



STANDARD OPERATING PROCEDURES

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ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AIR SAMPLES BY VIKING SPECTRATRAK 620 GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to describe the analysis of air or headspace samples by gas chromatography/mass spectrometry (GC/MS) using the Viking SpectraTrak 620. This method is applicable to volatile organic compounds (VOCs) that are in a gas phase. This method is applicable to headspace samples, air samples, soil gas, Tedlar bags, and Summa canisters, but is not limited to these sampling methods. The VOCs that are routinely analyzed at levels as low as 5 nanoliters (nL), are listed in Appendix A, Table 1.

These are standard (i.e., typically applicable) operating procedures, which may be varied or changed as required, depending on site conditions, equipment limitations, or limitations imposed by the procedure or other considerations. The procedure described herein is a modified version of those described in United States Environmental Protection Agency (U.S. EPA) Methods TO-14⁽¹⁾ and 624⁽²⁾. In all instances, the specific procedures employed will be documented and included in the final report.

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

2.0 METHOD SUMMARY

The gas samples or standards are injected onto an absorbent trap, which is then thermally desorbed to transfer the sample onto a GC capillary column interfaced with a MS. The GC capillary column is temperature programmed to separate the method analytes, which are then detected by the MS. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a reference library database. Reference spectra and retention times for analytes are obtained by the analysis of calibration standards under the same conditions used for samples. The concentration of each identified analyte is determined by relating the MS response of the quantitation ion produced by that compound to the MS response of that compound from the multi-point linear regression calibration curve. Alternatively, the concentration of the analyte can be determined by comparing its response to the quantitation ion produced by a compound that is used as an internal standard. The use of internal standards helps to compensate for variation in instrument sensitivity or sample heterogeneity often encountered in the field.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

3.1 Tedlar Bags

The Tedlar bags most commonly used for sampling have a volume of 1-liter (L). When the sampling procedure is concluded, the Tedlar bags are stored in either a clean cooler or an opaque trash bag to prevent photo degradation. It is essential that sample analysis be undertaken within 48 hours, as after that time compounds may diffuse from the bag or undergo physical or chemical alteration. Further information on Tedlar bag sampling may be found in ERT/SERAS SOP #2102, *Tedlar Bag Sampling*.



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3.2 Summa Canisters

After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to a laboratory for analysis. Upon receipt at the laboratory, the canister tag data is recorded. The initial sample canister pressure is recorded. The canister is pressurized with ultra-high purity nitrogen and the final pressure recorded. These values will be used to calculate a dilution factor for each sample canister. Sample holding times and expiration should be determined prior to initiating field activities. Sample stability may extend up to two months, depending upon sample matrix. Further information on Summa canister sampling may be found in ERT/SERAS SOP #1704, *Summa Canister Sampling*.

3.3 Headspace Samples

Liquid samples for headspace analysis are collected in 40 milliliter (mL) Volatile Organic Analysis (VOA) vials. The vials should be completely filled, with no visible air bubbles. Samples are stored out of direct light, in a cooler packed with ice immediately upon collection until analysis. Sample vials should be protected against breakage. Although, no holding time limits have been established for headspace samples, but it is recommended that headspace samples be analyzed as soon as possible.

3.4 Adsorption Tube Samples

Air samples, usually greater than 1 liter (L), are collected by drawing the air through an adsorption tube using a programmable sampling pump. Supelco Carbotrap 300 thermal desorption tubes are typically used, but any appropriate tube may be used. After recording the tube location and volume collected the tubes are placed in clean test tubes and sealed. If the sample tubes must be stored for more than a week, refrigeration is recommended. Maximum sample holding time is two weeks.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

The Viking SpectraTrak 620 is a complex instrument with interdependent components which all need to be operating properly in order for the unit to perform properly. Section 12.0 (Troubleshooting) of the *Viking SpectraTrak 620: Hardware and Software Operating Manual* should be consulted to solve potential problems. Additional assistance may be obtained by contacting Viking Instruments Corporation.

- Sample matrix interferences must be evaluated by the analyst on an individual case basis.
- Summa canister contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) should be thoroughly cleaned. Instructions for cleaning Summa canisters are described in ERT/SERAS SOP #1703, *Summa Canister Cleaning Procedures*.



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- Contamination of Tedlar bags is a major concern. Some of the possible contamination sources are addressed in Section 4.0 of the ERT/SERAS SOP #2102, *Tedlar Bag Sampling*.
- Contamination of liquid samples for headspace analysis can occur by diffusion of volatile organics through the septum. A field blank and trip blank should be shipped with the samples and analyzed to evaluate the extent, if any, of contamination.
- In general, high concentrations of short chain alkanes and alkenes in samples may interfere with the resolution and detector sensitivity for early-eluting chlorinated alkanes, chlorinated alkenes, and aromatic compounds.
- High levels of water vapor may cause a loss of resolution and detector sensitivity through part or all of a chromatogram.

5.0 EQUIPMENT/APPARATUS

- GC/MS - The Viking SpectraTrak 620 is a transportable, multi component system consisting of a gas chromatograph, mass spectrometer, and data system housed in a rugged case. The Hewlett-Packard HP 5971A MS is based on the model 5971A Mass Selective Detector. The HP 5971A uses a monolithic, fused silica mass filter with four electrically conductive hyperbolic surfaces. The analyzer can scan the mass range between 10 and 650 atomic mass units (amu) at eight selectable scanning speeds up to 2000 amu per second with 0.1 amu resolution.
- Sample Concentrator - The Tekmar model 4000 Dynamic Headspace Concentrator purge and trap unit with a Supelco VOCarb 3000 adsorption trap, and an adapter, (or an equivalent analytical system) allowing direct injection of the gas samples and standards into the gas stream during the purge cycle.
- Glass Syringes - Gas-tight syringes with Mininert Valve from 5 microliters (μL) to 1 liter (L) depending on sample and standard volumes used. (Hamilton Co. - Precision Sampling Corp., or equivalent)
- Adsorbent Trap - The VOCarb 3000 trap (Supelco, Inc. Cat. No. 2-1066) is commercially available. It consists of three 60/80 mesh adsorbent beds: 10 centimeter Carbopack B (granular graphitized carbon), 6-cm Carboxen 1000 (spherical porous carbon, 1200 square meter per gram, 0.48 gram per cubic centimeter), and 1-cm Carboxen 1001 (spherical porous graphitized carbon, 60/80 mesh, 500 square meter per gram, 0.61 gram per cubic centimeter). For initial conditioning, the trap is baked at 270^oC for 1 hour prior to use.
- Computer - A 486 DX/2 computer loaded with and capable of using HP EnviroQuant software.
- Gas Chromatography Column - Restek RT_x-volatiles, 20-meter long, 0.18 millimeter Internal Diameter, and 2.0 micrometer film thickness, or equivalent is used. (Restek Corp. or equivalent)

6.0 REAGENTS



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- Methanol - purge and trap grade. (Supelco, Inc. or equivalent)
- Gas Standards - Target compounds at one part per million volume/volume (ppmv/v) with the balance as ultra-pure nitrogen.
- Internal Standards - At one ppmv/v in ultra-pure nitrogen.

7.0 PROCEDURE

7.1 Daily GC/MS Tuning

At the beginning of each day, the GC/MS system should be tuned, either automatically or manually, using perfluorotributylamine (PFTBA) to set the proper mass calibration, mass resolution, and ion abundance ratios. After PFTBA tuning is successfully completed, an aliquot (up to 50 ng on column) of p-bromofluorobenzene (BFB) is analyzed to check the analytical system performance and confirm that the ion abundance ratios for BFB meet the requirements as stated in U.S. EPA Method 624⁽²⁾.

These criteria are in Appendix A, Table 2. These criteria must be met each day before any standards, blanks, or samples are analyzed.

7.2 GC/MS Calibration

7.2.1 Initial Calibration

Before any sample analysis is performed, the GC/MS is calibrated using certified standards that are contained in pressurized cylinders at approximate concentrations of 1 parts per million by volume (ppmv/v) in ultra-high purity nitrogen. To create a three point calibration curve, 5, 100, and 250 mL of the calibration standard mix should be injected individually, along with 100 mL of the internal standard mix. This will result in a calibration curve of 5 nL, 100 nL, and 250 nL (normalized to 1L) versus response factor for each individual target compound results. For each compound in the calibration, the retention times and relative abundances of the selected ions are stored on the hard disk of the GC/MS computer. This information is used to qualitatively and quantitatively identify the target compounds. The initial calibration is performed using a linear regression forced through zero. The correlation coefficient must be 0.900 or higher.

7.2.2 Continuing Calibration

The continuing calibration check can be used to verify the initial calibration, by the analysis of a single 100-nL standard. The final quantitated results should be within 25 percent of the known values from the initial calibration for all target compounds to be considered an acceptable continuing calibration.

7.3 Method Blank Analysis



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A method blank must be analyzed. If no target compounds are found at a level higher than the detection limit, then the method blank is considered acceptable and the sample analysis may proceed. A acceptable Method Blank must be established daily.

7.4 Instrument Conditions

7.4.1 Tekmar™ 4000 Dynamic Headspace Concentrator Conditions:

Purge Gas	Helium
Purge Gas Flow	30 mL/minute (min)
Valve Temperature	180° Celsius (°C)
Transfer Line Temperature	180°C
Purge Time	5 min (or as needed for sample introduction)
Desorb Preheat Temperature	245°C
Desorb Temperature	250°C
Desorb Time	0.5 min
Bake Temperature	260°C
Bake Time	6 min

7.4.2 Viking SpectraTrak 620 Chromatographic Conditions:

Carrier Gas	Helium
Head Pressure	6 pounds per square inch gauge (psig)
Column Flow	0.45 ml/min
Split Ratio	40:1
Initial Temperature	45°C (hold 0.5 min)
Ramp Rate	10°C per min
Final Temperature	145°C (hold 0.1 min)
Injector Temperature	120°C
Transfer Line Temperature	165°C
Source Temperature	170°C

7.5 Sample/Standard Introduction

Samples or standards (in the gas phase) are injected into the purge gas stream of the Tekmar 4000 Dynamic Headspace concentration during the purge cycle using a gas tight syringe and an adapter allowing direct injection into the purge gas stream. The purge cycle duration can be adjusted to allow a short pre-flush of the purge loop (about 15 to 30 seconds), injection of the sample or standard (at a flow rate across the trap not to exceed 100 mL/min), internal standards, and a final flush of the purge loop (15 to 30 seconds). Samples may be analyzed after the BFG tune check, initial standard calibration (or continuing calibration check), and the method blank check are all successfully completed.

7.5.1 Headspace Sample Introduction



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Fill a 40-mL VOA vial approximately half full with sample and seal with a Teflon-lined septum screw cap. Shake the capped vial vigorously for one minute. Allow to stand, undisturbed for at least 30 minutes at ambient temperature for vapor phase equilibration. Use a gas-tight syringe to extract an aliquot of headspace, insert the syringe needle through the vial septum to a distance approximately halfway between the liquid surface and the Teflon septum. Purge the syringe barrel 3 to 5 times by withdrawing and expelling a volume of headspace in slight excess of the volume anticipated to be used for analysis. Pull the exact

Volume needed into the syringe and inject into the sample injection adapter on the Tekmar 4000 Dynamic Headspace Concentrator during the sample purge cycle. The internal standard is then injected in the same manner.

7.5.2 Tedlar Bag Sample Introduction

Using a Luer-Lock fitting adapter, directly vent the sample from the Tedlar bag to a gas-tight syringe. Allow sample to fill the syringe with a volume slightly greater than the amount of sample to be used for analysis. Adjust the syringe to exactly the volume of sample needed and allow the pressure to equilibrate, then close the valve on the end of the syringe. The sample is then injected into the sample injection adapter on the Tekmar 4000 Dynamic Headspace Concentrator during the sample purge cycle. The internal standard is then injected in the same manner.

7.5.3 Summa Canister Sample Introduction

Remove the Swagelok cap and replace with a Swagelok nut with a septum inside. Gently open the Summa canister valve, insert a gas-tight syringe needle through the septum. Take care not to put the needle too far through the septum (into the valve). Allow the sample to fill the syringe to a volume slightly greater than the amount desired for analysis. Close the Summa canister valve. Adjust the syringe volume to exactly the desired volume and allow the pressure to equilibrate. The sample is now ready to be injected into the sample injection adapter on the Tekmar 4000 during the sample purge cycle. The internal standard is then injected in the same manner.

7.5.4 Adsorption Tube Sample Introduction

Air samples of known volumes are collected onto appropriate sample adsorption tubes. Afterwards, 50 nanograms (ng) of the internal standards, after GC/MS inlet split, are loaded onto each tube. The tube is attached to an auxiliary tube desorber and thermally desorbed and back flushed onto the trap of the Tekmar4000, during the sample purge cycle.

8.0 CALCULATIONS

Samples are identified and quantitated utilizing HP EnviroQuant software. This software uses reconstructed, extracted, ion chromatograms matched with retention time windows to tentatively identify



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and quantitate target compounds. This software can also perform library searches of other unknown compounds by comparing ion profiles against a National Institute of Standards and Testing (NIST) library.

The response factor (RF) is the slope of the line found by using linear regression forced through the origin. This line is the response ratio versus the amount ratio, where:

$$\begin{aligned}\text{Response Ratio (RR)} &= A_t/A_{IS} \\ \text{Amount Ratio (AR)} &= \text{Amt}_t/\text{Amt}_{IS}\end{aligned}$$

where:

$$\begin{aligned}\text{RF} &= \text{RR}/\text{AR} \\ A_t &= \text{Area response of the target compound} \\ A_{IS} &= \text{Area response of the internal standard} \\ \text{Amt}_{IS} &= \text{Amount of internal standard used in nL} \\ \text{Amt}_t &= \text{Amount of target compound used in nL}\end{aligned}$$

therefore:

$$\text{RF} = \text{RR}/\text{AR}$$

and :

$$\text{nL of sample target compound} = \frac{(A_t)(\text{Amt}_{IS})}{(A_{IS})(\text{RF})}$$

and:

$$\text{Sample concentration (ppbv/v)} = \frac{\text{Target Compound Volume (nL)}}{\text{Sample Volume (L)}}$$

where:

$$\text{Concentration (ppbv/v)} = \text{Concentration of the target compound in the sample in parts per billion by Volume}$$

9.0 QUALITY ASSURANCE/QUALITY CONTROL

1. Two criteria must be satisfied to verify the identification of a target compound:
 - a. Retention Time - The target compound's retention time (RT) in the sample must be within ± 0.50 minutes of the RT of the same compound in the standard.
 - b. Spectra - (1) All ions present in the reference standard mass spectra with a relative intensity greater than 10 percent (where the most abundant ion in the spectra equals 100 percent) must be present in the sample spectra. (2) The relative intensities of the ions specified above for the sample and the reference spectra must agree within ± 20 percent.



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2. The GC/MS is tuned daily for PFTBA to meet the abundance criteria for BFB as listed in U.S. EPA Method 624. The tune is adjusted when necessary.
3. An acceptable three point calibration of the standards must be performed before the analysis. A calibration is acceptable if the correlation coefficient is 0.900, or greater, for each compound.
4. A continuing calibration may be performed to confirm a previous initial calibration rather than analyzing a new set of initial calibration standards. A continuing calibration is acceptable if the final quantitated result for each target compound is within ± 25 percent of the true value.
5. Method blanks should be analyzed after the analysis of a standard analysis with higher target compound levels to check for carryover and for cleanliness of the system. All target compounds concentrations in the method blank must be below the method detection limit.

10.0 DATA VALIDATION

The data generated will be reviewed by a peer according to the Quality Assurance/Quality Control considerations listed in Section 9.0.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, Occupational Safety and Health Administration, and laboratory health and safety practices. More specifically, refer to ERT/SERAS SOP #3013, *SERAS Laboratory Safety Programs*.

12.0 REFERENCES

- (1) "Second Supplement to Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air", EPA/600/4-89/018, June 1988, Method TO14.
- (2) "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater", 40CFR136, Appendix A, Method 624 - Purgeables.

13.0 APPENDICES

Appendix A Tables

Table 1 Target Compounds Analyzed for Calibration

Table 2 GC/MS Performance Criteria for p-Bromofluorobenzene (EPA Method 624)



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APPENDIX A TABLES



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TABLE 1
Target Compounds Analyzed for Calibration

<u>Internal Standards</u>	<u>Quantitation Ions</u>
Bromochloromethane	128
p-Bromofluorobenzene	174

<u>Target Compounds</u>	<u>Quantitation Ions</u>
Chloromethane	50
Vinyl Chloride	62
Chloroethane	64
Trichlorofluoromethane	101
1,1-Dichloroethene	96
Dichloromethane	84
trans-1,2-Dichloroethene	96
1,1-Dichloroethane	63
Trichloromethane	83
1,1,1-Trichloroethane	97
Carbon Tetrachloride	117
1,2-Dichloroethane	62
Benzene	78
Trichloroethene	130
Bromodichloromethane	83
Dibromomethane	93
Toluene	91
1,1,2-Trichloroethane	97
Tetrachloroethene	164
Ethylbenzene	106
meta & para-Xylene	106
ortho-Xylene	106
Styrene	104
1,1,2,2-Tetrachloroethane	83
1,3,5-Trimethylbenzene	105



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TABLE 2

GC/MS Performance Criteria for p-Bromofluorobenzene (EPA Method 624)

<u>m/z</u>	<u>Ion Abundance Criteria</u>
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	Less than 2% of mass 174
174	Greater than 50% of mass 95
175	5-9% of mass 174
176	95-101% of mass 174
177	5-9% of mass 176

m/z = mass to charge ratio