FIELD ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN TEDLAR BAG AIR SAMPLES BY GC/MS (TRIAD GC/MS - Based on EPA TO-15A)

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* These sections affected by Revision 1.1

SUPERCEDES: SOP #1701; Revision 1.0; 11/7/05; US EPA Contract EP-W-09-031.

FIELD ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN TEDLAR BAG AIR SAMPLES BY GC/MS (TRIAD GC/MS - Based on EPA TO-15A)

1.0 SCOPE AND APPLICATION

The purpose of this standard operating procedure (SOP) is to describe the field Gas Chromatography/Mass Spectrometry (GC/MS) analysis of air samples collected in Tedlar bags. This procedure generates field screening data in parts per billion by volume (ppbv) and is based on Environmental Protection Agency (EPA) Compendium Method TO-15. 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. The field screening data may be definitively confirmed by the analysis of additional samples collected in SUMMA canisters and sent to a laboratory to be analyzed using methods and quality control (QC) criteria associated with definitive data. A list of the volatile organic compounds (VOCs) that may be analyzed by this method is presented in Table 1, Appendix A.

2.0 METHOD SUMMARY

Ambient air is drawn by vacuum into a Tedlar bag. An aliquot of sample is withdrawn from the bag using a glass syringe and subsequently injected into a modified purge & trap (P/T) concentrator. The VOCs are thermally desorbed from the trap, separated by GC and analyzed by positive ion electron impact MS.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

3.1 Sample Storage

Samples collected in Tedlar bags should be placed in a clean and cool environment (at room temperature) out of direct sunlight to prevent photo degradation. The bag samples should arrive at the mobile laboratory with the valve closed and an identification tag attached.

3.2 Holding Times

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.

Samples may be recorded on a chain of custody (COC) record (optional for screening locations) 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 or injection logbook 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 or in the injection logbook.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

- Structural isomers having co-eluting retention times and identical mass spectra will interfere with this method. The most common interference seen in these methods is between meta-xylene and para-xylene.

- Artifacts in Tedlar bags may result from improper cleaning procedures by the vendor, long term storage of clean Tedlar bags, sampling or sample storage.

- Organic compounds in the carrier gas, the GC/MS system, the sample preparation system or solvent vapors in the laboratory may contribute to contamination problems.

5.0 EQUIPMENT/APPARATUS

- Hewlett-Packard (HP) 6890 GC/5973 mass selective detector (MSD), equipped with Chem Station software, or equivalent

- Sample Concentrator, capable of ambient to approximately 350 degrees Centigrade ($^{\circ}$C) temperature range, equipped with a GC interface (OI Analytical P/T concentrator or equivalent)

- Restek Rtx-Volatile capillary column, 20 meter (m) long x 0.18 millimeter (mm)inner diameter (ID), 2.0 micron (um) film thickness, or equivalent

- Tedlar Bags , 1-liter (L), equipped with both sampling and injection valves (SKC, Inc. or equivalent).

- Glass Syringe, Micro-Mate hypodermic with Luer lock, 5, 10, 30, 50, 250, and 1000 milliliter (mL) (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).

6.0 REAGENTS

- Calibration standard, approximately 1.0 part per million by volume (ppmv) in nitrogen (Scott Specialty Gases, Inc., or equivalent)

- p-Bromofluorobenzene (BFB), approximately 1.0 ppmv in nitrogen (Scott Specialty Gases, Inc., or equivalent), used as the mass spectrometer performance standard

- Internal Standards, consisting of bromochloromethane (BCM), 1,4-difluorobenzene, and chlorobenzene-d_5, each at approximately 1.0 ppmv in nitrogen (Scott Specialty Gases, Inc., or equivalent)

- Perfluorotributylamine (PFTBA), for tuning the MS (Hewlett Packard, Inc., or equivalent)

- Helium, ultra high purity 99.999 - 99.9999 percent (%), used as the carrier and purge gas in the P/T GC/MS unit

- Nitrogen, ultra high purity 99.999% - 99.9999%, used for the preparation of blanks, dilution, and purging of Tedlar bags

7.0 PROCEDURES

7.1 GC/MS Operating Conditions

Example GC/MS operating conditions are as follows:

Initial Temperature	:	33°C
Initial Time	:	3.0 minutes
Ramp Rate	:	10.0°C/minute
Final Temperature	:	240°C
Final Time	:	0.5 minutes
Scan Rate	:	3.26 sec^{-1}
Mass Scan Range	:	35 to 260 atomic mass unit (amu)

Operating conditions for the concentrator and trap should be set according to the manufacturer's instructions. Example operating conditions for the concentrator are as follows:

Pre-Heat Temperature:	45_C
Pre-Heat time:	1 minute
Trap Purge Temperature	25_C
Purge Time:	10 minutes or as needed
Dry Purge Time:	1 minute
Desorb Temperature:	190_C
Desorb Time:	4 minutes
Bake Temperature:	200_C
Bake Time:	8 minutes
Transfer Line Temperature:	160_C

These parameters are subject to change based on chromatographic and analytical objectives.

7.2 Standard/Sample Injection

Introduce all standards and samples into the GC/MS system via a modified OI Analytical P/T concentrator. The standard or sample is first pre-concentrated in an adsorbent trap in the P/T unit. After the dry purge removes oxygen, the trap is thermally desorbed using helium so that all VOCs are swept onto the head of the GC column where VOCs are separated by temperature programming of the GC oven. In operation, a glass syringe is inserted into the hold-tip connected to a two-way valve assembly attached to the concentrator. When the vacuum pump is turned on and the two-way valve assembly is opened (Figure 1, Appendix B), the air in the syringe is drawn to the trap. After the injection, the pump is turned off and the two-way valve is closed. When the concentrator steps to desorb, the unit automatically starts GC/MS data acquisition.

7.3 GC/MS Tuning

- At the beginning of each day, the GC/MS system should be tuned, either automatically or manually, using PFTBA to set the proper mass calibration, mass resolution and ion abundance ratios. After PFTBA tuning is successfully completed, analyze 50 nanograms (ng) (7 mL) of BFB to check the analytical system performance and confirm that the ion abundance ratios for BFB meet the requirements listed in Table 2, Appendix A.

- Acquire the mass spectrum of BFB meeting the criteria in the following manner. Three scans (the peak apex 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.

7.4 Initial Calibration

Before any sample or blank analyses, calibrate the GC/MS system using target analytes and internal standards contained in pressurized cylinders or canisters at a nominal 1.0 ppmv concentration in nitrogen.

- A multipoint calibration, typically a 5-point calibration, should be established before sample injection. The initial calibration may include standards at 1, 5, 25, 50, and 100 nanoliter (nL). These concentrations result from injections of 1, 5, 25, 50, and 100 mL of the 1.0 ppmv calibration standard. One of the calibration standards should be near the quantitation limit (QL) for the compound(s) of interest. A minimum of three calibration standards must be used to generate a calibration curve.

- Internal standards are added by typically spiking with 10 mL (equivalent to 10 nL) of the nominal 1.0 ppmv internal standard mixture.

- Quantitation ions for target analytes are shown in Table 1, Appendix A. The primary ion should be used for quantitation unless interferences are present, in which case a secondary ion is used.

- Data generated by use of an average response factor ($RF_{average}$) or a linear regression forced through zero are acceptable. The preferred approach is to first create a calibration using the response factor (RF). Refer to Table 3, Appendix A. The initial calibration is acceptable when the calculated percent relative standard deviation (%RSD) for each analyte is less than or equal to (≤) 30.0% with at most two exceptions with a limit up to 40.0%. $RF_{average}$ is then used for calculating sample concentrations.

  Linear regression forced through zero (Table 4, Appendix A) may be used if the criteria for the $RF_{average}$ are not met. An acceptable correlation coefficient of ≥0.95 must be met for all target analytes.

- For each compound in the calibration, the retention time and relative abundance of selected ions are stored on the hard disk of the GC/MS computer to be used for compound identification.

- If the initial calibration 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.

7.5 Continuing Calibration

- For each day of analysis and after BFB criteria have been met, analyze a continuing calibration standard at the mid-point concentration to check that the initial calibration remains under control. For each target analyte, calculate the RF using the equation from Table 3, Appendix A. Compare this daily RF with the $RF_{average}$ from the initial calibration.

- Calculate the percent difference (%D) using the equation listed in Table 3, Appendix A. The continuing calibration is acceptable if the %D for all response factors (RFs) are within ± 30%. When using linear regression, compare the calculated concentration of the mid-level standard to the known concentration. Calculate a %D for each target analyte. The continuing calibration is acceptable if the %D for all response factors (RFs) are within ± 30%.

- If acceptance criteria are not met, re-analyze the continuing calibration check sample. If acceptance criteria are not met for the second check sample, the initial calibration must be re-analyzed.

7.6 Method (Instrument) and System Blanks

Method (Instrument) blanks are analyzed after the initial calibration standards and the continuing calibration standard and prior to any sample analyses to assess possible laboratory contamination.

- Measure 10 mL of the internal standards in a glass syringe and trap onto the concentrator. Proceed with analysis.

- System blanks may also be necessary after analyzing samples with high levels of VOC target analytes and/or non-target VOCs to ensure no carryover.

7.7 Tedlar Bag Analysis

Lot (Tedlar bag) are analyzed after the Method (Instrument) blank and prior to any sample analyses to assess possible contaminants from the Tedlar bag.

- Prior to use each Tedlar bag is purged three times with ultra-pure nitrogen. Using a nitrogen purged Tedlar bag, fill with nitrogen and hold for at least one-hour before analyzing.

- Using a Luer-Lock fitted adaptor, directly vent the nitrogen blank from the Tedlar bag to a glass syringe. The volume used for the Lot blank can range from 250 mL to 1000 mL. Allow the syringe to fill with a volume slightly greater than the amount to be used for analysis. Adjust to the exact sample volume required, allow the pressure to equilibrate, and close the valve at the syringe end.

- Place syringe in the Luer-Lock tip valve in the front of the concentrator and start pump to place onto the sorbent trap. Fill a glass syringe with 10 mL of the internal standard and place onto the sorbent trap. Proceed with analysis.

8.0 CALCULATIONS

Calculate the concentrations of target compounds in the air samples using the GC/MS computer software. The target compound calculation is presented in Table 5, Appendix A. All target analyte concentrations are reported to two significant figures.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

The following quality assurance/quality control (QA/QC) protocols apply to this procedure. The QA/QC requirements in this section may be waived by the Work Assignment Manager (WAM) or their designee depending on the data quality objectives of the project. All waivers must be documented in field logbooks or on a Work Assignment Field Change Form.

9.1 GC/MS Tuning and Performance Criteria

BFB must be analyzed each day of operation and must meet the BFB ion abundance criteria listed in Table 2, Appendix A.

9.2 Initial Calibration

An acceptable initial calibration must be performed using a minimum of three standards before sample analysis begins. The initial calibration range is acceptable if the %RSD is less than or equal to 30.0% for the $RF_{average}$ for each VOC; two compounds may have a %RSD up to 40.0%. When using linear regression, the correlation coefficient must be ≥ 0.95. Samples are quantitated using the $RF_{average}$ of each compound from the initial calibration or the linear regression formula.

9.3 Continuing Calibration

Once an initial calibration has been established, a continuing calibration standard must be analyzed on each day of sample analysis. The RF of the mid-level calibration standard is compared against the $RF_{average}$ from the current initial calibration when response factors are used for quantitation. The calculated concentrations of the mid-level calibration standard are compared to the known concentration when using linear regression. If the calculated %D for any VOC in the continuing calibration standard differs by more than ±30%, the continuing calibration must be reanalyzed. If the continuing calibration fails a second time, the initial calibration must be re-analyzed.

9.4 Blanks

The blanks should not contain any target analyte at concentrations above the limit of quantitation (lowest standard in initial calibration) or additional compounds which may co-elute or interfere with identification of the target analytes. If contamination is a problem, the source of the contamination must be investigated. Appropriate corrective actions should be taken and documented.

If an analyte found in the blank is also found in the associated samples, those sample results are to be

flagged as possibly contaminated.

9.5 Dilution Analysis

All target analyte concentrations should be within the calibration range. Use the results of the initial analysis to determine an appropriate dilution factor (DF). The DF should bring the target analyte concentration within the initial calibration range.

9.6 Replicate Analysis

One sample replicate should be analyzed each day of analysis. The sample should be randomly chosen and re-analyzed. Calculate the relative percent difference (RPD) for any concentration detected. The RPD is given as the absolute difference of the replicate values divided by their mean, expressed as a percentage.

9.7 Internal Standard Evaluation

Internal standards are added to all standards, blanks and samples. The area response for each internal standard must be within ±40% of the area response of the most recent calibration standard. In addition, the sample retention times must be within 20 seconds of the latest daily (24-hour) calibration check standard.

Internal standard responses and retention times should be evaluated immediately after data acquisition. If criteria are not met, inspect system for malfunctions and take corrective actions if necessary. Re-analyze the sample.

9.8 Target Compound Identification

Two criteria must be satisfied to verify the identification of a target compound:

- Retention Time - A sample target analyte retention time (RT) must be within ±0.50 minutes of the RT of the target analyte in the calibration standard. The calibration standard must be analyzed on the same 24 hour clock as the sample.

- Spectra - (1) All ions present in the standard mass spectra at a relative intensity greater than 10% (where the most abundant ion in the spectrum equals 100%) must be present in the sample spectrum, and (2) The relative intensities of the ions specified above must agree within ±20% between the sample and the reference spectra.

9.9 Tentatively Identified Compounds

A library search should be performed for tentatively identified compounds (TICs) present in method blanks, lot blanks, and samples for the purpose of tentative identification. In this case, the National Institute for Standards and Technology (NIST) Mass Spectral Library (or equivalent reference mass spectra system) should be used for identification search.

1. Guidelines for making tentative identification of a non-target compound:

   - Relative intensities of major ions greater than 10% of the most abundant ion in the reference spectrum should be present in the sample spectrum.
   - The relative intensities of the major ions should agree within ±20% between the standard and sample spectra. For example, if an ion has an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30-70%.
   - Molecular ions present in reference spectrum should be present in sample spectrum.
   - Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or the presence of co-eluting compounds.
   - 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 the presence of co-eluting compounds.
   - The peak area for the non-target compound is greater than 10% of the peak area of the nearest internal standard.

     NOTE: Data system library reduction programs can sometimes create these discrepancies.

2. If all of the above conditions for a compound are met, that compound will be reported as a TIC. If the mass spectral interpretation specialist indicates that 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 compound, if possible. Up to 20 TICs and/or unknowns may be reported.

3. An estimated concentration for TICs should be calculated using the internal standard method. The nearest internal standard free of interferences should be used for quantitation; a response factor of 1.0 will be used. All non-target analyte concentrations are reported to two significant figures.

9.10 Quantitation Limit

The lowest standard used in the initial calibration will be used for the quantitation limit or an elevated reporting limit may be used.

9.11 Manual Integrations

Manual integration of all target analytes, surrogates, and internal standards will be submitted for review. The manual integration results will be flagged with a "M" using the instrument software and verified during the data review process. Evidence of review will be documented on the Field Analytics Manual Integration Review Sheet (Figure 2, Appendix B). Documentation of the manual integration of quantitation ion peaks must be included in the data package. Refer to Scientific, Engineering, Response

and Analytical Services (SERAS) SERAS SOP #1001, *Chromatographic Peak Integration Procedures.*

9.12 Initial Demonstration of Capability

Initial proficiency in VOC 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.

9.13 Work Assignment Field Change Form

A Work Assignment Field Change Form must be generated to initiate any on-site 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

United States Environmental Protection Agency, 1999. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. EPA /625/R-96/010b, Office of Environmental Research and Development, Compendium Methods TO-15.

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

US EPA. 1999. *Statement of Work for Organic Analysis,* Document Number OLM04.2, Contract Laboratory Program.

13.0 APPENDICES

FIELD ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN TEDLAR BAG AIR SAMPLES BY GC/MS (TRIAD GC/MS - Based on EPA TO-15A)

A - Tables
B - Figures

APPENDIX A
Tables
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FIELD ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN TEDLAR BAG AIR SAMPLES BY GC/MS (TRIAD GC/MS - Based on EPA TO-15A)

TABLE 1. Typical Method Target Analytes (Quant Ions) and Corresponding Internal Standards

Bromochloromethane (49)

Propylene (41)
Chlorodifluoromethane (51)
Dichlorodifluoromethane (85)
Dichlorotetrafluoroethane (85)
Chloromethane (50)
Vinyl chloride (62)
1,3-Butadiene (39)
Bromomethane (94)
Chloroethane (64)
Trichlorofluoromethane (101)
Isopropyl alcohol (45)
Acetone (43)
Trichlorotrifluoroethane (151)
1,1-Dichloroethene (61)
Methylene chloride (49)
MTBE (73)
trans-1,2-Dichloroethene (61)
Hexane (57)
1,1-Dichloroethane (63)
2-Butanone (43)
cis-1,2-Dichloroethene (61)
Ethyl acetate (43)
Chloroform (83)
Tetrahydrofuran (42)
1,1,1-Trichloroethane (97)
Cyclohexane (56)

1,4-Difluorobenzene (114)

Carbon tetrachloride (117)
1,2-Dichloroethane (62)
Benzene (78)
Heptane (43)
Trichloroethene (130)
1,2-Dichloropropane (63)
1,4-Dioxane (88)
Methyl isobutyl ketone (43)
cis-1,3-Dichloropropene (75)

Chlorobenzene-d5 (117)

Toluene (91)
trans-1,3-Dichloropropene (75)
1,1,2-Trichloroethane (97)
2-Hexanone (43)
Tetrachloroethene (166)
Dibromochloromethane (127)
1,2-Dibromoethane (107)
Chlorobenzene (112)
Ethylbenzene (91)
m&p-Xylenes (91)
o-Xylene (91)
Styrene (104)
Bromoform (173)
1,1,2,2,-Tetrachloroethane (83)
4-Ethyltoluene (105)
1,3,5-Trimethylbenzene (105)
1,2,4-Trimethylbenzene (105)
1,3-Dichlorobenzene (146)
1,4-Dichlorobenzene (146)
1,2-Dichlorobenzene (146)
1,2,4-Trichlorobenzene (180)

TABLE 2. GC/MS Performance Criteria for p-Bromofluorobenzene*

m/z	Ion Abundance Criteria [1]
50	8.0 - 40% of mass 95
75	30 - 66% of mass 95
95	Base Peak, 100% relative abundance
96	5.0 - 9.0% of mass 95
173	Less than 2% of mass 174
174	50 - 120% of mass 95
175	4.0 - 9.0% of mass 174
176	93 - 101% of mass 174
177	5.0 - 9.0% of mass 176

[1] All ion abundances must be normalized to m/z 95, the nominal base peak.
Three scans (the peak apex 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.

* US EPA. 1999. *Statement of Work for Organic Analysis,* Document Number OLM04.2, Contract Laboratory Program.

TABLE 3. Average Response Calibration Equations

$$RRF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

where:

RF = Response factor
Ai = Area of analyte I
Ais = Area of internal standard
Ci = Concentration of analyte I
Cis = Concentration of internal standard

$$RF_{avg} = \frac{RF_1 + \ldots + RF_n}{n}$$

where:

$RF_{average}$ = Average response factor from initial calibration
n = Number of analysis

$$SD = \sqrt{\frac{\sum_{i=} (F_i + RF_{average})^2}{n -}}$$

$$(\%D = \frac{RF_{cc} - RF_{average}}{RF_{average}} x\ 100$$

where:

%D = Percent difference
RF_{cc} = Response factor of compound in continuing calibration
SD = Standard deviation

TABLE 4. Linear Regression Calibration Equations

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