



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 1 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

CONTENTS

- 1.0 SCOPE AND APPLICATION
 - 1.1 Principles of Operation
 - 1.1.1 Characteristic X-rays
 - 1.1.2 Scattered X-rays
 - 1.2 Sample Types
- 2.0 METHOD SUMMARY
- 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE
- 4.0 INTERFERENCES AND POTENTIAL PROBLEMS
 - 4.1 Sample Placement
 - 4.2 Sample Representivity
 - 4.3 Reference Analysis
 - 4.4 Chemical Matrix Effects (Due to the Chemical Composition of the Sample)
 - 4.5 Physical Matrix Effects (Due to Sample Morphology)
 - 4.6 Application Error
 - 4.7 Moisture Content
 - 4.8 Cases of Severe X-ray Spectrum Overlaps
- 5.0 EQUIPMENT / APPARATUS
 - 5.1 Description of the Spectrace 9000 System*
 - 5.2 Equipment and Apparatus List
 - 5.2.1 Spectrace 9000 Analyzer System
 - 5.2.2 Optional Items
 - 5.2.3 Limits and Precautions
 - 5.3 Peripheral Devices
 - 5.3.1 Communication Cable Connection
 - 5.3.2 Communication Port Setup
 - 5.3.3 User Software
 - 5.4 Instrument Maintenance
 - 5.4.1 Probe Window



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 2 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

- 5.4.2 Further Information and Troubleshooting
- 6.0 REAGENTS
- 7.0 PROCEDURE
 - 7.1 Prerequisites
 - 7.1.1 Gain Control
 - 7.1.2 Setting Data and Spectrum Store/Send Mode
 - 7.2 General Keys and Menu Software
 - 7.2.1 The Keyboard
 - 7.2.2 The Measure (Ready) Screen
 - 7.2.3 The Choose an Application Screen
 - 7.2.4 The Review Stored Results Screen
 - 7.2.5 The Review Stored Spectra Screen
 - 7.2.6 The More (Other Functions) Screen
 - 7.2.7 The Results Screen
 - 7.3 Preoperational Checks
 - 7.3.1 Energy Calibration and Energy Calibration Check*
 - 7.3.2 Resolution Check
 - 7.3.3 Blank (Zero) Sample Check
 - 7.3.4 Target Element Response Check
 - 7.4 Selecting Source Measuring Time
 - 7.4.1 Minimum Source Measuring Times
 - 7.4.2 Typical Minimum Detection Limits (MDLs) for the Soil Samples Application
 - 7.4.3 Typical Minimum Detection Limits (MDLs) for the Thin Samples Application
 - 7.5 Sample Handling and Presentation
 - 7.5.1 Soil Samples*
 - 7.5.2 Thin (Filter) Samples*
 - 7.5.3 Lead in Paint*
- 8.0 CALCULATIONS
- 9.0 QUALITY ASSURANCE / QUALITY CONTROL
 - 9.1 Precision



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 3 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

- 9.1.1 The Method Detection Limit (MDL) and Method Quantitation Limit (MQL)
- 9.2 Reporting Results*
- 9.3 Accuracy
 - 9.3.1 Matrix Considerations
- 10.0 DATA VALIDATION
 - 10.1 Confirmation Samples
 - 10.2 Recording Results
 - 10.3 Downloading Stored Results and Spectra
- 11.0 HEALTH AND SAFETY
- 12.0 REFERENCES
- 13.0 BIBLIOGRAPHY*
- 14.0 APPENDIX
 - A. Figures

* These sections affected by Revision 1.0

SUPERCEDES: SOP #1713, Revision 0.0; 01/26/95; U.S. EPA Contract 68-C4-0022.



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 4 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to serve as a guide to the start-up, check out, operation, calibration, and routine use of the Spectrace 9000 field portable x-ray fluorescence instrument for field use in screening hazardous or potentially hazardous inorganic materials. It is not intended to replace or diminish the use of the Spectrace 9000 Operating Instructions. The Operating Instructions contain additional information for optimizing instrument performance and for utilizing different applications.

The procedures contained herein are general operating guidelines which may be changed as required, depending on site conditions, equipment limitations, limitations imposed by Quality Assurance\Quality Control (QA\QC) procedure or other protocol limitations. In all instances, the procedures finally employed should be documented and included in the final report.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

1.1 Principles of Operation

X-ray Fluorescence (XRF) spectroscopy is a non destructive qualitative and quantitative analytical technique used to determine the chemical composition of samples. In a source excited XRF analysis, primary X-rays emitted from a sealed radioisotope source are utilized to irradiate samples. During interaction with samples, source X-rays may either undergo scattering (dominating process) or absorption by sample atoms in a process known as the photoelectric effect (absorption coefficient). This phenomenon originates when incident radiation knocks out an electron from the innermost shell of an atom creating a vacancy. The atom is excited and releases its surplus energy almost instantly by filling the vacancy with an electron from one of the higher energy shells. This rearrangement of electrons is associated with the emission of X-rays characteristic (in terms of energy) of the given atom. This process is referred to as emission of fluorescent X-rays (fluorescent yield). The overall efficiency of the fluorescence process is referred to as excitation efficiency and is proportional to the product of the absorption coefficient and the fluorescent yield.

1.1.1 Characteristic X-rays

The Spectrace 9000 utilizes characteristic X-ray lines originating from the innermost shells of the atoms: K, L, and occasionally M. The characteristic X-ray lines of the K series are the most energetic lines for any element and, therefore, are the preferred analytical lines. The K lines are always accompanied by the L and M lines of the same element. However, with energies much lower than those of the K lines, they can usually be neglected for those elements for which the K lines are analytically useful. For heavy elements such as cerium (Ce) (atomic number [Z]=58), to uranium (U, Z=92), the L lines are the preferred lines for analysis. The L_{α} and L_{β} lines have almost equal intensities, and the choice of one or the other depends on what interfering lines might be present. A source just energetic enough to excite the L lines will not excite the K lines of the same element. The M lines will appear together with the L lines.

The Spectrace 9000 Operating Instructions contain a table that identifies the X-rays (K or L) and elements measured for each excitation source.



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 5 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

An X-ray source can excite characteristic X-rays from an element only if the source energy is greater than the absorption edge energy for the particular line group of the element (e.g., K absorption edge, L absorption edge, M absorption edge). The absorption edge energy is somewhat greater than the corresponding line energy. The K absorption edge energy is approximately the sum of the K, L, and M line energies, and the L absorption edge energy is approximately the sum of the L and M line energies of the particular element.

Energies of the characteristic fluorescent X-rays are converted (within the detector) into a train of electric pulses, the amplitudes of which are linearly proportional to the energy. An electronic multichannel analyzer (electronic unit) measures the pulse amplitudes, which is the basis of a qualitative X-ray analysis. The number of counts at a given energy is representative of element concentration in a sample and is the basis for quantitative analysis.

1.1.2 Scattered X-rays

The source radiation is scattered from the sample by two physical processes: coherent or elastic scattering (no energy loss), and Compton or inelastic scattering (small energy loss). Thus, source backscatter (background signal) consists of two components with X-ray lines close together. The higher energy line is equal to the source energy. Since the whole sample takes part in scattering, the scattered X-rays usually yield the most intense lines in the spectrum. Furthermore, the scattered X-rays have the highest energies in the spectrum and, therefore, contribute most of the total measured intensity signal.

1.2 Sample Types

Solid and liquid samples can be analyzed for elements aluminum (Al) through uranium (U) with proper X-ray source selection and instrument calibration. Typical environmental applications are:

- Heavy metals in soil (in-situ or samples collected from the surface or from bore hole drillings, etc.), sludges, and liquids (e.g., lead (Pb) in gasoline)
- Light elements in liquids (e.g., phosphorus [P], sulphur [S], and chlorine [Cl] in organic solutions)
- Heavy metals in industrial waste stream effluents
- PCB in transformer oil by Cl analysis
- Heavy metal air particulates collected on membrane filters, either from personnel samplers or from high volume samplers.
- Lead (Pb) in paint

2.0 METHOD SUMMARY



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 6 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

The Spectrace 9000 Portable XRF Analyzer employs three radioactive isotope sources: iron-55 (Fe-55), cadmium-109 (Cd-109), and americium-241 (Am-241) for the production of primary X-rays. Each source emits a specific set of primary X-rays which excite a corresponding range of elements in a sample. When more than one source can excite the element of interest, the appropriate source is selected according to its excitation efficiency for the element of interest. See page 1-2 of the Spectrace 9000 Operating Instructions for a chart of source type versus element range.

The sample is positioned in front of the source-detector window and sample measurement is initiated which exposes the sample to primary radiation from the source. Fluorescent and backscattered X-rays from the sample enter through the beryllium (Be) detector window and are counted in the high resolution mercuric iodide (HgI₂) detector.

Elemental concentrations are computed using a Fundamental Parameter (FP) algorithm of the form:

$$\text{Concentration} = R \times S \times (1 + \text{SUM}\{A_n \times C_n\})$$

"R" is the measured analyte X-ray intensity relative to the pure element; "S" is a calculated sensitivity coefficient. The quantity SUM {} is a summation of "n"-element absorption-enhancement terms containing calculated alpha-coefficients and iteratively computed element concentrations. The Spectrace 9000 utilizes FP XRF calibrations derived from theoretical considerations (as opposed to empirical data). The menu-driven software in the Spectrace 9000 supports multiple XRF calibrations called "applications." Each application is a complete analysis configuration including elements to be measured, interfering elements in the sample, and a set of FP calibration coefficients.

The measurement time of each source is user-selectable. The shorter source measurement times (15 -30s) are generally used for initial screening and hot spot delineation, while longer measurement times (30 - 500s) are typically used for higher precision and accuracy requirements.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

This SOP specifically describes equipment operating procedures for the Spectrace 9000; hence, this section is not applicable to this SOP.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

The total method error for XRF analysis is defined as the square root of the sum of squares of both instrument precision and user or application related error. Generally, the instrument precision is the least significant source of error in XRF analysis. User- or application-related error is generally more significant and will vary with each site and method used. The components of the user or application related error are the following.

4.1 Sample Placement

This is a potential source of error because the X-ray signal decreases as the distance from the radioactive source is increased. However, this error is minimized by maintaining the same distance for each sample.

4.2 Sample Representivity



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 7 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

In order to accurately characterize site conditions, samples collected must be representative of the site or area under investigation. Representative soil sampling ensures that a sample or group of samples accurately reflects the concentration of the contaminant(s) of concern at a given time and location. Analytical results from representative samples reflect the variation in pollutant presence and concentration range throughout a site. Variables affecting sample representativeness include: (1) geologic variability, (2) contaminant concentration variability, (3) collection and preparation variability, and (4) analytical variability. Attempts should be made to minimize these sources of variability. For additional information on representative sampling, refer to the "Removal Program Representative Sampling Guidance, Volume 1 - Soil."⁽¹⁾

4.3 Reference Analysis

Soil chemical and physical matrix effects may be corrected by using site-specific soil samples which have been analyzed by Inductively-Coupled Plasma (ICP) or Atomic Absorption (AA) spectroscopy as calibration samples. A major source of error can result if these samples are not representative of the site and/or if the analytical error is large. Additionally, when comparing XRF results with reference analyses results, the efficiency of the sample digestion reference analysis should be considered. Some digestion methods may breakdown different sample matrices more efficiently than others.

4.4 Chemical Matrix Effects (Due to the Chemical Composition of the Sample)

Chemical matrix effects result from differences in concentrations of interfering elements. These effects appear as either spectral interferences (peak overlaps) or as X-ray absorption/enhancement phenomena. Both effects are common in soils contaminated with heavy metals. For example, iron (Fe) tends to absorb copper (Cu) X-rays, reducing the intensity of Cu measured by the detector. This effect can be corrected mathematically through the use of FP coefficients.

4.5 Physical Matrix Effects (Due to Sample Morphology)

Physical matrix effects are the result of variations in the physical character of the sample. They include parameters such as particle size, uniformity, homogeneity, and surface condition. For example, consider a sample in which the analyte exists in the form of very fine particles within a matrix composed of much coarser material. If two separate aliquots of the sample are prepared in such a way that the matrix particles in one are much larger than in the other, then the relative volume of analyte occupied by the analyte-containing particles will be different in each. When measured, a larger amount of the analyte will be exposed to the source X-rays in the sample containing finer matrix particles; this results in a higher intensity reading for that sample and, consequently, an apparently higher measured concentration for that element.

4.6 Application Error

Generally, the error in the application calibration model is insignificant (relative to the other sources of error) **PROVIDED** the instrument's operating instructions are followed correctly. However, if the sample matrix varies significantly from the design of the application, the error may become significant (e.g., using the soils application to analyze a 50 percent iron mine tailing sample).



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 8 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

4.7 Moisture Content

Sample moisture content will affect the analytical accuracy of soils or sludges. The overall error may be secondary when the moisture range is small (5-20 percent), or it may be a major source of error when measuring the surface of soils that are saturated with water.

4.8 Cases of Severe X-ray Spectrum Overlaps

When present in the sample, certain X-ray lines from different elements can be very close in energy and, therefore, can interfere by producing a severely overlapped spectrum.

The typical spectral overlaps are caused by the K_{β} line of element Z-1 (or as with heavier elements, Z-2 or Z-3) overlapping with the K_{α} line of element Z. This is the so-called K_{α}/K_{β} interference. Since the $K_{\alpha}:K_{\beta}$ intensity ratio for the given element usually varies from 5:1 to 7:1, the interfering element, Z-1, must be present in large concentrations in order to disturb the measurement of analyte Z. For example, the presence of large concentrations of vanadium (V) could disturb the measurement of chromium (Cr). The V K_{α} and K_{β} energies are 4.951 and 5.427 Kev, respectively. The Cr K_{α} energy is 5.41 Kev. The resolution of the detector is approximately 270 eV. Therefore, large amounts of V in a sample will result in spectral overlap of the V K_{β} with the Cr K_{α} peak (see Figure 1, Appendix A) and the measured X-ray spectrum will include TOTAL counts for Cr plus V lines.

Other interferences arise from K/L, K/M, and L/M line overlaps. While these are less common, the following are examples of severe overlap:

As $K_{\alpha}/Pb L_{\alpha}$, S $K_{\alpha}/Pb M_{\alpha}$

In the arsenic (As)/lead case, Pb can be measured from the Pb L_{β} line, and arsenic from either the As K_{α} or the As K_{β} line; this way the unwanted interference can be corrected. However, due to the limits of mathematical corrections, measurement sensitivity is reduced. Generally, arsenic concentrations can not be efficiently calculated in samples with Pb:As ratios of 10:1 or more. This may result in zero arsenic being reported regardless of what the actual concentration is.

The Spectrace 9000 uses overlap factors to correct for X-ray spectral overlaps for the elements of interest for a given application.

5.0 EQUIPMENT / APPARATUS

5.1 Description of the Spectrace 9000 System

The analyzer utilizes the method of Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry to determine the elemental composition of soils, sludges, aqueous solutions, oils, and other waste materials.

The Spectrace 9000 analyzer includes three compact, sealed radiation sources contained in a measuring probe: Fe-55, Cd-109, and Am-241. The analyzer software automatically selects which sources to use as well as measurement time for each source based on stored information for each application. The probe



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 9 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

is equipped with a high resolution HgI_2 detector, which is connected by cable to an environmentally sealed electronic module.

The electronic unit provides internal non volatile memory for storage of 120 spectra and 300 multi-element analysis reports. An RS-232 serial port is provided for downloading data and spectra to a peripheral device. The multi-element analysis reports and the 2000-channel spectra can be displayed on the instrument's LCD panel. The replaceable and rechargeable internal battery provides for field-portable operation.

The Spectrace 9000 is supplied with four factory-installed FP-based applications (calibrations). The "Soil Samples" application is for analysis of soils where the balance of the sample (that portion not directly measured by the instrument) is silica (SiO_2). The "Thin Film" application is for analysis of thin films such as air monitoring filters or wipes. The "PbK in Paint" application is for analyzing Pb in paint films and is reasonably independent of the type of substrate. Finally, the "Fine Particle Soil" application is for analysis of prepared soil samples that have been ground into fine particles (typically, less than 120 mesh). Spectrace Instruments will also develop new applications to meet user specific requirements (e.g., adding elements to the "Soil Samples" application). The PC-based Spectrace 9000 Application Generator software may also be used to develop new applications.

The Spectrace 9000 can be powered from a 115-volt (or 220-volt) wall outlet or from its 4-hour capacity battery. It can be operated in temperatures ranging from 32 to 120° Fahrenheit (F). Furthermore, the probe and electronic unit may be exposed to a light rain. However, additional protection is provided when the system (electronic unit and probe) is contained in the optional water repellant carrying case.

5.2 Equipment and Apparatus List

5.2.1 Spectrace 9000 Analyzer System

The complete Spectrace 9000 Analyzer System includes:

- Analyzer unit for data acquisition, processing, and display
- Hand-held probe including:
 - High-resolution HgI_2 detector
 - Three excitation sources (^{55}Fe , ^{109}Cd , ^{241}Am)
 - Safety cover
- Probe laboratory stand with the following:
 - Base for table top use
 - Safety shield over sample
 - Positioning fixtures for standard 30-mm and 40-mm X-ray sample cups
- Interconnecting cable
- RS-232C Serial I/O Interface cable



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 10 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

- Two blank check samples
- Pure element check samples
- Battery charger
- Battery pack
- System carrying/shipping case
- Spectrace 9000 Operating Instructions, application software, and utilities software. The application software is specific to each unit and cannot be interchanged between different units. The software is identified by the serial number of the unit.

5.2.2 Optional Items

- 31-mm diameter sample cups
- XRF polypropylene film, 0.2 mil thick
- Field carrying case
- Peripheral devices such as a printer and IBM compatible Personal Computer (PC)
- Spare probe window assembly
- Spare battery pack, charger, and charger adaptor (required to charge spare battery outside of electronic unit)

See the Spectrace 9000 Accessories Price List for additional options.

For mobile lab or laboratory X-ray sample preparation accessories (such as drying ovens, grinders, sieves, etc.), consult general laboratory equipment suppliers.

5.2.3 Limits and Precautions

The probes should be handled in accordance with the following radiological control practices.

1. The probe should always be in contact with the surface of the material being analyzed, and that material should completely cover the probe opening (aperture) when the sources are exposed. Do not remove a sample or move the probe while the indicators show **SOURCE ON**.

SOURCE ON indicators are:



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 11 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

- the message on the screen "**SOURCE ON**"
 - the flashing light at the base of the probe.
2. When the sources are exposed, under no circumstances should the probe be pointed at the operator or surrounding personnel.
 3. Do not place any part of the operator's or co-worker's bodies in line of exposure when the sources are exposed or partially covered.
 4. The probe must be covered with the safety cover or laboratory safety shield when not in use.
 5. Spectrace Instruments must be notified immediately of any condition or concern relative to the probe's structural integrity, source shielding, source switching condition, or operability.
 6. The appropriate state agency or the Nuclear Regulatory Commission (NRC) office must be notified immediately of any damage to the radioactive source, or any loss or theft of the device (see factory supplied data on radiological safety).
 7. Labels or instructions on the probe(s) must not be altered or removed.
 8. The user must not attempt to open the probe.
 9. The source(s) in the probe must be leak-tested every 6 months as described in the Spectrace 9000 Operating Instructions. The leak test certificates must be kept on file, and a copy must accompany the instrument at all times.
 10. The probe laboratory safety shield assembly must be used when the probe is inverted for measuring samples contained in cups.
 11. During operation, the probe must be kept at least 10 feet from computer monitors and any other source of radio frequency (RF). Some monitors have very poor RF shielding and will affect measurement results.
 12. The Spectrace 9000 should not be dropped or exposed to conditions of excessive shock or vibration.
 13. The electronic unit should be left on whenever the battery charger is connected to it. If the electronic unit is shut off with the battery charger plugged in, the battery may be damaged due to overcharging.

Additional precautions include:

1. The probe cable must never be pulled while unplugging the probe. The probe plug



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 12 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

should be grasped at the ribbed metal connector and squeezed and pulled gently while the connector is unplugged. The connector must never be forced when plugging in the connector.

2. The handle of the electronic unit must not be rotated unless the release buttons on each side of the handle are depressed.
3. The Spectrace 9000 should not be stored at an ambient temperature below -4°F or above 110°F .
4. The battery charging unit should only be used indoors in dry conditions.
5. Battery packs should be changed only in dry conditions.

5.3 Peripheral Devices

The Spectrace 9000 may be used with a wide range of peripheral devices for electronic data capture or printed readout as long as they are compatible with the RS-232 serial I/O protocol. Such devices include terminals, printers, electronic data loggers, personal computers, etc.

5.3.1 Communication Cable Connection

Plug the 25-pin connector of the RS-232 Serial I/O cable into the Spectrace 9000 25-pin connector (the connection just below the display screen on the electronic unit) and the 9-pin connector of the cable into the serial port of the receiving device.

5.3.2 Communication Port Setup

To communicate with an external device, the Spectrace 9000 **MUST** be set at the same baud rate, word length, and parity as the receiving device. The Spectrace 9000 allows you to select various configurations for these parameters in the communication (Comm.) port setup portion of the More submenu (which can be accessed from the main menu).

The default COM setup for application and utilities software is 9600,N,8,1.

5.3.3 User Software

Refer to your PC software manual for details on additional settings that may be required for proper interfacing between the Spectrace 9000 and your particular software.

5.4 Instrument Maintenance

5.4.1 Probe Window

When the probe window becomes damaged or punctured, it should be replaced as soon as



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 13 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

possible to prevent dust and moisture from entering the probe. Replacement window assemblies can be ordered from Spectrace Instruments. Note the location of the window aperture; it is closer to one end of the window plate. Simply unscrew the old window plate, press any corner of it, and remove it. Stretch the O-ring for 10 seconds, and lay it back in the groove. The O-ring must lie flat in the groove in order for the new window plate to be installed. Install the new window assembly in the same manner as the old. If the surface of the window plate is not flush with the face of the probe, the O-ring has probably come out of the groove. Remove the assembly, and try the same procedure again.

5.4.2 Further Information and Troubleshooting

Refer to the Spectrace 9000 Operating Instructions for additional detailed operational and/or maintenance and troubleshooting instructions. If no solution is found in the manual, contact Spectrace Instruments for assistance.

An instrument log should be maintained to document specific corrective actions taken to alleviate any instrumental problems, or for recording any service that has been performed.

6.0 REAGENTS

Generally, calibration standards are not necessary for site screening and extent of contamination analyses with the Spectrace 9000. Optionally, an application (only the Soil Sample application will be discussed here) can be optimized or verified to be 1:1 proportional to another analytical (reference) method (see Section 9.3 and 10.1). This can be done by analyzing a suitable set of Site-Specific Calibration Standards (SSCS) or Standard Reference Materials (SRMs) and performing a regression analysis on the reference (dependent) and the Spectrace 9000 results (independent) for each element of concern. SSCS and SRMs must be representative of the sample matrix to be analyzed by XRF, for example, National Institute of Standards and Technology (NIST) SRMs 2709, 2710, and 2711 for the soil application. In an application, any element's calibration can be adjusted by entering the desired slope and offset (intercept) in the Adjust Calibration menu. If any element's calibration has been adjusted in an application, "adj" will appear on the results screen. An adjusted element calibration can always be changed back to the initial slope and offset values of 1 and 0, respectively.

7.0 PROCEDURE

7.1 Prerequisites

If the Spectrace 9000 will be used in a location where AC power outlets are conveniently accessible, connect the battery charger to the electronic unit and plug the charger cord into the outlet. The probe cable must be connected before switching on the power. Plugging and unplugging this cable with the power on can damage the detector.

To connect the battery, set the electronics unit on its face and use a flat blade screwdriver to loosen the two one-quarter turn fasteners on the back. Remove the battery pack. Inside, find the cord with the red cap covering the three-pronged plug. Remove the cap and plug it into the battery pack. Put the battery pack into the unit and tighten the fasteners.



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 14 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

Apply power to the Spectrace 9000 by pressing the <ON> button. The electronic unit may not come on with the battery charger hooked up if the battery has been totally drained. The drained battery may require a 10 minute charge prior to startup. In a few seconds the display shows the version of software. If necessary, adjust the contrast knob located on the underside of the front display. This knob can be turned so far that the display appears blank.

The initial screen displays for about 10 seconds and then a prompt will ask if the time and date are set correctly. The date **MUST** be set correctly otherwise serious errors in source-decay compensation can result. Additionally, results tables include the time and date of analysis. The main menu appears after the time and date screens.

If a "battery low" message appears, recharge or change the battery before proceeding, or operate the unit using line voltage.

Allow the Spectrace 9000 to warm up for approximately 30 minutes after it has been turned on before performing analysis.

7.1.1 Gain Control

Automatic gain compensation is a feature of both Soil and Thin Samples applications, which allows operation of the instrument over a wide range of ambient temperatures and from one day to another without standardization. To maintain gain control compensation, it is necessary to occasionally operate with a minimum acquisition time of 50 seconds on the Cd-109 source. If the automatic gain control fails or is out of range, an error message will appear on the screen. If the error message continues to appear after repeat analyses, then the Cd-109 measurement time should be checked and/or an energy calibration should be performed. If the problem continues, contact Spectrace Instruments for help.

7.1.2 Setting Data and Spectrum Store/Send Mode

The Set store/send modes option is located in the More screen which can be accessed from the main menu. Data and/or Spectrum storage must be enabled for automatic on-board storing to occur. Sufficient memory is available to store up to 300 sets of analysis results and up to 120 spectra (40 samples since each sample has three spectra). When the available memory is full, the respective spectra or results storage mode is automatically disabled. The spectra or results memory must be cleared (deleted) and the respective store mode enabled before results and/or spectra can be stored again.

7.2 General Keys and Menu Software

This section outlines the general keys and basic menu software. Flow charts which describe the menu structure in detail are located on pages 4-13 through 4-17 in the Spectrace 9000 Operating Instructions.

7.2.1 The Keyboard

The row of numeric keys under the LCD screen performs functions defined by labels (a menu)



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 15 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

written to the bottom line of the display by the Spectrace 9000 software. As the operator moves through the various menus, the keys are redefined to provide an efficient user interface.

The keypad to the right of the screen is used for numeric entry. The <Cont/Pause> key (referred to as the <Cont>) is used:

- to enter information as an <Enter> key
- to begin an analysis
- to pause an analysis in progress

The left arrow <←> key is used to edit entries before pressing <Cont>.

7.2.2 The Measure (Ready) Screen

This main menu selection displays the application name, revision date, measurement time for each source, and accesses other options (see flow diagrams in Spectrace 9000 Operating Instructions).

7.2.3 The Choose an Application Screen

This main menu selection lists the applications currently loaded in the unit. Applications are selected and source measurement times may be modified in this screen (see flow diagrams in Spectrace 9000 Operating Instructions).

7.2.4 The Review Stored Results Screen

This main menu selection lists the stored results. *Up* and *Down* scroll are used on many screens. When *Up* and *Down* are displayed, pressing the <0> (zero) key will toggle to *PgUP* and *PgDN* for rapid movement through long lists. Stored results may be reviewed, deleted, or downloaded to the COM port (see flow diagrams in Spectrace 9000 Operating Instructions).

7.2.5 The Review Stored Spectra Screen

This main menu selection lists the stored spectra which may be deleted or transmitted to the COM port (see flow diagrams in Spectrace 9000 Operating Instructions). Spectra may be displayed in the *Examine Spectrum* portion of the More screen (accessed from the main menu) or in the *Examine Spectrum* selection from the Results screen under the *More Options* menu selection.

7.2.6 The More (Other Functions) Screen

This main menu selection lists the following functions:

- *Set clock/calendar*
- *Comm. port setup*
- *Set store/send modes*



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 16 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

- *Application maintenance*
- *Examine spectrum*

7.2.7 The Results Screen

The Results screen is displayed at the end of the analysis. If the automatic *Store Results* mode is enabled, the operator will be prompted for sample identification (*ID*) before the Results screen is displayed. *Up* or *Down* scrolls the screen to view more results. When *Up* and *Down* are displayed, pressing the <0> (zero) key will toggle to *PgUP* and *PgDN* for rapid movement through long lists. *Send* transmits results to the COM port. *Store* prompts for an ID and then stores results in memory. *Measr* will immediately begin another analysis cycle. *Opts* displays the first of two screens listing special options under the Results screen (the second screen is located under *More Opts* of the first screen. See flow diagrams in Spectrace 9000 Operating Instructions). The most frequently used functions are the *Examine Spectrum* and *Enable/Disable Display Thresholds* located on the second screen of options.

7.3 Preoperational Checks

7.3.1 Energy Calibration Check

An energy calibration should be performed after an instrument is shipped and periodically (approximately every 2-4 weeks) to ensure proper energy calibration. The *Energy Calibration* function is located in the *Options* section of the Measure Screen. The operator will be prompted to place the safety shield on the probe and then initiate a 600- second analysis that will update the X-ray energy calibration.

The energy calibration check is performed in the field daily and after an energy calibration to verify proper energy calibration. To perform an energy calibration check, place the safety shield on the probe. Select the *Soil Samples* application and measure the safety shield using a minimum acquisition time of 60 seconds for each source. Save the results and spectra for documentation. Select *Opts*, *More Options*, and then *Examine Spectrum*. Examine the spectrum of each source. Locate and record the centroid KeV (using the x12 horizontal magnification, X6 for Fe-55) for each of the following peaks:

Source	Peak	Theoretical (KeV)	Specification (KeV)
Cd-109	Pb L-alpha	10.54	10.50 - 10.58
	Pb L-beta	12.61	12.57 - 12.65
	Pb L-gamma	14.76	14.72 - 14.80
	Source line	22.10	22.06 - 22.14
Fe-55	S K-alpha	2.31	2.29 - 2.33



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 17 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

	Source line	5.89	5.87 - 5.91
Am-241	Pb L-alpha	10.54	10.49 - 10.59
	Pb L-beta	12.61	12.56 - 12.66
	Source line	59.5	59.3 - 59.7

Perform an *Energy calibration* (see Spectrace 9000 Operating Instructions) and then do another energy calibration check if any of the peaks fail to meet specification. The energy calibration check should be performed once at the beginning of the day, after an energy calibration, after loading an application, and whenever the instrument exhibits a persistent drift.

7.3.2 Resolution Check

The resolution check examines the detector's ability to resolve X-ray energies. This should be performed once at the beginning of the day. Select the *Soil Samples* application, and measure a sample of pure iron using a minimum acquisition time of 60 seconds for the Cd-109 source. Save the results and spectra for documentation. Select *Examine spectrum* under the More Options section of the Results screen. Examine the Cd-109 spectrum. Locate and record the maximum peak counts (must be >1000 counts) of the iron K-alpha peak (6.4 KeV) using the x12 horizontal magnification (see Figure 2, Appendix A). Divide the maximum peak counts by two. Examine the right (high energy) side of the peak and record the counts and KeV of the channel with counts less than or equal to one-half the maximum peak count value (channel B, Figure 2). Examine the left (low energy) side of the peak and record the counts and KeV of the channel with counts less than or equal to one-half the maximum peak count value (channel A, Figure 2). Subtract the left-side KeV from the right-side KeV (KeV at B - KeV at A, Figure 2). The difference should be less than 0.300 KeV. If the unit fails to meet this specification, call Spectrace Instruments for assistance.

7.3.3 Blank (Zero) Sample Check

The blank (Zero) sample check is performed to monitor the instrument's zero drift in the selected application. The blank sample check and the *Acquire Background Data* operation (discussed below) only apply to the application currently selected. This should be done once at the beginning of the day, after an energy calibration, after loading an application, and whenever the instrument exhibits a persistent drift on a blank or low-level sample.

Mount the probe in the laboratory stand and select the *Soil Samples* application. Disable the display thresholds. This will permit results less than one standard deviation (STD) to be displayed (even negatives). Measure the quartz blank provided with the unit (or a "clean" sand sample) using a minimum acquisition time of 60 seconds for each source. Review the results table. All elemental results for target elements with atomic number 24 (Cr) and higher in the periodic table should be within 3 standard deviations of zero ($0 \pm 3 \cdot |\text{STD}|$); all non-target element results should be within 5 standard deviations ($0 \pm 5 \cdot |\text{STD}|$). Repeat the measurement if the unit fails to meet these specifications. If several elements continue to be significantly out of these specifications, check the probe window and the blank sample for contamination or perform the *Acquire background data* operation located in the Measure (Ready) screen option.



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 18 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

Perform the blank (Zero) sample check again. Save the results and spectra for documentation. Enable the display thresholds prior to sample analysis after the blank sample check procedure is completed.

7.3.4 Target Element Response Check

The purpose of the target element response check is to ensure that the instrument and the selected application are working properly prior to performing sample analysis. This check should be performed at the beginning of the day. Use low, mid, and high samples, or standards with known concentrations for some or all of the target elements to be checked. Select a low sample near the quantitation limit of the target elements. Select a mid sample near the site action level and a high sample near the maximum concentration of the target elements expected on site.

These samples should be measured using the same source acquisition times that will be used for sample analysis. Save the sample check results and spectra for documentation.

7.4 Selecting Source Measuring Time

The source measuring time may be modified under the Measure screen. **Zero (seconds) measuring time should never be selected for any source for any application.** Generally, the element detection limit is reduced by 50 percent for every four-fold (x4) increase in source measuring time. Although counting statistics improve as measurement time increases, the practical upper limit for typical applications is 600 to 800 seconds. The elements are grouped together according to the radioisotope used for their excitation with typical minimum detection limits shown in Sections 7.4.2. and 7.4.3.

Automatic gain compensation is a feature of both the Soil and Thin Samples applications and allows operation of the instrument over a wide range of ambient temperatures and from one day to another without standardization. To maintain this gain control compensation, it is necessary to occasionally operate with a minimum acquisition time of 50 seconds on the Cd-109 source.

The *Real/live* option toggles between real time (elapsed clock time) and live time (actual time the instrument is counting). The latter adds time to the analysis to correct for the time the system is busy processing pulses.

7.4.1 Minimum Source Measuring Times

A minimum measuring time (real or live) of 15 seconds for the Fe-55 source, 30 seconds for the Cd-109 source, and 10 seconds for the Am-241 source is recommended when using the Soil Samples application. Measuring times for a source that excites a target element can be increased if lower detection limits are required.

When using the Thin Samples application, the measuring time for any source may be reduced to 10 seconds if the source does not excite a target element since this application does not correct for interelement effects. If a source excites a target element, a minimum measuring time (real or live) of 60 seconds for the Fe-55 source, 60 seconds for the Cd-109 source, and 120 seconds for the Am-241 source is recommended.



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 19 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

A minimum of 60 seconds is recommended for the Cd-109 source when using the PbK in Paint application.

7.4.2 Typical Minimum Detection Limits (MDLs) for the Soil Samples Application

For source measuring times of 60 seconds, typical element MDLs (in milligram per kilogram, mg/kg) for the Soil Samples application are:

Source	Element	MDL (mg/kg)
Fe-55	Potassium (K)	325
	Calcium (Ca)	150
	Titanium (Ti)	110
	Chromium (CrLo)	180
Cd-109	Chromium (CrHi) 525	
	Manganese (Mn)	410
	Iron (Fe)	225
	Cobalt (Co)	205
	Nickel (Ni)	125
	Copper (Cu)	90
	Zinc (Zn)	70
	Mercury (Hg)	60
	Arsenic (As)	50
	Selenium (Se)	35
	Lead (Pb)	30
	Rubidium (Rb)	10
	Strontium (Sr)	10
	Zirconium (Zr)	10
Molybdenum (Mo)	10	
Am-241	Cadmium (Cd)	180
	Tin (Sn) 100	
	Antimony (Sb)	65
	Barium (Ba)	20

NOTE: These typical MDLs are provided as an aid for selecting source measurement times; observed values for a given situation may vary depending on the matrix of the soil standard used to calculate MDLs, age of sources, moisture content, and other factors discussed in Section 4.

Generally, the detection limit is reduced by 50 percent for every four-fold (x4) increase in source measuring time. Additionally, more elements may be added to the Soil Samples application. Contact Spectrace Instruments for information about modifications to applications.

7.4.3 Typical Minimum Detection Limits (MDLs) for the Thin Samples Application

For source measuring times of 200 seconds for the Fe-55 and Cd-109 sources, and 800 seconds for the Am-241 source, typical element MDLs (in microgram per square centimeter, $\mu\text{g}/\text{cm}^2$) for the Thin Samples application are:



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 20 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

Source	Element	MDL ($\mu\text{g}/\text{cm}^2$)
Fe-55	Potassium (K)	0.40
	Calcium (Ca)	0.20
	Titanium (Ti)	0.15
	Chromium (CrLo)	0.40
Cd-109	Chromium (CrHi)	0.90
	Manganese (Mn)	0.65
	Iron (Fe)	0.65
	Cobalt (Co)	0.50
	Nickel (Ni)	0.30
	Copper (Cu)	0.65
	Zinc (Zn)	0.40
	Mercury (Hg)	0.45
	Arsenic (As)	0.40
	Selenium (Se)	0.15
	Lead (Pb)	0.50
	Rubidium (Rb)	0.10
	Strontium (Sr)	0.10
	Zirconium (Zr)	0.15
Molybdenum (Mo)	0.10	
Am-241	Cadmium (Cd)	2.5
	Tin (Sn)	2.5
	Antimony (Sb)	1.5
	Barium (Ba)	0.70

NOTE: These typical MDLs are provided as an aid for selecting source measurement times; observed values for a given situation may vary depending on the thin sample standard used to calculate MDLs, age of sources, and other factors discussed in Section 4.

Generally, the detection limit is reduced by 50 percent for every four-fold (x4) increase in source measuring time. Use of thick filters or filters with high background or contamination will result in higher MDLs and require a background subtraction. Additionally, more elements may be added to the Thin Samples application. Contact Spectrace Instruments for information about modifications to applications.

7.5 Sample Handling and Presentation

When making XRF measurements, be sure to maintain constant measurement geometry in order to minimize variations in analysis results. Document any anomalies in measurement geometry, sample surface morphology, moisture content, sample grain size, and matrix (see Section 4.0).

7.5.1 Soil Samples

Soil samples may be analyzed either in-situ or in X-ray sample cups (after preparation). The Soil Samples application assumes the sample to be infinitely thick. For in-situ measurements this is almost always the case. However, for sample cup measurements it is advisable to fill the cup nearly full and tap it on the bench to compact the soil. This ensures that the sample is as



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 21 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

uniformly thick as possible from analysis to analysis. The Spectrace 9000 laboratory stand and safety shield should be used when analyzing sample cups.

An area for in-situ analysis should be prepared by removing large rocks and debris. The soil surface should be rendered flat and compact prior to analysis. The Spectrace 9000 probe should be held firmly on the ground to maximize instrument contact with the ground. The probe should not be moved during analysis. Analysis of water saturated soils should be avoided. A thin layer of 0.2-mil polypropylene XRF film may be mounted on the surface probe to minimize contamination. Use of varying thicknesses of plastic (bags) have been shown to interfere in the light element (low atomic number) measurement and may affect the FP calibration of the other element concentrations.⁽²⁾ Additionally, plastic may contain significant levels of target element contamination.

Course-grained soil conditions or nuggets of contaminated material may preclude a truly representative sample and adversely affect the analysis results (typically by under reporting the target element). Such samples should be prepared before analysis. Preparation consistency is important to minimize variation in analytical results.

This application is specifically designed for soil with the assumption that the balance of the material is silica. If samples with a much lighter (lower atomic number) balance are analyzed, the results will typically be elevated by a factor of two to four. Contact Spectrace Instruments for help in analysis of different matrices.

7.5.2 Thin (Filter) Samples

The Thin Samples application is for analysis of thin samples such as filters or wipes. The detection limits are affected by the thickness of the substrate. Best results are obtained on the thinnest substrates. Always use the probe safety cover when measuring thin samples. This is not only for user safety, but also ensures a controlled background environment and provides a reference signal for the automatic gain control. Probe safety covers should never be interchanged between instruments.

Filters and wipes should be prescreened before use to establish background and contamination levels. Care should be used to prevent zinc oxide contamination from disposable gloves. Small 37-mm filters can be mounted between two layers of 0.2-mil thick polypropylene XRF film on 40-mm XRF cups for analysis. Larger filters can be placed on the probe with a sheet of 0.2-mil thick polypropylene XRF film between the filter and probe surface to prevent the window from being contaminated, and the probe safety cover should be placed over the filter prior to analysis. Filters should be presented loaded side down and wrinkle free.

7.5.3 Lead in Paint

The area selected for analysis should be smooth, representative and free of surface dirt. The Spectrace 9000 probe should be held firmly on the surface to maximize instrument contact. The probe should not be moved during analysis.

When used for specimen application (e.g., on paint chips or nonbacked films) remember to use the probe safety cover. In the PbK Application, a thick neutral sample, such as the quartz disk



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 22 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

(blank), should be positioned behind the specimen before the safety lid is closed. Otherwise, the PbK X-rays excited in the safety cover will be sensed by the detector. In this application, do not perform the *Acquire background data* option from the list of options under the Ready screen.

8.0 CALCULATIONS

The Spectrace 9000 is a direct readout instrument that does not require any calculations.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

9.1 Precision

The precision of the method is monitored by reading a low- or mid-target element concentration sample (or SSCS or SRMs selected as described in Sections 6.0) at the start and end of sample analysis and after approximately every tenth sample. (A daily total of seven measurements is recommended.) Determining the precision around the site action level can be extremely important if the XRF results are to be used in an enforcement action. Therefore, selection of a sample with a target element concentration at or near the site action level or level of concern is recommended. The sample is analyzed by the instrument for the normal field analysis time, and the results are recorded. The standard deviation for each target element is calculated. The relative standard deviation (RSD) of the sample mean can be used to calculate precision. The RSD should be within ± 20 percent for the data to be considered adequately precise.⁽³⁾

9.1.1 The Method Detection Limit (MDL) and Method Quantitation Limit (MQL)

The MDL and MQL may be calculated from the measurement of either a low or blank sample, (or a SSCS or SRMs selected as described in section 6.0), at the start and end of sample analysis, and after approximately every tenth sample (a daily total of seven measurements is recommended). Alternatively, the quartz blank or "clean" sand may be used if a blank soil or sediment sample is unavailable.

Disable the display thresholds. This will permit results less than one standard deviation (STD) to be displayed (even negatives). Measure the sample using the same application and measuring time used for the samples. Enable the display thresholds prior to analyzing the next sample.

The sample standard deviation of the mean for each target element is calculated. If the standard deviation has a fractional component, round up to the next whole number prior to calculating the MDL and MQL.

The definition of the MDL is three times the calculated standard deviation value.

The definition of the MQL is 10 times the calculated standard deviation value.

9.2 Reporting Results

All raw XRF data should be reported including the individual results of multiple analyses of samples and sampling points. The average and concentration range of each multiple analysis should also be reported.

A "reported" value for each analysis or average of multiple analyses should be processed in the following manner.



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 23 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

1. Round the value to the same degree of significance contained in the SSCS or SRM sample assay values (usually two) if the element's calibration has been adjusted (see Section 6.0). Round to 2 significant figures for sample results. DO NOT round results for standards used to determine MDL or RSD values (use raw data).
2. Report all values less than the MDL as not detected (U).
3. OPTIONAL: Flag and note all values greater than or equal to the MDL and less than the MQL (usually with a "J" next to the reported value).
4. Report all values equal to or greater than the MDL and within the linear calibration range (if the element's calibration has been adjusted, see section 6.0).
5. If SSCS were used and the calibration was adjusted, flag and note all values above the linear calibration range (ie, values greater than the highest concentration used in the calibration adjustment procedure).

9.3 Accuracy

Accuracy, relative to a specific digestion method and elemental analysis procedure, is determined by submitting an XRF analyzed sample (prepared sample cups may be submitted) for AA or ICP analysis at a laboratory.

The on-site analysis of soils by XRF instrumentation should be considered a screening effort only (QA1 data). Data derived from the instrument should be used with discretion. Confirmatory analyses on a subset of the screening samples (minimum 10 percent) can be used to determine if the XRF data meets QA2 data objectives. The confirmation samples should ideally be selected randomly from the sample set and include a number of samples at or near the critical level. The results of the metal analysis (dependent) and the XRF analysis (independent) are evaluated with a regression analysis. The correlation factor (R^2) should be 0.7 or greater.⁽³⁾

XRF results may be multiplied by the slope prior to substitution for metal analysis results in contouring, kriging programs, or removal volume estimates. Correcting the XRF results based on confirmatory analyses should only be undertaken after careful consideration. It must be understood that the confirmatory analysis (AA or ICP) is an estimate of the concentration of metal contamination and is dependent upon the specific instrumentation and sampling methodology used. Since XRF is a total elemental technique, any comparison with referee results must account for the possibility of variable extraction, dependent upon the digestion method used and its ability to dissolve the waste or mineral form in question.

9.3.1 Matrix Considerations

Other types of QA/QC verification should include verification that the instrument calibration is appropriate for the specific site to be assessed. This includes verification of potential multiple soil matrix types that may exist at a site. Matrix differences which affect the XRF measurement include large variations in calcium content, which may be encountered when going from siliceous to calcareous soils, as well as large variations in iron content.



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 24 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

10.1 Confirmation Samples

Confirmation samples are recommended at a minimum rate of 10 percent and are required if QA2 data objectives have been established for site activities.⁽³⁾ Ideally, the sample cup that was analyzed by XRF should be the same sample that is submitted for AA/ICP analysis. When confirming an in-situ analysis, collect a sample from a 6-inch by 6-inch area for both an XRF measurement and confirmation analysis.

The XRF and metals results are analyzed with a regression analysis using a statistical program (such as SAS®) or a spreadsheet with the intercept calculated in the regression. The correlation factor (coefficient of determination, COV) between XRF and AA/ICP data must be 0.7 or greater for QA2 data objectives.⁽³⁾

10.2 Recording Results

Record all results and monitoring activities in a laboratory or field notebook. Alternatively, record results electronically on a hard drive or floppy disk.

10.3 Downloading Stored Results and Spectra

Results (analytical reports) and spectra which have been stored in the Spectrace 9000 internal memory should be downloaded and captured in disk files on a PC (see section 5). Spectrace Instruments provides software for this purpose. Additionally, they provide software to prepare results or spectra for importing into a spreadsheet. Refer to the instructions provided with the programs for details on their operation.

Alternatively, other software with terminal data logging capabilities may be used to capture results and spectra to disk files.

After capturing results to a file, print a copy and save both the disk files and the printout for future reference and documentation purposes.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, corporate and/or any other applicable health and safety practices.



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 25 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

12.0 REFERENCES

- (1) U.S. EPA/ERT, "Representative Sampling Guidance, Volume 1 - Soil," November, 1991 (OSWER Directive 9360.4-10).
- (2) Kalnicky, Dennis, "Effects of Thickness Variations on XRF Analyses of Soil Samples When Using Plastic Bags as Measurement Containers," U.S. EPA Contract No. 68-03-3482, March, 1992.
- (3) U.S. EPA/ERT, Quality Assurance Technical Information Bulletin. "Field-Portable X-Ray Fluorescence," Volume 1, Number 4, May, 1991.

13.0 BIBLIOGRAPHY

1. Spectrace 9000 Portable XRF Analyzer Operating Instructions, Revision 0.3, January, 1992.
2. Bernick, Mark , P. Berry, G. Voots, G. Prince, et. al. , "A High Resolution Portable XRF HgI₂ Spectrometer for Field Screening of Hazardous Metal Wastes," Pacific-International Congress on X-ray Analytical Methods, August, 1991.
3. Bernick, Mark "Thin Film Standard Evaluation of the OEI X-MET 880 HEPS Probe and the Spectrace 9000 Field Portable X-ray Fluorescence Analyzers," U.S. EPA Contract No. 68-03-3482, March, 1992.
4. Andreas, C.M. and W. Coakley, "X-ray Fluorescence Spectrometry: Uses and Applications at Hazardous Waste Sites," HMCRI Research and Development Conference, San Francisco, California, February, 1992.
5. P. Berry, S. Little, G. Voots, M. Bernick, G. Prince, "XRF Determination of Lead in Paint, Soil, and Sampled Particulates with Field Portable Instrumentation", American Chemical Society-Division of Environmental Chemistry, August, 1992.
6. Bernick, Mark, D. Idler, L. Kaelin, D. Miller, J. Patel, G. Prince, "An Evaluation of Field Portable XRF Soil Preparation Methods," Second International Symposium on Field Screening Methods for Hazardous and Toxic Chemicals, February, 1991.
7. Dzubay, T. Ed, "X-ray Fluorescence Analysis of Environmental Samples," Ann Arbor Science, 1977, p. 310.
8. Chappell, R., Davis, A., Olsen, R, "Portable X-ray Fluorescence as a Screening Tool for Analysis of Heavy Metals in Soils and Mine Wastes," Proceedings Conference Management of Uncontrolled Hazardous Waste Sites, Washington, D.C., 1986, p 115.
9. Piorek, Stan, Rhodes, J., "A New Calibration Technique for X-ray Analyzers Used in Hazardous Waste Screening," Proceedings 5th National RCRA/Superfund Conference, April 1988, Las Vegas, NV.
10. "Data Quality Objectives for Remedial Response Activities," EPA\540\G-87\004, March 1987.
11. Rhodes, J., Stout, J., Schlinder, J., and Piorek, S., "Portable X-ray Survey Meters for *In-Situ* Trace Element Monitoring of Air Particulates," American Society for Testing and Materials, Special Technical Publication 786, 1982, pp. 70 - 82.



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 26 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

12. Piorek, S., Rhodes, J., "*In-Situ* Analysis of Waste Water Using Portable Pre-concentration Techniques and a Portable XRF Analyzer," Presented at the Electron Microscopy and X-ray Applications to Environmental and Occupational Health Analysis Symposium, Penn. State Univ., Oct. 14 - 17, 1980.
13. Piorek, S., Rhodes, J., "Hazardous Waste Screening Using a Portable X-ray Analyzer," Presented at the Symposium on Waste Minimization and Environmental Programs within D.O.D., American Defense Preparedness Assoc., Long Beach, CA., April 1987.
14. "Field-Portable X-Ray Fluorescence," U.S. EPA/ERT Quality Assurance Technical Information Bulletin, Vol. 1, No. 4, May 1991.
15. Kalnicky, D., "Effects of Thickness Variations on XRF Analyses of Soil Samples When Using Plastic Bags as Sample Containers," U.S. EPA Contract no. 68-03-3482, March, 1992.
16. Kalnicky, D., "Hazardous Materials Characterization with Field Portable XRF: Observations and Recommendations," U.S. EPA Contract no. 68-03-3482, March, 1992.
17. Kalnicky, D., "XRF Method Development, Analysis of PCB in Oil Using Field Portable XRF Instrumentation," U.S. EPA Contract no. 68-03-3482, July, 1992.
18. Kalnicky, D. J., Patel, J., and Singhvi, R., "Factors Affecting Comparability of Field XRF and Laboratory Analyses of Soil Contaminants," presented at the Denver X-ray Conference, Colorado Springs, CO, August, 1992.
19. Kalnicky, D. J., Soroka, J. M., Singhvi, R., and Prince, G., "XRF Analyzers, Field-Portable," in Encyclopedia of Environmental Analysis and Remediation, R. A. Meyers, ed., John Wiley & Sons, Inc., New York, 1998, Vol. 8, pp. 5315-5342, ISBN 0-471-11708-0.



STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 27 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

APPENDIX A

Figures

SOP #1713

April 1999

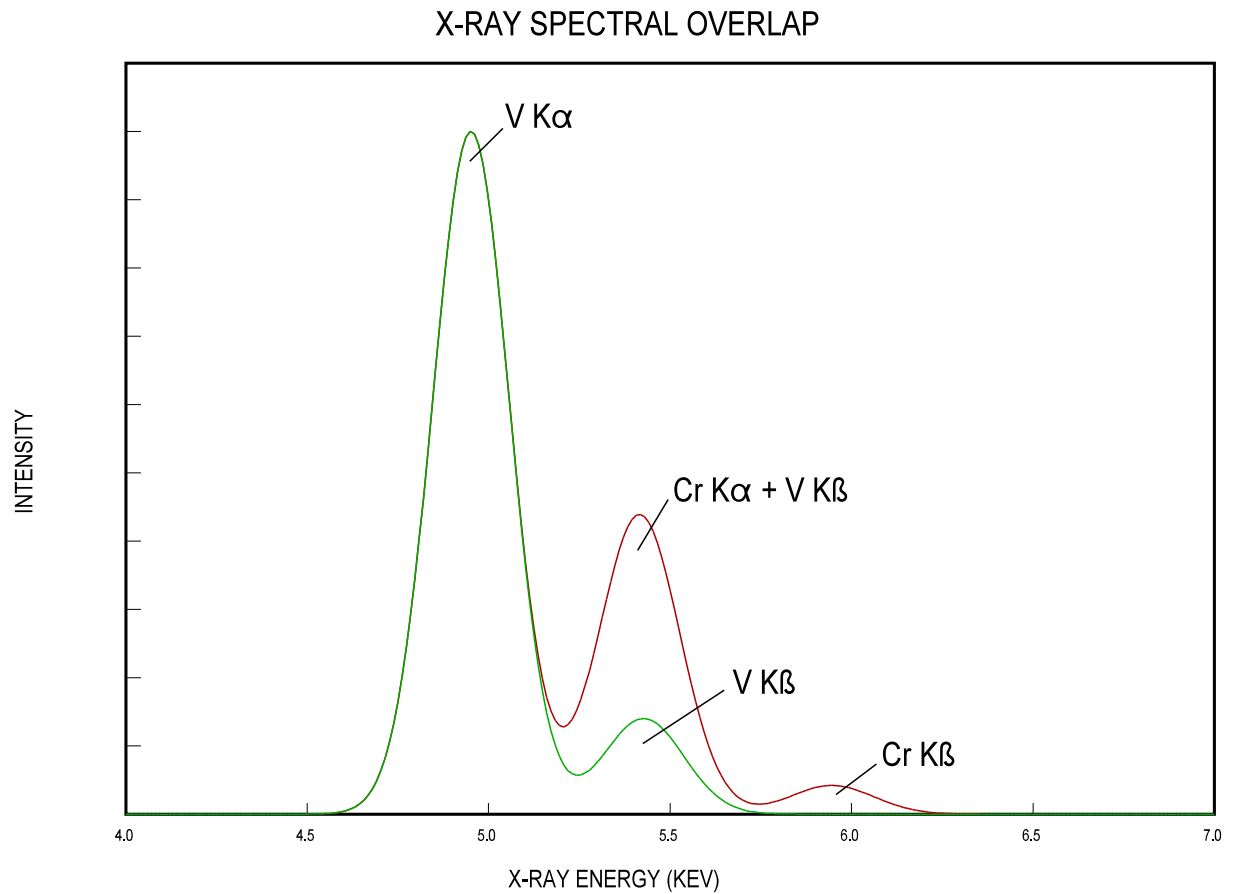


STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 28 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

FIGURE 1. X-Ray Spectral Plot Showing Overlap of Vanadium K_{β} X-Rays in the Chromium K_{α} Measurement Region.





STANDARD OPERATING PROCEDURES

SOP: 1713
PAGE: 29 of 32
REV: 1.0
DATE: 05/13/99

SPECTRACE 9000 FIELD PORTABLE X-RAY FLUORESCENCE OPERATING PROCEDURE

FIGURE 2. Iron X-Ray Spectrum Illustrating Detector Resolution Measurement

