.3.3 Protect all standards from light.

7.2.3.4 Samples, sample extracts, and standards must be stored separately.

7.2.3.5 The Contractor is responsible for maintaining and verifying the integrity of standard solutions prior to use. Storage of standard solutions in the freezer may cause some compounds to precipitate. This means at a minimum, the standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in solution. Additional steps may be necessary to ensure all components are in solution.

7.2.4 Temperature Records for Storage of Standards

7.2.4.1 The temperature of all standard storage refrigerators/freezers shall be recorded daily.

7.2.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

7.2.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators/freezers.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in 1 L (or 1 quart) amber glass containers, fitted with screw-caps lined with polytetrafluoroethylene (PTFE). If amber containers are not available, the samples should be protected from light. Soil samples may be collected in glass containers or closed end tubes (e.g., brass sleeves) in sufficient quantity to perform the analysis. The specific requirements for site sample collection are outlined by the Region.

8.1.2 All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until extraction.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete reconciled data package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3 Procedure for Sample Extract Storage

8.3.1 Sample extracts must be protected from light and stored at 4°C (±2°C) until 365 days after delivery of a complete reconciled data package to USEPA.

8.3.2 Sample extracts must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3.3 Samples, sample extracts, and standards must be stored separately.

8.4 Records for Sample and Sample Extract Storage

8.4.1 The temperature of all sample and sample extract storage refrigerators shall be recorded daily.

8.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

8.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators.

8.5 Contract Required Holding Times

8.5.1 Extraction of water samples by separatory funnel procedures must be completed within 5 days of the Validated Time of Sample Receipt (VTSR). Extraction of water samples by continuous liquid-liquid extraction must be started within 5 days of VTSR. Extraction of soil/sediment samples must be completed within 10 days of VTSR.

8.5.2 As part of USEPA's Quality Assurance (QA) program, USEPA may provide Performance Evaluation (PE) Samples as standard extracts that the Contractor is required to prepare per instructions provided by USEPA. PE samples must be prepared and analyzed concurrently with the samples in the Sample Delivery Group (SDG). The extraction holding time (5 days after VTSR for water samples, 10 days after VTSR for

soil/sediment samples) does not apply for PE samples received as standard extracts.

8.5.3 Analysis of sample extracts must be completed within 40 days following the start of extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Gas Chromatograph (GC) Operating Conditions

9.1.1 The following are the GC analytical conditions. The conditions are recommended, unless otherwise noted.

Carrier Gas:	Helium (Hydrogen may be used, Section 6.10.1.5)
Column Flow:	5 mL/min.
Make-up Gas:	Argon/Methane (P-5 or P-10) or N_2 (required)
Injector Temperature:	> 200°C (Section 9.1.5)
Injection Technique:	On-column
Injection Volume:	1 or 2 µl (Section 9.1.3)
Injector:	Grob-type, splitless
Initial Temperature:	150°C
Initial Hold Time:	0.5 min.
Temperature Ramp:	5°C to 6°C/min.
Final Temperature:	275°C
Final Hold Time:	After decachlorobiphenyl has eluted

9.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples [including Laboratory Control Samples (LCSs), and Matrix Spike and Matrix Spike Duplicates (MS/MSDs)], and required blanks (method/sulfur cleanup/instrument).

9.1.3 The same injection volume, 1.0 or 2.0 µL, must be used for all standards, samples (including LCSs and MS/MSDs), and required blanks (method/sulfur cleanup/instrument).

9.1.4 The linearity of the Electron Capture Detector (ECD) may be greatly dependent on the flow rate of the make-up gas. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector.

9.1.5 Cold (ambient temperature) on-column injectors that allow injection directly onto a 0.53 mm ID column may be used as long as the initial calibration and calibration verification technical acceptance criteria are met.

9.2 Initial Calibration

9.2.1 Summary of Initial Calibration

Prior to sample (including LCSs and MS/MSDs) and required blank (method/sulfur cleanup/instrument) analysis, each GC/ECD system must be initially calibrated at a minimum of five concentrations for

single component analytes, Toxaphene, and surrogates in order to determine instrument sensitivity and the linearity of GC response.

9.2.2 Frequency of Initial Calibration

Each GC/ECD system must be initially calibrated upon award of the contract, whenever major instrument maintenance or modification is performed (e.g., column replacement or repair, cleaning or replacement of ECD, etc.), or if the calibration verification technical acceptance criteria have not been met.

9.2.3 Procedure for Initial Calibration

9.2.3.1 Set up the GC/ECD system as described in Section 9.1.

9.2.3.2 Prepare the initial calibration standards using the procedures, analytes, and concentrations according to Section 7.2.

9.2.3.3 All standards, sample (including LCSs and MS/MSDs), and required blank (method/sulfur cleanup) extracts must be allowed to warm to ambient temperature before analysis.

9.2.3.4 Choose the appropriate initial calibration sequence (1 or 2), as given below. If two Individual Standard Mixtures are used, choose sequence 2. The appropriate calibration sequence is determined by the results of the Resolution Check Mixture (Section 9.2.5.2). All steps pertaining to the initial calibration sequence must be performed uninterrupted with no more than the length of one chromatographic run separating any step.

NOTE: The steps pertaining to Instrument Blank and Performance Evaluation Mixture (PEM) are used as part of the calibration verification as well (Section 9.3).

INITIAL CALIBRATION SEQUENCE 1

1. Resolution Check
2. Performance Evaluation Mixture (PEM)
3. Toxaphene CS1
4. Toxaphene CS2
5. Toxaphene CS3
6. Toxaphene CS4
7. Toxaphene CS5
8. CS1 Individual Standard Mix C
9. CS2 Individual Standard Mix C
10. CS3 Individual Standard Mix C
11. CS4 Individual Standard Mix C
12. CS5 Individual Standard Mix C
13. Instrument Blank
14. PEM

INITIAL CALIBRATION SEQUENCE 2

1. Resolution Check
2. Performance Evaluation Mixture (PEM)
3. Toxaphene CS1
4. Toxaphene CS2
5. Toxaphene CS3
6. Toxaphene CS4
7. Toxaphene CS5
8. CS1 Individual Standard Mix A
9. CS1 Individual Standard Mix B
10. CS2 Individual Standard Mix A
11. CS2 Individual Standard Mix B
12. CS3 Individual Standard Mix A
13. CS3 Individual Standard Mix B
14. CS4 Individual Standard Mix A
15. CS4 Individual Standard Mix B
16. CS5 Individual Standard Mix A
17. CS5 Individual Standard Mix B
18. Instrument Blank
19. PEM

9.2.4 Calculations for Initial Calibration

9.2.4.1 During the initial calibration sequence, absolute Retention Times (RTs) are determined for all single component pesticides, surrogates, and three to five major peaks of Toxaphene.

9.2.4.2 For each single component pesticide, an RT is measured in each of the five calibration standards for all Individual Standard Mixtures C for initial calibration sequence 1 or A and B for initial calibration sequence 2). **If initial calibration sequence 2 is used then the RT for the surrogates is measured from each of the five analyses of Individual Standard Mixture A during the initial calibration.** For Toxaphene, an RT is measured in each of the five calibration standards for the major peaks (3, 4, or 5). The Mean Absolute RT ($\overline{RT}$) is calculated for each single component pesticide, surrogate, and Toxaphene as the average of the five values. Calculate an $\overline{RT}$ for each single component pesticide, surrogate, and Toxaphene using Equation 1.

EQ. 1 Mean Absolute Retention Time Calculation

$$\overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n}$$

Where,

$\overline{RT}$ = Mean Absolute Retention Time of analyte.

RT_i = Absolute Retention Time of analyte.

n = Number of measurements (5).

9.2.4.3 An RT window is calculated for each single component analyte and surrogate and for the major peaks (3, 4 or 5) of Toxaphene using Table 1. Windows are centered around the $\overline{RT}$ for the analyte established during the initial calibration. Analytes are identified when peaks are observed in the RT window for the compound on both GC columns.

9.2.4.4 The linearity of the instrument is determined by calculating a Percent Relative Standard Deviation (%RSD) of the Calibration Factors (CFs) from a five-point calibration curve for each of the single component pesticides and surrogates. Either peak area or peak height may be used to calculate the CFs used in the %RSD equation. For example, it <u>is</u> permitted to calculate linearity for Endrin based on peak area and to calculate linearity for Aldrin based on peak height. It is <u>not</u> permitted within a %RSD calculation for an analyte to use the CFs calculated from both peak area and peak height. For example, it is <u>not</u> permitted to calculate the CF for the CS1 Standard for Endrin using peak height and calculate the CS3 and CS5 Standard CFs for Endrin using peak area.

9.2.4.5 Calculate the CFs for each single component pesticide and surrogates over the initial calibration range using Equation 2. The CFs for surrogates are calculated from the five analyses of the Individual Standard Mixture. If two Individual Standard Mixtures are used, calculate the CFs for surrogates from Individual Standard Mixture A only.

EQ. 2 Calibration Factors

$$CF = \frac{\text{Peak area (or Height) of the standard}}{\text{Mass Injected (ng)}}$$

9.2.4.6 Calculate the Mean CF ($\overline{CF}$) and the %RSD of the CF for each single component pesticide and surrogate over the initial calibration range using Equations 3 and 4.

EQ. 3 Mean Calibration Factor

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

EQ. 4 Percent Relative Standard Deviation of the Calibration Factors

$$\%RSD = \frac{SD_{CF}}{\overline{CF}} \times 100$$

$$SD_{CF} = \sqrt{\frac{\sum_{i=1}^{n} \left(CF_i - \overline{CF}\right)^2}{(n-1)}}$$

Where,

%RSD = Percent Relative Standard Deviation.

SD_{CF} = Standard Deviation of Calibration Factors.

CF_i = Calibration Factor.

$\overline{CF}$ = Mean Calibration Factor.

n = Total number of values (5).

9.2.4.7 A CF is calculated for each peak in a selected set of three to five major peaks for Toxaphene using Equation 2. The Mean CF and the %RSD of the CFs for each selected Toxaphene peak are calculated using Equations 3 and 4.

9.2.4.8 Calculate the Percent Breakdown (%Breakdown) of DDT, the Percent Breakdown of Endrin, and the combined breakdown of DDT and Endrin in the PEM using Equations 5, 6, 7, and 8.

EQ. 5 Amount Found

$$\text{Amount found (ng)} = \frac{\text{Peak area (or Peak height) of compound in PEM}}{\overline{CF}}$$

Where,

$\overline{CF}$ = Mean Calibration Factor from the initial calibration (area/ng).

NOTE: If during the initial calibration, linearity was determined based on peak area for the compound, then the $\overline{CF}$ must be based on peak area. If during the initial calibration, the linearity for the compound was determined based on peak height for the compound, then the $\overline{CF}$ must be based on peak height.

EQ. 6 Percent Breakdown of DDT

$$\text{\%Breakdown DDT} = \frac{\text{Amount found (ng) (DDD+DDE)}}{\text{Amount (ng) of DDT injected}} \times 100$$

EQ. 7 Percent Breakdown of Endrin

$$\text{\%Breakdown Endrin} = \frac{\text{Amount found (ng) (endrin aldehyde + endrin ketone)}}{\text{Amount (ng) of endrin injected}} \times 100$$

EQ. 8 Combined Percent Breakdown of DDT and Endrin

$$\text{Combined \%Breakdown} = \text{\%Breakdown DDT} + \text{\%Breakdown Endrin}$$

9.2.4.9 Calculate the Percent Difference (%Difference) between the calculated and nominal concentrations of each pesticide and surrogate in the PEM using Equations 5 and 9.

EQ. 9 Percent Difference Between the Calculated and Nominal Concentrations

$$\%Difference = \frac{C_{calc} - C_{nom}}{C_{nom}} \times 100$$

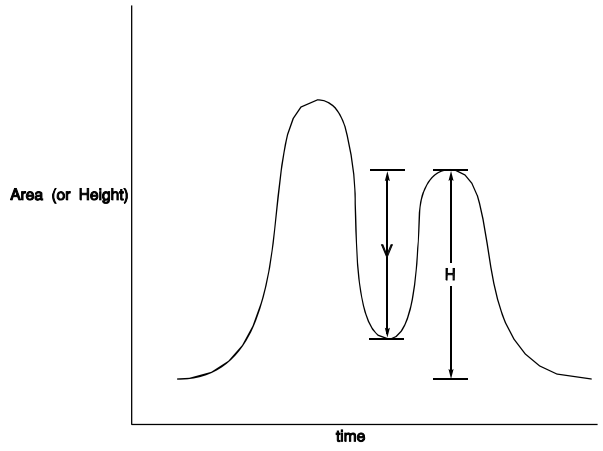
Where,

%Difference = Percent Difference.

C_{calc} = Calculated concentration of each analyte from the analysis of the standard. (Amount found (ng) in Eq. 5).

C_{nom} = Nominal concentration of each analyte.

9.2.4.10 Calculate the resolution between the analytes in the Resolution Check Mixture, PEM, and CS3 Standard concentrations of the Individual Standard Mixtures, using Equation 10.



EQ. 10 Percent Resolution

$$\%Resolution = \frac{V}{H} \times 100$$

Where,

V = Depth of the valley between the two peaks. The depth of the valley is measured along a vertical line from the level of the apex of the shorter peak to the floor of the valley between the two peaks.

H = Height of the shorter of the adjacent peaks.

9.2.5 Technical Acceptance Criteria for Initial Calibration

All initial calibration technical acceptance criteria apply independently to each GC column.

9.2.5.1 The initial calibration sequence must be analyzed according to the procedure and in the order listed in Section 9.2.3, at the concentrations listed in Section 7.2.2, and at the frequency listed in Section 9.2.2. The GC/ECD operating conditions optimized in Section 9.1 must be followed.

9.2.5.2 The resolution between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 80.0% for all analytes for the primary column and greater than or equal to 50% for the confirmation column in order to use one Individual Standard Mixture (C). If two Individual Standard Mixtures (A and B) are to be used, then the resolution between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 60.0% for both GC columns.

9.2.5.3 All single component pesticides and surrogates in both runs of the PEM must be greater than or equal to 90.0% resolved on each column.

9.2.5.4 The absolute RTs of each of the single component pesticides and surrogates in both runs of the PEM must be within the RT window determined from the five-point initial calibration in Section 9.2.4.3.

9.2.5.5 The Percent Difference between the calculated amount (amount found) and the nominal amount (amount added) for each of the single component pesticides and surrogates in both of the PEM runs of each GC column must be greater than or equal to -25.0% and less than or equal to 25.0% using Equation 9.

9.2.5.6 The Percent Breakdown of DDT and Endrin in each of the PEM runs must be less than or equal to 20.0%. The combined breakdown of DDT and Endrin must be less than or equal to 30.0%.

9.2.5.7 The %RSD of the CFs for each single component target compound must be less than or equal to 20.0%, except alpha-BHC and delta-BHC. The %RSD of the CFs for alpha-BHC and delta-BHC must be less than or equal to 25.0%. The %RSD of the CFs for the two surrogates must be less than or equal to 30.0%. Up to two single component target compounds (not surrogates) per column may exceed the maximum %RSD of 20.0% (25.0% for alpha-BHC and delta-BHC), but those compounds must have a %RSD of less than or equal to 30.0%. The %RSD of the CFs for Toxaphene must be less than or equal to 30.0%.

9.2.5.8 If one Individual Standard Mixture (C) is used then the resolution between any two adjacent peaks in the CS3 Individual Standard Mixture C must be at least 80% for the primary column and 50% for the secondary column. If two Individual Standard Mixtures (A and B) are used, then the resolution between any two adjacent peaks in the CS3 Individual Standard Mixtures (A and B) must be greater than or equal to 90% on both columns.

9.2.5.9 All instrument blanks must meet the technical acceptance criteria in Section 12.1.4.5.

9.2.5.10 The identification of single component pesticides by GC methods is based primarily on RT data. The RT of the apex of a peak can only be verified from an on-scale chromatogram. The identification of Toxaphene by GC methods is based primarily on recognition of patterns of RTs displayed on a chromatogram. Therefore, the following requirements apply to all data presented for single component and Toxaphene:

- The chromatograms that result from the analyses of the Resolution Check Mixture, the PEM, and the Individual Standard Mixtures during the initial calibration sequence must display the single component analytes present in each standard at

greater than 10% of full scale, but less than 100% of full scale;

- The chromatograms for at least one of the five analyses of each Individual Standard Mixture from the initial calibration sequence must display the single component analytes at greater than 50% and less than 100% of full scale;

- The chromatogram for at least one of the analyses of the Toxaphene standard analyzed during the initial calibration sequence must display the peaks chosen for identification at greater than 25% and less than 100% of full scale;

- For all Resolution Check Mixtures, PEMs, Individual Standard Mixtures, and blanks, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl; and

- If a chromatogram is replotted electronically to meet requirements, the scaling factor used must be displayed on the chromatogram.

9.2.6 Corrective Action for Initial Calibration

9.2.6.1 If the technical acceptance criteria for the initial calibration are not met, inspect the system for problems. It may be necessary to change the column, bake-out the detector, clean the injection port, or take other corrective actions to achieve the technical acceptance criteria.

9.2.6.2 Contamination should be suspected as a cause if the detector cannot achieve acceptable linearity using this method. In the case of low-level contamination, baking-out the detector at elevated temperature (350°C) should be sufficient to achieve acceptable performance. In the case of heavy contamination, passing hydrogen through the detector for 1-2 hours at elevated temperature may correct the problem. In the case of severe contamination, the detector may require servicing by the ECD manufacturer. CAUTION: DO NOT OPEN THE DETECTOR. THE ECD CONTAINS RADIOCHEMICAL SOURCES.

9.2.6.3 If a laboratory cleans out a detector using elevated temperature, the ECD electronics must be turned off during the bake out procedure.

9.2.6.4 After bake out or hydrogen reduction, the detector must be recalibrated using the initial calibration sequence.

9.2.6.5 Initial calibration technical acceptance criteria MUST be met before any samples (including LCSs and MS/MSDs) and required blanks (method/sulfur cleanup/instrument) are analyzed. Any samples or required blanks analyzed when the initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.3 Calibration Verification

9.3.1 Summary of Calibration Verification

Three types of analyses are used to verify the calibration and evaluate instrument performance, instrument blanks, PEMs, and the CS3 Individual Standard Mixture(s). A calibration verification consists of an instrument blank and PEM or an instrument blank and the CS3 Individual Standard Mixture(s). Sample (including LCS and MS/MSD) and required blank (method/sulfur cleanup) data are not acceptable unless bracketed by acceptable analyses of instrument blanks, PEMs, and both Individual Standard Mixtures.

9.3.2 Frequency of Calibration Verification

9.3.2.1 An instrument blank and the PEM must bracket one end of a 12-hour period during which sample and required blank data are collected, and a second instrument blank and the CS3 Individual Standard Mixture(s) must bracket the other end of the 12-hour period. If Individual Standard Mixtures A and B were used in the associated initial calibration sequence, then CS3 Individual Standard Mixtures A and B must be used for the calibration verification. If Individual Standard Mixture C was used in the associated initial calibration sequence, then CS3 Individual Standard Mixture C must be used in the calibration verification.

9.3.2.2 For the 12-hour period immediately following the initial calibration sequence, the instrument blank and the PEM that are the last two steps in the initial calibration sequence bracket the front end of that 12-hour period. The injection of the instrument blank starts the beginning of the 12-hour period (Section 9.2.3.4). Samples (including LCSs and MS/MSDs) and required blanks (method/sulfur cleanup) may be injected for 12 hours from the injection of the instrument blank. The first injections immediately after that 12-hour period must be an instrument blank and the CS3 Individual Standard Mixture(s). The instrument blank must be analyzed first, before the standard(s). If two Individual Standard Mixtures are used they may be analyzed in either order (A, B or B, A).

9.3.2.3 The analyses of the instrument blank and CS3 Individual Standard Mixture(s) immediately following one 12-hour period may be used to begin the subsequent 12-hour period, provided that they meet the technical acceptance criteria in Section 9.3.5. In that instance, the subsequent 12-hour period must be bracketed by the acceptable analyses of an instrument blank and a PEM, in that order. Those two analyses may in turn be used to bracket the front end of yet another 12-hour period. This progression may continue every 12 hours until such time as any of the instrument blanks, PEMs, or Individual Standard Mixture(s) fails to meet the technical acceptance criteria in Section 9.3.5. The 12-hour time period begins with the injection of the instrument blank.

9.3.2.4 If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an acceptable instrument blank and PEM must be analyzed in order to start a new sequence. This requirement applies even if no analyses were performed since that standard was injected.

9.3.2.5 The requirements for running the instrument blanks, PEM, and CS3 Individual Standard Mixture(s) are waived when no samples (including LCSs and MS/MSDs), dilutions, reanalyses, required blanks (method/sulfur cleanup), and Toxaphene standards are analyzed during that 12-hour period. To resume analysis, using the existing initial calibration, the Contractor must first

analyze an instrument blank and PEM that meet the technical acceptance criteria.

9.3.2.6 If the entire 12-hour period is not required for the analyses of all samples and blanks to be reported and all data collection is to be stopped, the sequence must be ended with either the instrument blank/PEM combination or the instrument blank/CS3 Individual Standard Mixture(s) combination, whichever was due to be performed at the end of the 12-hour period.

9.3.2.7 No more than 14 hours may elapse from the injection beginning the opening Continuing Calibration Verification (CCV) and the injection ending the closing CCV (PEM or Individual Standard Mixture).

9.3.3 Procedure for Calibration Verification

9.3.3.1 All standards and blanks must warm to ambient temperature prior to analysis.

9.3.3.2 Analyze the instrument blank, PEM, and the CS3 Individual Standard Mixture(s) at the required frequencies (Section 9.3.2).

9.3.4 Calculations for Calibration Verification

9.3.4.1 For each analysis of the PEM used to demonstrate calibration verification, calculate the Percent Difference between the amount of each analyte (including the surrogates) found in the PEM and the nominal amount, using Equation 9.

9.3.4.2 For each analysis of the PEM used to demonstrate calibration verification, calculate the Percent Breakdown of Endrin and DDT, and the combined breakdown, using Equations 5, 6, 7, and 8.

9.3.4.3 For each analysis of the CS3 Individual Standard Mixture(s) used to demonstrate calibration verification, calculate the Percent Difference between the CF of each analyte (including the surrogates) in the standard mixture and the $\overline{CF}$ from the initial calibration, using Equation 11. Do not attempt to calculate the breakdown of Endrin and DDT in the Individual Standard Mixtures, as these standards contain the breakdown products as well as the parent compounds.

EQ. 11 Percent Difference Between the Calibration Factor and the Mean Calibration Factor

$$\%Difference = \frac{CF - \overline{CF}}{\overline{CF}} \times 100$$

Where,

%Difference = Percent Difference.

CF = Calibration Factor for CS3 Standard used for Calibration Verification.

$\overline{CF}$ = Mean Calibration Factor.

9.3.5 Technical Acceptance Criteria for Calibration Verification

All calibration verification technical acceptance criteria apply independently to each GC column.

9.3.5.1 The PEMs, Individual Standard Mixtures, and instrument blanks must be analyzed at the required frequency (Section 9.3.2), on a GC/ECD system that has met the initial calibration technical acceptance criteria.

9.3.5.2 All single component pesticides and surrogates in the PEMs used to demonstrate calibration verification must be greater than or equal to 90.0% resolved. If one Individual Standard Mixture is used, the resolution between any two adjacent peaks in the CS3 Individual Standard Mixture C must be at least 80% for the primary column and 50% for the secondary column. If two Individual Standard Mixtures are used, the resolution between any two adjacent peaks in the CS3 Individual Standard Mixture A and B used to demonstrate calibration verification must be greater than or equal to 90.0% for both columns.

9.3.5.3 The absolute RT for each of the single component pesticides and surrogates in the PEMs and CS3 Individual Standard Mixture(s) used to demonstrate calibration verification must be within the RT windows determined from the five-point initial calibration in Section 9.2.4.3.

9.3.5.4 The Percent Difference between the calculated amount (amount found) and the nominal amount (amount added) for each of the single component pesticides and surrogates in the PEM used to demonstrate calibration verification must be greater than or equal to -25.0% and less than or equal to 25.0%.

9.3.5.5 The Percent Breakdown of 4,4'-DDT in the PEM must be less than or equal to 20.0% on each column. The Percent Breakdown of Endrin in the PEM must be less than or equal to 20.0% on each column. The combined breakdown of DDT and Endrin must be less than or equal to 30.0% on each column.

9.3.5.6 The Percent Difference between the CF of each of the single component pesticides and surrogates in the mid-point concentration of the Individual Standard Mixtures used to demonstrate calibration verification, and the $\overline{CF}$ from the initial calibration must be greater than or equal to -20.0% and less than or equal to 20.0%.

9.3.5.7 All instrument blanks must meet the technical acceptance criteria in Section 12.1.4.5.

9.3.5.8 The identification of single component pesticides by GC methods is based primarily on RT data. Since the RT of the apex of a peak can only be verified from an on-scale chromatogram, the following requirements must be met for calibration verification to be acceptable:

- The chromatograms that result from the analyses of the PEM and the Individual Standard Mixtures must display the single component analytes present in each standard at greater than 10% of full scale but less than 100% of full scale;
- For any PEM, Individual Standard Mixture, or blank, the baseline of the chromatogram must return to below 50% of full

scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl;

- If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram; and

- If the chromatogram of any standard or blank needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram(s) must be submitted in the data package.

9.3.5.9 A Toxaphene calibration verification standard (CS3) must be analyzed on the same instrument upon its detection in a sample. This standard must be analyzed within 72 hours of the analytes detection in a valid 12-hour period. The Percent Difference between the CF of each peak used to identify Toxaphene in the calibration verification standard and the $\overline{CF}$ from the initial calibration must be greater than or equal to -20.0% and less than or equal to 20.0%.

9.3.6 Corrective Action for Calibration Verification

9.3.6.1 If the technical acceptance criteria for the calibration verification are not met, inspect the system for problems and take corrective action to achieve the technical acceptance criteria.

9.3.6.2 Major corrective actions, such as replacing the GC column or baking out the detector, will require that a new initial calibration be performed that meets the technical acceptance criteria in Section 9.2.5.

9.3.6.3 Minor corrective actions may not require performing a new initial calibration, provided that a new analysis of the standard (PEM or Individual Standard Mixtures) that originally failed the criteria, and an associated instrument blank immediately after the corrective action, do meet all the technical acceptance criteria.

9.3.6.4 If a PEM or Individual Standard Mixture does not meet the technical acceptance criteria listed above, it must be reinjected immediately. If the second injection of the PEM or Individual Standard Mixture meets the criteria, sample analysis may continue. If the second injection does not meet the criteria, all data collection must be stopped. Appropriate corrective action must be taken, and a new initial calibration sequence must be run before more sample data are collected.

9.3.6.5 If an instrument blank does not meet the technical acceptance criteria listed in Section 12.1.4.5, all data collection must be stopped. Appropriate corrective action must be taken to clean out the system, and an acceptable instrument blank must be analyzed before more sample data are collected.

9.3.6.6 Analysts are reminded that running an instrument blank and a PEM or Individual Standard Mixtures once every 12 hours are the minimum contract requirements. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to run instrument blanks and standards more often to avoid discarding data.

9.3.6.7 If a successful instrument blank and PEM cannot be run after an interruption in analysis (Section 9.3.2.6), an acceptable initial calibration must be run before sample data may be collected. All acceptable sample (including LCS and MS/MSDs) and required blank (method/sulfur cleanup) analyses must be preceded and followed by acceptable standards and instrument blanks, as described in Section 9.3.2.

9.3.6.8 Calibration verification technical acceptance criteria must be met before any samples (including the LCSs and MS/MSDs) and required blanks (method/sulfur cleanup) are reported. Any samples and required blanks associated with a calibration verification that did not meet the technical acceptance criteria will require reanalysis at no additional cost to USEPA.

10.0 PROCEDURE

The Contractor must have the capability to perform all of the sample cleanup procedures presented in this Exhibit, including those included by reference. The Contractor may use any of the procedures or combinations of procedures to cleanup the samples prior to analysis, unless the Contractor is specifically directed by the Region to use a particular cleanup procedure or combination of cleanup procedures.

The Contractor must demonstrate that each cleanup procedure is capable of producing data that meets the technical acceptance criteria for the method, including Method Detection Limits (MDLs) and any precision and recovery limits.

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to apprise them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 Multi-phase Samples

If multi-phase samples (e.g., a two-phase liquid sample, oily, sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region.

10.1.2.1 If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample;
- Separate the phases of the sample and analyze each phase separately. SMO will provide EPA Sample Numbers for the additional phases, if required;
- Separate the phases and analyze one or more of the phases, but not all of the phases. SMO will provide EPA Sample Numbers for the additional phases, if required; or
- Do not analyze the sample.

10.1.2.2 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do any of the following:

- Separate the phase(s) and analyze the phase(s) that is(are) amenable to analysis. SMO will provide EPA Sample Numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.3 No other change in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Extraction of Water Samples

Water samples may be extracted by either separatory funnel procedure or a continuous liquid-liquid extraction procedure. If an emulsion prevents acceptable solvent recovery with the separatory funnel procedure, continuous liquid-liquid extraction must be employed. Allow the samples to warm to ambient temperature.

10.1.3.1 Separatory Funnel Extraction

10.1.3.1.1 Measure out each 1 L sample aliquot in a separate graduated cylinder. Measure and record the pH of the sample with wide range pH paper and adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring pH adjustment must be noted in the SDG Narrative. Place the sample aliquot into a 2 L separatory funnel.

10.1.3.1.2 Using a syringe or a volumetric pipet, add 3.0 mL of the surrogate solution (Section 7.2.2.1) to all water samples.

10.1.3.1.3 Rinse the graduated cylinder with 30 mL of methylene chloride and transfer the rinsate to the separatory funnel. If the sample container is empty, rinse the container with 30 mL of methylene chloride and add the rinsate to the separatory funnel. If the sample container is not rinsed, then add another 30 mL of methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 minutes, with periodic venting to release excess pressure.

NOTE: The total volume of solvent used for extraction is 60 mL. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than 1/3 the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration through glass wool, centrifugation, or other physical means. Drain the methylene chloride into a 250 mL Erlenmeyer flask.

10.1.3.1.4 Add a second 60 mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Proceed to Section 10.2.

10.1.3.2 Continuous Liquid-Liquid Extraction

10.1.3.2.1 Continuous Liquid-Liquid Extraction Without Hydrophobic Membrane

10.1.3.2.1.1 Follow the manufacturer's instructions for set-up.

10.1.3.2.1.2 Add methylene chloride to the bottom of the extractor and fill it to a depth of at least 1 inch above the bottom sidearm.

10.1.3.2.1.3 Measure out each 1 L sample aliquot in a separate, clean graduated cylinder; transfer the aliquot to the continuous extractor. Measure the pH of the sample with wide range pH paper or a pH meter and record the pH. Adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, as required. Samples requiring the pH adjustment must be noted in the SDG Narrative.

NOTE: With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and the water layer in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

10.1.3.2.1.4 Using a syringe or volumetric pipet, add 3.0 mL of the surrogate standard spiking solution (Section 7.2.2.1) into the sample and mix well.

10.1.3.2.1.5 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor. If the sample container is empty, rinse the container with 50 mL of methylene chloride and add the rinsate to the continuous extractor.

10.1.3.2.1.6 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 5-15 mL/minute. (recommended); optimize the extraction drip rate. Extract for a <u>minimum</u> of 18 hours.

NOTE 1: When a minimum drip rate of 10-15 mL/minute is maintained throughout the extraction, the extraction time may be reduced to a minimum of 12 hours. Allow to cool, then detach the distillation flask. Proceed to Section 10.2.

NOTE 2: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor.

10.1.3.2.2 Continuous Liquid-Liquid Extraction With Hydrophobic Membrane

10.1.3.2.2.1 Follow the manufacturer's instructions for set-up.

10.1.3.2.2.2 Measure out each 1 L sample aliquot in a separate, clean graduated cylinder. If the sample container is empty, rinse the container with 50 mL of methylene chloride and add the rinsate to the continuous extractor. If the sample container is not rinsed, add 50 mL of methylene chloride to the continuous extractor. Slowly transfer the aliquot to the continuous extractor. Measure the pH of the sample with

wide range pH paper or a pH meter and record the pH. Adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, as required. Samples requiring pH adjustment must be noted in the SDG Narrative.

10.1.3.2.2.3 Using a syringe or volumetric pipet, add 3.0 mL of the surrogate standard spiking solution (Section 7.2.2.1) into the sample and mix well.

10.1.3.2.2.4 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor.

10.1.3.2.2.5 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 6 hours.

NOTE 1: Due to the smaller volume of solvent used during the extraction process, some sample matrices (e.g., oily samples, samples containing a high concentration of surfactants) may create an emulsion that will consume the solvent volume, preventing efficient extraction of the sample. When this occurs, add additional solvent to ensure efficient extraction of the sample, and extend the extraction time for a minimum of 6 hours. If the sample matrix prevents the free flow of solvent through the membrane, then the non-hydrophobic membrane continuous liquid-liquid type extractor must be used. Allow to cool, then detach the distillation flask. Proceed to Section 10.2.

NOTE 2: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor. Using the hydrophobic membrane, it may not be necessary to dry the extract with sodium sulfate.

NOTE 3: If low surrogate recoveries occur, assure that 1) the apparatus was properly assembled to prevent leaks; 2) the drip rate/solvent cycling was optimized; 3) there was proper cooling for condensation of solvent. Document the problem and the corrective action.

NOTE 4: Alternate continuous liquid-liquid extractor types that meet the requirements of the analytical method may also be used. If using alternate extractors or design types, follow the manufacturer's instructions for set-up. Optimize the extraction procedure.

10.1.4 Soil/Sediment Samples

Mix samples thoroughly, especially composite samples. Discard any foreign objects such as sticks, leaves, and rocks. Also, decant and discard any standing aqueous phase.

10.1.4.1 pH Determination

Transfer 50 g of soil/sediment to a 100 mL beaker. Add 50 mL of water and stir the solution with a magnetic stirrer for 1 hour. Determine the pH of the sample by using a combination glass electrode and pH meter while the sample is stirred. Report the pH value on the appropriate data sheet. If the pH of the soil/sediment is greater than 9 or less than 5, document any subsequent problems in the analysis related to pH in the SDG Narrative, but do not attempt to adjust the pH of the sample. Discard the portion of the sample used for pH determination.

NOTE: If insufficient weight of soil/sediment is received, use a smaller 1:1 ratio of grams of sample to milliliters of water for the pH determination, and note in the SDG Narrative.

10.1.4.2 Percent Moisture

Weigh 5-10 g of the soil/sediment to the nearest 0.01 g into a tared crucible or aluminum weighing pan. Determine the weight percent volatilized by drying overnight at 105°C (hereafter referred to as Percent Moisture). After the sample is dry, remove the sample and pan and allow them to cool in a desiccator before weighing. Calculate the Percent Moisture according to Equation 12 below. Concentrations of individual analytes will be reported relative to the dry weight of soil/sediment.

CAUTION: Gases volatilized from some soil/sediment samples may require that this drying procedure be carried out in a hood.

EQ. 12 Percent Moisture

$$\%\text{Moisture} = \frac{\text{grams of wet sample - grams of dry sample}}{\text{grams of wet sample}} \times 100$$

10.1.4.3 Extraction of Soil/Sediment Samples

10.1.4.3.1 Three procedures are provided for the extraction of pesticide compounds from soil/sediment samples:

- Ultrasonic extraction;
- [Automated] Soxhlet extraction; and
- Pressurized fluid extraction.

The Contractor shall use one of the above procedures for the extraction of soil/sediment samples.

NOTE: All soil/sediment samples in a Case must be extracted by the same procedure.

10.1.4.3.2 For soil/sediment sample extractions, perform the following steps rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample, to the nearest 0.1 g, into a 400 mL beaker. Add 60 g of anhydrous powdered or granulated sodium sulfate, or add 30 g of Hydromatrix, or sufficient quantity, and mix well to produce a sandy texture. Proceed to Section 10.1.4.3.3 for ultrasonic extraction, Section

10.1.4.3.4 for automated Soxhlet extraction, or Section 10.1.4.3.5 for pressurized fluid extraction. As applicable, follow the manufacturer's instructions for use of all extraction equipment.

NOTE: For samples extracted by the Pressurized Fluid Extraction procedure (Section 10.1.4.3.5) the use of sodium sulfate is not recommended.

10.1.4.3.3 Ultrasonic Extraction

10.1.4.3.3.1 Add 3.0 mL of surrogate solution to the sample, then immediately add 100 mL of 1:1 (v/v) acetone/methylene chloride.

10.1.4.3.3.2 Place the bottom surface of the tip of the 3/4 inch tapered disruptor horn about 1/2 inch below the surface of the solvent, but above the sediment layer. Do not use a microtip probe.

10.1.4.3.3.3 Sonicate for 3 minutes using a 3/4 inch disruptor horn at full power, (output control knob at 10) with pulse on, and percent duty cycle knob set at 50.0%.

NOTE: These settings refer to the Model W-385. When using a sonicator other than Model W-385, refer to the manufacturer's instructions for appropriate output settings.

10.1.4.3.3.4 Decant and filter extracts through Whatman No. 41 (or equivalent) filter paper using vacuum filtration or centrifuge and decant extraction solvent.

10.1.4.3.3.5 Repeat the extraction two more times with two additional 100 mL portions of 1:1 (v/v) acetone/methylene chloride. Before each extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or, very carefully, with the tip of the unenergized probe. Decant the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 (v/v) acetone/methylene chloride. Proceed to Section 10.2.

10.1.4.3.4 [Automated] Soxhlet Extraction

The Contractor may use either automated or non-automated Soxhlet extraction. The following procedure is based on the use of a Soxtec HT-6 automated Soxhlet extraction system. When using a different system, refer to the instructions provided by the manufacturer for the appropriate procedure.

10.1.4.3.4.1 Check the heating oil level in the automated Soxhlet unit and add oil if needed. Follow the manufacturer's instructions to set the temperature on the service unit. Press the "MAINS" button and observe that the switch lamp is now "ON". Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/minutes to prevent solvent loss through the condensers.

10.1.4.3.4.2 Transfer the entire sample from the beaker (Section 10.1.4.3.2) to the thimble. Add 3.0 mL of surrogate solution to the sample.

10.1.4.3.4.3 Immediately transfer the thimbles containing the weighed samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.

10.1.4.3.4.4 Insert the extraction cups containing boiling chips, and load each with an appropriate volume 1:1 (v/v) acetone/methylene chloride. Using the cup holder, lower the locking handle, ensuring that the safety catch engages. The cups are now clamped into position.

NOTE: The seals must be pre-rinsed or pre-extracted with extraction solvent prior to initial use.

10.1.4.3.4.5 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 minutes. The condenser valves must be in the "OPEN" position. Extract for the preset time.

10.1.4.3.4.6 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set timer for 60 minutes. Condenser valves are still open. Extract for the preset time. After rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.

10.1.4.3.4.7 When all but 2-5 mL of solvent have been collected, open the system and remove the cups. Transfer the contents of the cups to graduated, conical-bottom glass tubes. Rinse the cups with methylene chloride and add the rinsates to the glass tubes. Proceed to Section 10.2.

10.1.4.3.5 Pressurized Fluid Extraction

10.1.4.3.5.1 Transfer the entire sample from the beaker (Section 10.1.4.3.2) to an extraction cell of the appropriate size for the aliquot. Add 3.0 mL of surrogate solution to the sample.

10.1.4.3.5.2 Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer.

10.1.4.3.5.3 Place a pre-cleaned collection vessel in the instrument for each sample, as described by the instrument manufacturer. The total volume of the collected extract will depend on the specific instrumentation and the extraction procedure recommended by the manufacturer and may range from 0.5 - 1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract.

10.1.4.3.5.4 The following are recommended extraction conditions:

Oven temperature:	100°C
Pressure:	1500-2000 psi
Static time:	5 min. (after 5 min. pre-heat equilibration)
Flush volume:	60% of the cell volume
Nitrogen purge:	60 sec. at 150 psi (purge time may be extended for larger cells)
Static cycles:	1

10.1.4.3.5.5 Optimize the extraction conditions, as needed, according to the manufacturer's instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. Any pressure in the range of 1500-2000 psi should suffice. An appropriate amount of 1:1 (v/v) acetone/methylene chloride should be used to achieve the conditions in Section 10.1.4.3.5.4.

10.1.4.3.5.6 Once established, the same pressure should be used for all samples in the same SDG.

10.1.4.3.5.7 Begin the extraction according to the manufacturer's instructions. Collect each extract in a clean vial. Allow the extracts to cool after the extractions are complete. Proceed to Section 10.2.

10.2 Extract Concentration

10.2.1 Concentration by Kuderna-Danish (K-D)

10.2.1.1 Assemble a K-D concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all the target pesticides listed in Exhibit C.

10.2.1.2 For water samples, transfer the extract to a K-D concentrator by pouring the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate.

10.2.1.2.1 For soil/sediment samples, directly transfer the extract to the K-D concentrator.

10.2.1.2.2 Rinse the Erlenmeyer flask (for both water and soil/sediment samples) and the column (for water samples) with at least two 20-30 mL portions of methylene chloride to complete the quantitative transfer.

10.2.1.3 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60-70°C recommended) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed

with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-30 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 3-5.0 mL for water samples (and less than 10 mL for soil/sediment samples), remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

10.2.1.4 For water extracts that do not require Gel Permeation Chromatography (GPC) cleanup, and for water and soil/sediment extracts that have been through the GPC cleanup step, proceed with the hexane exchange described in Section 10.2.2.

10.2.1.5 For water extracts that require GPC cleanup, remove the Snyder column, rinse the flask and its lower joint, collect the rinsate in the concentrator tube, and adjust the volume to 10.0 mL with methylene chloride. Proceed to Section 10.3.1.

10.2.1.6 For soil/sediment extracts that have not been cleaned-up using GPC, it is absolutely necessary to further reduce the volume of all soil/sediment extracts to 1 mL in order to remove most of the acetone. This is best accomplished using the nitrogen evaporation technique (Section 10.2.3.2). The presence of acetone will cause a dead volume to develop in the GPC column and thus will cause loss of surrogates and analytes during GPC cleanups. Adjust the soil/sediment extract volume to 10 mL with methylene chloride. Proceed to Section 10.3.1 for mandatory GPC.

10.2.2 Solvent Exchange into Hexane

This procedure applies to both extracts of water samples and extracts of soil/sediment samples.

10.2.2.1 With the extract in a K-D apparatus, momentarily remove the Snyder column, add 50.0 mL of hexane and a new boiling chip, and re-attach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as described previously (Section 10.2.1), but increase the temperature of the water bath (80-90°C is recommended). When the apparent volume of liquid reaches 3-5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

10.2.2.2 Remove the Snyder column; using 1-2 mL of hexane, rinse the flask and its lower joint into the concentrator tube. Complete quantitative transfer of the extract to a 10 mL vial by using hexane.

10.2.2.3 For samples that have <u>not</u> been subjected to GPC cleanup, adjust the volume of the hexane extract to 10 mL. For samples that <u>have</u> been subjected to GPC cleanup, concentrate the hexane extract to 5.0 mL using a Micro Snyder Column or nitrogen evaporation, as described in Section 10.2.3.1 or 10.2.3.2, then proceed to Section 10.3.2 for Florisil cartridge cleanup.

10.2.3 Final Concentration of Extract

Two different techniques are permitted to concentrate the extract to volume before Florisil cleanup or extract volume before instrumental analysis. They are the Micro Snyder Column and the Nitrogen

Evaporation Technique. If the Region requests lower Contract Required Quantitation Limits (CRQLs) than those listed in Exhibit C Pesticides, the extracts may be further concentrated (2.0 mL instead of 10 mL when GPC cleanup is not required, or 1.0 mL instead of 5.0 mL when GPC is required), provided a proper MDL study (see Sections 7.2.2.5 and 12.4) is performed. The MDL study must demonstrate that the lower CRQLs can be achieved.

NOTE: If the Region requests lower CRQLs than those listed in Exhibit C Pesticides, sufficient surrogate spiking solution must be added to samples [including LCS and Matrix Spike and Matrix Spike Duplicate (MS/MSD)] and blanks, such that the expected surrogate concentrations after final concentration of the extract are 12 times the surrogate concentrations in the low standard (CS1) of the associated initial calibration.

10.2.3.1 Micro Snyder Column Concentration

Add another one or two clean boiling chips to the concentrator tube and attach a two-ball Micro Snyder Column. Pre-wet the Snyder column by adding about 0.5 mL of hexane to the top of the column. Place the K-D apparatus in a hot water bath (80-90°C recommended) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse its flask and lower joint into the concentrator tube with 0.2 mL of hexane. If GPC cleanup is needed and not yet performed, adjust the volume to 10.0 mL with methylene chloride and proceed to Section 10.3.1 for GPC cleanup. For water samples that do not require GPC cleanup, adjust the volume to 10.0 mL with hexane and proceed to Section 10.3.2 for Florisil cleanup. For soil/sediment samples that have already undergone GPC cleanup, adjust the volume with hexane to 5.0 mL and proceed to Section 10.3.2 for Florisil cleanup. If no further cleanup is needed, adjust the volume with hexane to the same volume of the aliquot used for Florisil and/or sulfur cleanup (1.0 or 2.0 mL) and proceed to Section 10.4 for Gas Chromatograph/Electron Capture Detector (GC/ECD) analysis.

10.2.3.2 Nitrogen Evaporation Technique (taken from ASTM Method D5812)

10.2.3.2.1 Place the Concentrator tube in a warm water bath (30-35°C recommended) and evaporate the solvent volume to the final volume by blowing a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon) onto the solvent. DO NOT ALLOW THE EXTRACT TO GO DRY.

If GPC cleanup is needed and not yet performed, adjust the volume to 10 mL with methylene chloride and proceed to Section 10.3.1 for GPC cleanup. For water samples that do not require GPC cleanup, adjust the volume to 10.0 mL with hexane and proceed to Section 10.3.2 for Florisil cleanup. For soil/sediment samples that have already undergone GPC cleanup, adjust the volume with hexane to 5.0 mL and proceed to Section 10.3.2 for Florisil cleanup. If no further cleanup is needed, adjust the volume with hexane to the same volume of the aliquot

used for Florisil and/or sulfur cleanup (1.0 or 2.0 mL) and proceed to Section 10.4 for GC/ECD analysis.

10.2.3.2.2 Gas lines from the gas source to the evaporation apparatus must be stainless steel, copper, or polytetrafluoroethylene (PTFE) tubing. Plastic tubing must not be used between the carbon trap and the sample as it may introduce interferences. The internal wall of new tubing must be rinsed several times with hexane and then dried prior to use.

10.2.3.2.3 During evaporation, the tube solvent level must be kept below the water level of the bath.

10.3 Cleanup Procedures

There are three cleanup procedures specified in this method: GPC; Florisil cartridge; and sulfur cleanup. GPC must be performed for all soil/sediment extracts. GPC must be performed for water extracts that contain higher molecular weight contaminants that interfere with the analysis of the target analytes. Florisil cartridge cleanup is mandatory for all extracts. Sulfur cleanup must be performed for all sample extracts contaminated with sulfur. Method blanks must be subjected to the same cleanup procedures as the samples [including Laboratory Control Samples (LCSs) and MS/MSDs]. The following cleanup methods may be used in addition to those described here, so long as all technical acceptance criteria are met: SW-846 methods 3610B (Alumina); 3630C (Silica Gel); and 3650B (Acid/Base Partition).

10.3.1 Sample Cleanup by GPC

10.3.1.1 Introduction

GPC is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of natural (and synthetic) macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated.

10.3.1.2 GPC Column Preparation

Prepare the GPC column using Bio Beads. Alternate column packings may be used if 1) the column packings have equivalent or better performance than the Bio Beads and meet the technical acceptance criteria for GPC calibration and GPC calibration checks, and 2) the column packings do not introduce contaminants/artifacts into the sample that interfere with the analysis of the pesticide compounds. Follow the manufacturer's instructions for preparation of the GPC column.

10.3.1.3 Calibration of GPC

10.3.1.3.1 Summary of GPC Calibration

10.3.1.3.1.1 The GPC calibration procedure is based on monitoring the elution of standards with an ultraviolet (UV) detector connected to the GPC column.

10.3.1.3.1.2 The UV detector calibration procedure described in Section 10.3.1.3.3 is needed for the analyses of organochlorine pesticides and Toxaphene listed in Exhibit C. IT MUST NOT

BE USED FOR THE ANALYSIS OF GAS CHROMATOGRAPH/MASS SPECTROMETRY (GC/MS) EXTRACTABLES OR OTHER ANALYTES WITHOUT A RECOVERY STUDY.

10.3.1.3.2 Frequency of GPC Calibration

Each GPC system must be calibrated upon award of the contract, when the GPC calibration verification solution fails to meet criteria, when the column is changed, when channeling occurs, and once every 7 days.

10.3.1.3.3 Procedure for GPC Calibration

Follow the manufacturer's instructions for operating the GPC system. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte Retention Times (RTs) and must be monitored.

10.3.1.3.3.1 Using a 10 mL syringe, load the calibration solution (Section 7.2.2.8.1) onto the GPC. Determine the elution times for Bis(2-ethylhexyl)phthalate, methoxychlor, and perylene. Bis(2-ethylhexyl)phthalate will elute first; perylene will elute last.

Choose a "DUMP" time that removes greater than 85% of the phthalate. Choose a "COLLECT" time so that greater than 95% of the methoxychlor is collected, and continue to collect until just prior to the elution time of sulfur. Use a "WASH" time of 10 minutes.

NOTE: The "DUMP" and "COLLECT" times must be adjusted to compensate for the difference in volume of the lines between the detector and the collection flask.

Reinject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

Analyze a GPC blank of methylene chloride. Concentrate the methylene chloride that passed through the system during the collect cycle using a K-D evaporator. Exchange the solvent to hexane and analyze the concentrate by GC/ECD according to the procedure in Section 10.2.2 (usual protocol). Assuming that the blank represents the extract from a 1 L water sample, calculate the analyte concentrations using Equation 14.

10.3.1.3.4 Technical Acceptance Criteria for GPC Calibration

10.3.1.3.4.1 The GPC system must be calibrated at the frequency described in Section 10.3.1.3.2. The UV trace must meet the following requirements:

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution;

- Corn oil and phthalate peaks should exhibit greater than 85% resolution;
- Phthalate and methoxychlor peaks should exhibit greater than 85% resolution;
- Methoxychlor and perylene peaks should exhibit greater than 85% resolution; and
- Perylene and sulfur peaks must not be saturated and should exhibit greater than 90% baseline resolution.

10.3.1.3.4.2 The solvent flow rate and column pressure must be within the manufacturer's specified ranges.

10.3.1.3.4.3 The RTs for bis (2-ethylhexyl) phthalate and perylene must not vary more than ±5% between calibrations. If the RT shift is greater than 5%, take corrective action. Excessive RT shifts are caused by the following:

- Poor laboratory temperature control or system leaks;
- An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight; and/or
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

10.3.1.3.4.4 The analyte concentrations in a GPC blank must be less than the Contract Required Quantitation Limit (CRQL) of any compound in Exhibit C (Pesticides).

10.3.1.3.4.5 A copy of the two most recent UV traces of the calibration solution must be submitted with the data for the associated samples. If UV traces using the same GPC system are submitted with data for analysis of samples for semivolatile compounds, no additional UV traces are required.

10.3.1.3.5 Corrective Action for GPC Calibration

10.3.1.3.5.1 If the flow rate and/or column pressure do not fall within the manufacturer's specified ranges, a new column should be prepared.

10.3.1.3.5.2 A UV trace that does not meet the criteria in Section 10.3.1.3.4 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

10.3.1.3.5.3 If the concentration of any target compound in the GPC blank is equal to, or exceeds the CRQL listed in Exhibit C (Pesticides), pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

10.3.1.4 GPC Calibration Verification

10.3.1.4.1 Summary of GPC Calibration Verification

The GPC calibration must be routinely verified with two check mixtures (Sections 7.2.2.8.1 and 7.2.2.8.2).

10.3.1.4.2 Frequency of GPC Calibration Verification

10.3.1.4.2.1 The calibration verification must be performed at least once every 7 days (immediately following the GPC Calibration) whenever samples, including MS/MSDs, and blanks, are cleaned up using the GPC.

10.3.1.4.2.2 Some samples may contaminate the SX-3 Bio Beads and change the retention volume of the GPC column. Therefore, system calibration and analyte recovery must be checked whenever a sample causes significant discoloration of the GPC column. Even if no darkening is visible, GPC calibration must be checked not less than once every 7 days.

10.3.1.4.3 Procedure for GPC Calibration Verification

The instructions below are for a GPC injection loop of 5 mL. If a 2 mL injection loop is used, the Contractor should adjust the volume to 4 mL instead of 10 mL before injection extract on the GPC.

10.3.1.4.3.1 The pesticide GPC calibration verification solution contains the following six compounds in methylene chloride: gamma-BHC (Lindane), Heptachlor and Aldrin, each at a concentration of 20 ng/mL for a 5 mL GPC loop (50 ng/mL when a 2 mL GPC loop is used); and 4,4'-DDT, Endrin, and Dieldrin at 40 ng/mL (100 ng/mL for a 2 mL loop).

10.3.1.4.3.2 Load the 5 mL sample loop by using a 10 mL syringe containing 8 mL of the pesticide GPC calibration verification solution. Fractions are collected in an auto sequence by using the GPC program established by the UV detector calibration procedure (Section 10.3.1.3).

10.3.1.4.3.3 The collected GPC calibration verification fraction is transferred to a K-D apparatus, and the collection vessel is rinsed with two additional 10 mL portions of methylene chloride to complete the transfer. The volume of methylene chloride is reduced according to Section 10.2.1. After cooling, the solvent is exchanged to hexane according to the instructions in Section 10.2.2. The final volume is adjusted to 10 mL, and the sample is analyzed by GC according to the procedure in Section 10.4. The analysis must be performed on only one of the GC columns used for sample analysis.

10.3.1.4.3.4 The recovery of each single component analyte must be determined for evaluation and reporting purposes. Calculate the Percent Recovery of each single component analyte using Equation 13 in Section 10.3.2.2.3.

10.3.1.4.4 Technical Acceptance Criteria for GPC Calibration Verification

The recovery of each of the single component analytes must be between 80-110%.

10.3.1.4.5 Corrective Action for GPC Calibration Verification

The Contractor may continue to use the GPC column if the technical acceptance criteria for the GPC calibration verification are met. If the recoveries are out of the acceptance window, the columns must be replaced and the GPC recalibrated according to the instructions in Section 10.3.1.3 before proceeding with any GPC cleanup on samples (including LCSs and MS/MSDs) and required method blanks.

10.3.1.5 Daily UV Calibration Check (Optional)

The calibration of the GPC may be monitored daily by use of the UV-GPC calibration solution (Section 7.2.2.8.1) and the UV detector calibration procedure (Section 10.3.1.3.3). The UV detector should be used to monitor the elution times for the phthalate, methoxychlor, and perylene, respectively. The precalibrated GPC program should "DUMP" greater than 85% of the phthalate and should "COLLECT" greater than 95% of the methoxychlor and perylene. Significant changes in elution times of the analytes (e.g., greater than 0.5 minutes) indicate that the column is out of calibration and must be recalibrated or replaced.

10.3.1.6 Sample Cleanup by GPC

10.3.1.6.1 Introduction to Sample Cleanup by GPC

10.3.1.6.1.1 It is very important to have consistent laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not consistent, RTs will shift, and the "DUMP" and "COLLECT" times determined by the calibration standard will no longer will be appropriate. The ideal laboratory temperature, to prevent outgassing of the methylene chloride, is 22°C.

10.3.1.6.1.2 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of 1:1 (v/v) glycerol/water solution must be diluted and loaded into several loops. Similarly, extracts containing more than 40 mg/mL of non-volatile residue must be diluted and loaded into several loops. The non-volatile residue may be determined by evaporating a 100 µL aliquot of the extract to dryness in a tared aluminum weighing pan, or another suitable container. When multiple loops/runs are necessary for an individual sample, be sure to combine all of the sample eluates collected.

10.3.1.6.1.3 Systems using automated injection devices to load the sample on the column must be carefully monitored to assure that the required amount is injected onto the column. Viscous extracts, or extracts containing a large amounts of non-volatile residue will cause problems with injecting the proper amount of sample extract onto the column using automated injection systems. After the sample extract has been processed, the remaining sample extract in an injection vial must be checked to assure that the proper amount of extract was injected on the column before proceeding with the sample analysis. If the proper amount of extract was not injected, the sample must be reprepared and the sample extract must be either diluted and loaded into several loops or the sample extract must be injected manually.

10.3.1.6.2 Frequency of Sample Cleanup by GPC

GPC cleanup must be performed at least once for each soil/sediment extract, water extracts that contain high molecular weight contaminants that interfere with the analysis of the target analytes, and all associated Quality Control (QC) samples (blanks, LCSs, and MS/MSDs). If the cleanup procedure is inadequate, contact SMO.

10.3.1.6.3 Procedure for Sample Cleanup by GPC

10.3.1.6.3.1 Particles greater than 5 microns may scratch the valve, which may result in a system leak and cross contamination of sample extracts in the sample loops. To avoid such problems, filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container (e.g., a 15 mL culture tube with a PTFE-lined screw-cap). Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. Draw a minimum of 8 mL of extract into a 10 mL syringe.

NOTE: Some GPC instrument manufacturer's recommend using a smaller micron size filter disc. In this instance, follow the manufacturer's recommended operating instructions.

10.3.1.6.3.2 INTRODUCTION OF PARTICULATES OR GLASS WOOL INTO THE GPC SWITCHING VALVES MAY REQUIRE FACTORY REPAIR OF THE APPARATUS.

10.3.1.6.3.3 Follow the manufacturer's instructions for operation of the GPC system being utilized.

NOTE: These instructions were written for a 5 mL GPC injection loop. A 2 mL injection loop may be used in place of a 5 mL injection loop. If a 2 mL loop is used, concentrate the 10 mL extract to 4 mL, and then inject 2 mL from the 4 mL.

10.3.1.6.3.4 If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action, following the manufacturer's recommendations. The problem must be resolved prior to loading sample extracts.

10.3.1.6.3.5 After loading each sample loop, wash the loading port with methylene chloride to minimize cross contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

10.3.1.6.3.6 After loading all sample loops, process each sample using the collect and dump cycle times established in Section 10.3.1.3.3.1.

10.3.1.6.3.7 Collect each sample in a 250 mL Erlenmeyer flask covered with aluminum foil to reduce solvent evaporation, or directly into a K-D evaporator. Monitor sample volumes

collected. Changes in sample volumes collected may indicate one or more of the following problems:

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure;
- Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used; and/or
- Leaks in the system or significant variances in room temperature.

10.3.1.6.3.8 After the appropriate GPC fraction has been collected for each sample, concentrate the extract as per Section 10.2.1 and proceed to solvent exchange into hexane as described in Section 10.2.2 and Florisil cleanup in 10.3.2.

10.3.1.6.3.9 Any samples that were loaded into two or more loops must be recombined before proceeding with concentration.

10.3.2 Florisil Cleanup

10.3.2.1 Introduction

Florisil cartridge cleanup significantly reduces matrix interference caused by polar compounds and is required for all extracts. The same volume of the concentrated extract taken for Florisil cleanup must be maintained after Florisil cleanup (1 or 2 mL).

10.3.2.2 Florisil Cartridge Performance Check

10.3.2.2.1 Summary of Florisil Cartridge Performance Check

Every lot number of Florisil cartridges must be tested before they are used for sample cleanup.

10.3.2.2.2 Frequency of Florisil Cartridge Performance Check

Cartridge performance check must be conducted at least once on each lot of cartridges used for sample cleanup or every 6 months, whichever is most frequent.

10.3.2.2.3 Procedure for Florisil Cartridge Performance Check

Add 0.5 mL of 2,4,5-trichlorophenol solution (0.1 µg/mL in acetone; Section 7.2.2.7) and 0.5 mL of Individual Standard Mixture A or C (mid-point concentration; Section 7.2.2.5) to 4 mL of hexane. Reduce the volume to 0.5 mL using nitrogen (Section 10.2.3.2). Place the mixture onto the top of a washed Florisil cartridge, and elute it with 9 mL of hexane/acetone [(90:10)(V/V)]. Use two additional 1 mL hexane rinses to ensure quantitative transfer of the standard from the cartridge. Concentrate to a final volume of 1 mL and analyze the solution by GC/ECD using at least one of the GC columns specified for sample analysis. Determine the recovery of each analyte for evaluation and reporting purposes. Calculate the Percent Recovery (%R) using Equation 13.

EQ. 13 Percent Recovery

$$\text{Percent Recovery} = \frac{(Q_d \times DF)}{Q_a} \times 100$$

Where,

Q_d = Quantity determined by analysis.

Q_a = Quantity added.

DF = Dilution Factor

NOTE: For Florisil Cartridge Performance Check, use DF = 1.0 in calculations.

10.3.2.2.4 Technical Acceptance Criteria for Florisil Cartridge Performance Check

10.3.2.2.4.1 The cartridge performance check solution must be analyzed on a GC/ECD meeting the initial calibration and calibration verification technical acceptance criteria.

10.3.2.2.4.2 The lot of Florisil cartridges is acceptable if all pesticides are recovered at 80-120%, if the recovery of trichlorophenol is less than 5%, and if no peaks interfering with the target analytes are detected.

10.3.2.2.5 Corrective Action for Florisil Cartridge Performance Check

Any lot of Florisil cartridges that does not meet the criteria above must be discarded and a new lot, meeting criteria, must be used for sample cleanup.

10.3.2.3 Sample Cleanup by Florisil Cartridge

The required Florisil cartridge size and the final volume of the extract after Florisil cleanup are a function of the GC autosampler that a laboratory uses. If the autosampler operates reliably with 1.0 mL of sample extract, then a 500 mg cartridge is used and the required final volume is 1.0 mL. If the autosampler requires more sample, prepare 2.0 mL of sample extract using a 1 g cartridge. Manual injection requires only a 1.0 mL final extract and a 500 mg cartridge.

10.3.2.3.1 Frequency of Sample Cleanup by Florisil Cartridge

All samples (including LCSs and MS/MSDs) and method blank extracts are required to be cleaned up by the Florisil cartridge technique.

10.3.2.3.2 Procedure for Sample Cleanup by Florisil Cartridge

10.3.2.3.2.1 Attach the vacuum manifold to a water aspirator or to a vacuum pump with a trap installed between the manifold and the vacuum source. Adjust the vacuum pressure in the manifold to between 5 and 10 lbs of vacuum.

10.3.2.3.2.2 Place one Florisil cartridge into the vacuum manifold for each sample extract.

10.3.2.3.2.3 Prior to cleanup of samples, the cartridges must be washed with hexane/acetone (90:10). This is accomplished by placing the cartridge on the vacuum manifold, by pulling a vacuum, and by passing at least 5 mL of the hexane/acetone solution through the cartridge. While the cartridges are being washed, adjust the vacuum applied to each cartridge so that the flow rate through each cartridge is approximately equal. DO NOT ALLOW THE CARTRIDGES TO GO DRY AFTER THEY HAVE BEEN WASHED.

10.3.2.3.2.4 After the cartridges on the manifold are washed, the vacuum is released, and a rack containing labeled 10 mL volumetric flasks is placed inside the manifold. Care must be taken to ensure that the solvent line from each cartridge is placed inside of the appropriate volumetric flask as the manifold top is replaced.

10.3.2.3.2.5 After the volumetric flasks are in place, the vacuum to the manifold is restored, and a volume of extract equal to the required final volume (1.0 or 2.0 mL) from each sample, blank, or Matrix Spike extract is transferred to the top frit of the appropriate Florisil cartridge. This must equal the final volume after Florisil cleanup.

10.3.2.3.2.6 Because the volumes marked on concentrator tubes are not necessarily accurate at the 1 mL level, the use of a syringe or a volumetric pipet is required to transfer the extract to the cleanup cartridge.

10.3.2.3.2.7 The pesticides in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL volumetric flasks held in the rack inside the vacuum manifold.

10.3.2.3.2.8 Transfer the eluate in each volumetric flask to a clean centrifuge tube or 10 mL vial. Use two additional 1 mL hexane rinses to ensure quantitative transfer of the cartridge eluate.

10.3.2.3.2.9 Adjust the extract to the same 1 or 2 mL aliquot volume as was taken for cleanup using either of the blowdown technique (Section 10.2.3.1 or 10.2.3.2). Measure the final volume with a syringe or by transferring the extract to a volumetric flask.

10.3.2.3.2.10 If sulfur cleanup is to be performed, proceed to Section 10.3.3. Otherwise, transfer the sample to a GC vial and label the vial. The extract is ready for GC/ECD analysis.

10.3.3 Sulfur Cleanup

10.3.3.1 Introduction

10.3.3.1.1 Sulfur contamination will cause a rise in the baseline of a chromatogram and may interfere with the analyses of the later eluting pesticides. If crystals of sulfur are evident or if the presence of sulfur is suspected, sulfur removal must be performed. Interference which is due to sulfur is not acceptable. Sulfur can be removed by one of two methods,

according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and remove the sample extract with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean centrifuge tube or clean concentrator tube before proceeding with further sulfur cleanup.

10.3.3.1.2 If only part of a set of samples require sulfur cleanup, then, a sulfur cleanup blank is required for that part of the set (Section 12.1.3).

10.3.3.2 Frequency of Sulfur Cleanup

Sulfur removal is required for all sample extracts that contain sulfur.

10.3.3.3 Procedure for Sulfur Cleanup

10.3.3.3.1 Removal of Sulfur using Tetrabutylammonium (TBA) Sulfite

10.3.3.3.1.1 The TBA Sulfite procedure removes elemental sulfur by conversion to the thiosulfate ion, which is water-soluble. TBA sulfite causes the least amount of degradation to a broad range of pesticides and organics compounds, while mercury may degrade organophosphorus and some organochlorine pesticides. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

10.3.3.3.1.2 Add 2.0 mL TBA Sulfite Reagent, 1.0 mL 2-propanol, and approximately 0.65 g of sodium sulfite crystals to the extract and shake for at least 5 minutes on the wrist shaker and observe. An excess of sodium sulfite must remain in the sample extract during the procedure. If the sodium sulfite crystals are entirely consumed add one or two more aliquots (approximately 0.65 g) to the extract and observe. Place the samples on the wrist shaker for 45 minutes observing at 15-minute intervals to make sure that the sodium sulfite is not consumed. Add 5 mL organic free water and shake for 10-15 minutes. Place the samples into the centrifuge and spin at a setting and duration appropriate to spin down the solids. Transfer the hexane layer to a clean 10 mL and cap. The extract transferred to the vial still represents the 1.0 or 2.0 mL final volume.

10.3.3.3.2 Copper Technique

Add approximately 2 g of cleaned copper powder to the extract in the centrifuge or concentrator tube (2 g will fill the tube to about the 0.5 mL mark). Mix the copper and extract for at least 1 minute on a mechanical shaker. Separate the extract from the copper powder by drawing off the extract with a disposable pipet, and transfer the extract to a clean vial. The extract transferred to the vial still represents the 1.0 or 2.0 mL final volume. The separation of the extract from the copper powder is necessary to prevent degradation of the pesticides. If the copper appears bright, proceed to Section 10.4 and analyze the extracts. If the copper changes color, repeat the sulfur removal procedure as necessary.

10.4 GC/ECD Analysis

10.4.1 Introduction

10.4.1.1 Before samples (including LCSs and MS/MSDs) and required blanks (method/sulfur cleanup) can be analyzed, the instrument must meet the initial calibration and calibration verification technical acceptance criteria. All sample extracts, required blanks, and calibration standards must be analyzed under the same instrumental conditions. All sample extracts, required blank extracts, and standard/spiking solutions must be allowed to warm to ambient temperature before preparation/analysis. Sample analysis on two different non-equivalent GC columns (see Section 6.26.1.3) is required for all samples and blanks.

10.4.1.2 Set up the GC/ECD system per the requirements in Section 9.1. Unless ambient temperature on-column injection is used (Section 9.1), the injector must be heated to at least 200°C. The optimized GC conditions from Section 9.1 must be used.

10.4.2 Procedure for Sample Analysis by GC/ECD

The injection must be made on-column by using either automatic or manual injection. 1.0 or 2.0 µL injector volumes may be used provided that all associated standards, samples, and blanks use the same injection volume. The same injection volume must be used for all standards, samples (including LCSs and MS/MSDs), and blanks associated with the same initial calibration. If a single injection is used for two GC columns attached to a single injection port, it may be necessary to use an injection volume greater than 2 µL. However, the same injection volume must be used for all analyses.

10.4.2.1 Analytical Sequence

All acceptable samples must be analyzed within a valid analysis sequence as given below.

NOTE: The injection # will depend on whether initial calibration sequence 1 or 2 is used. The analytical sequence specific to using the initial calibration sequence 1 is depicted in bold font.

Time	Injection #	Material Injected
	1-17	First 17 steps of the initial calibration sequence 2
	1-12	**First 12 steps of the initial calibration sequence 1**
0 hr.	18	Instrument Blank at end of initial calibration sequence 2
	13	**Instrument Blank at end of initial calibration sequence 1**
	19	PEM at end of initial calibration sequence 2
	14	**PEM at end of initial calibration sequence 1**
	20	First sample if using initial calibration sequence 2

Time	Injection #	Material Injected
	15	**First sample if using initial calibration sequence 1**
	.	Subsequent samples
	.	
	.	
12 hrs.	.	Last Sample
	1st injection past 12 hours	Instrument blank
	2nd and 3rd injections past 12 hours	Individual Standard Mixtures A and B
	2nd injection past 12 hours	**Individual Standard Mixture C**
	.	Sample
	.	
	.	
	.	Subsequent samples
	.	
Another 12 hrs.	.	Last Sample
	1st injection past 12 hours	Instrument blank
	2nd injection past 12 hours	PEM
	.	Sample
	.	
	.	Subsequent samples
	.	
Another 12 hrs.	.	Last Sample
	1st injection past 12 hours	Instrument blank
	2nd and 3rd injections past 12 hours	Individual Standard Mixtures A and B
	2nd injection past 12 hours	**Individual Standard Mixture C**
	.	Sample
	.	
	etc.	

10.4.2.1.1 For initial calibration sequence 2, the first 12 hours are counted from injection #18 (the Instrument Blank at the end of the initial calibration sequence), not from injection #1. Samples and required blanks may be injected until 12:00 hours have elapsed. All subsequent 12-hour periods are timed from the injection of the instrument blank that brackets the front end of the samples. If more than 12 hours elapse between the injection of two instrument blanks that bracket a 12-hour period in which samples or required blanks are analyzed then the time between the injection of the second instrument blank and the preceding sample may not exceed the length of one chromatographic run. While the 12-hour period may not be

exceeded, the laboratory may run instrument blanks and standards more frequently, for instance, to accommodate staff working on 8-hour shifts. No more than 14 hours may elapse from the injection beginning the opening Continuing Calibration Verification (CCV) (instrument blank) and the injection ending the closing CCV (PEM or Individual Standard Mixture).

10.4.2.1.2 After the initial calibration, the analysis sequence may continue as long as acceptable instrument blanks, PEMs, and Individual Standard Mixtures (A and B) or C are analyzed at the required frequency. This analysis sequence shows only the minimum required blanks and standards. More blanks and standards may be run at the discretion of the Contractor; however, the blanks and standards must also satisfy the criteria presented in Section 9 in order to continue the run sequence.

10.4.2.1.3 An analysis sequence must also include all samples and required blank analyses, but the Contractor may decide at what point in the sequence they are to be analyzed.

10.4.2.1.4 The requirements for the analysis sequence apply to both GC columns and for all instruments used for these analyses.

10.4.3 Sample Dilutions

10.4.3.1 All samples must be analyzed at the most concentrated level that is consistent with achieving satisfactory chromatography as defined in Section 11.3 (injection taken from the 1.0 or 2.0 mL final extract after the cleanup steps).

10.4.3.2 If the response of any single component pesticide is greater than the response of the high standard (CS5) of the initial calibration range on **both** GC columns, then the extract must be diluted. The response of the pesticide compound(s) in the diluted extract must be between the initial calibration low-point (CS1) and high-point (CS5) standards for the lower column response of the two analyses.

10.4.3.3 If the response of any Toxaphene peak used for quantitation is greater than the response of the corresponding Toxaphene peak in the high standard (CS5) on **both** columns, then the sample must be diluted to have the response of the same peak be between the mid-point (CS3) and high-point (CS5) standards of Toxaphene.

10.4.3.4 If dilution is employed solely to bring a peak within the calibration range or to get the Toxaphene pattern on scale, the results for both the greater and the less concentrated extracts must be reported. The resulting changes in quantitation limits and surrogate recovery must be reported also for the diluted samples.

10.4.3.5 If the Dilution Factor (DF) is greater than 10, an additional extract 10 times more concentrated than the diluted sample extract must be analyzed and reported with the sample data. If the DF is less than or equal to 10, but greater than 1, the results of the original undiluted analysis must also be reported.

10.4.3.6 If the analysis of the most concentrated extract does not meet the requirement for dilution in Section 10.4.3.2 and 10.4.3.3, then the analysis is at no additional cost to USEPA.

10.4.3.7 When diluted, the chromatographic data for the single component pesticide must be able to be reported at greater than 10% of full scale but less than 100% of full scale.

10.4.3.8 When diluted, Toxaphene must be able to be reported at greater than 25% of full scale but less than 100% of full scale.

10.4.3.9 Samples with analytes detected at a level greater than the high calibration point must be diluted until the response is within the linear range established during calibration, or to a maximum of 1:100,000.

10.4.3.10 If the response is still above the high calibration point after the dilution of 1:100,000, the Contractor shall contact SMO immediately.

10.4.3.11 Use the results of the original analysis to determine the approximate DF required to get the largest analyte peak (for the lower of the two column responses) within the initial calibration range.

10.4.3.12 Sample dilutions must be made quantitatively. Dilute the sample extract with hexane.

10.4.3.13 If more than two analyses (i.e., from the original sample extract and more than one dilution, or from the most concentrated dilution analyzed and further dilutions) are required to get all target compounds within the calibration range, contact SMO for guidance.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

11.1.1.1 The laboratory will identify single component analyte peaks based on the Retention Time (RT) windows established during the initial calibration sequence. Single component analytes are identified when peaks are observed in the RT window for the analyte on both Gas Chromatograph (GC) columns.

11.1.1.2 A set of three or four major peaks is selected for Toxaphene. RT windows for each peak are determined from the initial calibration analysis. Identification of Toxaphene in the sample is based on pattern recognition in conjunction with the elution of three or four sample peaks within the RT window of the corresponding peaks of the standard on both GC columns.

11.1.1.3 If Toxaphene is detected in a sample then a Toxaphene CS3 standard must be run within 72 hours of its detection in a sample chromatogram, within a valid 12-hour sequence.

11.1.1.4 The choice of the peaks used for Toxaphene identification and the recognition of those peaks may be complicated by the environmental alteration of Toxaphene, and by the presence of coeluting analytes, matrix interferences, or both. Because of the alteration of Toxaphene in the environment, it may give patterns in samples similar to, but not identical with, those of the standards.

11.1.2 Gas Chromatography/Mass Spectrometry (GC/MS) Confirmation

11.1.2.1 Any pesticide listed in Exhibit C (Pesticides) for which a concentration is reported from GC/Electron Capture Detector (GC/ECD) analysis must have the identification confirmed by GC/MS if the concentration is sufficient for that purpose. The following paragraphs are to be used as guidance in performing GC/MS confirmation. If the Contractor fails to perform GC/MS confirmation as appropriate, USEPA may require reanalysis of any affected samples at no additional cost to USEPA.

11.1.2.2 The GC/MS confirmation may be accomplished by one of three general means:

- Examination of the semivolatile GC/MS library search results [i.e., Tentatively Identified Compound (TIC) data]; or
- A second analysis of the semivolatile extract; or
- Analysis of the pesticide extract, following any solvent exchange and concentration steps that may be necessary.

11.1.2.3 The semivolatile GC/MS analysis procedures outlined in Exhibit D (Analytical Methods for Semivolatiles) are based on the injection into the instrument of approximately 10 ng of a target compound in a 2.0 µL volume. The semivolatile Contract Required Quantitation Limit (CRQL) values in Exhibit C (Semivolatiles) are based on the sample concentration that corresponds to an on-column concentration (extract concentration) of 5.0 ng/µL of target analyte. Although these are quantitation limits, and the detection of analytes and generation of reproducible mass spectra

will routinely be possible at levels 3-10 times lower, the sample matrix may prevent detection of target analytes at less than 5.0 ng/µL. If any single component pesticide has an on-column concentration of greater than or equal to 5.0 ng/µL for both columns, then GC/MS confirmation is required. Similarly, for Toxaphene, if an individual peak concentration is greater than or equal to 125 ng/µL for both columns then GC/MS confirmation is required.

11.1.2.3.1 For water samples prepared according to the method described in Section 10, 10.0 ng/2.0 µL corresponds to a sample concentration of 50.0 µg/L for single component pesticides and a sample concentration of 1250 µg/L for Toxaphene.

11.1.2.3.2 For soil/sediment samples prepared according to the method described in Section 10, the corresponding sample concentration is 1700 µg/kg for single component pesticides and 42000 µg/kg for Toxaphene.

11.1.2.4 In order to confirm the identification of Toxaphene, the laboratory must also analyze a reference standard for Toxaphene. In order to demonstrate the ability of the GC/MS system to identify Toxaphene, the concentration of the standard should be 125 ng/µL.

11.1.2.5 To facilitate the confirmation of the single component pesticide analytes from the semivolatile library search data, the laboratory may wish to include these analytes in the semivolatile continuing calibration standard at a concentration of 5.0 ng/µL or less. Do not include Toxaphene in the semivolatile initial and continuing calibration standard. If added to this GC/MS standard, the response factors, RTs, etc., for these analytes would be reported on the GC/MS quantitation report, but <u>not</u> on the GC/MS calibration data reporting forms. As only a single concentration of each analyte would be analyzed, no linearity (%RSD) or Percent Difference criteria would be applied to the response factors for these additional analytes.

11.1.2.6 The Contractor is advised that library search results from the NIST (2002 release or later) mass spectral library will not likely list the name of the pesticide analyte as it appears in this analytical method, hence, the mass spectral interpretation specialist is advised to compare the Chemical Abstracts Service (CAS) Registry Numbers for the pesticides to those from the library search routine.

11.1.2.7 If the analyte cannot be confirmed from the semivolatile library search data for the original semivolatile GC/MS analysis, the laboratory may analyze another aliquot of the semivolatile sample extract after further concentration of the aliquot. This second aliquot must either be analyzed as part of a routine semivolatile GC/MS analysis, including instrument performance checks (DFTPP), calibration standards containing the pesticides as described in Section 11.1.2.5, or it must be analyzed along with separate reference standards for the analytes to be confirmed.

11.1.2.8 If the analyte cannot be confirmed by either the procedures in Sections 11.1.2.5 or 11.1.2.7, then an aliquot of the extract prepared for the GC/ECD analysis must be analyzed by GC/MS, following any necessary solvent exchange and concentration steps. As in Section 11.1.2.4, analysis of a reference standard is

required if the GC/MS continuing calibration standard does not contain the analyte to be confirmed.

11.1.2.9 Regardless of which of the three approaches above is used for GC/MS confirmation, the appropriate blank must also be analyzed by GC/MS to demonstrate that the presence of the analyte was not the result of laboratory contamination. If the confirmation is based on the analysis of the semivolatile extract, then the semivolatile method blank extracted with the sample must also be analyzed. If the confirmation is based on the analysis of the extract prepared for the GC/ECD analysis, then the pesticide method blank extracted with the sample must be analyzed.

11.1.2.10 If the identification of the analyte cannot be confirmed by any of the GC/MS procedures above, and the concentration calculated from the GC/ECD analysis is greater than, or equal to, the concentration of the reference standard analyzed by GC/MS, then report the analyte as undetected, adjust the sample quantitation limit (the value associated with the "U" qualifier) to a sample concentration equivalent to the concentration of the GC/MS reference standard, and qualify the results on Form I with one of the laboratory-defined qualifiers ("X," "Y," or "Z"). In this instance, define the qualifier explicitly in the Sample Delivery Group (SDG) Narrative, and describe the steps taken to confirm the analyte in the SDG Narrative.

11.1.2.11 For GC/MS confirmation of single component analytes, the required deliverables are copies of the library search results (best TIC matches) or analyte spectrum and the spectrum of the reference standard. For Toxaphene, spectra of three characteristic peaks are required for both the sample component and the reference standard.

11.1.2.12 The purpose of the GC/MS analysis for the single component pesticides is for identification. The purpose of the GC/MS analysis for Toxaphene is to confirm the presence of chlorinated camphenes. The GC/MS analytical results for the pesticides shall not be used for quantitation and the GC/MS results shall not be reported on Form I and Form X. The exception noted in Section 11.1.2.10 applies only to analytes that cannot be confirmed above the reference standard concentration.

11.2 Calculations

11.2.1 Target Compounds

11.2.1.1 Quantitation for all analytes and surrogates must be performed and reported for each GC column.

11.2.1.2 Manual integration of peaks (e.g., measuring peak height with a ruler) is only permitted when accurate electronic integration of peaks cannot be done. If manual integration of peaks is required, it must be documented in the SDG Narrative.

11.2.1.3 The Contractor must quantitate each single component analyte and surrogate based on the Mean Calibration Factors ($\overline{CF}$s) from the most recent initial calibration. Do not use the analyses of the Individual Standard Mixtures used to demonstrate calibration verification for quantitation of samples.

11.2.1.4 The Contractor must quantitate Toxaphene based on the Mean Calibration Factors ($\overline{CF}$s) from the most recent initial calibration.

11.2.1.5 The chromatograms of all samples [including Laboratory Control Samples (LCSs), Matrix Spikes and Matrix Spike Duplicates (MS/MSDs)], standards, and required blanks must be reviewed by a qualified pesticide analyst before they are reported.

11.2.1.6 Calculate the sample concentration and on-column concentration of the single component pesticides and surrogates by using the following equations.

11.2.1.6.1 Water

11.2.1.6.1.1 EQ. 14 Concentration Calculation of Target Compounds in Water Samples

$$\text{Concentration } \mu g/L = \frac{(A_x)\,(V_t)\,(DF)\,(GPC)}{(\overline{CF})\,(V_o)\,(V_i)}$$

Where,

A_x = Response (peak area or height) of the compound to be measured.

$\overline{CF}$ = Mean Calibration Factor from the initial calibration (area/ng).

V_{in} = Volume of extract loaded onto GPC column.

V_{out} = Volume of extract collected after GPC cleanup.

V_t = Volume of concentrated extract (µL). (If GPC is <u>not</u> performed, then V_t = 10,000 µL. If GPC is performed, then $V_t = V_{out}$.

V_i = Volume of extract injected (µL). (If a single injection is made onto two columns, use ½ the volume in the syringe as the volume injected onto each column).

$GPC = \frac{V_{in}}{V_{out}}$ = Gel Permeation Chromatography factor. (If no GPC is performed, GPC = 1.0)

V_o = Volume of water extracted (mL). (NOTE: for instrument blanks and sulfur cleanup blanks, assume a 1,000 mL volume).

DF = Dilution Factor. The DF is defined as follows:

$$\frac{\text{µL most concentrated extract used to make dilution + µL clean solvent}}{\text{µL most concentrated extract used to make dilution}}$$

If no dilution is performed, DF = 1.0.

The $\overline{CF}$s used in Equations 14 - 17 are those from the most recent initial calibration. If the CFs used to determine the linearity of the initial calibration were based on peak area, then the concentration of the analyte in the sample

must be based on peak area. Similarly, if peak height was used to determine linearity, use peak height to determine the concentration in the sample.

11.2.1.6.1.2 EQ. 15 On-Column Concentration of Water Sample Extract

$$\text{On-Column Concentration (ng/µL)} = \frac{(A_x)}{(\overline{CF})\,(V_i)}$$

Where,

A_x = Same as EQ. 14.

$\overline{CF}$ = Same as EQ. 14.

V_i = Volume of extract injected (µL). (If a single injection is made onto two columns, use ½ the volume in the syringe as the volume injected onto each column).

11.2.1.6.2 Soil/Sediment

11.2.1.6.2.1 EQ. 16 Concentration of Target Compounds in Soil/Sediment Samples

$$\text{Concentration µg/Kg (Dry weight basis)} = \frac{(A_x)\,(V_t)\,(DF)\,(GPC)}{(\overline{CF})\,(V_i)\,(W_s)\,(D)}$$

Where,

A_x = Same as EQ. 14.

$\overline{CF}$ = Same as EQ. 14.

V_t = Same as EQ. 14.

V_i = Volume of extract injected (µL). (If a single injection is made onto two columns, use ½ the volume in the syringe as the volume injected onto each column).

W_S = Weight of sample extracted (g).

DF = Same as EQ. 14.

D = % dry weight or $\frac{100-\%\text{Moisture}}{100}$

GPC = Same as EQ. 14.

11.2.1.6.2.2 EQ. 17 On-Column Concentration of Soil Sample Extract

$$\text{On-Column Concentration (ng/µL)} = \frac{(A_x)}{(\overline{CF})\,(V_i)}$$

Where,

A_x = Same as EQ. 14.

$\overline{CF}$ = Same as EQ. 14.

V_i = Volume of extract injected (µL). (If a single injection is made onto two columns, use ½ the volume in the syringe as the volume injected onto each column).

11.2.1.7 The lower of the two concentrations calculated for each single component pesticide is reported on Form I. In addition, the concentrations calculated for both the GC columns are reported on Form X, along with a Percent Difference (%Difference) comparing the two concentrations. The Percent Difference is calculated according to Equation 18.

EQ. 18 Percent Difference Between Concentrations on Both GC Columns

$$\%D = \frac{Conc_H - Conc_L}{Conc_L} \times 100$$

Where,

$Conc_H$ = The higher of the two concentrations for the target compound in question.

$Conc_L$ = The lower of the two concentrations for the target compound in question.

NOTE: Using this equation will result in Percent Difference values that are always positive.

11.2.1.8 The quantitation of Toxaphene must be accomplished by comparing the heights or the areas of each of the three or four major peaks of in the sample with the CF for the same peaks established during the initial calibration sequence. The concentration of Toxaphene is calculated by using Equations 14 and 16, where A_x is the area for each of the major peaks. The concentration of each peak is determined and then a mean concentration for the three or four major peaks is determined on each column.

11.2.1.9 The reporting requirement for Toxaphene is similar to that for the single component analytes, except that the lower <u>mean</u> concentration (from three or four peaks) is reported on Form I, and the two mean concentrations reported on Form X. The two mean concentrations are compared by calculating the Percent Difference using Equation 18.

11.2.2 CRQL Calculation

11.2.2.1 Water Samples

EQ. 19 CRQL for Water Samples

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{\text{Contract Sample Vol (1000 mL)}}{V_o} \times DF \times \frac{Vt}{(V_c)}$$

Where,

Contract CRQL = The CRQL value reported in Exhibit C (Pesticides).

V_o = Same as EQ. 14.

DF = Same as EQ. 14.

V_t = Same as EQ. 14.

V_C = Contract concentrated extract volume [10,000 µL if Gel Permeation Chromatography (GPC) was <u>not</u> performed and $V_c = V_{out}$ if GPC was performed].

11.2.2.2 Soil/Sediment Samples

EQ. 20 CRQL for Soil/Sediment Samples

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{\text{Contract Sample Wt. (30 g)}}{W_s} \times DF \times \frac{Vt}{V_c} \times \frac{100}{(100 - M_p)}$$

Where,

Contract CRQL = The CRQL value reported in Exhibit C (Pesticides).

W_S = Same as EQ. 16.

DF = Same as EQ. 16.

V_t = Same as EQ. 16.

V_c = Same as EQ. 19.

M_P = Percent Moisture.

11.2.3 Surrogate Recoveries

11.2.3.1 The concentrations of the surrogates are calculated separately for each GC column in a similar manner as the other analytes, using Equations 14 and 16. Use the $\overline{CF}$s from the initial calibration. If two Individual Standard Mixtures are used, $\overline{CF}$s from Individual Standard Mixture A are to be used.

11.2.3.2 The recoveries of the surrogates are calculated for each GC column according to Equation 13, Percent Recovery (%R).

11.3 Technical Acceptance Criteria for Sample Analyses

The requirements below apply independently to each GC column and to all instruments used for these analyses (see exception in Section 11.3.8). Quantitation must be performed on each GC column.

11.3.1 Samples must be analyzed under the GC/ECD operating conditions in Section 9.1. The instrument must have met all initial calibration and calibration verification technical acceptance criteria. Samples must be cleaned-up, when required, with GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration verification. Samples must be cleaned-up using Florisil that meets the technical acceptance criteria for Florisil. Sample data must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, Performance Evaluation Mixtures (PEMs), and Individual Standard Mixture(s), as described in Section 10.4.2.1.

11.3.2 The sample must be extracted and analyzed within the contract holding times.

11.3.3 The LCS associated with the samples must meet the LCS technical acceptance criteria.

11.3.4 The samples must have an associated method blank meeting the method blank technical acceptance criteria. If a sulfur cleanup blank is associated with the samples, that blank must meet the sulfur cleanup blank technical acceptance criteria.

11.3.5 The RT for each of the surrogates must be within the RT window as calculated in Section 9.2.4.3, for both GC columns.

11.3.6 The Percent Recovery for the surrogates must be between 30-150%, inclusive. Up to one surrogate may fail this criteria per column.

NOTE: The surrogate recovery requirements do not apply to a sample that has been diluted.

11.3.7 No target compound responses may exceed the upper limit responses of the initial calibration or else extracts must be diluted and reanalyzed (Section 10.4.3).

11.3.8 A Toxaphene calibration verification standard (CS3) must be analyzed on the same instrument upon its detection in a sample. This standard must be analyzed within 72 hours of the analytes detection in a valid 12-hour period.

11.3.9 The identification of single component pesticides by GC methods is based primarily on RT data. The RT of the apex of a peak can only be verified from an on-scale chromatogram. The identification of Toxaphene by GC methods is based primarily on recognition of the pattern of RTs displayed on a chromatogram. Therefore, the following requirements apply to all data presented for single component analytes and Toxaphene.

11.3.9.1 When no compounds are identified in a sample, the chromatograms from the analyses of the sample extract must use the same scaling factor as was used for the low-point standard of the initial calibration associated with those analyses.

11.3.9.2 Chromatograms must display single component pesticides detected in the sample at less than full scale.

11.3.9.3 Chromatograms must display the largest peak of Toxaphene detected in the sample at less than full scale.

11.3.9.4 If an extract must be diluted (Section 10.4.3), chromatograms must display single component pesticides between 10-100% of full scale.

11.3.9.5 If an extract must be diluted (Section 10.4.3), chromatograms must display Toxaphene between 25-100% of full scale.

11.3.9.6 For any sample or blank, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.

11.3.9.7 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample analysis technical acceptance criteria MUST be met before data are reported. Samples contaminated from laboratory sources or associated with a contaminated method blank or sulfur cleanup blank will require reextraction and reanalysis at no additional cost to USEPA. Any samples analyzed that do not meet the technical acceptance criteria will require reextraction and/or reanalysis at no additional cost to USEPA.

11.4.2 If the sample analysis technical acceptance criteria are not met, check calculations, surrogate solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the technical acceptance criteria, in which case, the affected samples must be reanalyzed at no additional cost to USEPA after the corrective action.

11.4.3 The extract from samples that were cleaned up by GPC using an automated injection system and that have both surrogate recoveries outside the lower surrogate acceptance limits must be checked to assure that the proper amount was injected on the GPC column. If insufficient volume was injected, the sample must be reprepared and reanalyzed at no additional cost to USEPA.

11.4.4 If sample chromatograms have a high baseline or interfering peaks, inspect the system to determine the cause of the problem (e.g., carryover, column bleed, dirty ECD, contaminated gases, leaking septum, etc.). After correcting the problem, analyze an instrument blank to demonstrate that the system is functioning properly. Reanalyze the sample extracts. If the problem with the samples still exists, then those samples must be reextracted and reanalyzed. Samples that cannot be made to meet the given specifications after one reextraction and minimum three-step cleanup (GPC, Florisil, and sulfur cleanups) are reported in the SDG Narrative and do not require further analysis.

12.0 QUALITY CONTROL (QC)

12.1 Blank Analyses

12.1.1 Introduction

There are two types of blanks required by this method: the method blank and the instrument blank. A separate sulfur cleanup blank may also be required if some, but not all of the samples are subjected to sulfur cleanup. Samples that are associated with a sulfur cleanup blank are also associated with the method blank with which they were extracted. Both the method and sulfur cleanup blanks must meet the respective technical acceptance criteria for the sample analysis technical acceptance criteria to be met.

NOTE: Under no circumstances should blanks (method/instrument/sulfur cleanup) be analyzed at a dilution (i.e., blanks should always have a DF = 1.0).

12.1.2 Method Blank

12.1.2.1 Summary of Method Blank

A method blank is a volume of a clean reference matrix (reagent water for aqueous samples, or purified sodium sulfate or Hydromatrix for soil/sediment samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

12.1.2.2 Frequency of Method Blank

A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples [excluding Matrix Spike and Matrix Spike Duplicates (MS/MSDs), Performance Evaluation (PE) samples, and Laboratory Control Samples (LCSs)]. In addition, a method blank shall:

- Be extracted by the same procedure used to extract samples; and
- Be analyzed on each Gas Chromatograph/Electron Capture Detector (GC/ECD) system used to analyze associated samples.

12.1.2.3 Procedure for Method Blank

For water samples, measure 1.0 L of reagent water for each method blank aliquot and spike with 3.0 mL of the surrogate spiking solution (Section 7.2.2.1). For soil/sediment samples, measure 30 g of sodium sulfate or Hydromatrix and spike with 3.0 mL of the surrogate spiking solution. Extract, concentrate, and analyze the method blank according to Section 10.

12.1.2.4 Calculations for Method Blank

Calculate method blank results according to Section 11.

12.1.2.5 Technical Acceptance Criteria for Method Blank

12.1.2.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.1.2.5.2 All method blanks must be prepared and analyzed at the frequency described in Section 12.1.2.2, using the procedure in Section 12.1.2.3 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria. Method blanks must undergo Gel Permeation Chromatography (GPC) cleanup, when required, on a GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration checks. Method blanks must be cleaned-up using Florisil meeting the technical acceptance criteria for Florisil.

12.1.2.5.3 Method blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, Performance Evaluation Mixtures (PEMs), and Individual Standard Mixtures, as described in Section 10.4.2.1.

12.1.2.5.4 The concentration of the target compounds [Exhibit C (Pesticides)] in the method blank must be less than the Contract Required Quantitation Limit (CRQL) for each target compound.

12.1.2.5.5 The method blank must meet all sample technical acceptance criteria in Sections 11.3.5 and 11.3.9.

12.1.2.5.6 Surrogate recoveries must fall within the acceptance window of 30-150%. These limits are <u>not</u> advisory.

12.1.2.5.7 Method blanks must be analyzed at the original concentration only (i.e., DF = 1.0).

12.1.2.6 Corrective Action for Method Blank

12.1.2.6.1 If a method blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out of QC limits.

12.1.2.6.2 If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. Further, all samples (including LCSs, MS/MSDs, and PE samples) processed with a method blank that does not meet the method blank technical acceptance criteria (i.e., contaminated) will require reextraction and reanalysis at no additional cost to USEPA. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.

12.1.2.6.3 If surrogate recoveries in the method blank do not meet the technical acceptance criteria listed in Section 12.1.2.5.6, first reanalyze the method blank. If the surrogate recoveries do not meet the technical acceptance criteria after reanalysis, then the method blank and all samples (including LCSs, MS/MSDs, and PE samples) associated with that method blank must be reextracted and reanalyzed at no additional cost to USEPA.

12.1.2.6.4 If the method blank fails to meet a technical acceptance criteria other than Sections 12.1.2.5.4 and 12.1.2.5.6, then the problem is an instrument problem. Correct the instrument problem, recalibrate the instrument (if necessary) and reanalyze the method blank.

12.1.3 Sulfur Cleanup Blank

12.1.3.1 Summary of Sulfur Cleanup Blank

The sulfur cleanup blank is a modified form of the method blank. The sulfur cleanup blank is hexane spiked with the surrogates and passed through the sulfur cleanup and analysis procedures. The purpose of the sulfur cleanup is to determine the levels of contamination associated with the separate sulfur cleanup steps.

12.1.3.2 Frequency of Sulfur Cleanup Blank

The sulfur cleanup blank is prepared when only part of a set of samples extracted together requires sulfur removal. A method blank is associated with the entire set of samples. The sulfur cleanup blank is associated with the part of the set that required sulfur cleanup. If all the samples associated with a given method blank are subjected to sulfur cleanup, then no separate sulfur cleanup blank is required.

12.1.3.3 Procedure for Sulfur Cleanup Blank

The concentrated volume of the blank must be the same as the final volume of the samples associated with the blank. The sulfur blank must also contain the surrogates at the same concentrations as the sample extracts (assuming 100.0% recovery). Therefore, add 0.6 mL of the surrogate spiking solution (Section 7.2.2.1) to 1.4 mL of hexane in a clean vial.

12.1.3.3.1 Proceed with the sulfur removal (Section 10.3.3) using the same technique (mercury or copper) as the samples associated with the blank.

12.1.3.3.2 Analyze the sulfur blank according to Section 10.4.2.

12.1.3.4 Calculations for Sulfur Cleanup Blank

12.1.3.4.1 Assuming that the material in the sulfur blank resulted from the extraction of a 1 L water sample, calculate the concentration of each analyte using Equation 14 in Section 11.2.1.6.1.1. Compare the results to the CRQL values in Exhibit C (Pesticides).

12.1.3.4.2 See Section 11.2 for the equations for the other calculations.

12.1.3.5 Technical Acceptance Criteria for Sulfur Cleanup Blanks

12.1.3.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each column.

12.1.3.5.2 All sulfur cleanup blanks must be prepared and analyzed at the frequency described in Section 12.1.3.2 using the procedure in Section 12.1.3.3 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.1.3.5.3 Sulfur cleanup blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs, and Individual Standard Mixtures, as described in Section 10.4.2.1.

12.1.3.5.4 The concentration of the target compounds [Exhibit C (Pesticides)] in the sulfur cleanup blank must be less than the CRQL for each target compound.

12.1.3.5.5 The sulfur cleanup blank must meet all sample technical acceptance criteria in Sections 11.3.5 and 11.3.9.

12.1.3.5.6 Surrogate recoveries must fall within the acceptance windows of 30-150%. These limits are not advisory.

12.1.3.6 Corrective Action for Sulfur Cleanup Blank

12.1.3.6.1 If a sulfur cleanup blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out-of-control.

12.1.3.6.2 If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. Further, all samples processed with a sulfur cleanup blank that does not meet the sulfur cleanup blank technical acceptance criteria (i.e., contaminated) will require reextraction and reanalysis at no additional cost to USEPA. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.

12.1.3.6.3 If surrogate recoveries in the sulfur cleanup blank do not meet the technical acceptance criteria in Section 12.1.3.5.6, first reanalyze the sulfur cleanup blank. If the surrogate recoveries do not meet the technical acceptance criteria after reanalysis, then the sulfur cleanup blank and all samples associated with that sulfur cleanup blank must be re-prepared/reextracted and reanalyzed at no additional cost to USEPA.

12.1.3.6.4 If the sulfur cleanup blank fails to meet a technical acceptance criteria other than Sections 12.1.3.5.4 and 12.1.3.5.6, then the problem is an instrument problem. Correct the instrument problem, recalibrate the instrument (if necessary), and reanalyze the sulfur cleanup blank.

12.1.4 Instrument Blank

12.1.4.1 Summary of Instrument Blank

An instrument blank is a volume of clean solvent spiked with the surrogates and analyzed on each GC column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis, particularly with regard to carryover of analytes from standards or highly contaminated samples into other analyses.

12.1.4.2 Frequency of Instrument Blank

The first analysis in a 12-hour analysis sequence (Section 9.3.2) must be an instrument blank. All groups of acceptable sample analyses are to be preceded and followed by acceptable instrument blanks (Section 10.4.2.1). If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an instrument blank must be analyzed to initiate a new 12-hour sequence (Section 9.3.2).

12.1.4.3 Procedure for Instrument Blank

12.1.4.3.1 Prepare the instrument blank by spiking the surrogates into hexane or iso-octane for a concentration of 20.0 ng/mL of tetrachloro-m-xylene and 40.0 ng/mL of decachlorobiphenyl.

12.1.4.3.2 Analyze the instrument blank according to Section 10.4, at the frequency listed in Section 12.1.4.2.

12.1.4.4 Calculations for Instrument Blank

12.1.4.4.1 Assuming that the material in the instrument blank resulted from the extraction of a 1 L water sample, calculate the concentration of each analyte using Equation 14 in Section 11.2.1.6.1.1. Compare the results to the CRQL values for water samples in Exhibit C (Pesticides).

12.1.4.4.2 See Section 11.2 for the equations for the other calculations.

12.1.4.5 Technical Acceptance Criteria for Instrument Blanks

12.1.4.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed and reported independently on Form I PEST for each GC column.

12.1.4.5.2 All instrument blanks must be prepared and analyzed at the frequency described in Section 12.1.4.2, using the procedure in Section 10.4 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.1.4.5.3 The concentration of each target compound [Exhibit C (Pesticides)] in the instrument blank must be less than the CRQL for that analyte.

12.1.4.5.4 The instrument blank must meet all sample technical acceptance criteria in Sections 11.3.5 and 11.3.9.

12.1.4.5.5 Instrument blanks must be analyzed at the original concentration only (i.e., DF = 1.0).

12.1.4.6 Corrective Action for Instrument Blank

12.1.4.6.1 If compounds are detected at concentrations greater than the CRQL, or the surrogate Retention Times (RTs) are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples that were run between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be run before additional data are collected. All samples (including LCSs, MS/MSDs, and PE samples) and required blanks that were run after the last acceptable instrument blank must

be reinjected during a valid run sequence and must be reported at no additional cost to USEPA.

12.2 Laboratory Control Sample (LCS)

12.2.1 Summary of LCS

The LCS is an internal laboratory QC sample designed to assess [on a Sample Delivery Group (SDG)-by-SDG basis] the capability of the Contractor to perform the analytical method listed in this Exhibit.

12.2.2 Frequency of LCS

The LCS must be prepared, extracted, analyzed, and reported once for every 20 field samples of a similar matrix, per SDG. The LCS must be extracted and analyzed concurrently with the samples in the SDG using the same extraction protocol, cleanup procedure, and instrumentation as the samples in the SDG.

12.2.3 Procedure for LCS

For water samples, measure 1.0 L of reagent water and spike with 1.0 mL of the LCS spiking solution and 3.0 mL of the surrogate spiking solution (Section 7.2.2). For soil/sediment samples, measure 30 g of a clean reference matrix (e.g., sodium sulfate, Hydromatrix, sand) and spike with 1.0 mL of the LCS spiking solution and 3.0 mL of the surrogate spiking solution. Extract, concentrate, and analyze the LCS according to Section 10.

12.2.4 Calculations for LCS

12.2.4.1 Calculate the results according to Section 11.

12.2.4.2 Calculate individual compound recoveries of the LCS using Equation 13.

12.2.5 Technical Acceptance Criteria For LCS

12.2.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.2.5.2 The LCS must be analyzed at the frequency described in Section 12.2.2 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.2.5.3 The LCS must be prepared as described in Section 12.2.3.

12.2.5.4 The LCS must meet all sample technical acceptance criteria in Sections 11.3.5, 11.3.7, and 11.3.9.

12.2.5.5 The Percent Recovery (%R) for each of the compounds in the LCS (water and soil/sediment) must be within the recovery limits listed in Table 2.

12.2.5.6 Surrogate recoveries must fall within the acceptance windows of 30-150%. These limits are <u>not</u> advisory.

12.2.6 Corrective Action for LCS

12.2.6.1 If the LCS technical acceptance criteria for the surrogates or the LCS compound recovery are not met, check calculations, the

surrogate and LCS solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the surrogate and LCS recovery criteria.

12.2.6.2 LCS technical acceptance criteria MUST be met before data are reported. LCS contamination from laboratory sources or any LCS analyzed not meeting the technical acceptance criteria will require reextraction and reanalysis of the LCS at no additional cost to USEPA.

12.2.6.3 All samples (including MS/MSD and PE samples) and required blanks, prepared and analyzed in an SDG with an LCS that does not meet the technical acceptance criteria, will also require reextraction and reanalysis at no additional cost to USEPA.

12.3 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

12.3.1 Summary of MS/MSD

To evaluate the effects of the sample matrix on the methods used for pesticide analyses, USEPA has prescribed a mixture of pesticide target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method.

12.3.2 Frequency of MS/MSD Analysis

12.3.2.1 An MS/MSD must be extracted and analyzed for every 20 field samples of a similar matrix in an SDG.

12.3.2.2 As part of USEPA's Quality Assurance/Quality Control (QA/QC) program, water rinsate samples and/or field blanks may be delivered to a laboratory for analysis. Do not perform MS/MSD analysis on a water rinsate sample or field blank.

12.3.2.3 If the USEPA Region requesting an MS/MSD designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample volume remaining to perform an MS/MSD, then the Contractor shall choose another sample to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify the Sample Management Office (SMO) that insufficient sample was received and identify the USEPA sample selected for the MS/MSD analysis. SMO shall contact the Region for confirmation immediately after notification. The rationale for the choice of another sample other than the one designated by USEPA shall be documented in the SDG Narrative.

12.3.2.4 If there is insufficient sample volume remaining in any of the samples in an SDG to perform the requested MS/MSD, the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD be performed, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative.

12.3.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.3.2.1, the Contractor shall contact SMO. SMO will contact the Region to determine which samples should have MS/MSD performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If

this procedure is not followed, the Contractor will not be paid for MS/MSD analysis performed at a greater frequency than required by the contract.

12.3.2.6 When a Contractor receives only PE samples, no MS/MSD shall be performed within that SDG.

12.3.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the requested MS/MSD analysis when the Region did not designate a sample to be used for this purpose.

12.3.3 Procedure for Preparing MS/MSD

12.3.3.1 For water samples, measure out two additional 1 L aliquots of the sample chosen for spiking. Adjust the pH of the samples (if required) and fortify each with 1.0 mL of the matrix spiking solution and 3.0 mL of the surrogate spiking solution (Section 7.2.2). Extract, concentrate, cleanup, and analyze the MS/MSD according to Section 10.

12.3.3.2 For soil/sediment samples, weigh out two additional 30 g aliquots of the sample chosen for spiking. Add 1.0 mL of the matrix spiking solution and 3.0 mL of the surrogate spiking solution (Section 7.2.2). Extract, concentrate, cleanup, and analyze the MS/MSD according to Section 10.

12.3.3.3 MS/MSD samples must be analyzed at the same concentration as the most concentrated extract for which the original sample results will be reported. Do not dilute the MS/MSD samples further to get either spiked or non-spiked analytes within calibration range.

12.3.4 Calculations for MS/MSD

The Percent Recoveries and the Relative Percent Difference (RPD) between the recoveries of each of the compounds in the MS/MSD samples will be calculated and reported by using the following equations:

EQ. 21 Percent Recovery of Spike Compounds in MS/MSD Samples

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike Sample Result.

SR = Original Sample Result.

SA = Spike Added.

EQ. 22 Relative Percent Difference Between MS/MSD Spike Recoveries

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where,

RPD = Relative Percent Difference.

MSR = Matrix Spike Recovery.

MSDR = Matrix Spike Duplicate Recovery.

12.3.5 Technical Acceptance Criteria for MS/MSD

12.3.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.3.5.2 All MS/MSDs must be prepared and analyzed at the frequency described in Section 12.3.2, using the procedure above and in Section 10, on a GC/ECD system meeting the initial calibration, calibration verification, and blank technical acceptance criteria. MS/MSDs must be cleaned up with GPC, when required, on a GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration checks. MS/MSDs must be cleaned-up using Florisil meeting the technical acceptance criteria for Florisil. MS/MSDs must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs, and Individual Standard Mixture(s) (A, B, or C) as described in Section 10.4.2.1.

12.3.5.3 The samples must be extracted and analyzed within the contract required holding times.

12.3.5.4 The RT for each of the surrogates must be within the RT window as calculated in Section 9 for both GC columns.

12.3.5.5 The limits for Matrix Spike compound recovery and RPD are given in Table 3. As these limits are only advisory, no further action by the laboratory is required. However, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from USEPA.

12.3.6 Corrective Action for MS/MSD

Any MS/MSD which fails to meet the technical acceptance criteria in Sections 12.3.5.1, 12.3.5.2, and 12.3.5.4 must be reanalyzed at no additional cost to USEPA.

12.4 Method Detection Limit (MDL) Determination

12.4.1 Before any field samples are analyzed under the contract, the MDL for each single compound pesticide target compound and Toxaphene shall be determined on each instrument used for analysis. MDL determination is matrix- and level-specific (i.e., the MDL shall be determined for water and soil samples). The MDLs must be verified annually thereafter (see Section 12.4.2 for MDL verification procedures), until the contract expires or is terminated, or after major

instrument maintenance. Major instrument maintenance includes, but is not limited to, cleaning or replacement of the detector and replacement of the GC column.

12.4.2 To determine the MDLs, the Contractor shall run an MDL study following the procedures specified in 40 CFR Part 136. The Contractor shall analyze the MDL samples on each instrument used for field sample analyses. MDL verification for water samples is achieved by analyzing a single reagent water blank (see method blank for water samples in Section 12.1.2) spiked with each single component pesticide target compound and Toxaphene at a concentration equal to two times the analytically determined MDL. MDL verification for soil samples is achieved by analyzing a single purified solid matrix blank (see method blank for soil samples in Section 12.1.2) spiked with each single component pesticide target compound and Toxaphene at a concentration equal to 2 times the analytically determined MDL. Each target compound must produce a response and meet the criteria in Section 11.1.1. Samples used for MDL determination and verification must be subjected to the same extraction and cleanup procedures used for field samples. The resulting chromatograms of each target compound must meet the qualitative identification criteria outlined in Sections 11.1.1 for both columns.

12.4.3 The determined concentration of the MDL must be less than the CRQL.

12.4.4 All documentation for the MDL studies shall be maintained at the laboratory and provided to USEPA upon written request.

13.0 METHOD PERFORMANCE

Not Applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, USEPA recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036, (202) 872-4386.

15.0 WASTE MANAGEMENT

USEPA requires that laboratory waste management practices be consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, to comply with the letter and spirit of any sewer discharge permits and regulations, and to comply with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

16.1 American Society of Testing and Materials. Standard Test Method for Determination of Organochlorine Pesticides in Water by Capillary Column Gas Chromatography. D5812-96(2002)e1.

16.2 US Environmental Protection Agency. Organochlorine Pesticides by Gas Chromatography. SW-846 Method 8081B, Revision 2. January 1998.

16.3 US Environmental Protection Agency. Separatory Funnel Liquid-Liquid Extraction. SW-846 Method 3510C, Revision 3. December 1996.

16.4 US Environmental Protection Agency. Continuous Liquid-Liquid Extraction. SW-846 Method 3520C, Revision 3. December 1996.

16.5 US Environmental Protection Agency. Automated Soxhlet Extraction. SW-846 Method 3541, Revision 0. September 1994.

16.6 US Environmental Protection Agency. Pressurized Fluid Extraction (PFE). SW-846 Method 3545A, Revision 1. January 1998.

16.7 US Environmental Protection Agency. Ultrasonic Extraction. SW-846 Method 3550C, Revision 3. November 2000.

16.8 US Environmental Protection Agency. Alumina Cleanup. SW-846 Method 3610B, Revision 2. December 1996.

16.9 US Environmental Protection Agency. Silica Gel Cleanup. SW-846 Method 3630C, Revision 3. December 1996.

16.10 US Environmental Protection Agency. Gel-Permeation Cleanup. SW-846 Method 3640A, Revision 1. September 1994.

16.11 US Environmental Protection Agency. Acid-Base Partition Cleanup. SW-846 Method 3650B, Revision 2. December 1996.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

Retention Time Windows for Single Component Analytes, Toxaphene, and Surrogates

Compound	RT Window (minutes)
alpha-BHC	± 0.05
beta-BHC	± 0.05
gamma-BHC (Lindane)	± 0.05
delta-BHC	± 0.05
Heptachlor	± 0.05
Aldrin	± 0.05
alpha-Chlordane	± 0.07
gamma-Chlordane	± 0.07
Heptachlor epoxide	± 0.07
Dieldrin	± 0.07
Endrin	± 0.07
Endrin aldehyde	± 0.07
Endrin ketone	± 0.07
4,4'-DDD	± 0.07
4,4'-DDE	± 0.07
4,4'-DDT	± 0.07
Endosulfan I	± 0.07
Endosulfan II	± 0.07
Endosulfan sulfate	± 0.07
Methoxychlor	± 0.07
Toxaphene	± 0.07
Tetrachloro-m-xylene	± 0.05
Decachlorobiphenyl	± 0.10

Table 2

Laboratory Control Sample Recovery Limits

Compound	Percent Recovery
gamma-BHC	50-120
Heptachlor epoxide	50-150
Dieldrin	30-130
4,4'-DDE	50-150
Endrin	50-120
Endosulfan sulfate	50-120
gamma-Chlordane	30-130

NOTE: The recovery limits for any of the compounds in the LCS may be expanded at any time during the period of performance if USEPA determines that the limits are too restrictive.

Table 3

Matrix Spike Recovery and
Relative Percent Difference Limits

Compound	Percent Recovery Water	RPD Water	Percent Recovery Soil	RPD Soil
gamma-BHC (Lindane)	56-123	0-15	46-127	0-50
Heptachlor	40-131	0-20	35-130	0-31
Aldrin	40-120	0-22	34-132	0-43
Dieldrin	52-126	0-18	31-134	0-38
Endrin	56-121	0-21	42-139	0-45
4,4'-DDT	38-127	0-27	23-134	0-50

Table 4

Concentration Levels of Calibration Standards

Compound	Concentration (ng/mL)				
	CS1	CS2	CS3	CS4	CS5
alpha-BHC	5.0	10	20	40	80
gamma-BHC	5.0	10	20	40	80
Heptachlor	5.0	10	20	40	80
Endosulfan I	5.0	10	20	40	80
Dieldrin	10	20	40	80	160
Endrin	10	20	40	80	160
4,4'-DDD	10	20	40	80	160
4,4'-DDT	10	20	40	80	160
Methoxychlor	50	100	200	400	800
beta-BHC	5.0	10	20	40	80
delta-BHC	5.0	10	20	40	80
Aldrin	5.0	10	20	40	80
Heptachlor-epoxide	5.0	10	20	40	80
4,4'-DDE	10	20	40	80	160
Endosulfan II	10	20	40	80	160
Endosulfan sulfate	10	20	40	80	160
Endrin ketone	10	20	40	80	160
Endrin aldehyde	10	20	40	80	160
alpha-Chlordane	5.0	10	20	40	80
gamma-Chlordane	5.0	10	20	40	80
Tetrachloro-m-xylene	5.0	10	20	40	80
Decachlorobiphenyl	10	20	40	80	160
Toxaphene	500	1000	2000	4000	8000

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EXHIBIT D

ANALYTICAL METHOD FOR THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS

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Exhibit D - Analytical Methods for Semivolatiles

Table of Contents

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1.0 SCOPE AND APPLICATION

1.1 In 1978, US Environmental Protection Agency (USEPA) Headquarters and Regional representatives designed analytical methods for the analysis of semivolatiles in hazardous waste samples. These methods were based on USEPA Method 625, Base/Neutral and Acids. In 1980, these methods were adopted for use in the Contract Laboratory Program (CLP). As the requirements of Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) evolved, the CLP methods, as well as their precedent USEPA 600 Series methods, established the basis for other USEPA methods to perform the analysis of semivolatiles contained in hazardous waste samples (i.e., SW-846). The following CLP method has continuously improved to incorporate technological advancements promulgated by USEPA, and has continued to set the standard for the preparation, extraction, isolation, identification, and reporting of semivolatiles at hazardous waste sites.

1.2 The analytical method that follows is designed to analyze water and soil/sediment samples from hazardous waste sites for the semivolatile organic compounds on the Target Compound List (TCL) [see Exhibit C (Semivolatiles)]. It covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to Gas Chromatography (GC). The method involves solvent extraction of the matrix sample, characterization to determine the appropriate analytical protocol to be used, followed by appropriate cleanup procedure and GC/Mass Spectrometry (MS) analysis to determine the semivolatile organic compounds present in the sample. In addition, if requested, sample extracts will be analyzed for a select group of compounds, including Polynuclear Aromatic Hydrocarbons (PAHs) and pentachlorophenol by GC/MS, using the Selected Ion Monitoring (SIM) technique. If a SIM analysis is requested, a full scan analysis using the low-level method must be performed <u>first</u>. If all PAHs and pentachlorophenol are detected during the full scan analysis using the low-level method, then a SIM analysis is not to be performed and this should be documented in the SDG Narrative.

1.3 This analytical method provides the use of SW-846 Methods 3520C (Revision 3, December 1996); 3541 (Revision 0, September 1994); 3545A (Revision 1, January 1998); and 3550C (Revision 3, November 2000) for the extraction of soil/sediment samples. The method includes the use of Deuterated Monitoring Compounds (DMCs) for precision and accuracy assessment.

1.4 Problems have been associated with the following compounds analyzed by this method.

1.4.1 Dichlorobenzidine and 4-chloroaniline can be subject to oxidative losses during solvent concentration.

1.4.2 Hexachlorocyclopentadiene is subject to thermal decomposition in the GC inlet, chemical reactions in acetone solution, and photochemical decomposition.

1.4.3 N-nitrosodiphenylamine decomposes in the GC inlet forming diphenylamine and consequently, may be detected as diphenylamine.

2.0 SUMMARY OF METHOD

2.1 Water

A 1 L aliquot of sample is acidified to pH 2.0, mixed with Deuterated Monitoring Compounds (DMCs), and extracted with methylene chloride using a continuous liquid-liquid extractor. Separatory funnel extraction is NOT permitted. The methylene chloride extract is dried with sodium sulfate (or an equivalent drying agent such as Hydromatrix™), concentrated, subjected to Gel Permeation Chromatography (GPC) (GPC is required when higher molecular weight compounds are present that interfere with the analyses of target compounds; GPC is optional for all other circumstances), and analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) for extractable organics.

2.2 Low-Level Soil/Sediment

A 30 g portion of soil/sediment is mixed with anhydrous powdered sodium sulfate (or Hydromatrix) and DMCs, and extracted with 1:1 methylene chloride/acetone solution using an ultrasonic probe, a Soxhlet extractor, or a pressurized fluid extractor. The extract is concentrated, subjected to GPC cleanup, and analyzed by GC/MS for extractable organics.

The Contractor must determine whether a soil/sediment sample should be analyzed by the low-level or medium-level method, using a USEPA-approved screening procedure or an in-house laboratory screening procedure.

2.3 Medium-Level Soil/Sediment

Approximately 1 g portion of soil/sediment is mixed with anhydrous powdered sodium sulfate (or Hydromatrix) and DMCs in a vial and extracted with methylene chloride. The methylene chloride extract is subjected to GPC cleanup and optional silica gel cleanup (SW-846 Method 3630C), prior to analysis by GC/MS for extractable organics.

2.4 Internal standards are added to all samples, standards, requested Matrix Spike and Matrix Spike Duplicates (MS/MSDs), and blanks. The target compounds and DMCs are identified in the samples and blanks by analyzing standards that contain all target compounds, DMCs, and internal standards under the same conditions and comparing resultant mass spectra and GC Retention Times (RTs). A Relative Response Factor (RRF) is established for each target compound and DMC during the initial and continuing calibrations by comparing the mass spectral response from the Extracted Ion Current Profile (EICP) for the primary quantitation ion produced by that compound to the mass spectra response for the primary quantitation ion produced by the associated internal standard compound. Each identified target compound and DMC is quantitated by comparing the instrument response for the compound in the sample, standard, requested MS/MSD, or blank with the instrument response of the associated internal standard, while taking into account the Mean RRF ($\overline{RRF}$) from the most recent initial calibration, the sample weight/volume, the moisture content of soil samples, and any sample dilutions.

2.5 Non-target compounds are identified by comparing the resultant mass spectra from the non-target compounds to mass spectra contained in the NIST (2002 release or later), Wiley (1991 release or later), or equivalent mass spectral library. Non-target compounds are quantitated by comparing the mass spectra response from the Reconstructed Ion Chromatogram (RIC) for the non-target compound peaks to the mass spectra response produced by the nearest internal standard. An RRF of 1 is assumed.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts and/or elevated baselines in the Extracted Ion Current Profiles (EICPs). All of the materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of Occupational Safety & Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should be made available to all personnel involved in the chemical analyses.

5.2 Specifically, concentrated sulfuric acid presents some hazards and is moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this analytical method is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Glassware

6.1.1 Continuous Liquid-Liquid Extractors - Equipped with polytetrafluoroethylene (PTFE) or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf extractor) or hydrophobic membrane-based extractor.

6.1.2 Beakers - 400 mL.

6.1.3 Syringes - 2 µL, 10 µL, 0.1 mL, 0.2 mL, 0.5 mL. 1 mL, 5 mL, and 10 mL with Luer-lok fitting.

6.1.4 Glass Scintillation Vials - At least 20 mL with screw-cap and PTFE or aluminum foil liner.

6.1.5 Pasteur Pipets - 1 mL glass, disposable.

6.1.6 Vial and Caps - Amber glass, 2 mL capacity with PTFE-lined screw-cap, 2 mL capacity for Gas Chromatograph (GC) auto sampler.

Vials for collection of extracts - 40 mL or 60 mL, pre-cleaned, open top screw-cap with PTFE-lined silicone septum.

6.1.7 Drying Column - 19 mm ID chromatographic column with coarse frit (substitution of a small pad of borosilicate glass wool for the frit will help prevent cross contamination of sample extracts).

6.1.8 Class A Graduated Cylinder - 100 mL.

6.1.9 Class A Volumetric Flasks - 10 mL.

6.2 Kuderna-Danish (K-D) Apparatus

6.2.1 Concentrator Tubes - 15 mL and 10 mL graduated. Calibration must be checked at the volumes employed in the test. Ground-glass stoppers are used to prevent evaporation of extracts.

6.2.2 Evaporative Flasks - 500 mL. Attach to concentrator tube with springs.

6.2.3 Snyder Column - Three-ball macro.

6.2.4 Snyder Column - Two-ball micro.

6.3 Spatula - Stainless steel or PTFE.

6.4 Balances - Analytical, capable of accurately weighing ±0.0001 g, and one capable of weighing 100 g (±0.01 g). The balances must be calibrated with Class S weights or known reference weights once per each 12-hour work shift. The balances must be calibrated with Class S weights at a minimum of once per month. The balances must also be checked annually by a certified technician.

6.5 Ultrasonic Cell Disrupters - 300 watt with pulsing capability, 1/2 inch tapered disrupter horn, 1/8 inch standard tapered microtip probe, and 3/4 inch tapered high gain "Q" disrupter horn, or 3/4 inch standard solid disrupter horn.

NOTE: In order to ensure that sufficient energy is transferred to the sample during extraction, the microtip probe or horn shall be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

6.6 Sonabox Acoustic Enclosure (or equivalent) - For use with disrupter to decrease noise level.

6.7 Pressurized Fluid Extraction Device - Dionex Accelerated Solvent Extractor (ASE-300) or equivalent with appropriately sized extraction cells. Currently, 100 mL cells are available that will accommodate greater than 30 g samples. Cells should be made of stainless steel or other material capable of withstanding the pressure environments (2000+ psi) necessary for this procedure.

6.7.1 Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.8 Automated Soxhlet Extraction System - With temperature-controlled oil bath. Silicone oil must not be used because it destroys the rubber parts. The apparatus must be used in a hood.

6.8.1 Cellulose or Glass Extraction Thimble - 26 mm ID x 60 mm.

6.8.2 Glass Extraction Cups.

6.8.3 Thimble Adapters.

6.8.4 Viton Seals.

6.9 Vacuum Filtration Apparatus

6.9.1 Buchner Funnel.

6.9.2 Filter Paper - Whatman No. 41 or equivalent.

6.10 Borosilicate Glass Wool - Rinsed with methylene chloride.

6.11 Test Tube Rack

6.12 Silicon Carbide Boiling Chips - Approximately 10/40 mesh. Heat to 400°C for 30 min. or Soxhlet extract with methylene chloride. PTFE boiling chips solvent rinsed prior to use are acceptable.

6.13 Water Bath - Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

6.14 Oven - Drying.

6.15 Desiccator.

6.16 Crucibles - Porcelain.

6.17 Nitrogen Evaporation Device - Equipped with a water bath that can be maintained at 35-40°C. To prevent the release of solvent fumes into the laboratory, the nitrogen evaporator device must be used in a hood.

6.18 pH Paper - Including narrow range capable of measuring a pH of 2.0.

6.19 pH Meter - With a combination glass electrode. Calibrate according to manufacturer's instructions. The pH meter shall be calibrated prior to each use.

6.20 Gel Permeation Chromatography (GPC) Cleanup System

6.20.1 GPC System - Systems that perform satisfactorily have been assembled from the following components - a High Performance Liquid Chromatograph (HPLC) pump, an auto sampler or a valving system with sample loops, and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements of Section 10.3.3.

NOTE: GPC cleanup is required for all soil/sediment extracts, and for water extracts containing higher molecular weight contaminants that interfere with the analyses of the target compounds.

6.20.2 Chromatographic Column - 700 mm x 25 mm ID glass column. Flow is upward. To simplify switching from the ultraviolet (UV) detector during calibration to the GPC collection device during extract cleanup, an optional double 3-way valve may be attached so that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

6.20.3 Guard Column (optional) - 5 cm, with appropriate fittings to connect the inlet side of the analytical column.

6.20.4 Bio Beads (SX-3) - 200-400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, or equivalent). An additional 5 g of Bio Beads are required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

6.20.5 Ultraviolet Detector - Fixed wavelength (254 nm) with a semi-prep flow-through cell.

6.20.6 Strip Chart Recorder, recording integrator, or laboratory data system.

6.20.7 Syringe Filter Assembly disposable - 5 micron filter discs.

NOTE: Consult the instrument operation manual to determine the proper filter disc to use in the system. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

6.21 Gas Chromatograph/Mass Spectrometer (GC/MS) System

6.21.1 Gas Chromatograph - The GC system must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout the temperature program operations. The system must be suitable for splitless injection and have all required accessories including syringes, analytical columns, and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants or flow controllers with rubber components are not to be used.

6.21.2 Gas Chromatography Column - Minimum length 30 m x 0.25 mm ID (or 0.32 mm) bonded-phase silicon coated fused silica capillary column DB-5 (J&W Scientific); RTX-5, RTX-5 Sil Ms (Restek); Zebron ZB-5 (Phenomenex); SPB-5 (Supelco); AT-5 (Alltech); HP-5 (Agilent); CP-Sil 8CB (Chrompack); 007-2 (Quadrex); BP-5 (SGE); or equivalent. Note that this is a minimum requirement for column length. Longer columns may be used. Although a film thickness of 1.0 µm is recommended because of its larger capacity, a film thickness of 0.25 µm may be used. A description of the GC column used for analysis shall be provided in the SDG Narrative.

6.21.2.1 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantification of the compounds listed in Exhibit C (Semivolatiles).
- The analytical results generated using the column meet the initial and continuing calibration verification technical acceptance criteria listed in the analytical method, and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Semivolatiles).
- The column can accept up to 160 ng of each compound listed in Exhibit C (Semivolatiles), without becoming overloaded.
- The column provides equal or better resolution of the compounds listed in Exhibit C (Semivolatiles), than columns listed in Section 6.21.2.

6.21.2.2 As applicable, follow the manufacturer's instructions for use of its product.

6.21.2.3 The Contractor must maintain documentation that the column met the criteria in Section 6.21.2.1. The minimum documentation is as follows:

6.21.2.3.1 Manufacturer provided information concerning the performance characteristics of the column.

6.21.2.3.2 Reconstructed ion chromatograms and data system reports generated on the GC/MS used for Contract Laboratory Program (CLP) analyses:

- From blanks that demonstrate that there are no contaminants that interfere with the semivolatile analysis when using the column.
- For initial calibration standards analyzed using the column.
- For Continuing Calibration Verification (CCV) standards analyzed using the column.

6.21.2.3.3 Based on the Contractor-generated data described in Section 6.21.2.3.2, the Contractor must complete a written review, signed by the Laboratory Manager, certifying that:

- The column performance meets the technical acceptance criteria in Sections 9.3.5 and 9.4.5.

- The low-point initial calibration standard analysis has adequate sensitivity to meet the semivolatile CRQLs.
- The high-point initial calibration standard analysis was not overloaded.
- The column does not introduce contaminants that interfere with the identification and/or quantitation of compounds listed in Exhibit C (Semivolatiles).

6.21.2.4 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request by the USEPA Regional CLP Project Officer (CLP PO).

6.21.2.5 **PACKED COLUMNS CANNOT BE USED.**

6.21.3 Mass Spectrometer

Must be capable of scanning from 35-500 amu every 1 sec. or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum that meets the tuning acceptance criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet. The system must be capable of Selected Ion Monitoring (SIM). The instrument must be vented to the outside of the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.21.4 GC/MS Interface

The Contractor may use any GC/MS interface that provides acceptable sensitivity at CRQLs. However, direct insertion of the GC column into the Mass Spectrometer source is the recommended interface. GC/MS interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

6.21.5 Data System

A computer system interfaced to the MS that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundance versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The NIST (2002 release or later), Wiley (1991 release or later), or equivalent mass spectral library shall be used as the reference library. The operational data system must be capable of and is required to flag all data files that have been edited manually by laboratory personnel.

6.21.6 Data Storage Device

Data storage devices must be suitable for long-term, off-line storage of data.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent Water - Reagent water is defined as water in which an interferent is not observed at or above the Contract Required Quantitation Limit (CRQL) for each analyte of interest. Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g (1 lb) of activated carbon.

7.1.2 Sulfuric Acid Solution (H_2SO_4) - (1+1) slowly add 50 mL of concentrated H_2SO_4 (sp. gr. 1.84; 18 N) to 50 mL of reagent water.

7.1.3 Acetone, methanol, methylene chloride, iso-octane, 2-propanol, and toluene - pesticide residue analysis grade or equivalent.

7.1.4 Sodium Sulfate - Powdered or granular anhydrous reagent grade, heated at 400°C for 4 hours in a shallow tray, cooled in a desiccator, and stored in a glass bottle.

OR

Hydromatrix - Diatomaceous earth-based material rinsed with methylene chloride and dried at 400°C for 4 hours in a shallow tray, cooled in a desiccator, and stored in a glass bottle.

CAUTION: An open container of sodium sulfate may become contaminated during storage in the laboratory.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 7. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor that are immediately ampulated in glass vials may be retained for 2 years from preparation date. The expiration date of the ampulated standards, upon the breaking of the glass seal, is 6 months (or sooner, if the standard has degraded or evaporated).

7.2.2 Stock Standard Solutions

7.2.2.1 Stock standard solutions are defined as standards that are to be used to produce working standards. They may be in the form of single compounds or mixtures. They may be purchased or prepared in methylene chloride or another suitable solvent.

7.2.3 Working Standards

7.2.3.1 Deuterated Monitoring Compound (DMC) Standard Spiking Solution

7.2.3.1.1 Prepare a DMC standard spiking solution in methanol to contain the following compounds shown:

DMC

Phenol-d_5

Bis(2-chloroethyl)ether-d_8

2-Chlorophenol-d_4

4-Methylphenol-d_8

Nitrobenzene-d_5

2-Nitrophenol-d_4

2,4-Dichlorophenol-d_3

4-Chloroaniline-d_4

Dimethylphthalate-d_6

Acenaphthylene-d_8

4-Nitrophenol-d_4

Fluorene-d_{10}

4,6-Dinitro-methylphenol-d_2

Anthracene-d_{10}

Pyrene-d_{10}

Benzo(a)pyrene-d_{12}

Fluoranthene-d_{10} [Selected Ion Monitoring (SIM) analysis]

2-Methylnapthalene-d_{10} (SIM analysis)

7.2.3.1.2 DMC standards are added to all samples, blanks, requested Matrix Spike and Matrix Spike Duplicates (MS/MSDs), and calibration solutions. The SIM compounds can be added as part of the DMC standard spiking solution or added separately to all standards, samples, and blanks that require SIM analysis. The DMC standard spiking solution must be prepared every 12 months, or sooner if the solution has degraded or concentrated.

7.2.3.2 Matrix Spiking Solution

7.2.3.2.1 The matrix spiking solution consists of the following:

Bases/Neutrals	Acids
Acenaphthene	Pentachlorophenol
2,4-Dinitrotoluene	Phenol
Pyrene	2-Chlorophenol
N-Nitroso-di-n-propylamine	4-Chloro-3-methylphenol
	4-Nitrophenol

7.2.3.2.2 Prepare a spiking solution that contains each of the base/neutral and acid compounds listed above in methanol (see Section 12.2.3 for appropriate concentrations).

7.2.3.2.3 For SIM analyses, the laboratory has the option of using the matrix spiking solution in Section 7.2.3.2.1 or preparing a matrix spiking solution containing only acenaphthene, pyrene,

and pentachlorophenol in methanol (see Section 12.2.3 for appropriate concentrations).

7.2.3.3 Gel Permeation Chromatography (GPC) Calibration and GPC Continuing Calibration Verification Solution

7.2.3.3.1 Prepare a calibration solution in methylene chloride containing the following analytes at the minimum concentration listed (in elution order):

Compound	Concentration (mg/mL)
Corn oil	25.0
Bis(2-ethylhexyl)phthalate	0.5
Methoxychlor	0.1
Perylene (CAS # 198-55-0)	0.02
Sulfur (CAS # 7704-34-9)	0.08

NOTE: Sulfur is not very soluble in methylene chloride, but it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

7.2.3.4 Instrument Performance Check Solution

Prepare a solution containing decafluorotriphenylphosphine (DFTPP) in methylene chloride. The solution may be incorporated into the calibration standard used as the mid-level initial calibration standard and the continuing calibration standard verification standard, or may be prepared as a single analyte solution. If DFTPP is incorporated into the calibration standard, then an aliquot of the DFTPP solution is to be added to the autosampler vial containing either the initial calibration mid-level standard, or Continuing Calibration Verification (CCV) before calibration analysis. The DFTPP must be analyzed using the same Gas Chromatograph (GC) and Mass Spectrometer run conditions as is used for the calibration analysis. The DFTPP solutions are to be prepared such that 50 ng of DFTPP is injected onto the column.

7.2.3.5 Initial and Continuing Calibration Solutions

7.2.3.5.1 Calibration standards are to be prepared at a minimum of five concentration levels in methylene chloride at concentrations that are applicable to the sensitivity of the instrument. For most operations, the calibrations standards are to be prepared at 5.0, 10, 20, 40 and 80 ng/µL for each target compound and associated DMCs (see Table 7). These levels are based upon 1.0 mL final volume extracts for samples not undergoing GPC cleanup, and 0.5 mL final volume extracts for those samples undergoing GPC cleanup. Other concentration levels may be used for more sensitive instrumentation and final extract levels. For example, a laboratory may use a final extract volume of 1.0 mL for samples undergoing GPC cleanup, and a low calibration standard of 2.5 ng/µL. The alternate calibration standards and final volumes may be used as long as the following requirements are met:

(a) The laboratory can demonstrate that the CRQL for each analyte listed in Exhibit C can be reached using the calibration and final volume scheme. This demonstration is made when there is formal documentation of laboratory Method Detection Limit (MDL) studies indicating that the calculated MDL for each target analyte is below the required CRQL for that analyte when using the laboratory's specific final volume and calibration level scheme.

(b) All five calibration levels are in the same ratio as that shown above (e.g., if a lab were using a 1.0 ng/µL low standard, then the other calibration levels must be 2.0, 4.0, 8.0, and 16 ng/µL).

Each calibration standard should contain each target compound. Each DMC may be added to the other calibration standards, or may be contained in a separate mixture and combined with the calibration standards in the autosampler vials just prior to analysis. Seven target compounds and two DMCs (2,4-Dinitrophenol, Pentachlorophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline, 4-Nitrophenol, 4,6-Dinitro-2-methylphenol, 4-Nitrophenol-d_4, and 4,6-Dinitro-2-methylphenol-d_2) will require only a four-point initial calibration at 10, 20, 40, and 80 ng/µL since detection at less than 10 ng/µL is difficult. The USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB) Organic Program Manager (PM) has the authority to disallow certain alternative calibration standard concentrations or final extract volume schemes if it is felt that it is inappropriate or that it may lead to questionable data.

NOTE: 1.0 or 2.0 µL injections of all calibration standards may be used. All samples analyzed must have been injected at the same volume (1.0 or 2.0 µL) as the calibration standard.

7.2.3.5.2 If the optional analysis of Polynuclear Aromatic Hydrocarbons (PAHs) and pentachlorophenol using the Selected Ion Monitoring (SIM) technique is to be performed, prepare calibration standards at a minimum of five concentration levels that are applicable to the sensitivity of the instrument. For most operations, the calibrations standards are to be prepared at 0.10, 0.20, 0.40, 0.80, and 1.0 ng/µL for each target compound of interest and the associated DMCs (see Table 8). Pentachlorophenol will require only a four-point initial calibration at 0.20, 0.40, 0.80, and 1.0 ng/µL.

NOTE: 1.0 or 2.0 µL injections of all calibration standards may be used. All samples analyzed must have been injected at the same volume (1.0 or 2.0 µL) as the calibration standard.

7.2.3.5.3 The CCV standard should be at or near the mid-point concentration level of the calibration standards, normally 20 ng/µL. If the optional analysis of PAHs/pentachlorophenol by SIM is to be performed, the CCV standard should be at or near the mid-point calibration level, normally 0.40 ng/µL.

7.2.3.5.4 To facilitate the confirmation of single component pesticides from the semivolatile library search data [see Exhibit D (Pesticides), Section 11.1.2], the laboratory may include the

single component pesticide target compounds listed in Exhibit C (Pesticides), Section 3.0, in the semivolatile CCV standard. The laboratory may add any or all of these compounds to the semivolatile CCV standard, but at a concentration of 10 ng/µL or less. Do not include the Aroclor or Toxaphene mixtures in the semivolatile initial and continuing calibration verification standards. If added to this Gas Chromatograph/Mass Spectrometer (GC/MS) standard, these additional analytes are not reported on the semivolatile calibration form (Form VII), but must be included in the quantitation report for the CCV standard. As only a single point calibration would be performed, no Percent Relative Standard Deviation (%RSD) or Percent Difference (%Difference) criteria would apply to these additional analytes.

7.2.3.6 Internal Standard Solution

7.2.3.6.1 Prepare an internal standard solution containing each of the following compounds in methylene chloride: 1,4-dichlorobenzene-d_4; naphthalene-d_8; acenaphthene-d_{10}; phenanthrene-d_{10}; chrysene-d_{12}; and perylene-d_{12}. It may be necessary to use 5-10% toluene in this solution and a few minutes of ultrasonic mixing in order to dissolve all the constituents. Just prior to full scan analysis by GC/MS, add sufficient amount of the internal standard solution to an aliquot of the water, low-level, or medium-level soil sample extracts to result in a 20 ng/µL concentration of each internal standard.

7.2.3.6.2 If the optional analysis of PAHs/pentachlorophenol by SIM is to be performed, just prior to SIM analysis the Contractor shall add sufficient amount of the internal standard solution to an aliquot of the water or low-level sample extracts to result in a 0.40 ng/µL concentration of each internal standard. 1,4-dichlorobenzene-d_4 is not required to be evaluated as an internal standard when performing SIM analysis.

7.3 Storage of Standard Solutions

7.3.1 Store the stock standard solutions at 4°C (±2°C) in polytetrafluoroethylene (PTFE)-lined screw-cap amber bottles. Fresh standards should be prepared every 12 months at a minimum.

7.3.2 Store the working standards at 4°C (±2°C) in PTFE-sealed containers. The solution should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner if comparison with Quality Control (QC) check samples indicates a problem.

7.3.3 The CCV standard should be stored at 4°C (±2°C). The solution should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner if comparison with Quality Control (QC) check samples indicates a problem.

7.3.4 Refrigeration of the GPC calibration solution may cause the corn oil to precipitate. Before use, allow the solution to stand at room temperature until the corn oil dissolves. Replace this calibration solution every 6 months, or more frequently if necessary.

7.3.5 Protect all standards from light. Samples, sample extracts, and standards must be stored separately.

7.3.6 The Contractor is responsible for maintaining and verifying the integrity of standard solutions prior to use. Storage of standard

solutions in the freezer may cause some compounds to precipitate. This means, at a minimum, the standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in solution. Additional steps may be necessary to ensure all components are in solution.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in 1 L (or 1 quart) amber glass containers, fitted with polytetrafluoroethylene (PTFE)-lined screw-caps. If amber containers are not available, the samples should be protected from light. Soil samples may be collected in glass containers or closed-end tubes (e.g., brass sleeves) in sufficient quantity to perform the analysis. The specific requirements for site sample collection are outlined by the Region.

8.1.2 All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until extraction.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3 Procedure for Sample Extract Storage

8.3.1 Sample extracts must be protected from light and stored at 4°C (±2°C) until 365 days after delivery of a complete, reconciled data package to USEPA.

8.3.2 Samples, sample extracts, and standards must be stored separately.

8.4 Contract Required Holding Times

8.4.1 Extraction of water samples shall be started within 5 days of Validated Time of Sample Receipt (VTSR). Extraction of soil/sediment samples shall be completed within 10 days of VTSR.

8.4.2 As part of USEPA's Quality Assurance (QA) program, USEPA may provide Performance Evaluation (PE) samples as standard extracts that the Contractor is required to prepare per the instructions provided by USEPA. PE samples must be prepared and analyzed concurrently with the samples in the Sample Delivery Group (SDG). The extraction holding time (5 days after VTSR for water and 10 days after VTSR for soil/sediment) does not apply to PE samples received as standard extracts.

8.4.3 Extracts of water and soil/sediment samples must be analyzed within 40 days following extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

9.1.1 Gas Chromatograph (GC)

9.1.1.1 The following are only suggested gas chromatographic analytical conditions. Other conditions may be used, provided that all technical acceptance criteria in Sections 9.3.5, 9.4.5, and 11.3 are met. For example, newer columns that are stable at temperatures of up to 370°C may be used. The use of these columns would decrease run time while still providing adequate resolution.

Initial Column Temperature Hold	40°C for 4 min.
Column Temperature Program	40-270°C at 10°C/min.
Final Column Temperature Hold	270°C; Hold Required: 3 min. after all compounds listed in Exhibit C (Semivolatiles), have eluted
Injector Temperature	250-300°C
Transfer Line Temperature	250-300°C
Source Temperature	According to manufacturer's specifications
Injector	Grob-type, splitless
Sample Volume	1 or 2 µL
Carrier Gas	Helium at 30 cm/sec.

9.1.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, blanks, and Matrix Spike and Matrix Spike Duplicates (MS/MSDs).

9.1.2 Mass Spectrometer (MS)

The following are the required MS analytical conditions:

Electron Energy	70 volts (nominal)
Mass Range	35 to 500 amu
Ionization Mode	Electron Ionization (EI)
Scan Time	Not to exceed 1 sec. per scan

NOTE: For SIM analyses the laboratory is to use professional judgment and the instrument manufacturer's instructions and guidelines in choosing an appropriate single ion scan or dwell time (usually 50 to 500 msec per ion).

9.2 GC/MS Mass Calibration (Tuning) and Ion Abundance

9.2.1 Summary of GC/MS Instrument Performance Check

The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibration such as perfluoro-tri-n-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.3.4). Prior to the analysis of any samples, including MS/MSDs, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing decafluorotriphenylphosphine (DFTPP).

NOTE: The requirement to analyze the instrument performance check solution does not apply when the optional analysis of Polyaromatic Hydrocarbons (PAHs)/pentachlorophenol is to be performed.

9.2.2 Frequency of GC/MS Instrument Performance Check

9.2.2.1 The instrument performance check solution must be analyzed once at the beginning of each 12-hour period during which samples or standards are analyzed. However, in cases where a closing Continuing Calibration Verification (CCV) can be used as an opening CCV for the next 12-hour time period, then an additional DFTPP tune is not required and the 12-hour time period begins with the injection of the CCV.

9.2.2.2 The 12-hour time period for a GC/MS system instrument performance check and calibration standards (initial or continuing calibration verification criteria) begins at the moment of injection of the DFTPP analysis that the laboratory submits as documentation of a compliant instrument performance check. However, in cases where a closing CCV can be used as an opening CCV for the next 12-hour period, then an additional DFTPP tune is not required, and the 12-hour period begins with the injection of the CCV. The time period ends after 12 hours have elapsed according to the system clock.

NOTE: For the optional analysis of PAHs/pentachlorophenol by the Selected Ion Monitoring technique (SIM), the 12-hour time period begins at the moment of injection of the first initial calibration standard or at the moment of injection of the CCV standard, if initial calibration is not to be performed. The time period ends after 12 hours have elapsed according to the system clock.

9.2.3 Procedure for GC/MS Instrument Performance Check

The analysis of the instrument performance check solution may be performed as an injection of 50 ng of DFTPP into the GC/MS or by adding a sufficient amount of DFTPP to the calibration standards to result in an on-column amount of 50 ng of DFTPP (Section 7.2.3.4) and analyzing the calibration standard.

9.2.4 Technical Acceptance Criteria for GC/MS Instrument Performance Check

9.2.4.1 The GC/MS system must be tuned at the frequency described in Section 9.2.2.

9.2.4.2 The abundance criteria listed in Table 1 must be met for a 50 ng injection of DFTPP. The mass spectrum of DFTPP must be acquired in the following manner: three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be

accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. Do not subtract part of the DFTPP peak.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical GC/MS instrument run conditions.

9.2.5 Corrective Action for GC/MS Instrument Performance Check

9.2.5.1 If the GC/MS instrument performance check technical acceptance criteria are not met, re-tune the GC/MS system. It may be necessary to clean the ion source, clean quadrupoles, or take other actions to achieve the technical acceptance criteria.

9.2.5.2 The instrument performance check technical acceptance criteria MUST be met before any standards, samples, including MS/MSDs, or required blanks are analyzed. Any standards, samples, or required blanks analyzed when the instrument performance check technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

Prior to the analysis of samples and required blanks, and after the instrument performance check technical acceptance criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations (Section 7.2.3.5.1) to determine instrument sensitivity and the linearity of GC/MS response for the semivolatile target and Deuterated Monitoring Compounds (DMCs). Each initial calibration standard contains all the semivolatile target compounds, DMCs, and internal standards.

NOTE: For optional analysis of PAHs/pentachlorophenol using the SIM technique, the GC/MS system must be calibrated at a minimum of five concentrations (Section 7.2.3.5.2), prior to the analysis of samples and required blanks, to determine instrument sensitivity and linearity. The calibration standards contain all the PAHs and pentachlorophenol, the associated DMCs, and internal standards.

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be initially calibrated upon award of the contract, whenever the Contractor takes corrective action that may change or affect the initial calibration criteria (e.g., ion source cleaning or repairs, column replacement, etc.), or if the CCV technical acceptance criteria have not been met.

9.3.2.2 If time still remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. It is not necessary to analyze a continuing calibration standard within this 12-hour time period.

9.3.3 Procedure for Initial Calibration

9.3.3.1 All standard/spiking solutions and blanks must be allowed to warm to ambient temperature before preparation or analysis.

9.3.3.2 Prepare five calibration standards containing all the semivolatile target and DMCs at the concentrations described in Section 7.2.3.5.

9.3.3.3 Add sufficient amount of internal standard solution (Section 7.2.3.6) to aliquots of calibration standards to result in a 20 ng/µL concentration of each internal standard. The internal standards specified in Section 7.2.3.6 should permit most of the semivolatile target compounds to have Relative Retention Times (RRTs) of 0.80 to 1.20, using the assignments of internal standards to target compounds given in Table 2.

9.3.3.4 Analyze each calibration standard by injecting 1.0 or 2.0 µL of standard.

9.3.4 Calculations for Initial Calibration

9.3.4.1 Calculate the Relative Response Factors (RRFs) for each semivolatile target and DMC using Equation 1 and the primary characteristic ions found in Table 3. Assign the target compounds and DMCs to the internal standard according to Table 2. For internal standards, use the primary ion listed in Table 3 unless interferences are present. If interferences prevent the use of the primary ion for a given internal standards, use the secondary ion(s) listed in Table 3.

NOTE: Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion.

EQ. 1 Relative Response Factor Calculation

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where,

A_x = Area of the characteristic ion for the compound to be measured (Table 3).

A_{is} = Area of the characteristic ion for specific internal standard (Table 3).

C_{is} = Amount of the internal standard injected (ng).

C_x = Amount of the target compound or DMC injected (ng).

9.3.4.2 The Mean Relative Response Factor ($\overline{RRF}$) must be calculated for all compounds. Calculate the Percent Relative Standard Deviation (%RSD) of the RRF values for the initial calibration using Equation 2.

EQ. 2 Percent Relative Standard Deviation Calculation

$$\%RSD = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{n-1}}$$

Where,

X_i = Each individual value used to calculate the mean.

$\overline{X}$ = The mean of n values.

n = The total number of values.

9.3.5 Technical Acceptance Criteria for Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.3.5.1 and at the frequency described in Section 9.3.2 on a GC/MS system meeting the instrument performance technical acceptance criteria.

NOTE: All initial calibration standards for the optional analysis of PAHs/pentachlorophenol by the SIM technique must be analyzed at the concentration levels described in Section 7.2.3.5.2 and at the frequency described in Section 9.3.2.

9.3.5.2 The RRF at each calibration concentration for each semivolatile target compound and DMC must be greater than or equal to the compound's minimum acceptable RRF listed in Table 4.

9.3.5.3 The %RSD of the RRFs over the initial calibration range for each semivolatile target compound and DMC that has a required %RSD must be less than or equal to the %RSD listed in Table 4.

9.3.5.4 Up to four target compounds and DMCs (excluding those with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Section 9.3.5.2 but these compounds must still meet the minimum RRF requirements of 0.010. Up to four target compounds and DMCs (excluding those with maximum %RSD requirements of 40.0%) may fail to meet the criteria listed in Section 9.3.5.3 but these compounds must still meet the maximum %RSD requirements of 40.0%.

9.3.5.5 For the optional analysis of PAHs/pentachlorophenol using the SIM technique, two target compounds and DMCs (excluding those with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Section 9.3.5.2 but these compounds must still meet the minimum RRF requirements of 0.010. Up to two target compounds and DMCs (excluding those with maximum %RSD requirements of 40.0%) may fail to meet the requirements criteria listed in Section 9.3.5.3 but these compounds must still meet the maximum %RSD requirements of 40.0%.

9.3.5.6 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument

manual to determine how saturation is indicated for your instrument.

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If any technical acceptance criteria for initial calibration are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the acceptance criteria.

9.3.6.2 Initial calibration technical acceptance criteria must be met before any samples or required blanks are analyzed. Any samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.4 Continuing Calibration Verification

9.4.1 Summary of Opening and Closing Continuing Calibration Verification

Prior to the analysis of samples and required blanks and after instrument performance check technical acceptance criteria and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing a CCV standard (opening CCV) to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the analytical method. The CCV standard contains all the semivolatile target compounds, DMCs, and internal standards. After all samples and blanks have been analyzed, and before the end of the 12-hour time period, a closing CCV using the same standard as for the opening CCV is required. The same injection volume must be used for all standards, samples, and blanks.

NOTE: For the optional analysis of PAHs/pentachlorophenol using SIM, each GC/MS system must be routinely checked by analyzing a CCV standard (opening CCV), prior to the analysis of samples and required blanks, and after initial calibration technical acceptance criteria have been met. The continuing calibration standard for optional analysis of PAHs/pentachlorophenol contains the PAHs and pentachlorophenol, the associated DMCs, and internal standards. After all samples and blanks have been analyzed, and before the end of the 12-hour time period, a closing CCV using the same standard conditions as for the opening CCV is required.

9.4.2 Frequency of Continuing Calibration Verification

9.4.2.1 Each GC/MS used for analysis must be calibrated once every 12-hour time period of operation. The 12-hour time period begins with the injection of DFTPP for full scan analysis followed by the injection of the opening CCV. If a closing CCV meets the technical acceptance criteria for an opening CCV and samples are analyzed within the next 12-hour time period, then an additional DFTPP tune is not required and the 12-hour time period begins with that calibration verification. If the closing CCV does not meet the technical acceptance criteria for an opening CCV, then a DFTPP tune, followed by an opening CCV, is required and the next 12-hour time period begins with the DFTPP tune.

9.4.2.2 If time still remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed.

9.4.2.3 After the injection of all samples and required blanks, and before the end of the 12-hour period, another injection of the CCV solution is required (closing CCV). The closing CCV used to bracket the end of a 12-hour analytical sequence may be used as the opening CCV for a new 12-hour analytical sequence, provided that all technical acceptance criteria are met for an opening CCV in Section 9.4.5.

9.4.3 Procedure for Continuing Calibration Verification

9.4.3.1 All standard/spiking solutions and blanks must be allowed to warm to ambient temperature before preparation or analysis.

9.4.3.2 Add sufficient amount of internal standard solution (Section 7.2.3.6) to an aliquot of CCV standard to result in 20 ng/µL concentration of each internal standard. The internal standards specified in Section 7.2.3.6 should permit most of the semivolatile target compounds to have RRTs of 0.80 to 1.20, using the assignments of internal standards to target compounds given in Table 2.

9.4.3.3 Analyze the CCV standard by injecting 1.0 or 2.0 µL of standard.

9.4.4 Calculations for Continuing Calibration Verification

9.4.4.1 Calculate an RRF for each semivolatile target compound and DMC using Equation 1 and the primary characteristic ions found in Table 3. For internal standards, use the primary ions listed in Table 3 unless interferences are present. If interferences prevent the use of the primary ion for a given internal standard, use the secondary ion(s) listed in Table 3.

9.4.4.2 Calculate the Percent Difference (%Difference) between the $\overline{RRF}$ from the most recent initial calibration and the continuing calibration verification RRF for each semivolatile target compound and DMC using Equation 3.

EQ. 3 Relative Response Factor Percent Difference Calculation

$$\%\ \text{Difference}_{RRF} = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

Where,

$\overline{RRF_i}$ = Mean Relative Response Factor from the most recent initial calibration meeting technical acceptance criteria.

RRF_c = Relative Response Factor from CCV standard.

9.4.5 Technical Acceptance Criteria for Opening and Closing Continuing Calibration Verification (CCV)

9.4.5.1 The opening and closing CCV standard must be analyzed at or near the mid-point concentration level of the calibration standards, normally 20 ng/µL, at the frequency described in Section 9.4.2, on a GC/MS system meeting the instrument performance check and the initial calibration technical acceptance criteria.

NOTE: For the optional analysis of PAHs/pentachlorophenol, the opening and closing CCV standard must be analyzed at or near the mid-point concentration level of the calibration range for SIM analysis, normally 0.40 ng/µL, at the frequency described in Section 9.4.2, and on a GC/MS system meeting the initial calibration technical acceptance criteria.

9.4.5.2 For an opening CCV, the RRF for each semivolatile target compound and DMC must be greater than or equal to the compound's minimum acceptable RRF listed in Table 4. For a closing CCV, the RRF for each semivolatile target compound and DMC must be greater than or equal to 0.010.

9.4.5.3 For an opening CCV, the RRF Percent Difference for each semivolatile target compound and DMC that must be within the inclusive range listed in Table 4. For a closing CCV, the RRF Percent Difference for each semivolatile target compound and DMC must be in the inclusive range of ±50.

9.4.5.4 For an opening CCV, up to four target compounds and DMCs (excluding those compounds with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Section 9.4.5.2 but these compounds must still meet the minimum RRF requirements of 0.010. Up to four target compounds and DMCs (excluding those with maximum Percent Difference requirements of ±40.0%) may fail to meet the requirements listed in Section 9.4.5.3 but these compounds must still meet the maximum Percent Difference requirements of ±40.0%. For a closing CCV, all target compounds and DMCs must meet the requirements listed in Sections 9.4.5.2 and 9.4.5.3.

9.4.5.5 For the optional analysis of PAHs/pentachlorophenol using the SIM technique, up to two target compounds and DMCs (excluding those with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Section 9.4.5.2 but these compounds must still meet the minimum RRF requirements of 0.010. Up to two target compounds and DMCs (excluding those with maximum Percent Difference requirements of ±40.0%) may fail to meet the criteria listed in Section 9.4.5.3 but these compounds must still meet the maximum Percent Difference requirements of ±40.0%. All PAH and phenolic compounds must meet the criteria listed in Sections 9.4.5.2 and 9.4.5.3 for a closing CCV.

9.4.5.6 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.4.6 Corrective Action for Opening and Closing CCV

9.4.6.1 If the opening CCV technical acceptance criteria in Sections 9.4.5.2 and 9.4.5.3 are not met, recalibrate the GC/MS instrument according to Section 9.3. If the closing CCV technical acceptance criteria in Sections 9.4.5.2 and 9.4.5.3 are not met, then all samples and blanks analyzed within that 12-hour time period must be reanalyzed at no additional cost to USEPA. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the CCV technical acceptance criteria.

9.4.6.2 CCV technical acceptance criteria MUST be met before any samples or required blanks, are analyzed. Any samples or required blanks

analyzed when CCV criteria have not been met will require reanalysis at no additional cost to USEPA.

10.0 PROCEDURE

The Contractor must have the capability to perform all of the sample cleanup procedures presented in this Exhibit, including those included by reference. The Contractor may use any of the procedures or combinations of procedures to cleanup the samples prior to analysis, unless the Contractor is specifically directed by the Region to use a particular cleanup procedure or combination of cleanup procedures.

The Contractor must demonstrate that each cleanup procedure is capable of producing data that meets the technical acceptance criteria for the method, including Method Detection Limits (MDLs) (see Section 12.3) and any precision and recovery limits.

NOTE: If Selected Ion Monitoring (SIM) analysis is requested for a sample, a full scan analysis at the regular concentration levels must be performed on that sample prior to the SIM analysis. For all SIM target compounds detected at or above Contract Required Quantitation Limits (CRQLs) during the full scan analysis, a SIM analysis is not to be performed for that target compound. Any SIM analyses not performed for this reason must be noted in the Sample Delivery Group (SDG) Narrative.

10.1 Sample Preparation

10.1.1 If an insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to apprise them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed, or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.2 If multi-phase samples (e.g., a two-phase liquid sample, oily, sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample;
- Separate the phases of the sample and analyze each phase separately. SMO will provide EPA Sample Numbers for the additional phases;
- Separate the phases and analyze one or more of the phases, but not all of the phases. SMO will provide EPA Sample Numbers for the additional phases, if required; or
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside the scope), the Region may require the Contractor to do any of the following:

- Separate the phase(s) and analyze the phase(s) that is(are) amenable to analysis. SMO will provide EPA Sample Numbers for the additional phases, if required.

- Do not analyze the sample.

10.1.2.2 No other change in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Water Samples

10.1.3.1 Continuous liquid-liquid extraction is used to extract the samples. Separatory funnel extraction or other manual extraction techniques cannot be used. Allow the sample to come to ambient temperature.

10.1.3.2 Continuous Liquid-Liquid Extraction Without Hydrophobic Membrane

10.1.3.2.1 Follow the manufacturer's instructions for set-up.

10.1.3.2.2 Add methylene chloride to the bottom of the extractor and fill it to a depth of at least 1 inch above the bottom sidearm.

10.1.3.2.3 Measure out a 1.0 L sample aliquot in a separate, clean graduated cylinder; transfer the aliquot to the continuous extractor. Measure and record the initial pH of the sample with a pH meter or narrow range pH paper. Adjust the pH to 2.0 with 1:1 sulfuric acid and record the final pH.

NOTE: With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and the water layer in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

10.1.3.2.4 Using a syringe or volumetric pipet, add a sufficient amount of the Deuterated Monitoring Compound (DMC) standard spiking solution to result in the addition of 40 µg of each DMC and 0.4 µg of the SIM DMCs (fluoranthene-d_{10} and 2-methylnapthalene-d_{10})(Section 7.2.3.1) into the sample and mix well.

10.1.3.2.5 Rinse the graduated cylinder with 50 mL of methylene chloride and transfer the rinsate to the continuous extractor. If the sample was received in a 1 L container, rinse the empty container with 50 mL of methylene chloride and add rinsate to the continuous extractor.

10.1.3.2.6 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 5-15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 18 hours.

NOTE 1: When a minimum drip rate of 10-15 mL/minute is maintained throughout the extraction, the extraction time may be reduced to a minimum of 12 hours. Allow to cool then detach the distillation flask. Proceed to Section 10.2.

NOTE 2: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor.

10.1.3.3 Continuous Liquid-Liquid Extraction With Hydrophobic Membrane

10.1.3.3.1 Follow the procedure in Sections 10.1.3.2.1 - 10.1.3.2.6 but reduce the amount of methylene chloride used to 50 mL and extract for a minimum of 6 hours.

10.1.3.3.2 Due to the smaller volume of solvent used during the extraction process, some sample matrices (e.g., oily samples, samples containing a high concentration of surfactants) may create an emulsion that will consume the solvent volume, preventing the efficient extraction of the sample. When this occurs, add additional solvent to assure efficient extraction of the sample and extend the extraction time by a minimum of 6 hours. If the sample matrix prevents the free flow of solvent through the membrane, then the non-hydrophobic membrane continuous liquid-liquid type extractor must be used.

10.1.3.3.3 It may not be necessary to dry the extract with sodium sulfate, if the hydrophobic membrane type extractor is used.

10.1.3.4 If low DMC recoveries occur, assure: 1) the apparatus was properly assembled to prevent leaks; 2) the drip rate/solvent cycling was optimized; and 3) there was proper cooling for condensation of solvent.

10.1.3.5 Alternate continuous liquid-liquid extractor types that meet the requirements of the analytical method may also be used. If using alternate extractors or design types, follow the manufacturer's instruction for set-up.

10.1.4 Soil/Sediment Samples

Decant and discard any water layer on a sediment sample. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

10.1.4.1 pH Determination

Transfer 50 g of soil/sediment to a 100 mL beaker. Add 50 mL of water and stir for 1 hour. Determine the pH of the sample with a pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil/sediment is greater than 11 or less than 5, document this in the SDG Narrative. Discard this portion of the sample.

NOTE: If limited sample weight (less than 50 g) is received, use a smaller 1:1 ratio of grams of soil/sediment sample to mLs of water for the pH determination. Note this in the SDG Narrative.

10.1.4.2 Percent Moisture

Immediately after weighing the sample for extraction, weigh 5-10 g of the soil/sediment into a tared crucible. Determine the Percent Moisture (%Moisture) by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual

analytes will be reported relative to the dry weight of soil/sediment.

NOTE: If a soil sample has greater than 65% moisture, the laboratory may use up to 50 g of soil sample in order to achieve the expected CRQLs. The amount of sample used and the Percent Moisture should be noted in the SDG Narrative.

EQ. 4 Percent Moisture Calculation

$$\%\ \text{Moisture} = \frac{\text{grams of wet sample - grams of dry sample}}{\text{grams of wet sample}} \times 100$$

10.1.4.3 Mandatory Determination of Concentration Level

The Contractor must determine whether a soil/sediment sample should be analyzed by the low-level or medium-level soil/sediment method. It is the responsibility of the Contractor to analyze the sample at the correct level.

- Assume the sample is low-level and analyze a 30 g sample. An analysis using the wrong level because of incorrect assumption will not be billable to USEPA.
- Use USEPA screening procedures or an in-house laboratory screening procedure. The procedure must be documented and available for review during on-site laboratory evaluation, or when requested by the USEPA Regional Contract Laboratory Program Project Officer (CLP PO).

10.1.4.4 Low-Level Soil/Sediment Samples

10.1.4.4.1 Three procedures are provided for the extraction of semivolatile compounds from soil/sediment samples:

- Ultrasonic extraction;
- [Automated] Soxhlet extraction; and
- Pressurized fluid extraction.

The Contractor shall use one of the above procedures for the extraction of soil/sediment samples.

NOTE: All soil/sediment samples in a Case must be extracted by the same procedure.

10.1.4.4.2 For soil/sediment sample extractions, perform the following steps rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample to the nearest 0.1 g, into a 400 mL beaker. Add 60 g of anhydrous powdered or granulated sodium sulfate, or 30 g of Hydromatrix, and mix well to produce a sandy texture. Proceed to Section 10.1.4.4.3 for ultrasonic extraction, Section 10.1.4.4.4 for automated Soxhlet extraction, or Section 10.1.4.4.5 for pressurized fluid extraction.

NOTE: For samples extracted by the Pressurized Fluid Extraction procedure (Section 10.1.4.3.5) the use of sodium sulfate is not recommended.

10.1.4.4.3 Ultrasonic Extraction

10.1.4.4.3.1 Add a sufficient amount of the DMC standard spiking solution to result in the addition of 40 µg of each DMC and 0.4 µg of the SIM DMCs (fluoranthene-d_{10} and 2-methylnapthalene-d_{10})(Section 7.2.3.1) to the sample, then immediately add 100 mL of 1:1 v/v methylene chloride/acetone.

10.1.4.4.3.2 Place the bottom of the tip of the 3/4 inch tapered disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer. Do not use a microtip probe.

10.1.4.4.3.3 Sonicate for 3 minutes using a 3/4 inch disrupter horn at full power, (output control knob at 10) with pulse on and percent duty cycle knob set at 50%.

Decant and filter extracts through Whatman No. 41 (or equivalent) filter paper using vacuum filtration or centrifuge and decant extraction solvent.

10.1.4.4.3.4 Repeat the extraction two more times with two additional 100 mL portions of 1:1 v/v methylene chloride/acetone. Before each extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or very carefully with the tip of the unenergized probe. Decant the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 v/v methylene chloride/acetone.

10.1.4.4.3.5 If the sample is to be screened following the low-level preparation method prior to Gel Permeation Chromatography (GPC), proceed to the appropriate screening procedure. Otherwise, proceed to Section 10.2.

10.1.4.4.4 [Automated] Soxhlet Extraction

10.1.4.4.4.1 The Contractor may use either automated or non-automated Soxhlet extraction. Check the heating oil level in the automated Soxhlet unit and add oil if needed. Follow the manufacturer's instructions to set the temperature on the service unit. Press the "MAINS" button and observe that the switch lamp is now "ON". Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/minute to prevent solvent loss through the condensers.

10.1.4.4.4.2 Transfer the entire sample from the beaker (Section 10.1.4.4.2) to the thimble. Add a sufficient amount of the DMC standard spiking solution to result in the addition of 40 µg of each DMC and 0.4 µg of each SIM DMC (fluoranthene-d_{10} and 2-methylnapthalene-d_{10}) (Section 7.2.3.1) to the sample.

10.1.4.4.4.3 Immediately transfer the thimbles containing the weighed samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.

10.1.4.4.4.4 Insert the extraction cups containing boiling chips, and load each with appropriate volume of extraction solvent (1:1 v/v methylene chloride/acetone). Using the cup holder, lower the

locking handle, ensuring that the safety catch engages. The cups are now clamped into position.

NOTE: The seals must be pre-rinsed or pre-extracted with extraction solvent prior to initial use.

10.1.4.4.4.5 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 min. The condenser valves must be in the "OPEN" position. Extract for the preset time.

10.1.4.4.4.6 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set the timer for 60 min. Condenser valves are still open. Extract for the preset time. After rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.

10.1.4.4.4.7 When all but 2-5 mL of the solvent have been collected, open the system and remove the cups. Transfer the contents of the cups to graduated, conical-bottom glass tubes. Rinse the cups with methylene chloride and add the rinsates to the glass tubes.

10.1.4.4.4.8 If the sample is to be screened following the low-level preparation method prior to GPC, proceed to the appropriate screening procedure. Otherwise, proceed to Section 10.2.

10.1.4.4.5 Pressurized Fluid Extraction

10.1.4.4.5.1 Transfer the entire sample from the beaker (Section 10.1.4.4.2) to an extraction cell of the appropriate size for the aliquot. Add sufficient amount of the DMC standard spiking solution to result in the addition of 40 µg of each DMC and 0.4 µg for each SIM DMC (fluoranthene-d_{10} and 2-methylnapthalene-d_{10} (Section 7.2.3.1) to the sample.

10.1.4.4.5.2 Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer.

10.1.4.4.5.3 Place a pre-cleaned collection vessel in the instrument for each sample, as described by the instrument manufacturer. The total volume of the collected extract will depend on the specific instrumentation and the extraction procedure recommended by the manufacturer and may range from 0.5 - 1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract.

10.1.4.4.5.4 The following are recommended extraction conditions.

Extraction Conditions	
Oven temperature	100°C
Pressure	1500-2000 psi
Static time	5 min. (after 5 min. pre-heat equilibration)
Flush volume	60% of the cell volume
Nitrogen purge	60 sec. at 150 psi (purge time may be extended for larger cells)
Static cycles	1

10.1.4.4.5.5 Optimize the extraction conditions as needed, according to the manufacturer's instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. Any pressure in the range of 1500-2000 psi should suffice. An appropriate amount of 1:1 (v/v) acetone/methylene chloride should be used to achieve the conditions in Section 10.1.4.4.5.4.

10.1.4.4.5.6 Once established, the same pressure should be used for all samples in the same SDG.

10.1.4.4.5.7 Begin the extraction according to the manufacturer's instructions. Collect each extract in a clean vial. Allow the extracts to cool after the extractions are complete.

10.1.4.4.5.8 If the sample is to be screened following the low-level preparation method prior to GPC, proceed to the appropriate screening procedure. Otherwise, proceed to Section 10.2.

10.1.4.5 Medium-Level Soil/Sediment Samples

10.1.4.5.1 The procedure described below is for the extraction of soil/sediment samples by the ultrasonic method (Section 10.1.4.4.3). The Contractor may also use the [automated] Soxhlet extraction or pressurized fluid extraction procedures described in Sections 10.1.4.4.4 and 10.1.4.4.5, respectively. The requirements of this analytical method must be met at all times [i.e., sample weight used for medium-level soil/sediment extraction and original CRQLs for medium-level soils]. As applicable, follow the manufacturer's instructions for the use of all extraction equipment.

NOTE: All medium-level soil/sediment samples in a Case must be extracted by the same procedure.

10.1.4.5.2 Transfer approximately 1 g (record weight to the nearest 0.1 g) of sample to a 20 mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

10.1.4.5.3 Add 2.0 g or sufficient quantity of anhydrous powdered or granulated sodium sulfate or Hydromatrix to the sample in the 20 mL vial and mix well to produce a sandy texture.

10.1.4.5.4 DMCs are added to all samples, Matrix Spike and Matrix Spike Duplicates (MS/MSDs), and blanks. Add a sufficient amount of the DMC standard spiking solution to result in the addition of 40 µg of each DMC excluding the two SIM DMCs (fluoranthene-d_{10} and 2-methylnapthylene-d_{10}) (Section 7.2.3.1) to the sample mixture.

10.1.4.5.5 Immediately add sufficient methylene chloride to the sample so that the total volume is approximately 10 mL and disrupt the sample with the 1/8 inch tapered microtip ultrasonic probe for 2 minutes at output control setting 5, in continuous mode. Before extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. Decant and filter extract through Whatman No. 41 (or equivalent) filter paper

using vacuum filtration or centrifuge and decant extraction solvent.

NOTE: Concentration of the extracts of soil/sediment samples prepared by the medium-level procedure described above may not be necessary. Proceed to Section 10.2.1.6 if no extract concentration is to be performed.

10.2 Concentrating the Extract

Note that low-level soil/sediment samples prepared by the procedure described in Section 10.1.4.4 will result in extracts containing a mixture of acetone and methylene chloride. Because all soil/sediment sample extracts MUST be subjected to GPC cleanup prior to analysis, the majority of the acetone must be removed from the extract, otherwise, it will have adverse effects on the GPC column. To remove the acetone from the soil/sediment sample extract, follow the steps in Section 10.2.1, then concentrate to 1.0 mL using the nitrogen evaporation technique in Section 10.2.2.2.

10.2.1 Concentration by Kuderna-Danish (K-D)

10.2.1.1 Assemble a K-D apparatus by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D, if equivalency is demonstrated for all the semivolatile target compounds listed in Exhibit C (Semivolatiles).

10.2.1.2 For water samples, transfer the extract to a K-D concentrator by pouring the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate.

10.2.1.2.1 For soil/sediment samples, directly transfer the extract to the K-D concentrator.

10.2.1.2.2 Rinse the Erlenmeyer flasks (for both water and soil/sediment samples) and the column (for water samples) with 20-30 mL of methylene chloride to complete the quantitative transfer.

10.2.1.3 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top of the column. Place the K-D apparatus in a hot water bath (60-70°C recommended) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-15 minutes. At the proper rate of distillation, the balls of the column will chatter actively, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 or 2 mL of methylene chloride. A 5 mL syringe is recommended for this operation.

10.2.1.4 For water samples that do not require GPC cleanup, proceed to final concentration of extract (Section 10.2.2). Oily water samples require GPC.

10.2.1.5 For water samples that require GPC, adjust the volume of the extract to 10.0 mL with methylene chloride and proceed with GPC cleanup (Section 10.3).

10.2.1.6 For soil/sediment samples, adjust the volume of the extract to 10.0 mL with methylene chloride and proceed with GPC cleanup (Section 10.3).

10.2.1.7 For water samples or soil/sediment samples that have undergone GPC, proceed to final concentration of extract (Section 10.2.2).

10.2.2 Final Concentration of Extract

Two different concentration techniques are permitted to obtain the final extract volume, Micro Snyder Column and Nitrogen Evaporation techniques:

10.2.2.1 Micro Snyder Column Technique

Add another one or two clean boiling chips to the concentrator tube and attach a two-ball Micro Snyder Column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60-70°C recommended) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation, the balls of the column will chatter actively, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL (0.4 mL for low-level soil/sediment samples or water samples that have undergone GPC), remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the evaporative flask and its lower joint into the concentrator tube with 0.2 mL (O.1 mL for low-level soil/sediment samples and water samples that have undergone GPC) of methylene chloride. Adjust the final volume to 1.0 mL (0.5 mL for low-level soil/sediment samples and water samples that have undergone GPC) with methylene chloride. Transfer the extract to the polytetrafluoroethylene (PTFE)-sealed screw-cap bottle, label the bottle, and store at 4°C (±2°C).

10.2.2.2 Nitrogen Evaporation Technique (Taken from ASTM Method D3086)

The following method may be used for final concentration of the semivolatile extract instead of the procedure in Section 10.2.2.1. Place the concentrator tube in a warm water bath (30-35°C recommended) and evaporate the solvent volume to just below 1 mL (below 0.5 mL for low-level soil/sediment samples and water samples that have undergone GPC) by blowing a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon) above the extract.

CAUTION: Gas lines from the gas source to the evaporation apparatus must be stainless steel, copper, or PTFE tubing. New plastic tubing must not be used between the carbon trap and the sample since it may introduce interferences.

The internal wall of the concentrator tube must be rinsed down several times with methylene chloride during the operation. During evaporation, the tube solvent level must be kept below the

water level of the bath. The extract must never be allowed to become dry.

10.2.2.3 Final Extract Volumes

The final extract volumes in Sections 10.2.2.3.1 and 10.2.2.3.2 are recommended volumes. If more sensitive Gas Chromatograph/Mass Spectrometer (GC/MS) systems are employed, then the larger extract volumes (less concentrated extracts) may be used, provided that the CRQLs for all target compounds can be achieved, and that all DMCs and internal standards have an expected extract concentration that is at the mid-point of the calibration curve.

10.2.2.3.1 Water

For water samples that did not undergo GPC, the extract must be brought to a final volume of 1.0 mL with methylene chloride. Remove boiling chips before adjusting final volume. For water samples that underwent GPC, the extract must be brought to a final volume equal to V_{out} (volume of extract collected from GPC cleanup) with methylene chloride [concentrating the extract to 0.5 mL will result in no loss of sensitivity despite the volume of extract (5 mL) not recovered after GPC].

10.2.2.3.2 Soil/Sediment

Adjust the final volume for low-level and medium-level soil/sediment samples to equal V_{out} with methylene chloride. For example, if V_{out} equals 0.5 mL, then the final volume must be adjusted to 0.5 mL. Concentrating the extract to 0.5 mL will result in no loss of sensitivity despite the volume of extract not recovered after GPC cleanup. Remove boiling chips before adjusting final volume.

10.2.2.3.3 Transfer the extract to a PTFE-sealed screw-cap bottle, label the bottle, and store at 4°C (±2°C).

10.3 Sample Cleanup by Gel Permeation Chromatography (GPC)

10.3.1 Introduction

10.3.1.1 GPC is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of natural macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated.

10.3.1.2 GPC must be performed for all soil/sediment extracts. GPC must be performed for water extracts that contain higher molecular weight contaminants that interfere with the analysis of the target analytes. In addition, GPC must be performed for all associated blanks, and MS/MSDs. If the cleanup procedure is inadequate, contact SMO.

10.3.2 GPC Column Preparation

Prepare the GPC column using Bio Beads. Alternative column packings may be used if 1) the column packings have equivalent or better performance than the Bio Beads and meet the technical acceptance criteria for GPC calibration and GPC Continuing Calibration Verification (CCV), and 2) the column packings do not introduce

contaminants/artifacts into the sample that interfere with the analysis of the semivolatile compounds. Follow the manufacturer's instructions for preparation of the GPC column.

10.3.3 Calibration of GPC

10.3.3.1 Summary of GPC Calibration and GPC Continuing Calibration Verification

The GPC calibration procedure and GPC CCV procedure are based on monitoring the elution of standards with a UV detector connected to the GPC column.

10.3.3.2 Frequency of GPC Calibration and GPC Continuing Calibration Verification

Each GPC system must be calibrated upon award of a contract, when the column is changed, when channeling occurs, and once every 7 days [GPC CCV] when samples, including MS/MSDs and blanks, are cleaned up using GPC.

10.3.3.3 Procedure for GPC Calibration and GPC Continuing Calibration Verification

Follow the manufacturer's instructions for operating the GPC system. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte Retention Times (RTs) and must be monitored.

10.3.3.3.1 Using a 10 mL syringe, load the calibration solution (Section 7.2.3.3) onto the GPC. Establish appropriate "COLLECT" and "DUMP" time periods to ensure collection of all target analytes. Initiate column eluate collection just before elution of bis(2-ethylhexyl)phthalate and after the elution of corn oil. Stop eluate collection shortly after the elution of perylene. Collection should be stopped before sulfur elutes. Use a "WASH" time of 10 minutes after the elution of sulfur. Each laboratory is required to establish its specific time sequences.

10.3.3.3.2 Re-inject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

10.3.3.3.3 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

10.3.3.3.4 Analyze a GPC blank of methylene chloride after each GPC calibration or each GPC CCV. Concentrate the methylene chloride that passes through the system during the collect cycle using a K-D evaporator. Add internal standards at the appropriate concentration and analyze the concentrate by Gas Chromatograph/Mass Spectrometer (GC/MS).

10.3.4 Technical Acceptance Criteria for GPC Calibration and GPC Continuing Calibration Verification

10.3.4.1 The GPC system must be calibrated and verified at the frequency described in Section 10.3.3.2. The UV trace must meet the following requirements:

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and the phthalate peaks should exhibit greater than 85% resolution.
- The phthalate and methoxychlor peaks should exhibit greater than 85% resolution.
- Methoxychlor and perylene peaks should exhibit greater than 85% resolution.
- Perylene and sulfur peaks must not be saturated and should exhibit greater than 90% baseline resolution.

10.3.4.2 The solvent flow rate and column pressure must be within the manufacturer's specified ranges.

10.3.4.3 If the RT shift is greater than 5% between calibrations take corrective action. Excessive RT shifts are caused by the following:

- Poor laboratory temperature control or system leaks.
- An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight.
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

10.3.4.4 A copy of the two most recent ultraviolet (UV) traces of the calibration solution from the same GPC system (instrument, column, conditions) must be submitted with the data for the associated samples.

10.3.4.5 The analyte concentrations in the GPC blank must be less than the CRQL for all target compounds in Exhibit C (Semivolatiles), except bis(2-ethylhexyl)phthalate, which must be less than 5 times the CRQL.

10.3.5 Corrective Action for GPC Calibration and GPC Continuing Calibration Verification

10.3.5.1 If the requirements in Section 10.3.4 cannot be met, the column may be cleaned by processing several 5 mL volumes of butylchloride through the system. Butylchloride removes the discoloration and particles that may have precipitated out of the methylene chloride extracts. If a guard column is being used, replace it with a new one. This may correct the problem. If column maintenance does not restore the performance of the column, the column must be repacked with new packing and recalibrated. It may be necessary to obtain a new lot of Bio Beads if the column fails all criteria.

10.3.5.2 If the GPC blank exceeds the requirements in Section 10.3.4.5, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

10.4 Sample Extract Cleanup by GPC

10.4.1 It is very important to have constant laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not constant, RTs will shift, and the "DUMP" and "COLLECT" times determined by the calibration standard will no longer be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22°C.

10.4.2 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol/water solution must be diluted and loaded into several loops. Similarly, extracts containing more than 40 mg/mL of non-volatile residue must be diluted and loaded into several loops. The non-volatile residue may be determined by evaporating a 100 µL aliquot of the extract to dryness in a tared aluminum weighing pan, or other suitable container. Systems using automated injection devices to load the sample on the column must be carefully monitored to assure that the required amount is being injected on the column. Viscous extracts or extracts containing a large amount of non-volatile residue will cause problems with an automated injection system's ability to inject the proper amount of sample extract on a column. After the sample extract has been processed, the remaining sample extract in the injection vial must be checked before proceeding with extract cleanup to assure that the proper amount was injected on the column. If the proper amount of extract was not injected, the sample must be re-prepared at no additional cost to USEPA, and the sample extract must either be diluted and loaded into several loops, or the sample extract must be injected manually.

NOTE: When multiple loops/runs are necessary for an individual sample, be sure to combine all of the sample eluates collected from each run.

10.4.3 Frequency of GPC Sample Cleanup

GPC cleanup must be performed once for each soil/sediment extract and for water extracts that contain high molecular weight contaminants that interfere with the analysis of the target analytes. GPC cleanup on the method blank must be performed after all associated samples have been cleaned up (GPC sequence: calibration, sample 1, sample 2, etc., method blank, calibration verification).

10.4.4 Procedure for GPC Sample Cleanup

10.4.4.1 Particles greater than 5 micron may scratch the valve, which may result in a system leak and cross contamination of sample extracts in the sample loops. To avoid such problems, filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container (e.g., a 15 mL culture tube with a PTFE-lined screw-cap). Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. Draw a minimum of 8 mL of extract into a 10 mL syringe.

NOTE: Some GPC instrument manufacturers recommend using a smaller micron size filter. Follow the manufacturer's recommended operating instructions.

10.4.4.2 Introduction of particulates or glass wool into the GPC switching valves may require factory repair of the apparatus.

10.4.4.3 Follow the manufacturer's instructions for operation of the GPC system being utilized. A 2 mL injection loop may be used in place of a 5 mL injection loop. If a 2 mL injection loop is used, concentrate the sample extract to 4 mL instead of 10 mL and inject 2 mL instead of 5 mL.

10.4.4.4 If the sample is difficult to load, part of the system may be blocked. Take appropriate corrective action, following the manufacturer's recommendations. The problem must be resolved prior to loading sample extracts.

10.4.4.5 After loading each sample loop, wash the loading port with methylene chloride to minimize cross-contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

10.4.4.6 After loading all the sample loops, process each sample using the "COLLECT" and "DUMP" cycle time established in Section 10.3.3.3.1.

10.4.4.7 Collect each sample in a 250 mL Erlenmeyer flask, covered with aluminum foil to reduce solvent evaporation, or directly into a K-D evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems.

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure.
- Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used.
- Leaks in the system or significant variances in room temperature.

10.4.4.8 Any samples that were loaded into two or more loops must be recombined before proceeding with concentration.

10.5 Final Concentration

Concentrate the extract as per Section 10.2.2. After removing boiling chips, final volumes should be brought to the volumes stated in Section 10.2.2.3.

10.6 Sample Analysis by Gas Chromatograph/Mass Spectrometer (GC/MS)

10.6.1 Sample extracts shall be analyzed only after the GC/MS system has met the instrument performance check, initial calibration, and CCV requirements. The same instrument conditions must be employed for the analysis of samples as were used for calibration.

10.6.2 The internal standard solution is added to an aliquot of each sample extract. Add sufficient amount of the internal standard solution (Section 7.2.3.6) to each accurately measured aliquot of water, low-level, or medium-level soil/sediment sample extract to result in 20 ng/µL concentration of each internal standard.

NOTE: In order to make provision for sample dilutions and/or optional analysis of Polyaromatic Hydrocarbons

(PAHs)/pentachlorophenol by the Selected Ion Monitoring (SIM) technique, if requested, the internal standard solution must be added to aliquots of sample extracts, not the entire extract.

10.6.3 If the optional analysis of PAHs/pentachlorophenol by SIM is to be performed, the Contractor shall add sufficient amount of the internal standard solution to each accurately measured aliquot of water and low- level soil/sediment sample extract to result in a 0.40 ng/µL concentration of each internal standard.

10.6.4 If sample extracts are to be diluted, add internal standards after dilution. Internal standards must be added to maintain the required 20 ng/µL (0.40 ng/µL for the optional analysis of PAHs/pentachlorophenol by SIM) of each internal standard in the extract volume.

10.6.5 Inject 1.0 or 2.0 µL of the sample extract into the GC/MS. This volume must contain each internal standard at a concentration of 20 ng/µL (0.40 ng/µL for optional analysis of PAHs/pentachlorophenol by SIM).

10.6.6 Sample Dilutions

10.6.6.1 If the response of any target compound in any sample exceeds the response of the same target compound in the high standard of the initial calibration, that sample extract must be diluted. Add the internal standard solution to the diluted extract for a concentration of 20 ng/µL (0.40 ng/µL for optional analysis of PAHs/pentachlorophenol by SIM) of each internal standard, and analyze the diluted extract. Guidance in performing dilution and exceptions to this requirement are given below.

10.6.6.2 Use the results of the original analysis to determine the approximate Dilution Factor (DF) required to get the largest analyte peak within the initial calibration range.

10.6.6.3 The DF chosen must keep the response of the largest peak for a target compound in the upper half of the calibration range of the instrument.

10.6.6.4 The maximum DF permitted for low-level soils is 30.0. If a low-level soil sample requires a DF greater than 30.0 to bring target compounds within the calibration range, then the medium-level method shall be utilized.

10.6.6.5 If more than two analyses (i.e., from the original sample extract and more than one dilution, or from the most concentrated dilution analyzed and further dilutions) are required to get all target compounds within the calibration range, contact SMO for guidance.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

11.1.1.1 The compounds listed in the Target Compound List (TCL) in Exhibit C (Semivolatiles), shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of the standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

- Elution of the sample analyte within the Gas Chromatograph (GC) Relative Retention Time (RRT) unit window established from the 12-hour calibration standard.
- Correspondence of the sample analyte and calibration standard component mass spectra.

11.1.1.2 For establishing correspondence of the GC RRT, the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For samples analyzed during the same 12-hour time period as the initial calibration standards, compare the analyte Retention Times (RTs) to those from the 20 ng/µL [0.40 ng/µL for the optional Polyaromatic Hydrocarbons (PAHs)/pentachlorophenol analysis] calibration standard. Otherwise, use the corresponding opening Continuing Calibration Verification standard. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using Extracted Ion Current Profiles (EICPs) for ions unique to the component of interest.

11.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained from a calibration standard on the Contractor's Gas Chromatograph/Mass Spectrometer (GC/MS) meeting the daily instrument performance requirements for decafluorotriphenylphosphine (DFTPP) are required. Once obtained, these standard spectra may be used for identification purposes only if the Contractor's GC/MS meets the DFTPP daily instrument performance requirements.

11.1.1.4 The requirement for qualitative verification by comparison of mass spectra are as follows:

- All ions present in the standard mass spectrum at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.
- The relative intensities of ions specified in the paragraph above must agree within ±20% between the standard and sample spectra (e.g., For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70%).
- Ions greater than 10% in the sample spectrum, but not present in the standard spectrum, must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their

spectra. When target compounds are below Contract Required Quantitation Limits (CRQLs) but the spectrum meets the identification criteria, report the concentration with a "J". For example, if the CRQL is 5.0 µg/L and concentration of 3.0 µg/L is calculated, report as "3.0J".

11.1.1.5 If a compound cannot be verified by all of the spectral identification criteria in Sections 11.1.1.1 - 11.1.1.4, but in the technical judgement of the mass spectra interpretation specialist the identification is correct, then the Contractor shall report the identification and proceed with quantitation.

11.1.2 Qualitative Identification of Non-Target Compounds

11.1.2.1 A library search shall be executed for non-target sample components for the purpose of tentative identification. The NIST (2002 release or later), Wiley (1991 release or later), or equivalent mass spectral library, shall be used as the reference library.

11.1.2.2 All organic compounds that have not been positively identified as semivolatile target analytes using the procedures detailed in Section 11.1.1, or that are not Deuterated Monitoring Compounds (DMCs) or internal standards shall be tentatively identified via a forward search of the NIST, Wiley, or equivalent mass spectral library. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer-generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

11.1.2.3 Up to 30 non-alkane Tentatively Identified Compounds (TICs) of greatest apparent concentration shall be reported on Form I SV-TIC. Peaks that are tentatively identified as straight-chain, branched, or cyclic alkanes, and are alone or part of an alkane series, shall be reported as "total alkanes" on Form I SV-TIC. An alkane is defined as any hydrocarbon with the generic formula C_nH_{2n+2} (straight-chain or branched) or C_nH_{2n} (cyclic) that contains only C-H and C-C single bonds. The concentrations of each of the alkanes is to be summed and reported as a single result for the "total alkanes". Documentation for the tentative identification of each alkane shall be supplied in the hard copy deliverable packages. The alkanes are not to be counted as part of the 30 compounds individually reported as TICs on Form I SV-TIC. Carbon dioxide and compounds with responses less than 10% of the internal standard in which they are to be quantified (as determined by inspection of the peak areas or height) are not to be reported (nor are they to be counted as part of the 30 compounds that are to be reported).

11.1.2.4 Peaks that are suspected to be aldol-condensation reaction products (i.e., 4-methyl-4-hydroxy-2-pentanone and 4-methyl-3-pentene-2-one) shall be searched, reported, and counted as part of the 30 most intense non-target semivolatile compounds, and qualified with an "A" flag on Form I SV-TIC.

11.1.2.5 Rules for Making Tentative Identification

11.1.2.5.1 For compounds to be reported, as per the instructions in Section 11.1.2.3., identification (as generated by the library search program) of those receiving a library search match of

85% or higher should be considered a "probable match". The compound should be reported with the identification generated by the search program unless the mass spectral interpretation specialist feels there is just evidence not to report the compound as identified by the library search program.

11.1.2.5.2 If the library search produces more than one compound at or above 85%, report the compound with the highest percent match (report first compound if the percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels there is just evidence not to report the compound with the highest match. Do not report DMCs, internal standards, or analytes that are on the semivolatile target analyte list, unless the library search produces only one compound having a match of greater than 85%, and that compound is identified as a DMC, internal standard, or semivolatile target analyte.

11.1.2.5.3 If the library search produces a series of obvious isomer compounds with library search matches greater than 85% (e.g., tetramethyl naphthalenes), the compound with the highest library search percent match should be reported (or first compound if library search matches are the same).

11.1.2.5.4 If the mass spectral interpretation specialist has just evidence to support reporting a compound with a tentative identification of something other than that generated by the library search program (with a library search result of 85% or greater), the laboratory shall include in the Sample Delivery Group (SDG) Narrative the justification for not reporting a compound as listed by the search program. This narrative shall detail explicitly why a library search generated identification for a compound was rejected. If a TIC has obvious isomer analogs, the laboratory shall include in the SDG narrative a statement indicating that the exact isomer configuration, as reported, may not be absolutely accurate.

11.1.2.5.5 If the library search produces no matches at or above 85%, the mass spectral interpretation specialist is encouraged to make a valid tentative identification of the compound. If no valid tentative identification can be made, the compound should be reported as "unknown". The mass spectral interpretation specialist should give additional classification of the unknown, if possible (e.g., "unknown aromatic compound", "unknown chlorinated compound", etc.).

11.1.2.6 Qualitative identification on non-target compounds is not required when performing SIM analyses.

11.2 Calculations

11.2.1 Target Compounds

11.2.1.1 Target compounds identified shall be quantitated by the internal standard method. The internal standard used shall be the one assigned to that analyte for quantitation (Table 2). The EICP area of primary characteristic ions of analytes listed in Table 3 are used for quantitation.

11.2.1.2 It is expected that situations will arise when the automated quantitation procedures in the GC/MS software provide inappropriate quantitations. This normally occurs when there is

compound coelution, baseline noise, or matrix interferences. In these circumstances, the Contractor must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific TCL compound. The area integrated shall not include baseline background noise. The area integrated shall not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet Quality Control (QC) criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instance of manual integration must be documented in the SDG Narrative.

11.2.1.3 In all instances where the data system report has been edited or where manual integration or quantitation has been performed, the GC/MS Operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the integration scan range. The GC/MS Operator shall also mark each integrated area with the letter "M" on the quantitation report. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all compounds listed in Exhibit C (Semivolatiles), internal standards, and DMCs.

11.2.1.4 The requirements listed in Sections 11.2.1.1 - 11.2.1.3 apply to all standards, samples, and blanks.

11.2.1.5 The Mean Relative Response Factor ($\overline{RRF}$) from the initial calibration is used to calculate the concentration in the sample. Secondary ion quantitation is allowed ONLY when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reason in the SDG Narrative. The area of a secondary ion cannot be used for the area of a primary ion unless a $\overline{RRF}$ is calculated using the secondary ion.

11.2.1.6 Calculate the concentration in the sample using the $\overline{RRF}$ and Equations 5 and 6.

11.2.1.6.1 Water

EQ. 5 Concentration of Water Sample

$$\text{Concentration } \mu g/L = \frac{(A_x)\,(I_s)\,(V_t)\,(DF)\,(GPC)}{(A_{is})\,(\overline{RRF})\,(V_o)\,(V_i)}$$

Where,

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

I_s = Amount of internal standard injected in ng.

V_o = Volume of water extracted in mL.

V_i = Volume of extract injected in µL.

V_t = Volume of the concentrated extract in µL (If GPC Cleanup is performed, $V_t = V_{out}$).

$\overline{RRF}$ = Mean Relative Response Factor determined from the initial calibration standard.

$GPC = \frac{V_{in}}{V_{out}}$ = GPC factor. (If no GPC is performed, GPC = 1).

V_{in} = Volume of extract loaded onto GPC column.

V_{out} = Volume of extract collected after GPC cleanup.

DF = Dilution Factor. The DF for analysis of water samples for semivolatiles by this method is defined as follows:

$$DF = \frac{\text{µL most conc. extract used to make dilution + µL clean solvent}}{\text{µL most conc. extract used to make dilution}}$$

If no dilution is performed, DF = 1.0.

11.2.1.6.2 Soil/Sediment

EQ. 6 Concentration of Soil/Sediment Sample

$$\text{Concentration µg/Kg (Dry weight basis)} = \frac{(A_x)\,(I_s)\,(V_t)\,(DF)\,(GPC)}{(A_{is})\,(\overline{RRF})\,(V_i)\,(W_s)\,(D)}$$

Where,

A_x, I_s, A_{is}, V_{in}, and V_{out} are as given for water, above.

V_t = Volume of the concentrated extract in µL (If no GPC Cleanup is performed, then V_t = 1000 µL. If GPC Cleanup is performed, then $V_t = V_{out}$).

V_i = Volume of the extract injected in µL.

$$D = \frac{100 - \%\ \text{Moisture}}{100}$$

W_s = Weight of sample extracted in g.

$GPC = \frac{V_{in}}{V_{out}}$ = GPC Factor

$\overline{RRF}$ = Mean Relative Response Factor determined from the initial calibration standard.

DF = Dilution Factor. The DF for analysis of soil/sediment samples for semivolatiles by this method is defined as follows:

$$DF = \frac{\text{µL most conc. extract used to make dilution + µL clean solvent}}{\text{µL most conc. extract used to make dilution}}$$

If no dilution is performed, DF = 1.0.

A GPC factor of 2.0 is used to account for the amount of extract that is not recovered from the mandatory use of GPC cleanup. Concentrating the extract collected after GPC to 0.5 mL maintains the sensitivity of the soil/sediment method.

11.2.2 Non-Target Compound

An estimated concentration for non-target compounds tentatively identified shall be quantitated by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used. The equations for calculating concentration are the same as Equations 5 and 6. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compounds to be measured and the internal standard. An $\overline{RRF}$ of 1 is to be assumed. The resulting concentration shall be qualified as "J" (estimated, due to lack of a compound specific response factor), and "N" (presumptive evidence of presence), indicating the quantitative and qualitative uncertainties associated with this non-target component. An estimated concentration should be calculated for all TICs as well as those identified as unknowns.

11.2.3 CRQL Calculations

11.2.3.1 Water Samples

EQ. 7 Aqueous Adjusted CRQL

$$\underset{\text{CRQL}}{\text{Adjusted}} = \underset{\text{CRQL}}{\text{Contract}} \times \frac{(V_x)\,(V_t)\,(DF)}{(V_o)\,(V_c)}$$

Where,

V_t, DF, and V_o are as given in Equation 5.

V_x = Contract sample volume (1000 mL).

V_c = Contract concentrated extract volume (1000 µL if GPC is not performed. If GPC was performed, then $V_c = V_{out}$).

11.2.3.2 Soil/Sediment Samples

EQ. 8 Soil/Sediment Adjusted CRQL

$$\underset{\text{CRQL}}{\text{Adjusted}} = \underset{\text{CRQL}}{\text{Contract}} \times \frac{(W_x)\,(V_t)\,(DF)}{(W_s)\,(V_c)\,(D)}$$

Where,

V_t and DF = As given in Equation 5.

W_s and D = As given in Equation 6.

W_x = Contract sample weight (30 g for low-level soil/sediment samples and 1.0 g for medium-level soil/sediment samples).

V_c = Contract concentrated extract volume (If GPC is required, $V_c = V_{out}$).

11.2.4 Deuterated Monitoring Compound (DMC) Recoveries

11.2.4.1 Calculate DMC recoveries for all samples, blanks, and Matrix Spike and Matrix Spike Duplicates (MS/MSDs). Determine if recovery is within limits (Table 6) and report on the appropriate form.

11.2.4.2 Calculate the concentrations of the DMCs using the same equations as used for the target compounds. Calculate the recovery of each DMC using the following equation:

EQ. 9 DMC Percent Recovery Calculation

$$\%\ \text{Recovery} = \frac{(\text{Concentration (or amount) found} \times DF)}{\text{Concentration (or amount) spiked}} \times 100$$

Where,

DF = Same as EQ. 5.

11.3 Technical Acceptance Criteria for Sample Analysis

11.3.1 The samples must be analyzed on a GC/MS system meeting the instrument performance check, initial calibration, CCV, and blank technical acceptance criteria. The sample must undergo cleanup procedures, when required, on a GPC meeting the technical acceptance criteria for GPC calibration.

11.3.2 The sample must be extracted and analyzed within the contract holding times.

11.3.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

11.3.4 The Percent Recoveries of DMCs in a sample must be within the recovery limits listed in Table 6. Up to four DMCs per sample may fail to meet the recovery limits listed in Table 6 but all Percent

Recoveries must be greater than zero. If the optional analysis of PAHs and pentachlorophenol using the Selected Ion Monitoring (SIM) technique is to be performed, both SIM DMCs must meet the recovery limits in Table 6.

NOTE: The DMC recovery requirements do not apply to samples that have been diluted.

11.3.5 The instrumental response (EICP area) for each of the internal standards in the sample must be within the range of 50.0% and 200% of the response of the internal standard in the most recent opening CCV standard analysis.

11.3.6 The RT shift for each of the internal standards must be within ±0.50 min. (30 seconds) between the sample and the most recent opening CCV standard analysis.

11.3.7 Excluding those ions in the solvent front, no ion may saturate the detector. No target compound concentration may exceed the upper limit of the initial calibration range unless a more dilute aliquot of the sample extract is also analyzed according to the procedures in Section 10.6.6.

11.4 Corrective Action for Sample Analysis

11.4.1 Corrective Action for Sample Analysis

The sample technical acceptance criteria **must** be met before data are reported. Samples contaminated from laboratory sources, or sample results submitted not meeting the sample technical acceptance criteria, will require reextraction and/or reanalysis at no additional cost to USEPA.

11.4.2 Corrective action for failure to meet instrument performance checks and initial and continuing calibration verification must be completed before the analysis of samples.

11.4.3 Corrective Action for DMC Recoveries that Fail to Meet Their Acceptance Criteria (Section 11.3.4, Table 6)

11.4.3.1 If the DMC recoveries in a sample fail to meet the acceptance criteria specified in Section 11.3.4, check calculations, sample preparation logs, DMC standard spiking solutions, and the instrument operation.

- If the calculations were incorrect, correct them and verify that the DMC recoveries meet their acceptance criteria.
- If the sample preparation logs indicate that the incorrect amount of DMC standard spiking solution was added to the sample, then reextract and reanalyze the sample after adding the correct amount of DMC standard spiking solution.
- If the DMC standard spiking solution was improperly prepared, concentrated, or degraded, re-prepare the solution, and reextract and reanalyze the sample.
- If the DMC recoveries were outside the lower acceptance limit and the extract from the sample were cleaned up on a GPC using an automated injection system, the Contractor shall verify that the proper amount was injected on the GPC column.

If insufficient sample volume was injected on the GPC, the sample must be re-prepared and reanalyzed.

- If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. Verify that the DMC recoveries meet their acceptance criteria.

- If the instrument malfunction affected the calibrations, recalibrate the instrument before reanalyzing the sample extract.

11.4.3.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

11.4.3.2.1 Reextract and reanalyze the sample. EXCEPTION: If DMC recoveries in a sample used for an MS/MSD were considered unacceptable, then it should be reextracted/reanalyzed only if DMC recoveries met the acceptance criteria in <u>both</u> the MS/MSD analyses.

11.4.3.2.2 If the DMC recoveries meet acceptance criteria in the reextracted/reanalyzed sample, then the problem was within the Contractor's control. Therefore, submit only data from the reextraction/reanalysis.

11.4.3.2.3 If the DMC recoveries fail to meet the acceptance criteria in the reextracted/reanalyzed sample, then submit data from both analyses. Distinguish between the initial analysis and the reextraction/reanalysis on all deliverables, using the suffixes in Exhibit B, Section 3.3.7.1.

11.4.4 Corrective Action for Internal Standard Compound Responses that Fail to Meet Their Acceptance Criteria (Sections 11.3.6 and 11.3.7)

11.4.4.1 If the internal standards in a sample fail to meet their acceptance criteria, check calculations, internal standard solutions, and instrument operation.

- If the calculations were incorrect, correct them, and verify that the internal standard responses meet their acceptance criteria.

- If the internal standard solution was improperly prepared, concentrated, or degraded, re-prepare solutions and reanalyze another aliquot of the sample extract after adding the correct amount of the freshly prepared internal standard solution.

- If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract.

- If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

11.4.4.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

11.4.4.2.1 Reanalyze the sample extract. EXCEPTION: If internal standard compound recoveries in the original sample used for a Matrix

Spike and/or Matrix Spike Duplicate were outside the acceptance windows, then it should be reanalyzed only if internal standard compound recoveries met the internal standard acceptance criteria in both the MS/MSD analysis.

11.4.4.2.2 If the internal standard compound recoveries meet acceptance criteria in the reanalyzed sample extract, then the problem was within the Contractor's control. Therefore, submit only data from the reanalysis.

11.4.4.2.3 If the internal standard compound recoveries fail to meet their acceptance windows in the reanalyzed sample extract, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables using the suffixes in Exhibit B.

11.4.5 Corrective Action for Internal Standard Compound RTs Outside Acceptance Criteria (Section 11.3.6)

11.4.5.1 If the internal standard compound RTs are not within their acceptance criteria, check the instrument for malfunctions. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

11.4.5.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

11.4.5.2.1 Reanalyze the sample extract.

EXCEPTION: If the internal standard compound RTs in a sample used for a Matrix Spike and/or Matrix Spike Duplicate were outside the acceptance criteria, then it should be reanalyzed only if the internal standard compound RTs were within the acceptance criteria in <u>both</u> of the MS/MSD analyses.

11.4.5.2.2 If the internal standard compound RTs are within the acceptance criteria in the reanalyzed sample extract, then the problem was within the Contractor's control. Therefore, submit only data from the reanalysis with the internal standard compound RTs within the acceptance limits.

11.4.5.2.3 If the internal standard compound RTs are outside the acceptance criteria in the reanalyzed sample extract, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables, using the suffixes in Exhibit B, Section 3.3.7.1.

12.0 QUALITY CONTROL (QC)

12.1 Method Blanks

12.1.1 Summary of Method Blanks

A method blank is a volume of a clean reference matrix (reagent water for water samples, or purified sodium sulfate or Hydromatrix for soil/sediment samples) spiked with sufficient amount of internal standard solution (Section 7.2.3.6) and Deuterated Monitoring Compound (DMC) standard spiking solution (Section 7.2.3.1) and carried through the entire analytical procedure. The internal standard solution is added just prior to full scan analysis by Gas Chromatograph/Mass Spectrometer (GC/MS). The volume or weight of the reference matrix must be approximately equal to the volume of weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

12.1.2 Frequency of Method Blanks

A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples [excluding Matrix Spike and Matrix Spike Duplicates (MS/MSDs) and Performance Evaluation (PE) samples]. In addition, a method blank shall:

- Be extracted by the same procedure used to extract samples; and
- Be analyzed on each GC/MS system used to analyze associated samples and conditions (i.e., GC/MS settings).

12.1.3 Procedure for Method Blank Preparation

12.1.3.1 For semivolatile analyses, a method blank for water samples consists of 1.0 L volume of reagent water spiked with a sufficient amount of the DMC standard spiking solution to result in the addition of 40 µg of each DMC and 0.4 µg of each Selected Ion Monitoring (SIM) DMC (Section 7.2.3.1). For low-level and medium-level soil/sediment samples, a method blank consists of 1 g (medium-level) and 30 g (low-level) of sodium sulfate or Hydromatrix spiked with sufficient amount of the DMC standard spiking solution to result in the addition of 40 µg of each DMC and 0.4 µg (low-level) of each SIM DMC. Extract, concentrate, cleanup, and analyze the blank according to procedures for water and soil samples.

12.1.3.2 Under no circumstances should method blanks be analyzed at a dilution (i.e., method blanks should always have a DF = 1.0).

12.1.4 Technical Acceptance Criteria for Method Blank Analysis

12.1.4.1 All blanks must be extracted and analyzed at the frequency described in Section 12.1.2 on a GC/MS system meeting the decafluorotriphenylphosphine (DFTPP), initial calibration, and CCV technical acceptance criteria.

12.1.4.2 The Percent Recovery (%Recovery) of each of the DMCs in the blank must be within the acceptance limits listed in Table 6. These limits are <u>not</u> advisory.

12.1.4.3 The blank must meet the sample acceptance criteria listed in Sections 11.3.5 through 11.3.7.

12.1.4.4 A method blank for semivolatile analysis for low-level soil and water samples must contain less than five times the CRQL of the bis (2-ethylhexyl) phthalate listed in Exhibit C (Semivolatiles). For all other target compounds the method blank must contain less than the Contract Required Quantitation Limit (CRQL) of any single target compound [Exhibit C (Semivolatiles)]. For medium-level soils, the method blank must contain less than the CRQL of any single target compound.

12.1.4.5 All method blanks must be analyzed at the original concentration only (i.e., DF = 1.0).

12.1.5 Corrective Action for Method Blanks

12.1.5.1 If a method blank does not meet the technical acceptance criteria for method blank analysis, the Contractor shall consider the analytical system to be out-of-control.

12.1.5.2 If contamination is the problem, then the source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvent, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in the GC/MS be eliminated. Samples associated with the contaminated blank must be reextracted and reanalyzed at no additional cost to USEPA.

12.1.5.3 If DMC recoveries in the method blank do not meet the acceptance criteria listed in Section 12.1.4.2 and Table 6, first reanalyze the method blank. If the DMC recoveries do not meet the acceptance criteria after reanalysis, the method blank and all samples associated with that method blank must be reextracted and reanalyzed at no additional cost to USEPA.

12.1.5.4 If the method blank does not meet internal standard response requirements listed in Section 11.3.5, follow the corrective action procedure outlined in Section 11.4.4.1. The Contractor shall resolve and document the resolution of the problem before proceeding with sample analysis.

12.1.5.5 If the method blank does not meet the Retention Time (RT) requirements for internal standards (Section 11.3.6), check the instrument for malfunction and recalibrate. Reanalyze the method blank. Sample analyses cannot proceed until the method blank meets these requirements.

12.2 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the methods used for semivolatile analyses, USEPA has prescribed a mixture of semivolatile target compounds to be spiked into two aliquots of a sample and analyzed in accordance with the appropriate method.

12.2.2 Frequency of MS/MSD Analyses

12.2.2.1 An MS/MSD shall be analyzed if requested by the Region [through the Sample Management Office (SMO)] or specified on the Traffic Report/Chain of Custody Record (TR/COC). If requested, a Matrix Spike and a Matrix Spike Duplicate must be performed for each group of 20 field samples in a Sample Delivery Group (SDG), or each SDG, whichever is most frequent. An MS/MSD should be analyzed for each sample matrix (water/soil) and each level (low/med). For the optional analysis by the SIM method, MS/MSD will not be required unless specifically requested by the Region.

12.2.2.2 As part of USEPA's Quality Assurance/Quality Control (QA/QC) program, water rinsate samples and/or field/trip blanks (field QC) may accompany soil/sediment samples and/or water samples that are delivered to the laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the field QC samples.

12.2.2.3 If the USEPA Region requesting MS/MSD designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample remaining to perform an MS/MSD, then the Contractor shall choose another sample on which to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify SMO that insufficient sample was received and identify the USEPA sample selected for the MS/MSD analysis. SMO shall contact the Region for confirmation immediately after notification. The rationale for the choice of another sample other than the one designated by USEPA shall be documented in the SDG Narrative.

12.2.2.4 If there is insufficient sample remaining in any of the samples in an SDG to perform the requested MS/MSD, then the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD be performed, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.2.2.1, then the Contractor shall contact SMO. SMO will contact the Region to determine which samples should have an MS/MSD analysis performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If this procedure is not followed, the Contractor will not be paid for MS/MSD analysis performed at a greater frequency than required by the contract.

12.2.2.6 When a Contractor receives only PE samples, no MS/MSD shall be performed within that SDG.

12.2.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the requested MS/MSD analysis if the Region did not designate samples to be used for this purpose. If the PE sample is an ampulated standard, the ampulated PE sample is not considered to be another matrix type.

12.2.3 Procedure for Preparing MS/MSD

12.2.3.1 Water Samples

For water samples, prepare two additional 1.0 L aliquots of the sample chosen for spiking in two continuous extractors. Add a sufficient amount of the DMC standard spiking solution and the matrix spiking solution to each aliquot to result in the addition of 40 µg of each DMC (0.40 µg of each SIM DMC) and 40 µg of each Matrix Spike compound (0.40 µg of each Matrix Spike compound for SIM analysis). Extract, concentrate, cleanup, and analyze the MS/MSD according to the procedures for water samples (Section 10.1.3).

12.2.3.2 Soil/Sediment Samples - Low-Level

For low-level soil/sediment samples, prepare two additional 30 g aliquots (record weight to nearest 0.1 g) of the sample chosen for spiking in the two 400 mL beakers. Add 60 g of anhydrous powdered sodium sulfate or 30 g of Hydromatrix to each aliquot. Mix well. Add a sufficient amount of the DMC standard spiking solution and the matrix spiking solution to each aliquot, to result in the addition of 40 µg of each DMC (0.40 µg of each SIM DMC) and 40 µg of each Matrix Spike compound (0.40 µg of each Matrix Spike compound for SIM analysis), then follow the appropriate extraction procedure in Section 10.1.4.4. Extract, concentrate, cleanup, and analyze the MS/MSD according to the procedures for low-level soil samples.

12.2.3.3 Soil/Sediment Samples - Medium-Level

For medium-level soil/sediment samples, prepare two additional 1.0 g aliquots (record weight to nearest 0.1 g) of the sample chosen for spiking in two, 20 mL vials. Add 2.0 g of anhydrous powdered sodium sulfate or 1.0 g of Hydromatrix to each aliquot. Mix well. Add a sufficient amount of DMC standard spiking solution and the matrix spiking solution to result in the addition of 40 µg of each DMC and 40 µg of each Matrix Spike compound, and proceed with the appropriate extraction procedure (Section 10.1.4.5). Extract, concentrate, cleanup, and analyze the MS/MSD according to the procedures for medium-level samples.

12.2.3.4 If MS/MSD are requested for the optional SIM method, 0.40 µg of only acenaphthene, pentachlorophenol, and pyrene Matrix Spike compounds is required; however, a Matrix Spike solution containing the full list (Section 7.2.3.2.1) at 0.40 µg of each Matrix Spike compound may be used.

12.2.4 Dilution of MS/MSD

Before any MS/MSD analysis, analyze the original sample, then analyze the MS/MSD at the same concentration as the most concentrated extract for which the original sample results will be reported. For example, if the original sample is to be reported at a 1:1 dilution and a 1:10 dilution, then analyze and report the MS/MSD at a 1:1 dilution only. However, if the original sample is to be reported at a 1:10 dilution and a 1:100 dilution, then the MS/MSD must be analyzed and reported at a 1:10 dilution only. Do <u>not</u> further dilute the MS/MSD samples to get either spiked or non-spiked analytes within calibration range. Dilution of the sample must be performed in accordance to the conditions in Section 10.6.6.

NOTE: In cases where SIM MS/MSD is requested, if the sample designated for SIM MS/MSD analysis has all SIM target compounds detected during the full scan analysis, then the laboratory must contact SMO to determine if another sample should be chosen for SIM MS/MSD analysis. In this case, both sets of SIM MS/MSD analyses will be billable. If the Region does not request another sample for SIM MS/MSD, the original SIM MS/MSD analysis is still billable.

12.2.5 Calculations for MS/MSD

12.2.5.1 Calculate the recovery of each Matrix Spike compound in the MS/MSD samples and report on the appropriate forms. Calculate the concentrations of the Matrix Spike compounds using the same equations as used for target compounds (Equations 5 and 6). Calculate the recovery of each Matrix Spike compound as follows:

EQ. 10 Matrix Spike Recovery Calculation

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike Sample Result.

SR = Sample Result.

SA = Spike Added.

12.2.5.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each compound in the MS/MSD as follows:

EQ. 11 Relative Percent Difference Calculation

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where,

RPD = Relative Percent Difference.

MSR = Matrix Spike Recovery.

MSDR = Matrix Spike Duplicate Recovery.

12.2.6 Technical Acceptance Criteria for MS/MSD

12.2.6.1 If requested, all MS/MSDs must be prepared and analyzed at the frequency described in Section 12.2.2. All MS/MSDs must be analyzed on a GC/MS system meeting DFTPP, initial and continuing calibration verification technical acceptance criteria, and the method blank technical acceptance criteria. The MS/MSD must

undergo cleanup procedures when required on a Gel Permeation Chromatograph (GPC) meeting the technical acceptance criteria for GPC calibration.

12.2.6.2 The MS/MSD must have an associated method blank meeting the blank technical acceptance criteria.

12.2.6.3 The MS/MSD must be extracted and analyzed within the contract holding time.

12.2.6.4 The RT shift for each of the internal standards must be within ±0.50 minutes (30 seconds) between the MS/MSD sample and the most recent opening CCV standard analysis.

12.2.6.5 The limits for Matrix Spike compound recovery and RPD are given in Table 5. As these limits are only advisory, no further action by the laboratory is required; however, frequent failure to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from USEPA.

12.2.7 Corrective Action for MS/MSD

Any MS/MSD that fails to meet the technical acceptance criteria in Sections 12.2.6.1, 12.2.6.2, and 12.2.6.4 must be reanalyzed at no additional cost to USEPA. Only data from the MS/MSD that meets the technical acceptance criteria in Section 12.2.6 should be submitted.

12.3 Method Detection Limit (MDL) Determination

12.3.1 Before any field samples are analyzed under the contract, the MDL for each semivolatile target compound shall be determined on each instrument used for analysis. MDL determination is matrix-specific and level-specific (i.e., the MDL shall be determined for water, low-level soil and medium-level soils). The MDLs must be verified annually thereafter (see Section 12.3.2 for MDL verification procedures), until the contract expires or is terminated, or after major instrument maintenance. Major instrument maintenance includes, but is not limited to: cleaning or replacement of the mass spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), electron multiplier (or similar device), and GC column.

12.3.2 To determine the MDLs, the Contractor shall run an MDL study following the procedures specified in 40 CFR Part 136. The Contractor shall analyze the MDL samples on each instrument used for field sample analyses. MDL verification for water samples is achieved by analyzing a single reagent water blank (see method blank for water samples in Section 12.1) spiked with each semivolatile target compound at a concentration equal to two times the analytically determined MDL. Each target compound must produce a response and meet the criteria in Section 11.1.1. MDL verification for low-level soil samples is achieved by analyzing a single purified solid matrix blank (see method blank for low-level soil samples in Section 12.1) spiked with each semivolatile target compound at a concentration equal to 1-4 times the analytically determined MDL. MDL verification for medium-level soil samples is achieved by analyzing a single purified solid matrix blank (see method blank for medium-level soil samples in Section 12.1) spiked with each semivolatile target compound at a concentration equal to two times the analytically determined MDL. Samples used for MDL determination and verification must be subjected to the same extraction and cleanup procedures used for field samples. The resulting mass spectra of

each target compound must meet the qualitative identification criteria outlined in Sections 11.1.1 through 11.1.2.5.5.

12.3.3 The determined concentration of the MDL must be less than the CRQL.

12.3.4 All documentation for the MDL studies shall be maintained at the laboratory and provided to USEPA upon written request.

13.0 METHOD PERFORMANCE

Not Applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, USEPA recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to Laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington D.C. 20036, (202) 872-4386.

15.0 WASTE MANAGEMENT

USEPA requires that laboratory waste management practices be consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). SW-846 Method 8270C. Revision 3. December 1996.

16.2 US Environmental Protection Agency. Continuous Liquid-Liquid Extraction. SW-846 Method 3520C. Revision 3. December 1996.

16.3 US Environmental Protection Agency. Automated Soxhlet Extraction. SW-846 Method 3541. Revision 0. September 1994.

16.4 US Environmental Protection Agency. Pressurized Fluid Extraction (PFE). SW-846 Method 3545A. Revision 1. January 1998.

16.5 US Environmental Protection Agency. Ultrasonic Extraction. SW-846 Method 3550C. Revision 3. November 2000.

16.6 US Environmental Protection Agency. Silica Gel Cleanup. SW-846 Method 3630C. Revision 3. December 1996.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

Decafluorotriphenylphosphine Key Ions and
Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	10.0 - 80.0% of mass 198
68	Less than 2.0% of mass 69
69	Present
70	Less than 2.0% of mass 69
127	10.0 - 80.0% of mass 198
197	Less than 2.0% of mass 198
198	Base peak 100% relative abundance (see Note)
199	5.0 - 9.0% of mass 198
275	10.0 - 60.0% of mass 198
365	Greater than 1.0% of mass 198
441	Present but less than mass 443
442	50.0 - 100% of mass 198
443	15.0 - 24.0% of mass 442

NOTE: All ion abundances MUST be normalized to m/z 198, the nominal base peak, even though the ion abundance of m/z 442 may be up to 100% that of m/z 198.

Table 2

Semivolatile Internal Standards With Corresponding
Target and Deuterated Monitoring Compounds Assigned for Quantitation

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Benzaldehyde	Nitrobenzene	Hexachlorocyclopentadiene
Phenol	Isophorone	2,4,6-Trichlorophenol
Bis(2-chloroethyl) ether	2-Nitrophenol	2,4,5-Trichlorophenol
2-Chlorophenol	2,4-Dimethylphenol	2,3,4,6-Tetrachlorophenol
2-Methylphenol	Bis(2-chloroethoxy)methane	1,1'-Biphenyl
2,2'-Oxybis-(1-chloro-propane)	2,4-Dichlorophenol	2-Chloronaphthalene
Acetophenone	4-Chloroaniline	2-Nitroaniline
4-Methylphenol	Hexachlorobutadiene	Dimethylphthalate
N-Nitroso-di-n-propylamine	Caprolactam	Acenaphthylene
Hexachloroethane	4-Chloro-3-methylphenol	3-Nitroaniline
Phenol-d_5 (DMC)	2-Methylnaphthalene	Acenaphthene
Bis(2-chloroethyl)ether-d_8 (DMC)	Naphthalene	2,4-Dinitrophenol
2-Chlorophenol-d_4 (DMC)	Nitrobenzene-d_5 (DMC)	4-Nitrophenol
4-Methylphenol-d_8 (DMC)	2-Nitrophenol-d_4 (DMC)	Dibenzofuran
	2,4-Dichlorophenol-d_3 (DMC)	2,4-Dinitrotoluene
	4-Chloroaniline-d_4 (DMC)	2,6-Dinitrotoluene
	2-Methylnapthalene-d_{10} (SIM- DMC)	1,2,4,5-Tetrachlorobenzene
		Diethylphthalate
		4-Chlorophenyl-phenylether
		Fluorene
		4-Nitroaniline
		Acenaphthylene-d_8 (DMC)
		4-Nitrophenol-d_4 (DMC)
		Dimethylphthalate-d_6 (DMC)
		Fluorene-d_{10} (DMC)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4,6-Dinitro-2-methylphenol	Pyrene	Di-n-octylphthalate
N-Nitrosodiphenylamine	Butylbenzylphthalate	Benzo(b)fluoranthene
4-Bromophenyl-phenylether	3,3'-Dichlorobenzidine	Benzo(k)fluoranthene
Hexachlorobenzene	Benzo(a)anthracene	Benzo(a)pyrene
Atrazine	Bis(2-ethylhexyl)phthalate	Indeno(1,2,3-cd)pyrene
Pentachlorophenol	Chrysene	Dibenzo(a,h)anthracene
Phenanthrene	Pyrene-d_{10} (DMC)	Benzo(g,h,i)perylene
Anthracene		Benzo(a)pyrene-d_{12} (DMC)
Carbazole		
Di-n-butylphthalate		
Fluoranthene		
4,6-Dinitro-2-methylphenol-d_2 (DMC)		
Anthracene-d_{10} (DMC)		
Fluoranthene-d_{10} (SIM-DMC)		

Table 3

Characteristic Ions for Semivolatile
Target Compounds, Deuterated Monitoring Compounds, and Internal Standards

Parameter	Primary Quantitation Ion	Secondary Ion(s)
Benzaldehyde	77	105, 106
Phenol	94	65, 66
Bis(2-chloroethyl)ether	93	63, 95
2-Chlorophenol	128	64, 130
2-Methylphenol	108	107
2,2'-Oxybis-(l-chloropropane)	45	77, 79
Acetophenone	105	77, 51
4-Methylphenol	108	107
N-Nitroso-di-n-propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	107	121, 122
Bis(2-chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
Caprolactam	113	55, 56
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
1,1'-Biphenyl	154	153, 76
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Dimethylphthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150
1,2,4,5-Tetrachlorobenzene	216	214, 179, 108, 143, 218
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249

Table 3

Characteristic Ions for Semivolatile
Target Compounds, Deuterated Monitoring Compounds,
and Internal Standards (Con't)

Parameter	Primary Quantitation Ion	Secondary Ion(s)
Atrazine	200	173, 215
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Carbazole	167	166, 139
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
Bis(2-ethylhexyl)phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-octyl phthalate	149	none
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenzo(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
2,3,4,6-Tetrachlorophenol	232	131, 230, 166, 234, 168
Deuterated Monitoring Compounds		
Phenol-d_5	99	71, 42
Bis(2-chloroethyl)ether-d_8	67	99, 69
2-Chlorophenol-d_4	132	134, 68, 66
4-Methylphenol-d_8	113	115, 54
Nitrobenzene-d_5	128	82, 54
2-Nitrophenol-d_4	143	69, 41, 42
2,4-Dichlorophenol-d_3	165	167, 101
4-Chloroaniline-d_4	131	133, 69
Dimethylphthalate-d_6	166	78
Acenaphthylene-d_8	160	80, 158
4-Nitrophenol-d_4	143	113, 41, 42
Fluorene-d_{10}	176	174, 87, 86
4,6-Dinitro-2-methylphenol-d_2	200	170, 52
Anthracene-d_{10}	188	94, 80
Pyrene-d_{10}	212	106, 104
Benzo(a)pyrene-d_{12}	264	132, 118
Fluoranthene-d_{10} (SIM)	212	106,104
2-Methylnapthalene-d_{10} (SIM)	152	151

Table 3

Characteristic Ions for Semivolatile
Target Compounds, Deuterated Monitoring Compounds,
and Internal Standards (Con't)

Parameter	Primary Quantitation Ion	Secondary Ion(s)
Internal Standards		
1,4-Dichlorobenzene-d_4	152	115
Naphthalene-d_8	136	68
Acenaphthene-d_{10}	164	162, 160
Phenanthrene-d_{10}	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265

Table 4

Relative Response Factor Criteria for Initial and Continuing Calibration Verification of Semivolatile Target Compounds and Deuterated Monitoring Compounds

Semivolatile Compounds	Minimum RRF[1]	Maximum %RSD	Maximum %Diff[1]
Benzaldehyde	0.010	40.0	±40.0
Phenol	0.800	20.0	±25.0
Bis(2-chloroethyl)ether	0.700	20.0	±25.0
2-Chlorophenol	0.800	20.0	±25.0
2-Methylphenol	0.700	20.0	±25.0
2,2'-Oxybis-(1-chloropropane)	0.010	40.0	±40.0
Acetophenone	0.010	40.0	±40.0
4-Methylphenol	0.600	20.0	±25.0
N-Nitroso-di-n-propylamine	O.500	20.0	±25.0
Hexachloroethane	0.300	20.0	±25.0
Nitrobenzene	0.200	20.0	±25.0
Isophorone	0.400	20.0	±25.0
2-Nitrophenol	0.100	20.0	±25.0
2,4-Dimethylphenol	O.200	20.0	±25.0
Bis(2-chloroethoxy)methane	0.300	20.0	±25.0
2,4-Dichlorophenol	0.200	20.0	±25.0
Naphthalene	0.700	20.0	±25.0
4-Chloroaniline	0.010	40.0	±40.0
Hexachlorobutadiene	0.010	40.0	±40.0
Caprolactam	0.010	40.0	±40.0
4-Chloro-3-methylphenol	0.200	20.0	±25.0
2-Methylnaphthalene	0.400	20.0	±25.0
Hexachlorocyclopentadiene	0.010	40.0	±40.0
2,4,6-Trichlorophenol	0.200	20.0	±25.0
2,4,5-Trichlorophenol	0.200	20.0	±25.0
1,1'-Biphenyl	0.010	40.0	±40.0
2-Chloronaphthalene	0.800	20.0	±25.0
2-Nitroaniline	0.010	40.0	±40.0
Dimethylphthalate	0.010	40.0	±40.0
2,6-Dinitrotoluene	0.200	20.0	±25.0
Acenaphthylene	0.900	20.0	±25.0
3-Nitroaniline	0.010	40.0	±40.0
Acenaphthene	0.900	20.0	±25.0
2,4-Dinitrophenol	0.010	40.0	±40.0
4-Nitrophenol	0.010	40.0	±40.0
Dibenzofuran	0.800	20.0	±25.0
2,4-Dinitrotoluene	0.200	20.0	±25.0
Diethylphthalate	0.010	40.0	±40.0
1,2,4,5-Tetrachlorobenzene	0.010	40.0	±40.0
4-Chlorophenyl-phenylether	0.400	20.0	±25.0
Fluorene	0.900	20.0	±25.0
4-Nitroaniline	0.010	40.0	±40.0
4,6-Dinitro-2-methylphenol	0.010	40.0	±40.0
4-Bromophenyl-phenyl ether	0.100	20.0	±25.0
N-Nitrosodiphenylamine	0.010	40.0	±40.0
Hexachlorobenzene	0.100	20.0	±25.0

Table 4

Relative Response Factor Criteria for Initial and Continuing Calibration Verification of Semivolatile Target Compounds and Deuterated Monitoring Compounds (Con't)

Semivolatile Compounds	Minimum RRF[1]	Maximum %RSD	Maximum %Diff[1]
Atrazine	0.010	40.0	±40.0
Pentachlorophenol	0.050	20.0	±25.0
Phenanthrene	0.700	20.0	±25.0
Anthracene	0.700	20.0	±25.0
Carbazole	0.010	40.0	±40.0
Di-n-butylphthalate	0.010	40.0	±40.0
Fluoranthene	0.600	20.0	±25.0
Pyrene	0.600	20.0	±25.0
Butylbenzylphthalate	0.010	40.0	±40.0
3,3'-Dichlorobenzidine	0.010	40.0	±40.0
Benzo(a)anthracene	0.800	20.0	±25.0
Chrysene	0.700	20.0	±25.0
Bis(2-ethylhexyl)phthalate	0.010	40.0	±40.0
Di-n-octylphthalate	0.010	40.0	±40.0
Benzo(b)fluoranthene	0.700	20.0	±25.0
Benzo(k)fluoranthene	0.700	20.0	±25.0
Benzo(a)pyrene	0.700	20.0	±25.0
Indeno(1,2,3-cd)pyrene	0.500	20.0	±25.0
Dibenzo(a,h)anthracene	0.400	20.0	±25.0
Benzo(g,h,i)perylene	0.500	20.0	±25.0
2,3,4,6-Tetrachlorophenol	0.100	20.0	±25.0
Deuterated Monitoring Compounds			
Phenol-d_5	0.010	20.0	±25.0
Bis(2-chloroethyl)ether-d_8	0.010	20.0	±25.0
2-Chlorophenol-d_4	0.010	20.0	±25.0
4-Methylphenol-d_8	0.010	20.0	±25.0
Nitrobenzene-d_5	0.010	20.0	±25.0
2-Nitrophenol-d_4	0.010	20.0	±25.0
2,4-Dichlorophenol-d_3	0.010	20.0	±25.0
4-Chloroaniline-d_4	0.010	40.0	±40.0
Dimethylphthalate-d_6	0.010	40.0	±40.0
Acenaphthylene-d_8	0.010	20.0	±25.0
4-Nitrophenol-d_4	0.010	40.0	±40.0
Fluorene-d_{10}	0.010	20.0	±25.0
4,6-Dinitro-2-methylphenol-d_2	0.010	40.0	±40.0
Anthracene-d_{10}	0.010	20.0	±25.0
Pyrene-d_{10}	0.010	20.0	±25.0
Benzo(a)pyrene-d_{12}	0.010	20.0	±25.0
Fluoranthene-d_{10} (SIM)	0.010	20.0	±25.0
2-Methylnapthalene-d_{10} (SIM)	0.010	20.0	±25.0

[1] For a closing CCV, all target compounds and DMCs must meet a minimum RRF of 0.010 and a maximum %Difference of ±50.0.

Table 5

Matrix Spike Recovery and
Relative Percent Difference Limits

Compound	%Recovery Water	RPD Water	%Recovery Soil/Sediment	RPD Soil/Sediment
Phenol	12-110	0-42	26-90	0-35
2-Chlorophenol	27-123	0-40	25-102	0-50
N-Nitroso-di-n-propylamine	41-116	0-38	41-126	0-38
4-Chloro-3-methylphenol	23-97	0-42	26-103	0-33
Acenaphthene	46-118	0-31	31-137	0-19
4-Nitrophenol	10-80	0-50	11-114	0-50
2,4-Dinitrotoluene	24-96	0-38	28-89	0-47
Pentachlorophenol	9-103	0-50	17-109	0-47
Pyrene	26-127	0-31	35-142	0-36

Table 6

Deuterated Monitoring Compound Recovery Limits

Compound	% Recovery For Water Samples	% Recovery For Soil Samples
Phenol-d_5	39-106	17-103
Bis(2-chloroethyl)ether-d_8	40-105	12-98
2-Chlorophenol-d_4	41-106	13-101
4-Methylphenol-d_8	25-111	8-100
Nitrobenzene-d_5	43-108	16-103
2-Nitrophenol-d_4	40-108	16-104
2,4-Dichlorophenol-d_3	37-105	23-104
4-Chloroaniline-d_4	1-145	1-145
Dimethylphthalate-d_6	47-114	43-111
Acenaphthylene-d_8	41-107	20-97
4-Nitrophenol-d_4	33-116	16-166
Fluorene-d_{10}	42-111	40-108
4,6-Dinitro-2-methylphenol-d_2	22-104	1-121
Anthracene-d_{10}	44-110	22-98
Pyrene-d_{10}	52-119	51-120
Benzo(a)pyrene-d_{12}	32-121	43-111
Fluoranthene-d_{10} (SIM)	50-150	50-150
2-Methylnapthalene-d_{10} (SIM)	50-150	50-150

Table 7

Semivolatile Deuterated Monitoring Compounds
and the Associated Target Compounds

Phenol-d_5 (DMC)	**2-Chlorophenol-d_4 (DMC)**	**2-Nitrophenol-d_4 (DMC)**
Benzaldehyde	2-Chlorophenol	Isophorone
Phenol		2-Nitrophenol

Bis(2-Chloroethyl) ether-d_8 (DMC)	**4-Methylphenol-d_8 (DMC)**	**4-Chloroaniline-d_4 (DMC)**
Bis(2-chloroethyl)ether	2-Methylphenol	4-Chloroaniline
2,2'-Oxybis(1-chloropropane)	4-Methylphenol	Hexachlorocyclopentadiene
Bis(2-chloroethoxy)methane	2,4-Dimethylphenol	3,3'-Dichlorobenzidine

Nitrobenzene-d_5 (DMC)	**2,4-Dichlorophenol-d_3 (DMC)**	**Dimethylphthalate-d_6 (DMC)**
Acetophenone	2,4-Dichlorophenol	Caprolactam
N-Nitroso-di-n-propylamine	Hexachlorobutadiene	1,1'-Biphenyl
Hexachloroethane	4-Chloro-3-methylphenol	Dimethylphthalate
Nitrobenzene	2,4,6-Trichlorophenol	Diethylphthalate
2,6-Dinitrotoluene	2,4,5-Trichlorophenol	Di-n-butylphthalate
2,4-Dinitrotoluene	1,2,4,5-Tetrachlorobenzene	Butylbenzylphthalate
N-Nitrosodiphenylamine	Pentachlorophenol	Bis(2-ethylhexyl) phthalate
	2,3,4,6-Tetrachlorophenol	Di-n-octylphthalate

Fluorene-d_{10} (DMC)	**Anthracene-d_{10} (DMC)**	**Pyrene-d_{10} (DMC)**
Dibenzofuran	Hexachlorobenzene	Fluoranthene
Fluorene	Atrazine	Pyrene
4-Chlorophenyl-phenylether	Phenanthrene	Benzo(a)anthracene
4-Bromophenyl-phenylether	Anthracene	Chrysene
Carbazole		

Acenaphthylene-d_8 (DMC)	**4-Nitrophenol-d_4 (DMC)**	**Benzo(a)pyrene-d_{12} (DMC)**
Naphthalene	2-Nitroaniline	Benzo(b)fluoranthene
2-Methylnaphthalene	3-Nitroaniline	Benzo(k)fluoranthene
2-Chloronaphthalene	2,4-Dinitrophenol	Benzo(a)pyrene
Acenaphthylene	4-Nitrophenol	Indeno(1,2,3-cd)pyrene
Acenaphthene	4-Nitroaniline	Dibenzo(a,h)anthracene
		Benzo(g,h,i)perylene

4,6-Dinitro-2-methylphenol-d_2 (DMC)
4,6-Dinitro-2-methylphenol

Table 8

Semivolatile Deuterated Monitoring Compounds and the Associated Target Compounds for Selected Ion Monitoring Analysis

Fluoranthene-d_{10}	**2-Methylnaphthalene-d_{10}**
Fluoranthene	Napthalene
Pyrene	2-Methylnaphthalene
Benzo(a)anthracene	Acenapthylene
Chrysene	Acenaphthene
Benzo(b)fluoranthene	Fluorene
Benzo(k)fluoranthene	Pentachlorophenol
Benzo(a)pyrene	Phenanthrene
Indeno(1,2,3-cd)pyrene	Anthracene
Dibenzo(a,h)anthracene	
Benzo(g,h,i)perylene	

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EXHIBIT D

ANALYTICAL METHOD FOR THE ANALYSIS OF LOW/MEDIUM CONCENTRATIONS
OF VOLATILE ORGANIC COMPOUNDS

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1.0 SCOPE AND APPLICATION

1.1 In 1978, US Environmental Protection Agency (USEPA) Headquarters and Regional representatives designed analytical methods for the analysis of volatiles in hazardous waste samples. These methods were based on USEPA Method 624, Purgeables. In 1980, these methods were adopted for use in the Contract Laboratory Program (CLP). As the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) evolved, the CLP methods, as well as their precedent USEPA 600 Series methods, established the basis for other USEPA methods to perform the analysis of volatiles contained in hazardous waste samples (i.e., SW-846). The following CLP method has continuously improved to incorporate technological advancements promulgated by USEPA, and has continued to set the standard for the preparation, extraction, isolation, identification, and reporting of volatiles at hazardous waste sites.

1.2 The analytical method that follows is designed to analyze water and soil/sediment samples from hazardous waste sites for the volatile organic compounds on the Target Compound List (TCL) in Exhibit C (Low/Medium Volatiles). The method includes sample preparation and analysis to determine the approximate concentration of organic constituents in the sample. The actual analysis is based on a purge-and-trap Gas Chromatograph/Mass Spectrometer (GC/MS) method for aqueous and medium-level soil samples and closed-system purge-and-trap for low-level soil samples.

1.3 Problems have been associated with the following compounds analyzed by this method.

- Chloromethane, vinyl chloride, bromomethane, and chloroethane can display peak broadening if the compounds are not delivered to the GC column in a tight band.
- Acetone, hexanone, 2-butanone, 4-methyl-2-pentanone, and 1,4-dioxane have poor purge efficiencies.
- 1,1,1-trichloroethane and all the dichloroethanes can dehydrohalogenate during storage or analysis.
- Chloromethane may be lost if the purge flow is too fast.
- Bromoform is one of the compounds most likely to be adversely affected by cold spots and/or active sites in the transfer lines. Response of its quantitation ion (m/z 173) is directly affected by tuning of 4-bromofluorobenzene (BFB) at ions m/z 174/176. Increasing the m/z 174/176 ratio within the specified Quality Control (QC) limits may improve bromoform response.

2.0 SUMMARY OF METHOD

2.1 Water

An inert gas is bubbled through a 5 mL sample contained in a specifically designed purging chamber at ambient temperature. Higher purge temperatures may be used, provided that all technical acceptance criteria are met for all standards, samples, and blanks. The same purge conditions must be used for all associated standards, samples, and blanks. The purgeable compounds are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeable compounds onto a Gas Chromatographic (GC) column. The GC is temperature-programmed to separate the purgeable compounds which are then detected with a Mass Spectrometer (MS).

2.2 Low-Level Soil/Sediment

Low-level volatile organic compounds are generally determined by analyzing approximately 5 g of sample, in a pre-weighed vial with a septum-sealed screw-cap (see Section 6.0) that already contains a stirring bar.

NOTE: The sodium bisulfate preservative may be used under limited circumstances. 5.0 mL of sodium bisulfate solution (Section 7.1.3) is added to each sample when preservation by sodium bisulfate is requested by the Region.

The entire vial is placed into the instrument carousel. Immediately before analysis, organic-free reagent water, Deuterated Monitoring Compounds (DMCs), and internal standards are automatically added without opening the sample vial. The vial containing the sample is heated to the suggested temperature of 40°C and the volatiles are purged through a sorbent trap using an inert gas combined with agitation of the sample. Higher purge temperatures may be required for the analysis of certain target compounds (i.e., 1,4-dioxane). When purging is complete, the trap is heated and backflushed with helium to desorb the purgeable compounds onto a GC column. The GC is temperature-programmed to separate the purgeable compounds which are then detected with an MS.

2.3 Medium-Level Soil/Sediment

A soil sample of 5 g is collected, preserved in methanol and/or extracted with methanol. An aliquot of the methanol extract is added to 5 mL of reagent water. An inert gas is bubbled through this solution in a specifically designed purging chamber at ambient temperature. The purgeable compounds are effectively transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeable compounds onto a GC column. The GC is temperature-programmed to separate the purgeable compounds which are then detected with an MS.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method Interferences

Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks as described in Section 12. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride, fluorocarbons, and other common laboratory solvents) through the septum seal into the sample during storage and handling. Therefore, these samples must be stored separately from other laboratory samples and standards, and must be analyzed in a room whose atmosphere is demonstrated to be free of all potential contaminants that will interfere with the analysis.

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device. The trap and other parts of the system are also subjected to contamination; therefore, frequent bake-out and purging of the entire system may be required.

4.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine the presence of methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all Gas Chromatography (GC) carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken. At the time of sample receipt, the Contractor must prepare two 40 mL VOA vials containing reagent water and/or inert sand to be stored with each group of samples (Section 12.1.1.2).

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should be made available to all personnel involved in the chemical analyses.

5.2 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene; carbon tetrachloride; chloroform; vinyl chloride; and 1,4-dioxane. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this analytical method is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Sample Containers

The specific required sample containers will depend on the purge-and-trap system to be employed. Several systems are commercially available. Some systems employ 40 mL clear vials with a special frit and equipped with two polytetrafluoroethylene (PTFE)-faced silicone septa. Other systems permit the use of any good quality glass vial that is large enough to contain at least 5 g of soil or solid material and at least 10 mL of water, and that can be sealed with a screw-cap containing a PTFE-faced silicone septum. The Contractor shall consult the purge-and-trap system manufacturer’s instructions regarding suitable specific vials, septa, caps, and mechanical agitation devices.

6.2 Glassware

6.2.1 Syringes - 25 mL glass hypodermic syringes with a Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used). 5.0, 1.0, and 0.5 mL syringes, gas-tight with shut-off valve.

6.2.2 Syringe Valve - Two-way, with Luer ends (three each), if applicable to the purging device.

6.2.3 Micro Syringes - 25 µL with a 2 inch x 0.006 inch ID, 22 gauge beveled needle. 10 µL, 100 µL.

6.2.4 Disposable Pasteur Pipets.

6.2.5 Volumetric Flasks - Class A, 10 mL and 100 mL, with ground glass stoppers.

6.2.6 60 mL, septum-sealed glass vials to collect samples for screening, percent moisture determination.

6.2.7 40 mL, screw-cap, PTFE-lined, septum-sealed glass vials. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

6.2.8 Vials and Caps - Assorted sizes.

6.2.9 Bottle - 15 mL, screw-cap, with PTFE capliner.

6.3 pH Paper - Wide range

6.4 Magnetic Stirring Bars

PTFE or glass-coated, of the appropriate size to fit the sample vials. Consult the manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. Consult the manufacturer of the purging device and the stirring bars for suggested cleaning procedures.

6.5 Balances

Balances must be analytical and capable of accurately weighing ±0.0001 g. The balances must be calibrated with Class S weights or known reference weights once per each 12-hour work shift. The balances must be calibrated with Class S weights at a minimum of once per month. The balances must also be annually checked by a certified technician.

6.6 Purge-and-Trap Device

The purge-and-trap device consists of three separate pieces of equipment: the sample purge chamber, the trap, and the desorber. This device either manually or automatically: samples an appropriate volume (e.g., 5.0 mL from the vial), adds DMCs, matrix spikes and internal standards to the sample and transfers the sample to the purge device. This device also purges the volatile organic compounds (VOCs) using an inert gas stream and traps the released VOCs for subsequent desorption into the Gas Chromatograph (GC). For low-level soil samples, the purge-and-trap device consists of: a unit that automatically adds water, DMCs, and internal standards to a hermetically sealed vial containing the sample; purges the volatile compounds using an inert gas stream while agitating the contents of the vial; and traps the released volatile compounds for subsequent desorption into the GC. Such systems are commercially available from several sources and shall meet the following specifications.

NOTE: The purge-and-trap device must be capable of accepting 40 mL closed-system purge-and-trap sample vials from the field, which are not to be opened during the analytical process.

6.6.1 The sample purge chamber must be designed to accept 5 mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column.

6.6.2 For soil samples, the purging device should be capable of accepting a vial large enough to contain a 5 g soil/sediment sample plus a magnetic stirring bar and 10 mL of water. The device must be capable

of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample during purging (e.g., using a magnetic stirring bar, sonication, or other means). The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed volatile compounds to the GC.

6.6.3 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inches (2.667 mm). The trap must be packed to contain (starting from the inlet) 0.5 cm silanized glass wool, and the following minimum lengths of absorbent:

- 8 cm of 2,6-diphenylene oxide polymer (60/80 mesh chromatographic grade Tenax GC or equivalent).
- 1 cm methyl silicone packing, 3.0% OV-1 on Chromasorb W, 60/80 mesh (or equivalent).
- 8 cm of silica gel, 35/60 mesh (or equivalent).
- 7 cm of coconut charcoal.

6.6.4 Alternate sorbent traps may be used if:

- The trap packing materials do not introduce contaminants that interfere with identification and quantitation of the compounds listed in Exhibit C (Low/Medium Volatiles).
- The analytical results generated using the trap meet the initial and continuing calibration verification technical acceptance criteria listed in the analytical method and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Low/Medium Volatiles).
- The trap can accept up to 1000 ng of each compound listed in Exhibit C (Low/Medium Volatiles) without becoming overloaded.

6.6.4.1 The alternate trap must be designed to optimize performance. Follow manufacturer's instructions for the use of its product. Before use of any trap, other than the one specified in Section 6.6.3, the Contractor must first meet the criteria listed in Section 6.6.4. Once this has been demonstrated, the Contractor must document its use in each SDG Narrative by specifying the trap composition (packing material/brand name, amount of packing material). Other sorbent traps include, but are not limited to, Tenax/Silica Gel/Carbon Trap from USEPA Method 524.2, Tenax - GC/Graphpac-D Trap (Alltech) or equivalent, and Vocarb 4000 Trap (Supelco) or equivalent.

6.6.4.2 The Contractor must maintain documentation that the alternate trap meets the criteria listed in Section 6.6.4. The minimum documentation requirements are as follows:

6.6.4.2.1 Manufacturer provided information concerning the performance characteristics of the trap.

6.6.4.2.2 Reconstructed ion chromatograms and data system reports generated on the Contractor's Gas Chromatograph/Mass

Spectrometer (GC/MS) used for Contract Laboratory Program (CLP) analyses:

- From instrument blank analyses that demonstrate there are no contaminants that interfere with the volatile analysis when using the alternate trap;
- From initial and continuing calibration verification standards analyzed using the trap specified in Section 6.6.3.

6.6.4.2.3 Based on Contractor-generated data described above, the Contractor must complete a written comparison/review, that has been signed by the Laboratory Manager certifying that:

- The alternate trap performance meets the technical acceptance criteria listed in Sections 9.3.5 and 9.4.5;
- The low-point initial calibration standard analysis has adequate sensitivity to meet the low/medium volatile CRQLs;
- The high-point initial calibration standard analysis was not overloaded; and
- The alternate trap materials do not introduce contaminants that interfere with the identification and/or quantitation of the compounds listed in Exhibit C (Low/Medium Volatiles).

6.6.4.2.4 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request of the USEPA Regional Contract Laboratory Program Project Officer (CLP PO).

6.6.5 The purge-and-trap apparatus may be assembled as a separate unit or be an integral unit coupled with a GC.

6.6.6 The desorber should be capable of rapidly heating the trap to 180°C. The polymer section of the trap should not be heated higher than 180°C and the remaining sections should not exceed 220°C during bake-out mode.

6.7 Gas Chromatograph/Mass Spectrometer (GC/MS) System

6.7.1 Gas Chromatograph - The GC system must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout desorption and temperature program operations. The system must include or be interfaced to a purge-and-trap system as specified in Section 6.6 and have all required accessories including syringes, analytical columns, and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants, or flow controllers with rubber components are not to be used.

6.7.2 GC Columns - A description of the column used for analysis shall be provided in the SDG Narrative.

6.7.2.1 Minimum length 30 m x 0.53 mm ID VOCOL, or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.7.2.2 Minimum length 30 m x 0.53 mm ID DB-624, or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.7.2.3 Minimum length 30 m x 0.53 mm ID AT-624, or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.7.2.4 Minimum length 30 m x 0.53 mm ID Rtx-624, or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.7.2.5 Minimum length 30 m x 0.53 mm ID BP-624, or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.7.2.6 Minimum length 30 m x 0.53 mm ID CP-Select 624CB, or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.7.3 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantitation of the compounds listed in Exhibit C (Low/Medium Volatiles).
- The analytical results generated using the column meet the initial and continuing calibration verification technical acceptance criteria listed in the analytical method, and the CRQLs listed in Exhibit C (Low/Medium Volatiles).
- The column provides equal or better resolution of the compounds listed in Exhibit C (Low/Medium Volatiles) than the columns listed in Section 6.7.2.

6.7.3.1 As applicable, follow the manufacturer's instructions for use of its product.

6.7.3.2 The Contractor must maintain documentation that the column met the criteria in Section 6.7.3. The minimum documentation is as follows:

6.7.3.2.1 Manufacturer provided information concerning the performance characteristics of the column.

6.7.3.2.2 Reconstructed ion chromatograms and data system reports generated on the GC/MS used for the CLP analyses:

- From instrument blanks that demonstrate that there are no contaminants that interfere with the volatile analysis when using the alternate column; and
- From initial and continuing calibration verification standards analyzed using the alternate column.

6.7.3.2.3 Based on the Contractor-generated data described above, the Contractor shall complete a written review, signed by the Laboratory Manager, certifying that:

- The column performance meets the technical acceptance criteria in Sections 9.3.5 and 9.4.5;
- The low-point initial calibration standard analysis has adequate sensitivity to meet the low/medium volatile CRQLs;
- The high-point initial calibration standard analysis was not overloaded; and

- The column does not introduce contaminants that interfere with the identification and/or quantitation of compounds listed in Exhibit C (Low/Medium Volatiles).

6.7.3.2.4 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request by the USEPA Regional CLP PO.

6.7.4 **PACKED COLUMNS CANNOT BE USED.**

6.7.5 Mass Spectrometer

Must be capable of scanning from 35 to 300 atomic mass unit (amu) every 2 seconds or less utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum that meets all the 4-bromofluorobenzene (BFB) GC/MS performance check technical acceptance criteria in Table 1 when 50 ng of BFB are injected through the GC inlet. The instrument conditions required for the acquisition of the BFB mass spectrum are given in Section 9.

NOTE: To ensure sufficient precision of mass spectral data, the MS scan rate should allow acquisition of at least five spectra while a sample compound elutes from the GC. The purge-and-trap GC/MS system must be in a room whose atmosphere is demonstrated to be free of all potential contaminants that will interfere with the analysis. The instrument must be vented to the outside of the facility or to a trapping system which prevents the release of contaminants into the instrument room.

6.7.6 GC/MS Interface

Any GC/MS interface that gives acceptable calibration points at 25 ng or less (for non-ketone target compounds), per injection for each of the parameters of interest, and achieves all acceptance criteria, may be used. GC to MS interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

6.7.7 Data System

A computer system interfaced to the MS that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The NIST (2002 release or later), Wiley (1991 release or later), or equivalent mass spectral library shall be used as the reference library. The operational data system must be capable of flagging all data files that have been edited manually by laboratory personnel.

6.7.8 Data Storage Device

Data storage devices must be suitable for long-term, off-line storage of data.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

7.1.1 Reagent Water - Reagent water is defined as water in which an interferant is not observed at or above the Contract Required Quantitation Limit (CRQL) for each compound of interest.

7.1.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing approximately 453 g (1 lb) of activated carbon.

7.1.1.2 Reagent water may also be generated using a water purification system.

7.1.1.3 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a polytetrafluoroethylene (PTFE)-lined septum and cap.

7.1.2 Methanol - Pesticide quality or equivalent.

7.1.3 Sodium Bisulfate Solution - 2.0 g of ACS reagent grade or equivalent sodium bisulfate is dissolved for every 5.0 g of water.

7.2 Standards

The Contractor must provide all standards to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit E. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer’s expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions, prepared by the Contractor which are immediately ampulated in glass vials, may be retained for 2 years from the preparation date. Upon breaking the glass seal, the expiration times listed in Sections 7.2.1 - 7.3 will apply. The Contractor is responsible for assuring that the integrity of the standards has not degraded (see Section 7.3.5).

7.2.1 Stock Standard Solutions

Stock standard solutions are defined as standards that are to be used to produce working standards. They may be in the form of single compounds or mixtures. They may be prepared in methanol from pure standard materials, or purchased as pre-made solutions. Prepare fresh stock standards every 6 months, or sooner if the standard has degraded or evaporated.

7.2.2 Working Standards

7.2.2.1 Instrument Performance Check Solution

Prepare the instrument performance check solution containing 4-bromofluorobenzene (BFB). If the BFB solution is added to the mid-level calibration standard (50 µg/L for non-ketones and 100 µg/L for ketones) add a sufficient amount of BFB to result in a 10 µg/L concentration of BFB (50 ng on-column). The BFB must be analyzed using the GC and Mass Spectrometer (MS) run conditions as is used for the calibration analysis.

7.2.2.2 Calibration Standard Solution

Prepare the working calibration standard solution containing all of the purgeable target compounds in methanol [Exhibit C (Low/Medium Volatiles)]. Prepare a fresh calibration standard solution monthly, or sooner if the solution has degraded or evaporated. The recommended concentration of the target compounds is 100 µg/mL.

NOTE: The Contractor may prepare a calibration standard containing all of the non-ketones and a separate standard containing the ketones.

7.2.2.3 Internal Standard Spiking Solution

Prepare an internal standard spiking solution containing 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4 in methanol. Add a sufficient amount of the internal standard solution to samples, including Matrix Spike and Matrix Spike Duplicates (MS/MSD), blanks, and calibration standards to result in the addition of 0.25 µg of each internal standard. Prepare a fresh internal standard solution monthly, or sooner if the solution has degraded or evaporated.

7.2.2.4 Deuterated Monitoring Compound (DMC) Spiking Solution

Prepare a DMC spiking solution in methanol (or in deuterated methanol) containing the compounds listed below: DMCs are to be added to each sample and blank, as well as initial calibration standards and Continuing Calibration Verification (CCV) standards. For samples and blanks, add sufficient amount of DMC solution to each sample to result in the addition of 0.25 µg of each non-ketone DMC, 0.50 µg for each ketone DMC, and 6.25 µg for 1,4-dioxane-d_8 DMC. For calibration standards, add sufficient amounts of DMC solution to each 5 mL aliquot of calibration standard to result in the concentrations listed in Section 7.2.2.6.2 (initial calibration) and Section 7.2.2.6.4 (continuing calibration verification). Prepare a fresh DMC solution every month, or sooner if the standard has degraded.

Compound

Vinyl chloride-d_3

Chloroethane-d_5

1,1-Dichloroethene-d_2

2-Butanone-d_5

Chloroform-d

1,2-Dichloroethane-d_4

Benzene-d_6

1,2-Dichloropropane-d_6

Toluene-d_8

trans-1,3-Dichloropropene-d_4

2-Hexanone-d_5

1,4-Dioxane-d_8

1,1,2,2-Tetrachloroethane-d_2

1,2-Dichlorobenzene-d_4

7.2.2.5 Matrix Spiking Solution

If MS/MSD analysis is requested at the time of scheduling, prepare a spiking solution in methanol that contains the following compounds at a concentration of 12.5 µg/mL: 1,1-dichloroethene; trichloroethene; chlorobenzene; toluene; and benzene. Prepare fresh spiking solution monthly, or sooner if the solution has degraded or evaporated.

7.2.2.6 Initial and Continuing Calibration Verification Standards

7.2.2.6.1 Add a sufficient amount of each working standard to a 5 mL aliquot of reagent water to produce the desired calibration standard concentrations listed in Section 7.2.2.6.2 and 7.2.2.6.4.

7.2.2.6.2 Prepare five aqueous initial calibration standard solutions containing all of the purgeable target compounds and the DMCs at the following levels: all non-ketone target compounds and their associated DMCs (see Table 7) at 5.0, 10, 50, 100, and 200 µg/L; all ketones and their associated DMCs (see Table 7) at 10, 20, 100, 200, and 400 µg/L; 1,4-dioxane and 1,4-dioxane-d_8 DMC at 100, 200, 1250, 2000, and 4000 µg/L. All three xylene isomers (o-, m-, and p-xylene) must be present in the calibration standards. The o-xylene calibration standard concentrations must be at 5.0, 10, 50, 100, and 200 µg/L, while the concentration of the m-, plus p-xylene isomers must total 5.0, 10, 50, 100, and 200 µg/L.

NOTE: The concentrations listed above are based on a 5 mL volume. If 10 mL volumes are to be used (i.e., low-level soil samples) then the concentrations of the standards must be reduced in half to ensure the same on-column amount of each analyte.

7.2.2.6.3 Calibration standards may be prepared in a volumetric flask or in the syringe used to inject the standard into the purging device.

7.2.2.6.4 The CCV standard should be at or near the mid-point concentration level of the calibration standards, 50 µg/L for non-ketones and their associated DMCs, 100 µg/L for ketones and their associated DMCs, and 1250 for 1,4-dioxane and its associated DMCs.

NOTE: The concentrations listed above are based on a 5 mL volume. If 10 mL volumes are to be used (i.e., low-level soil samples) then the concentrations of the standards must be reduced in half to ensure the same on-column amount of each analyte.

7.2.2.6.5 The methanol contained in each of the aqueous calibration standards must not exceed 1.0% by volume.

7.3 Storage of Standard Solutions

7.3.1 Store the stock standards in PTFE-sealed screw-cap bottles with zero headspace at -10°C to -20°C, and protect the standards from light.

7.3.2 Aqueous standards may be stored for up to 24 hours if held in PTFE-sealed screw-cap vials with zero headspace at 4°C (±2°C). Protect the standards from light. If not stored as such, the standards must be discarded after 1 hour unless they are set up to be purged by an autosampler. When using an autosampler, the standards may be kept up to 12 hours in purge tubes connected via the autosampler to the purge-and-trap device.

7.3.3 If standards are purchased and stored in ampulated vials, they may be stored up to 2 years after the preparation date.

7.3.4 Purgeable standards must be stored separately from other standards, samples, and blanks.

7.3.5 The Contractor is responsible for maintaining the integrity of standard solutions and verifying prior to use. This means that standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in the solution.

7.3.6 Temperature Records for Storage of Standards

7.3.6.1 The temperature of all standards storage refrigerators/freezers shall be recorded daily.

7.3.6.2 Temperature excursion shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

7.3.6.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators/freezers.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Soil/Sediment Samples

NOTE: For soil samples received in pre-prepared closed-system purge-and-trap sample vials (Section 10.1.4) or pre-weighed glass vials that are to be stored at -7°C, ensure that the samples are placed on their side prior to being frozen.

8.1.1.1 Soil/Sediment samples may be received from the field either in pre-prepared closed-system purge-and-trap sample vials, pre-weighed glass vials, or in field core sampling/storage containers (e.g., EnCore™ or equivalent). Samples received in pre-prepared closed-system vials may arrive with no added preservative in 5 mL of water, or preserved with sodium bisulfate. Samples in pre-weighed glass vials may be preserved with 5 mL of methanol (medium-level samples only). Only vials that are thoroughly sealed may be used for medium-level soil analysis.

8.1.1.2 For samples received in pre-prepared closed-system purge-and-trap vials or pre-weighed glass vials, the Contractor should receive at least three such vials per field sample, plus at least one additional 60 mL sealed glass vial containing sample with minimum headspace. For samples received in field core sampling containers, the Contractor should receive at least three such containers per field sample, plus at least one additional 60 mL sealed glass vial containing sample with minimum headspace. If the minimum amount of containers have not been sent by the field samplers, the Contractor is to immediately contact the Sample Management Office (SMO) for instructions. A total of four vials per field sample is the recommended amount of vials the Contractor should receive.

NOTE: If Matrix Spike and Matrix Spike Duplicate (MS/MSD) analysis is required for a particular sample, eight additional field core containers or glass vials should be sent by the field samplers. Contact SMO if insufficient sample for MS/MSD analysis has been provided.

8.1.1.2.1 For each preserved sample, samplers should send approximately 5 g (weight excluding preservative) of sample containing preservative in a pre-weighed glass vial. The Contractor shall weigh this vial immediately upon receipt and then store at less than -7°C. If a medium-level analysis of the sample is necessary, use this vial.

8.1.1.3 Samples received in pre-prepared closed-system purge-and-trap vials without preservative are to be analyzed within 24 hours of sample receipt, or they must be stored at less than -7°C until time of analysis. Ensure that the samples are clean of external dirt and moisture prior to weighing.

8.1.1.4 In limited cases, preservation with sodium bisulfate may be required. Samples received in pre-prepared closed-system purge-and-trap vials preserved with sodium bisulfate shall be stored at 4°C (±2°C) until time of analysis. Samples preserved with sodium bisulfate should be accompanied by field documentation recording the initial weight of the vial with preservative.

8.1.1.5 Medium-level samples may be received in pre-weighed vials preserved with methanol. If the volume of methanol in the vial does not appear to be equal to 5 mL, or if the vial appears to be dry, the Contractor shall immediately contact SMO, who will contact the Region. Samples preserved with methanol should be accompanied by field documentation recording the initial weight of the vial with methanol. Samples received preserved with methanol shall be stored at 4°C (±2°C) until time of analysis. Samples received without preservative are to be analyzed within 24 hours of sample receipt, or they must be stored at less than -7°C until time of preparation and analysis.

8.1.1.6 For samples received in field core sampling/storage containers, the Contractor shall transfer the contents of the three containers for each sample, immediately upon receipt, to a pre-prepared closed-system purge-and-trap vial, and record the date and time of transfer. The transferred samples are to be analyzed within 24 hours of sample receipt, or they must be stored at less than -7°C.

8.1.2 Water Samples

8.1.2.1 Water samples should be collected in glass containers having a total volume of at least 40 mL with a polytetrafluoroethylene (PTFE)-lined septum and an open top screw-cap. Headspace should be avoided. The containers should be filled in such a manner that no air bubbles pass through the sample as the container is being filled. The samples are preserved to a pH of less than or equal to 2 at time of collection. Water samples shall be stored at 4°C (±2°C) until time of analysis. A total of two vials per field sample is the recommended amount the Contractor should receive.

NOTE: If MS/MSD analysis is required for a particular sample, two additional vials should be sent by the field samplers. Contact SMO if insufficient sample for MS/MSD analysis has been provided.

8.2 Sample Storage

8.2.1 Unpreserved low/medium soil samples must be protected from light and stored at less than -7°C from the time of receipt until time of analysis. Store unused sample aliquots at less than -7°C until 60 days after delivery of a reconciled, complete Sample Data Package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 Sodium bisulfate preserved low/medium soil samples and water samples must be protected from light and stored at 4°C (±2°C), in a refrigerator used only for storage of volatile samples, in an atmosphere demonstrated to be free of all potential contaminants, until 60 days after delivery of a reconciled, complete Sample Data Package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2.1 Aqueous storage blanks shall be stored [at 4°C (±2°C)] with preserved low/medium soil samples and water samples within an Sample Delivery Group (SDG) until all such samples are analyzed. Inert sand storage blanks shall be stored at less than -7°C with unpreserved low/medium soil samples until all such samples are analyzed.

8.2.3 Samples, sample extracts, and standards must be stored separately. Volatile standards must be stored separately from semivolatile, pesticide, and Aroclor standards.

8.3 Temperature Records and Sample Storage

8.3.1 The temperature of all sample storage refrigerators and freezers shall be recorded daily.

8.3.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

8.3.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators.

8.4 Contract Required Holding Times

Analysis of water and soil/sediment samples must be completed within 10 days of Validated Time of Sample Receipt (VTSR). Analysis of unpreserved, unfrozen soil/sediment samples must be completed within 24 hours of VTSR. As part of USEPA's Quality Assurance (QA) program, USEPA may provide Performance Evaluation (PE) samples that the Contractor is required to prepare per the instructions provided by USEPA. PE samples must be prepared and analyzed concurrently with the samples in the SDG. The contract-required 10 day holding time does not apply to PE samples.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

9.1.1 Purge-and-Trap

9.1.1.1 The following are the recommended purge-and-trap analytical conditions. The conditions are recommended unless otherwise noted.

Purge Conditions

Purge Gas:	Helium or Nitrogen
Purge Time:	11.0 ±0.1 min.
Purge Flow Rate:	25-40 mL/min.
Purge Temperature:	Ambient temperature for water or medium-level soil/sediment samples (required for medium-level soil/sediment samples, suggested for water samples), and 40°C low-level soil/sediment samples. Higher purge temperatures may be used, provided that technical acceptance criteria are met for all standards, samples, and blanks. Certain target compounds, such as methyl tert-butyl ether (MTBE), may decompose at high purge temperatures in samples that have been acid preserved.

Desorb Conditions

Desorb Temperature:	180°C
Desorb Flow Rate:	15 mL/min. (4 mL/min. for low-level soil samples).
Desorb Time:	4.0 ±0.1 min.

Trap Reconditioning Conditions

Reconditioning Temperature:	180°C
Reconditioning Time:	7.0 ±0.1 min. (minimum). A longer time may be required to bake contamination or water from the system.

9.1.1.2 Assemble a purge-and-trap device that meets the specification in Section 6.6 and that is connected to a Gas Chromatograph/Mass Spectrometer (GC/MS) system.

9.1.1.3 Before initial use, condition the trap overnight at 180°C by backflushing with at least 20 mL/minute flow of inert gas according to the manufacturer's recommendations. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, condition the trap for 10 minutes at 180°C while backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to the analysis of samples and blanks.

9.1.1.4 For low-level soil samples, establish the purge-and-trap instrument operating conditions. Adjust the instrument to inject 10 mL of reagent water, to heat the sample to 40°C for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer. Once established, the same purge-and-

trap conditions must be used for the analysis of all standards, samples, and blanks.

9.1.1.5 Optimize purge-and-trap conditions for sensitivity and to minimize cross-contamination between samples. Once optimized, the same purge-and-trap conditions must be used for the analysis of all standards, samples, and blanks.

NOTE: In certain situations, a heated purge may be used for water samples provided that all standards, samples, and blanks are run under the same conditions and all technical acceptance criteria can be met.

9.1.1.6 A moisture reduction/water management system may be used to improve the chromatographic performance by controlling moisture or water if:

- The system does not introduce contaminants that interfere with identification and quantitation of compounds listed in Exhibit C (Low/Medium Volatiles);
- The analytical results generated when using the moisture reduction/water management system meet the initial and continuing calibration verification technical acceptance criteria listed in the analytical method and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Low/Medium Volatiles);
- All calibration standards, samples, and blanks are analyzed under the same conditions; and
- The Contractor performs acceptably on the Performance Evaluation (PE) samples using this system.

9.1.2 Gas Chromatograph (GC)

9.1.2.1 The following are the recommended GC analytical conditions. These conditions are recommended unless otherwise noted.

Capillary Columns

Carrier Gas:	Helium
Flow Rate:	15 mL/min.
Initial Temperature:	10°C
Initial Hold Time:	1.0 - 5.0 (±0.1) min.
Ramp Rate:	6°C/min.
Final Temperature:	160°C
Final Hold Time:	Until 3 min. after all compounds listed in Exhibit C (Low/Medium Volatiles) elute (required).

9.1.2.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, blanks, and Matrix Spikes and Matrix Spike Duplicates (MS/MSDs).

9.1.2.3 If the gaseous compounds chloromethane, bromomethane, vinyl chloride, and chloroethane fail to exhibit narrow, symmetrical peak shape, are not separated from the solvent front, or are not resolved greater than 90.0% from each other, then a subambient

oven controller must be used, and the initial temperature must be less than or equal to 10°C.

9.1.3 Mass Spectrometer (MS)

The following are the required MS analytical conditions:

Electron Energy:	70 volts (nominal)
Mass Range:	35-300 amu
Ionization Mode:	Electron Ionization (EI)
Scan Time:	To give at least 5 scans per peak, not to exceed 2 sec. per scan for capillary column.

9.2 GC/MS Calibration (Tuning) and Ion Abundance

9.2.1 Summary of GC/MS Performance Check

9.2.1.1 The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibrant such as perfluoro-tri-n-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.2.1).

9.2.1.2 Prior to the analysis of any samples, including MS/MSDs, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing 4-bromofluorobenzene (BFB).

9.2.2 Frequency of GC/MS Performance Check

The instrument performance check solution must be injected once at the beginning of each 12-hour period, during which samples or standards are to be analyzed. The 12-hour time period for GC/MS performance check, calibration standards (initial or continuing calibration verification), blank, and sample analysis begins at the moment of injection of the BFB analysis that the laboratory submits as documentation of a compliant instrument performance check. However, in cases where a closing Continuing Calibration Verification (CCV) can be used as an opening CCV for the next 12-hour period, then an additional BFB tune is not required and the 12-hour period begins with the injection of the CCV. The time period ends after 12 hours have elapsed according to the system clock.

9.2.3 Procedure for GC/MS Performance Check

9.2.3.1 The analysis of the instrument performance check solution may be performed as follows:

- As an injection of up to 50 ng of BFB into the GC/MS.
- By adding sufficient amount of BFB solution (Section 7.2.2.1) to 5 mL of reagent water to result in a 10 µg/L concentration of BFB.
- By adding sufficient amount of BFB solution to a calibration standard to result in a 10 µg/L concentration of BFB.

9.2.4 Technical Acceptance Criteria for GC/MS Performance Check

9.2.4.1 The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not background subtract part of the BFB peak.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a BFB analysis must be run under identical GC/MS instrument run conditions.

9.2.4.2 The analysis of the instrument performance check solution must meet the ion abundance criteria given in Table 1.

9.2.5 Corrective Action for GC/MS Performance Check

9.2.5.1 If the BFB technical acceptance criteria are not met, retune the GC/MS system. It may also be necessary to clean the ion source, clean the quadrupole rods, or take other corrective actions to achieve the technical acceptance criteria.

9.2.5.2 BFB technical acceptance criteria must be met before any standards, samples, including MS/MSDs or required blanks, are analyzed. Any samples or required blanks analyzed when tuning technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

Prior to the analysis of samples and required blanks, and after the instrument performance check solution criteria have been met, each GC/MS system must be calibrated at five concentrations to determine instrument sensitivity and the linearity of GC/MS response for the purgeable target and Deuterated Monitoring Compounds (DMCs).

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be calibrated upon award of the contract whenever the Contractor takes corrective action which may change or affect the initial calibration criteria (e.g., ion source cleaning or repair, column replacement, etc.) or if the CCV acceptance criteria have not been met.

9.3.2.2 If time remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples and blanks may be analyzed. It is not necessary to analyze another CCV standard. A method blank is required.

9.3.3 Procedure for Initial Calibration

9.3.3.1 Assemble a purge-and-trap device that meets the specifications in Section 6.6. Condition the device as described in Section 9.1.1.

9.3.3.2 Connect the purge-and-trap device to the GC. The GC must be operated using temperature and flow rate parameters equivalent to those in Section 9.1.2.

9.3.3.3 Add sufficient amount of the internal standard solution (Section 7.2.2.3) to each of the five aqueous calibration standard solutions (Section 7.2.2.6.2) containing the DMCs for a

concentration of 50.0 µg/L at the time of purge. Analyze each calibration standard according to Section 10.

9.3.3.4 Separate initial calibration and continuing calibration verification must be performed for water samples and low-level soil/sediment samples if different purge conditions are used (unheated purge vs. heated purge). Extracts of medium-level soil/sediment samples may be analyzed using the calibrations of water samples if the same purge conditions are used.

The laboratory may run different matrices in the same 12-hour time period under the same tune, as long as separate calibration verifications are performed for each matrix within that 12-hour period.

9.3.4 Calculations for Initial Calibration

9.3.4.1 Calculate the Relative Response Factor (RRF) for each volatile target and DMC using Equation 1. The primary characteristic ions used for quantitation are listed in Table 2. If an interference prevents the use of a primary ion for a given internal standard, use a secondary ion listed in the same table. Assign the target compounds and DMCs to an internal standard according to Table 3.

NOTE: Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion.

EQ. 1 Relative Response Factor Calculation

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where,

A_x = Area of the characteristic ion [Extracted Ion Current Profile (EICP)] for the compound to be measured (see Table 2).

A_{is} = Area of the characteristic ion (EICP) for the specific internal standard (see Table 2).

C_{is} = Concentration of the internal standard.

C_x = Concentration of the compound to be measured.

9.3.4.2 Calculating the RRFs of the xylenes requires special attention. Report an RRF for m,p-xylene and one for o-xylene. On capillary columns, the m,p-xylene isomers coelute. Therefore, when calculating the RRF in the equation above, use the area response (A_x) and concentration (C_x) of the peak from o-xylene and A_x and C_x of the peak from m,p-xylene isomers respectively.

9.3.4.3 The Mean Relative Response Factor ($\overline{RRF}$) must be calculated for all compounds.

9.3.4.4 Calculate the Percent Relative Standard Deviation (%RSD) of the RRF values for each purgeable target and DMC over the initial calibration range using Equation 2 in conjunction with Equations 3 and 4.

EQ. 2 Percent Relative Standard Deviation Calculation

$$\%RSD = \frac{SD_{RRF}}{\overline{X}} \times 100$$

Where,

SD_{RRF} = Standard Deviation of initial calibration Relative Response Factors (per compound) from EQ. 3.

$\overline{X}$ = Mean value of the initial calibration Relative Response Factors (per compound).

9.3.4.5 Equation 3 is the general formula for Standard Deviation (SD) for a statistically small set of values.

EQ. 3 Standard Deviation Calculation

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{(n-1)}}$$

Where,

X_i = Each individual value used to calculate the mean.

$\overline{X}$ = The mean of n values.

n = Total number of values.

9.3.4.6 Equation 4 is the general formula for the mean of a set of values.

EQ. 4 Mean Value Calculation

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

Where,

X_i = Value.

$\overline{X}$ = Mean value.

n = Number of values.

9.3.5 Technical Acceptance Criteria for Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.2.6, and at the frequency described in Section 9.3.2 on a GC/MS system meeting the BFB technical acceptance criteria.

9.3.5.2 The RRF at each calibration concentration for each purgeable target and DMC must be greater than or equal to the compound's minimum acceptable RRF listed in Table 4.

9.3.5.3 The %RSD for each target or DMC listed in Table 4 must be less than or equal to that value listed.

9.3.5.4 Up to two target compounds and DMCs (excluding those with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Section 9.3.5.2 but these compounds must still meet the minimum RRF requirements of 0.010. Up to two target compounds and DMCs (excluding those with maximum %RSD requirements of 40.0%) may fail to meet the criteria listed in Section 9.3.5.3 but these compounds must still meet the maximum %RSD requirements of 40.0%. The exceptions are 1,4-dioxane and 1,4-dioxane-d_8, which must have a minimum RRF greater than or equal to 0.0050 and the %RSD must be less than or equal to 50.0%.

9.3.5.5 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, service the purge-and-trap device, or take other corrective actions to achieve the technical acceptance criteria.

9.3.6.2 Initial calibration technical acceptance criteria must be met before any samples, including MS/MSDs or required blanks, are analyzed. Any samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.4 Continuing Calibration Verification

9.4.1 Summary of Opening and Closing Continuing Calibration Verification (CCV)

Prior to the analysis of samples and required blanks and after BFB tune and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing an opening CCV containing all the purgeable target compounds, DMCs, and internal standards to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the analytical method. A closing CCV using the same standard conditions as for the opening CCV is required after all samples and blanks have been analyzed, and before the end of the 12-hour time period.

9.4.2 Frequency of Continuing Calibration Verification

9.4.2.1 The 12-hour time period begins with the injection of BFB, followed by the injection of the opening CCV solution. BFB may be added to the CCV solution, in which case only one injection is necessary. If a closing CCV meets the technical acceptance criteria for an opening CCV (Section 9.4.5) and samples are analyzed within that subsequent 12-hour time period, then an additional BFB tune is not required and the 12-hour time period begins with that calibration verification. If the closing CCV does not meet the technical

acceptance criteria for an opening CCV, then a BFB tune, followed by an opening CCV is required and the next 12-hour time period begins with the BFB tune.

9.4.2.2 If time remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. A method blank is required. Quantitate all sample and blank results using the mean RRF obtained from the initial calibration standard.

9.4.2.3 After the injection of all samples and required blanks, and before the end of the 12-hour period, another injection of the CCV solution is required (closing CCV). The closing CCV used to bracket the end of a 12-hour analytical sequence may be used as the opening CCV for a new 12-hour analytical sequence, provided that all technical acceptance criteria are met for an opening CCV in Section 9.4.5.

9.4.3 Procedure for Continuing Calibration Verification

9.4.3.1 Set up the purge-and-trap GC/MS system per the requirements in Section 9.1.1.

9.4.3.2 Add a sufficient amount of the internal standard solution (Section 7.2.2.3) to the 5 mL syringe or volumetric flask containing the CCV (Section 7.2.2.6.4) to result in a concentration of 50 µg/L. Analyze the CCV standard according to Section 10.

9.4.3.3 All samples, required blanks, and standard/spiking solutions must be allowed to warm to ambient temperature before analysis.

9.4.3.4 For low-level soil samples, the CCV standard shall be prepared in the same manner as the initial calibration standard of the same concentration as specified in Section 9.3.3.3.

9.4.4 Calculations for Continuing Calibration Verification

9.4.4.1 Calculate an RRF for each target compound and DMC according to Section 9.3.4.1.

9.4.4.2 Calculate the Percent Difference (%Difference) between the CCV RRF_c and the most recent initial calibration $\overline{RRF_i}$ for each purgeable target compound and DMC using Equation 5.

EQ. 5 Percent Difference Calculation

$$\%Difference = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

Where,

RRF_c = Relative Response Factor from current CCV standard.

$\overline{RRF_i}$ = Mean Relative Response Factor from the most recent initial calibration.

9.4.5 Technical Acceptance Criteria for Opening and Closing CCV

9.4.5.1 The concentration of the low/medium volatile organic target and DMCs in the opening and closing CCV must be at or near the mid-point concentration level of the calibration standards, 50 µg/L for non-ketones, 100 µg/L for ketones, and 1250 µg/L for 1,4-dioxane based on 5 mL volumes. The opening and closing CCV standard must be analyzed at the frequency described in Section 9.4.2 on a GC/MS system meeting the BFB (Section 9.2.4) and initial calibration (Section 9.3.5) technical acceptance criteria.

9.4.5.2 For an opening CCV, the RRF for each purgeable target and DMC must be greater than, or equal to, the compound's minimum acceptable RRF listed in Table 4. For a closing CCV, the RRF for each purgeable target and DMC must be at least 0.010 (except for 1,4-dioxane and its associated DMC 1,4-dioxane-d_8, which must be at least 0.0050).

9.4.5.3 For an opening CCV, the RRF Percent Difference for each purgeable target compound and DMC listed in Table 4 must be less than, or equal to, the value listed. For a closing CCV, the RRF Percent Difference for each purgeable target and DMC must be in the inclusive range of ±50%.

9.4.5.4 For an opening CCV, up to two target compounds and DMCs (excluding those compounds with minimum RRF requirements of 0.010) may fail the criteria listed in Section 9.4.5.2 but these compounds must still meet the minimum RRF requirements of 0.010. Up to two target compounds and DMCs (excluding those compounds with maximum Percent Difference requirements of ±40.0%) may fail to meet the requirements listed in Section 9.4.5.3 but these compounds must still meet the maximum Percent Difference requirements of ±40.0%. The exceptions are 1,4-dioxane and 1,4-dioxane-d_8, which must have a minimum RRF greater than or equal to 0.0050 and the Percent Difference must be within the inclusive range of ±50.0%. For a closing CCV, all target compounds and DMCs must meet the requirements listed in Sections 9.4.5.2 and 9.4.5.3.

9.4.5.5 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.4.6 Corrective Action for Opening and Closing Continuing Calibration Verification (CCV)

9.4.6.1 If the opening CCV technical acceptance criteria are not met, recalibrate the GC/MS instrument according to Section 9.3. If the closing CCV technical acceptance criteria are not met, then all samples and blanks analyzed within that 12-hour time period must be reanalyzed at no additional cost to USEPA. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the CCV technical acceptance criteria.

9.4.6.2 CCV technical acceptance criteria **MUST** be met before any samples, including MS/MSDs or required blanks, are analyzed. Any samples or required blanks analyzed when CCV technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90%, of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to notify them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multi-phase samples (e.g., two-phase liquid sample, oily, sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample;
- Separate the phases of the sample and analyze each phase separately. SMO will provide EPA Sample Numbers for the additional phases, if required;
- Separate the phases and analyze one or more of the phases, but not all of the phases. SMO will provide EPA Sample Numbers for the additional phases, if required; or
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do any of the following:

- Separate the phases and analyze the phase(s) that is(are) amenable to analysis. SMO will provide EPA Sample Numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Water Samples

10.1.3.1 Prior to the analysis of samples, establish the appropriate purge-and-trap Gas Chromatograph/Mass Spectrometer (GC/MS) operating conditions, as outlined in Section 9.1. Samples shall be analyzed only after the GC/MS system has met the instrument performance check, initial calibration, and Continuing Calibration Verification (CCV) requirements. Also prior to sample analysis, a method blank must be analyzed that meets blank technical acceptance criteria in Section 12.1.4. All samples, required blanks, and standard/spiking solutions must be allowed to warm to ambient temperature before analysis. All samples, required blanks, and calibration standards must be analyzed under the same instrument conditions.

10.1.3.2 If time remains in the 12-hour period (as described in Section 9.3.2), samples may be analyzed without analysis of a CCV standard.

10.1.3.3 Adjust the purge gas (helium) flow rate to 25-40 mL/minute. Variations from this flow rate may be necessary to achieve better purging and collection efficiencies for some compounds, particularly chloromethane and bromoform.

10.1.3.4 If the autosampler can automatically sample the appropriate volume then Sections 10.1.3.5 to 10.1.3.7 are performed by the autosampler.

10.1.3.5 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample or standard bottle that has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5 mL. This process of taking an aliquot destroys the validity of the sample for future analysis so, if there is only one VOA vial, the analyst must fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time as the analyst has determined that the first sample has been analyzed properly. Filling one 5 mL syringe would allow the use of only one syringe. If an analysis is needed from the second 5 mL syringe, it must be performed within 24 hours. Care must also be taken to prevent air from leaking into the syringe.

10.1.3.6 Add a sufficient amount of Deuterated Monitoring Compound (DMC) spiking solution (Section 7.2.2.4) and a sufficient amount of internal standard spiking solution (Section 7.2.2.3) through the valve bore of the syringe, then close the valve. The DMCs and internal standards may be mixed and added as a single spiking solution.

NOTE: Purge-and-trap instrumentation that allows internal standard and DMCs to be automatically added to each sample is widely available.

Some of this instrumentation may be set-up by the manufacturer to add only 1 µL of internal standard or DMCs. The 1 µL addition of standards will be allowed if the addition is done solely in an automated manner, and if the final concentration of the following standards in the 5 mL water sample can be met: 50 µg/L for internal standards; the concentrations listed in Section 7.2.2.6.2 for DMCs in the initial calibration; and the concentrations listed in Section 7.2.2.6.4 for DMCs in the CCV.

10.1.3.7 Attach the valve assembly on the syringe to the valve on the sample purger. Open the valves and inject the sample into the purging chamber.

10.1.3.8 Close both valves and purge the sample for 11.0 (±0.1) minutes at ambient temperature.

10.1.3.9 Sample Desorption - After the 11-minute purge, attach the trap to the GC, adjust the purge-and-trap system to desorb mode, initiate the temperature program sequence of the GC, and start data acquisition. Introduce the trapped material into the GC column by rapidly heating the trap to 180°C while backflushing the trap with

inert gas at 15 mL/min. for 4.0 ±0.1 minutes. While the trapped material is being introduced into the GC, empty the sample purger and rinse it with reagent water. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high purgeable levels, it may be necessary to wash out the sample purger with a detergent solution, rinse it with reagent water, and then dry it in an oven at 105°C.

10.1.3.10 Trap Reconditioning - After desorbing the sample, recondition the trap for a minimum of 7.0 (±0.1) minutes at 180°C by returning the purge-and-trap system to purge mode. Trap temperatures up to 220°C may be employed. However, higher temperatures will shorten the useful life of the trap.

10.1.3.11 Gas Chromatography - Hold the column temperature at 10°C for 1.0 - 5.0 min., then program at 6°C/min. to 160°C and hold until 3 minutes after all target volatile compounds have eluted.

NOTE: Once an initial hold time has been chosen and the GC operating conditions optimized, the same GC condition must be used for the analysis.

10.1.3.12 Termination of Data Acquisition - 3 minutes after all the purgeable target compounds have eluted from the GC, terminate the MS data acquisition and store data files on the data system storage device. Use appropriate data output software to display full range mass spectra and appropriate Extracted Ion Current Profiles (EICPs).

10.1.4 Low-Level Soil/Sediment Samples

10.1.4.1 The Contractor should strive to analyze soil/sediment samples at the lowest dilution, unless directed otherwise. If samples are received as sealed VOA vials or containers, they are to be analyzed according to Section 10.1.4.2 (Method 5035), unless screening analysis indicates samples are to be analyzed as medium-level samples. If the results of medium-level analysis indicate that all target compound concentrations are below the medium-level Contract Required Quantitation Limit (CRQL) in Exhibit C (Low/Medium Volatiles), then the samples must be analyzed as low-level samples. If samples are originally analyzed by the low-level method, and any target compound in the sample exceeds the response of the same target compound in the high standard, then the sample is to be reanalyzed by the medium-level method. In this scenario, the low-level analysis, the medium-level analysis, and any dilution of the medium-level samples are billable. If the laboratory suspects that any target compound is at a concentration that may result in instrument performance problems when analyzed using the low-level method, SMO should be contacted for further guidance.

If USEPA specifically requests the laboratory to analyze a sample only by the medium-level protocol (i.e., methanol extraction technique), the laboratory is not obligated to perform the low-level analysis. The request to the laboratory is to be made on the Traffic Report/Chain of Custody Record (TR/COC). After receiving a TR/COC with this specific request, the laboratory is to confirm the request through SMO.

10.1.4.2 The following steps apply to the preparation of vials used for the analysis of low-level soil/sediment samples by the closed-system purge-and-trap equipment described in this method. If samples are

received in closed-system purge vials, proceed to Section 10.1.4.8.

NOTE: There should be three field core sampling/storage containers for each field sample. The contents of two of the field core containers are to be transferred immediately upon sample receipt and processed using the steps outlined in Sections 10.1.4.3 - 10.1.4.8. One of these prepared samples is then to be used as the primary sample, while the other is to be used as a back-up sample, if necessary. The contents of the third field core container shall be transferred immediately upon sample receipt to a tared dry closed-system purge-and-trap container (i.e., no preservative solution or stirring bar is to be added), weighed according to Section 10.1.4.8, and then stored at less than -7°C. This sample shall be used for the medium concentration level methanol extraction procedure as described in Section 10.1.4.1, if results of the original analysis indicate that medium-level extraction is warranted.

10.1.4.3 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

10.1.4.4 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted vials are used, seal both ends as recommended by the manufacturer.

10.1.4.5 Affix a label to each vial and weigh the prepared vial to the nearest 0.01 g. Record the tare weight and final weight.

10.1.4.6 Because volatile organics will partition into the headspace of the vial and will be lost when the vial is opened, DMCs, Matrix Spikes, and internal standards should only be added to vials after the sample has been added to the vial. The standards should be introduced either manually by puncturing the septum with a small-gauge needle or automatically by the purge-and-trap system just prior to analysis.

10.1.4.7 Using the sample collection device, transfer the contents (approximately 5 g) into the sample vial. This sample transfer must be performed rapidly to minimize loss of volatile compounds. Quickly brush any soil off the vial and immediately seal the vial with the septum and screw-cap. The soil vial is hermetically sealed and must remain so in order to guarantee the integrity of the sample. Gloves must be worn when handling the sample vial since the vial has been tared. Record the date and time of sample transfer onto the pre-prepared vials and submit with the data package.

10.1.4.8 Weigh the vial and contents to the nearest 0.01 g and record this weight. Sample weight is determined by subtracting the sample vial tared weight determined above from this final weight. For samples received in closed-system purge vials, the tared weights should have been provided by the field sampler. If tared weights are not provided, contact SMO for further guidance.

10.1.4.9 Prior to sample purge, all soil/sediment samples must be allowed to warm to ambient temperature. For those samples that have been stored in freezing compartments and will be analyzed by the low concentration level protocol, 5 mL of reagent water must be added

to the vials without disturbing the hermetic seal of the sample vial.

NOTE: An additional 5 mL of reagent water will be added to the vial as per Section 10.1.4.10. All low-level soil samples should have a total sample volume (reagent water and preservative) of 10 mL.

Shake all vials containing aqueous solutions gently to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel according to the manufacturer's instructions.

10.1.4.10 Without disturbing the hermetic seal on the sample vial, add 5 mL reagent water, add sufficient amount of the internal standard spiking solution (Section 7.2.2.3) and the DMC spiking solution (Section 7.2.2.4). All samples, including Matrix Spike and Matrix Spike Duplicates (MS/MSDs), standards, and blanks, within an SDG, must have the same amount of reagent water added. Do not increase/change the amount of DMC and internal standard solution added. Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as described by the manufacturer.

10.1.4.11 Purge the sample with helium or another inert gas at a flow rate of 20 to 40 mL/minute for 11 minutes while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

10.1.4.12 If a non-cryogenic interface is to be utilized, place the purge-and-trap system in the desorb mode after the 11-minute purge, and preheat the trap to 180°C without a flow of desorption gas. Start the flow of desorption gas at 10 mL/minute for about 4 minutes. Begin the temperature program of the GC and start data acquisition.

10.1.4.13 If a cryogenic interface is to be utilized, place the purge-and-trap system in the desorb mode after the 11-minute purge, making sure that the cryogenic interface is at -150°C or lower, and rapidly heat the trap to 180°C while backflushing with an inert gas at 4 mL/minute for about 5 minutes. At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C. Begin the temperature program of the GC and start the data acquisition.

10.1.4.14 After desorbing the sample for 4-5 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 180°C. After approximately 10 minutes, turn off the trap heater and halt the purge flow through the trap. When the trap is cool (ambient temperature), the next sample can be analyzed.

10.1.5 Medium-Level Soil/Sediment Samples

NOTE: If the only acceptable vial received is the one without headspace, contact SMO for further guidance.

10.1.5.1 The medium-level soil/sediment method is based on extracting the soil/sediment sample with methanol. An aliquot of the methanol extract is added to reagent water containing the DMCs and the

internal standards. The reagent water containing the methanol extract is purged at ambient temperature.

10.1.5.2 Prior to the analysis of samples, establish the appropriate purge-and-trap GC/MS operating conditions, as outlined in Section 9.1. Because the methanol extract and reagent water mixture is purged at ambient temperature, the instrument performance check, initial calibration, and CCV for water samples may be used for analyses of medium-level soil/sediment sample extracts.

10.1.5.3 Weigh the vial and contents to the nearest 0.01 g and record this weight. Sample weight is determined by subtracting the sample vial tared weight determined in Sections 10.1.4.3 - 10.1.4.5. For samples received in closed-system purge vials, the tared weights should have been provided by the field sampler. If tared weights are not provided, contact SMO for further guidance.

NOTE: If a methanol preserved sample is to be analyzed, weigh the sample vial and contents to the nearest 0.1 g and record the weight. Record any discrepancies between laboratory-determined weight and sampler-determined weight in the SDG Narrative and utilize the sampler-determined weight in any calculations. Proceed to Section 10.1.5.6.

10.1.5.4 Quickly add 5 mL of methanol to the vial. Cap and shake for 2 minutes.

NOTE: The steps in Sections 10.1.5.3 and 10.1.5.4 must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

10.1.5.5 Let the solution settle. Then, using a disposable pipette, transfer approximately 1 mL of extract into a GC vial for storage. The remainder may be discarded. The 1 mL extract may be stored in the dark at 4°C (±2°C) prior to the analysis.

10.1.5.6 Add 100 µL volume of methanol extract to the 4.9 mL of reagent water for analysis. Otherwise, estimate the concentration range of the sample from the low-level analysis or from the in-house screening procedure to determine the appropriate volume. A 100 µL of methanol extract is the maximum volume that can be added to the 4.9 mL of reagent water for medium-level analysis. If less than 100 µL of methanol extract is used, a volume of clean methanol must be used so that the volumes of methanol extract and clean methanol total 100 µL.

10.1.5.7 Remove the plunger from a 5 mL Luer-Lok type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5 mL. Pull the plunger back to 5 mL to allow volume for the addition of sample and standards, and add sufficient amount of DMC spiking solution (Section 7.2.2.4) and sufficient amount of internal standard spiking solution (Section 7.2.2.3). Also add the volume of methanol extract determined in Section 10.1.5.6 and a volume of clean methanol to total 100 µL (excluding methanol in DMC/internal standard solutions).

10.1.5.8 Attach the syringe-syringe valve assembly to the syringe valve on the purge device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

10.1.5.9 Proceed with the analysis as outlined in Sections 10.1.3.8 - 10.1.3.12.

10.1.6 Sample Dilutions

10.1.6.1 The Contractor shall analyze samples undiluted, or at minimal dilution. Samples may be diluted because of target compound responses exceeding the response of the same target compound in the high standard, or because of excessive matrix interference that hinders accurate quantitation. It is highly recommended that screening analysis be performed prior to sample analysis to determine estimated compound concentration and matrix problems.

NOTE 1: If the laboratory has evidence or highly suspects, because of sample color or other physical properties, that a sample may contain high concentrations of either target or non-target compounds, then SMO shall be contacted immediately. SMO will seek Regional recommendations for diluted analysis.

NOTE 2: Secondary ion quantitation is only allowed when there are sample interferences with the primary quantitation ion, not when saturation occurs. If secondary ion quantitation is used, calculate a Relative Response Factor (RRF) using the area response (EICP) from the most intense secondary ion which is free of sample interferences, and document the reasons in the SDG Narrative.

10.1.6.2 For water samples, samples may be diluted to keep target compound concentrations within the calibrated range and/or to keep baseline height from the earliest eluting peak from exceeding one-half the relative height of the highest peak in the chromatogram. If dilution is required due to baseline drift, the laboratory must submit chromatograms in which the highest peak is set to full scale. If the baseline rises less than 10% in the diluted analysis, the sample has been overdiluted. The Contractor must receive prior approval from the USEPA Regional Contract Laboratory Program Project Officer (CLP PO) of sample origin via SMO to perform more than two dilutions of a sample.

10.1.6.3 For soil samples analyzed by the low-level method, if the response of any target compound in the sample exceeds the response of the same target compound in the high standard, then a new sample must be prepared and analyzed by the medium-level method (Section 10.1.5).

10.1.6.4 The Dilution Factor (DF) chosen must keep the responses of the volatile target compounds that required dilutions in the upper half of the calibration range.

10.1.6.5 All dilutions must be made just prior to GC/MS analysis of the sample. Until the diluted sample is in a gas-tight syringe, all steps in the dilution procedure must be performed without delay.

10.1.6.6 For water samples, all dilutions are made in volumetric flasks. Select the volumetric flask that will allow for the necessary dilution (10-100 mL). Intermediate dilutions may be necessary for extremely large dilutions. Calculate the approximate volume of reagent water that will be added to the selected volumetric flask and add slightly less than this quantity of reagent water to the flask.

10.1.6.7 For water samples, inject the proper aliquot from the syringe prepared in Section 10.1.3.5 into the volumetric flask. Only aliquots of 1 mL increments are permitted. Dilute the aliquot to the mark on the flask with reagent water. Cap the flask, invert, and shake three times.

10.1.6.8 Fill a 5 mL syringe with the diluted sample as in Section 10.1.3.5. If this is an intermediate dilution, use it and repeat the above procedure to achieve larger dilutions.

10.1.6.9 If more than two analyses (i.e., from the original sample and more than one dilution, or from the most concentrated dilution analyzed and further dilutions) are required to get all target compounds within the calibration range, contact SMO for guidance.

10.2 pH Determination (Water Samples)

Once the sample aliquots have been taken from the VOA vial, the pH of the water sample must be determined. The purpose of the pH determination is to ensure that all VOA samples were acidified in the field. Test the pH by placing one or two drops of sample on the pH paper (do **not** add pH paper to the vial). Record the pH of each sample, and report these data in the SDG Narrative, following the instructions in Exhibit B. No pH adjustment is to be performed by the Contractor.

10.3 Percent Moisture Determination

It is highly recommended that the Percent Moisture (%Moisture) determination only be made after the analyst has determined that no sample aliquots will be taken from the 60 mL vial for further analysis. This is to minimize the loss of volatiles and to avoid sample contamination from the laboratory atmosphere.

Immediately after weighing the sample for analysis, weigh 5-10 g of the soil/sediment into a tared crucible. Determine the Percent Moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of soil/sediment.

EQ. 6 Percent Moisture Calculation

$$\%\text{Moisture} = \frac{\text{grams of wet sample - grams of dry sample}}{\text{grams of wet sample}} \times 100$$

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

11.1.1.1 The compounds listed in the Target Compound List (TCL) in Exhibit C (Low/Medium Volatiles) shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of the standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

- Elution of the sample component at the same Gas Chromatograph (GC) Relative Retention Time (RRT) as the standard component; and
- Correspondence of the sample component and standard component mass spectra.

11.1.1.2 For establishing correspondence of the GC RRT, the sample component RRT must compare within ±0.06 RRT units of the RRT of the corresponding continuing calibration standard component. For reference, the standard must be run in the same 12-hour time period as the sample. If samples are analyzed during the same 12-hour time period as the initial calibration standards, use the RRT values from the 50 µg/L standard. Otherwise, use the corresponding opening Continuing Calibration Verification (CCV) standard. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, then the RRT should be assigned by using Extracted Ion Current Profiles (EICP) or ions unique to the component of interest.

11.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/Mass Spectrometer (MS) are required. Once obtained, these standard spectra may be used for identification purposes, **only** if the Contractor's GC/MS meets the daily instrument performance requirements for 4-bromofluorobenzene (BFB). These standard spectra may be obtained from the run used to obtain reference RRTs.

11.1.1.4 The guidelines for qualitative verification by comparison of mass spectra are as follows:

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) **must** be present in the sample spectrum.
- The relative intensities of ions specified in the above paragraph must agree within ±20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70%).
- Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the adjusted Contract

Required Quantitation Limit (CRQL), report the actual value followed by a "J" (e.g., "3J").

11.1.1.5 If a compound cannot be verified by all of the spectral identification criteria listed in Section 11.1.1.4, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification and proceed with quantitation.

11.1.2 Qualitative Identification of Non-Target Compounds

11.1.2.1 A library search shall be executed for non-target sample components for the purpose of tentative identification. The NIST (2002 release or later), Wiley (1991 release or later), or equivalent mass spectral library, shall be used as the reference library.

11.1.2.2 All organic compounds that have not been positively identified as volatile target analytes using the procedures detailed in Section 11.1, or that are not Deuterated Monitoring Compounds (DMCs) or internal standards shall be tentatively identified via a forward search of the NIST, Wiley, or equivalent mass spectral library. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer-generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

11.1.2.3 Up to 30 non-alkane Tentatively Identified Compounds (TICs) of greatest apparent concentration shall be reported on Form I VOA-TIC. Peaks that are tentatively identified as straight-chain, branched, or cyclic alkanes, and are alone or part of an alkane series, shall be reported as "total alkanes" on Form I VOA-TIC. An alkane is defined as any hydrocarbon with the generic formula C_nH_{2n+2} (straight-chain or branched) or C_nH_{2n} (cyclic) that contains only C-H and C-C single bonds. The concentrations of each of the alkanes is to be summed and reported as a single result for the "total alkanes". Documentation for the tentative identification of each alkane shall be supplied in the hard copy deliverable packages. The alkanes are not to be counted as part of the 30 compounds individually reported as tentative identified compounds on Form I VOA-TIC. Carbon dioxide and compounds with responses less than 10% of the internal standard in which they are to be qualified (as determined by inspection of the peak areas or height) are not to be reported (nor are they to be counted as part of the 30 compounds that are to be reported).

11.1.2.4 Rules for making tentative identification:

11.1.2.4.1 For compounds to be reported, as per the instructions in Section 11.1.2.3., identification (as generated by the library search program) of those receiving a library search match of 85% or higher should be considered a "probable match". The compound should be reported with the identification generated by the search program unless the mass spectral interpretation specialist feels there is <u>just evidence</u> not to report the compound as identified by the library search program.

11.1.2.4.2 If the library search produces more than one compound at or above 85%, report the compound with the highest percent match (report first compound if the percent match is the same for two

or more compounds), unless the mass spectral interpretation specialist feels there is just evidence not to report the compound with the highest match. Do not report DMCs, internal standards, or analytes that are on the volatile target analyte list, unless the library search produces only one compound having a match of greater than 85%, and that compound is identified as a DMC, internal standard, or volatile target analyte.

11.1.2.4.3 If the library search produces a series of obvious isomer compounds with library search matches greater that 85% (e.g., tetramethyl naphthalenes), the compound with the highest library search percent match should be reported (or first compound if library search matches are the same).

11.1.2.4.4 If the mass spectral interpretation specialist has just evidence to support reporting a compound with a tentative identification of something other than that generated by the library search program (with a library search result of 85% or greater), the laboratory shall include in the Sample Delivery Group (SDG) Narrative the justification for not reporting a compound as listed by the search program. This narrative shall detail explicitly why a library search generated identification for a compound was rejected. If a TIC has obvious isomer analogs, the laboratory shall include in the SDG narrative a statement indicating that the exact isomer configuration, as reported, may not be absolutely accurate.

11.1.2.4.5 If the library search produces no matches at or above 85%, the mass spectral interpretation specialists is encouraged to make a valid tentative identification of the compound. If no valid tentative identification can be made, the compound should be reported as "unknown". The mass spectral interpretation specialist should give additional classification of the unknown, if possible (e.g., "unknown aromatic compound", "unknown chlorinated compound", etc.).

11.2 Calculations

11.2.1 Target Compounds

11.2.1.1 Identified target compounds shall be quantified by the internal standard method using Equation 7 or 8. The internal standard used shall be that which is assigned in Table 3. The Mean Relative Response Factor ($\overline{RRF}$) from the initial calibration standard is used to calculate the concentration in the sample.

11.2.1.2 Water

EQ. 7 Water Concentration Calculation

$$\text{Concentration } (\mu g/L) = \frac{(A_x)\ (I_s)\ (DF)}{(A_{is})\ (\overline{RRF})\ (V_o)}$$

Where,

A_x = Area of the characteristic ion (EICP) for the compound to be measured. The primary quantitation ions for the target compounds, internal standards, and DMCs are listed in Table 2.

A_{is} = Area of the characteristic ion (EICP) for the internal standard. The target compounds are listed with their associated internal standards in Table 3.

I_s = Amount of internal standard added, in ng.

$\overline{RRF}$ = Mean Relative Response Factor from the initial calibration.

V_o = Total volume of water purged, in mL.

DF = Dilution Factor. The DF for analysis of water samples for volatiles by this method is defined as the ratio of the number of mL of water purged (i.e., V_o above) to the number of mL of the original water sample used for purging. For example, if 2.0 mL of sample is diluted to 5.0 mL with reagent water and purged, DF = 5.0 mL/2.0 mL = 2.5. If no dilution is performed, DF = 1.0.

11.2.1.3 Low-Level Soil/Sediment

EQ. 8 Low-Level Soil/Sediment Concentration Calculation

$$\text{Concentration } (\mu g/Kg) \text{ (dry weight basis)} = \frac{(A_x)\ (I_s)\ (DF)}{(A_{is})\ (\overline{RRF})\ (W_s)\ (D)}$$

Where,

A_x, I_s, A_{is}, and DF are as given for water, Equation 7.

$\overline{RRF}$ = Mean Relative Response Factor from the heated purge of the initial calibration.

$$D = \frac{100 - \%\text{Moisture}}{100}$$

W_s = Weight of sample added to the purge tube, in g.

11.2.1.4 Medium-Level Soil/Sediment

EQ. 9 Medium-Level Soil/Sediment Concentration Calculation

$$\text{Concentration } \mu g/Kg \text{ (dry weight basis)} = \frac{(A_x)(I_s)(AV_t)(1000)(DF)}{(A_{is})(\overline{RRF})(V_a)(W_s)(D)}$$

Where,

A_x, I_s, A_{is} are as given for water, Equation 7.

$\overline{RRF}$ = Mean Relative Response Factor from the **ambient** temperature purge of the initial calibration.

AV_t = Adjusted total volume of the methanol extract plus soil water in milliliters (mL) determined by:

$$AV_t = V_t + \{W_s - [W_s(D)]\}$$

Where V_t = total volume of methanol extract in milliliters (mL). This volume is typically 10 mL, even though only 1.0 mL is transferred to the vial in Section 10.1.5.5. The quantity derived from $\{W_s - [W_s(D)]\}$ is the soil water volume and is expressed in mL.

V_a = Volume of the aliquot of the sample methanol extract (i.e., sample extract not including the methanol added to equal 100 µL), in microliters (µL) added to reagent water for purging.

W_s = Weight of soil/sediment extracted, in g.

$$D = \frac{100 - \%Moisture}{100}$$

DF = Dilution Factor. The DF for analysis of soil/sediment samples for volatiles by the medium-level method is defined as:

$$\frac{\mu L \text{ most conc. extract used to make dilution} + \mu L \text{ clean solvent}}{\mu L \text{ most conc. extract used to make dilution}}$$

11.2.1.5 For water, low-level and medium-level soil/sediment samples, xylenes are to be reported as "m,p-xylenes" and "o-xylene". Because m- and p-xylene isomers coelute, special attention must be given to the quantitation of the xylenes. In quantitating sample concentrations, be sure to use the correct corresponding Relative Response Factor (RRF) values.

NOTE: The area of each peak (i.e., the peaks for o-xylene and m,p-xylene) must appear on the complete quantitation report.

11.2.1.6 The stereoisomers, trans-1,2-dichloroethene, and cis-1,2-dichloroethene are to be reported separately.

11.2.1.7 Secondary ion quantitation is allowed **only** when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the SDG Narrative. A secondary ion cannot be used unless an RRF is calculated using the secondary ion.

11.2.1.8 The requirements listed in Sections 11.2.1.9 and 11.2.1.10 apply to all standards, samples including Matrix Spikes and Matrix Spike Duplicates (MS/MSDs) and blanks.

11.2.1.9 It is expected that situations will arise where the automated quantitation procedures in the GC/MS software provide inappropriate quantitations. This normally occurs when there is compound coelution, baseline noise, or matrix interferences. In these circumstances, the Contractor must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific target compound, DMC, or internal standard compound. The area integrated shall not include baseline background noise. The area integrated shall also not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet Quality Control (QC) criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instances of manual integration must be documented in the SDG Narrative.

11.2.1.10 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS Operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the integration scan range. The GC/MS Operator shall also mark each integrated area with the letter "M" on the quantitation report. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all compounds listed in Exhibit C (Low/Medium Volatiles), internal standards, and DMCs.

11.2.2 Non-Target Compounds

11.2.2.1 An estimated concentration for non-target TICs shall be determined by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

11.2.2.2 The formulas for calculating non-target compound concentrations are the same as in Sections 11.2.1.2, 11.2.1.3, and 11.2.1.4. Total area counts (or peak heights) from the total Reconstructed Ion Chromatograms (RICs) are to be used for both the non-target compound to be measured (A_x) and the internal standard (A_{is}). An RRF of 1.0 is to be assumed. The value from this quantitation shall be qualified as "J" (estimated due to the lack of a compound-specific RRF), and "N" (presumptive evidence of presence), indicating the quantitative and qualitative uncertainties associated with this non-target compound. An estimated concentration must be calculated for all TICs, as well as those identified as unknowns.

11.2.3 CRQL Calculations

11.2.3.1 Water

EQ. 10 Water Adjusted CRQL Calculation

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{V_x}{V_o} \times DF$$

Where,

Contract CRQL = Exact CRQL values in Exhibit C of the Statement of Work (SOW).

V_o and DF are as given in Equation 7.

V_x = Contract Sample Volume (5.0 mL).

11.2.3.2 Low-Level Soil/Sediment

EQ. 11 Low-Level Soil Adjusted CRQL Calculation

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{(W_x)}{(W_s)(D)}$$

Where,

W_s and D are as given in Equation 8.

W_x = Contract Sample Weight (5.0 g).

11.2.3.3 Medium-Level Soil/Sediment

EQ. 12 Medium-Level Soil/Sediment Adjusted CRQL Calculation

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{(W_x)(V_t)(V_y)(1000)(DF)}{(W_s)(V_c)(V_a)(D)}$$

Where,

V_t, DF, W_s, V_a and D are as given in Equation 9.

W_x = Contract Sample Weight (5.0 g).

V_y = Contract Soil Aliquot Volume from soil methanol extract (100 µL).

V_c = Contract Soil Methanol Extract Volume (5,000 µL).

11.2.4 Deuterated Monitoring Compound (DMC) Recoveries

11.2.4.1 Calculate the concentration of each DMC using the same equation as used for target compounds.

11.2.4.2 Calculate the recovery of each DMC in all samples and blanks using Equation 13. Report the recoveries on the appropriate forms.

EQ. 13 DMC Percent Recovery Calculation

$$\%R = \frac{Q_d \times DF}{Q_a} \times 100$$

Where,

Q_d = Concentration or amount determined by analysis.

Q_a = Concentration or amount added to sample/blank.

DF = Same as EQ. 9.

11.2.5 Internal Standard Responses and Retention Times (RTs)

Internal standard responses and RTs in all samples must be evaluated during, or immediately after, data acquisition. Compare the sample/blank internal standard responses and RTs to the opening CCV internal standard responses and RTs. For samples and blanks analyzed during the same 12-hour time period as the initial calibration standards, compare the internal standard responses and RTs against the 50 µg/L calibration standard.

The EICP of the internal standards must be monitored and evaluated for each sample including MS/MSDs and blanks.

11.3 Technical Acceptance Criteria for Sample Analysis

11.3.1 The samples must be analyzed on a GC/MS system meeting the BFB, initial calibration, CCV, and blank technical acceptance criteria.

11.3.2 The sample and any required dilution must be analyzed within the contract holding time.

11.3.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

11.3.4 The Percent Recovery of each of the DMCs in the sample must be within the acceptance windows in Table 5. The recovery limits for 1,4-dioxane-d_8 are advisory. Up to three DMCs, excluding 1,4-dioxane-d_8, per sample may fail to meet the recovery limits listed in Table 5.

11.3.5 The EICP area for each of the internal standards in the sample must be within the range of 50.0% and 200% of its response in the most recent opening CCV standard analysis.

11.3.6 The RT shift for each of the internal standards in the sample must be within ±0.50 minutes (30 seconds) of its RT recent opening CCV standard analysis.

11.3.7 Excluding those ions in the solvent front, no ion may saturate the detector. No target compound concentration may exceed the upper

limit of the initial calibration range unless a more diluted aliquot of the sample is also analyzed according to the procedures in Section 10.1.6.

11.3.8 The Contractor must demonstrate that there is no carryover from a contaminated sample before data from subsequent analyses may be submitted. After a sample that contains a target compound at a level exceeding the initial calibration range, the Contractor must either:

- Analyze an instrument blank immediately after the contaminated sample. If an autosampler is used, an instrument blank must also be analyzed using the same purge inlet that was used for the contaminated sample. The instrument blanks must meet the technical acceptance criteria for blank analysis (see Section 12.1.4); or

- Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample and that exceeded the calibration range. The maximum carryover criteria are as follows: the sample must not contain a concentration above the adjusted CRQL for the target compounds that exceeded the limits in the contaminated sample. If an auto sampler is used, the next sample analyzed using the same purge inlet that was used for the contaminated sample must also meet the maximum contamination criteria.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample technical acceptance criteria must be met before data are reported. Samples contaminated from laboratory sources or any samples not meeting the sample technical acceptance criteria will require reanalysis at no additional cost to USEPA.

11.4.2 Corrective actions for failure to meet instrument performance checks, initial calibration, CCV, and method blanks must be completed before the analysis of samples.

11.4.3 Corrective Action for DMCs and Internal Standard Compounds that Fail to Meet Acceptance Criteria

11.4.3.1 If the technical acceptance criteria for any of the internal standards and DMCs are not met:

- Check all calculations, instrument logs, the DMC and internal standard compound spiking solutions, and the instrument operation. If the calculations were incorrect, correct the calculations and verify that the DMC recoveries and internal standard compound responses meet acceptance criteria.

- If the instrument logs indicate that the incorrect amount of DMC or internal standard compound spiking solution was added, then reanalyze the sample after adding the correct amount of DMC and internal standard spiking solutions.

- If the DMC spiking solution or internal standard compound spiking solution was improperly prepared, concentrated, or degraded, re-prepare the solutions and reanalyze the samples.

- If the instrument malfunctioned, correct the instrument problem and reanalyze the sample. If the instrument malfunction affected the calibration, recalibrate the

instrument before re-analyzing the sample. Verify that the DMC recoveries meet acceptance criteria.

11.4.3.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If DMC recoveries or internal standard compound responses in a sample used for a MS/MSD were outside the acceptance criteria, then it should be reanalyzed only if DMC recoveries and internal standard compound responses met acceptance criteria in both the MS/MSD analyses.

- If the DMC recoveries and the internal standard compound responses meet the acceptance criteria in the reanalyzed sample, then the problem was within the Contractor's control. Therefore, submit data only from the reanalysis.

- If the DMC recoveries and/or the internal standard compound responses fail to meet the acceptance windows in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables using the suffixes in Exhibit B.

11.4.4 Corrective Action for Internal Standard Compound RTs Outside Acceptance Criteria

11.4.4.1 If the internal standard compound RTs are not within their acceptance criteria, check the instrument for malfunctions. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample. If the instrument malfunction affected the calibration, recalibrate the instrument before re-analyzing the samples.

11.4.4.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If the internal standard compound RTs in a sample used for a MS or MSD were outside the acceptance criteria, then it should be reanalyzed only if the internal standard compound RTs were within the acceptance criteria in both the MS/MSD analyses.

- If the internal standard compound RTs are within the acceptance criteria, then the problem was within the Contractor's control. Therefore, submit only data from the reanalysis when the internal standard compound RTs are within the acceptance limits.

- If the internal standard compound RTs are outside the acceptance criteria in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables, using the suffixes in Exhibit B.

11.4.5 All samples to be reported to USEPA must meet the maximum carryover criteria in Section 11.3.8. If any sample fails to meet these criteria, each subsequent analysis must be checked for cross-contamination. The analytical system is considered contaminated until a sample has been analyzed that meets the maximum carryover

criteria or an instrument blank has been analyzed that meets the technical acceptance criteria for blanks. If an instrument blank is not analyzed between consecutive samples that have the same compound with a concentration exceeding the calibration range then the second sample must be appropriately diluted as in Section 10.1.6.4 and analyzed. If in the dilution this compound is detected at levels at or below the adjusted CRQL then all samples analyzed after the second sample that fail to meet maximum carryover criteria must be reanalyzed. If in the dilution this compound is detected within the calibration range then no further corrective action is required.

12.0 QUALITY CONTROL (QC)

12.1 Blank Analyses

12.1.1 Summary

There are three different types of blanks required by this method.

12.1.1.1 Method Blank - A volume of a clean reference matrix (reagent water for water samples or a purified solid matrix for soil/sediment samples) spiked with sufficient amount of internal standard spiking solution (Section 7.2.2.3) and Deuterated Monitoring Compound (DMC) solution (Section 7.2.2.4), and carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of the method blank is to determine the levels of contamination associated with processing and analysis of samples.

NOTE: For soil/sediment samples, if any samples are prepared without the sodium bisulfate preservative, a method blank will be prepared in the same manner and run in the same 12-hour sequence as the unpreserved samples.

12.1.1.2 Storage Blank - A volume of a clean reference matrix [reagent water for water samples and preserved soil samples stored at 4°C (±2°C) or inert sand for soil samples stored at less than -7°C] spiked with sufficient amount of internal standard spiking solution (Section 7.2.2.3) and DMC solution (Section 7.2.2.4), and analyzed after all samples in the Sample Delivery Group (SDG) have been analyzed. Upon receipt of the first samples in an SDG), two vials with a clean reference matrix are stored with the samples in the SDG under the same conditions. After all samples in the SDG have been analyzed, the storage blank is analyzed. The storage blank indicates whether contamination may have occurred during storage of samples.

NOTE: If the SDG contains samples stored at 4°C (±2°C) and samples stored at less than -7°C, two storage blanks will be prepared, one for each condition.

12.1.1.3 Instrument Blank - A 5.0 mL aliquot of reagent water spiked with sufficient amount of internal standard spiking solution (Section 7.2.2.3) and DMC solution (Section 7.2.2.4) that is added to the sample vial and carried through the entire analytical procedure. Instrument blanks are analyzed after a sample/dilution that contains a target compound exceeding the calibration range. The results from the instrument blank analysis indicate whether there is contamination from a previous sample.

12.1.2 Frequency of Blank Analyses

12.1.2.1 The method blank **must** be analyzed at least once during every 12-hour time period on each Gas Chromatograph/Mass Spectrometer (GC/MS) system used for volatile analysis (see Section 9.2.2 for the definition of the 12-hour time period).

12.1.2.2 The method blank **must** be analyzed after the opening Continuing Calibration Verification (CCV) and before any samples, including Matrix Spike and Matrix Spike Duplicates (MS/MSDs), dilutions, or storage blanks are analyzed. The method blank must be analyzed after the initial calibration sequence if samples are analyzed before the 12-hour period expires. A method blank must be analyzed in each 12-hour time period in which samples, including dilutions, MS/MSDs, and storage blanks from an SDG are analyzed.

12.1.2.3 A minimum of one storage blank must be analyzed per matrix type (1 for soil and 1 for water sample) after all samples for the SDG stored in the same manner have been analyzed, unless the SDG contains only ampulated Performance Evaluation (PE) samples. Analysis of a storage blank is not required for SDGs that contain only ampulated PE samples.

12.1.2.4 The Contractor must demonstrate that there is no carryover from contaminated samples before data from subsequent analyses may be used. Samples may contain target compounds at levels exceeding the calibration range. An instrument blank must be analyzed after the sample that exceeds the calibration range (also in the same purge inlet if an autosampler is used) or a sample that meets the maximum contamination criteria in Section 11.3.8 must be analyzed. For these purposes, if the instrument blank meets the technical acceptance criteria for blank analyses or the sample meets the maximum contamination criteria, the system is considered to be uncontaminated. If the instrument blank or sample does not meet the criteria (i.e., contaminated), the system must be decontaminated. Until an instrument blank meets the blank technical acceptance criteria or a sample meets the maximum carryover criteria, any samples analyzed since the original contaminated sample will require reanalysis at no additional cost to USEPA.

NOTE: Only the instrument blank that demonstrates that there was no carryover from the previous sample or the instrument blank that demonstrates that the system is clean (Section 12.1.4.6) must be reported. Instrument blanks analyzed during the instrument decontamination process that exceed the requirements listed in Section 11.3.8 do not need to be reported.

12.1.3 Procedure for Blank Analyses

12.1.3.1 For water samples, method blanks shall be analyzed in the same manner as the associated samples, following the procedure described in Section 10.1.3.

12.1.3.2 For low-level soil samples, method blanks shall be analyzed in the same manner as the associated samples, following the procedure described in Section 10.1.4.

12.1.3.3 For medium-level soil samples, method blanks shall be analyzed in the same manner as the associated samples, following the procedure described in Section 10.1.5.

12.1.3.4 Storage/instrument blanks shall be analyzed in the same manner as the associated samples following the procedures outlined in Section 10.1.

12.1.3.5 Under no circumstances should blanks (storage/instrument/method) be analyzed at a dilution (i.e., blanks should always have a DF = 1.0).

12.1.3.6 Identify and quantitate analytes according to Section 11.0.

12.1.4 Technical Acceptance Criteria for Blank Analyses

12.1.4.1 All blanks must be analyzed on a GC/MS system meeting the 4-bromofluorobenzene (BFB), initial calibration, and CCV technical acceptance criteria and at the frequency described in Section 12.1.2.

12.1.4.2 The storage blank must be analyzed on a GC/MS system that also meets the technical acceptance criteria for the method blank.

12.1.4.3 The Percent Recovery (%R) of each of the DMCs in a blank must be within the acceptance windows in Table 5. The recovery limits for 1,4-dioxane-d_8 are advisory.

12.1.4.4 The Extracted Ion Current Profile (EICP) area for each of the internal standards in a blank must be within the range of 50.0% and 200% of the response of the internal standards in the most recent opening CCV standard analysis.

12.1.4.5 The Retention Time (RT) shift for each of the internal standards in a blank must be within ±0.50 min. (30 sec.) of its RT in the most recent opening CCV standard analysis.

12.1.4.6 The concentration of each target compound found in the blank must be less than the Contract Required Quantitation Limit (CRQL) listed in Exhibit C (Low/Medium Volatiles), except for methylene chloride, acetone, and 2-butanone which must be less than 2 times the respective CRQL. The concentration of each target compound in the instrument blank must be less than its CRQL listed in Exhibit C (Low/Medium Volatiles).

12.1.5 Corrective Action for Blank Analyses

12.1.5.1 It is the Contractor's responsibility to ensure that method interferences caused by the contaminants in solvents, reagents, glassware, laboratory air, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in Gas Chromatograms, be eliminated. If a Contractor's blanks exceed the criteria in Section 12.1.4.6, the Contractor must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures **MUST** be taken and documented before further analysis proceeds.

12.1.5.2 Any method blank that fails to meet the technical acceptance criteria must be reanalyzed. Further, all samples processed within the 12-hour time period with a method blank that does not meet the blank technical acceptance criteria will require reanalysis at no additional cost to USEPA.

Any instrument blank that fails to meet any technical acceptance criteria described in Sections 12.1.4.3 - 12.1.4.6 requires

reanalysis of the samples analyzed after the instrument blank having any target compounds detected at levels above the adjusted CRQL.

12.1.5.3 If the storage blank does not meet the technical acceptance criteria for blank analyses in Sections 12.1.4.1 - 12.1.4.5, correct system problems and reanalyze the storage blank. If the storage blank does not meet the criteria in Section 12.1.4.6, reanalyze the storage blank to determine whether the contamination occurred during storage or during analyses. If, upon reanalysis, the storage blank meets the criteria in Section 12.1.4.6, the problem occurred during the analysis and the reanalyzed storage blank results must be reported. If upon reanalysis, the storage blank did not meet the criteria in Section 12.1.4.6, the problem occurred during storage. The Laboratory Manager or their designee must address the problem in the SDG Narrative and discuss the corrective actions implemented to prevent future occurrences.

NOTE: A copy of the storage blank data must also be retained by the Contractor and be made available for inspection during on-site laboratory evaluations.

12.2 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the methods used for volatile analyses, USEPA has prescribed a mixture of volatile target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method.

12.2.2 Frequency of MS/MSD

12.2.2.1 An MS/MSD shall be analyzed if requested by the Region [through the Sample Management Office (SMO)] or specified on the Traffic Report/Chain of Custody Record (TR/COC). If requested, a Matrix Spike and a Matrix Spike Duplicate must be performed for each group of 20 field samples in an SDG, or each SDG, whichever is most frequent.

12.2.2.2 As a part of USEPA's Quality Assurance/Quality Control (QA/QC) program, water rinsate samples and/or field/trip blanks (field QC) may accompany soil/sediment samples and/or water samples that are delivered to a laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the field QC samples.

12.2.2.3 If the USEPA Region designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample, less than the required amount to perform an MS/MSD, then the Contractor shall choose another sample to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify SMO that insufficient sample was received and identify the USEPA sample selected for the MS/MSD analysis. SMO shall contact the Region for confirmation immediately after notification. The rationale for the choice of a sample other than the one designated by the Region shall be documented in the SDG Narrative.

12.2.2.4 If an insufficient number of sample vials were received to perform an MS/MSD, and MS/MSD are required, then the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD is required, or specify an alternate means

of performing the MS/MSD analysis. SMO will notify the Contractor of the resolution. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than required by the contract, the Contractor shall contact SMO. SMO will contact the Region to determine which samples should have an MS/MSD analysis performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If this procedure is not followed, the Contractor will not be paid for MS/MSD analysis performed at a greater frequency than required by the contract.

12.2.2.6 When a Contractor receives **only** PE sample(s), no MS/MSD shall be performed within that SDG.

12.2.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the MS/MSD when the Region did not designate samples to be used for this purpose. SMO will notify the Contractor of the chosen sample. The Contractor shall document the decision in the SDG Narrative.

12.2.3 Procedure for Preparing MS/MSD

12.2.3.1 To prepare an MS/MSD for water samples, add 20 µL of the Matrix Spiking solution (Section 7.2.2.5) to each of the 5 mL aliquots of the sample chosen for spiking. Process samples according to Sections 10.1.3.5 - 10.1.3.12. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each Matrix Spike compound.

12.2.3.2 To prepare an MS/MSD for low-level soil/sediment samples, add 20 µL of the Matrix Spiking solution (Section 7.2.2.5) either manually by puncturing the septum with a small-gauge needle or automatically by the purge-and-trap system just prior to analysis. Analyze the MS/MSD samples by the procedure described in Section 10.1.4. Do not further dilute MS/MSD samples to get either spiked or non-spiked analytes within calibration range.

12.2.3.3 To prepare an MS/MSD for medium-level soil/sediment samples, add 4.0 mL of methanol and 1.0 mL of Matrix Spiking solution to each of the two aliquots of the soil/sediment sample chosen for spiking.

NOTE: In the cases where methanol has been added as a preservative, do not add additional methanol. Add only 1.0 mL of Matrix spiking solution to each of the two aliquots of the soil/sediment sample chosen for spiking.

Process samples according to Sections 10.1.5.6 - 10.1.5.9. This results in a 2,500 µg/kg concentration of each Matrix Spike compound when added to a 5 g sample. Add a 100 µL aliquot of this extract to 5 mL of water for purging (as per Sections 10.1.5.6 and 10.1.5.7).

NOTE: Before performing an MS/MSD analysis, analyze the sample used for MS/MSD. If the sample analysis requires dilution, the aliquots for the MS/MSD shall be prepared at the same dilution as the least diluted analysis for which the sample results will be reported to USEPA. Sample dilutions must be performed in accordance with Section 10.1.6. Do **not** further

dilute MS/MSD samples to get **either** spiked **or** non-spiked analytes within calibration range.

12.2.4 Calculations for MS/MSD

12.2.4.1 Calculate the concentrations of the Matrix Spike compounds using the same equations as used for target compounds (Equations 7, 8, and 9). Calculate the recovery of each Matrix Spike compound as follows:

EQ. 14 Matrix Spike Recovery Calculation

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spiked Sample Result.

SR = Sample Result.

SA = Spike Added.

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each compound in the MS/MSD as follows:

EQ. 15 Relative Percent Difference Calculation

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where,

MSR = Matrix Spike Recovery.

MSDR = Matrix Spike Duplicate Recovery.

The vertical bars in the formula above indicate the absolute value of the difference.

12.2.5 Technical Acceptance Criteria for MS/MSD

12.2.5.1 All MS/MSDs must be analyzed on a GC/MS system meeting the BFB, initial calibration and continuing calibration verification technical acceptance criteria, blank technical acceptance criteria, and at the frequency described in Section 12.2.2.

12.2.5.2 The MS/MSD must be analyzed within the contract holding time.

12.2.5.3 The RT shift for each of the internal standards in the MS/MSD must be within ±0.50 minutes (30 seconds) of its RT and the most recent opening CCV standard analysis.

12.2.5.4 The limits for Matrix Spike compound recovery and RPD are given in Table 6. As these limits are only advisory, no further action by the laboratory is required. However, frequent failures to meet

the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from USEPA.

12.2.6 Corrective Action for MS/MSD

Any MS/MSD that does not meet the technical acceptance criteria in Sections 12.2.5.1 and 12.2.5.3, must be reanalyzed at no additional cost to USEPA.

12.3 Method Detection Limit (MDL) Determination

12.3.1 Before any field samples are analyzed under the contract, the MDL for each volatile target compound shall be determined on each instrument used for analysis. MDL determination is matrix-specific and level-specific (i.e., the MDL shall be determined for water, low-level soil and medium-level soils). The MDLs must be verified annually thereafter (see Section 12.3.2 for MDL verification procedures), until the contract expires or is terminated, or after major instrument maintenance. Major instrument maintenance includes, but is not limited to, cleaning or replacement of the mass spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), electron multiplier (or similar device), GC column, and replacement or overhaul of the purge-and-trap device.

12.3.2 To determine the MDLs, the Contractor shall run an MDL study following the procedures specified in 40 CFR Part 136. The Contractor shall analyze the MDL samples on each instrument used for field sample analyses. MDL verification for water samples is achieved by analyzing a single reagent water blank (see method blank for water samples in Section 12.1) spiked with each volatile target compound at a concentration equal to 1-4 times the analytically determined MDL. Each target compound must produce a response and meet the criteria in Section 11.1.1. MDL verification for low-level soil samples is achieved by analyzing a single purified solid matrix blank (see method blank for low-level soil samples in Section 12.1) spiked with each volatile target compound at a concentration equal to two times the analytically determined MDL. MDL verification for medium-level soil samples is achieved by analyzing a single purified solid matrix blank (see method blank for medium-level soil samples in Section 12.1) spiked with each volatile target compound at a concentration equal to two times the analytically determined MDL. The resulting mass spectra of each target compound must meet the qualitative identification criteria outlined in Section 11.1.1.

12.3.3 The determined concentration of the MDL must be less than the CRQL.

12.3.4 All documentation for the MDL studies shall be maintained at the laboratory and provided to USEPA upon written request.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, USEPA recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington D.C., 20036, (202) 872-4386.

15.0 WASTE MANAGEMENT

USEPA requires that laboratory waste management practices be consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

US Environmental Protection Agency. Purge-and-Trap for Aqueous Samples. Method 5030C. Revision 2. May 2003.

US Environmental Protection Agency. Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples. Method 5035A. July 2002.

US Environmental Protection Agency. Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). Method 8260B. Revision 2. December 1996.

US Environmental Protection Agency. Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry. Method 524.2. August 1992.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

4-bromofluorobenzene Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15.0 - 40.0% of mass 95
75	30.0 - 80.0% of mass 95
95	base peak, 100% Relative Abundance
96	5.0 - 9.0% of mass 95 (see NOTE)
173	less than 2.0% of mass 174
174	50.0 - 120% of mass 95
175	5.0 - 9.0% of mass 174
176	95.0 - 101% of mass 174
177	5.0 - 9.0% of mass 176

NOTE: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95.

Table 2

Characteristic Ions for Trace Volatile Target Compounds

Target Compound	Primary Quantitation Ion	Secondary Ion(s)
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl chloride	62	64
Bromomethane	94	96
Chloroethane	64	66
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61, 63
1,1,2-Trichloro-1,2,2-trifluoroethane	101	85, 151
Acetone	43	58
Carbon disulfide	76	78
Methyl acetate	43	74
Methylene chloride	84	49, 86
trans-1,2-Dichloroethene	96	61, 98
Methyl tert-butyl ether	73	43, 57
1,1-Dichloroethane	63	65, 83
cis-1,2-Dichloroethene	96	61, 98
2-Butanone	43*	72
Chloroform	83	85
Bromochloromethane	128	49, 130, 51
1,1,1-Trichloroethane	97	99, 61
Cyclohexane	56	69, 84
Carbon tetrachloride	117	119
Benzene	78	-
1,2-Dichloroethane	62	98
1,4-Dioxane	88	43,58
Trichloroethene	95	97, 132, 130
Methylcyclohexane	83	55, 98
1,2-Dichloropropane	63	112
Bromodichloromethane	83	85, 127
cis-1,3-Dichloropropene	75	77
4-Methyl-2-pentanone	43	58, 100
Toluene	91	92
trans-1,3-Dichloropropene	75	77
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Tetrachloroethene	164	129, 131, 166
2-Hexanone	43	58, 57, 100
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Chlorobenzene	112	77, 114
Ethylbenzene	91	106
m,p-Xylene	106	91
o-Xylene	106	91
Styrene	104	78

*m/z 43 is used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

Table 2

Characteristic Ions for Trace Volatile Target Compounds (Con't)

Analyte	Primary Quantitation Ion	Secondary Ion(s)
Bromoform	173	175, 254
Isopropylbenzene	105	120, 77
1,1,2,2-Tetrachloroethane	83	85, 131
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene	146	111, 148
1,2-Dibromo-3-chloropropane	75	157, 155
1,2,4-Trichlorobenzene	180	182, 145
1,2,3-Trichlorobenzene	180	182, 145
Deuterated Monitoring Compounds		
Vinyl chloride-d_3	65	67
Chloroethane-d_5	69	71, 51
1,1-Dichloroethene-d_2	63	98, 65
2-Butanone-d_5	46	77
Chloroform-d	84	86, 47, 49
1,2-Dichloroethane-d_4	65	67, 51
Benzene-d_6	84	82, 54, 52
1,2-Dichloropropane-d_6	67	65, 46, 42
Toluene-d_8	98	100, 42
trans-1,3-Dichloropropene-d_4	79	81, 42
2-Hexanone-d_5	63	46
1,4-Dioxane-d_8	96	51, 66
1,1,2,2-Tetrachloroethane-d_2	84	86
1,2-Dichlorobenzene-d_4	152	150
Internal Standards		
1,4-Dichlorobenzene-d_4	152	115, 150
1,4-Difluorobenzene	114	63, 88
Chlorobenzene-d_5	117	82, 119

Table 3

Volatile Target Compounds and Deuterated Monitoring Compounds with Corresponding Internal Standards for Quantitation

1,4-Difluorobenzene (IS)	Chlorobenzene-d_5 (IS)	1,4-Dichlorobenzene-d_4 (IS)
Dichlorodifluoromethane	1,1,1-Trichloroethane	Bromoform
Chloromethane	Cyclohexane	1,3-Dichlorobenzene
Vinyl chloride	Carbon tetrachloride	1,4-Dichlorobenzene
Bromomethane	Benzene	1,2-Dichlorobenzene
Chloroethane	Trichloroethene	1,2-Dibromo-3-chloropropane
Trichlorofluoromethane	Methylcyclohexane	1,2,4-Trichlorobenzene
1,1-Dichloroethene	1,2-Dichloropropane	1,2,3-Trichlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	Bromodichloromethane	1,2-Dichlorobenzene-d_4 (DMC)
Acetone	cis-1,3-Dichloropropene	
Carbon disulfide	4-Methyl-2-pentanone	
Methyl acetate	Toluene	
Bromochloromethane	trans-1,3-Dichloropropene	
Methylene chloride	1,1,2-Trichloroethane	
trans-1,2-Dichloroethene	Tetrachloroethene	
Methyl tert-butyl ether	2-Hexanone	
1,1-Dichloroethane	Dibromochloromethane	
cis-1,2-Dichloroethene	1,2-Dibromoethane	
2-Butanone	Chlorobenzene	
Chloroform	Ethylbenzene	
1,2-Dichloroethane	m,p-Xylene	
1,4-Dioxane	o-Xylene	
Vinyl chloride-d_3 (DMC)	Styrene	
Chloroethane-d_5 (DMC)	Isopropylbenzene	
1,1-Dichloroethene-d_2 (DMC)	1,1,2,2-Tetrachloroethane	
2-Butanone-d_5 (DMC)	Benzene-d_6 (DMC)	
Chloroform-d (DMC)	1,2-Dichloropropane-d_6 (DMC)	
1,2-Dichloroethane-d_4 (DMC)	trans-1,3-Dichloropropene-d_4 (DMC)	
1,4-Dioxane-d_8 (DMC)	Toluene-d_8 (DMC)	
	2-Hexanone-d_5 (DMC)	
	1,1,2,2-Tetrachloroethane-d_2 (DMC)	

Table 4

Relative Response Factor Criteria for Initial and Opening Continuing Calibration Verification of Volatile Organic Compounds

Volatile Compound	Minimum RRF[1]	Maximum %RSD	Maximum %Diff[1]
Dichlorodifluoromethane	0.010	40.0	±40.0
Chloromethane	0.010	40.0	±40.0
Vinyl chloride	0.100	20.0	±25.0
Bromomethane	0.100	20.0	±25.0
Chloroethane	0.010	40.0	±40.0
Trichlorofluoromethane	0.010	40.0	±40.0
1,1-Dichloroethene	0.100	20.0	±25.0
1,1,2-Trichloro-1,2,2-trifluoroethane	0.010	40.0	±40.0
Acetone	0.010	40.0	±40.0
Carbon disulfide	0.010	40.0	±40.0
Methyl acetate	0.010	40.0	±40.0
Methylene chloride	0.010	40.0	±40.0
trans-1,2-Dichloroethene	0.010	40.0	±40.0
Methyl tert-butyl ether	0.010	40.0	±40.0
1,1-Dichloroethane	0.200	20.0	±25.0
cis-1,2-Dichloroethene	0.010	40.0	±40.0
2-Butanone	0.010	40.0	±40.0
Bromochloromethane	0.050	20.0	±25.0
Chloroform	0.200	20.0	±25.0
1,1,1-Trichloroethane	0.100	20.0	±25.0
Cyclohexane	0.010	40.0	±40.0
Carbon tetrachloride	0.100	20.0	±25.0
Benzene	0.400	20.0	±25.0
1,2-Dichloroethane	0.100	20.0	±25.0
1,4-Dioxane	0.0050	50.0	±50.0
Trichloroethene	0.300	20.0	±25.0
Methylcyclohexane	0.010	40.0	±40.0
1,2-Dichloropropane	0.010	40.0	±40.0
Bromodichloromethane	0.200	20.0	±25.0
cis-1,3-Dichloropropene	0.200	20.0	±25.0
4-Methyl-2-pentanone	0.010	40.0	±40.0
Toluene	0.400	20.0	±25.0

Table 4

Relative Response Factor Criteria for Initial and Opening Continuing Calibration Verification of Volatile Organic Compounds (Con't)

Volatile Compound	Minimum RRF[1]	Maximum %RSD	Maximum %Diff[1]
trans-1,3-Dichloropropene	0.100	20.0	±25.0
1,1,2-Trichloroethane	0.100	20.0	±25.0
Tetrachloroethene	0.100	20.0	±25.0
2-Hexanone	0.010	40.0	±40.0
Dibromochloromethane	0.100	20.0	±25.0
1,2-Dibromoethane	0.010	40.0	±40.0
Chlorobenzene	0.500	20.0	±25.0
Ethylbenzene	0.100	20.0	±25.0
m,p-Xylene	0.300	20.0	±25.0
o-Xylene	0.300	20.0	±25.0
Styrene	0.300	20.0	±25.0
Bromoform	0.050	20.0	±25.0
Isopropylbenzene	0.010	40.0	±40.0
1,1,2,2-Tetrachloroethane	0.300	20.0	±25.0
1,3-Dichlorobenzene	0.600	20.0	±25.0
1,4-Dichlorobenzene	0.500	20.0	±25.0
1,2-Dichlorobenzene	0.400	20.0	±25.0
1,2-Dibromo-3-chloropropane	0.010	40.0	±40.0
1,2,4-Trichlorobenzene	0.200	20.0	±25.0
1,2,3-Trichlorobenzene	0.200	20.0	±25.0
Deuterated Monitoring Compounds			
Vinyl chloride-d_3	0.010	20.0	±25.0
Chloroethane-d_5	0.010	40.0	±40.0
1,1-Dichloroethene-d_2	0.010	20.0	±25.0
2-Butanone-d_5	0.010	40.0	±40.0
Chloroform-d	0.010	20.0	±25.0
1,2-Dichloroethane-d_4	0.010	20.0	±25.0
Benzene-d_6	0.010	20.0	±25.0
1,2-Dichloropropane-d_6	0.010	40.0	±40.0
Toluene-d_8	0.010	20.0	±25.0

Table 4

Relative Response Factor Criteria for Initial and Opening Continuing Calibration Verification of Volatile Organic Compounds (Con't)

Deuterated Monitoring Compounds	Minimum RRF[1]	Maximum	Maximum %Diff[1]
trans-1,3-Dichloropropene-d_4	0.010	20.0	±25.0
2-Hexanone-d_5	0.010	40.0	±40.0
1,4-Dioxane-d_8	0.0050	50.0	±50.0
1,1,2,2-Tetrachloroethane-d_2	0.010	20.0	±25.0
1,2-Dichlorobenzene-d_4	0.010	20.0	±25.0

[1]For a closing CCV, all target compounds and DMCs must meet a minimum RRF of 0.010 and a maximum percent difference of ± 50.0, except for 1,4-dioxane and 1,4-dioxane-d_8, which must meet a minimum RRF of 0.0050 and a maximum Percent Difference of ± 50.0.

Table 5

Deuterated Monitoring Compound Recovery Limits

Compound	Percent Recovery for Water Samples	Percent Recovery for Soil Samples
Vinyl chloride-d_3	65-131	(68-122)
Chloroethane-d_5	71-131	(61-130)
1,1-Dichloroethene-d_2	55-104	(45-132)
2-Butanone-d_5	49-155	(20-182)
Chloroform-d	78-121	(72-123)
1,2-Dichloroethane-d_4	78-129	(79-122)
Benzene-d_6	77-124	(80-121)
1,2-Dichloropropane-d_6	79-124	(74-124)
Toluene-d_8	77-121	(78-121)
trans-1,3-Dichloropropene-d_4	73-121	(72-130)
2-Hexanone-d_5	28-135	(17-184)
1,4-Dioxane-d_8	50-150	(50-150)
1,1,2,2-Tetrachloroethane-d_2	73-125	(56-161)
1,2-Dichlorobenzene-d_4	80-131	(70-131)

NOTE: The recovery limits for any of the compounds listed above may be expanded at any time during the period of performance if USEPA determines that the limits are too restrictive.

Table 6

Matrix Spike Recovery and
Relative Percent Difference Limits

Compound	Percent Recovery Water	RPD Water	Percent Recovery Soil	RPD Soil
1,1-Dichloroethene	61-145	0-14	59-172	0-22
Trichloroethene	71-120	0-14	62-137	0-24
Benzene	76-127	0-11	66-142	0-21
Toluene	76-125	0-13	59-139	0-21
Chlorobenzene	75-130	0-13	60-133	0-21

Table 7

Volatile Deuterated Monitoring Compounds and the Associated Target Compounds

Chloroethane-d_5 (DMC)	**1,2-Dichloropropane-d_6 (DMC)**	**1,2-Dichlorobenzene-d_4 (DMC)**
Dichlorodifluoromethane	Cyclohexane	Chlorobenzene
Chloromethane	Methylcyclohexane	1,3-Dichlorobenzene
Bromomethane	1,2-Dichloropropane	1,4-Dichlorobenzene
Chloroethane	Bromodichloromethane	1,2-Dichlorobenzene
Carbon disulfide		1,2,4-Trichlorobenzene
		1,2,3-Trichlorobenzene

1,4-Dioxane-d_8 (DMC)	**trans-1,3-Dichloropropene-d_4 (DMC)**	**Chloroform-d (DMC)**
1,4-Dioxane	cis-1,3-Dichloropropene	1,1-Dichloroethane
	trans-1,3-Dichloropropene	Bromochloromethane
	1,1,2-Trichloroethane	Chloroform
		Dibromochloromethane
		Bromoform

2-Butanone-d_5 (DMC)	**1,1-Dichloroethene-d_2 (DMC)**	**2-Hexanone-d_5 (DMC)**
Acetone	trans-1,2-Dichloroethene	4-Methyl-2-pentanone
2-Butanone	cis-1,2-Dichloroethene	2-Hexanone

Vinyl chloride-d_3 (DMC)	**Benzene-d_6 (DMC)**	**1,1,2,2-Tetrachloroethane-d_2 (DMC)**
Vinyl chloride	Benzene	1,1,2,2-Tetrachloroethane
		1,2-Dibromo-3-chloropropane

1,2-Dichloroethane-d_4 (DMC)	**Toluene-d_8 (DMC)**
Trichlorofluoromethane	Trichloroethene
1,1-Dichloroethene	Toluene
1,1,2-Trichloro-1,2,2-trifluoroethane	Tetrachloroethene
Methyl acetate	Ethylbenzene
Methylene chloride	o-Xylene
Methyl tert-butyl ether	m,p-Xylene
1,1,1-Trichloroethane	Styrene
Carbon tetrachloride	Isopropylbenzene
1,2-Dibromoethane	
1,2-Dichloroethane	

EXHIBIT D

ANALYTICAL METHOD FOR THE ANALYSIS OF TRACE CONCENTRATIONS OF VOLATILE ORGANIC COMPOUNDS

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Exhibit D - Analytical Methods for Trace Volatiles

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1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze water samples containing trace concentrations of the volatile compounds listed in the Target Compound List (TCL) in Exhibit C (Trace Volatiles). The majority of the samples are expected to be obtained from drinking water and well/groundwater type sources around Superfund sites. The method is based on EPA Method 524.2. The sample preparation and analysis procedures included in this method are based on purge-and-trap Gas Chromatograph/Mass Spectrometer (GC/MS) techniques.

In addition, if requested, samples will be analyzed for a select group of compounds by GC/MS, using the Selected Ion Monitoring (SIM) technique. If trace SIM is requested for 1,4-dioxane, 1,2-dibromoethane, and 1,2-dibromo-3-chloropropane, a full scan analysis using the trace method should be performed first. If the three target compounds are detected at or above the CRQL (for trace level) during the full scan analysis using the trace method, then a SIM analysis is not to be performed and this should be documented in the Sample Delivery Group (SDG) Narrative.

1.2 Problems that have been associated with the following compounds analyzed by this method include:

- Chloromethane, vinyl chloride, bromomethane, and chloroethane may display peak broadening if the compounds are not delivered to the GC column in a tight band.

- Acetone, hexanone, 2-butanone, 4-methyl-2-pentanone, and 1,4-dioxane have poor purge efficiencies.

- 1,1,1-Trichloroethane and all of the dichloroethanes may dehydrohalogenate during storage or analysis.

- Tetrachloroethane and 1,1-dichloroethane may be degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

- Chloromethane may be lost if the purge flow is too fast.

- Bromoform is one of the compounds most likely to be adversely affected by cold spots and/or active sites in the transfer lines. Response of its quantitation ion (m/z 173) is directly affected by the tuning of 4-bromofluorobenzene (BFB) at ions m/z 174/176. Increasing the m/z 174/176 ratio within the specified Quality Control (QC) limits may improve bromoform response.

- Due to the lower quantitation limits required by this method, extra caution must be exercised when identifying compounds.

2.0 SUMMARY OF METHOD

2.1 An inert gas is bubbled through a 25 mL sample contained in a specially designed purging chamber at ambient temperature causing the purgeables to be transferred from the water/aqueous phase to the vapor phase. Higher purge temperatures may be used, provided that all technical acceptance criteria are met for all standards, samples, and blanks. The same purge conditions must be used for all associated standards, samples, and blanks. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a Gas Chromatograph (GC) wide-bore capillary column. The GC is temperature programmed to separate the purgeables, which are then detected with a Mass Spectrometer (MS).

2.2 Deuterated Monitoring Compounds (DMCs) and internal standards are added to all samples and blanks. The target compounds and DMCs are identified in the samples and blanks by analyzing standards that contain all target compounds, DMCs, and internal standards under the same conditions and comparing resultant mass spectra and GC Retention Times (RTs). A Mean Relative Response Factor ($\overline{RRF}$) is established for each target compound and DMC during the initial calibration. The mass spectra response from the Extracted Ion Current Profile (EICP) for the primary quantitation ion produced by that compound is compared to the mass spectral response for the primary quantitation ion produced by the associated internal standard compound. Each identified target compound and DMC is quantitated by comparing the instrument response for the compound in the sample or blank with the instrument response of the associated internal standard, while taking into account the $\overline{RRF}$, the sample volume, and any sample dilutions.

2.3 Non-target compounds are identified by comparing the resultant mass spectra from the non-target compounds to mass spectra contained in the NIST (2002 release or later), Wiley (1991 release or later), or equivalent mass spectral library. Non-target compounds are quantitated by comparing the mass spectra response from the total ion chromatograms to the mass spectra response of the nearest internal standard compound. An RRF of 1 is assumed.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method Interferences

Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks as described in Section 12. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.2 Samples can be contaminated by diffusion of purgeable organics (particularly methylene chloride, fluorocarbons, and other common laboratory solvents) through the septum seal into the sample during storage and handling. Therefore, these samples must be stored separately from other laboratory samples and standards and must be analyzed in a room in which the atmosphere is demonstrated to be free of all potential contaminants that will interfere with the analysis.

4.3 Contamination by carryover can occur whenever high-level and trace-level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it must either be followed by analysis of an instrument blank, or the next sample must be closely monitored to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105°C. The trap and other parts of the system are also subject to contamination; therefore, frequent bake-out and purging of the entire system may be required.

4.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all Gas Chromatography (GC) carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Office of Safety and Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analyses.

5.2 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene; carbon tetrachloride; chloroform; vinyl chloride; and 1,4-dioxane. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of the analytical method is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Glassware

6.1.1 Syringes - 25 mL, gas-tight with shut-off valve. Micro syringes - 10 µL and larger, 0.006 inch (0.15 mm) ID needle.

6.1.2 Syringe Valve - Two-way, with Luer ends (three each), if applicable to the purging device.

6.1.3 Pasteur Pipets - Disposable.

6.1.4 Vials and Caps - Assorted sizes.

6.1.5 Volumetric Flasks, Class A with ground-glass stoppers.

6.1.6 Bottles - 15 mL, screw-cap, with polytetrafluoroethylene (PTFE) cap liner.

6.2 pH Paper - Wide range.

6.3 Balances

Balances must be analytical and capable of accurately weighing ±0.0001 g. The balance must be calibrated with Class S weights or known reference weights once per each 12-hour work shift. The balance must be calibrated with Class S weights at a minimum of once per month. The balance must also be annually checked by a certified technician.

6.4 Purge-and-Trap Device

The purge-and-trap device consists of three separate pieces of equipment: the sample purge chamber, the trap, and the desorber. This

device either manually or automatically samples an appropriate volume (e.g., 25 mL from the vial); adds DMCs, Matrix Spikes, and internal standards to the sample; and transfers the sample to the purge device. The purge device also purges the volatile organic compounds (VOCs) using an inert gas stream and traps the released VOCs for subsequent desorption into the Gas Chromatograph (GC). Such systems are commercially available from several sources and shall meet the following specifications.

6.4.1 The sample purge chamber must be designed to accept 25 mL samples with a water column at least 10 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column.

6.4.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch (2.667 mm). The trap must be packed to contain the following minimum lengths of absorbents: (starting from inlet) 0.5 cm silanized glass wool, 1 cm methyl silicone, 8 cm of 2,6-diphenylene oxide polymer (Tenax-GC, 60/80 mesh), 8 cm of silica gel (Davison Chemical, 35/60 mesh, grade 15 or equivalent), 7 cm of coconut charcoal, and 0.5 cm silanized glass wool. A description of the trap used for analysis shall be provided in the SDG Narrative.

6.4.3 The desorber must be capable of rapidly heating the trap to 180°C. The polymer section of the trap should not be heated higher than 180°C and the remaining sections should not exceed 220°C during bake-out mode.

6.4.4 Trap Packing

6.4.4.1 2,6-Diphenylene Oxide Polymer, 60/80 mesh chromatographic grade (Tenax GC or equivalent).

6.4.4.2 Methyl Silicone Packing, 3.0% OV-1 on Chromosorb W, 60/80 mesh (or equivalent).

6.4.4.3 Silica Gel, 35/60 mesh,(or equivalent).

6.4.4.4 Coconut Charcoal.

6.4.4.5 Alternate sorbent traps may be used if:

- The trap packing materials do not introduce contaminants that interfere with identification and quantitation of the compounds listed in Exhibit C (Trace Volatiles);
- The analytical results generated using the trap meet the initial calibration and continuing calibration verification technical acceptance criteria listed in the analytical method and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Trace Volatiles); or
- The trap can accept up to 1000 ng of each compound listed in Exhibit C (Trace Volatiles) without becoming overloaded.

6.4.4.5.1 The alternate trap must be designed to optimize performance. Follow the manufacturer's instructions for the use of its product. Before use of any trap other than the one specified in Section 6.4.2, the Contractor must first meet the criteria

listed in Section 6.4.4.5. Once this has been demonstrated, the Contractor must document its use in each SDG Narrative by specifying the trap composition (packing material/brand name, amount of packing material). Other sorbent traps include, but are not limited to: Tenax/Silica Gel/Carbon Trap from EPA Method 524.2, Tenax - GC/Graphpac-D Trap (Alltech) or equivalent, and Vocarb 4000 Trap (Supelco) or equivalent.

6.4.4.5.2 The Contractor must maintain documentation that the alternate trap meets the criteria listed in Section 6.4.4.5. The minimum documentation requirements are as follows:

6.4.4.5.2.1 Manufacturer-provided information concerning the performance characteristics of the trap.

6.4.4.5.2.2 Reconstructed ion chromatograms and data system reports generated on the Contractor's Gas Chromatograph/Mass Spectrometer (GC/MS) used for Contract Laboratory Program (CLP) analyses:

- From instrument blank analyses that demonstrate that there are no contaminants that interfere with the volatile analysis when using the alternate trap; and
- From initial calibration and continuing calibration verification standards analyzed using the trap specified in Section 6.4.4.

6.4.4.5.2.3 Based on Contractor-generated data described above, the Contractor must complete a written comparison/review, that has been signed by the Laboratory Manager, certifying that:

- The alternate trap performance meets the technical acceptance criteria listed in Sections 9.3.5 and 9.4.5;
- The low-point initial calibration standard analysis has adequate sensitivity to meet the volatile CRQLs;
- The high-point initial calibration standard analysis was not overloaded; and
- The alternate trap materials do not introduce contaminants that interfere with the identification and/or quantitation of the compounds listed in Exhibit C (Trace Volatiles).

6.4.4.5.2.4 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request of the Regional USEPA CLP Project Officer (CLP PO).

6.4.5 The purge-and-trap apparatus may be assembled as a separate unit or be an integral unit coupled with a GC.

6.5 Gas Chromatograph/Mass Spectrometer (GC/MS) System

6.5.1 Gas Chromatograph - The GC system must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout desorption and temperature program operations. The system must include or be interfaced to a purge-and-trap system as specified in Section 6.4 and have all required accessories including syringes, analytical columns, and gases. All GC carrier gas lines must be constructed from stainless steel or

copper tubing. Non-PTFE thread sealants, or flow controllers with rubber components, are not to be used. The column oven must be cooled to 10°C if adequate separation of gaseous compounds is not achieved (Section 9.1.2.3); therefore, a subambient oven controller is required.

6.5.2 Gas Chromatography Columns

A description of the column used for analysis shall be provided in the SDG Narrative.

6.5.2.1 Minimum length 30 m x 0.53 mm ID VOCOL (Supelco) or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.5.2.2 Minimum length 30 m x 0.53 mm ID DB-624 (J & W Scientific) or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.5.2.3 Minimum length 30 m x 0.53 mm ID AT-624 (Alltech) or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.5.2.4 Minimum length 30 m x 0.53 mm ID Rtx-624 (Restek) or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.5.2.5 Minimum length 30 m x 0.53 mm ID BP-624 (SGE) or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.5.2.6 Minimum length 30 m x 0.53 mm ID CP-Select 624CB (Chrompack) or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.5.3 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantitation of the compounds listed in Exhibit C (Trace Volatiles);
- The analytical results generated using the column meet the initial calibration and continuing calibration verification technical acceptance criteria listed in the analytical method, and the CRQLs listed in Exhibit C (Trace Volatiles);
- The column can accept up to 1000 ng of each compound listed in Exhibit C (Trace Volatiles) without becoming overloaded; and
- The column provides equal or better resolution of the compounds listed in Exhibit C (Trace Volatiles) than the columns listed in Section 6.5.2.

6.5.3.1 As applicable, follow the manufacturer's instructions for use of its product.

6.5.3.2 The Contractor must maintain documentation that the column met the criteria in Section 6.5.3. The minimum documentation is as follows:

6.5.3.2.1 Manufacturer provided information concerning the performance characteristics of the column.

6.5.3.2.2 Reconstructed ion chromatograms and data system reports generated on the GC/MS used for the CLP analyses:

- From instrument blanks that demonstrate that there are no contaminants that interfere with the volatile analysis when using the column; and

- From initial calibration and continuing calibration verification standards analyzed using the alternate column.

6.5.3.3 Based on the Contractor-generated data described above, the Contractor shall complete a written comparison/review, signed by the Laboratory Manager, certifying that:

- The alternate column performance meets the technical acceptance criteria in Sections 9.3.5 and 9.4.5;

- The low-point initial calibration standard analysis has adequate sensitivity to meet the volatile CRQLs;

- The high-point initial calibration standard analysis was not overloaded; and

- The column does not introduce contaminants that interfere with the identification and/or quantitation of compounds listed in Exhibit C (Trace Volatiles).

6.5.3.4 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request of the USEPA Regional CLP PO.

6.5.4 **PACKED COLUMNS CANNOT BE USED.**

6.5.5 Mass Spectrometer (MS)

The MS must be capable of scanning from 35-300 amu every 2 seconds or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the 4-bromofluorobenzene (BFB) GC/MS performance check technical acceptance criteria in Table 1.

NOTE: To ensure sufficient precision of mass spectral data, the MS scan rate must allow acquisition of at least five spectra while a sample compound elutes from the GC. The purge-and-trap GC/MS system must be in a room whose atmosphere is demonstrated to be free of all potential contaminants that will interfere with the analysis. The system must be capable of Selected Ion Monitoring (SIM). The instrument must be vented to outside the facility or to a trapping system which prevents the release of contaminants into the instrument room.

6.5.6 GC/MS Interface

Any GC/MS interface may be used that gives acceptable calibration points at 12.5 ng or less per injection for each of the purgeable non-ketone target compounds and Deuterated Monitoring Compounds (DMCs) and achieves all acceptable performance criteria. GC/MS interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

6.5.7 Data System

A computer system must be interfaced to the MS that allows the continuous acquisition and storage on machine-readable media of all

mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching of any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows comparing sample spectra against reference library spectra. The NIST (2002 release or later), Wiley (1991 release or later), or equivalent mass spectral library shall be used as the reference library. The data system must be capable of flagging all data files that have been edited manually by laboratory personnel.

6.5.8 Data Storage Device

Data storage devices must be suitable for long-term, off-line storage of data.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

7.1.1 Reagent Water - Reagent water is defined as water in which an interferant is not observed at or above the Contract Required Quantitation Limit (CRQL) for each compound of interest.

7.1.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g (1 lb) of activated carbon.

7.1.1.2 Reagent water may be generated using a water purification system.

7.1.1.3 Reagent water may be prepared by boiling water for 15 minutes Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle, seal with a polytetrafluoroethylene (PTFE)-lined septum, and cap.

7.1.2 Methanol - High Performance Liquid Chromatography (HPLC) quality or equivalent - Each lot of methanol used for analysis under the contract must be purged with nitrogen and must be demonstrated to be free of contaminants that interfere with the measurement of purgeable compounds listed in Exhibit C (Trace Volatiles).

7.2 Standards

The Contractor must provide all standards to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit E. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard

solutions prepared by the Contractor that are immediately ampulated in glass vials may be retained for 2 years from preparation date. Upon breaking the glass seal, the expiration times listed in Sections 7.2.1.1 to 7.2.2.2 will apply. The Contractor is responsible for assuring that the integrity of the standards has not degraded (Section 7.2.3.5).

7.2.1 Stock Standard Solutions

Stock standard solutions are defined as standards that are to be used to produce working standards. They may be in the form of single compounds or mixtures. They may be purchased or prepared in methanol from pure standard materials.

7.2.1.1 Prepare fresh stock standards every 6 months, or sooner if standard has degraded or evaporated.

7.2.2 Working Standards

7.2.2.1 Instrument Performance Check Solution

Prepare the instrument performance check solution containing 4-bromoflurobenzene (BFB) in methanol. If the BFB solution is added to the mid-level calibration standard (5.0 µg/L for non-ketones and 50 µg/L for ketones), add a sufficient amount of BFB to result in a 2.0 µg/L concentration of BFB (50 ng BFB on-column). The BFB must be analyzed using the same GC and Mass Spectrometer (MS) run conditions as is used for the calibration analysis.

7.2.2.2 Calibration Standard Solution

Prepare single or multiple working calibration standard solution(s) containing all of the purgeable target compounds [Exhibit C (Trace Volatiles)]in methanol. Prepare fresh calibration standards every month, or sooner if the standard has degraded.

7.2.2.3 Internal Standard Spiking Solution

Prepare an internal standard spiking solution containing 1,4-dichlorobenzene-d_4, chlorobenzene-d_5, and 1,4-difluorobenzene in methanol. Add a sufficient amount of the internal standard solution to 25 mL of samples, blanks, and calibration standards to result in a 5.0 µg/L concentration. Prepare a fresh internal standard solution every month, or sooner if the standard had degraded. If analysis using the Selected Ion Monitoring (SIM) technique is required, add sufficient amount of the internal standard solution to 25 mL of samples, blanks, and calibration standards to result in a 0.50 µg/L concentration of each internal standard.

7.2.2.4 Deuterated Monitoring Compound (DMC) Spiking Solution

Prepare a DMC spiking solution in methanol (or in deuterated methanol) containing the compounds listed below: DMCs are to be added to each sample and blank, as well as initial calibration standards and Continuing Calibration Verification (CCV) standards. For samples and blanks, add sufficient amount of DMC solution to each 25 mL of sample to result in a concentration of 5.0 µg/L of each non-ketone DMC, 50 µg/L for each ketone DMC, and 250 µg/L for 1,4-dioxane-d_8 DMC. If SIM analysis is required, add sufficient amount of DMC solution to each sample and blank to result in a

concentration of 0.50 µg/L for each non-ketone DMC, and 25 µg/L for 1,4-dioxane-d_8 DMC. For calibration standards, add sufficient amounts of DMC solution to each 25 mL aliquot of calibration standard to result in the concentrations listed in Section 7.2.2.6.2 (initial calibration) and Section 7.2.2.6.4 (CCV). Prepare a fresh DMC solution every month, or sooner if the standard has degraded.

Compound
Vinyl chloride-d_3
Chloroethane-d_5
1,1-Dichloroethene-d_2
2-Butanone-d_5
Chloroform-d
1,2-Dichloroethane-d_4
Benzene-d_6
1,2-Dichloropropane-d_6
Toluene-d_8
trans-1,3-Dichloropropene-d_4
2-Hexanone-d_5
1,4-Dioxane-d_8
1,1,2,2-Tetrachloroethane-d_2
1,2-Dichlorobenzene-d_4

7.2.2.5 Matrix Spiking Solution

If Matrix Spike and Matrix Spike Duplicate (MS/MSD) analysis is requested at the time of scheduling, prepare a spiking solution in methanol that contains the following compounds at a concentration of 12.5 µg/mL: 1,1-dichloroethene; trichloroethene; chlorobenzene; toluene; and benzene. Prepare fresh spiking solution monthly, or sooner if the solution has degraded or evaporated.

7.2.2.6 Initial and Continuing Calibration Standard

7.2.2.6.1 Add a sufficient amount of each working standard to a 25 mL aliquot of reagent water to produce the desired calibration standard concentrations listed in Section 7.2.2.6.2 or 7.2.2.6.4.

7.2.2.6.2 Prepare five aqueous initial calibration standard solutions containing all of the purgeable target compounds, and the DMCs at the suggested following levels: all non-ketone target compounds and associated DMCs (see Table 7), except 1,4-dioxane, at 0.50, 1.0, 5.0, 10, and 20 µg/L; all ketones and their associated DMCs (see Table 7) at 5.0, 10, 50, 100, and 200 µg/L; and 1,4-dioxane and its associated DMC (see Table 7), 1,4-dioxane-d_8 at 20, 40, 250, 400, and 800 µg/L. All three xylene isomers (o-, m-, and p-xylene) must be present in the calibration standards. The o-xylene calibration standard concentrations must be at 0.50, 1.0, 5.0, 10 and 20 µg/L, while the concentration of the m-, plus the p-xylene isomers must **total** 0.50, 1.0, 5.0, 10, and 20 µg/L.

If analysis by the SIM technique is requested for 1,4-dioxane, prepare calibration standards containing 1,4-dioxane and its associated DMC (see Table 8) at concentrations of 2.0, 4.0, 25, 40, and 80 µg/L. If analysis by the SIM technique is requested for all other compounds of interest, prepare calibration standards containing the compounds of interest and their associated DMCs (see Table 8) at concentrations of 0.050, 0.10, 0.50, 1.0, and 2.0 µg/L.

7.2.2.6.3 Calibration standards may be prepared in a volumetric flask or in the syringe used to inject the standard into the purging device.

7.2.2.6.4 For CCV (beginning and ending CCV), the aqueous CCV standard shall be at a concentration equivalent to the mid-level calibration standard listed in Section 7.2.2.6.2 (i.e., 5.0 µg/L for non-ketones, 50 µg/L for ketones, 250 µg/L for 1,4-dioxane, 25 µg/L for 1,4-dioxane by the SIM technique, and 0.50 µg/L for other compounds analyzed by the SIM technique).

7.2.2.6.5 The methanol contained in each of the aqueous calibration standards must not exceed 1% by volume.

7.2.3 Storage of Standard Solutions

7.2.3.1 Store the stock standards in PTFE-sealed screw-cap bottles with zero headspace at -10°C to -20°C, and protect the standards from light.

7.2.3.2 Aqueous standards may be stored up to 24 hours if held in PTFE-sealed screw-cap vials with zero headspace at 4°C (±2°C) and protected from light. If not so stored, they must be discarded after 1 hour unless they are set up to be purged by an autosampler. When using an autosampler, the standards may be kept up to 12 hours in purge tubes connected via the autosampler to the purge-and-trap device. If standards are purchased and stored as ampulated vials, they may be stored indefinitely.

7.2.3.3 If standards are purchased and stored in ampulated vials, they may be stored up to 2 years after the preparation date.

7.2.3.4 Purgeable standards must be stored separately from other standards, samples, and blanks.

7.2.3.5 The Contractor is responsible for maintaining and verifying the integrity of standard solutions prior to use. This means that standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in the solution.

7.2.4 Temperature Records for Storage of Standards

7.2.4.1 The temperature of all standard storage refrigerators/freezers shall be recorded daily.

7.2.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

7.2.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in glass containers having a total volume of at least 40 mL with a polytetrafluoroethylene (PTFE)-lined septum and an open top screw-cap. Headspace should be avoided. The specific requirements for site sample collection are outlined by the Region. If Selected Ion Monitoring (SIM) is requested, an additional sample aliquot will be collected.

8.1.2 The containers must be filled in such a manner that no air bubbles pass through the sample as the container is being filled. Seal the vial so that no air bubbles are entrapped in it.

8.1.3 Water samples are preserved to a pH of 2 at the time of collection.

8.1.4 All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until analysis.

8.1.5 If SIM analysis is requested, a total of four vials per field sample is the recommended amount of vials the contractor should receive. If SIM analysis is not requested then a total of two vials per field sample is the recommended amount of vials the Contractor should receive. An additional two vials are required if Matrix Spike and Matrix Spike Duplicates (MS/MSDs) are to be performed on that sample.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants and in a refrigerator used only for storage of volatile samples received under the contract.

8.2.3 All volatile samples in a Sample Delivery Group (SDG) must be stored together in the same refrigerator.

8.2.4 Storage blanks shall be stored with samples until all samples within an SDG are analyzed.

8.2.5 Samples, sample extracts, and standards must be stored separately.

8.2.6 Trace volatile standards must be stored separately from semivolatile, pesticide, and Aroclor standards.

8.3 Temperature Records for Sample Storage

8.3.1 The temperature of all sample storage refrigerators shall be recorded daily.

8.3.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

8.3.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators.

8.4 Contract Required Holding Times

Analysis of water samples must be completed within 10 days of Validated Time of Sample Receipt (VTSR). As part of USEPA's Quality Assurance (QA) program, USEPA may provide Performance Evaluation (PE) samples as standard extracts which the Contractor is required to prepare per the instructions provided by USEPA. PE samples must be prepared and analyzed concurrently with the samples in the SDG. The contract-required 10-day holding time does not apply to PE samples received as standard extracts.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

9.1.1 Purge-and-Trap

9.1.1.1 The following are the recommended purge-and-trap analytical conditions. The conditions below are suggested, but other conditions may be used, provided that all technical acceptance criteria are met for all standards, samples, and blanks:

<u>Purge Conditions</u>	
Purge Gas:	Helium or Nitrogen
Purge Time:	11.0 ±0.1 min.
Purge Flow Rate:	25-40 mL/min.
Purge Temperature:	*Ambient temperature
<u>Desorb Conditions</u>	
Desorb Temperature:	180°C
Desorb Flow Rate:	15 mL/min.
Desorb Time:	4.0 ±0.1 min.
<u>Trap Reconditioning Conditions</u>	
Reconditioning Temperature:	180°C
Reconditioning Time:	7.0 ±0.1 min. (minimum). A longer time may be required to bake contamination or water from the system.

* NOTE: Higher purge temperatures may be used provided that all technical acceptance criteria are met for all standards, samples, and blanks. Certain target compounds, such as methyl tert-butyl ether (MTBE), may decompose at high purge temperatures in samples that have been acid preserved.

9.1.1.2 Before initial use, condition the trap overnight at 180°C by backflushing with at least 20 mL/minute flow of inert gas. Do not vent the trap effluent onto the analytical column. Prior to daily use, condition the trap by heating at 180°C for 10 minutes while backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to the analysis of samples and blanks.

9.1.1.3 Optimize purge-and-trap conditions for sensitivity and to minimize cross-contamination between samples. Once optimized, the same purge-and-trap conditions must be used for the analysis of all standards, samples, and blanks.

9.1.1.4 A moisture reduction/water management system may be used to improve the chromatographic performance by controlling moisture or water if:

- The system does not introduce contaminants that interfere with identification and quantitation of compounds listed in Exhibit C (Trace Volatiles);
- The analytical results generated when using the moisture reduction/water management system meet the initial calibration and continuing calibration verification technical acceptance criteria listed in the analytical method and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Trace Volatiles);
- All calibration standards, samples, and blanks are analyzed under the same conditions; and
- The Contractor performs acceptably on the Performance Evaluation (PE) samples using this system.

9.1.2 Gas Chromatograph (GC)

9.1.2.1 The following are the recommended GC analytical conditions. The conditions are recommended unless otherwise noted:

Capillary Columns	
Carrier Gas:	Helium
Flow Rate:	15 mL/min.
Initial Temperature:	10°C
Initial Hold Time:	1.0 - 5.0 (±0.1) min.
Ramp Rate:	6°C/min.
Final Temperature:	160°C
Final Hold Time:	Until 3 min. after all compounds listed in Exhibit C (Trace Volatiles) elute (required)

9.1.2.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, and blanks.

9.1.2.3 If the gaseous compounds chloromethane, bromomethane, vinyl chloride, and chloroethane fail to exhibit narrow, symmetrical peak shape, are not separated from the solvent front, or are not resolved greater than 90.0% from each other, then a subambient oven controller must be used, and the initial temperature must be less than or equal to 10°C.

9.1.3 Mass Spectrometer (MS)

The following are the required MS analytical conditions:

Electron Energy:	70 volts (nominal)
Mass Range:	35-300 amu
Ionization Mode:	Electron Ionization (EI)
Scan Time:	To give at least five scans per peak, not to exceed 2 sec. per scan for capillary column.

9.2 Instrument Performance Check -- 4-bromofluorobenzene (BFB)

9.2.1 Summary of Instrument Performance Check

9.2.1.1 The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibrant such as perfluoro-tri-n-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.2.1).

9.2.1.2 Prior to the analysis of any samples, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing BFB.

This requirement does not apply when samples are analyzed by the Selected Ion Monitoring (SIM) technique.

9.2.2 Frequency of Instrument Performance Check

The instrument performance check solution must be injected once at the beginning of each 12-hour period, during which samples, blanks, or standards are to be analyzed. The 12-hour time period for GC/MS performance check, calibration standards (initial calibration or continuing calibration verification), blank, and sample analysis begins at the moment of injection of the BFB analysis that the laboratory submits as documentation of a compliant instrument performance check. However, in cases where a closing Continuing Calibration Verification (CCV) can be used as an opening CCV for the next 12-hour period, then an additional BFB tune is not required, and the 12-hour period begins with the injection of the CCV. The time period ends after 12 hours have elapsed according to the system clock.

9.2.3 Procedure for Instrument Performance Check

The analysis of the instrument performance check solution may be performed as follows:

- As an injection of up to 50 ng of BFB into the GC/MS.
- By adding a sufficient amount of BFB solution to the mid-level calibration standard (5.0 µg/L for non-ketones and 50 µg/L for ketones) to result in a 2.0 µg/L concentration of BFB.
- By adding a sufficient amount of BFB solution (Section 7.2.2.1) to 25 mL of reagent water to result in a 2.0 µg/L concentration of BFB.

9.2.4 Technical Acceptance Criteria for Instrument Performance Check

9.2.4.1 The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan, the scan immediately preceding, and the scan immediately following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the beginning of the elution of BFB. Do not background subtract part of the BFB peak.

NOTE: All subsequent standards, samples, and blanks associated with a BFB analysis must use identical GC/MS instrument run conditions.

9.2.4.2 The analysis of the instrument performance check solution must meet the ion abundance criteria given in Table 1.

9.2.5 Corrective Action for Instrument Performance Check

9.2.5.1 If the BFB technical acceptance criteria are not met, retune the GC/MS system. It may also be necessary to clean the ion source, clean the quadrupole rods, or take other corrective actions to achieve the technical acceptance criteria.

9.2.5.2 BFB technical acceptance criteria **must** be met before any standards, samples, or required blanks are analyzed. Any samples or required blanks analyzed when tuning technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

Prior to the analysis of samples and required blanks and after the instrument performance check technical acceptance criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations to determine instrument sensitivity and the linearity of GC/MS response for the purgeable target and Deuterated Monitoring Compounds (DMCs).

NOTE: For analysis using the SIM technique, the GC/MS system must be calibrated at a minimum of five concentrations (Section 7.2.2.6.2), prior to the analysis of samples and required blanks, to determine instrument sensitivity and linearity.

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be calibrated upon award of the contract, whenever the Contractor takes corrective action that may change or affect the initial calibration criteria (i.e., ion source cleaning or repair, column replacement, etc.), or if the CCV technical acceptance criteria have not been met.

9.3.2.2 If time remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples and blanks may be analyzed. It is not necessary to analyze a CCV standard within this 12-hour time period. A method blank is required. Quantitate all samples and blank results using the Mean Relative Response Factor ($\overline{RRF}$) from the initial calibration. Compare Quality Control (QC) criteria such as internal standard area response change and Retention Time (RT) shift to the initial calibration standard that is the same concentration as the CCV.

9.3.3 Procedure for Initial Calibration

9.3.3.1 Assemble a purge-and-trap device that meets the specifications in Section 6.4. Condition the device as described in Section 9.1.1.

9.3.3.2 Connect the purge-and-trap device to the GC. The GC must be operated using temperature and flow rate parameters equivalent to those in Section 9.1.2.

9.3.3.3 All samples, blanks, and standard/spiking solutions must be allowed to warm to ambient temperature before analysis.

9.3.3.4 Add sufficient amount of the internal standard solution (Section 7.2.2.3) to each of the five aqueous calibration standard solutions (Section 7.2.2.6.2) containing the DMCs (Section 7.2.2.4) at the time of purge. Analyze each calibration standard according to Section 10.

9.3.4 Calculations for Initial Calibration

Calculating the Relative Response Factors (RRFs) of the xylenes requires special attention. Report an RRF for m,p-xylene and one for o-xylene. On capillary columns, the m,p-xylene isomers coelute. Therefore, when calculating the RRF in the equation below, use the area response (Ax) and concentration (Cx) of the peak from o-xylene and A_x and C_x of the peak from the m,p-xylene isomers respectively.

9.3.4.1 Calculate the RRF for each purgeable target compound and DMC using Equation 1. See Table 3 to associate purgeable target compounds and DMCs with the proper internal standard. See Table 4 for primary quantitation ions to be used for each purgeable target compound, DMC, and internal standard compound.

NOTE: Unless otherwise stated, the area response is that of the primary quantitation ion.

EQ. 1 Relative Response Factor Calculation

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where,

A_x = Area of the characteristic ion (EICP) for the compound to be measured (Table 4).

A_{is} = Area of the characteristic ion (EICP) for the specific internal standard (Table 4).

C_{is} = Concentration of the internal standard.

C_x = Concentration of the compound to be measured.

9.3.4.2 The $\overline{RRF}$ must be calculated for all compounds.

9.3.4.3 Calculate the Percent Relative Standard Deviation (%RSD) of RRF values for each purgeable target compound and DMC over the initial calibration range using Equation 2 in conjunction with Equations 3 and 4.

EQ. 2 Percent Relative Standard Deviation Calculation

$$\%RSD = \frac{SD_{RRF}}{\overline{X}} \times 100$$

Where,

SD_{RRF} = Standard deviation of initial calibration RRFs (per compound) from EQ. 3.

$\overline{X}$ = Mean value of the initial calibration RRFs (per compound).

9.3.4.4 Equation 3 is the general formula for Standard Deviation (SD) for a statistically small set of values.

EQ. 3 Standard Deviation Calculation

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(X_i - \overline{X}\right)^2}{n-1}}$$

Where,

X_i = Each individual value used to calculate the mean.

$\overline{X}$ = The mean of n values.

n = Total number of values.

9.3.4.5 Equation 4 is the general formula for the mean of a set of values.

EQ. 4 Mean Value Calculation

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

Where,

X_i = Value.

$\overline{X}$ = Mean value.

n = Number of values.

9.3.5 Technical Acceptance Criteria For Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.2.6.2, and at the frequency described in Section 9.3.2 on a GC/MS system meeting the BFB technical acceptance criteria (Section 9.2.4).

9.3.5.2 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the instrument manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.3.5.3 The RRF at each calibration concentration for each purgeable target and DMC that has a required minimum RRF value must be greater than or equal to the compound's minimum acceptable RRF listed in Table 2.

9.3.5.4 The %RSD for each target or DMC listed in Table 2 must be less than or equal to that value listed.

9.3.5.5 Up to two target compounds and DMCs (excluding those with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Section 9.3.5.3 but these compounds must still meet the minimum RRF requirements of 0.010. Up to two target compounds and DMCs (excluding those with maximum %RSD requirements of 40.0%) may fail to meet the criteria listed in Section 9.3.5.4 but these compounds must still meet the maximum %RSD requirements of 40.0%. The exceptions are 1,4-dioxane and 1,4-dioxane-d_8, which must have a minimum RRF greater than or equal to 0.0050 and the %RSD must be less than or equal to 50.0%.

9.3.5.6 For analysis using the SIM technique, all target compounds and DMCs must meet a minimum RRF criterion of 0.010 and have a %RSD less than or equal to 50%. The exceptions are 1,4-dioxane and 1,4-dioxane-d_8, which must meet a minimum RRF of 0.0050.

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, service the purge-and-trap device, or take other corrective actions to achieve the technical acceptance criteria.

9.3.6.2 Initial calibration technical acceptance criteria **MUST** be met before any samples or required blanks are analyzed. Any samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.4 Continuing Calibration Verification

9.4.1 Summary of Opening and Closing Continuing Calibration Verification (CCV)

Prior to the analysis of samples and required blanks and after BFB tune and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing an opening CCV containing all the purgeable target compounds, DMCs, and internal standards to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the analytical method. After all samples and blanks have been analyzed and before the end of the 12-hour time period a closing CCV using the same standard conditions as for the opening CCV is required.

NOTE: For analysis using the SIM technique, prior to the analysis of samples and required blanks, and after initial calibration technical acceptance criteria have been met, each GC/MS system

must be routinely checked by analyzing a CCV standard (25 µg/L for 1,4-dioxane and its associated DMC, and 0.50 µg/L for all other target compounds and associated DMCs).

9.4.2 Frequency of Continuing Calibration Verification

9.4.2.1 The 12-hour time period begins with the injection of BFB, followed by the injection of the opening CCV solution. BFB may be added to the CCV solution, in which case only one injection is necessary. If a closing CCV meets the technical acceptance criteria for an opening CCV (Sections 9.4.5.2 and 9.4.5.3) and samples are analyzed within that subsequent 12-hour time period, then an additional BFB tune is not required and the 12-hour time period begins with that calibration verification. If the closing CCV does not meet the technical acceptance criteria for an opening CCV, then a BFB tune followed by an opening CCV is required and the next 12-hour time period begins with the BFB tune.

9.4.2.2 If time remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. A method blank is required. Quantitate all sample and blank results using the $\overline{RRF}$ from the initial calibration.

9.4.2.3 After the injection of all samples and required blanks, and before the end of the 12-hour period another injection of the CCV solution is required (closing CCV). The closing CCV used to bracket the end of a 12-hour analytical sequence may be used as the opening CCV for a new 12-hour analytical sequence, provided that all technical acceptance criteria are met for an opening CCV in Section 9.4.5.

9.4.3 Procedure for Continuing Calibration Verification

9.4.3.1 Set up the purge-and-trap GC/MS system per the requirements in Section 9.1.

9.4.3.2 All samples, required blanks, and standard/spiking solutions must be allowed to warm to ambient temperature before analysis.

9.4.3.3 Add sufficient amount of internal standard solution (Section 7.2.2.3) to the 25 mL syringe or volumetric flask containing the CCV (7.2.2.6.4). Analyze the CCV according to Section 10.

9.4.4 Calculations for Continuing Calibration Verification

9.4.4.1 Calculate an RRF for each target compound and DMC according to Section 9.3.4.1.

9.4.4.2 Calculate the Percent Difference (%Difference) between the CCV RRF and the most recent initial calibration $\overline{RRF}$ for each purgeable target and DMC using Equation 5.

EQ. 5 Percent Difference Calculation

$$\%Difference = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

Where,

RRF_c = Relative Response Factor from current CCV standard.

$\overline{RRF_i}$ = Mean Relative Response Factor from the most recent initial calibration.

9.4.5 Technical Acceptance Criteria for Opening and Closing Continuing Calibration Verification (CCV)

9.4.5.1 The concentration of the trace volatile organic target compounds and DMCs in the opening and closing CCV must be at or near the mid-point concentration level of the calibration standards, (5.0 µg/L for non-ketones, 50 µg/L for ketones, and 250 µg/L for 1,4-dioxane). The opening and closing CCV must be analyzed at the frequency described in Section 9.4.2 on a GC/MS system meeting the BFB (Section 9.2.4) and the initial calibration (Section 9.3.5) technical acceptance criteria.

NOTE: For analysis using the SIM technique, the concentration of 1,4-dioxane and the DMC 1,4-dioxane-d_8 in the opening and closing CCV standard must be at or near the mid-point concentration level of the calibration standards (25 µg/L). The concentration for the remaining target compounds and DMCs must be 0.50 µg/L. The opening and closing CCV standard must be analyzed at the frequency described in Section 9.4.2 on a GC/MS system meeting the initial calibration technical acceptance criteria.

9.4.5.2 For an opening CCV, The RRF for each purgeable target and DMC must be greater than, or equal to, the compound's minimum acceptable RRF listed in Table 4. For a closing CCV, The RRF for each purgeable target and DMC must be at least 0.010 (except for 1,4-dioxane and its associated DMC, 1,4-dioxane-d_8, which must be at least 0.0050).

9.4.5.3 For an opening CCV, the RRF Percent Difference for each purgeable target compound and DMC listed in Table 2 must be within the inclusive range of the value listed. For a closing CCV, the RRF Percent Difference for each purgeable target and DMC must be in the inclusive range of 50.

9.4.5.4 For an opening CCV, up to two target compounds and DMCs (excluding those compounds with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Section 9.4.5.2 but these compounds must still meet the minimum RRF requirements of 0.010. Up to two target compounds and DMCs (excluding those compounds with maximum Percent Difference requirements of ±40.0%) may fail to meet the requirements listed in Section 9.4.5.3 but these compounds must still meet the maximum Percent Difference requirements of ±40.0%. The exceptions are 1,4-dioxane and 1,4-dioxane-d_8, which must have a minimum RRF greater than or equal to 0.0050 and the Percent Difference must be within the inclusive range of ±50.0%. For a

closing CCV, all target compounds and DMCs must meet the requirements listed in Sections 9.4.5.2 and 9.4.5.3.

9.4.5.5 For analysis using the SIM technique, all target compounds and DMCs must meet a minimum RRF criterion of 0.010 and have a maximum Percent Different of ±50%. The exceptions are 1,4-dioxane and 1,4-dioxane-d_8 which must meet a minimum RRF of 0.0050.

9.4.5.6 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.4.6 Corrective Action for Opening and Closing Continuing Calibration Verification (CCV)

9.4.6.1 If the opening CCV technical acceptance criteria are not met, recalibrate the GC/MS instrument according to Section 9.3. If the closing CCV technical acceptance criteria are not met, then all samples and blanks analyzed within that 12-hour time period must be reanalyzed at no additional cost to USEPA. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the CCV technical acceptance criteria.

9.4.6.2 Opening CCV technical acceptance criteria MUST be met before any samples or required blanks are analyzed. Any samples or required blanks analyzed when opening CCV technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

10.0 PROCEDURE

10.1 Summary of Sample Analysis

10.1.1 This method is designed for analysis of samples that contain trace concentrations of the target compounds listed in Exhibit C (Trace Volatiles). It is expected that the samples will come from drinking water and well/groundwater type sources around Superfund sites. If, upon inspection of a sample, the Contractor suspects that the sample is not amenable to this method, contact the Sample Management Office (SMO). SMO will contact the Region for instructions.

NOTE: If SIM analysis is requested for a sample, a full scan analysis at trace level must be performed on that sample prior to SIM analysis. For all SIM target compounds detected at or above CRQLs during the full scan analysis, a SIM analysis is <u>not</u> to be performed for that target compound. Any SIM analyses not performed for this reason must be noted in the Sample Delivery Group (SDG) Narrative.

10.1.2 Prior to the analysis of samples, establish the appropriate purge-and-trap Gas Chromatograph/Mass Spectrometer (GC/MS) operating conditions, as outlined in Section 9.1, analyze the instrument performance check solution (Section 9.2), and calibrate the GC/MS system according to Sections 9.3 through 9.4.6. Also prior to sample analysis, a method blank must be analyzed that meets blank technical acceptance criteria in Section 12.1.5. All samples, required blanks, and standard/spiking solutions must be allowed to warm to ambient temperature before analysis. All samples, required blanks, and calibration standards must be analyzed under the same instrument conditions.

10.1.3 If insufficient sample volume (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact SMO to apprise them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.2 Procedure for Sample Analysis

10.2.1 If the autosampler can automatically sample the appropriate volume then Sections 10.2.2 - 10.2.4 are performed by the autosampler. The pH determination procedure listed in Section 10.2.3 must still be performed manually.

10.2.2 Remove the plunger from a 25 mL syringe that has a closed syringe valve attached. Open the sample or standard container that has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Invert the syringe, open the syringe valve, and vent any residual air while adjusting the sample volume to 25.0 mL. This process of taking an aliquot destroys the validity of the sample for future analysis, unless the excess sample is immediately transferred to a smaller vial with zero headspace and stored at 4°C (±2°C).

10.2.3 For analysis by the Selected Ion Monitoring (SIM) technique, add a sufficient amount of the Deuterated Monitoring Compound (DMC) standard solution (Section 7.2.2.4) and a sufficient amount of

internal standard spiking solution (Section 7.2.2.3) through the valve bore of the syringe, then close the valve. Invert the syringe 3 times.

Add a sufficient amount of the DMC standard solution (Section 7.2.2.4) and a sufficient amount of internal standard spiking solution (Section 7.2.2.3) through the valve bore of the syringe, then close the valve. Invert the syringe 3 times.

Once the sample aliquots have been taken from the VOA vial, the pH of the water sample must be determined. The purpose of the pH determination is to ensure that all VOA samples were acidified in the field. Test the pH by placing one or two drops of sample on the pH paper (do not add pH paper to the vial). Record the pH of each sample and report these data in the SDG Narrative, following the instructions in Exhibit B. No pH adjustment is to be performed by the Contractor.

10.2.4 Attach the valve assembly on the syringe to the valve on the sample purger. Open the valves and inject the sample into the purging chamber.

10.2.5 Close both valves and purge the sample for 11.0 (±0.1) minutes at ambient temperature.

10.2.6 Sample Desorption - After the 11-minute purge, attach the trap to the GC, adjust the purge-and-trap system to the desorb mode, initiate the temperature program sequence of the GC and start data acquisition. Introduce the trapped material to the GC column by rapidly heating the trap to 180°C while backflushing the trap with inert gas at 15 mL/minute for 4.0 ±0.1 minutes. While the trapped material is being introduced into the GC, empty the sample purger and rinse it with reagent water. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high purgeable levels, it may be necessary to wash out the sample purger with a detergent solution, rinse it with reagent water, and then dry it in an oven at 105°C.

10.2.7 Trap Reconditioning - After desorbing the sample, recondition the trap for a minimum of 7.0 ±0.1 minutes at 180°C by returning the purge-and-trap system to purge mode.

10.2.8 Gas Chromatography - Hold the column temperature at 10°C for 1.0 - 5.0 minutes, then program at 6°C/minute to 160°C and hold until 3 minutes after all target volatile compounds have eluted.

NOTE: Once an initial hold time has been chosen and the GC operating conditions optimized, the same GC condition must be used for the analysis.

10.2.9 Termination of Data Acquisition - 3 minutes after all the purgeable target compounds have eluted from the GC, terminate the MS data acquisition and store data files on the data system storage device. Use appropriate data output software to display full range mass spectra and appropriate Extracted Ion Current Profiles (EICPs).

10.2.10 Dilutions

10.2.10.1 An original undiluted analysis must be made and results reported for all samples. If the peak response for any target compound in any sample exceeds the peak response in the highest standard in the initial calibration, a new aliquot of that sample must be diluted and purged. Guidance for performing dilutions and

exceptions to this requirement are given in Sections 10.2.10.2 - 10.2.10.8.

NOTE 1: If the laboratory has evidence or highly suspects, because of sample color or other physical properties, that a sample may contain high concentrations of either target or non-target compounds, then SMO shall be contacted immediately. SMO will seek Regional recommendations for diluted analysis.

NOTE 2: Secondary ion quantitation is only allowed when there are sample interferences with the primary quantitation ion, not when saturation occurs. If secondary ion quantitation is used, calculate a Relative Response Factor (RRF) using the area response (EICP) from the most intense secondary ion which is free of sample interferences, and document the reasons in the SDG Narrative.

10.2.10.2 Use the results of the original analysis to determine the approximate Dilution Factor (DF) required to get the largest analyte peak within the calibration range.

10.2.10.3 The DF chosen must keep the concentration of the trace volatile target compounds that required dilution in the upper half of the initial calibration range.

10.2.10.4 All dilutions must be made just prior to GC/MS analysis of the sample. Until the diluted sample is in a gas-tight syringe, all steps in the dilution procedure must be performed without delay.

10.2.10.5 Samples may be diluted in a volumetric flask or in a 25 mL Luer-Lok syringe.

10.2.10.6 To dilute the sample in a volumetric flask, use the following procedure:

10.2.10.6.1 Select the volumetric flask that will allow for necessary dilution (25-100 mL).

10.2.10.6.2 Calculate the approximate volume of reagent water that will be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.

10.2.10.6.3 Inject the proper sample aliquot from a syringe into the volumetric flask. Only aliquots of 1 mL increments are permitted. Dilute the aliquot to the mark with reagent water. Cap the flask and invert it 3 times.

10.2.10.6.4 Fill a 25 mL syringe with the diluted sample and analyze according to Section 10.2.

10.2.10.7 To dilute the sample in a 25 mL syringe, use the following procedure:

10.2.10.7.1 Calculate the volume of the reagent water necessary for the dilution. The final volume of the diluted sample should be 25 mL.

10.2.10.7.2 Close the syringe valve, remove the plunger from the syringe barrel, and pour reagent water into the syringe barrel to just short of overflowing.

10.2.10.7.3 Replace the syringe plunger and compress the water.

10.2.10.7.4 Invert the syringe, open the syringe valve, and vent any residual air. Adjust the water volume to the desired amount.

10.2.10.7.5 Adjust the plunger to the 25 mL mark to accommodate the sample aliquot. Inject the proper aliquot of sample from another syringe through the valve bore of the 25 mL syringe. Close the valve and invert 3 times. Analyze according to Section 10.2.

10.2.10.8 If more than two analyses (i.e., from the original sample and more than one dilution, or from the most concentrated dilution analyzed and further dilutions) are required to get all target compounds within the calibration range, contact SMO for guidance.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification of Target Compounds

11.1.1 The compounds listed in the Target Compound List (TCL) [Exhibit C (Trace Volatiles)], shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

- Elution of the sample component at the same Gas Chromatograph (GC) Relative Retention Time (RRT) as the standard component; and
- Correspondence of the sample component and calibration standard component mass spectra.

11.1.2 For establishing correspondence of the GC RRT, the sample component RRT must be within ±0.06 RRT units of the RRT of the standard component. For reference, the standard must be run in the same 12-hour time period as the sample. If samples are analyzed during the 12-hour time period as the initial calibration, use the RRT values from the 5.0 µg/L standard [0.50 µg/L standard for Selected Ion Monitoring (SIM) analysis]. Otherwise, use the corresponding opening Continuing Calibration Verification (CCV) standard. For SIM analysis, use the RRT values of the median concentration standard. If coelution of interfering compounds prohibits accurate assignment of the sample component RRT from the total ion chromatogram, then the RRT should be assigned using the Extracted Ion Current Profile (EICP) for ions unique to the component of interest.

11.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/Mass Spectrometer (MS) are required. Once obtained, these standard spectra may be used for identification purposes, only if the Contractor's GC/MS meets the daily instrument performance requirements for 4-bromofluorobenzene (BFB). These standard spectra may be obtained from the standard analysis that was also used to obtain the RRTs.

11.1.4 The guidelines for qualitative verification by comparison of mass spectra are as follows:

11.1.4.1 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

11.1.4.2 The relative intensities of ions specified in Section 11.1.4.1 must agree within ±20% between the standard and sample spectra (i.e., for an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30-70%).

11.1.4.3 Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the adjusted Contract Required Quantitation Limit (CRQL), report the actual value followed by a "J" (e.g., "0.3J").

11.1.4.4 If a compound cannot be verified by all of the spectral identification criteria listed in Section 11.1.4, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification and proceed with quantitation.

11.2 Qualitative Identification of Non-Target Compounds

11.2.1 A library search shall be executed for non-target sample components for the purpose of tentative identification. The NIST (2002 release or later) or equivalent mass spectral library, shall be used as the reference library.

11.2.2 All organic compounds that have not been positively identified as volatile target analytes using the procedures detailed in Section 11.1, or that are not Deuterated Monitoring Compounds (DMCs) or internal standards shall be tentatively identified via a forward search of the NIST, Wiley, or equivalent mass spectral library. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer-generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

11.2.3 Up to 30 non-alkane Tentatively Identified Compounds (TICs) of greatest apparent concentration shall be reported on Form I VOA-TIC. Peaks that are tentatively identified as straight-chain, branched, or cyclic alkanes, and are alone or part of an alkane series, shall be reported as "total alkanes" on Form I VOA-TIC. An alkane is defined as any hydrocarbon with the generic formula C_nH_{2n+2} (straight-chain or branched) or C_nH_{2n} (cyclic) that contains only C-H and C-C single bonds. The concentrations of each of the alkanes is to be summed and reported as a single result for the "total alkanes". Documentation for the tentative identification of each alkane shall be supplied in the hard copy deliverable packages. The alkanes are not to be counted as part of the 30 compounds individually reported as TICs on Form I VOA-TIC. Carbon dioxide and compounds with responses less than 10% of the internal standard in which they are to be quantified (as determined by inspection of the peak areas or height) are not to be reported (nor are they to be counted as part of the 30 compounds that are to be reported).

11.2.4 Rules for making tentative identification:

11.2.4.1 For compounds to be reported, as per the instructions in Section 11.2.3, identification (as generated by the library search program) of those receiving a library search match of 85% or higher should be considered a "probable match". The compound

should be reported with the identification generated by the search program unless the mass spectral interpretation specialist feels there is just evidence not to report the compound as identified by the library search program.

11.2.4.2 If the library search produces more than one compound at or above 85%, report the compound with the highest percent match (report first compound if the percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels there is just evidence not to report the compound with the highest match. Do not report DMCs, internal standards, or analytes that are on the volatile target analyte list, unless the library search produces only one compound having a match of greater than 85%, and that compound is identified as a DMC, internal standard, or volatile target analyte.

11.2.4.3 If the library search produces a series of obvious isomer compounds with library search matches greater than 85% (e.g., tetramethyl naphthalenes), the compound with the highest library search percent match should be reported (or first compound if library search matches are the same).

11.2.4.4 If the mass spectral interpretation specialist has just evidence to support reporting a compound with a tentative identification of something other than that generated by the library search program (with a library search result of 85% or greater), the laboratory shall include in the Sample Delivery Group (SDG) Narrative the justification for not reporting a compound as listed by the search program. This narrative shall detail explicitly why a library search generated identification for a compound was rejected. If a tentatively identified compound has obvious isomer analogs, the laboratory shall include in the SDG narrative a statement indicating that the exact isomer configuration, as reported, may not be absolutely accurate.

11.2.4.5 If the library search produces no matches at or above 85%, the mass spectral interpretation specialists is encouraged to make a valid tentative identification of the compound. If no valid tentative identification can be made, the compound should be reported as "unknown". The mass spectral interpretation specialist should give additional classification of the unknown, if possible (e.g., "unknown aromatic compound", "unknown chlorinated compound", etc.).

11.3 Calculations

11.3.1 Target Compounds

11.3.1.1 Identified target compounds shall be quantified by the internal standard method using Equation 6. The internal standard used shall be that which is assigned in Table 3. The Mean Relative Response Factor ($\overline{RRF}$) from the initial calibration standard is used to calculate the concentration in the sample. When a target compound concentration is below its CRQL but the spectra meets the identification criteria, report the concentration with a "J". For example, if the CRQL is 0.50 µg/L and a concentration of 0.30 µg/L is calculated, report as "0.30 J". Report ALL sample concentration data as UNCORRECTED for blanks.

EQ. 6 Water Concentration Calculation

$$\text{Concentration in ug/L} = \frac{(A_x)\ (I_s)\ (DF)}{(A_{is})\ (\overline{RRF})\ (V_o)}$$

Where,

A_x = Area of the characteristic ion (EICP) for the compound to be measured. The primary quantitation ions for the target compounds, internal standards, and the DMCs are listed in Table 4.

A_{is} = Area of the characteristic ion (EICP) for the internal standard. The target compounds are listed with their associated internal standards in Table 3.

I_s = Amount of internal standard added in ng.

$\overline{RRF}$ = Mean Relative Response Factor from the initial calibration standard.

V_o = Total volume of water purged, in mL.

DF = Dilution Factor. The DF for analysis of water samples for volatiles by this method is defined as the ratio of the number of mL of water purged (i.e., V_o above) to the number of mL of the original water sample used for purging. For example, if 5.0 mL of sample is diluted to 25.0 mL with reagent water and purged, DF = 25.0 mL/5 mL = 5.0. If no dilution is performed, DF = 1.0.

11.3.1.2 Xylenes are to be reported as "m,p-xylene" and "o-xylene". Because m- and p-xylene isomers coelute, special attention must be given to the quantitation of the xylenes. In quantitating sample concentrations, be sure to use the correct corresponding RRF values.

NOTE: The area of each peak (i.e., the peaks for o-xylene and m,p-xylene) must appear on the quantitation report.

11.3.1.3 The stereoisomers, trans-1,2-dichloroethene, and cis-1,2-dichloroethene, are to be reported separately.

11.3.1.4 The requirements listed in Sections 11.3.1.5 and 11.3.1.6 apply to all standards, samples, and blanks.

11.3.1.5 It is expected that situations will arise where the automated quantitation procedures in the GC/MS software provide inappropriate quantitation. This normally occurs when there is compound coelution, baseline noise, or matrix interferences. In these circumstances the Contractor must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific target compound, DMC, or internal standard compound. The area integrated shall not include baseline background noise. The area integrated shall not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is

not to be used solely to meet Quality Control (QC) criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instances of manual integration must be documented in the SDG Narrative.

11.3.1.6 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the integration scan range. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all compounds listed in Exhibit C (Trace Volatiles), internal standards, and DMCs.

11.3.2 Non-Target Compounds

11.3.2.1 An estimated concentration for non-target compounds tentatively identified shall be determined by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

11.3.2.2 Equation 6 is also used for calculating non-target compound concentrations. Total area counts (or peak heights) from the total Reconstructed Ion Chromatograms (RICs) are to be used for both the non-target compound to be measured (A_x) and the internal standard (A_{is}). An RRF of 1.0 is to be assumed. The value from this quantitation shall be qualified by a "J" (estimate due to lack of a compound-specific RRF), and "N" (presumptive evidence of presence), indicating the qualitative and quantitative uncertainties associated with this non-target compound. An estimated concentration must be calculated for all TICs, as well as those identified as unknowns.

11.3.3 CRQL Calculation

Calculate the adjusted CRQL for trace volatiles by using Equation 7.

EQ. 7 Water Adjusted CRQL Calculation

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{V_c}{V_o} \times DF$$

Where,

Contract CRQL = Exact CRQL values in Exhibit C of the Statement of Work (SOW).

V_o = Total volume of water purged in mL.

NOTE: Must not exceed the contract sample volume.

V_c = Contract sample volume in mL (25 mL).

DF = Same as EQ. 6.

11.3.4 Deuterated Monitoring Compound (DMC) Recoveries

11.3.4.1 Calculate the concentration of each DMC using the same equation as used for target compounds (Equation 6).

11.3.4.2 Calculate the recovery of each DMC in all samples and blanks using Equation 8. Report the recoveries on the appropriate forms.

EQ. 8 DMC Percent Recovery Calculation

$$\%R = \frac{Q_d \times DF}{Q_a} \times 100$$

Where,

Q_d = Concentration or amount determined by analysis.

Q_a = Concentration or amount added to sample/blank.

DF = Same as EQ. 6.

11.3.5 Internal Standard Responses and Retention Times (RTs)

Internal standard responses and RTs in all samples and blanks must be evaluated during or immediately after data acquisition. Compare the sample/blank internal standard responses and RTs to the opening CCV internal standard responses and RTs. For samples and blanks analyzed during the same 12-hour time period as the initial calibration standards, compare the internal standard responses and RTs against the initial calibration standard with non-ketone concentrations of 5.0 µg/L, ketone concentrations of 50 µg/L, and a 1,4-dioxane concentration of 250 µg/L (25 µg/L concentration of 1,4-dioxane and 0.5 µg/L concentration for other compounds analyzed by SIM). The EICP of the internal standards must be monitored and evaluated for each sample and blank.

11.4 Technical Acceptance Criteria for Sample Analysis

11.4.1 The sample must be analyzed on a GC/MS system meeting the BFB, initial calibration, CCV, and blank technical acceptance criteria. Do not apply BFB criteria to SIM analysis.

11.4.2 The sample and any required dilution must be analyzed within the contract required holding time.

11.4.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

11.4.4 The Percent Recovery (%R) of each of the DMCs in the sample must be within the acceptance windows in Table 5. The recovery limits for 1,4-dioxane-d_8 are advisory. Up to three DMCs, excluding 1,4-dioxane-d_8, per sample may fail to meet the recovery limits listed in Table 5. For SIM analysis, all DMCs must meet the recovery limits listed in Table 5.

11.4.5 The EICP area for each of the internal standards in the sample must be within the range of 60.0% and 140% of its response in the most recent opening CCV standard analysis.

11.4.6 The RT shift for each of the internal standards in the sample must be within ±0.33 minutes (20.0 seconds) of its RT in the most recent opening CCV standard analysis.

11.4.7 Excluding those ions in the solvent front, no ion may saturate the detector. No peak response of any target compound in any sample should exceed the peak response of the highest standard in the initial calibration, unless a more diluted aliquot of the sample is also analyzed according to the procedures in Section 10.2.10.

11.4.8 The Contractor must demonstrate that there is no carryover from a contaminated sample before data from subsequent analyses may be submitted. After a sample that contains a target compound at a level exceeding the initial calibration range, or a non-target compound at a concentration greater than 100 µg/L, or saturated ions from a compound (excluding the compound peaks in the solvent front), the Contractor must either:

11.4.8.1 Analyze an instrument blank immediately after the contaminated sample. If an autosampler is used, an instrument blank must also be analyzed using the same purge inlet that was used for the contaminated sample. The instrument blanks must meet the technical acceptance criteria for blank analysis (Section 12.1.5);

or

Monitor the analyzed sample immediately after the contaminated sample for all the compounds that were in the contaminated sample and that exceeded the limits above. The maximum carryover criteria are as follows: the sample must not contain a concentration above the CRQL for the target compounds, or above 2 µg/L for the non-target compounds that exceeded the limits in the contaminated sample. If an autosampler is used, the next sample analyzed using the same purge inlet that was used for the contaminated sample must also meet the maximum carryover criteria.

11.5 Corrective Action for Sample Analysis

11.5.1 Sample technical acceptance criteria must be met before data are reported. Samples contaminated from laboratory sources or any samples not meeting the sample technical acceptance criteria will require reanalysis at no additional cost to USEPA.

11.5.2 Corrective actions for failure to meet technical acceptance criteria for instrument performance checks, initial calibration, continuing calibration verification, and method blanks must be completed before the analysis of samples.

11.5.3 If the technical acceptance criteria for any of the internal standards and DMCs are not met, check calculations, internal standard and DMC spiking solutions, and instrument performance. It may be necessary to bake-out the system to remove the water from the purge-and-trap transfer lines, to recalibrate the instrument, or take other corrective action procedures to meet the technical acceptance criteria.

11.5.4 Sample reruns performed as a result of suspected matrix interference beyond the scope of the method will be evaluated on a case-by-case basis for payment purposes by the USEPA Contract Laboratory Program Project Officer (CLP PO). Send a copy of the SDG Narrative (including the Contract Number), a description of the situation, and the requested action to the CLP PO.

11.5.5 If the contractor needs to analyze more than one sample dilution other than the original analysis to have all the target compounds within the initial calibration range, contact the Sample Management Office (SMO). SMO will contact the Region for instruction.

11.5.6 All samples to be reported to USEPA must meet the maximum carryover criteria in Section 11.4.8. If any sample fails to meet these criteria, each subsequent analysis must be checked for cross contamination. The analytical system is considered contaminated until a sample has been analyzed that meets the maximum carryover criteria or an instrument blank has been analyzed that meets the technical acceptance criteria for blanks. If an instrument blank is not analyzed between consecutive samples that have the same compound with a concentration exceeding the calibration range, then the second sample must be appropriately diluted as in Section 10.2.10 and analyzed. If in the dilution this compound is detected at levels at or below the adjusted CRQL, then all samples analyzed after the second sample that fail to meet maximum carryover criteria must be reanalyzed. If in the dilution this compound is detected within the calibration range, then no further corrective action is needed.

12.0 QUALITY CONTROL (QC)

12.1 Blank Analyses

12.1.1 Summary of Blank Analyses

There are three different types of blanks required by this method.

12.1.1.1 Method Blank - 25 mL of reagent water spiked with sufficient amount of internal standard spiking solution (Section 7.2.2.3) and Deuterated Monitoring Compound (DMC) solution (Section 7.2.2.4), and carried through the entire analytical procedure. The purpose of the method blank is to determine the levels of contamination associated with processing and analysis of samples.

12.1.1.2 Storage Blank - Upon receipt of the first samples in a Sample Delivery Group (SDG), two 40 mL screw-cap VOA vials with a polytetrafluoroethylene (PTFE)-faced silicone septum are filled with reagent water (80 mL total). The vials are stored with the samples in the SDG under the same conditions. A 25.0 mL aliquot of this reagent water is spiked with sufficient amount of internal standard spiking solution (Section 7.2.2.3) and DMC solution (Section 7.2.2.4), and analyzed after all samples in the SDG have been analyzed. The storage blank indicates whether contamination may have occurred during storage of samples.

12.1.1.3 Instrument Blank - 25 mL of reagent water spiked with sufficient amount of internal standard spiking solution (Section 7.2.2.3) and DMC solution (Section 7.2.2.4), and carried through the entire analytical procedure. Instrument blanks are analyzed after a sample/dilution that contains a target compound exceeding the calibration range. The results from the instrument blank analysis indicate whether there is contamination from a previous sample.

12.1.2 Frequency of Blank Analyses

12.1.2.1 The method blank must be analyzed at least once during every 12-hour time period on each Gas Chromatograph/Mass Spectrometer (GC/MS) system used for trace volatile analysis (see Section 9.2.2 for the definition of the 12-hour time period).

12.1.2.2 The method blank must be analyzed after the Continuing Calibration Verification (CCV) and before any samples or storage blanks are analyzed. The method blank must be analyzed after the initial calibration sequence if samples are analyzed before the 12-hour time period expires. A method blank must be analyzed in each 12-hour time period in which samples (including dilutions) and storage blanks from an SDG are analyzed.

12.1.2.3 A minimum of one storage blank must be analyzed per SDG, after all samples for the SDG have been analyzed, unless the SDG contains only ampulated Performance Evaluation (PE) samples. Analysis of a storage blank is not required for SDGs that contain only ampulated PE samples.

12.1.2.4 The Contractor must demonstrate that there is no carryover from contaminated samples before data from subsequent analyses may be used. Samples may contain target compounds at levels exceeding the initial calibration range or non-target compounds at concentrations greater than 100 µg/L, or ions from a compound that saturate the detector (excluding the compound peaks in the solvent front). An instrument blank must be analyzed immediately after

the contaminated sample (also in the same purge inlet if an autosampler is used), or a sample that meets the maximum carryover criteria in Section 11.4.8 must be analyzed. For these purposes, if the instrument blank meets the technical acceptance criteria for blank analysis or the sample meets the maximum carryover criteria, the system is considered to be uncontaminated. If the instrument blank or sample does not meet the criteria (i.e., contaminated), the system must be decontaminated. Until an instrument blank meets the blank technical acceptance criteria or a sample meets the maximum carryover criteria, any samples analyzed since the original contaminated sample will require reanalysis at no additional cost to USEPA.

NOTE: Only the instrument blank that demonstrates that there was no carryover from the previous sample or the instrument blank that demonstrates that the system is clean (Section 12.1.5.6) must be reported. Instrument blanks analyzed during the instrument decontamination process that exceed the requirements listed in Section 11.4.8 do not need to be reported.

12.1.3 Procedure for Blank Analyses

12.1.3.1 Method blanks shall be analyzed in the same manner as the associated samples, following the procedure described in Section 10.2.

12.1.3.2 Under no circumstances should blanks be analyzed at a dilution (i.e., blanks should always have a DF=1.0).

12.1.4 Calculations for Blank Analyses

Perform data analysis and calculations according to Section 11.

12.1.5 Technical Acceptance Criteria for Blank Analyses

12.1.5.1 All blanks must be analyzed on a GC/MS system meeting the 4-bromofluorobenzene (BFB), initial calibration, and continuing calibration verification technical acceptance criteria, and at the frequency described in Section 12.1.2.

12.1.5.2 The storage blank must be analyzed on a GC/MS system that also meets the technical acceptance criteria for the method blank.

12.1.5.3 The Percent Recovery (%R) of each of the DMCs in the blank must be within the acceptance windows in Table 5. The recovery limits for 1,4-dioxane-d_8 are advisory.

12.1.5.4 The Extracted Ion Current Profile (EICP) area for each of the internal standards in the blank must be within the range of 60.0% and 140% of its response in the most recent opening CCV standard analysis.

12.1.5.5 The Retention Time (RT) shift for each of the internal standards in the blank must be within ±0.33 minutes (20.0 seconds) of its RT in the most recent opening CCV standard analysis.

12.1.5.6 The concentration of each target compound found in the storage and method blanks must be less than the Contract Required Quantitation Limit (CRQL) listed in Exhibit C (Trace Volatiles), except for methylene chloride, acetone, and 2-butanone, which must be less than 2 times the respective CRQL. The concentration of each

target compound in the instrument blank must be less than its CRQL listed in Exhibit C (Trace Volatiles). The concentration of non-target compounds in all blanks must be less than 2.0 µg/L.

12.1.5.7 All blanks (storage/instrument/method) must be analyzed at the original concentration only (i.e., DF=1.0).

12.1.6 Corrective Action for Blank Analyses

12.1.6.1 It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, laboratory air, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms, be eliminated. If a Contractor's blanks exceed the criteria in Section 12.1.5.6, the Contractor must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds.

12.1.6.2 Any method blank that fails to meet the technical acceptance criteria must be reanalyzed. Further, all samples processed within the 12-hour time period with a method blank that does not meet the blank technical acceptance criteria will require reanalysis at no additional cost to USEPA.

12.1.6.3 Any instrument blank that fails to meet the technical acceptance criteria described in Section 12.1.5.6 requires reanalysis of the samples analyzed after the instrument blank having any target compounds detected at levels above the CRQLs at no additional cost to USEPA.

12.1.6.4 If the storage blank does not meet the technical acceptance criteria for blank analyses in Sections 12.1.5.1 to 12.1.5.6, correct system problems and reanalyze the storage blank. If the storage blank does not meet the criteria in Section 12.1.5.6, reanalyze the blank to determine whether the contamination occurred during storage or during analyses. If upon reanalysis, the storage blank meets the criteria in Section 12.1.5.6, the problem occurred during the analysis and the reanalyzed storage blank results must be reported. If upon reanalysis the storage blank did not meet the criteria in Section 12.1.5.6, the problem occurred during storage. The Laboratory Manager or their designee must address the problem in the SDG Narrative and discuss the corrective actions implemented to prevent future occurrences.

NOTE: A copy of the storage blank data must be retained by the Contractor and be made available for inspection during on-site laboratory evaluations.

12.2 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the method used for trace volatile analysis, USEPA has prescribed a mixture of volatile target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method, upon request.

12.2.2 Frequency of MS/MSD

12.2.2.1 An MS/MSD shall be analyzed if requested by the Region [through the Sample Management Office (SMO)] or specified on the Traffic Report/Chain of Custody Record (TR/COC). If requested, a MS/MSD must be performed for each group of 20 field samples in an SDG, or each SDG, whichever is most frequent. The Contractor shall not perform MS/MSD analysis when using the Selected Ion Monitoring (SIM) technique.

12.2.2.2 As part of USEPA's Quality Assurance/Quality Control (QA/QC) program, water rinsate samples and/or field/trip blanks (field QC) may be delivered to a laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the field QC samples.

12.2.2.3 If the USEPA Region requesting MS/MSD designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample, less than the required amount, remaining to perform an MS/MSD, then the Contractor shall choose another sample to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify SMO that insufficient sample was received and identify the USEPA sample selected for the MS/MSD analysis. SMO shall contact the Region for confirmation immediately after notification. The rationale for the choice of a sample other than the one designated by the Region shall be documented in the SDG Narrative.

12.2.2.4 If an insufficient number of sample vials were received to perform an MS/MSD, and MS/MSD are required, then the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD is required, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the resolution. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.2.2.1, the Contractor shall contact SMO. SMO will contact the Region to determine which samples should have an MS/MSD performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If this procedure is not followed, the Contractor will not be paid for MS/MSD analysis performed at a greater frequency than required by the contract.

12.2.2.6 When a Contractor receives **only** Performance Evaluation (PE) sample(s), no MS/MSD shall be performed within that SDG.

12.2.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the requested MS/MSD analysis when the Region did not designate samples to be used for this purpose.

12.2.3 Procedure for Preparing MS/MSD

12.2.3.1 If requested, add 10 µL of the matrix spiking solution (Section 7.2.2.5) to each of the 25 mL aliquots of the sample chosen for spiking. Process the samples according to Section 10.1. Disregarding any dilutions, this is equivalent to a concentration of 5 µg/L of each Matrix Spike compound.

12.2.3.2 MS/MSD samples must be analyzed at the same concentration as the most concentrated aliquot for which the original sample results

will be reported. Sample dilutions must be performed in accordance with Section 10.2.10. Do **not** further dilute MS/MSD samples to get **either** spiked **or** non-spiked analytes within calibration range.

12.2.4 Calculations for MS/MSD

12.2.4.1 Calculate the concentrations of the Matrix Spike compounds using the same equations as used for target compounds (Equation 6). Calculate the recovery of each Matrix Spike compound as follows:

EQ. 9 Matrix Spike Recovery Calculation

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spiked Sample Result.

SR = Sample Result.

SA = Spike Added.

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each compound in the MS/MSD as follows:

EQ. 10 Relative Percent Difference Calculation

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where,

MSR = Matrix Spike Recovery.

MSDR = Matrix Spike Duplicate Recovery.

12.2.5 Technical Acceptance Criteria for MS/MSD

12.2.5.1 If requested, all MS/MSD must be prepared and analyzed at the frequency described in Section 12.2.2. All MS/MSDs must be analyzed on a GC/MS system meeting the BFB, initial calibration, and continuing calibration verification technical acceptance criteria, and the blank technical acceptance criteria.

12.2.5.2 The MS/MSD must be analyzed within the contract holding time.

12.2.5.3 The RT shift for each of the internal standards in the MS/MSD must be within ±0.33 minutes (20 seconds) of its RT in the most recent opening CCV standard analysis.

12.2.5.4 The limits for Matrix Spike compound recovery and RPD are given in Table 6. As these limits are only advisory, no further action by the laboratory is required. However, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from USEPA.

12.2.6 Corrective Action for MS/MSD

Any MS/MSD that does not meet the technical acceptance criteria in Sections 12.2.5.1 and 12.2.5.3 must be reanalyzed at no additional cost to USEPA.

12.3 Method Detection Limit (MDL) Determination

12.3.1 Before any field samples are analyzed under the contract, the MDL for each volatile target compound shall be determined on each instrument used for analysis. MDL determination is level-specific (i.e., the MDL shall be determined for trace and trace SIM levels). The MDLs must be verified annually thereafter (see Section 12.3.2 for MDL verification procedures), until the contract expires or is terminated, or after major instrument maintenance. Major instrument maintenance includes, but is not limited to, cleaning or replacement of the mass spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), electron multiplier (or similar device), GC column, and replacement or overhaul of the purge-and-trap device.

12.3.2 To determine the MDLs, the Contractor shall run an MDL study following the procedures specified in 40 CFR Part 136. The Contractor shall analyze the MDL samples on each instrument used for field sample analyses. MDL verification is achieved by analyzing a single reagent water blank spiked with each volatile target compound at a concentration equal to 1-4 times the analytically determined MDL. Each target compound must produce a response and meet the criteria in Section 11.1. The resulting mass spectra of each target compound must meet the qualitative identification criteria outlined in Sections 11.1.1 through 11.1.4.3.

12.3.3 The determined concentration of the MDL must be less than the CRQL.

12.3.4 All documentation for the MDL studies shall be maintained at the laboratory and provided to USEPA upon written request.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, USEPA recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington D.C., 20036, (202) 872-4386.

15.0 WASTE MANAGEMENT

USEPA requires that laboratory waste management practices be consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

US Environmental Protection Agency. Purge-and-Trap for Aqueous Samples. Method 5030C. Revision 3. May 2003.

US Environmental Protection Agency. Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). Method 8260B. Revision 2. December 1996.

US Environmental Protection Agency. Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry. Method 524.2. August 1992.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

4-bromofluorobenzene Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	15.0 - 40.0% of mass 95
75	30.0 - 80.0% of mass 95
95	base peak, 100% Relative Abundance
96	5.0 - 9.0% of mass 95 (see NOTE)
173	less than 2.0% of mass 174
174	50.0 - 120% of mass 95
175	5.0 - 9.0% of mass 174
176	95.0 - 101% of mass 174
177	5.0 - 9.0% of mass 176

NOTE: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95.

Table 2

Technical Acceptance Criteria for Initial and Opening Continuing Calibration Verification for Trace Volatile Organic Compounds

Volatile Compound	Minimum RRF[1]	Maximum %RSD	Maximum %Diff[1]
Dichlorodifluoromethane	0.010	40.0	±40.0
Chloromethane	0.010	40.0	±40.0
Vinyl chloride	0.100	30.0	±30.0
Bromomethane	0.100	30.0	±30.0
Chloroethane	0.010	40.0	±40.0
Trichlorofluoromethane	0.010	40.0	±40.0
1,1-Dichloroethene	0.100	30.0	±30.0
1,1,2-Trichloro-1,2,2-trifluoroethane	0.010	40.0	±40.0
Acetone	0.010	40.0	±40.0
Carbon disulfide	0.010	40.0	±40.0
Methyl acetate	0.010	40.0	±40.0
Methylene chloride	0.010	40.0	±40.0
trans-1,2-Dichloroethene	0.010	40.0	±40.0
Methyl tert-butyl ether	0.010	40.0	±40.0
1,1-Dichloroethane	0.200	30.0	±30.0
cis-1,2-Dichloroethene	0.010	40.0	±40.0
2-Butanone	0.010	40.0	±40.0
Bromochloromethane	0.050	30.0	±30.0
Chloroform	0.200	30.0	±30.0
1,1,1-Trichloroethane	0.100	30.0	±30.0
Cyclohexane	0.010	40.0	±40.0
Carbon tetrachloride	0.100	30.0	±30.0
Benzene	0.400	30.0	±30.0
1,2-Dichloroethane	0.100	30.0	±30.0
1,4-Dioxane	0.0050	50.0	±50.0
Trichloroethene	0.300	30.0	±30.0
Methylcyclohexane	0.010	40.0	±40.0
1,2-Dichloropropane	0.010	40.0	±40.0
Bromodichloromethane	0.200	30.0	±30.0
cis-1,3-Dichloropropene	0.200	30.0	±30.0
4-Methyl-2-pentanone	0.010	40.0	±40.0
Toluene	0.400	30.0	±30.0
trans-1,3-Dichloropropene	0.100	30.0	±30.0
1,1,2-Trichloroethane	0.100	30.0	±30.0
Tetrachloroethene	0.100	30.0	±30.0
2-Hexanone	0.010	40.0	±40.0
Dibromochloromethane	0.100	30.0	±30.0
1,2-Dibromoethane	0.010	40.0	±40.0
Chlorobenzene	0.500	30.0	±30.0
Ethylbenzene	0.100	30.0	±30.0
m,p-Xylene	0.300	30.0	±30.0
o-Xylene	0.300	30.0	±30.0
Styrene	0.300	30.0	±30.0
Bromoform	0.050	30.0	±30.0

Table 2

Technical Acceptance Criteria for Initial and Opening Continuing Calibration Verification for Trace Volatile Organic Compounds (Con't)

Volatile Compound	Minimum RRF[1]	Maximum %RSD	Maximum %Diff[1]
Isopropylbenzene	0.010	40.0	±40.0
1,1,2,2-Tetrachloroethane	0.100	30.0	±30.0
1,3-Dichlorobenzene	0.400	30.0	±30.0
1,4-Dichlorobenzene	0.400	30.0	±30.0
1,2-Dichlorobenzene	0.400	30.0	±30.0
1,2-Dibromo-3-chloropropane	0.010	40.0	±40.0
1,2,4-Trichlorobenzene	0.200	30.0	±30.0
1,2,3-Trichlorobenzene	0.200	30.0	±30.0
Deuterated Monitoring Compounds			
Vinyl chloride-d_3	0.010	30.0	±30.0
Chloroethane-d_5	0.010	40.0	±40.0
1,1-Dichloroethene-d_2	0.010	30.0	±30.0
2-Butanone-d_5	0.010	40.0	±40.0
Chloroform-d	0.010	30.0	±30.0
1,2-Dichloroethane-d_4	0.010	30.0	±30.0
Benzene-d_6	0.010	30.0	±30.0
1,2-Dichloropropane-d_6	0.010	40.0	±40.0
Toluene-d_8	0.010	30.0	±30.0
trans-1,3-Dichloropropene-d_4	0.010	30.0	±30.0
2-Hexanone-d_5	0.010	40.0	±40.0
1,4-Dioxane-d_8	0.0050	50.0	±50.0
1,1,2,2-Tetrachloroethane-d_2	0.010	30.0	±30.0
1,2-Dichlorobenzene-d_4	0.010	30.0	±30.0

[1]For a closing CCV, all target compounds and DMCs must meet a minimum RRF of 0.010 and a maximum percent difference of ±50.0, except for 1,4-dioxane and 1,4-dioxane-d_8, which must meet a minimum RRF of 0.0050 and a maximum Percent Difference of ±50.0.

Table 3

Trace Volatile Target Compounds and Deuterated Monitoring Compounds with Corresponding Internal Standards for Quantitation

1,4-Difluorobenzene (IS)	Chlorobenzene-d_5 (IS)	1,4-Dichlorobenzene-d_4 (IS)
Dichlorodifluoromethane	1,1,1-Trichloroethane	Bromoform
Chloromethane	Cyclohexane	1,3-Dichlorobenzene
Vinyl chloride	Carbon tetrachloride	1,4-Dichlorobenzene
Bromomethane	Benzene	1,2-Dichlorobenzene
Chloroethane	Trichloroethene	1,2-Dibromo-3-chloropropane
Trichlorofluoromethane	Methylcyclohexane	1,2,4-Trichlorobenzene
1,1-Dichloroethene	1,2-Dichloropropane	1,2,3-Trichlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	Bromodichloromethane	1,2-Dichlorobenzene-d_4 (DMC)
Acetone	cis-1,3-Dichloropropene	
Carbon disulfide	4-Methyl-2-pentanone	
Methyl acetate	Toluene	
Bromochloromethane	trans-1,3-Dichloropropene	
Methylene chloride	1,1,2-Trichloroethane	
trans-1,2-Dichloroethene	Tetrachloroethene	
Methyl tert-butyl ether	2-Hexanone	
1,1-Dichloroethane	Dibromochloromethane	
cis-1,2-Dichloroethene	1,2-Dibromoethane	
2-Butanone	Chlorobenzene	
Chloroform	Ethylbenzene	
1,2-Dichloroethane	m,p-Xylene	
1,4-Dioxane	o-Xylene	
Vinyl chloride-d_3 (DMC)	Styrene	
Chloroethane-d_5 (DMC)	Isopropylbenzene	
1,1-Dichloroethene-d_2 (DMC)	1,1,2,2-Tetrachloroethane	
2-Butanone-d_5 (DMC)	Benzene-d_6 (DMC)	
Chloroform-d (DMC)	1,2-Dichloropropane-d_6 (DMC)	
1,2-Dichloroethane-d_4 (DMC)	trans-1,3-Dichloropropene-d_4 (DMC)	
1,4-Dioxane-d_8 (DMC)	Toluene-d_8 (DMC)	
	2-Hexanone-d_5 (DMC)	
	1,1,2,2-Tetrachloroethane-d_2 (DMC)	

Table 4

Characteristic Ions for Trace Volatile Target Compounds

Target Compound	Primary Quantitation Ion	Secondary Ion(s)
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl chloride	62	64
Bromomethane	94	96
Chloroethane	64	66
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61, 63
1,1,2-Trichloro-1,2,2-trifluoroethane	101	85, 151
Acetone	43	58
Carbon disulfide	76	78
Methyl acetate	43	74
Methylene chloride	84	49, 86
trans-1,2-Dichloroethene	96	61, 98
Methyl tert-butyl ether	73	43, 57
1,1-Dichloroethane	63	65, 83
cis-1,2-Dichloroethene	96	61, 98
2-Butanone	43*	72
Chloroform	83	85
Bromochloromethane	128	49, 130, 51
1,1,1-Trichloroethane	97	99, 61
Cyclohexane	56	69, 84
Carbon tetrachloride	117	119
Benzene	78	-
1,2-Dichloroethane	62	98
1,4-Dioxane	88	43,58
Trichloroethene	95	97, 132, 130
Methylcyclohexane	83	55, 98
1,2-Dichloropropane	63	112
Bromodichloromethane	83	85, 127
cis-1,3-Dichloropropene	75	77
4-Methyl-2-pentanone	43	58, 100
Toluene	91	92
trans-1,3-Dichloropropene	75	77
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Tetrachloroethene	164	129, 131, 166
2-Hexanone	43	58, 57, 100
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Chlorobenzene	112	77, 114
Ethylbenzene	91	106
m,p-Xylene	106	91
o-Xylene	106	91
Styrene	104	78

*m/z 43 is used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

Table 4

Characteristic Ions for Trace Volatile Target Compounds (Con't)

Analyte	Primary Quantitation Ion	Secondary Ion(s)
Bromoform	173	175, 254
Isopropylbenzene	105	120, 77
1,1,2,2-Tetrachloroethane	83	85, 131
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene	146	111, 148
1,2-Dibromo-3-chloropropane	75	157, 155
1,2,4-Trichlorobenzene	180	182, 145
1,2,3-Trichlorobenzene	180	182, 145
Deuterated Monitoring Compounds		
Vinyl chloride-d_3	65	67
Chloroethane-d_5	69	71, 51
1,1-Dichloroethene-d_2	63	98, 65
2-Butanone-d_5	46	77
Chloroform-d	84	86, 47, 49
1,2-Dichloroethane-d_4	65	67, 51
Benzene-d_6	84	82, 54, 52
1,2-Dichloropropane-d_6	67	65, 46, 42
Toluene-d_8	98	100, 42
trans-1,3-Dichloropropene-d_4	79	81, 42
2-Hexanone-d_5	63	46
1,4-Dioxane-d_8	96	51, 66
1,1,2,2-Tetrachloroethane-d_2	84	86
1,2-Dichlorobenzene-d_4	152	150
Internal Standards		
1,4-Dichlorobenzene-d_4	152	115, 150
1,4-Difluorobenzene	114	63, 88
Chlorobenzene-d_5	117	82, 119

Table 5

Deuterated Monitoring Compound Recovery Limits

Compound	Percent Recovery Limits
Vinyl chloride-d_3	65-131
Chloroethane-d_5	71-131
1,1-Dichloroethene-d_2	55-104
2-Butanone-d_5	49-155
Chloroform-d	78-121
1,2-Dichloroethane-d_4	78-129
Benzene-d_6	77-124
1,2-Dichloropropane-d_6	79-124
Toluene-d_8	77-121
trans-1,3-Dichloropropene-d_4	73-121
2-Hexanone-d_5	28-135
1,4-Dioxane-d_8	50-150
1,1,2,2-Tetrachloroethane-d_2	73-125
1,2-Dichlorobenzene-d_4	80-131

NOTE: The recovery limits for any of the compounds listed above may be expanded at any time during the period of performance if USEPA determines that the limits are too restrictive. The recovery limits for 1,4-dioxane-d_8 are advisory.

Table 6

Matrix Spike Recovery and Relative Percent Difference Limits

Compound	Percent Recovery	RPD
1,1-Dichloroethene	61-145	0-14
Benzene	76-127	0-11
Trichloroethene	71-120	0-14
Toluene	76-125	0-13
Chlorobenzene	75-130	0-13

Table 7

Volatile Deuterated Monitoring Compounds and the Associated Target Compounds

Chloroethane-d_5 (DMC)	**1,2-Dichloropropane-d_6 (DMC)**	**1,2-Dichlorobenzene-d_4 (DMC)**
Dichlorodifluoromethane	Cyclohexane	Chlorobenzene
Chloromethane	Methylcyclohexane	1,3-Dichlorobenzene
Bromomethane	1,2-Dichloropropane	1,4-Dichlorobenzene
Chloroethane	Bromodichloromethane	1,2-Dichlorobenzene
Carbon disulfide		1,2,4-Trichlorobenzene
		1,2,3-Trichlorobenzene

1,4-Dioxane-d_8 (DMC)	**trans-1,3-Dichloropropene-d_4 (DMC)**	**Chloroform-d (DMC)**
1,4-Dioxane	cis-1,3-Dichloropropene	1,1-Dichloroethane
	trans-1,3-Dichloropropene	Bromochloromethane
	1,1,2-Trichloroethane	Chloroform
		Dibromochloromethane
		Bromoform

2-Butanone-d_5 (DMC)	**1,1-Dichloroethene-d_2 (DMC)**	**2-Hexanone-d_5 (DMC)**
Acetone	trans-1,2-Dichloroethene	4-Methyl-2-pentanone
2-Butanone	cis-1,2-Dichloroethene	2-Hexanone

Vinyl chloride-d_3 (DMC)	**Benzene-d_6 (DMC)**	**1,1,2,2-Tetrachloroethane-d_2 (DMC)**
Vinyl chloride	Benzene	1,1,2,2-Tetrachloroethane
		1,2-Dibromo-3-chloropropane

1,2-Dichloroethane-d_4 (DMC)	**Toluene-d_8 (DMC)**
Trichlorofluoromethane	Trichloroethene
1,1-Dichloroethene	Toluene
1,1,2-Trichloro-1,2,2-trifluoroethane	Tetrachloroethene
Methyl acetate	Ethylbenzene
Methylene chloride	o-Xylene
Methyl tert-butyl ether	m,p-Xylene
1,1,1-Trichloroethane	Styrene
Carbon tetrachloride	Isopropylbenzene
1,2-Dibromoethane	
1,2-Dichloroethane	

Table 8

Volatile Deuterated Monitoring Compounds and the Associated Target Compounds for Selected Ion Monitoring Analysis

1,4-Dioxane-d_8 (DMC)	**1,1,2,2-Tetrachloroethane-d_2 (DMC)**	**1,2-Dichloroethane-d_4 (DMC)**
1,4-Dioxane	1,2-Dibromo-3-chloropropane	1,2-Dibromoethane

EPA/625/R-96/010b

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-15

Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

Center for Environmental Research Information
Office of Research and Development
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Method TO-15
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DISCLAIMER

METHOD TO-15

Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

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METHOD TO-15

Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

1. Scope

1.1 This method documents sampling and analytical procedures for the measurement of subsets of the 97 volatile organic compounds (VOCs) that are included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. VOCs are defined here as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25°C and 760 mm Hg. Table 1 is the list of the target VOCs along with their CAS number, boiling point, vapor pressure and an indication of their membership in both the list of VOCs covered by Compendium Method TO-14A (1) and the list of VOCs in EPA's Contract Laboratory Program (CLP) document entitled: *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites (2)*.

Many of these compounds have been tested for stability in concentration when stored in specially-prepared canisters (see Section 8) under conditions typical of those encountered in routine ambient air analysis. The stability of these compounds under all possible conditions is not known. However, a model to predict compound losses due to physical adsorption of VOCs on canister walls and to dissolution of VOCs in water condensed in the canisters has been developed (3). Losses due to physical adsorption require only the establishment of equilibrium between the condensed and gas phases and are generally considered short term losses, (i.e., losses occurring over minutes to hours). Losses due to chemical reactions of the VOCs with cocollected ozone or other gas phase species also account for some short term losses. Chemical reactions between VOCs and substances inside the canister are generally assumed to cause the gradual decrease of concentration over time (i.e., long term losses over days to weeks). Loss mechanisms such as aqueous hydrolysis and biological degradation (4) also exist. No models are currently known to be available to estimate and characterize all these potential losses, although a number of experimental observations are referenced in Section 8. Some of the VOCs listed in Title III have short atmospheric lifetimes and may not be present except near sources.

1.2 This method applies to ambient concentrations of VOCs above 0.5 ppbv and typically requires VOC enrichment by concentrating up to one liter of a sample volume. The VOC concentration range for ambient air in many cases includes the concentration at which continuous exposure over a lifetime is estimated to constitute a 10^{-6} or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at 10^{-6} risk concentrations, the total risk may be significantly greater.

1.3 This method applies under most conditions encountered in sampling of ambient air into canisters. However, the composition of a gas mixture in a canister, under unique or unusual conditions, will change so that the sample is known not to be a true representation of the ambient air from which it was taken. For example, low humidity conditions in the sample may lead to losses of certain VOCs on the canister walls, losses that would not happen if the humidity were higher. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water-soluble compounds. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence an absolute storage stability cannot be assigned to a specific gas. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs can be recovered from canisters near their original concentrations after storage times of up to thirty days (see Section 8).

1.4 Use of the Compendium Method TO-15 for many of the VOCs listed in Table 1 is likely to present two difficulties: (1) what calibration standard to use for establishing a basis for testing and quantitation, and (2) how

to obtain an audit standard. In certain cases a chemical similarity exists between a thoroughly tested compound and others on the Title III list. In this case, what works for one is likely to work for the other in terms of making standards. However, this is not always the case and some compound standards will be troublesome. The reader is referred to the Section 9.2 on standards for guidance. Calibration of compounds such as formaldehyde, diazomethane, and many of the others represents a challenge.

1.5 Compendium Method TO-15 should be considered for use when a subset of the 97 Title III VOCs constitute the target list. Typical situations involve ambient air testing associated with the permitting procedures for emission sources. In this case sampling and analysis of VOCs is performed to determine the impact of dispersing source emissions in the surrounding areas. Other important applications are prevalence and trend monitoring for hazardous VOCs in urban areas and risk assessments downwind of industrialized or source-impacted areas.

1.6 Solid adsorbents can be used in lieu of canisters for sampling of VOCs, provided the solid adsorbent packings, usually multisorbent packings in metal or glass tubes, can meet the performance criteria specified in Compendium Method TO-17 which specifically addresses the use of multisorbent packings. The two sample collection techniques are different but become the same upon movement of the sample from the collection medium (canister or multisorbent tubes) onto the sample concentrator. Sample collection directly from the atmosphere by automated gas chromatographs can be used in lieu of collection in canisters or on solid adsorbents.

2. Summary of Method

2.1 The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister. Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

2.2 After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to the laboratory for analysis.

2.3 Upon receipt at the laboratory, the canister tag data is recorded and the canister is stored until analysis. Storage times of up to thirty days have been demonstrated for many of the VOCs (5).

2.4 To analyze the sample, a known volume of sample is directed from the canister through a solid multisorbent concentrator. A portion of the water vapor in the sample breaks through the concentrator during sampling, to a degree depending on the multisorbent composition, duration of sampling, and other factors. Water content of the sample can be further reduced by dry purging the concentrator with helium while retaining target compounds. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The sample is then released by thermal desorption and carried onto a gas chromatographic column for separation.

As a simple alternative to the multisorbent/dry purge water management technique, the amount of water vapor in the sample can be reduced below any threshold for affecting the proper operation of the analytical system by

reducing the sample size. For example, a small sample can be concentrated on a cold trap and released directly to the gas chromatographic column. The reduction in sample volume may require an enhancement of detector sensitivity.

Other water management approaches are also acceptable as long as their use does not compromise the attainment of the performance criteria listed in Section 11. A listing of some commercial water management systems is provided in Appendix A. One of the alternative ways to dry the sample is to separate VOCs from condensate on a low temperature trap by heating and purging the trap.

2.5 The analytical strategy for Compendium Method TO-15 involves using a high resolution gas chromatograph (GC) coupled to a mass spectrometer. If the mass spectrometer is a linear quadrupole system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN mode) or by monitoring select ion monitoring mode (SIM) of compounds on the target list. If the mass spectrometer is based on a standard ion trap design, only a scanning mode is used (note however, that the Selected Ion Storage (SIS) mode for the ion trap has features of the SIM mode). Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound. This establishes the compound concentration that exists in the sample.

Mass spectrometry is considered a more definitive identification technique than single specific detectors such as flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), or a multidetector arrangement of these (see discussion in Compendium Method TO-14A). The use of both gas chromatographic retention time and the generally unique mass fragmentation patterns reduce the chances for misidentification. If the technique is supported by a comprehensive mass spectral database and a knowledgeable operator, then the correct identification and quantification of VOCs is further enhanced.

3. Significance

3.1 Compendium Method TO-15 is significant in that it extends the Compendium Method TO-14A description for using canister-based sampling and gas chromatographic analysis in the following ways:

- Compendium Method TO-15 incorporates a multisorbent/dry purge technique or equivalent (see Appendix A) for water management thereby addressing a more extensive set of compounds (the VOCs mentioned in Title III of the CAAA of 1990) than addressed by Compendium Method TO-14A. Compendium Method TO-14A approach to water management alters the structure or reduces the sample stream concentration of some VOCs, especially water-soluble VOCs.
- Compendium Method TO-15 uses the GC/MS technique as the only means to identify and quantitate target compounds. The GC/MS approach provides a more scientifically-defensible detection scheme which is generally more desirable than the use of single or even multiple specific detectors.
- In addition, Compendium Method TO-15 establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent sampling and analytical equipment. There are several new and viable commercial approaches for water management as noted in Appendix A of this method on which to base a VOC monitoring technique as well as other approaches to sampling (i.e., autoGCs and solid

adsorbents) that are often used. This method lists performance criteria that these alternatives must meet to be acceptable alternatives for monitoring ambient VOCs.
- Finally, Compendium Method TO-15 includes enhanced provisions for inherent quality control. The method uses internal analytical standards and frequent verification of analytical system performance to assure control of the analytical system. This more formal and better documented approach to quality control guarantees a higher percentage of good data.

3.2 With these features, Compendium Method TO-15 is a more general yet better defined method for VOCs than Compendium Method TO-14A. As such, the method can be applied with a higher confidence to reduce the uncertainty in risk assessments in environments where the hazardous volatile gases listed in the Title III of the Clean Air Act Amendments of 1990 are being monitored. An emphasis on risk assessments for human health and effects on the ecology is a current goal for the U.S. EPA.

4. Applicable Documents

4.1 ASTM Standards

- **Method D1356** *Definitions of Terms Relating to Atmospheric Sampling and Analysis*.
- **Method E260** *Recommended Practice for General Gas Chromatography Procedures*.
- **Method E355** *Practice for Gas Chromatography Terms and Relationships*.
- **Method D5466** *Standard Test Method of Determination of Volatile Organic Compounds in Atmospheres (Canister Sampling Methodology)*.

4.2 EPA Documents

- *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II*, U. S. Environmental Protection Agency, EPA-600/R-94-038b, May 1994.
- *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA-600/4-83-027, June 1983.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-14, Second Supplement*, U. S. Environmental Protection Agency, EPA-600/4-89-018, March 1989.
- *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites*, U. S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C., Draft Report, June 1990.
- *Clean Air Act Amendments of 1990*, U. S. Congress, Washington, D.C., November 1990.

5. Definitions

[Note: Definitions used in this document and any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, E260, and E355. Aside from the definitions given below, all pertinent abbreviations and symbols are defined within this document at point of use.]

5.1 Gauge Pressure—pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or psi. Zero gauge pressure is equal to atmospheric (barometric) pressure.

5.2 Absolute Pressure—pressure measured with reference to absolute zero pressure, usually expressed in units of kPa, or psi.

5.3 Cryogen—a refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Typical cryogens are liquid nitrogen (bp -195.8°C), liquid argon (bp -185.7°C), and liquid CO_2 (bp -79.5°C).

5.4 Dynamic Calibration—calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system from a manifold through which the gas standards are flowing.

5.5 Dynamic Dilution—means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with humidified zero air in a manifold so that a flowing stream of calibration mixture is available at the inlet of the analytical system.

5.6 MS-SCAN—mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

5.7 MS-SIM—mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

5.8 Qualitative Accuracy—the degree of measurement accuracy required to correctly identify compounds with an analytical system.

5.9 Quantitative Accuracy—the degree of measurement accuracy required to correctly measure the concentration of an identified compound with an analytical system with known uncertainty.

5.10 Replicate Precision—precision determined from two canisters filled from the same air mass over the same time period and determined as the absolute value of the difference between the analyses of canisters divided by their average value and expressed as a percentage (see Section 11 for performance criteria for replicate precision).

5.11 Duplicate Precision—precision determined from the analysis of two samples taken from the same canister. The duplicate precision is determined as the absolute value of the difference between the canister analyses divided by their average value and expressed as a percentage.

5.12 Audit Accuracy—the difference between the analysis of a sample provided in an audit canister and the nominal value as determined by the audit authority, divided by the audit value and expressed as a percentage (see Section 11 for performance criteria for audit accuracy).

6. Interferences and Contamination

6.1 Very volatile compounds, such as chloromethane and vinyl chloride can display peak broadening and co-elution with other species if the compounds are not delivered to the GC column in a small volume of carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing trap or at the head of the gas chromatographic column, mitigates this problem.

6.2 Interferences in canister samples may result from improper use or from contamination of: (1) the canisters due to poor manufacturing practices, (2) the canister cleaning apparatus, and (3) the sampling or analytical system. Attention to the following details will help to minimize the possibility of contamination of canisters.

6.2.1 Canisters should be manufactured using high quality welding and cleaning techniques, and new canisters should be filled with humidified zero air and then analyzed, after "aging" for 24 hours, to determine cleanliness. The cleaning apparatus, sampling system, and analytical system should be assembled of clean, high quality components and each system should be shown to be free of contamination.

6.2.2 Canisters should be stored in a contaminant-free location and should be capped tightly during shipment to prevent leakage and minimize any compromise of the sample.

6.2.3 Impurities in the calibration dilution gas (if applicable) and carrier gas, organic compounds out-gassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with Buna-N rubber components must be avoided.

6.2.4 Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses. Whenever a high concentration (>25 ppbv of a trace species) sample is encountered, it should be followed by an analysis of humid zero air to check for carry-over contamination.

6.2.5 In cases when solid sorbents are used to concentrate the sample prior to analysis, the sorbents should be tested to identify artifact formation (see Compendium Method TO-17 for more information on artifacts).

7. Apparatus and Reagents

[Note: Compendium Method To-14A list more specific requirements for sampling and analysis apparatus which may be of help in identifying options. The listings below are generic.]

7.1 Sampling Apparatus

[Note: Subatmospheric pressure and pressurized canister sampling systems are commercially available and have been used as part of U.S. Environmental Protection Agency's Toxic Air Monitoring Stations (TAMS), Urban Air Toxic Monitoring Program (UATMP), the non-methane organic compound (NMOC) sampling and analysis program, and the Photochemical Assessment Monitoring Stations (PAMS).]

7.1.1 Subatmospheric Pressure (see Figure 1, without metal bellows type pump).

7.1.1.1 Sampling Inlet Line. Stainless steel tubing to connect the sampler to the sample inlet.

7.1.1.2 Sample Canister. Leak-free stainless steel pressure vessels of desired volume (e.g., 6 L), with valve and specially prepared interior surfaces (see Appendix B for a listing of known manufacturers/resellers of canisters).

7.1.1.3 Stainless Steel Vacuum/Pressure Gauges. Two types are required, one capable of measuring vacuum (–100 to 0 kPa or 0 to - 30 in Hg) and pressure (0–206 kPa or 0–30 psig) in the sampling system and a second type (for checking the vacuum of canisters during cleaning) capable of measuring at 0.05 mm Hg (see Appendix B) within 20%. Gauges should be tested clean and leak tight.

7.1.1.4 Electronic Mass Flow Controller. Capable of maintaining a constant flow rate (± 10%) over a sampling period of up to 24 hours and under conditions of changing temperature (20–40°C) and humidity.

7.1.1.5 Particulate Matter Filter. 2-μm sintered stainless steel in-line filter.

7.1.1.6 Electronic Timer. For unattended sample collection.

7.1.1.7 Solenoid Valve. Electrically-operated, bi-stable solenoid valve with Viton® seat and O-rings. A Skinner Magnelatch valve is used for purposes of illustration in the text (see Figure 2).

7.1.1.8 Chromatographic Grade Stainless Steel Tubing and Fittings. For interconnections. All such materials in contact with sample, analyte, and support gases prior to analysis should be chromatographic grade stainless steel or equivalent.

7.1.1.9 Thermostatically Controlled Heater. To maintain above ambient temperature inside insulated sampler enclosure.

7.1.1.10 Heater Thermostat. Automatically regulates heater temperature.

7.1.1.11 Fan. For cooling sampling system.

7.1.1.12 Fan Thermostat. Automatically regulates fan operation.

7.1.1.13 Maximum-Minimum Thermometer. Records highest and lowest temperatures during sampling period.

7.1.1.14 Stainless Steel Shut-off Valve. Leak free, for vacuum/pressure gauge.

7.1.1.15 Auxiliary Vacuum Pump. Continuously draws air through the inlet manifold at 10 L/min. or higher flow rate. Sample is extracted from the manifold at a lower rate, and excess air is exhausted.

[Note: The use of higher inlet flow rates dilutes any contamination present in the inlet and reduces the possibility of sample contamination as a result of contact with active adsorption sites on inlet walls.]

7.1.1.16 Elapsed Time Meter. Measures duration of sampling.

7.1.1.17 Optional Fixed Orifice, Capillary, or Adjustable Micrometering Valve. May be used in lieu of the electronic flow controller for grab samples or short duration time-integrated samples. Usually appropriate only in situations where screening samples are taken to assess future sampling activity.

7.1.2 Pressurized (see Figure 1 with metal bellows type pump and Figure 3).

7.1.2.1 Sample Pump. Stainless steel, metal bellows type, capable of 2 atmospheres output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds.

[Note: An alternative sampling system has been developed by Dr. R. Rasmussen, The Oregon Graduate Institute of Science and Technology, 20000 N.W. Walker Rd., Beaverton, Oregon 97006, 503-690-1077, and is illustrated in Figure 3. This flow system uses, in order, a pump, a mechanical flow regulator, and a mechanical compensation flow restrictive device. In this configuration the pump is purged with a large sample flow, thereby eliminating the need for an auxiliary vacuum pump to flush the sample inlet.]

7.1.2.2 Other Supporting Materials. All other components of the pressurized sampling system are similar to components discussed in Sections 7.1.1.1 through 7.1.1.17.

7.2 Analytical Apparatus

7.2.1 Sampling/Concentrator System (many commercial alternatives are available).

7.2.1.1 Electronic Mass Flow Controllers. Used to maintain constant flow (for purge gas, carrier gas and sample gas) and to provide an analog output to monitor flow anomalies.

7.2.1.2 Vacuum Pump. General purpose laboratory pump, capable of reducing the downstream pressure of the flow controller to provide the pressure differential necessary to maintain controlled flow rates of sample air.

7.2.1.3 Stainless Steel Tubing and Stainless Steel Fittings. Coated with fused silica to minimize active adsorption sites.

7.2.1.4 Stainless Steel Cylinder Pressure Regulators. Standard, two-stage cylinder regulators with pressure gauges.

7.2.1.5 Gas Purifiers. Used to remove organic impurities and moisture from gas streams.

7.2.1.6 Six-port Gas Chromatographic Valve. For routing sample and carrier gas flows.

7.2.1.7 Multisorbent Concentrator. Solid adsorbent packing with various retentive properties for adsorbing trace gases are commercially available from several sources. The packing contains more than one type of adsorbent packed in series.

7.2.1.7.1A pre-packed adsorbent trap (Supelco 2-0321) containing 200 mg Carbopack B (60/80 mesh) and 50 mg Carbosieve S-III (60/80 mesh) has been found to retain VOCs and allow some water vapor to pass through (6). The addition of a dry purging step allows for further water removal from the adsorbent trap. The steps constituting the dry purge technique that are normally used with multisorbent traps are illustrated in Figure 4. The optimum trapping and dry purging procedure for the Supelco trap consists of a sample volume of 320 mL and a dry nitrogen purge of 1300 mL. Sample trapping and drying is carried out at 25°C. The trap is back-flushed with helium and heated to 220°C to transfer material onto the GC column. A trap bake-out at 260°C for 5 minutes is conducted after each run.

7.2.1.7.2 An example of the effectiveness of dry purging is shown in Figure 5. The multisorbent used in this case is Tenax/Ambersorb 340/Charcoal (7). Approximately 20% of the initial water content in the sample remains after sampling 500 mL of air. The detector response to water vapor (hydrogen atoms detected by atomic emission detection) is plotted versus purge gas volume. Additional water reduction by a factor of 8 is indicated at temperatures of 45°C or higher. Still further water reduction is possible using a two-stage concentration/dryer system.

7.2.1.8 Cryogenic Concentrator. Complete units are commercially available from several vendor sources. The characteristics of the latest concentrators include a rapid, "ballistic" heating of the concentrator to release any trapped VOCs into a small carrier gas volume. This facilitates the separation of compounds on the gas chromatographic column.

7.2.2 Gas Chromatographic/Mass Spectrometric (GC/MS) System.

7.2.2.1 Gas Chromatograph. The gas chromatographic (GC) system must be capable of temperature programming. The column oven can be cooled to subambient temperature (e.g., -50°C) at the start of the gas chromatographic run to effect a resolution of the very volatile organic compounds. In other designs, the rate of release of compounds from the focusing trap in a two stage system obviates the need for retrapping of compounds on the column. The system must include or be interfaced to a concentrator and have all required accessories including analytical columns and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with Buna-N rubber components must not be used.

7.2.2.2 Chromatographic Columns. 100% methyl silicone or 5% phenyl, 95% methyl silicone fused silica capillary columns of 0.25- to 0.53-mm I.D. of varying lengths are recommended for separation of many of the possible subsets of target compounds involving nonpolar compounds. However, considering the diversity of the target list, the choice is left to the operator subject to the performance standards given in Section 11.

7.2.2.3 Mass Spectrometer. Either a linear quadrupole or ion trap mass spectrometer can be used as long as it is capable of scanning from 35 to 300 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 50 ng or less of p-bromofluorobenzene (BFB) is analyzed.

7.2.2.3.1Linear Quadrupole Technology. A simplified diagram of the heart of the quadrupole mass spectrometer is shown in Figure 6. The quadrupole consists of a parallel set of four rod electrodes mounted in a square configuration. The field within the analyzer is created by coupling opposite pairs of rods together and applying radiofrequency (RF) and direct current (DC) potentials between the pairs of rods. Ions created in the ion source from the reaction of column eluates with electrons from the electron source are moved through the

parallel array of rods under the influence of the generated field. Ions which are successfully transmitted through the quadrupole are said to possess stable trajectories and are subsequently recorded with the detection system. When the DC potential is zero, a wide band of m/z values is transmitted through the quadrupole. This "RF only" mode is referred to as the "total-ion" mode. In this mode, the quadrupole acts as a strong focusing lens analogous to a high pass filter. The amplitude of the RF determines the low mass cutoff. A mass spectrum is generated by scanning the DC and RF voltages using a fixed DC/RF ratio and a constant drive frequency or by scanning the frequency and holding the DC and RF constant. With the quadrupole system only 0.1 to 0.2 percent of the ions formed in the ion source actually reach the detector.

7.2.2.3.2Ion Trap Technology. An ion-trap mass spectrometer consists of a chamber formed between two metal surfaces in the shape of a hyperboloid of one sheet (ring electrode) and a hyperboloid of two sheets (the two end-cap electrodes). Ions are created within the chamber by electron impact from an electron beam admitted through a small aperture in one of the end caps. Radio frequency (RF) (and sometimes direct current voltage offsets) are applied between the ring electrode and the two end-cap electrodes establishing a quadrupole electric field. This field is uncoupled in three directions so that ion motion can be considered independently in each direction; the force acting upon an ion increases with the displacement of the ion from the center of the field but the direction of the force depends on the instantaneous voltage applied to the ring electrode. A restoring force along one coordinate (such as the distance, r, from the ion-trap's axis of radial symmetry) will exist concurrently with a repelling force along another coordinate (such as the distance, z, along the ion traps axis), and if the field were static the ions would eventually strike an electrode. However, in an RF field the force along each coordinate alternates direction so that a stable trajectory may be possible in which the ions do not strike a surface. In practice, ions of appropriate mass-to-charge ratios may be trapped within the device for periods of milliseconds to hours. A diagram of a typical ion trap is illustrated in Figure 7. Analysis of stored ions is performed by increasing the RF voltage, which makes the ions successively unstable. The effect of the RF voltage on the ring electrode is to "squeeze" the ions in the xy plane so that they move along the z axis. Half the ions are lost to the top cap (held at ground potential); the remaining ions exit the lower end cap to be detected by the electron multiplier. As the energy applied to the ring electrode is increased, the ions are collected in order of increasing mass to produce a conventional mass spectrum. With the ion trap, approximately 50 percent of the generated ions are detected. As a result, a significant increase in sensitivity can be achieved when compared to a full scan linear quadrupole system.

7.2.2.4 GC/MS Interface. Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points for each of the analytes of interest and can be used to achieve all acceptable performance criteria may be used. Gas chromatograph to mass spectrometer interfaces constructed of all-glass, glass-lined, or fused silica-lined materials are recommended. Glass and fused silica should be deactivated.

7.2.2.5 Data System. The computer system that is interfaced to the mass spectrometer must allow the continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as a Selected Ion Current Profile (SICP). Software must also be available that allows integrating the abundance in any SICP between specified time or scan number limits. Also, software must be available that allows for the comparison of sample spectra with reference library spectra. The National Institute of Standards and Technology (NIST) or Wiley Libraries or equivalent are recommended as reference libraries.

7.2.2.6 Off-line Data Storage Device. Device must be capable of rapid recording and retrieval of data and must be suitable for long-term, off-line data storage.

7.3 Calibration System and Manifold Apparatus (see Figure 8)

7.3.1 Calibration Manifold. Stainless steel, glass, or high purity quartz manifold, (e.g.,1.25-cm I.D. x 66-cm) with sampling ports and internal baffles for flow disturbance to ensure proper mixing. The manifold should be heated to ~50°C.

7.3.2 Humidifier. 500-mL impinger flask containing HPLC grade deionized water.

7.3.3 Electronic Mass Flow Controllers. One 0 to 5 L/min unit and one or more 0 to 100 mL/min units for air, depending on number of cylinders in use for calibration.

7.3.4 Teflon Filter(s). 47-mm Teflon® filter for particulate collection.

7.4 Reagents

7.4.1 Neat Materials or Manufacturer-Certified Solutions/Mixtures. Best source (see Section 9).

7.4.2 Helium and Air. Ultra-high purity grade in gas cylinders. He is used as carrier gas in the GC.

7.4.3 Liquid Nitrogen or Liquid Carbon Dioxide. Used to cool secondary trap.

7.4.4 Deionized Water. High performance liquid chromatography (HPLC) grade, ultra-high purity (for humidifier).

8. Collection of Samples in Canisters

8.1 Introduction

8.1.1 Canister samplers, sampling procedures, and canister cleaning procedures have not changed very much from the description given in the original Compendium Method TO-14. Much of the material in this section is therefore simply a restatement of the material given in Compendium Method TO-14, repeated here in order to have all the relevant information in one place.

8.1.2 Recent notable additions to the canister technology has been in the application of canister-based systems for example, to microenvironmental monitoring (8), the capture of breath samples (9), and sector sampling to identify emission sources of VOCs (10).

8.1.3 EPA has also sponsored the development of a mathematical model to predict the storage stability of arbitrary mixtures of trace gases in humidified air (3), and the investigation of the SilcoSteel™ process of coating the canister interior with a film of fused silica to reduce surface activity (11). A recent summary of storage stability data for VOCs in canisters is given in the open literature (5).

8.2 Sampling System Description

8.2.1 Subatmospheric Pressure Sampling [see Figure 1 (without metal bellows type pump)].

8.2.1.1 In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.05 mm Hg (see Appendix C for discussion of evacuation pressure). When the canister is opened to the atmosphere containing the VOCs to be sampled, the differential pressure causes the sample to flow into the canister. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-weighted-average (TWA) samples (duration of 1-24 hours) taken through a flow-restrictive inlet (e.g., mass flow controller, critical orifice).

8.2.1.2 With a critical orifice flow restrictor, there will be a decrease in the flow rate as the pressure approaches atmospheric. However, with a mass flow controller, the subatmospheric sampling system can maintain a constant flow rate from full vacuum to within about 7 kPa (1.0 psi) or less below ambient pressure.

8.2.2 Pressurized Sampling [see Figure 1 (with metal bellows type pump)].

8.2.2.1 Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. The sample is collected in a canister using a pump and flow control arrangement to achieve a typical 101-202 kPa (15-30 psig) final canister pressure. For example, a 6-liter evacuated canister can be filled at 10 mL/min for 24 hours to achieve a final pressure of 144 kPa (21 psig).

8.2.2.2 In pressurized canister sampling, a metal bellows type pump draws in air from the sampling manifold to fill and pressurize the sample canister.

8.2.3 All Samplers.

8.2.3.1 A flow control device is chosen to maintain a constant flow into the canister over the desired sample period. This flow rate is determined so the canister is filled (to about 88.1 kPa for subatmospheric pressure sampling or to about one atmosphere above ambient pressure for pressurized sampling) over the desired sample period. The flow rate can be calculated by:

$$F = \frac{P \times V}{T \times 60}$$

where:

F = flow rate, mL/min.
P = final canister pressure, atmospheres absolute. P is approximately equal to

$$\frac{\text{kPa gauge}}{101.2} + 1$$

V = volume of the canister, mL.
T = sample period, hours.

For example, if a 6-L canister is to be filled to 202 kPa (2 atmospheres) absolute pressure in 24 hours, the flow rate can be calculated by:

$$F = \frac{2 \times 6000}{24 \times 60} = 8.3 \text{ mL/min}$$

8.2.3.2 For automatic operation, the timer is designed to start and stop the pump at appropriate times for the desired sample period. The timer must also control the solenoid valve, to open the valve when starting the pump and to close the valve when stopping the pump.

8.2.3.3 The use of the Skinner Magnelatch valve (see Figure 2) avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve that would have to be energized during the entire sample period. The temperature rise in the valve could cause outgassing of organic compounds from the Viton® valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained either with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods, or with a conventional mechanical timer and a special pulse circuit. A simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer is illustrated in Figure 2(a). However, with this simple circuit, the valve may operate unreliably during brief power interruptions or if the timer is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 2(b).

8.2.3.4 The connecting lines between the sample inlet and the canister should be as short as possible to minimize their volume. The flow rate into the canister should remain relatively constant over the entire sampling period.

8.2.3.5 As an option, a second electronic timer may be used to start the auxiliary pump several hours prior to the sampling period to flush and condition the inlet line.

8.2.3.6 Prior to field use, each sampling system must pass a humid zero air certification (see Section 8.4.3). All plumbing should be checked carefully for leaks. The canisters must also pass a humid zero air certification before use (see Section 8.4.1).

8.3 Sampling Procedure

8.3.1 The sample canister should be cleaned and tested according to the procedure in Section 8.4.1.

8.3.2 A sample collection system is assembled as shown in Figures 1 and 3 and must be cleaned according to the procedure outlined in Sections 8.4.2 and 8.4.4.

[Note: The sampling system should be contained in an appropriate enclosure.]

8.3.3 Prior to locating the sampling system, the user may want to perform "screening analyses" using a portable GC system, as outlined in Appendix B of Compendium Method TO-14A, to determine potential volatile organics present and potential "hot spots." The information gathered from the portable GC screening analysis would be used in developing a monitoring protocol, which includes the sampling system location, based upon the "screening analysis" results.

8.3.4 After "screening analysis," the sampling system is located. Temperatures of ambient air and sampler box interior are recorded on the canister sampling field test data sheet (FTDS), as documented in Figure 9.

[Note: The following discussion is related to Figure 1]

8.3.5 To verify correct sample flow, a "practice" (evacuated) canister is used in the sampling system.

[Note: For a subatmospheric sampler, a flow meter and practice canister are needed. For the pump-driven system, the practice canister is not needed, as the flow can be measured at the outlet of the system.]

A certified mass flow meter is attached to the inlet line of the manifold, just in front of the filter. The canister is opened. The sampler is turned on and the reading of the certified mass flow meter is compared to the sampler mass flow controller. The values should agree within ±10%. If not, the sampler mass flow meter needs to be recalibrated or there is a leak in the system. This should be investigated and corrected.

[Note: Mass flow meter readings may drift. Check the zero reading carefully and add or subtract the zero reading when reading or adjusting the sampler flow rate to compensate for any zero drift.]

After 2 minutes, the desired canister flow rate is adjusted to the proper value (as indicated by the certified mass flow meter) by the sampler flow control unit controller (e.g., 3.5 mL/min for 24 hr, 7.0 mL/min for 12 hr). Record final flow under "CANISTER FLOW RATE" on the FTDS.

8.3.6 The sampler is turned off and the elapsed time meter is reset to 000.0.

[Note: Whenever the sampler is turned off, wait at least 30 seconds to turn the sampler back on.]

8.3.7 The "practice" canister and certified mass flow meter are disconnected and a clean certified (see Section 8.4.1) canister is attached to the system.

8.3.8 The canister valve and vacuum/pressure gauge valve are opened.

8.3.9 Pressure/vacuum in the canister is recorded on the canister FTDS (see Figure 9) as indicated by the sampler vacuum/pressure gauge.

8.3.10 The vacuum/pressure gauge valve is closed and the maximum-minimum thermometer is reset to current temperature. Time of day and elapsed time meter readings are recorded on the canister FTDS.

8.3.11 The electronic timer is set to start and stop the sampling period at the appropriate times. Sampling starts and stops by the programmed electronic timer.

8.3.12 After the desired sampling period, the maximum, minimum, current interior temperature and current ambient temperature are recorded on the FTDS. The current reading from the flow controller is recorded.

8.3.13 At the end of the sampling period, the vacuum/pressure gauge valve on the sampler is briefly opened and closed and the pressure/vacuum is recorded on the FTDS. Pressure should be close to desired pressure.

[Note: For a subatmospheric sampling system, if the canister is at atmospheric pressure when the field final pressure check is performed, the sampling period may be suspect. This information should be noted on the sampling field data sheet.]

Time of day and elapsed time meter readings are also recorded.

8.3.14 The canister valve is closed. The sampling line is disconnected from the canister and the canister is removed from the system. For a subatmospheric system, a certified mass flow meter is once again connected to the inlet manifold in front of the in-line filter and a "practice" canister is attached to the Magnelatch valve of the sampling system. The final flow rate is recorded on the canister FTDS (see Figure 9).

[Note: For a pressurized system, the final flow may be measured directly.]

The sampler is turned off.

8.3.15 An identification tag is attached to the canister. Canister serial number, sample number, location, and date, as a minimum, are recorded on the tag. The canister is routinely transported back to the analytical laboratory with other canisters in a canister shipping case.

8.4 Cleaning and Certification Program

8.4.1 Canister Cleaning and Certification.

8.4.1.1 All canisters must be clean and free of any contaminants before sample collection.

8.4.1.2 All canisters are leak tested by pressurizing them to approximately 206 kPa (30 psig) with zero air.

[Note: The canister cleaning system in Figure 10 can be used for this task.]

The initial pressure is measured, the canister valve is closed, and the final pressure is checked after 24 hours. If acceptable, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period.

8.4.1.3 A canister cleaning system may be assembled as illustrated in Figure 10. Cryogen is added to both the vacuum pump and zero air supply traps. The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The vacuum pump is started and the vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) are evacuated to <0.05 mm Hg (see Appendix B) for at least 1 hour.

[Note: On a daily basis or more often if necessary, the cryogenic traps should be purged with zero air to remove any trapped water from previous canister cleaning cycles.]

Air released/evacuated from canisters should be diverted to a fume hood.

8.4.1.4 The vacuum and vacuum/pressure gauge shut-off valves are closed and the zero air shut-off valve is opened to pressurize the canister(s) with humid zero air to approximately 206 kPa (30 psig). If a zero gas generator system is used, the flow rate may need to be limited to maintain the zero air quality.

8.4.1.5 The zero air shut-off valve is closed and the canister(s) is allowed to vent down to atmospheric pressure through the vent shut-off valve. The vent shut-off valve is closed. Repeat Sections 8.4.1.3 through 8.4.1.5 two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

8.4.1.6 At the end of the evacuation/pressurization cycle, the canister is pressurized to 206 kPa (30 psig) with humid zero air. The canister is then analyzed by a GC/MS analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.2 ppbv of targeted VOCs) should not be used. As a "blank" check of the canister(s) and cleanup procedure, the final humid zero air fill of 100% of the canisters is analyzed until the cleanup system and canisters are proven reliable (less than 0.2 ppbv of any target VOCs). The check can then be reduced to a lower percentage of canisters.

8.4.1.7 The canister is reattached to the cleaning manifold and is then reevacuated to <0.05 mm Hg (see Appendix B) and remains in this condition until used. The canister valve is closed. The canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting. The canister is now ready for collection of an air sample. An identification tag is attached to the inlet of each canister for field notes and chain-of-custody purposes. An alternative to evacuating the canister at this point is to store the canisters and reevacuate them just prior to the next use.

8.4.1.8 As an option to the humid zero air cleaning procedures, the canisters are heated in an isothermal oven not to exceed 100°C during evacuation of the canister to ensure that higher molecular weight compounds are not retained on the walls of the canister.

[Note: For sampling more complex VOC mixtures the canisters should be heated to higher temperatures during the cleaning procedure although a special high temperature valve would be needed].

Once heated, the canisters are evacuated to <0.05 mm Hg (see Appendix B) and maintained there for 1 hour. At the end of the heated/evacuated cycle, the canisters are pressurized with humid zero air and analyzed by a GC/MS system after a minimum of 12 hrs of "aging." Any canister that has not tested clean (less than 0.2 ppbv each of targeted compounds) should not be used. Once tested clean, the canisters are reevacuated to <0.05 mm Hg (see Appendix B) and remain in the evacuated state until used. As noted in Section 8.4.1.7, reevacuation can occur just prior to the next use.

8.4.2 Cleaning Sampling System Components.

8.4.2.1 Sample components are disassembled and cleaned before the sampler is assembled. Nonmetallic parts are rinsed with HPLC grade deionized water and dried in a vacuum oven at 50°C. Typically, stainless steel parts and fittings are cleaned by placing them in a beaker of methanol in an ultrasonic bath for 15 minutes. This procedure is repeated with hexane as the solvent.

8.4.2.2 The parts are then rinsed with HPLC grade deionized water and dried in a vacuum oven at 100°C for 12 to 24 hours.

8.4.2.3 Once the sampler is assembled, the entire system is purged with humid zero air for 24 hours.

8.4.3 Zero Air Certification.

[Note: In the following sections, "certification" is defined as evaluating the sampling system with humid zero air and humid calibration gases that pass through all active components of the sampling system. The system is "certified" if no significant additions or deletions (less than 0.2 ppbv each of target compounds) have occurred when challenged with the test gas stream.]

8.4.3.1 The cleanliness of the sampling system is determined by testing the sampler with humid zero air without an evacuated gas sampling canister, as follows.

8.4.3.2 The calibration system and manifold are assembled, as illustrated in Figure 8. The sampler (without an evacuated gas canister) is connected to the manifold and the zero air cylinder is activated to generate a humid gas stream (2 L/min) to the calibration manifold [see Figure 8(b)].

8.4.3.3 The humid zero gas stream passes through the calibration manifold, through the sampling system (without an evacuated canister) to the water management system/VOC preconcentrator of an analytical system.

[Note: The exit of the sampling system (without the canister) replaces the canister in Figure 11.]

After the sample volume (e.g., 500 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed and refocussed on a cold trap. This trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. The VOCs are refocussed prior to gas chromatographic separation. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC/MS (see Section 10) system. The analytical system should not detect greater than 0.2 ppbv of any targeted VOCs in order for the sampling system to pass the humid zero air certification test. Chromatograms (using an FID) of a certified sampler and contaminated sampler are illustrated in Figures 12(a) and 12(b), respectively. If the sampler passes the humid zero air test, it is then tested with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling (e.g., 0.5 to 2 ppbv) as outlined in Section 8.4.4.

8.4.4 Sampler System Certification with Humid Calibration Gas Standards from a Dynamic Calibration System

8.4.4.1 Assemble the dynamic calibration system and manifold as illustrated in Figure 8.

8.4.4.2 Verify that the calibration system is clean (less than 0.2 ppbv of any target compounds) by sampling a humidified gas stream, *without* gas calibration standards, with a previously certified clean canister (see Section 8.1).

8.4.4.3 The assembled dynamic calibration system is certified clean if less than 0.2 ppbv of any targeted compounds is found.

8.4.4.4 For generating the humidified calibration standards, the calibration gas cylinder(s) containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs is attached to the calibration system as illustrated in Figure 8. The gas cylinders are opened and the gas mixtures are passed through 0 to 10 mL/min certified mass flow controllers to generate ppb levels of calibration standards.

8.4.4.5 After the appropriate equilibrium period, attach the sampling system (containing a certified evacuated canister) to the manifold, as illustrated in Figure 8(b).

8.4.4.6 Sample the dynamic calibration gas stream with the sampling system.

8.4.4.7 Concurrent with the sampling system operation, realtime monitoring of the calibration gas stream is accomplished by the on-line GC/MS analytical system [Figure 8(a)] to provide reference concentrations of generated VOCs.

8.4.4.8 At the end of the sampling period (normally the same time period used for experiments), the sampling system canister is analyzed and compared to the reference GC/MS analytical system to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system.

8.4.4.9 A recovery of between 90% and 110% is expected for all targeted VOCs.

8.4.5 Sampler System Certification without Compressed Gas Cylinder Standards.

8.4.5.1 Not all the gases on the Title III list are available/compatible with compressed gas standards. In these cases sampler certification must be approached by different means.

8.4.5.2 Definitive guidance is not currently available in these cases; however, Section 9.2 lists several ways to generate gas standards. In general, Compendium Method TO-14A compounds (see Table 1) are available commercially as compressed gas standards.

9. GC/MS Analysis of Volatiles from Canisters

9.1 Introduction

9.1.1 The analysis of canister samples is accomplished with a GC/MS system. Fused silica capillary columns are used to achieve high temporal resolution of target compounds. Linear quadrupole or ion trap mass spectrometers are employed for compound detection. The heart of the system is composed of the sample inlet concentrating device that is needed to increase sample loading into a detectable range. Two examples of concentrating systems are discussed. Other approaches are acceptable as long as they are compatible with achieving the system performance criteria given in Section 11.

9.1.2 With the first technique, a whole air sample from the canister is passed through a multisorbent packing (including single adsorbent packings) contained within a metal or glass tube maintained at or above the surrounding air temperature. Depending on the water retention properties of the packing, some or most of the water vapor passes completely through the trap during sampling. Additional drying of the sample is accomplished after the sample concentration is completed by forward purging the trap with clean, dry helium or another inert gas (air is not used). The sample is then thermally desorbed from the packing and backflushed from the trap onto a gas chromatographic column. In some systems a "refocusing" trap is placed between the primary trap and the gas chromatographic column. The specific system design downstream of the primary trap depends on technical factors such as the rate of thermal desorption and sampled volume, but the objective in most cases is to enhance chromatographic resolution of the individual sample components before detection on a mass spectrometer.

9.1.3 Sample drying strategies depend on the target list of compounds. For some target compound lists, the multisorbent packing of the concentrator can be selected from hydrophobic adsorbents which allow a high percentage of water vapor in the sample to pass through the concentrator during sampling and without significant loss of the target compounds. However, if very volatile organic compounds are on the target list, the adsorbents required for their retention may also strongly retain water vapor and a more lengthy dry purge is necessary prior to analysis.

9.1.4 With the second technique, a whole air sample is passed through a concentrator where the VOCs are condensed on a reduced temperature surface (cold trap). Subsequently, the condensed gases are thermally desorbed and backflushed from the trap with an inert gas onto a gas chromatographic column. This concentration technique is similar to that discussed in Compendium Method TO-14, although a membrane dryer is not used. The sample size is reduced in volume to limit the amount of water vapor that is also collected (100 mL or less may be necessary). The attendant reduction in sensitivity is offset by enhancing the sensitivity of detection, for example by using an ion trap detector.

9.2 Preparation of Standards

9.2.1 Introduction.

9.2.1.1 When available, standard mixtures of target gases in high pressure cylinders must be certified traceable to a NIST Standard Reference Material (SRM) or to a NIST/EPA approved Certified Reference Material (CRM). Manufacturer's certificates of analysis must be retained to track the expiration date.

9.2.1.2 The neat standards that are used for making trace gas standards must be of high purity; generally a purity of 98 percent or better is commercially available.

9.2.1.3 Cylinder(s) containing approximately 10 ppmv of each of the target compounds are typically used as primary stock standards. The components may be purchased in one cylinder or in separate cylinders depending on compatibility of the compounds and the pressure of the mixture in the cylinder. Refer to manufacturer's specifications for guidance on purchasing and mixing VOCs in gas cylinders.

9.2.2 Preparing Working Standards.

9.2.2.1 Instrument Performance Check Standard. Prepare a standard solution of BFB in humidified zero air at a concentration which will allow collection of 50 ng of BFB or less under the optimized concentration parameters.

9.2.2.2 Calibration Standards. Prepare five working calibration standards in humidified zero air at a concentration which will allow collection at the 2, 5, 10, 20, and 50 ppbv level for each component under the optimized concentration parameters.

9.2.2.3 Internal Standard Spiking Mixture. Prepare an internal spiking mixture containing bromochloromethane, chlorobenzene-d_5, and 1,4-difluorobenzene at 10 ppmv each in humidified zero air to be added to the sample or calibration standard. 500 µL of this mixture spiked into 500 mL of sample will result in a concentration of 10 ppbv. The internal standard is introduced into the trap during the collection time for all calibration, blank, and sample analyses using the apparatus shown in Figure 13 or by equivalent means. The volume of internal standard spiking mixture added for each analysis must be the same from run to run.

9.2.3 Standard Preparation by Dynamic Dilution Technique.

9.2.3.1 Standards may be prepared by dynamic dilution of the gaseous contents of a cylinder(s) containing the gas calibration stock standards with humidified zero air using mass flow controllers and a calibration manifold. The working standard may be delivered from the manifold to a clean, evacuated canister using a pump and mass flow controller.

9.2.3.2 Alternatively, the analytical system may be calibrated by sampling directly from the manifold if the flow rates are optimized to provide the desired amount of calibration standards. However, the use of the canister as a reservoir prior to introduction into the concentration system resembles the procedure normally used to collect samples and is preferred. Flow rates of the dilution air and cylinder standards (all expressed in the same units) are measured using a bubble meter or calibrated electronic flow measuring device, and the concentrations of target compounds in the manifold are then calculated using the dilution ratio and the original concentration of each compound.

$$\text{Manifold Conc.} = \frac{(\text{Original Conc.})\ (\text{Std. Gas Flowrate})}{(\text{Air Flowrate}) + (\text{Std. Gas Flowrate})}$$

9.2.3.3 Consider the example of 1 mL/min flow of 10 ppmv standard diluted with 1,000 mL/min of humid air provides a nominal 10 ppbv mixture, as calculated below:

$$\text{Manifold Conc.} = \frac{(10\ \text{ppm})(1\ \text{mL/min})(1000\ \text{ppb/1 ppm})}{(1000\ \text{mL/min}) + (1\ \text{mL/min})} = 10\ \text{ppb}$$

9.2.4 Standard Preparation by Static Dilution Bottle Technique

[Note: Standards may be prepared in canisters by spiking the canister with a mixture of components prepared in a static dilution bottle (12). This technique is used specifically for liquid standards.]

9.2.4.1 The volume of a clean 2-liter round-bottom flask, modified with a threaded glass neck to accept a Mininert septum cap, is determined by weighing the amount of water required to completely fill up the flask. Assuming a density for the water of 1 g/mL, the weight of the water in grams is taken as the volume of the flask in milliliters.

9.2.4.2 The flask is flushed with helium by attaching a tubing into the glass neck to deliver the helium. After a few minutes, the tubing is removed and the glass neck is immediately closed with a Mininert septum cap.

9.2.4.3 The flask is placed in a 60°C oven and allowed to equilibrate at that temperature for about 15 minutes. Predetermined aliquots of liquid standards are injected into the flask making sure to keep the flask temperature constant at 60°C.

9.2.4.4 The contents are allowed to equilibrate in the oven for at least 30 minutes. To avoid condensation, syringes must be preheated in the oven at the same temperature prior to withdrawal of aliquots to avoid condensation.

9.2.4.5 Sample aliquots may then be taken for introduction into the analytical system or for further dilution. An aliquot or aliquots totaling greater than 1 percent of the flask volume should be avoided.

9.2.4.6 Standards prepared by this method are stable for one week. The septum must be replaced with each freshly prepared standard.

9.2.4.7 The concentration of each component in the flask is calculated using the following equation:

$$\text{Concentration, mg/L} = \frac{(V_a)(d)}{V_f}$$

where: V_a = Volume of liquid neat standard injected into the flask, µL.
d = Density of the liquid neat standard, mg/µL.
V_f = Volume of the flask, L.

9.2.4.8 To obtain concentrations in ppbv, the equation given in Section 9.2.5.7 can be used.

[Note: In the preparation of standards by this technique, the analyst should make sure that the volume of neat standard injected into the flask does not result in an overpressure due to the higher partial pressure produced by the standard compared to the vapor pressure in the flask. Precautions should also be taken to avoid a significant decrease in pressure inside the flask after withdrawal of aliquot(s).]

9.2.5 Standard Preparation Procedure in High Pressure Cylinders

[Note: Standards may be prepared in high pressure cylinders (13). A modified summary of the procedure is provided below.]

9.2.5.1 The standard compounds are obtained as gases or neat liquids (greater than 98 percent purity).

9.2.5.2 An aluminum cylinder is flushed with high-purity nitrogen gas and then evacuated to better than 25 in. Hg.

9.2.5.3 Predetermined amounts of each neat standard compound are measured using a microliter or gastight syringe and injected into the cylinder. The cylinder is equipped with a heated injection port and nitrogen flow to facilitate sample transfer.

9.2.5.4 The cylinder is pressurized to 1000 psig with zero nitrogen.

[Note: User should read all SOPs associated with generating standards in high pressure cylinders. Follow all safety requirements to minimize danger from high pressure cylinders.]

9.2.5.5 The contents of the cylinder are allowed to equilibrate (~24 hrs) prior to withdrawal of aliquots into the GC system.

9.2.5.6 If the neat standard is a gas, the cylinder concentration is determined using the following equation:

$$\text{Concentration, ppbv} = \frac{\text{Volume}_{\text{standard}}}{\text{Volume}_{\text{dilution gas}}} \times 10^9$$

[Note: Both values must be expressed in the same units.]

9.2.5.7 If the neat standard is a liquid, the gaseous concentration can be determined using the following equations:

$$V = \frac{nRT}{P}$$

and:

$$n = \frac{(mL)(d)}{MW}$$

where:
- V = Gaseous volume of injected compound at EPA standard temperature (25°C) and pressure (760 mm Hg), L.
- n = Moles.
- R = Gas constant, 0.08206 L-atm/mole °K.
- T = 298°K (standard temperature).
- P = 1 standard pressure, 760 mm Hg (1 atm).
- mL = Volume of liquid injected, mL.
- d = Density of the neat standard, g/mL.
- MW = Molecular weight of the neat standard expressed, g/g-mole.

The gaseous volume of the injected compound is divided by the cylinder volume at STP and then multiplied by 10^9 to obtain the component concentration in ppb units.

9.2.6 Standard Preparation by Water Methods.

[Note: Standards may be prepared by a water purge and trap method (14) and summarized as follows].

9.2.6.1 A previously cleaned and evacuated canister is pressurized to 760 mm Hg absolute (1 atm) with zero grade air.

9.2.6.2 The air gauge is removed from the canister and the sparging vessel is connected to the canister with the short length of 1/16 in. stainless steel tubing.

[Note: Extra effort should be made to minimize possible areas of dead volume to maximize transfer of analytes from the water to the canister.]

9.2.6.3 A measured amount of the stock standard solution and the internal standard solution is spiked into 5 mL of water.

9.2.6.4 This water is transferred into the sparge vessel and purged with nitrogen for 10 mins at 100 mL/min. The sparging vessel is maintained at 40°C.

9.2.6.5 At the end of 10 mins, the sparge vessel is removed and the air gauge is re-installed, to further pressurize the canister with pure nitrogen to 1500 mm Hg absolute pressure (approximately 29 psia).

9.2.6.6 The canister is allowed to equilibrate overnight before use.

9.2.6.7 A schematic of this approach is shown in Figure 14.

9.2.7 Preparation of Standards by Permeation Tubes.

9.2.7.1 Permeation tubes can be used to provide standard concentration of a trace gas or gases. The permeation of the gas can occur from inside a permeation tube containing the trace species of interest to an air stream outside. Permeation can also occur from outside a permeable membrane tube to an air stream passing through the tube (e.g., a tube of permeable material immersed in a liquid).

9.2.7.2 The permeation system is usually held at a constant temperature to generate a constant concentration of trace gas. Commercial suppliers provide systems for generation and dilution of over 250 compounds. Some commercial suppliers of permeation tube equipment are listed in Appendix D.

9.2.8 Storage of Standards.

9.2.8.1 Working standards prepared in canisters may be stored for thirty days in an atmosphere free of potential contaminants.

9.2.8.2 It is imperative that a storage logbook be kept to document storage time.

10. GC/MS Operating Conditions

10.1 Preconcentrator

The following are typical cryogenic and adsorbent preconcentrator analytical conditions which, however, depend on the specific combination of solid sorbent and must be selected carefully by the operator. The reader is referred to Tables 1 and 2 of Compendium Method TO-17 for guidance on selection of sorbents. An example of a system using a solid adsorbent preconcentrator with a cryofocusing trap is discussed in the literature (15). Oven temperature programming starts above ambient.

10.1.1 Sample Collection Conditions

Cryogenic Trap	**Adsorbent Trap**

Set point	-150°C	Set point	27°C
Sample volume	- up to 100 mL	Sample volume	- up to 1,000 mL
Carrier gas purge flow	- none	Carrier gas purge flow	- selectable

[Note: The analyst should optimize the flow rate, duration of sampling, and absolute sample volume to be used. Other preconcentration systems may be used provided performance standards (see Section 11) are realized.]

10.1.2 Desorption Conditions

Cryogenic Trap		**Adsorbent Trap**	
Desorb Temperature	120°C	Desorb Temperature	Variable
Desorb Flow Rate	~ 3 mL/min He	Desorb Flow Rate	~3 mL/min He
Desorb Time	<60 sec	Desorb Time	<60 sec

The adsorbent trap conditions depend on the specific solid adsorbents chosen (see manufacturers' specifications).

10.1.3 Trap Reconditioning Conditions.

Cryogenic Trap		**Adsorbent Trap**	
Initial bakeout	120°C (24 hrs)	Initial bakeout	Variable (24 hrs)
After each run	120°C (5 min)	After each run	Variable (5 min)

10.2 GC/MS System

10.2.1 Optimize GC conditions for compound separation and sensitivity. Baseline separation of benzene and carbon tetrachloride on a 100% methyl polysiloxane stationary phase is an indication of acceptable chromatographic performance.

10.2.2 The following are the recommended gas chromatographic analytical conditions when using a 50-meter by 0.3-mm I.D., 1 µm film thickness fused silica column with refocusing on the column.

Item	**Condition**	
Carrier Gas:	Helium	
Flow Rate:	Generally 1-3 mL/min as recommended by manufacturer	
Temperature Program:	Initial Temperature:	-50°C
	Initial Hold Time:	2 min
	Ramp Rate:	8° C/min
	Final Temperature:	200°C
	Final Hold Time:	Until all target compounds elute.

10.2.3 The following are the recommended mass spectrometer conditions:

Item	**Condition**

Electron Energy:	70 Volts (nominal)
Mass Range:	35-300 amu [the choice of 35 amu excludes the detection of some target compounds such as methanol and formaldehyde, and the quantitation of others such as ethylene oxide, ethyl carbamate, etc. (see Table 2). Lowering the mass range and using special programming features available on modern gas chromatographs will be necessary in these cases, but are not considered here.
Scan Time:	To give at least 10 scans per peak, not to exceed 1 second per scan].

A schematic for a typical GC/MS analytical system is illustrated in Figure 15.

10.3 Analytical Sequence

10.3.1 Introduction. The recommended GC/MS analytical sequence for samples during each 24-hour time period is as follows:

- Perform instrument performance check using bromofluorobenzene (BFB).
- Initiate multi-point calibration or daily calibration checks.
- Perform a laboratory method blank.
- Complete this sequence for analysis of ≤20 field samples.

10.4 Instrument Performance Check

10.4.1 Summary. It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. The GC/MS system is set up according to the manufacturer's specifications, and the mass calibration and resolution of the GC/MS system are then verified by the analysis of the instrument performance check standard, bromofluorobenzene (BFB).

10.4.2 Frequency. Prior to the analyses of any samples, blanks, or calibration standards, the Laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard containing BFB. The instrument performance check solution must be analyzed initially and once per 24-hour time period of operation.

The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or daily calibration check criteria) begins at the injection of the BFB which the laboratory records as documentation of a compliance tune.

10.4.3 Procedure. The analysis of the instrument performance check standard is performed by trapping 50 ng of BFB under the optimized preconcentration parameters. The BFB is introduced from a cylinder into the GC/MS via a sample loop valve injection system similar to that shown in Figure 13.

The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is conducted using a single scan prior to the elution of BFB.

10.4.4 Technical Acceptance Criteria. Prior to the analysis of any samples, blanks, or calibration standards, the analyst must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard as specified in Table 3.

10.4.5 Corrective Action. If the BFB acceptance criteria are not met, the MS must be retuned. It may be necessary to clean the ion source, or quadrupoles, or take other necessary actions to achieve the acceptance criteria.

10.4.6 Documentation. Results of the BFB tuning are to be recorded and maintained as part of the instrumentation log.

10.5 Initial Calibration

10.5.1 Summary. Prior to the analysis of samples and blanks but after the instrument performance check standard criteria have been met, each GC/MS system must be calibrated at five concentrations that span the monitoring range of interest in an initial calibration sequence to determine instrument sensitivity and the linearity of GC/MS response for the target compounds. For example, the range of interest may be 2 to 20 ppbv, in which case the five concentrations would be 1, 2, 5, 10 and 25 ppbv.

One of the calibration points from the initial calibration curve must be at the same concentration as the daily calibration standard (e.g., 10 ppbv).

10.5.2 Frequency. Each GC/MS system must be recalibrated following corrective action (e.g., ion source cleaning or repair, column replacement, etc.) which may change or affect the initial calibration criteria or if the daily calibration acceptance criteria have not been met.

If time remains in the 24-hour time period after meeting the acceptance criteria for the initial calibration, samples may be analyzed.

If time does not remain in the 24-hour period after meeting the acceptance criteria for the initial calibration, a new analytical sequence shall commence with the analysis of the instrument performance check standard followed by analysis of a daily calibration standard.

10.5.3 Procedure. Verify that the GC/MS system meets the instrument performance criteria in Section 10.4.

The GC must be operated using temperature and flow rate parameters equivalent to those in Section 10.2.2. Calibrate the preconcentration-GC/MS system by drawing the standard into the system. Use one of the standards preparation techniques described under Section 9.2 or equivalent.

A minimum of five concentration levels are needed to determine the instrument sensitivity and linearity. One of the calibration levels should be near the detection level for the compounds of interest. The calibration range should be chosen so that linear results are obtained as defined in Sections 10.5.1 and 10.5.5.

Quantitation ions for the target compounds are shown in Table 2. The primary ion should be used unless interferences are present, in which case a secondary ion is used.

10.5.4 Calculations.

[Note: In the following calculations, an internal standard approach is used to calculate response factors. The area response used is that of the primary quantitation ion unless otherwise stated.]

10.5.4.1 Relative Response Factor (RRF). Calculate the relative response factors for each target compound relative to the appropriate internal standard (i.e., standard with the nearest retention time) using the following equation:

$$RRF = \frac{A_x C_{is}}{A_{is} C_x}$$

where: RRF = Relative response factor.
A_x = Area of the primary ion for the compound to be measured, counts.
A_{is} = Area of the primary ion for the internal standard, counts.
C_{is} = Concentration of internal standard spiking mixture, ppbv.
C_x = Concentration of the compound in the calibration standard, ppbv.

[Note: The equation above is valid under the condition that the volume of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume of field and QC sample introduced into the trap is the same for each analysis. C_{is} and C_x must be in the same units.]

10.5.4.2 Mean Relative Response Factor. Calculate the mean RRF for each compound by averaging the values obtained at the five concentrations using the following equation:

$$\overline{RRF} = \sum_{i=1}^{n} \frac{x_i}{n}$$

where: $\overline{RRF}$ = Mean relative response factor.
x_i = RRF of the compound at concentration i.
n = Number of concentration values, in this case 5.

10.5.4.3 Percent Relative Standard Deviation (%RSD). Using the RRFs from the initial calibration, calculate the %RSD for all target compounds using the following equations:

$$\%RSD = \frac{SD_{RRF}}{\overline{RRF}} \times 100$$

and

$$SD_{RRF} = \sqrt{\sum_{i=1}^{N} \frac{(RRF_i - \overline{RRF})^2}{N - 1}}$$

where: SD_{RRF} = Standard deviation of initial response factors (per compound).
RRF_i = Relative response factor at a concentration level i.
$\overline{RRF}$ = Mean of initial relative response factors (per compound).

10.5.4.4 Relative Retention Times (RRT). Calculate the RRTs for each target compound over the initial calibration range using the following equation:

$$RRT = \frac{RT_c}{RT_{is}}$$

where: RT_c = Retention time of the target compound, seconds
RT_{is} = Retention time of the internal standard, seconds.

10.5.4.5 Mean of the Relative Retention Times ($\overline{RRT}$). Calculate the mean of the relative retention times ($\overline{RRT}$) for each analyte target compound over the initial calibration range using the following equation:

$$\overline{RRT} = \sum_{i=1}^{n} \frac{RRT}{n}$$

where: $\overline{RRT}$ = Mean relative retention time for the target compound for each initial calibration standard.

RRT = Relative retention time for the target compound at each calibration level.

10.5.4.6 Tabulate Primary Ion Area Response (Y) for Internal Standard. Tabulate the area response (Y) of the primary ions (see Table 2) and the corresponding concentration for each compound and internal standard.

10.5.4.7 Mean Area Response ($\overline{Y}$) for Internal Standard. Calculate the mean area response ($\overline{Y}$) for each internal standard compound over the initial calibration range using the following equation:

$$\overline{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$

where: $\overline{Y}$ = Mean area response.

Y = Area response for the primary quantitation ion for the internal standard for each initial calibration standard.

10.5.4.8 Mean Retention Times ($\overline{RT}$). Calculate the mean of the retention times ($\overline{RT}$) for each internal standard over the initial calibration range using the following equation:

$$\overline{RT} = \sum_{i=1}^{n} \frac{RT_i}{n}$$

where: $\overline{RT}$ = Mean retention time, seconds

RT = Retention time for the internal standard for each initial calibration standard, seconds.

10.5.5 Technical Acceptance Criteria for the Initial Calibration.

10.5.5.1 The calculated %RSD for the RRF for each compound in the calibration table must be less than 30% with at most two exceptions up to a limit of 40%.

[Note: This exception may not be acceptable for all projects. Many projects may have a specific target list of compounds which would require the lower limit for all compounds.]

10.5.5.2 The RRT for each target compound at each calibration level must be withiin 0.06 RRT units of the mean RRT for the compound.

10.5.5.3 The area response Y of at each calibration level must be within 40% of the mean area response $\overline{Y}$ over the initial calibration range for each internal standard.

10.5.5.4 The retention time shift for each of the internal standards at each calibration level must be within 20 s of the mean retention time over the initial calibration range for each internal standard.

10.5.6 Corrective Action.

10.5.6.1 Criteria. If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the initial calibration technical acceptance criteria.

10.5.6.2 Schedule. Initial calibration acceptance criteria *must* be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed.

10.6 Daily Calibration

10.6.1 Summary. Prior to the analysis of samples and blanks but after tuning criteria have been met, the initial calibration of each GC/MS system must be routinely checked by analyzing a daily calibration standard to ensure that the instrument continues to remain under control. The daily calibration standard, which is the nominal 10 ppbv level calibration standard, should contain all the target compounds.

10.6.2 Frequency. A check of the calibration curve must be performed once every 24 hours on a GC/MS system that has met the tuning criteria. The daily calibration sequence starts with the injection of the BFB. If the BFB analysis meets the ion abundance criteria for BFB, then a daily calibration standard may be analyzed.

10.6.3 Procedure. The mid-level calibration standard (10 ppbv) is analyzed in a GC/MS system that has met the tuning and mass calibration criteria following the same procedure in Section 10.5.

10.6.4 Calculations. Perform the following calculations.

[Note: As indicated earlier, the area response of the primary quantitation ion is used unless otherwise stated.]

10.6.4.1 Relative Response Factor (RRF). Calculate a relative response factor (RRF) for each target compound using the equation in Section 10.5.4.1.

10.6.4.2 Percent Difference (%D). Calculate the percent difference in the RRF of the daily RRF (24-hour) compared to the mean RRF in the most recent initial calibration. Calculate the %D for each target compound using the following equation:

$$\%D = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

where: RRF_c = RRF of the compound in the continuing calibration standard.

$\overline{RRF_i}$ = Mean RRF of the compound in the most recent initial calibration.

10.6.5 Technical Acceptance Criteria. The daily calibration standard must be analyzed at the concentration level and frequency described in this Section 10.6 and on a GC/MS system meeting the BFB instrument performance check criteria (see Section 10.4).

The %D for each target compound in a daily calibration sequence must be within ±30 percent in order to proceed with the analysis of samples and blanks. A control chart showing %D values should be maintained.

10.6.6 Corrective Action. If the daily calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the daily calibration technical acceptance criteria.

Daily calibration acceptance criteria must be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed. If the % D criteria are not met, it will be necessary to rerun the daily calibration sample.

10.7 Blank Analyses

10.7.1 Summary. To monitor for possible laboratory contamination, laboratory method blanks are analyzed at least once in a 24-hour analytical sequence. All steps in the analytical procedure are performed on the blank

using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis.

A laboratory method blank (LMB) is an unused, certified canister that has not left the laboratory. The blank canister is pressurized with humidified, ultra-pure zero air and carried through the same analytical procedure as a field sample. The injected aliquot of the blank must contain the same amount of internal standards that are added to each sample.

10.7.2 Frequency. The laboratory method blank must be analyzed after the calibration standard(s) and before any samples are analyzed.

Whenever a high concentration sample is encountered (i.e., outside the calibration range), a blank analysis should be performed immediately after the sample is completed to check for carryover effects.

10.7.3 Procedure. Fill a cleaned and evacuated canister with humidified zero air (RH >20 percent, at 25°C). Pressurize the contents to 2 atm.

The blank sample should be analyzed using the same procedure outlined under Section 10.8.

10.7.4 Calculations. The blanks are analyzed similar to a field sample and the equations in Section 10.5.4 apply.

10.7.5 Technical Acceptance Criteria. A blank canister should be analyzed daily.

The area response for each internal standard (IS) in the blank must be within ±40 percent of the mean area response of the IS in the most recent valid calibration.

The retention time for each of the internal standards must be within ±0.33 minutes between the blank and the most recent valid calibration.

The blank should not contain any target analyte at a concentration greater than its quantitation level (three times the MDL as defined in Section 11.2) and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte.

10.7.6 Corrective Action. If the blanks do not meet the technical acceptance criteria, the analyst should consider the analytical system to be out of control. It is the responsibility of the analyst to ensure that contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures need to be taken and documented before further sample analysis proceeds.

If an analyte in the blank is found to be out of control (i.e., contaminated) and the analyte is also found in associated samples, those sample results should be "flagged" as possibly contaminated.

10.8 Sample Analysis

10.8.1 Summary. An aliquot of the air sample from a canister (e.g., 500 mL) is preconcentrated and analyzed by GC/MS under conditions stated in Sections 10.1 and 10.2. If using the multisorbent/dry purge approach, adjust the dry purge volume to reduce water effects in the analytical system to manageable levels.

[Note: The analyst should be aware that pressurized samples of high humidity samples will contain condensed water. As a result, the humidity of the sample released from the canister during analysis will vary

in humidity, being lower at the higher canister pressures and increasing in humidity as the canister pressures decreases. Storage integrity of water soluble compounds may also be affected.]

10.8.2 Frequency. If time remains in the 24-hour period in which an initial calibration is performed, samples may be analyzed without analysis of a daily calibration standard.

If time does not remain in the 24-hour period since the injection of the instrument performance check standard in which an initial calibration is performed, both the instrument performance check standard and the daily calibration standard should be analyzed before sample analysis may begin.

10.8.3 Procedure for Instrumental Analysis. Perform the following procedure for analysis.

10.8.3.1 All canister samples should be at temperature equilibrium with the laboratory.

10.8.3.2 Check and adjust the mass flow controllers to provide correct flow rates for the system.

10.8.3.3 Connect the sample canister to the inlet of the GC/MS analytical system, as shown in Figure 15 [Figure 16 shows an alternate two stage concentrator using multisorbent traps followed by a trap cooled by a closed cycle cooler (15)]. The desired sample flow is established through the six-port chromatographic valve and the preconcentrator to the downstream flow controller. The absolute volume of sample being pulled through the trap must be consistent from run to run.

10.8.3.4 Heat/cool the GC oven and cryogenic or adsorbent trap to their set points. Assuming a six-port value is being used, as soon as the trap reaches its lower set point, the six-port chromatographic valve is cycled to the trap position to begin sample collection. Utilize the sample collection time which has been optimized by the analyst.

10.8.3.5 Use the arrangement shown in Figure 13, (i.e., a gastight syringe or some alternate method) introduce an internal standard during the sample collection period. Add sufficient internal standard equivalent to 10 ppbv in the sample. For example, a 0.5 mL volume of a mixture of internal standard compounds, each at 10 ppmv concentration, added to a sample volume of 500 mL, will result in 10 ppbv of each internal standard in the sample.

10.8.3.6 After the sample and internal standards are preconcentrated on the trap, the GC sampling valve is cycled to the inject position and the trap is swept with helium and heated. Assuming a focusing trap is being used, the trapped analytes are thermally desorbed onto a focusing trap and then onto the head of the capillary column and are separated on the column using the GC oven temperature program. The canister valve is closed and the canister is disconnected from the mass flow controller and capped. The trap is maintained at elevated temperature until the beginning of the next analysis.

10.8.3.7 Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak should be acquired. Scanning also allows identification of unknown compounds in the sample through searching of library spectra.

10.8.3.8 Each analytical run must be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound.

10.8.3.9 Secondary ion quantitation is allowed only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the laboratory record book.

10.8.4 Calculations. The equation below is used for calculating concentrations.

$$C_x = \frac{A_x C_{is} DF}{A_{is} \overline{RRF}}$$

where: C_x = Compound concentration, ppbv.

A_x = Area of the characteristic ion for the compound to be measured, counts.

A_{is} = Area of the characteristic ion for the specific internal standard, counts.

C_{is} = Concentration of the internal standard spiking mixture, ppbv

.

$\overline{RRF}$ = Mean relative response factor from the initial calibration.

DF = Dilution factor calculated as described in section 2. If no dilution is performed, DF = 1.

[Note: The equation above is valid under the condition that the volume (~500 µL) of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume (~500 mL) of field and QC sample introduced into the trap is the same for each analysis.]

10.8.5 Technical Acceptance Criteria.

[Note: If the most recent valid calibration is an initial calibration, internal standard area responses and RTs in the sample are evaluated against the corresponding internal standard area responses and RTs in the mid level standard (10 ppbv) of the initial calibration.]

10.8.5.1 The field sample must be analyzed on a GC/MS system meeting the BFB tuning, initial calibration, and continuing calibration technical acceptance criteria at the frequency described in Sections 10.4, 10.5 and 10.6.

10.8.5.2 The field samples must be analyzed along with a laboratory method blank that met the blank technical acceptance criteria.

10.8.5.3 All of the target analyte peaks should be within the initial calibration range.

10.8.5.4 The retention time for each internal standard must be within ±0.33 minutes of the retention time of the internal standard in the most recent valid calibration.

10.8.6 Corrective Action. If the on-column concentration of any compound in any sample exceeds the initial calibration range, an aliquot of the original sample must be diluted and reanalyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

- Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.
- The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

[Note: Analysis involving dilution should be reported with a dilution factor and nature of the dilution gas.]

10.8.6.1 Internal standard responses and retention times must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 20 sec from the latest daily (24-hour) calibration standard (or mean retention time over the initial calibration range), the GC/MS system must be inspected for malfunctions, and corrections made as required.

10.8.6.2 If the area response for any internal standard changes by more than ±40 percent between the sample and the most recent valid calibration, the GC/MS system must be inspected for malfunction and

corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

10.8.6.3 If, after reanalysis, the area responses or the RTs for all internal standards are inside the control limits, then the problem with the first analysis is considered to have been within the control of the Laboratory. Therefore, submit only data from the analysis with SICPs within the limits. This is considered the initial analysis and should be reported as such on all data deliverables.

11. Requirements for Demonstrating Method Acceptability for VOC Analysis from Canisters

11.1 Introduction

11.1.1 There are three performance criteria which must be met for a system to qualify under Compendium Method TO-15. These criteria are: the method detection limit of ≤0.5 ppbv, replicate precision within 25 percent, and audit accuracy within 30 percent for concentrations normally expected in contaminated ambient air (0.5 to 25 ppbv).

11.1.2 Either SIM or SCAN modes of operation can be used to achieve these criteria, and the choice of mode will depend on the number of target compounds, the decision of whether or not to determine tentatively identified compounds along with other VOCs on the target list, as well as on the analytical system characteristics.

11.1.3 Specific criteria for each Title III compound on the target compound list must be met by the analytical system. These criteria were established by examining summary data from EPA's Toxics Air Monitoring System Network and the Urban Air Toxics Monitoring Program network. Details for the determination of each of the criteria follow.

11.2 Method Detection Limit

11.2.1 The procedure chosen to define the method detection limit is that given in the *Code of Federal Regulations* (40 CFR 136 Appendix B).

11.2.2 The method detection limit is defined for each system by making seven replicate measurements of the compound of interest at a concentration near (within a factor of five) the expected detection limit, computing the standard deviation for the seven replicate concentrations, and multiplying this value by 3.14 (i.e., the Student's t value for 99 percent confidence for seven values). Employing this approach, the detection limits given in Table 4 were obtained for some of the VOCs of interest.

11.3 Replicate Precision

11.3.1 The measure of replicate precision used for this program is the absolute value of the difference between replicate measurements of the sample divided by the average value and expressed as a percentage as follows:

$$\text{percent difference} = \frac{|x_1 - x_2|}{\bar{x}} \times 100$$

where: x_1 = First measurement value.

x_2 = Second measurement value.

$\bar{x}$ = Average of the two values.

11.3.2 There are several factors which may affect the precision of the measurement. The nature of the compound of interest itself such as molecular weight, water solubility, polarizability, etc., each have some effect on the precision, for a given sampling and analytical system. For example, styrene, which is classified as a polar VOC, generally shows slightly poorer precision than the bulk of nonpolar VOCs. A primary influence on precision is the concentration level of the compound of interest in the sample, i.e., the precision degrades as the concentration approaches the detection limit. A conservative measure was obtained from replicate analysis of "real world" canister samples from the TAMS and UATMP networks. These data are summarized in Table 5 and suggest that a replicate precision value of 25 percent can be achieved for each of the target compounds.

11.4 Audit Accuracy

11.4.1 A measure of analytical accuracy is the degree of agreement with audit standards. Audit accuracy is defined as the difference between the nominal concentration of the audit compound and the measured value divided by the audit value and expressed as a percentage, as illustrated in the following equation:

$$\text{Audit Accuracy, \%} = \frac{\text{Spiked Value} - \text{Observed Value}}{\text{Spiked Value}} \times 100$$

11.4.2 Audit accuracy results for TAMS and UATMP analyses are summarized in Table 6 and were used to form the basis for a selection of 30 percent as the performance criterion for audit accuracy.

12. References

1. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-14A, Second Edition,* U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA 600/625/R-96/010b, January 1997.

2. Winberry, W. T., Jr., et al., *Statement-of-Work (SOW) for the Analysis of Air Toxics From Superfund Sites*, U. S. Environmental Protection Agency, Office of Solid Waste, Contract Laboratory Program, Washington, D.C., Draft Report, June 1990.

3. Coutant, R.W., *Theoretical Evaluation of Stability of Volatile Organic Chemicals and Polar Volatile Organic Chemicals in Canisters*, U. S. Environmental Protection Agency, EPA Contract No. 68-DO-0007, Work Assignment No. 45, Subtask 2, Battelle, Columbus, OH, June 1993.

4. Kelly, T.J., Mukund, R., Gordon, S.M., and Hays, M.J., *Ambient Measurement Methods and Properties of the 189 Title III Hazardous Air Pollutants*, U. S. Environmental Protection Agency, EPA Contract No. 68-DO-0007, Work Assignment 44, Battelle, Columbus, OH, March 1994.

5. Kelly T. J. and Holdren, M.W., "Applicability of Canisters for Sample Storage in the Determination of Hazardous Air Pollutants," *Atmos. Environ.*, Vol. 29, 2595-2608, May 1995.

6. Kelly, T.J., Callahan, P.J., Pleil, J.K., and Evans, G.E., "Method Development and Field Measurements for Polar Volatile Organic Compounds in Ambient Air," *Environ. Sci. Technol.*, Vol. 27, 1146-1153, 1993.

7. McClenny, W.A., Oliver, K.D. and Daughtrey, E.H.., Jr. "Dry Purging of Solid Adsorbent Traps to Remove Water Vapor Before Thermal Desorption of Trace Organic Gases," *J. Air and Waste Manag. Assoc.*, Vol. 45, 792-800, June 1995.

8. Whitaker, D.A., Fortmann, R.C. and Lindstrom, A.B. "Development and Testing of a Whole Air Sampler for Measurement of Personal Exposures to Volatile Organic Compounds," *Journal of Exposure Analysis and Environmental Epidemiology*, Vol. 5, No. 1, 89-100, January 1995.

9. Pleil, J.D. and Lindstrom, A.B., "Collection of a Single Alveolar Exhaled Breath for Volatile Organic Compound Analysis," *American Journal of Industrial Medicine*, Vol. 28, 109-121, 1995.

10. Pleil, J.D. and McClenny, W.A., "Spatially Resolved Monitoring for Volatile Organic Compounds Using Remote Sector Sampling," *Atmos. Environ.*, Vol. 27A, No. 5, 739-747, August 1993.

11. Holdren, M.W., et al., Unpublished Final Report, EPA Contract 68-DO-0007, Battelle, Columbus, OH. Available from J.D. Pleil, MD-44, U. S. Environmental Protection Agency, Research Triangle Park, NC, 27711, 919-541-4680.

12. Morris, C.M., Burkley, R.E. and Bumgarner, J.E., "Preparation of Multicomponent Volatile Organic Standards Using Dilution Bottles," *Anal. Letts*., Vol. 16 (A20), 1585-1593, 1983.

13. Pollack, A.J., Holdren, M.W., "Multi-Adsorbent Preconcentration and Gas Chromatographic Analysis of Air Toxics With an Automated Collection/Analytical System," in the *Proceedings of the 1990 EPA/A&WMA International Symposium of Measurement of Toxic and Related Air Pollutants*, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA/600/9-90-026, May 1990.

14. Stephenson, J.H.M., Allen, F., Slagle, T., "Analysis of Volatile Organics in Air via Water Methods" in *Proceedings of the 1990 EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants*, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA 600/9-90-026, May 1990.

15. Oliver, K. D., Adams, J. R., Davehtrey, E. H., Jr., McClenny, W. A., Young, M. J., and Parade, M. A., "Techniques for Monitoring Toxices VOCs in Air: Sorbent Preconcentration Closed-Cycle Cooler Cryofocusing, and GC/MS Analysis," *Environ. Sci. Technol.*, Vol. 30, 1938-1945, 1996.

APPENDIX A.

LISTING OF SOME COMMERCIAL WATER MANAGEMENT SYSTEMS USED WITH AUTOGC SYSTEMS

Tekmar Dohrman Company
7143 East Kemper Road
Post Office Box 429576
Cincinnati, Ohio 45242-9576
(513) 247-7000
(513) 247-7050 (Fax)
(800) 543-4461
[Moisture control module]

Entech Laboratory Automation
950 Enchanted Way No. 101
Simi Valley, California 93065
(805) 527-5939
(805) 527-5687 (Fax)
[Microscale Purge and Trap]

Dynatherm Analytical Instruments
Post Office Box 159
Kelton, Pennsylvania 19346
(215) 869-8702
(215) 869-3885 (Fax)
[Thermal Desorption System]

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380
(818) 787-4275 (Fax)
[Multi-adsorbent trap/dry purge]

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(770) 319-9999
(770) 319-0336 (Fax)
(800) 241-6898
[Controlled Desorption Trap]

Varian Chromatography System
2700 Mitchell Drive
Walnut Creek, California 94898
(510) 945-2196
(510) 945-2335 (FAX)
[Variable Temperature Adsorption Trap]

APPENDIX B.

COMMENT ON CANISTER CLEANING PROCEDURES

The canister cleaning procedures given in Section 8.4 require that canister pressure be reduced to <0.05mm Hg before the cleaning process is complete. Depending on the vacuum system design (diameter of connecting tubing, valve restrictions, etc.) and the placement of the vacuum gauge, the achievement of this value may take several hours. In any case, the pressure gauge should be placed near the canisters to determine pressure. The objective of requiring a low pressure evacuation during canister cleaning is to reduce contaminants. If canisters can be routinely certified (<0.2 ppbv for target compounds) while using a higher vacuum, then this criteria can be relaxed. However, the ultimate vacuum achieved during cleaning should always be <0.2mm Hg.

Canister cleaning as described in Section 8.4 and illustrated in Figure 10 requires components with special features. The vacuum gauge shown in Figure 10 must be capable of measuring 0.05mm Hg with less than a 20% error. The vacuum pump used for evacuating the canister must be noncontaminating while being capable of achieving the 0.05 mm Hg vacuum as monitored near the canisters. Thermoelectric vacuum gauges and turbomolecular drag pumps are typically being used for these two components.

An alternate to achieving the canister certification requirement of <0.2 ppbv for all target compounds is the criteria used in Compendium Method TO-12 that the total carbon count be <10ppbC. This check is less expensive and typically more exacting than the current certification requirement and can be used if proven to be equivalent to the original requirement. This equivalency must be established by comparing the total nonmethane organic carbon (TNMOC) expressed in ppbC to the requirement that individual target compounds be <0.2 ppbv for a series of analytical runs.

APPENDIX C.

LISTING OF COMMERCIAL MANUFACTURERS AND RE-SUPPLIERS OF SPECIALLY-PREPARED CANISTERS

BRC/Rasmussen
17010 NW Skyline Blvd.
Portland, Oregon 97321
(503) 621-1435

Meriter
1790 Potrero Drive
San Jose, CA 95124
(408) 265-6482

Restek Corporation
110 Benner Circle
Bellefonte, PA 16823-8812
(814) 353-1300
(800) 356-1688

Scientific Instrumentation Specialists
P.O. Box 8941
815 Courtney Street
Moscow, ID 83843
(208) 882-3860

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(404) 319-9999
(800) 241-6898

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380

APPENDIX D.

LISTING OF COMMERCIAL SUPPLIERS OF PERMEATION TUBES AND SYSTEMS

Kin-Tek
504 Laurel St.
Lamarque, Texas 77568
(409) 938-3627
(800) 326-3627

Vici Metronics, Inc.
2991 Corvin Drive
Santa Clara, CA 95051
(408) 737-0550

Analytical Instrument Development, Inc.
Rt. 41 and Newark Rd.
Avondale, PA 19311
(215) 268-3181

Ecology Board, Inc.
9257 Independence Ave.
Chatsworth, CA 91311
(213) 882-6795

Tracor, Inc.
6500 Tracor Land
Austin, TX
(512) 926-2800

Metronics Associates, Inc.
3201 Porter Drive
Standford Industrial Park
Palo Alto, CA 94304
(415) 493-5632

TABLE 1. VOLATILE ORGANIC COMPOUNDS ON THE TITLE III CLEAN AIR AMENDMENT LIST--MEMBERSHIP IN COMPENDIUM METHOD TO-14A LIST AND THE SOW-CLP LIST OF VOCs

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Methyl chloride (chloromethane); CH3Cl	74-87-3	-23.7	3.8 x 10	50.5	X	X
Carbonyl sulfide; COS	463-58-1	-50.0	3.7 x 10	60.1		
Vinyl chloride (chloroethene); C2H3Cl	75-01-4	-14.0	3.2 x 10	62.5	X	X
Diazomethane; CH2N2	334-88-3	-23.0	2.8 x 10	42.1		
Formaldehyde; CH2O	50-00-0	-19.5	2.7 x 10	30		
1,3-Butadiene; C4H6	106-99-0	-4.5	2.0 x 10	54		X
Methyl bromide (bromomethane); CH3Br	74-83-9	3.6	1.8 x 10	94.9	X	X
Phosgene; CCl2O	75-44-5	8.2	1.2 x 10	99		
Vinyl bromide (bromoethene); C2H3Br	593-60-2	15.8	l.l x 10	107		
Ethylene oxide; C2H4O	75-21-8	10.7	1.1 x 10	44		
Ethyl chloride (chloroethane); C2H5Cl	75-00-3	12.5	1.0 x 10	64.5	X	X
Acetaldehyde (ethanal); C2H4O	75-07-0	21.0	952	44		
Vinylidene chloride (1,1-dichloroethylene); C2H2Cl2	75-35-4	31.7	500	97	X	X
Propylene oxide; C3H6O	75-56-9	34.2	445	58		
Methyl iodide (iodomethane); CH3I	74-88-4	42.4	400	141.9		
Methylene chloride; CH2Cl2	75-09-2	40.0	349	84.9	X	X
Methyl isocyanate; C2H3NO	624-83-9	59.6	348	57.1		
Allyl chloride (3-chloropropene); C3H5Cl	107-05-1	44.5	340	76.5	X	X
Carbon disulfide; CS2	75-15-0	46.5	260	76		
Methyl tert-butyl ether; C5H12O	1634-04-4	55.2	249	86		
Propionaldehyde; C2H5CHO	123-38-6	49.0	235	58.1		
Ethylidene dichloride (1,1-dichloroethane); C2H4Cl2	75-34-3	57.0	230	99	X	

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Chloroprene (2-chloro-1,3-butadiene); C4H5Cl	126-99-8	59.4	226	88.5		
Chloromethyl methyl ether; C2H5ClO	107-30-2	59.0	224	80.5		
Acrolein (2-propenal); C3H4O	107-02-8	52.5	220	56		X
1,2-Epoxybutane (1,2-butylene oxide); C4H8O	106-88-7	63.0	163	72		
Chloroform; CHCl3	67-66-3	61.2	160	119	X	X
Ethyleneimine (aziridine); C2H5N	151-56-4	56	160.0	43		
1,1-Dimethylhydrazine; C2H8N2	57-14-7	63	157.0	60.0		
Hexane; C6H14	110-54-3	69.0	120	86.2	X	
1,2-Propyleneimine (2-methylaziridine); C3H7N	75-55-8	66.0	112	57.1		
Acrylonitrile (2-propenenitrile); C3H3N	107-13-1	77.3	100	53	X	
Methyl chloroform (1,1,1-trichloroethane); C2H3Cl3	71-55-6	74.1	100	133.4	X	X
Methanol; CH4O	67-56-1	65.0	92.0	32		X
Carbon tetrachloride; CCl4	56-23-5	76.7	90.0	153.8	X	X
Vinyl acetate; C4H6O2	108-05-4	72.2	83.0	86		X
Methyl ethyl ketone (2-butanone); C4H8O	78-93-3	79.6	77.5	72		X
Benzene; C6H6	71-43-2	80.1	76.0	78	X	X
Acetonitrile (cyanomethane); C2H3N	75-05-8	82	74.0	41.0		X
Ethylene dichloride (1,2-dichloroethane); C2H4Cl2	107-06-2	83.5	61.5	99	X	X
Triethylamine; C6H15N	121-44-8	89.5	54.0	101.2		
Methylhydrazine; CH6N2	60-34-4	87. 8	49.6	46.1		
Propylene dichloride (1,2-dichloropropane); C3H6Cl2	78-87-5	97.0	42.0	113	X	X
2,2,4-Trimethyl pentane C8H18	540-84-l	99.2	40.6	114		
1,4-Dioxane (1,4-Diethylene oxide); C4H8O2	123-91-1	101	37.0	88		
Bis(chloromethyl) ether; C2H4Cl2O	542-88-1	104	30.0	115		
Ethyl acrylate; C5H8O2	140-88-5	100	29.3	100		
Methyl methacrylate; C5H8O2	80-62-6	101	28.0	100.1		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmgHg)[1]	MW[1]	TO-14A	CLP-SOW
Methyl methacrylate; C5H8O2	80-62-101	101	28.0	100.1		
1,3-Dichloropropene; C3H4Cl2 (cis)	542-75-6	112	27.8	111	X	X
Toluene; C7H8	108-88-3	111	22.0	92	X	X
Trichloroethylene; C2HCl3	79-01-6	87.0	20.0	131.4	X	X
1,1,2-Trichloroethane; C2H3Cl3	79-00-5	114	19.0	133.4	X	X
Tetrachloroethylene; C2Cl4	127-18-4	121	14.0	165.8	X	X
Epichlorohydrin (1-chloro-2,3-epoxy propane); C3H5ClO	106-89-8	117	12.0	92.5		
Ethylene dibromide (1,2-dibromoethane); C2H4Br2	106-93-4	132	11.0	187.9	X	X
N-Nitroso-N-methylurea; C2H5N3O2	684-93-5	124	10.0	103		
2-Nitropropane; C3H7NO2	79-46-9	120	10.0	89		
Chlorobenzene; C6H5Cl	108-90-7	132	8.8	112.6	X	X
Ethylbenzene; C8H10	100-41-4	136	7.0	106	X	X
Xylenes (isomer & mixtures); C8H10	1330-20-7	142	6.7	106.2	X	X
Styrene; C8H8	100-42-5	145	6.6	104	X	X
p-Xylene; C8H10	106-42-3	138	6.5	106.2	X	X
m-Xylene; C8H10	108-38-3	139	6.0	106.2	X	X
Methyl isobutyl ketone (hexone); C6H12O	108-10-1	117	6.0	100.2		
Bromoform (tribromomethane); CHBr3	75-25-2	149	5.6	252.8		
l,l,2,2-Tetrachloroethane; C2H2Cl4	79-34-5	146	5.0	167.9	X	X
o-Xylene; C8H10	95-47-6	144	5.0	106.2	X	X
Dimethylcarbamyl chloride; C3H6ClNO	79-44-7	166	4.9	107.6		
N-Nitrosodimethylamine; C2H6N2O	62-75-9	152	3.7	74		
Beta-Propiolactone; C3H4O2	57-57-8	Decomposes at 162	3.4	72		
Cumene (isopropylbenzene); C9Hl2	98-82-8	153	3.2	120		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Cumene (isopropylbenzene); C9H12	98-82-8	153	3.2	120		
Acrylic acid; C3H4O2	79-10-7	141	3.2	72		
N,N-Dimethylformamide; C3H7NO	68-12-2	153	2.7	73		
1,3-Propane sultone; C3H6O3S	1120-71-4	180/30mm	2.0	122.1		
Acetophenone; C8H8O	98-86-2	202	1.0	120		
Dimethyl sulfate; C2H6O4S	77-78-1	188	1.0	126.1		
Benzyl chloride (a-chlorotoluene); C7H7Cl	100-44-7	179	1.0	126.6	X	X
1,2-Dibromo-3-chloropropane; C3H5Br2Cl	96-12-8	196	0.80	236.4		
Bis(2-Chloroethyl)ether; C4H8Cl2O	111-44-4	178	0.71	143		
Chloroacetic acid; C2H3ClO2	79-11-8	189	0.69	94.5		
Aniline (aminobenzene); C6H7N	62-53-3	184	0.67	93		
1,4-Dichlorobenzene (p-); C6H4Cl2	106-46-7	173	0.60	147	X	X
Ethyl carbamate (urethane); C3H7NO2	51-79-6	183	0.54	89		
Acrylamide; C3H5NO	79-06-1	125/25 mm	0.53	71		
N,N-Dimethylaniline; C8H11N	121-69-7	192	0.50	121		
Hexachloroethane; C2Cl6	67-72-1	Sublimes at 186	0.40	236.7		
Hexachlorobutadiene; C4Cl6	87-68-3	215	0.40	260.8	X	X
Isophorone; C9H14O	78-59-1	215	0.38	138.2		
N-Nitrosomorpholine; C4H8N2O2	59-89-2	225	0.32	116.1		
Styrene oxide; C8H8O	96-09-3	194	0.30	120.2		
Diethyl sulfate; C4H10O4S	64-67-5	208	0.29	154		
Cresylic acid (cresol isomer mixture);C7H8O	1319-77-3	202	0.26	108		
o-Cresol; C7H8O	95-48-7	191	0.24	108		
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	240	0.22	110		
Phenol; C6H6O	108-95-2	182	0.20	94		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	240	0.22	110		
Phenol; C6H6O	108-95-2	182	0.20	94		
1,2,4-Trichlorobenzene; C6H3Cl3	120-82-1	213	0.18	181.5	X	X
nitrobenzene; C6H5NO2	98-95-3	211	0.15	123		

[1]Vapor pressure (v.p.), boiling point (BP) and molecularweight (MW) data from:
(a)D. L. Jones and J. bursey, "Simultaneous Control of PM-10 and Hazardous Air Pollutants II: Rationale for Selection of Hazardous Air Pollutants as Potential Particulate Matter," Report EPA-452/R-93/013, U. S. Environmental Protection Agency, Research Triangle Park, NC. October 1992;
(b)R. C. Weber, P. A. Parker, and M. Bowser. Vapor Pressure Distribution of Selected Organic Chemicals, Report EPA-600/2-81-021, U. S. Environmental Protection Agency, Cincinnati, OH, February 1981; and
(c)R. C. Weast, ed., "CRC Handbook of Chemistry and Physics," 59th edition, CRC Press, Boca Raton, 1979.

TABLE 2. CHARACTERISTIC MASSES (M/Z) USED FOR QUANTIFYING THE TITLE III CLEAN AIR ACT AMENDMENT COMPOUNDS

Compound	CAS No.	Primary Ion	Secondary Ion
Methyl chloride (chloromethane); CH3Cl	74-87-3	50	52
Carbonyl sulfide; COS	463-S8-1	60	62
Vinyl chloride (chloroethene); C2H3Cl	7S-01-4	62	64
Diazomethane; CH2N2	334-88-3	42	41
Formaldehyde; CH2O	50-00-0	29	30
1,3-Butadiene; C4H6	106-99-0	39	54
Methyl bromide (bromomethane); CH3Br	74-83-9	94	96
Phosgene; CCl2O	75-44-5	63	65
Vinyl bromide (bromoethene); C2H3Br	593-60-2	106	108
Ethylene oxide; C2H4O	75-21-8	29	44
Ethyl chloride (chloroethane); C2H5Cl	75-00-3	64	66
Acetaldehyde (ethanal); C2H4O	75-07-0	44	29, 43
Vinylidene chloride (1,1-dichloroethylene); C2H2Cl2	75-35-4	61	96
Propylene oxide; C3H6O	75-56-9	58	57
Methyl iodide (iodomethane); CH3I	74-88-4	142	127
Methylene chloride; CH2Cl2	75-09-2	49	84, 86
Methyl isocyanate; C2H3NO	624-83-9	57	56
Allyl chloride (3-chloropropene); C3H5Cl	107-05-1	76	41, 78
Carbon disulfide; CS2	75-15-0	76	44, 78
Methyl tert-butyl ether; C5H12O	1634-04-4	73	41, 53
Propionaldehyde; C2H5CHO	123-38-6	58	29, 57
Ethylidene dichloride (1,1-dichloroethane); C2H4Cl2	75-34-3	63	65, 27
Chloroprene (2-chloro-1,3-butadiene); C4H5Cl	126-99-8	88	53, 90
Chloromethyl methyl ether; C2H5ClO	107-30-2	45	29, 49
Acrolein (2-propenal); C3H4O	107-02-8	56	55
1,2-Epoxybutane (1,2-butylene oxide); C4H8O	106-88-7	42	41, 72
Chloroform; CHCl3	67-66-3	83	85, 47
Ethyleneimine (aziridine); C2H5N	151-56-4	42	43
1,1-Dimethylhydrazine; C2H8N2	57-14-7	60	45, 59
Hexane; C6H14	110-54-3	57	41, 43
1,2-Propyleneimine (2-methylazindine); C3H7N	75-55-8	56	57, 42
Acrylonitrile (2-propenenitrile); C3H3N	107-13-1	53	52
Methyl chloroform (1,1,1 trichloroethane); C2H3Cl3	71-55-6	97	99, 61
Methanol; CH4O	67-56-1	31	29
Carbon tetrachloride; CCl4	56-23-5	117	119
Vinyl acetate; C4H6O2	108-05-4	43	86
Methyl ethyl ketone (2-butanone); C4H8O	78-93-3	43	72

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Benzene; C6H6	71-43-2	78	77,50
Acetonitrile (cyanomethane); C2H3N	75-05-8	41	40
Ethylene dichloride (1,2-dichloroethane); C2H4Cl2	107-06-2	62	64, 27
Triethylamine; C6H15N	121-44-8	86	58, 101
Methylhydrazine; CH6N2	60-34-4	46	31, 45
Propylene dichloride (1,2-dichloropropane); C3H6Cl2	78-87-5	63	41, 62
2,2,4-Trimethyl pentane; C8H18	540-84-1	57	41, 56
1,4-Dioxane (1,4 Diethylene oxide); C4H8O2	123-91-1	88	58
Bis(chloromethyl) ether; C2H4Cl2O	542-88-1	79	49, 81
Ethyl acrylate; C5H8O2	140-88-5	55	73
Methyl methacrylate; C5H8O2	80-62-6	41	69, 100
1,3-Dichloropropene; C3H4Cl2 (cis)	542-75-6	75	39, 77
Toluene; C7H8	108-88-3	91	92
Trichloethylene; C2HCl3	79-01-6	130	132, 95
1,1,2-Trichloroethane; C2H3Cl3	79-00-5	97	83, 61
Tetrachloroethylene; C2Cl4	127-18-4	166	164, 131
Epichlorohydrin (l-chloro-2,3-epoxy propane); C3H5ClO	106-89-8	57	49, 62
Ethylene dibromide (1,2-dibromoethane); C2H4Br2	106-93-4	107	109
N-Nitrso-N-methylurea; C2H5N3O2	684-93-5	60	44, 103
2-Nitropropane; C3H7NO2	79-46-9	43	41
Chlorobenzene; C6H5Cl	108-90-7	112	77, 114
Ethylbenzene; C8H10	100-41-4	91	106
Xylenes (isomer & mixtures); C8H10	1330-20-7	91	106
Styrene; C8H8	100-42-5	104	78, 103
p-Xylene; C8H10	106-42-3	91	106
m-Xylene; C8H10	108-38-3	91	106
Methyl isobutyl ketone (hexone); C6H12O	108-10-1	43	58, 100
Bromoform (tribromomethane); CHBr3	75-25-2	173	171, 175
1,1,2,2-Tetrachloroethane; C2H2Cl4	79-34-5	83	85
o-Xylene; C8H10	95-47-6	91	106
Dimethylcarbamyl chloride; C3H6ClNO	79-44-7	72	107
N-Nitrosodimethylamine; C2H6N2O	62-75-9	74	42
Beta-Propiolactone; C3H4O2	57-57-8	42	43
Cumene (isopropylbenzene); C9H12	98-82-8	105	120
Acrylic acid; C3H4O2	79-10-7	72	45, 55
N,N-Dimethylformamide; C3H7NO	68-12-2	73	42, 44
1,3-Propane sultone; C3H6O3S	1120-71-4	58	65, 122

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Acetophenone; C8H8O	98-86-2	105	77,120
Dimethyl sulfate; C2H6O4S	77-78-1	95	66,96
Benzyl chloride (a-chlorotoluene); C7H7Cl	100-44-7	91	126
1,2-Dibromo-3-chloropropane; C3H5Br2Cl	96-12-8	57	155, 157
Bis(2-Chloroethyl)ether; C4H8Cl2O	111-44-4	93	63, 95
Chloroacetic acid; C2H3ClO2	79-11-8	50	45, 60
Aniline (aminobenzene); C6H7N	62-53-3	93	66
1,4-Dichlorobenzene (p-); C6H4Cl2	106-46-7	146	148, 111
Ethyl carbamate (urethane); C3H7NO2	51-79-6	31	44, 62
Acrylamide; C3H5NO	79-06-1	44	55, 71
N,N-Dimethylaniline; C8H11N	121-69-7	120	77, 121
Hexachloroethane; C2Cl6	67-72-1	201	199, 203
Hexachlorobutadiene; C4Cl6	87-68-3	225	227, 223
Isophorone; C9H14O	78-59-1	82	138
N-Nitrosomorpholine; C4H8N2O2	59-89-2	56	86, 116
Styrene oxide; C8H8O	96-09-3	91	120
Diethyl sulfate; C4H10O4S	64-67-5	45	59, 139
Cresylic acid (cresol isomer mixture); C7H8O	1319-77-3		
o-Cresol; C7H8O	95-48-7	108	107
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	110	64
Phenol; C6H6O	108-95-2	94	66
1,2,4-Trichlorobenzene; C6H3Cl3	120-82-1	180	182, 184
Nitrobenzene; C6H5NO2	98-95-3	77	51, 123

TABLE 3. REQUIRED BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria[1]
50	8.0 to 40.0 Percent of m/e 95
75	30.0 to 66.0 Percent of m/e 95
95	Base Peak, 100 Percent Relative Abundance
96	5.0 to 9.0 Percent of m/e 95 (See note)
173	Less than 2.0 Percent of m/e 174
174	50.0 to 120.0 Percent of m/e 95
175	4.0 to 9.0 Percent of m/e 174
176	93.0 to 101.0 Percent of m/e 174
177	5.0 to 9.0 Percent of m/e 176

[1]All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

TABLE 4. METHOD DETECTION LIMITS (MDL)[1]

TO-14A List	Lab #1, SCAN	Lab #2, SIM
Benzene	0.34	0.29
Benzyl Chloride	--	--
Carbon tetrachloride	0.42	0.15
Chlorobenzene	0.34	0.02
Chloroform	0.25	0.07
1,3-Dichlorobenzene	0.36	0.07
1,2-Dibromoethane	--	0.05
1,4-Dichlorobenzene	0.70	0.12
1,2-Dichlorobenzene	0.44	--
1,1-Dichloroethane	0.27	0.05
1,2-Dichloroethane	0.24	--
1,1-Dichloroethene	--	0.22
cis-1,2-Dichloroethene	--	0.06
Methylene chloride	1.38	0.84
1,2-Dichloropropane	0.21	--
cis-1,3-Dichloropropene	0.36	--
trans-1,3-Dichloropropene	0.22	--
Ethylbenzene	0.27	0.05
Chloroethane	0.19	--
Trichlorofluoromethane	--	--
1,1,2-Trichloro-1,2,2-trifluoroethane		--
1,2-Dichloro-1,1,2,2-tetrafluoroethane	--	--
Dichlorodifluoromethane	--	--
Hexachlorobutadiene	--	--
Bromomethane	0.53	--
Chloromethane	0.40	--
Styrene	1.64	0.06
1,1,2,2-Tetrachloroethane	0.28	0.09
Tetrachloroethene	0.75	0.10
Toluene	0.99	0.20
1,2,4-Trichlorobenzene	--	--
1,1,1-Trichloroethane	0.62	0.21
1,1,2-Trichloroethane	0.50	--
Trichloroethene	0.45	0.07
1,2,4-Trimethylbenzene	--	--
1,3,5-Trimethylbenzene	--	--
Vinyl Chloride	0.33	0.48
m,p-Xylene	0.76	0.08
o-Xylene	0.57	0.28

[1]Method Detection Limits (MDLs) are defined as the product of the standard deviation of seven replicate analyses and the student's "t" test value for 99% confidence. For Lab #2, the MDLs represent an average over four studies. MDLs are for MS/SCAN for Lab #1 and for MS/SIM for Lab #2.

TABLE 5. SUMMARY OF EPA DATA ON REPLICATE PRECISION (RP) FROM EPA NETWORK OPERATIONS[1]

Monitoring Compound Identification	EPA's Urban Air Toxics Monitoring Program (UATMP)			EPA's Toxics Air Monitoring Stations (TAMS)		
	%RP	#	ppbv	%RP	#	ppbv
Dichlorodifluoromethane	--		--	13.9	47	0.9
Methylene chloride	16.3	07	4.3	19.4	47	0.6
1,2-Dichloroethane	36.2	31	1.6	--	--	--
1,1,1-Trichloroethane	14.1	44	1.0	10.6	47	2.0
Benzene	12.3	56	1.6	4.4	47	1.5
Trichloroethene	12.8	08	1.3	--	--	--
Toluene	14.7	76	3.1	3.4	47	3.1
Tetrachloroethene	36.2	12	0.8	--	--	--
Chlorobenzene	20.3	21	0.9	--	--	--
Ethylbenzene	14.6	32	0.7	5.4	47	0.5
m-Xylene	14.7	75	4.0	5.3	47	1.5
Styrene	22.8	59[2]	1.1	8.7	47	0.2[2]
o-Xylene	--		--	6.0	47	0.5
p-Xylene	--					
1,3-Dichlorobenzene	49.1	06	0.6	--	--	--
1,4-Dichlorobenzene	14.7	14	6.5	--	--	--

[1]Denotes the number of replicate or duplicate analysis used to generate the statistic. The replicate precision is defined as the mean ratio of absolute difference to the average value.
[2]Styrene and o-xylene coelute from the GC column used in UATMP. For the TAMS entries, both values were below detection limits for 18 of 47 replicates and were not included in the calculation.

TABLE 6. AUDIT ACCURACY (AA) VALUES[1] FOR SELECTED COMPENDIUM METHOD TO-14A COMPOUNDS

Selected Compounds From TO-14A List	FY-88 TAMS AA(%), N=30	FY-88 UATMP AA(%), N=3
Vinyl chloride	4.6	17.9
Bromomethane	--	6.4
Trichlorofluoromethane	6.4	--
Methylene chloride	8.6	31.4
Chloroform	--	4.2
1,2-Dichloroethane	6.8	11.4
1,1,1-Trichloroethane	18.6	11.3
Benzene	10.3	10.1
Carbon tetrachloride	12.4	9.4
1,2-Dichloropropane	--	6.2
Trichloroethene	8.8	5.2
Toluene	8.3	12.5
Tetrachloroethene	6.2	--
Chlorobenzene	10.5	11.7
Ethylbenzene	12.4	12.4
o-Xylene	16.2	21.2

[1]Audit accuracy is defined as the relative difference between the audit measurement result and its nominal value divided by the nominal value. N denotes the number of audits averaged to obtain the audit accuracy value. Information is not available for other TO-14A compounds because they were not present in the audit materials.

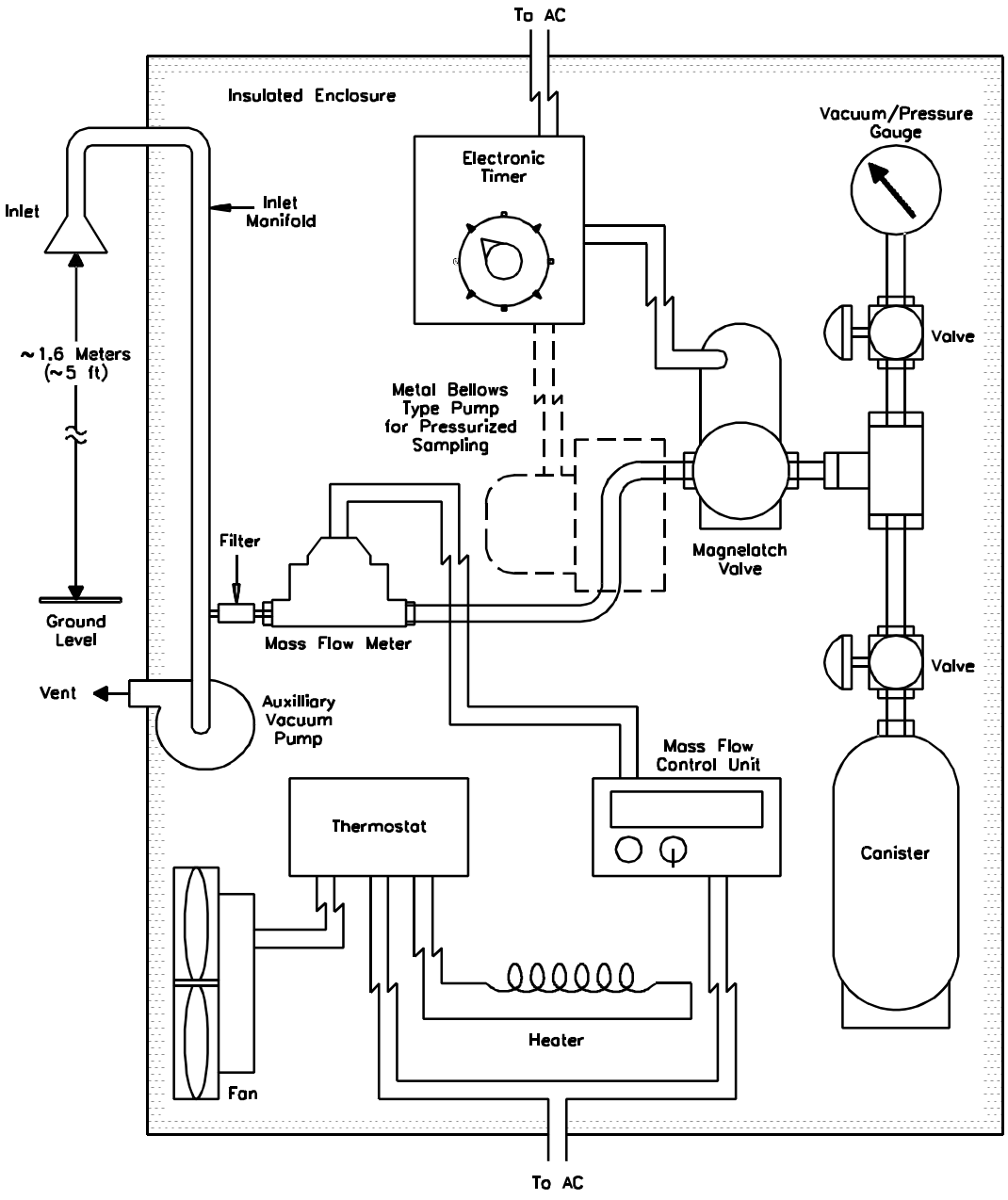
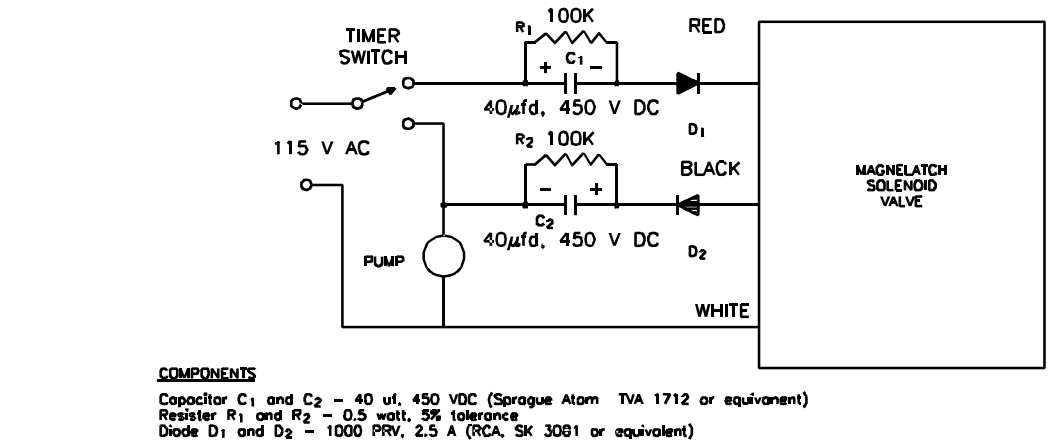
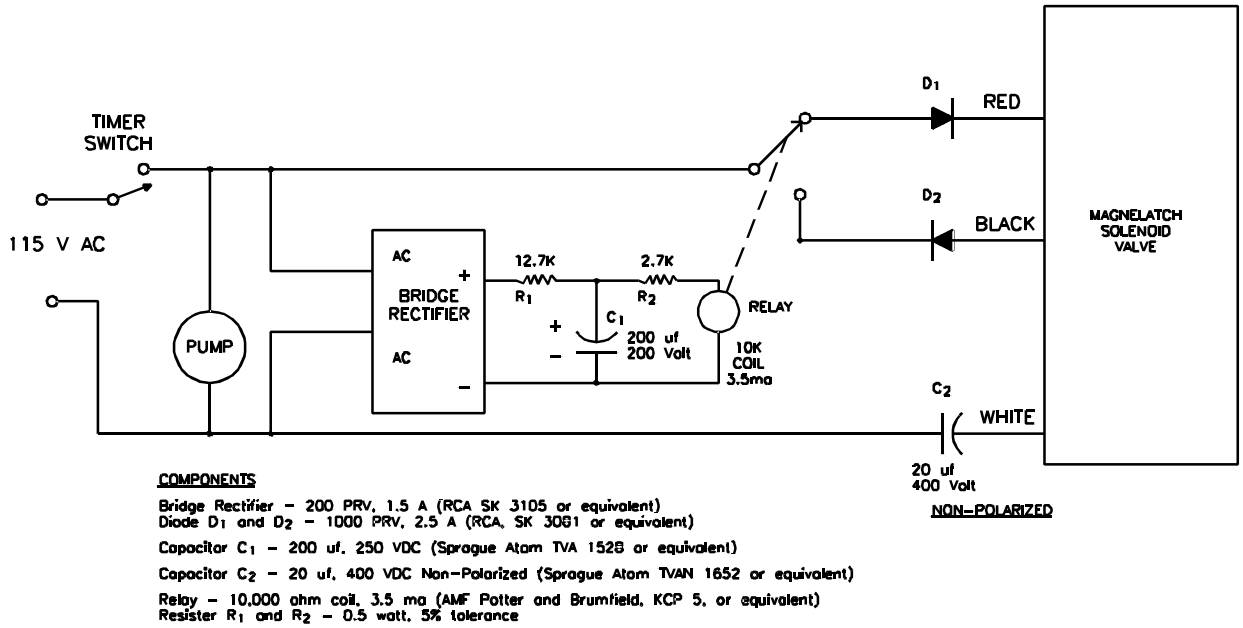


Figure 1. Sampler configuration for subatmospheric pressure or pressurized canister sampling.



(a). Simple Circuit for Operating Magnelatch Valve



(b). Improved Circuit Designed to Handle Power Interruptions

Figure 2. Electrical pulse circuits for driving Skinner magnelatch solenoid valve with mechanical timer.

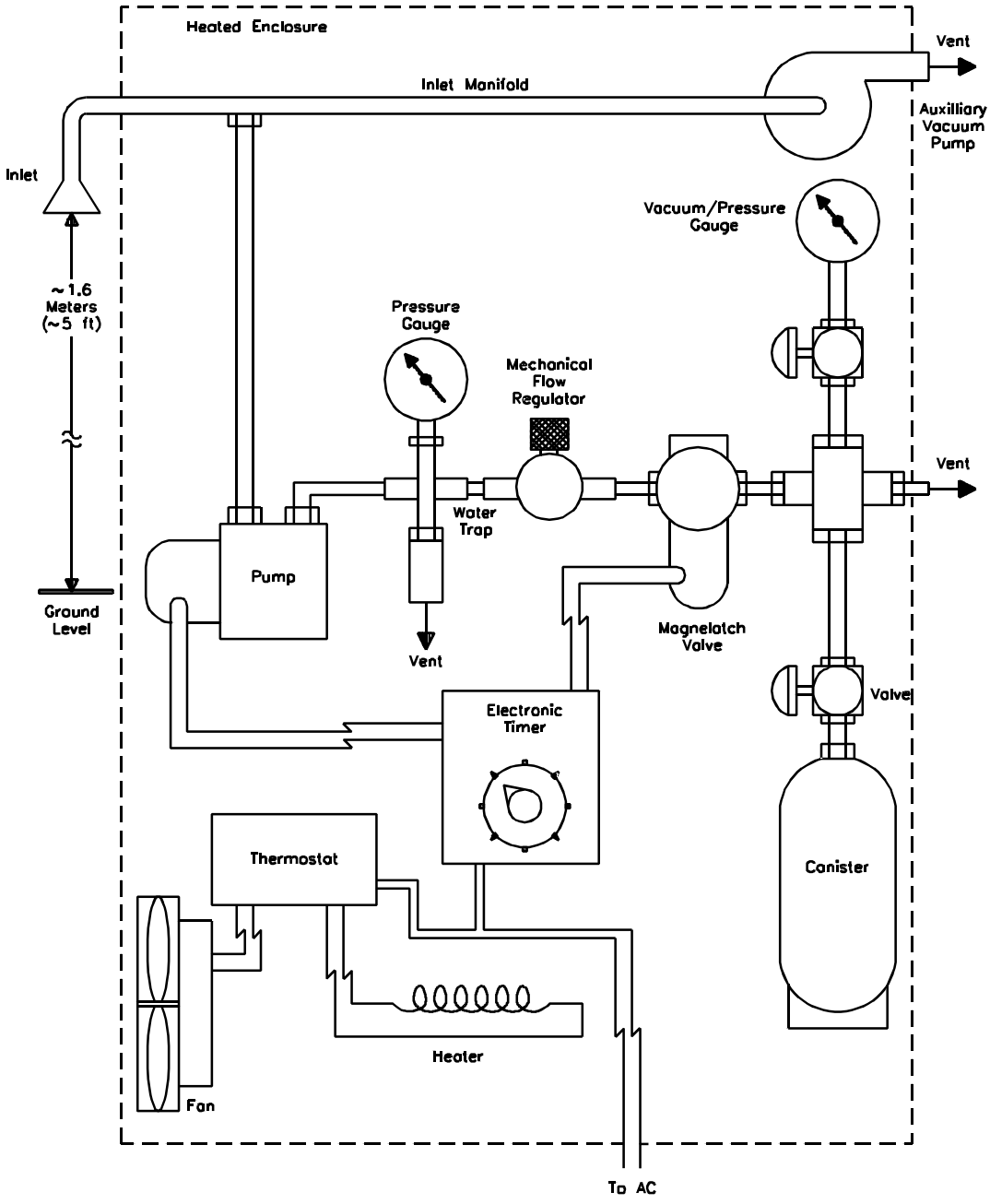


Figure 3. Alternative sampler configuration for pressurized canister sampling.

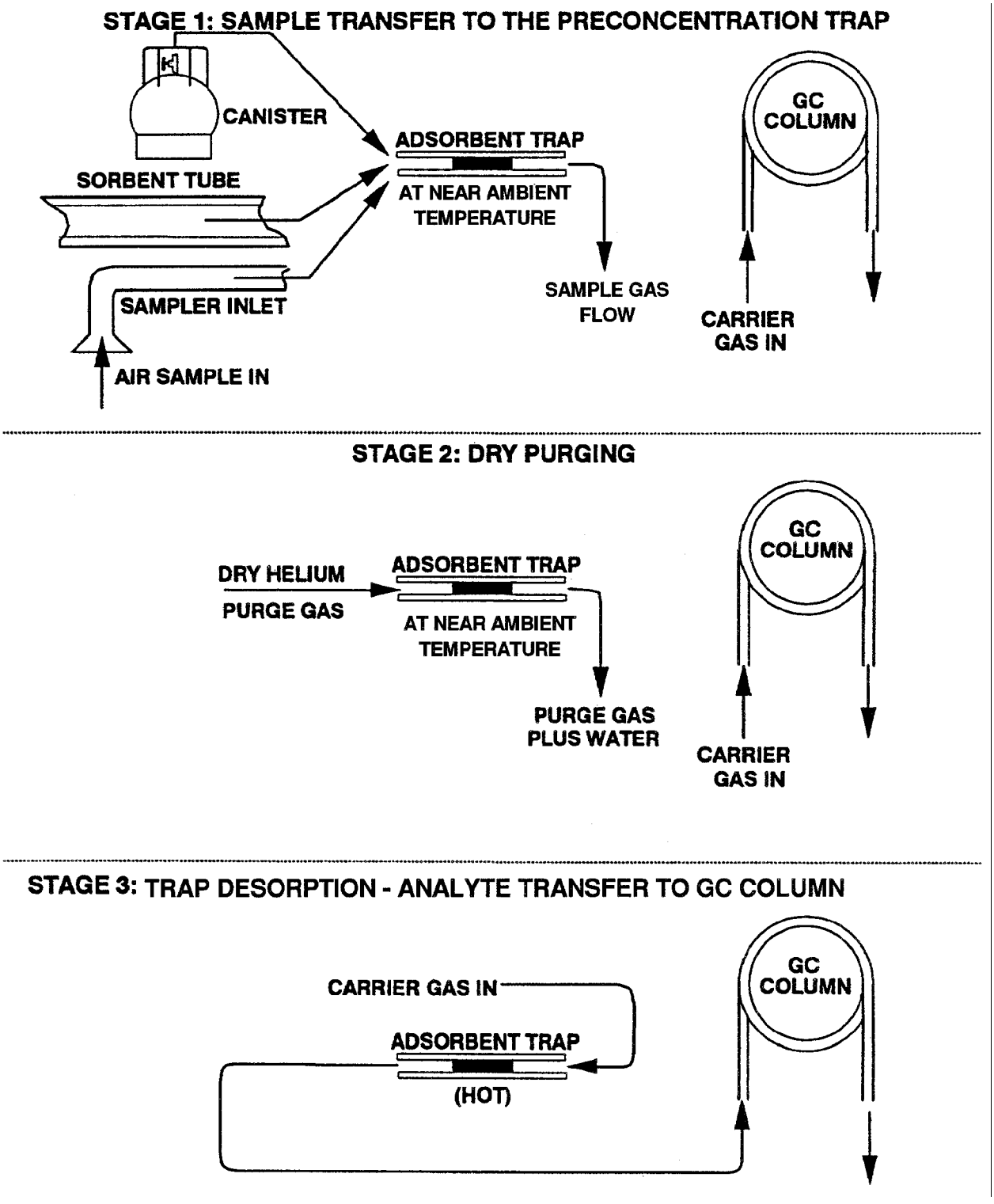


Figure 4. Illustration of three stages of dry purging of adsorbent trap.

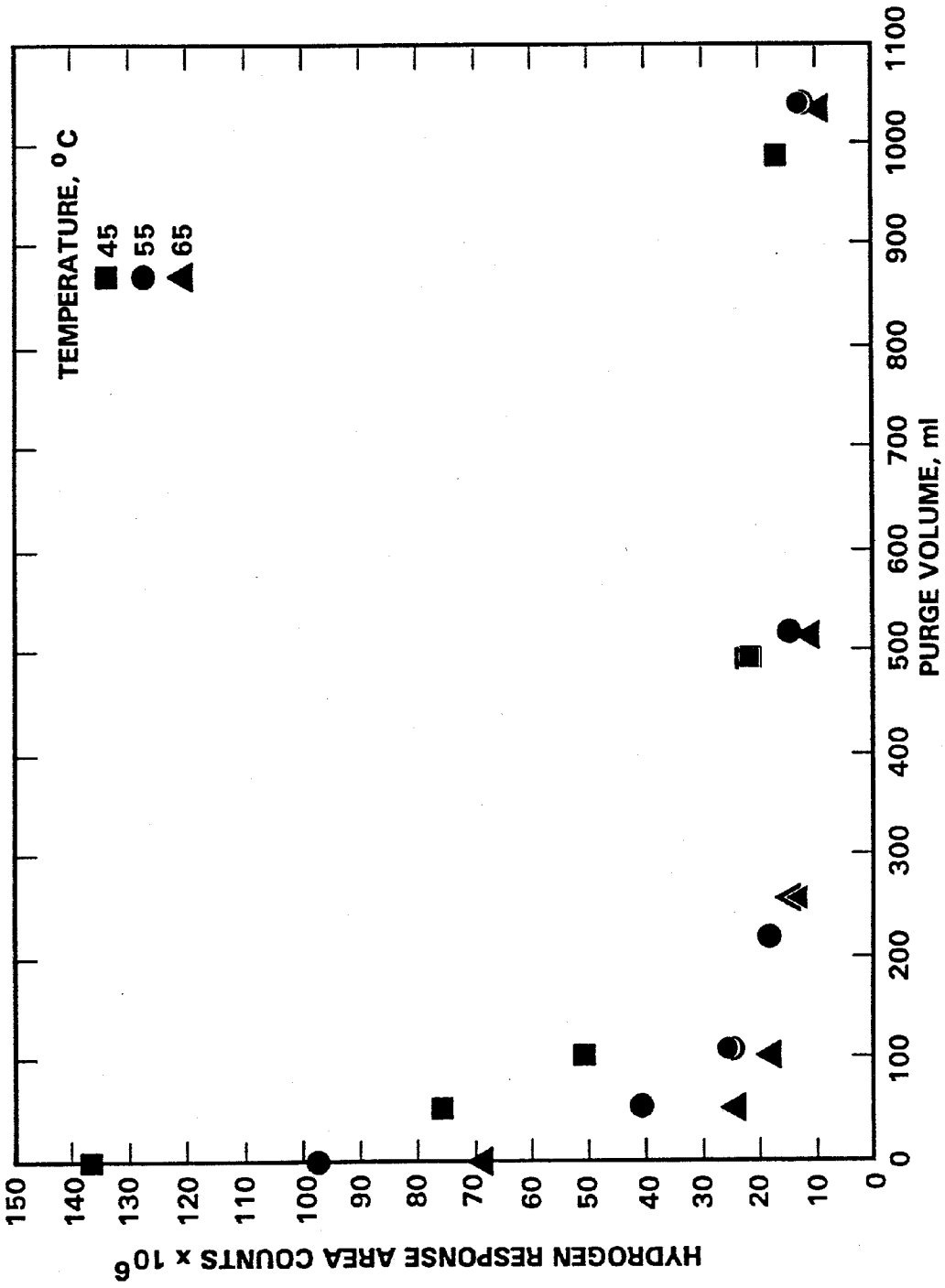


Figure 5. Residual water vapor on VOC concentrator vs. dry He purge volume.

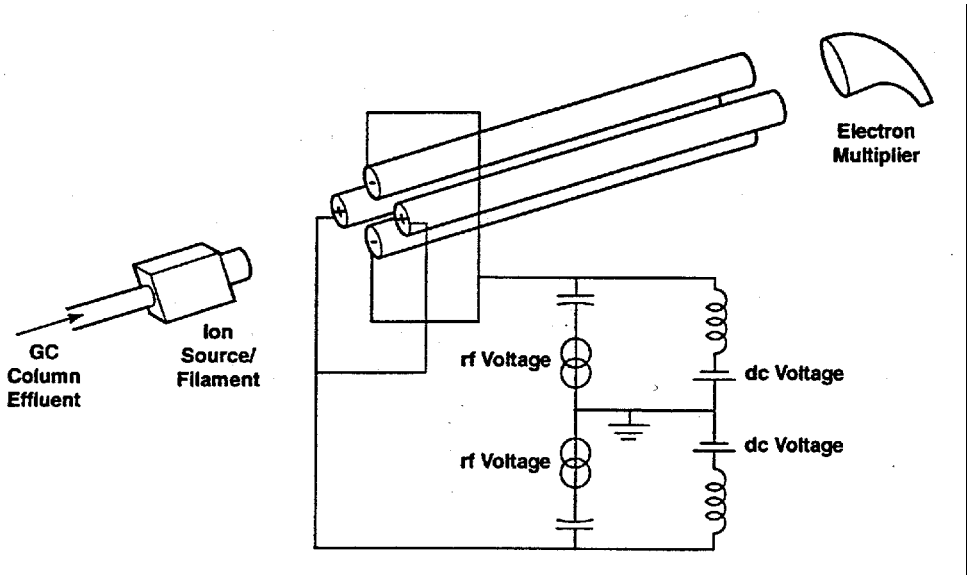


Figure 6. Simplified diagram of a quadrupole mass spectrometer.

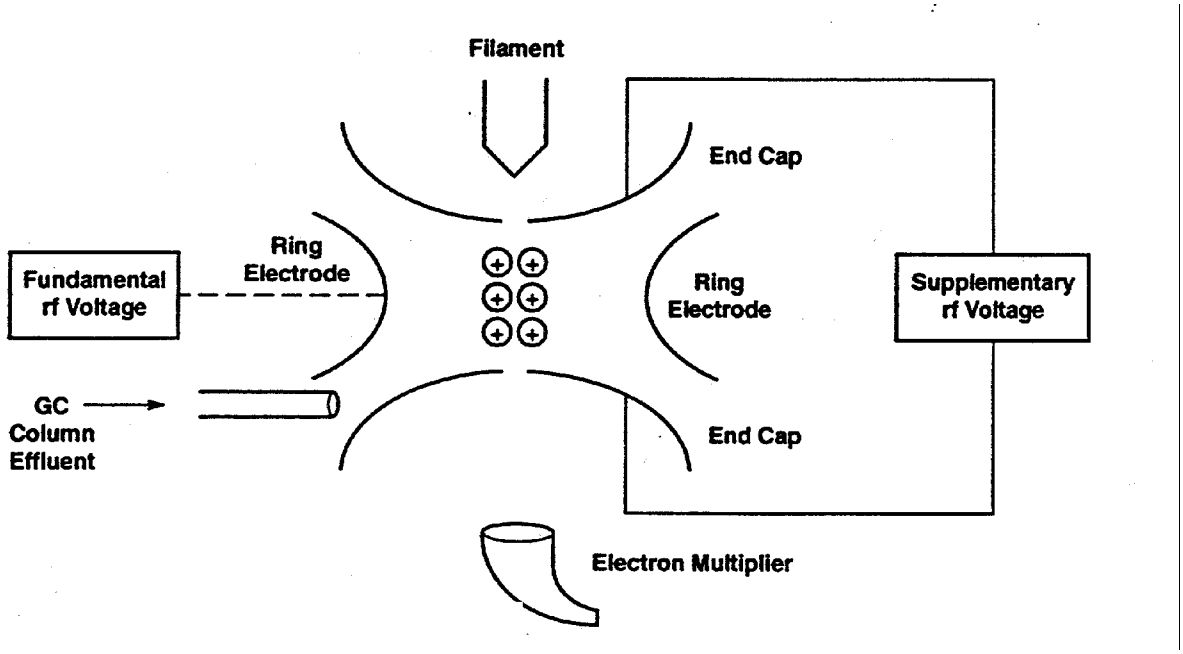


Figure 7. Simplified diagram of an ion trap mass spectrometer.

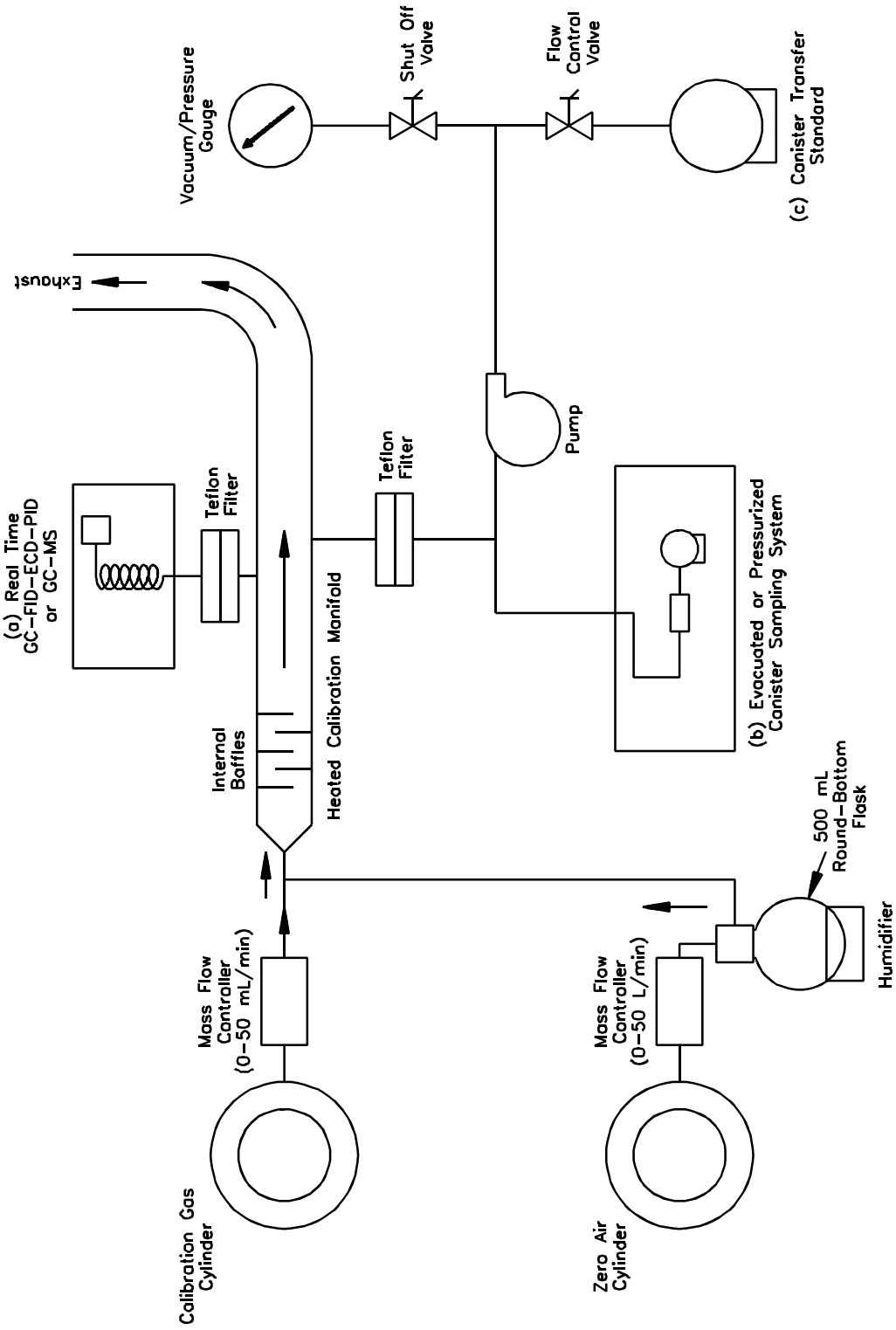


Figure 8. Schematic diagram of calibration system and manifold for (a) analytical system calibration, (b) testing canister sampling system and (c) preparing canister transfer standards.

COMPENDIUM METHOD TO-15
CANISTER SAMPLING FIELD TEST DATA SHEET

A.GENERAL INFORMATION

SITE LOCATION: _____
SITE ADDRESS: _____
_____
SAMPLING DATE: _____

SHIPPING DATE: _____
CANISTER SERIAL NO.: _____
SAMPLER ID: _____
OPERATOR: _____
CANISTER LEAK
CHECK DATE: _____

B. SAMPLING INFORMATION

	TEMPERATURE				PRESSURE	
	INTERIOR	AMBIENT	MAXIMUM	MINIMUM	CANISTER PRESSURE	
START						
STOP						

	SAMPLING TIMES		FLOW RATES		
	LOCAL TIME	ELAPSED TIME METER READING	MANIFOLD FLOW RATE	CANISTER FLOW RATE	FLOW CONTROLLER READOUT
START					
STOP					

SAMPLING SYSTEM CERTIFICATION DATE: _____
QUARTERLY RECERTIFICATION DATE: _____

C. LABORATORY INFORMATION

DATA RECEIVED: _____
RECEIVED BY: _____
INITIAL PRESSURE: _____
FINAL PRESSURE: _____
DILUTION FACTOR: _____
ANALYSIS
GC-FID-ECD DATE: _____
GC-MSD-SCAN DATE: _____
GC-MSD-SIM DATE: _____
RESULTS*: _____
_____
GC-FID-ECD: _____
GC-MSD-SCAN: _____
GC-MSD-SIM: _____

_____
SIGNATURE/TITLE

Figure 9. Canister sampling field test data sheet (FTDS).

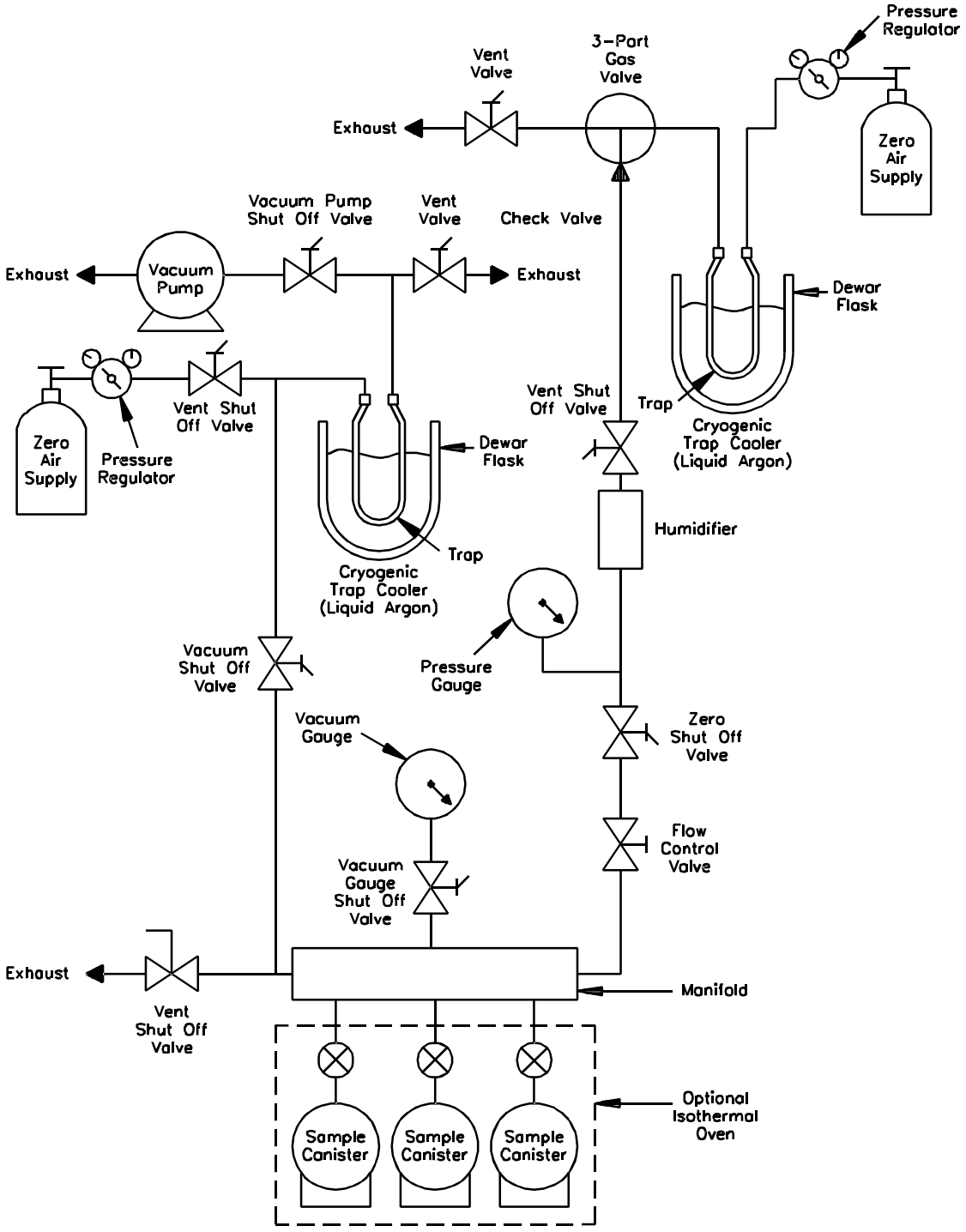


Figure 10. Canister cleaning system.

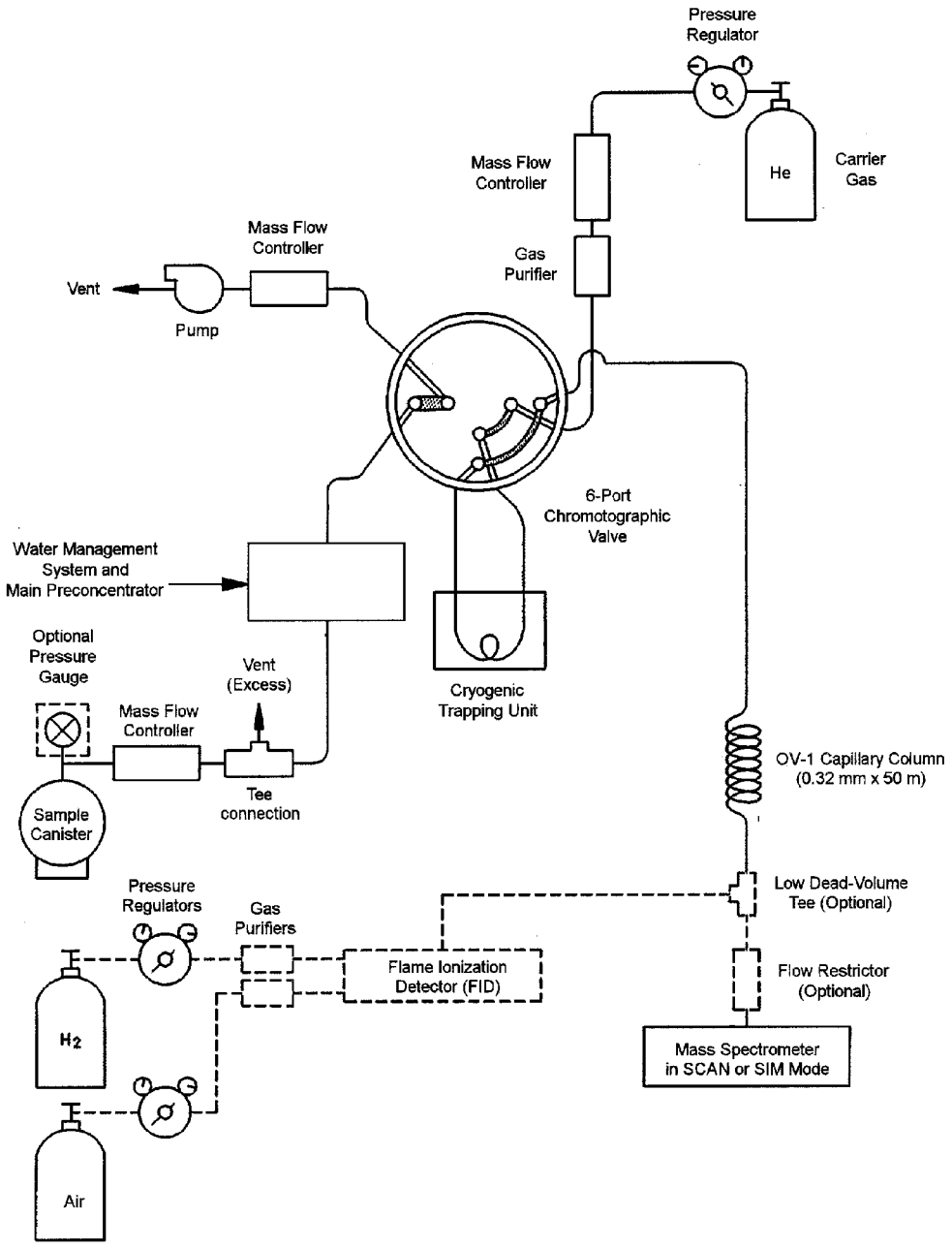
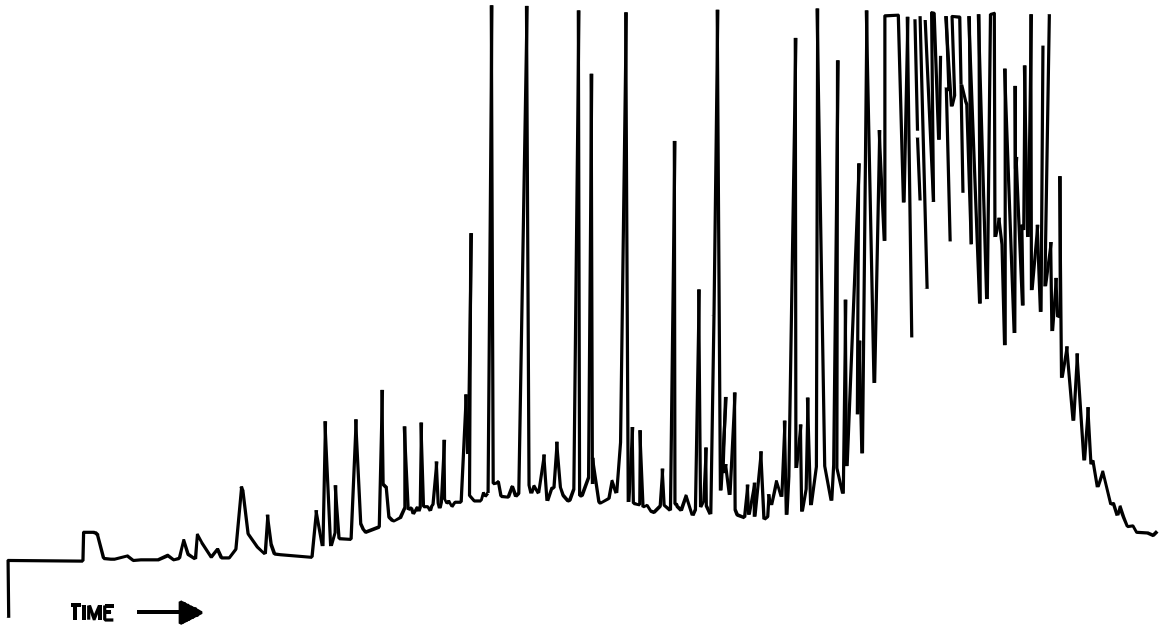


Figure 11. Canister analysis utilizing GC/MS/SCAN/SIM analytical system with optional flame ionization detector with 6-port chromatographic valve in the sample desorption mode.
[Alternative analytical system illustrated in Figure 16.]

(a). Certified Sampler



(b). Contaminated Sampler

Figure 12. Example of humid zero air test results for a clean sample canister (a) and a contaminated sample canister (b).

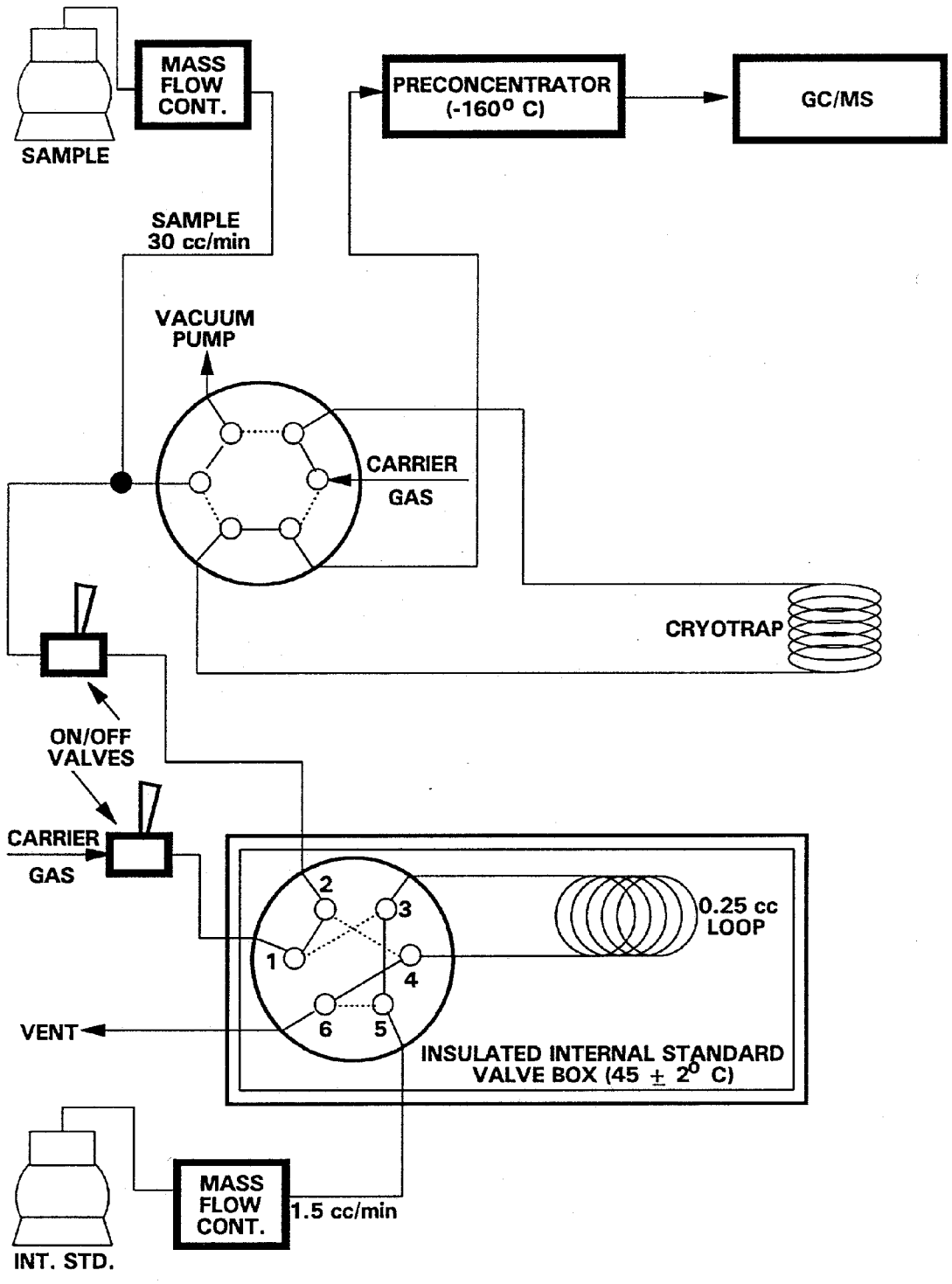


Figure 13. Diagram of design for internal standard addition.

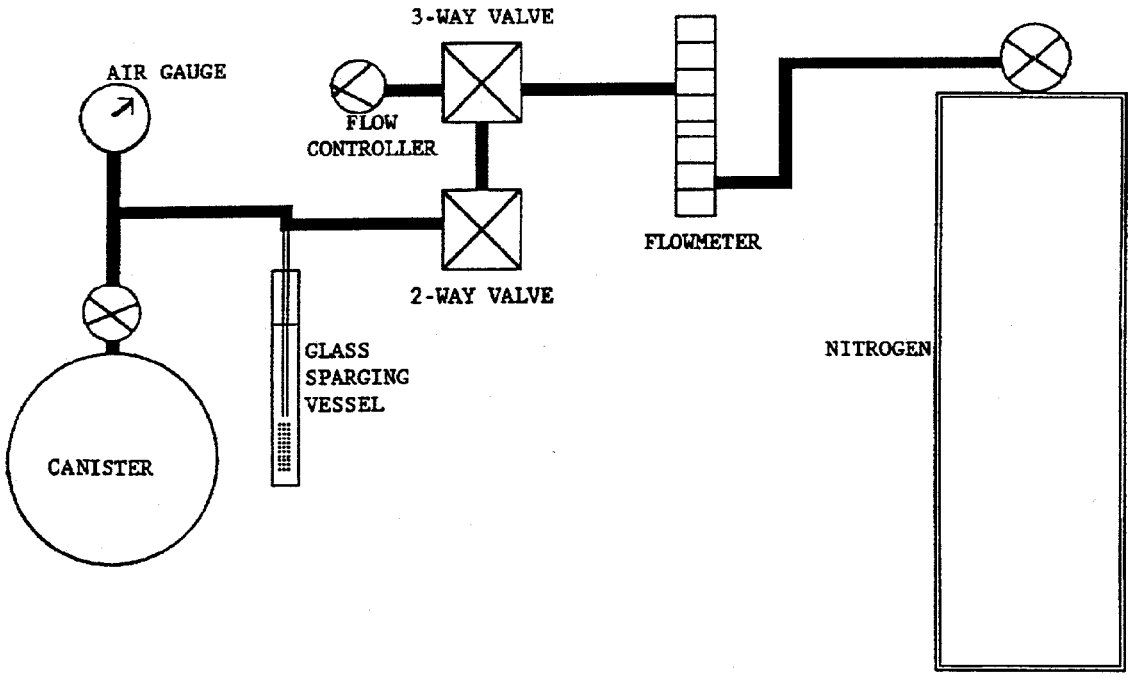


Figure 14. Water method of standard preparation in canisters.

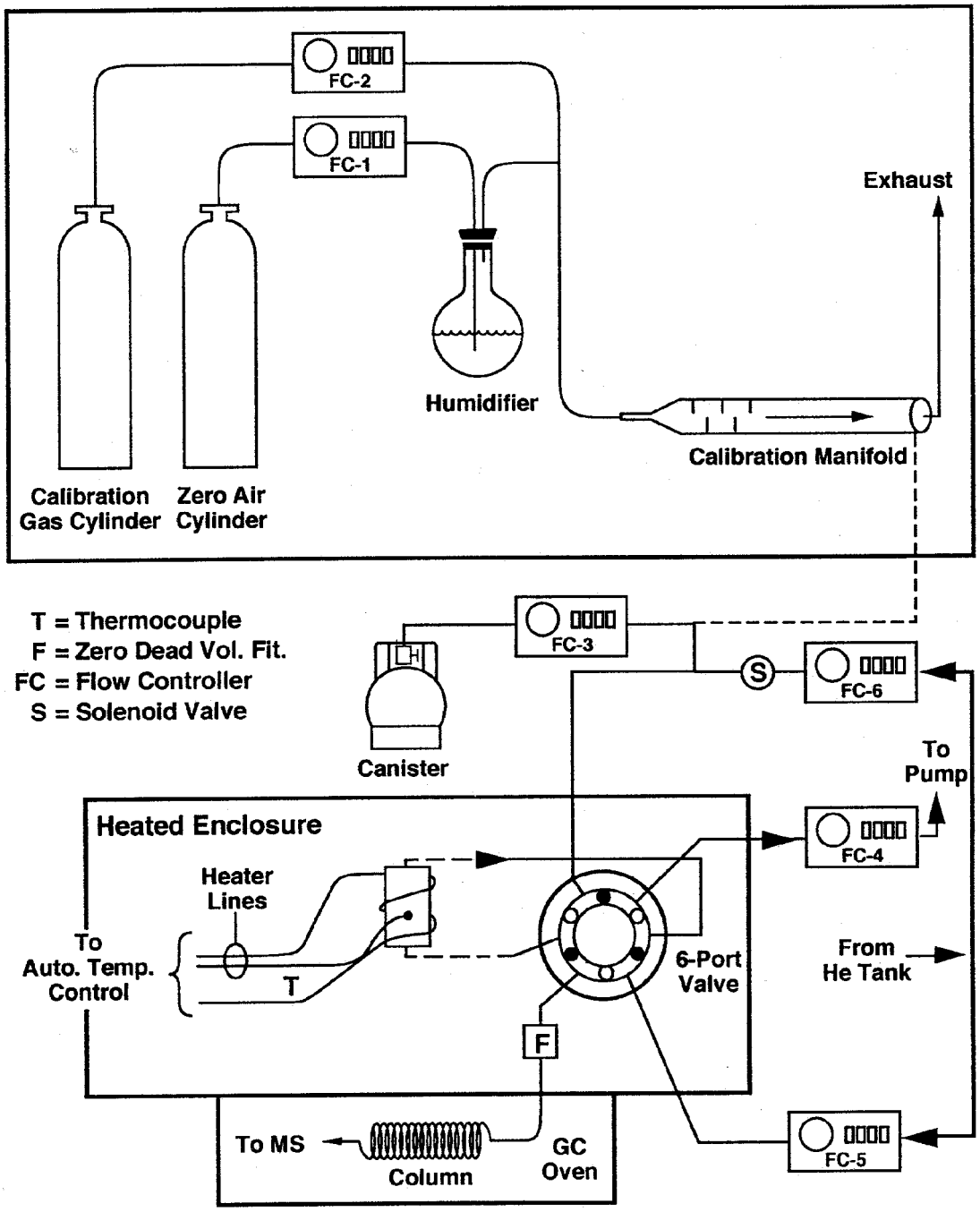


Figure 15. Diagram of the GC/MS analytical system.

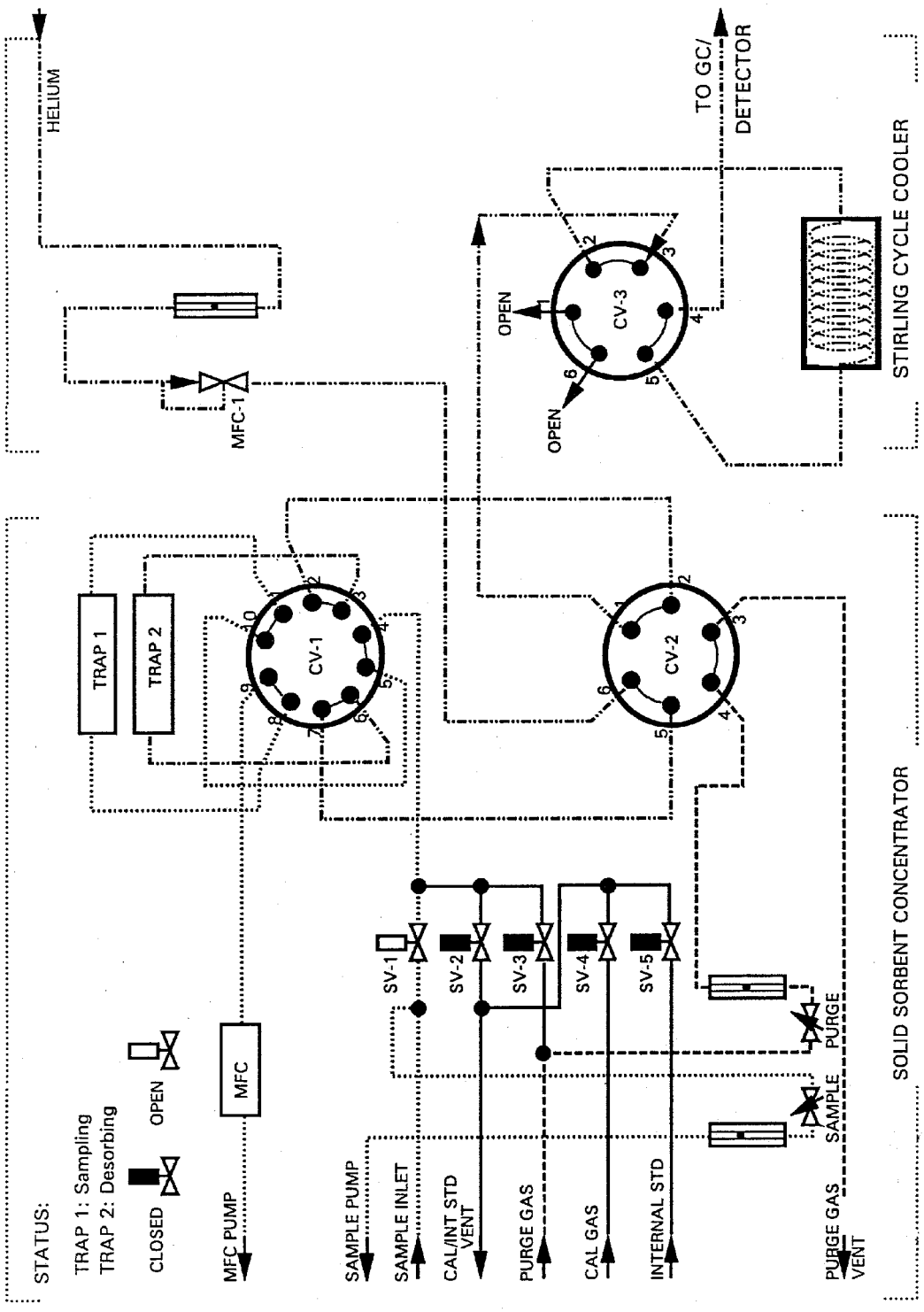


Figure 16. Sample flow diagram of a commercially available concentrator showing the combination of multisorbent tube and cooler (Trap 1 sampling; Trap 2 desorbing).