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MICRO GAS CHROMATOGRAPH ANALYSIS OF FIXED/PERMANENT GASES (TRIAD GC - Based on EPA Method 3C)

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* These sections affected by Revision 0.1

SUPERCEDES: SOP #1725; Revision 0.0; 12/31/02; U.S. EPA Contract EP-W-09-031..



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1.0 SCOPE AND APPLICATION

The purpose of this standard operating procedure (SOP) is to describe the Gas Chromatography (GC) analysis of vapor phase samples and is applicable to the analysis of Fixed/Permanent gases. The data generated using this SOP meets the Screening Data objective for a quick, preliminary assessment of site contamination, and provides analyte identification and quantification. Screening data without associated confirmation data are generally not considered to be data of known quality. A list of some of the gases that may be analyzed by this procedure can be found in Table 1, Appendix A.

2.0 METHOD SUMMARY

A vapor phase sample is collected by vacuum into a Tedlar bag. An aliquant of the sample is drawn into a glass syringe and then connected to the injection port of the micro GC for subsequent analysis.

An internal sampling pump pulls the sample from the glass syringe through a fixed sampling loop for a programmed period of time. Injection valves are activated and the sample is injected onto dual capillary columns. The GC oven is operated isothermally to separate the analytes present into discrete peaks, which are then detected with the dual micro thermal conductivity detectors (μ TCDs).

Data generated are stored electronically by Windows-based data system software. Compounds eluting from the GC columns are identified and quantified by comparing the retention time and response with those of standards stored in a reference library database. The databases are prepared by analyzing reference standards under the same conditions as the samples.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Samples are usually collected in Tedlar bags as per Scientific, Engineering, Response and Analytical Services (SERAS) SERAS SOP #2102, *Tedlar Bag Sampling*. Once samples collected, the Tedlar bag should be placed in a clean and cool environment (at room temperature) out of direct sunlight. The bag samples should arrive at the mobile laboratory with the valves closed and identification tags attached. Samples should be accompanied with a chain of custody (COC) record indicating sampling locations, sample numbers, date collected, sample matrix, and sample volumes. The COC record should agree with the information on the Tedlar[®] bag labels and discrepancies should be noted on the COC record at the time of receipt by the mobile laboratory. In addition, any obvious physical damage or contamination (e.g., broken valves, condensate in the bag, or bags being flat) should also be recorded on the COC record. In the event that COC is not provided, enter all available information in the injection logbook.

For best results, samples should be analyzed within the first 12 hours of collection. Samples must be analyzed within 24 to 48 hours after collection.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Since the TCD exhibits universal response and detects all gas components with a thermal conductivity different from the carrier gas, interferences may occur. The 3000A Micro GC detects the preselected compounds that can be



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identified by retention times stored within its internal library; therefore, large quantities of other vapors may be present, and seriously interfere with the analysis. The presence of many sample components may confuse the identification routine of the software and yield ambiguous results. Also, large quantities of sample vapors may overload the capillary columns, causing the retention times of the preselected compounds to fall outside of expected retention time windows.

5.0 EQUIPMENT/APPARATUS

- Gas chromatograph (GC), interfaced with dual columns, μ TCDs, and laptop computer (Agilent Technologies 3000A Micro GC equipped with Agilent Cerity QA-QC software or equivalent).
- Chromatographic column, capable of resolving gas components of interest. (J&W's HP PLOT U, HP PLOT MoleSieve or equivalent).
- Tedlar bags, 1- or 5-liter (L) equipped with sampling injection valves (SKC, Inc. or equivalent).
- Glass syringe, Micro-Mate hypodermic with Luer lock, various volume size (Popper & Son, Inc. or equivalent).
- Syringe needles, various gauges with Luer lock tip (Benton-Dickson Inc. or equivalent).
- Syringe sampling valves, on/off Teflon two way valves (Supelco, Inc., or equivalent).
- Regulators, for controlling gas cylinder pressures and flow rates (Scott Specialty Gases, Inc. or equivalent).
- Teflon tubing, diameter and length determined by connection requirements of cylinder and/or the GC.

6.0 REAGENTS

- Calibration gases, standard gas mixtures for compounds of interest (Scott Specialty Gases, Inc. or equivalent).
- Helium, ultra high purity 99.999 percent (%) - 99.9999%, for use as a carrier gas.

7.0 PROCEDURES

Prior to routine operation of the Micro GC, optimize the operational conditions according to manufacturers' specifications to provide good resolution and minimum analysis time. Table 2 summarizes suggested operating conditions for the Micro GC. Figure 1 shows the separation and retention times that can be achieved under these operating conditions. Operating conditions will vary based on the target compounds and requirements for optimal response.

7.1 Initial Calibration



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Before sample analysis begins, the Micro GC is calibrated by the external standard technique using certified gas standards containing the target compounds. Three or more different concentrations of the gas standard (s) are used to create a multipoint calibration. The concentration range should bracket the expected concentration of the target compounds, or define the working range of the detector.

The Agilent Cerity QA/QC software calculates and graphically displays the calibration curve (See Figure 2, Appendix B). Using a linear least square fit, the calibration curve is generated by plotting peak area/height versus concentration for each compound (See Table 3, Appendix A). The slope of the line is used as the response factor for subsequent quantitation. The correlation coefficient (r^2) measures the fit of the calibration curve and ranges from 0.00 to 1.00, where:

0.00 = no fit
1.000 = perfect fit

An acceptable calibration curve must have a correlation coefficient of 0.950 or higher.

7.2 Continuing Calibration

The calibration is to be verified each day analysis will be performed. A single point gas standard, typically the mid range standard, containing the compounds of interest is analyzed as a calibration check. Sample analyses may begin if the quantitated results for the calibration check is within 20% of the known concentration value. A new calibration curve must be generated if this criterion cannot be met (See Table 4, Appendix A).

7.3 Method Detection Limit

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. Typically, the MDL reflects the limit of quantitation (LOQ) that is the lowest standard concentration reported for each target compound. The LOQ value is dependent on the response of the target compound(s), sample matrix, and GC conditions. The actual LOQ required for each assignment is site specific and dictated by the data quality objectives of the project.

7.4 Column and Detector Conditioning

Over time, small amounts of contaminants accumulate especially in the column, and can cause peak tailing and retention time shifts. Periodic bake out of the column and detector is required to optimize the chromatography of the instrument. Follow manufacturers' specifications for column and detector conditioning. Table 5 summarizes the recommended parameters and instructions for use with the Agilent 3000A Micro GC.

8.0 CALCULATIONS

All calculations referred to in this SOP can be found in the tables of Appendix A.



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9.0 QUALITY ASSURANCE/QUALITY CONTROL

The following quality assurance/quality control procedures apply:

9.1 Initial Calibration

An acceptable multipoint (three or more) initial calibration must be performed before sample analysis begins. The initial calibration range is acceptable if the correlation coefficient is greater than or equal to (\geq) 0.950 for a linear regression calibration. Samples are quantitated using the linear regression formula produced by the system software (See Table 3, Appendix A).

9.2 Continuing Calibration

A single point continuing calibration, preferably a mid range standard, must be performed at the beginning of each day of sample analysis. The calculated value of the standard is compared to the known value. If the calculated value differs by more than plus or minus (\pm)20% from the known value, re-analyze the continuing calibration standard. If the second continuing calibration standard also fails, perform a new initial calibration. The equation for Percent Difference (%D) can be found in Table 4.

9.3 Limit of Quantitation

The lowest standard in the calibration curve will be used as the LOQ unless a higher reporting limit has been selected. The reporting limit will be defined by the project's data quality objectives.

9.4 Sample Analysis

Each sample must be analyzed, at a minimum, in duplicate. The average area and %D are then calculated and reported for each analyte in the sample (See Table 4, Appendix A). The results are acceptable when the peak areas for two consecutive injections have a \pm 5% difference. If this criterion is not achieved, analyze additional replicates until consistent areas are obtained.

Depending on the data quality objective stipulated in the work plan, at least 10% of the samples analyzed by this SOP may be submitted for confirmation by an outside laboratory for definitive confirmation.

9.5 Initial Demonstration of Capability

Initial proficiency in this analysis must be demonstrated by each analyst initially and each time significant changes are made in the procedure or for instrumentation. Each analyst will generate precision and accuracy data using a reference standard other than the source used for calibration. Four replicates of a well-mixed reference standard is analyzed using the procedures outlined in this SOP. Calculate the average mean in ppbv and the standard deviation (s) in ppbv. The Quality Assurance Officer (QAO) will tabulate the results from all of the analysts per matrix per parameter, and calculate control limits.

9.6 Work Assignment Field Change Form



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A Work Assignment Field Change Form must be generated to initiate any onsite change in the scope of a project. This form must document the original scope of work that is being changed, the new scope and the signatures of the SERAS Task Leader or their designee and the Work Assignment Manager.

10.0 DATA VALIDATION

The data is reviewed using the Quality Assurance/Quality Control considerations listed in Section 9.0 by the analyst prior to submittal to the client to ensure that the instrument has been operated in accordance with this SOP and manufacturer's recommendations and that all QA/QC checks have been performed. The Screening data objective requires that the calibration and detection limits be evaluated. All field analytical reports must be reviewed in accordance with Administrative Procedure (AP) #22, *Peer Review of SERAS Deliverables*.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow Environmental Protection Agency (EPA), Occupational Safety and Health Administration (OSHA) and corporate health and safety practices.

12.0 REFERENCES

"Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.1." 40 CFR Part 136, Appendix B.

"Determination of Carbon Dioxide, Methane, Nitrogen, and Oxygen from Stationary Sources." 40 CFR Part 60, Appendix A. Method 3C.

National Environmental Laboratory Accreditation Committee (NELAC), *Quality Systems*, current approved version.

13.0 APPENDICES

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- Figures



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TABLE 1. Columns installed in the Agilent 3000A Micro GC

HP-PLOT Molesieve Column A

- High resolution column for the analysis of permanent gases hydrogen (H₂), oxygen (O₂), nitrogen (N₂), carbon monoxide (CO), methane (CH₄) and noble gases.
- 4 meter (m) x 0.320 millimeter (mm) inner diameter (ID), 30 micron (μ) df, molecular sieve 5A PLOT
- Ideal for many applications, including routine air monitoring and analysis in less than 10 seconds.
- Temperature range: -60 to 300 degrees Centigrade (°C)

HP-PLOT U Column B

- Analysis of fixed gases and light hydrocarbons, CO₂, CH₄, ethane (C₂H₆), ethylene (C₂H₄), acetylene (C₂H₂), carbonyl sulfide (COS), sulfur dioxide (SO₂), natural gas, refinery gas, carbon isomers (C1 - C3), except propylene and propane.
- 4 m x 0.320 mm ID, 10μ df, HP-PLOT U
- Temperature range: -60 to 190°C



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TABLE 2. Typical Operating Parameters for the Agilent 3000A Micro GC

	Column	Column
	A	B
3000 GC Set points		
Sample Inlet Temperature (°C)	95	Same as A
Injector Temperature (°C)	90	90
Column Temperature (°C)	110	70
Sampling Time (s)	10	10
Inject Time (ms)	0	30
Run Time (s)	100	100
Post Run Time (s)	0	0
Pressure Equilibration Time (s)	1	1
Column Pressure (psi)	35	25
Post Run Pressure (psi)	35	25
Detector Filament	Enabled	Enabled
Detector Sensitivity	Standard	Standard
Detector Data Rate (Hz)	20	20
Baseline Offset (mV)	0	0
Backflush Time (s)	10	n/a
3000 GC Configuration	A	B
Injector Type	Backflush	Timed
Carrier Gas	Helium	Helium
Column Type	Molecular Sieve	Plot U
Detector Type	TCD	TCD
Inlet Type	Heated	Heated

- °C = Degrees Celsius
- s = Seconds
- ms = Milliseconds
- psi = Pounds per square inch
- Hz = Hertz (cycles per second)
- mV = Millivolts
- n/a = Not applicable
- TCD = Thermal conductivity detector



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TABLE 3. Equations for a Linear Regression Calibration

The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = mx + b$$

where:

- y = Instrument response
- m = Slope of line
- x = Concentration of the calibration standard
- b = The intercept

As can be seen in Figure 2, the line created by the calibration curve is forced through zero. The intercept, b, is equal to zero. The above equation then becomes:

$$y = mx$$

Using external standard quantitation, the regression equation is rearranged as shown below:

$$\frac{A_s (C_s)}{A_{is}} = m C_s$$

where:

- A_t = Area under the peak or peak height for the target analyte in the sample
- A_s = Area under the peak or peak height for the target analyte in the standard
- C_s = Concentration of the target analyte in the calibration standard
- m = Slope of the line



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TABLE 4. Equation for Percent Difference

Calculate and report the Percent Difference (%D) for each compound in the daily calibration check by the following equation:

$$\%D = \left[\frac{|A - B|}{3} \right] 100$$

where:

- %D = percent difference
- A = result from the calibration check
- B = known concentration for the compound

The vertical bars in the formula indicate the absolute value of the difference, therefore, value is always expressed as a positive value



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TABLE 5. Bake out conditions, frequency, and instructions for the Agilent 3000A Micro GC

Column type	Column Temperature °C	Duration, hours	Recommended frequency for general use
Alumina PLOT	180	8-12	Weekly
MolSieve 5A PLOT	180	8-12	Weekly
OV-1	180	2	Weekly
OV-1701	180	2	Weekly
PLOT Q	160	8-12	Weekly
PLOT U	160	8-12	Weekly
Stabilwax-DB	180	2	Weekly

1. In Agilent Cerity, create a method called "Bake out for 3000A". Use the values listed above to set the flow rates, run times, and temperatures. If the GC contains columns with different durations, create bake out method for each set of GC modules that use the same bake out time.
2. Turn the detector filaments ON.
3. Save the method.
4. Make sure carrier gas flow is ON (this protects the columns and detectors).
5. From Cerity's instrument view, download the method to the instrument.
6. Allow the method to run for the duration listed above.
7. After bake out is complete, load your analytical method and run a set of calibration samples.
8. Check the report. Adjust the calibration settings, retention times, and response factors as needed.
9. If the problem persists, replace the 10-micron inlet filter and rerun your calibration sample.



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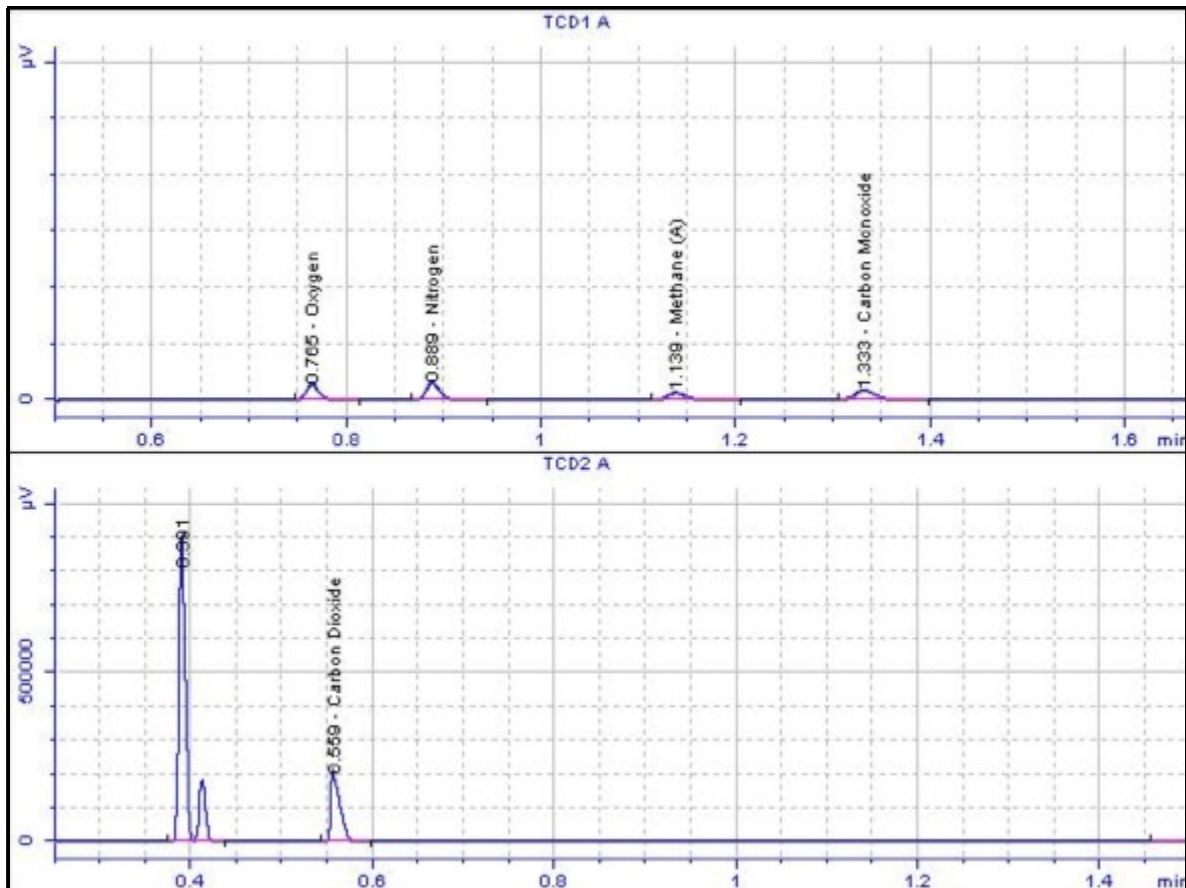


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FIGURE 1. Gas Chromatogram of Fixed Gases



Columns: A - HP-PLOT MoleSieve; B - HP-PLOT U
Program: Isothermal analysis, column A at 110°C and column B at 70°C for 100 seconds.
Detector: Thermal conductivity detector (TCD)



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FIGURE 2. Calibration Curve for Carbon Dioxide