

National Human Exposure Assessment Survey (NHEXAS)

Arizona Study

Quality Systems and Implementation Plan for Human Exposure Assessment

The University of Arizona
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Standard Operating Procedure

SOP-BCO-L-22.1

Title: Analysis of Three-Phase Multisorbent Samplers for Volatile
Organic Compounds

Source: The University of Arizona

U.S. Environmental Protection Agency
Office of Research and Development
Human Exposure & Atmospheric Sciences Division
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Analysis of Three-Phase Multisorbent Samplers for Volatile Organic Compounds

1.0 Purpose and Applicability

This standard operating procedure (SOP) describes methodology for the analysis of certain trace volatile organic compounds (VOCs) in air that are captured on carbon-based multisorbent tubes packed with Carbotrap C, Carbotrap (graphitized carbon blacks), and Carbosieve S-III (a carbon molecular sieve). The procedure involves thermal desorption of the adsorbed species and their analysis by high-resolution gas chromatography and low-resolution electron impact mass spectrometry (GC-MS). Table 1 presents a listing of the NHEXAS primary and secondary compounds that are quantified using this method. The table also lists those compounds that will be identified qualitatively but not quantified, i.e., only their presence or absence in a sample will be noted and reported.

2.0 Definitions

- 2.1 VOC: organic compound with saturation vapor pressure at 25 °C between 10^{-2} and 10^{-8} kPa.
- 2.2 Multi-bed sorbent: three-phase carbon-based sorbent packing material used to trap C_3 - C_{12} VOCs in air.
- 2.3 Active sampler: tube packed with carbon-based sorbents used to collect air samples for organic vapor analysis by drawing air at a known flow rate through the tube using a pump.

3.0 References

- 3.1 W.T. Winberry, Jr., N.T. Murphy, and R.M. Riggan, "Method TO-1: Method for the Determination of Volatile Organic Compounds in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS)," In: *Methods for Determination of Toxic Organic Compounds in Air: EPA Methods*; Noyes Data Corporation: Park Ridge, New Jersey, 1990.
- 3.2 "Standard Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method," Standard D 3687, American Society for Testing and Materials, Philadelphia, PA, Annual Book of ASTM Standards, 1989.

**Table 1. Compounds Fully Characterized or Identified
Only by GC-MS Analysis of Multisorbent Tubes.**

Compound	Quantification Mass (m/z)
Primary	
1,3-Butadiene	53
Benzene	78
Toluene	91
Trichloroethene	132
Secondary	
1,1-Dichloroethene	61
Dichloromethane	49
1,1-Dichloroethane	63
cis-1,2-Dichloroethene	61
Trichloromethane	83
1,2-Dichloroethane	62
1,1,1-Trichloroethane	97
Carbon tetrachloride	117
1,2-Dichloropropane	63
1,1,2-Trichloroethane	97
Tetrachloroethene	166
Chlorobenzene	112
Ethylbenzene	91
m-+p-Xylene	91
Styrene	104
1,1,2,2-Tetrachloroethane	83
o-Xylene	91
m-Dichlorobenzene	146
p-Dichlorobenzene	146
o-Dichlorobenzene	146
Present/Absent	
Methyl bromide	94
Ethyl chloride	64
Trichlorofluoromethane	101
3-Chloropropene	41
1,1,2-Trichloro-1,2,2-trifluoroethane	151
cis-1,3-Dichloropropene	75
trans-1,3-Dichloropropene	75
1,2-Dibromoethane	107
4-Ethyltoluene	105
1,3,5-Trimethylbenzene	105
1,2,4-Trimethylbenzene	105
Benzyl chloride	91
1,2,4-Trichlorobenzene	180
Hexachlorobutadiene	225

- 3.3 K.J. Krost, E.D. Pellizzari, S.G. Walburn, and S.A. Hubbard, "Collection and Analysis of Hazardous Organic Emissions," *Anal. Chem.*, **54**, 810-817 (1982).
- 3.4 A.J. Pollack, S.M. Gordon, and D.J. Moschandreas. March 1993. *Evaluation of Portable Multisorbent Air Samplers for Use with an Automated Multitube Analyzer*. Report EPA/600/R-93/053, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 91 pp.
- 3.5 P. Ciccioli, A. Cecinato, E. Brancaleoni, M. Frattoni, and A. Liberti, "Use of Carbon Adsorption Traps Combined with High Resolution Gas Chromatography-Mass Spectrometry for the Analysis of Polar and Non-Polar C₄-C₁₄ Hydrocarbons Involved in Photochemical Smog Formation," *J. High Res. Chromatogr.*, **15**, 75-84 (1992).
- 3.6 R.W. Bishop and R.J. Valis, "A Laboratory Evaluation of Sorbent Tubes for Use with a Thermal Desorption Gas Chromatography-Mass Selective Detection Technique," *J. Chromatogr. Sci.*, **28**, 589-593 (1990).
- 3.7 Hewlett Packard 5880 and 5890 GC Operator's Manuals, ND.
- 3.8 Hewlett Packard 5970 Mass Selective Detector Hardware Manual, ND.

4.0 Discussion

- 4.1 Ambient air is drawn through a sampling tube. The sampling tube, containing Carbotrap C, Carbotrap, and Carbosieve S-III, captures the VOCs in the air. The least retentive sorbent, Carbotrap C, traps the C₁₂ and larger hydrocarbon-based compounds, the Carbotrap traps the C₆-C₁₂ fraction, and the most retentive sorbent, Carbosieve S-III, traps the C₂-C₅ fraction.
- 4.2 For analysis, the sampler is placed in a heated chamber and purged with an inert gas (thermal desorption). The inert gas transfers the organic compounds from the sorbent bed onto a cold trap and subsequently onto a gas chromatographic (GC) column which is held initially at low temperature (-50°C). The GC column temperature is then increased (temperature programmed) and the components eluting from the column are identified and quantified by mass spectrometry (MS). Component identification is normally accomplished on the basis of the GC retention time and mass spectral fragmentation characteristics. For the present study, the VOCs of interest are those listed in Table 1.

5.0 Responsibilities

- 5.1 Fixed-location sampling of indoor and outdoor air for the target VOCs will be conducted by University of Arizona (UA) personnel as described in SOP UA-F-11.1.
- 5.2 The Sample Custodian at Battelle will be responsible for receiving the samples from UA and shall sign and date all forms accompanying the samples at the time of sample receipt. The Sample Custodian shall also be responsible for transferring custody of the samples to the appropriate Laboratory Analyst for analysis and shall archive the remaining samples on completion of the laboratory work.
- 5.3 Extraction, analysis, and calculations for the samples, as defined in this work instruction, will be performed by the Laboratory Analyst in the Atmospheric Sciences and Applied Technology Department at Battelle, under the direction of the Laboratory Director or his designee.
- 5.4 The Data Coordinator shall be responsible for checking that the Laboratory Analyst has completed the Sample Laboratory Data Sheet and for preparing Data Packages for shipment to UA.
- 5.5 The Laboratory Director at Battelle will be responsible for ensuring completion of the analyses in accordance with the work instruction and quality control requirements. He will also be responsible for approving the original and revisions to the method.
- 5.6 Any person who amends or alters this procedure is responsible for ensuring that the changes have been properly documented, the SOP changed, reviewed, and reissued.

6.0 Materials and Reagents

6.1 Materials

- 6.1.1 Dynatherm Analytical Instruments, Inc Model 10 Tube Conditioner, designed to accommodate Carbotrap 300 multibed sorbent sampler tubes.
- 6.1.2 50 m by 0.32 mm id fused silica column coated with nonpolar OV-1 (or equivalent) stationary phase.

- 6.1.3 Carbotrap 300 Thermal Desorption Tubes (Supelco, Catalog No. 2-0370), containing 20/40 Carbotrap C 300 mg), 20/40 Carbotrap B (200 mg), and 60/80 Carbosieve S-III (125 mg), in 0.635 cm od x 12 cm stainless steel tubes. (The original stainless steel tubes are 17.8 cm long as received from Supelco. Each tube is shortened to 12 cm by cutting 2.9 cm off each end of the tube with a tubing cutter.)
- 6.1.4 Automated Hewlett-Packard Model 5970 gas chromatograph/mass selective detector (MSD) equipped with a thermal desorber unit and a two-stage sorbent trap. The MSD may be operated in either the full-scan (SCAN) or selected ion monitoring (SIM) mode. In the SCAN mode, the MSD scans all masses repeatedly during the GC run between a lower and an upper mass limit. This mode is best suited for analyzing unknown compounds because it provides a complete mass spectrum for each GC peak. The mass spectrum may then be used to identify the compound using a computer-based compilation of standard spectra along with a suitable library search algorithm. In the SIM mode, the mass spectrometer monitors only preselected ions, rather than scanning all masses continuously between two mass limits. This results in increased sensitivity and improved quantitative analysis. With SIM, detection limits of ~0.01 ppbv are attainable. For the present purposes, the target compounds are monitored in the SIM mode.
- 6.1.5 Tylan mass flow controllers, with digital readout .
- 6.1.6 SKC constant flow sample pump.
- 6.1.7 Stopwatch.
- 6.1.8 Bubble flow meter, 25 mL.
- 6.1.9 Rotameter, 0-15 mL/min range.
- 6.1.10 Hamilton gas-tight syringes, 25-1000 μ L.
- 6.1.11 Liquid microliter syringes, 5-50 μ L, for injection of standards into GC-MS system.
- 6.1.12 Class A volumetric flasks, 10 mL.
- 6.1.13 Capillary pipettes, 50 mL.

6.1.14 Pasteur pipettes.

6.1.15 Low velocity laboratory fume hood.

6.1.16 Refrigerator.

6.1.17 Gas-phase dilution system.

6.1.18 Aadco clean air generator.

6.1.19 Nafion PermaPure tube (25 cm x 0.4 cm ID).

6.1.20 Omega CN9000 Temperature Controller, used to control the temperature of the Dynatherm tube desorber.

6.1.21 15.7-Liter aluminum high-pressure gas cylinder.

6.1.22 Mechanical rotary-vane roughing pump.

6.2 Reagents

6.2.1 Helium carrier gas (purity 99.995%).

6.2.2 Liquid nitrogen (commercial grade).

6.2.3 Zero-grade nitrogen gas cylinder.

6.2.4 Perfluorotributylamine (FC-43) for MS standardization.

6.2.5 Chemical standards (Aldrich Chemical Co.) for preparation of calibration standards.

7.0 Procedure

All relevant information relating to the analysis of samples, such as lot numbers, manufacturers of reagents and gases, etc., must be recorded contemporaneously on the "Sample Laboratory Data Sheet - Multisorbent/VOCs" (Figure 1) and compared against any control parameters. Any deviations noted require that the analysis be discontinued or justified via the analysts' best judgement.

7.1 Initial Preparations

7.1.1 Preparation of Target Compound Calibration Cylinder

- 7.1.1.1 Dilute calibration mixtures to calibrate the GC/FID system and passive samplers are prepared from Standard Reference Materials (SRM) from the National Institute of Standards and Technology (NIST), if available. If not available, a calibration cylinder is prepared in-house as follows.
- 7.1.1.2 Initially flush a 15.7-L aluminum cylinder with zero air, then evacuate the container to ~27 in. Hg with a roughing pump.
- 7.1.1.3 Prepare a table of the target compounds and their respective densities.
- 7.1.1.4 Use 1 μL of each compound to give concentrations of the individual compounds of approximately 175-350 ppbv under the conditions that apply here.
- 7.1.1.5 Using gloves and working at a fume hood, draw up 1 μL of each of the target compounds into a capillary pipette then inject into the evacuated cylinder via a heated injection port. (p-Dichlorobenzene, which is a solid at room temperature, cannot be introduced in this manner. It is weighed accurately on a balance, then dissolved in the liquid "cocktail" prepared from the remaining target compounds).
- 7.1.1.6 Zero-grade air is directed through the injection port to aid in the evaporation of the liquids.
- 7.1.1.7 After all the compounds have been injected, the injection port is removed and the tank is pressurized with zero-grade N_2 from a high-pressure gas cylinder to 1,014.7 psig. The effective volume of the gas in the cylinder is $(1014.7/14.7) \times 15.7 = 1,084 \text{ L}$.
- 7.1.1.8 The resulting concentrations for the primary and secondary target compounds are listed in Table 2.
- 7.1.1.9 The cylinder and regulator are wrapped with heating tape and maintained at 50°C to minimize sample adsorption.

Table 2. Concentrations of Target Compounds Prepared by Injecting 1 μ L of Each into Pressurized 15.7-L Cylinder.

Compound	Density (g/mL)	Amount Injected (g)	MW	Equivalent Analyte Volume at STP (L)	Cylinder Concentration (ppbv)
Benzene	0.874	8.74×10^{-4}	78	2.74×10^{-4}	253
Toluene	0.867	8.67×10^{-4}	92	2.30×10^{-4}	213
Trichloroethylene	1.464	14.64×10^{-4}	130	2.75×10^{-4}	254
1,1-Dichloroethene	1.213	12.13×10^{-4}	96	3.09×10^{-4}	285
Dichloromethane	1.325	13.25×10^{-4}	84	3.86×10^{-4}	356
1,1-Dichloroethane	1.256	12.56×10^{-4}	98	3.13×10^{-4}	289
cis-1,2-Dichloroethene	1.284	12.84×10^{-4}	96	3.27×10^{-4}	302
Trichloromethane	1.492	14.92×10^{-4}	118	3.09×10^{-4}	285
1,2-Dichloroethane	1.256	12.56×10^{-4}	98	3.13×10^{-4}	289
1,1,1-Trichloroethane	1.338	13.38×10^{-4}	132	2.48×10^{-4}	229
Carbon tetrachloride	1.594	15.94×10^{-4}	152	2.56×10^{-4}	236
1,2-Dichloropropane	1.156	11.56×10^{-4}	112	2.52×10^{-4}	233
1,1,2-Trichloroethane	1.435	14.35×10^{-4}	132	2.66×10^{-4}	245
Tetrachloroethene	1.623	16.23×10^{-4}	164	2.42×10^{-4}	223
Chlorobenzene	1.107	11.07×10^{-4}	112	2.42×10^{-4}	223
Ethylbenzene	0.867	8.67×10^{-4}	106	2.00×10^{-4}	185
m-+p-Xylene	0.867	8.67×10^{-4}	106	2.00×10^{-4}	185
Styrene	0.909	9.09×10^{-4}	104	2.14×10^{-4}	197
1,1,2,2-Tetrachloroethane	1.586	15.86×10^{-4}	166	2.34×10^{-4}	216
o-Xylene	0.870	8.70×10^{-4}	106	2.01×10^{-4}	185
m-Dichlorobenzene	1.288	12.88×10^{-4}	146	2.16×10^{-4}	199
p-Dichlorobenzene	1.241	12.41×10^{-4}	146	2.08×10^{-4}	192
o-Dichlorobenzene	1.306	13.06×10^{-4}	146	2.19×10^{-4}	202

7.1.1.10 To generate low ppbv (and pptv) concentrations for spiking the sorbent tubes and for on-line instrument calibration, the pressurized cylinder is attached to a gas phase dilutor.

7.1.1.11 Connect the Aadco air generator to the gas-phase dilutor to obtain the diluent gas.

- 7.1.1.12 Place a Nafion PermaPure tube (25 cm x 0.4 cm ID), immersed in distilled water, in line with the dilution system to humidify the standard gas stream.
- 7.1.1.13 Measure the dilution air flow rate with a Tylan digital mass flow controller and set the flow rate from the pressurized cylinder to provide the dilution desired.

7.1.2 GC-MS Instrument Set-Up

- 7.1.2.1 The thermal desorption-GC-MS system consists of a heated thermal desorption chamber attached via a six-port valve to a freeze-out loop, which is connected in turn to a capillary GC, a quadrupole mass spectrometer, and a data system. The thermal desorption module must be able to accommodate the particular sampler tube configuration of interest. Exposure of the sample to hot metal surfaces should be minimized, and only stainless steel or nickel surfaces should be used. The volume of the tubing and fittings leading from the sampler tube to the GC column must be kept as small as possible and all areas must be heated and well-swept by helium carrier gas.
- 7.1.2.2 The GC must be equipped with subambient temperature programming capability (using liquid nitrogen) to permit the use of an initial oven temperature of -50°C.
- 7.1.2.3 Helium purge flow (through the sampler tube) and carrier gas flow are set at approximately 36 mL/min and 1-2 mL/min, respectively.
- 7.1.2.4 Once the column and other system components are assembled and the various flows established, the column temperature is initially increased to about 250°C for at least 4 hours to condition the column.
- 7.1.2.5 The MS and data system are set according to the manufacturer's instructions. Electron ionization (70 eV) and an electron multiplier gain of about 10^5 should be used. Once the entire GC-MS system has been set up, the system is calibrated as described in Section 7.1.6. (Steps taken to validate the operation of the data system are described in the Appendix).

7.1.3 Routine GC-MS Tuning and Standardization

- 7.1.3.1 Twice weekly, the GC-MS system must be tuned according to manufacturer's instructions, to verify that acceptable performance criteria are achieved.
- 7.1.3.2 To tune the GC-MS, FC-43 is introduced directly into the ion source via the molecular leak. The instrumental parameters (i.e., lens voltages, resolution, etc.) are adjusted to give documented, standard relative abundances as well as acceptable resolution and peak shape (see Section 7.5). If any key ion abundance observed for the daily FC-43 mass tuning check differs by more than 10% absolute abundance from that observed during the previous daily tuning, the instrument must be retuned. If the criteria cannot be met, even after retuning the mass spectrometer, the ion source may require cleaning as per the manufacturer's instructions.
- 7.1.3.3 The performance criteria must be achieved before any blanks, standards, or samples are analyzed.
- 7.1.3.4 If routine calibration indicates a significant deviation from the performance criteria, the system must be tuned daily until stable and acceptable performance criteria are again achieved.

7.1.4 Concentration of Target Compounds in Calibration Cylinder

- 7.1.4.1 The concentrations of the target compounds in the calibration cylinder (Section 7.1.1) are determined by referencing it to a primary standard from NIST that contains the compounds of interest.
- 7.1.4.2 Measured volumes of the NIST primary standard and the calibration cylinder are injected into the GC-MSD system.
- 7.1.4.3 The response factors from the NIST primary standard are used to determine the concentrations of the target compounds in the calibration cylinder. These calculated concentrations are assumed to apply to the standard cylinder.

7.1.5 Preparation of Calibration Standards and Spiked Laboratory/Field Controls

- 7.1.5.1 Attach the pressurized standard cylinder and the Aadco air source to the gas phase dilutor.
- 7.1.5.2 Establish a gas flow through the dilutor at the predetermined concentration.
- 7.1.5.3 Attach a T-piece to the exit port of the gas phase dilutor.
- 7.1.5.4 Attach the multisorbent Carbotrap 300 sampler tube to an SKC sample pump that has been adjusted to provide the desired flow rate through the sampler tube.
- 7.1.5.5 Insert the sampler tube into the T-piece in the gas phase dilutor and secure the Swagelok nut and ferrule.
- 7.1.5.6 Turn on the sample pump and sample the spiked stream until the desired loading is achieved on the sample tube. Remove the sample tube and place Swagelok caps in each end of the tube.
- 7.1.5.7 Designate a pre-determined number of spiked sampler tubes (generally 10% of the number exposed in the field) as either laboratory or field controls and handle accordingly.

7.1.6 Calibration of the GC-MS System

- 7.1.6.1 Before analyzing a sample set, calibration runs are performed with the Instrument Calibration Cylinder (Section 7.1.1), under the same conditions used to analyze the field samples.
- 7.1.6.2 Calibration standards are used at four levels that bracket the concentration range of interest.
- 7.1.6.3 For the present purposes, a linear response corresponds to a correlation coefficient >0.98 for a linear least squares fit of the concentration/area response data.
- 7.1.6.4 Once response linearity has been demonstrated, an intermediate concentration standard near the expected levels for the components of interest is used for daily calibration purposes.

- 7.1.6.5 Responses of the target compounds should not vary by more than 10% from day-to-day. If greater variability is observed, more frequent calibration may be required to ensure the reliability of the measurements.
- 7.1.6.6 For each analyte, the average retention time is established manually from the individual retention times generated in the calibration runs. A calibration response factor is determined for the analyte by the computer.
- 7.1.6.7 The response for each target compound in the calibration standard is used to calculate a response factor from the following equation:

$$RF_c = \frac{C_c V_I}{R_c}$$

where RF_c = response factor for component (ng injected/peak area counts); C_c = concentration of component in calibration standard ($\mu\text{g/mL}$); V_I = volume of calibration standard injected (μL); and R_c = component response in calibration standard (peak area counts).

- 7.1.6.8 The RF values are tabulated and, provided the ratio of response to concentration is a constant over the working range (<10% RSD), linearity through the origin may be assumed and the average RF may be used in place of a calibration curve.
- 7.1.6.9 Experience with this system in the laboratory at Battelle has shown that, once the initial calibration has been established, a daily one-point calibration serves as a sufficient check of the stability of the GC-MS system.
- 7.1.6.10 After the single-point calibration, the analytical system is challenged with a humidified zero air stream, using a clean (blank) tube, to ensure the cleanliness of the system (i.e., levels of target VOCs must be <0.2 ppbv).

7.2 Preparation of Field Samplers and Blanks for Analysis

Set up a new manila folder labeled with the date of analysis and place all relevant information (written correspondence, identification of samples and associated computer data files, GC-MS plots, etc.) in the folder. This file will ultimately contain all information relating to the analysis and reports of the samples analyzed in the laboratory this day.

7.2.1 Preparation of Carbotrap 300 Multisorbent Sampler Tubes

- 7.2.1.1 Arrange the Carbotrap 300 multisorbent sampler tubes in sets of 10 in the order that the samplers are recorded on the VOCs Carbotrap 300 Sampler Analysis Data Sheet (Figure 2).
- 7.2.1.2 Inspect each sampler tube. If any defects, such as cracked culture tubes, caps, etc., are observed, note them in the "Comments" column of the Sampler Analysis Data Sheet.
- 7.2.1.3 If the culture tube or cap is broken so that air may have entered the sampler, the sample is voided and marked "NOT ANALYZED" in the Sampler Analysis Data Sheet.

7.2.2 Preparation of Field Blanks

- 7.2.2.1 Of the samplers taken to the field, 10% are set aside as unexposed field blanks and are analyzed with each set of samples.
- 7.2.2.2 Both laboratory blanks (unexposed samplers that remain in the laboratory during sampling) and field blanks (unexposed samplers sent into the field along with the samplers that are exposed) are analyzed.
- 7.2.2.3 The amount of each target compound (in ng) collected on exposed samplers must be corrected for the average amount measured on the designated blanks. Generally, it is found that properly conditioned carbon-based multisorbent tubes do not produce background peaks above the detection limit.
- 7.2.2.4 A control chart of the amount of each target VOC on the unexposed blanks will be kept with the VOCs/Carbotrap 300 Log

Book to ensure that there is no contamination of the sample batches.

- 7.2.2.5 Blank samplers should show peaks that are no greater than 5 ng per target compound. In practice, we find that clean sorbent tubes show background peaks that are generally below the detection limit.

7.3 Sampler Tube Analysis

- 7.3.1 For analysis of the sorbent tubes, an automated gas chromatographic system equipped with cryogenic preconcentration is used. The automated GC system incorporates a Hewlett-Packard Model 5880 gas chromatograph (GC) and parallel flame ionization detector (FID) and Hewlett-Packard 5970 mass selective detector (MSD). A modified Nutech Model 320 controller regulates the temperature of the cryogenic trap. A six port valve is used to move the cryogenic trap between collection mode and injection mode. The cryogenic trap is constructed of 20 cm x 0.2 cm ID stainless steel tubing packed with either silanized glass beads(60/80 mesh) or with material such as either Carbotrap B and Carbosieve S-III (Supelco) sorbents. Target compounds are chromatographically resolved with a 50 m x 0.32 mm id OV-1 fused silica column. Optimum analytical results are achieved with this column by temperature programming the GC oven from -50 °C to 200 °C at 8 °/min. The column exit flow is split to direct one-third of the flow to the MSD; the remaining flow passes through the FID. The MSD is operated in the selective ion mode (SIM) to monitor only preselected ions. As a result, increased sensitivity and improved quantitative analysis is achieved.
- 7.3.2 Initially remove the Swagelok cap from the end of the sorbent tube and place it in the Dynatherm desorber.
- 7.3.3 The exhaust port of the Dynatherm desorber is attached to a PermaPure Nafion drier. The drier is then attached to the heated transfer line (165°C) from the automated GC-MS system.
- 7.3.4 Prior to desorbing the sorbent tubes, the cryogenic preconcentrator on the GC-MS system is cooled to -150°C when a silanized glass beads (60/80 mesh) preconcentration trap is used or -15°C when a sorbent based preconcentration trap is used. The GC column is cooled to -50°C. The mass spectrometer and data system are set up for data acquisition in the SIM mode, as described in the manufacture's instructions. (The ionization

filament may need to be turned off during the initial 1-3 min of the run to allow air and other highly volatile components to elute. However, care must be taken to ensure that the filament is turned on in time to acquire data for the early-eluting target compounds, such as 1,3-butadiene).

- 7.3.5 After placing the six-port valve in the fill position to collect the desorption products from the sorbent tubes, the Dynatherm desorber is heated to 320°C with the Omega temperature controller for 10 min, with 36 mL/min of helium purging through the heated sorbent tube.
- 7.3.6 Following the 10 min heated purge of the sorbent tube, the six-port valve is moved to the inject position. The cryogenic trap is then heated to between 150°C and 250°C while flushing the trap with helium. The trapped compounds are then transferred to the OV-1 column, and the GC oven temperature program (-50°C to 200°C at 8°/min) is started as well as the MSD acquisition program.
- 7.3.7 After the final target compound elutes from the column, data acquisition is terminated.
- 7.3.8 Once a stable baseline has been achieved, the system may be readied for the next analysis.
- 7.3.9 Initial data processing generally involves (1) qualitatively determining the presence or absence of each target compound on the basis of a set of characteristic ions and retention times, and (2) quantification of each identified component by integrating the intensity of a characteristic ion and comparing the value to that of the calibration standard. In addition, for at least one GC-MS run, the system should be run in the full-scan mode in order to compare the individual mass spectra with reference spectra, to ensure correct instrument performance.
- 7.3.10 Place all laboratory-related worksheets in the current analysis folder in preparation for report generation.

7.4 Calculations

7.4.1 Calibration Curve

- 7.4.1.1 Data from calibration standards is used to calculate a response factor for each target compound. Ideally, the process involves analysis of at least three calibration levels of each component

during a given day and determination of the response factor (area/ng injected) from the linear least squares fit of a plot of ng injected vs. Peak area (for the characteristic ion). (In general, quantities of component greater than 1000 ng should not be injected because of column overloading and/or MS response nonlinearity). A standard personal computer program is used to fit a least squares regression equation of the form

$$Y = A + Bx$$

where Y = MS peak area (in area units, AU); x = level of the target compound standard (ng); A = intercept, and B = slope (AU/ng).

7.4.1.2 The correlation coefficient R^2 must be greater than 0.98. If this requirement is not met, re-evaluate the analysis and, if necessary, run another calibration curve.

7.4.1.3 If substantial nonlinearity is observed in the calibration curve, a nonlinear least squares fit should be used. This involves fitting the data to the following quadratic equation:

$$Y = A + Bx + Cx^2$$

where Y = MS peak area (in area units, AU); x = level of the target compound standard (ng); A , B , and C = coefficients in the equation.

7.4.2 Calculation of Target Compound Content of Blank or Control Samplers

7.4.2.1 The target compound content of unexposed (blank) samplers or control samples x_{un} must be calculated using the calibration coefficients from Section 7.4.1 and the measured peak areas of the sample Y_{un} for each compound of interest, i.e., for the linear-response case, analyte quantities are calculated from the equation:

$$x_{un} = \frac{(Y_{un} - A)}{B} (ng)$$

where x_{un} = is the target compound content of the unexposed sampler; and Y_{un} = the associated peak area for the target compound from the unexposed sampler. For the nonlinear case, the quantity of analyte is obtained from the equation:

$$Y_{un} = A + Bx_{un} + Cx_{un}^2$$

where A , B , and C = coefficients calculated from calibration curve in Section 7.4.1.

7.4.3 Calculation of Target Compound Content of Exposed Samplers

7.4.3.1 Use the calibration coefficients from Section 7.4.1 and the measured peak areas of the exposed sampler Y_{ex} for each compound of interest and correct for the content of unexposed samplers.

7.4.3.2 For the linear-response case:

$$x_{ex} = \frac{(Y_{ex} - A)}{B} - x_{un} \text{ (ng)}$$

where x_{ex} = is the target compound content of the exposed sampler; and x_{un} = the target compound content of the unexposed samplers (from Section 7.4.2).

7.4.4 Calculation of Sorbent Sampler Target Compound Concentration

7.4.4.1 The concentration of each target compound in the original air sample is calculated from the following equation:

$$C_{ex} = \frac{x_{ex}}{V_{air}}$$

where C_{ex} = calculated concentration of the target compound (ng/L); and V_{air} = total volume of air drawn through sampler tube, at standard conditions (25 °C and 760 mm of Hg). The total volume V_{air} at standard conditions is calculated from the equation:

$$V_{air} = V_{exptl} \left(\frac{P}{760} \right) \left(\frac{298}{273 + T} \right)$$

where V_{exptl} = total volume sampled at measured temperature and pressure (L); P = average barometric pressure (mm Hg); and T = average ambient temperature ($^{\circ}\text{C}$).

7.5 Quality Control

7.5.1 Instrument Tuning and Standardization

- 7.5.1.1 Refer to Section 7.1.3. These procedures provide a means of monitoring MS performance characteristics over time, and permanent records of the information are kept in the laboratory.

7.5.2 Calibration for Quantitative Analysis

- 7.5.2.1 Refer to the quantitative analysis calibration procedures in Sections 7.1.5 and 7.1.6. If quantitative responses (in area counts) of the lowest level standard mixture fall below the detection limits, the instrument and/or GC column and injector must be checked for performance degradation. The injector and/or ion source should be cleaned or the first 0.5 m of the column should be removed.
- 7.5.2.2 Those samples which were analyzed during the period when low level standards were not detected will be reanalyzed.

7.5.4 Precision, Bias, and Detection Limit

- 7.5.4.1 Precision and bias are largely dependent upon the precision and bias of the analytical procedure for each target compound, and the precision and bias of the sampling process.
- 7.5.4.2 Precision also depends greatly on the chemical; for thermal desorption introduction, repeatability is typically $\pm 20\%$ at a 300 ng level.
- 7.5.4.3 Method Accuracy: Prior to conducting a study with Carbotrap tubes, blank tubes are spiked with the compounds of interest and analyzed to determine the level of recovery of each compound. Percent bias is given by:

$$\% \text{ Bias} = \frac{X - Y}{X} 100$$

where X = expected level of target compound; and Y = measured level of target compound recovered in analysis. Recovery efficiencies for the target compounds are between 80 and 120%.

- 7.5.4.4 The limit of detection LOD for a target compound is obtained from the above data. It is defined as:

$$LOD = A + 3.3\sigma$$

where A = intercept (coefficient) from linear or quadratic least squares fit; and σ = standard deviation of the lowest concentration measurements. The method detection limit is about 0.3 ppbv. This is equivalent to the injection of a 5 ng sample collected from the passage of a 4 L air sample through a sorbent tube, and assuming a molecular weight of 100 for a typical target VOC. Both the range and limit of detection depend strongly on the properties of the individual compounds of interest.

- 7.5.4.5 Blank Sorbent Tubes: One unused sorbent tube (not a field blank) should be analyzed during each analytical study as a check on the background contribution from the sampler tube.

8.0 Records

- 8.1 All operations, maintenance and performance calibration data are stored in each instrument log book.
- 8.2 List each sample analyzed on the GC/MS in the instrument log book, including the date of data acquisition, project number, instrument conditions, file name, and floppy disk identification.
- 8.3 All analytical results are logged in specific project books and entered on the Carbotrap 300 Sampler Analysis Data Sheet (Figure 2). Directions for filling out the Analysis Data Sheet are as follows:
 - 8.3.1 Obtain a separate Analysis Data Sheet for each sample.

- 8.3.2 In the spaces provided, enter the sample code, the analysis date, the analyst's name, and the sample volume (in liters).
- 8.3.3 Enter the amounts obtained (in μg) for the field sample and the blank.
- 8.4 All data files are stored on Bernoulli disks for permanent record.
- 8.5 Hardcopy output of chromatograms and data reports are produced by the data system after each run.
- 8.6 Hard copies of the data will be stored in the analytical laboratory with the laboratory notebook.
- 8.7 Analysis results will be sent to UA after one-over-one review of the data.
- 8.8 All forms and logbooks shall also include the technician's signature, date, time of analysis, and method number.
- 8.9 All completed data forms and results will be submitted to the Laboratory Director where they will be checked and stored in a designated area.
- 8.10 All forms will be filled out in black ink. Any deletions or corrections shall be made by drawing a line through the error and shall be initialed by the technician making the correction.

Figure 1: "Sample Laboratory Data Sheet - Multisorbent/VOCs"

ITEM:	PARAMETER:
Date	_____
Analyst	_____
Standard Curve Number	_____
NIST Primary Gas Standard Lot No.	_____
Date Approved	_____
Calibration Gas Cylinder ID No.	_____
Date Approved	_____
Calibration Compounds Lot No.'s	ON BACK
Helium Gas Cylinder ID No.	_____
Date Approved	_____
Nitrogen Gas Cylinder ID No.	_____
Date Approved	_____
GC Column ID No.	OV-1, 50 m x 0.32 mm
Date Installed	_____
GC Carrier Gas Flow Rate	1.0 - 1.2 cm ³ /min
GC Temperature Program	-50°C - 200°C at 8°/min
Thermal Desorber Cycle	320°C for 10 min with pre-concentrator at -150°C and 36 mL/min He purge
MS (SIM): Filament Current	80 µA
EM Voltage	1.8 - 2.0 kV
Standard Curve Slope Value	XXX - XXY
Intercept	YYY - YYZ
Regression R ²	>0.98
No. of Cartridges Analyzed	_____
No. of Monitors Recorded	SAME AS ANALYZED
COMMENTS:	_____

Figure 1 (Continued).

COMPOUND	LOT NO.	DATE APPROVED	MANUFACTURER
1,3-Butadiene			
Benzene			
Toluene			
Trichloroethene			
1,1-Dichloroethene			
Dichloromethane			
1,1-Dichloroethane			
cis-1,2-Dichloroethene			
Trichloromethane			
1,2-Dichloroethane			
1,1,1-Trichloroethane			
Carbon tetrachloride			
1,2-Dichloropropane			
1,1,2-Trichloroethane			
Tetrachloroethene			
Chlorobenzene			
Ethylbenzene			
m-+p-Xylene			
Styrene			
1,1,2,2-Tetrachloroethane			
o-Xylene			
m-Dichlorobenzene			
p-Dichlorobenzene			
o-Dichlorobenzene			

Figure 2: Carbotrap 300 Sampler Analysis Data Sheet

Sample ID: _____

Date: _____

Active Sampling Time: _____ min

Sample Volume, V = _____ L

Compound	Amount, μg	MDL, μg
1,3-Butadiene		
Benzene		
Toluene		
Trichloroethene		
1,1-Dichloroethene		
Dichloromethane		
1,1-Dichloroethane		
cis-1,2-Dichloroethene		
Trichloromethane		
1,2-Dichloroethane		
1,1,1-Trichloroethane		
Carbon tetrachloride		
1,2-Dichloropropane		
1,1,2-Trichloroethane		
Tetrachloroethene		
Chlorobenzene		
Ethylbenzene		
m-+p-Xylene		
Styrene		
1,1,2,2-Tetrachloroethane		
o-Xylene		
m-Dichlorobenzene		
p-Dichlorobenzene		
o-Dichlorobenzene		

TURN OVER

Figure 2: (Continued)**Compounds Present/Absent**

Compound	Present/Absent
Methyl bromide	
Ethyl chloride	
Trichlorofluoromethane	
3-Chloropropene	
1,1,2-Trichloro-1,2,2-trifluoroethane	
cis-1,3-Dichloropropene	
trans-1,3-Dichloropropene	
1,2-Dibromoethane	
4-Ethyltoluene	
1,3,5-Trimethylbenzene	
1,2,4-Trimethylbenzene	
Benzyl chloride	
1,2,4-Trichlorobenzene	
Hexachlorobutadiene	

Appendix

Data System Validation

We have adopted a "holistic" approach to validate the computer system used in this SOP, based on the procedure described by Furman et al. (W.R. Furman, T.P. Layloff, and R.E. Tetzlaff, "Validation of Computerized Liquid Chromatographic Systems," J. AOAC Intl., 77, 1314-1318, 1994). This consists of tests to measure and evaluate the performance of the entire computerized GC/MS system under the conditions of its intended use, namely, the analysis of multisorbent samplers for VOCs.

The approach involves an initial characterization and calibration, and a running calibration. The initial characterization consists of generating 70-eV mass spectra for each of the target compounds and comparing the spectra with the corresponding standards in a computer-based spectral library (Wiley Registry of Mass Spectral Data, 5th Edition, containing 140,000 reference spectra and structures for over 118,000 compounds). The initial calibration is designed to evaluate system linearity and precision. Linearity is determined by using at least 4 standard mixtures to generate the response curve over the range of interest, as specified in the SOP. Precision is determined initially by making replicate injections (> 5) of a single standard mixture and calculating the standard deviation of the area responses.

After satisfactory linearity and precision data are obtained, a standard mixture is run at regular intervals so as to document that the system is not drifting or has undergone an unexpected change.

All data generated in evaluating the characterization of spectra and calibration of the system are maintained in a documentation file that is kept with the instrument.