

# National Human Exposure Assessment Survey (NHEXAS)

## *Arizona Study*

## Quality Systems and Implementation Plan for Human Exposure Assessment

The University of Arizona  
Tucson, Arizona 85721

Cooperative Agreement CR 821560

**Standard Operating Procedure**

**SOP-BCO-L-31.0**

**Title:** Analysis of Two-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  
Human Exposure Research Branch

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## Analysis of Two-Phase Multisorbent Samplers for Volatile Organic Compounds

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### 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 two-phase carbon-based multisorbent tubes packed with 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 (GC). Table 1 provides a list of the NHEXAS primary compounds that are characterized using this method.

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

| Compound  | Classification |
|-----------|----------------|
| Acetylene | Primary        |
| Ethylene  | Primary        |
| Propene   | Primary        |
| Propane   | Primary        |
| Isobutane | Primary        |
| 1-Butene  | Primary        |
| n-Butane  | Primary        |

### 2.0 Definitions

- 2.1 VOC: organic compound with saturation vapor pressure at 25°C between  $10^{-2}$  and  $10^{-8}$  kPa.
- 2.2 Two-phase multi-bed sorbent: carbon-based sorbent material used to collect  $C_2 - C_4$  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. Riggin, "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.
- 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 C<sub>4</sub>-C<sub>14</sub> 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 Varian 3600 GC Operator's Manuals, ND.

### 4.0 Discussion

- 4.1 Ambient air is drawn through a sampling tube. The sampling tube, containing the sorbents Carbotrap and Carbosieve S-III, captures the VOCs in the air over the range C<sub>2</sub> – C<sub>4</sub>.
- 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 a low temperature (-50°C). The GC column temperature then is increased ("temperature-programmed") and the components eluting from the column are identified and quantified using a flame ionization detector (FID). Component identification is normally accomplished on the basis of the GC retention time. 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/her 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/she 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 200 multibed sorbent sampler tubes.
- 6.1.2 50 m by 0.32 mm id fused silica PLOT column coated with  $\text{Al}_2\text{O}_3/\text{NaSO}_4$ .
- 6.1.3 Carbotrap 200 Stainless Steel Multi-Bed Thermal Desorption Tubes, containing 70/80 mesh glass beads, 20/40 mesh Carbotrap B, and 60/80 mesh Carbosieve S-III, in ¼" o.d. x 7" (18 cm) stainless steel.
- 6.1.4 Varian 3600 gas chromatograph (GC) equipped with a two-stage sorbent trap and flame ionization detector (FID). With the FID, detection limits of ~0.3 ppbv are attainable.
- 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  $\mu\text{L}$ .
- 6.1.11 Low velocity laboratory fume hood.
- 6.1.12 Refrigerator.
- 6.1.13 Gas-phase dilution system.
- 6.1.14 Aadco clean air generator (or equivalent).
- 6.1.15 Nafion PermaPure tube (25 cm x 0.4 cm id).
- 6.1.16 Omega CN9000 Temperature Controller, used to control the temperature of the Dynatherm tube desorber.

6.1.17 15.7-L aluminum high-pressure gas cylinder.

6.1.18 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 Gas cylinders of target gases (Matheson Gas Products) 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 Since all of the target compounds listed in Table 1 are gases, obtain a gas cylinder of each target gas.

7.1.1.4 Connect an injection port to the 15.7 L cylinder and turn on the heater to the injection port.

- 7.1.1.5 Using gloves and working at a fume hood, draw up 1 mL of each of the target gases into a gas-tight syringe and then inject it into the evacuated cylinder via the heated injection port.
- 7.1.1.6 Zero-grade air is directed through the injection port to aid in sweeping each gas into the 15.7 L cylinder.
- 7.1.1.7 After all the gases have been injected, the injection port is removed and the tank is pressurized with zero-grade N<sub>2</sub> from a high-pressure gas cylinder to 1,000 psig. The effective volume of the gas in the cylinder is  $(1014.7 \text{ psia}/14.7 \text{ psia}) \times 15.7 = 1,084 \text{ L}$ .
- 7.1.1.8 The resulting concentrations for the primary 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 mL of Each Pure Gas into Pressurized 15.7-L Cylinder.**

| Compound  | Cylinder Concentration (ppbv) |
|-----------|-------------------------------|
| Acetylene | 920                           |
| Ethylene  | 920                           |
| Propene   | 920                           |
| Propane   | 920                           |
| Isobutane | 920                           |
| 1-Butene  | 920                           |
| n-Butane  | 920                           |

- 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-FID Instrument Set-Up**

- 7.1.2.1 The thermal desorption GC/FID 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 with FID, 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 GC/FID data system is set according to the manufacturer's instructions. Once the entire GC/FID 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 Concentration of Target Compounds in Calibration Cylinder**

- 7.1.3.1 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.
- 7.1.2.2 Measured volumes of the NIST primary standard and the calibration cylinder are injected into the GC/FID system.
- 7.1.3.3 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.

### **7.1.4 Preparation of Calibration Standards and Spiked Laboratory/Field Controls**

- 7.1.4.1 Attach the pressurized standard cylinder and the Aadco air source to the gas phase dilutor.
- 7.1.4.2 Establish a gas flow through the dilutor at the predetermined concentration.
- 7.1.4.3 Attach a T-piece to the exit port of the gas phase dilutor.
- 7.1.4.4 Attach the multisorbent Carbotrap 200 sampler tube to an SKC sample pump that has been adjusted to provide the desired flow rate through the sampler tube.
- 7.1.4.5 Insert the sampler tube into the T-piece in the gas phase dilutor and secure the Swagelok nut and ferrule.
- 7.1.4.6 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 on each end of the tube.
- 7.1.4.7 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.

### 7.1.5 Calibration of the GC/FID System

- 7.1.5.1 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.
- 7.1.5.2 Calibration standards are used at four levels that bracket the concentration range of interest.
- 7.1.5.3 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.
- 7.1.5.4 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.
- 7.1.5.5 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.
- 7.1.5.6 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.
- 7.1.5.7 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 (mL); and  $R_c$  = component response in calibration standard (peak area counts).

- 7.1.5.8 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.

- 7.1.5.9 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 GCFID system.
- 7.1.5.10 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/FID 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 200 Multisorbent Sampler Tubes**

- 7.2.1.1 Arrange the Carbotrap 200 multisorbent sampler tubes in sets of 10 in the order that the samplers are recorded on the VOCs Carbotrap 200 Sampler Analysis Data Sheet (Figure 2).
- 7.2.1.2 Inspect each sampler tube. If any defects, such as cracked caps, etc., are observed, note them in the "Comments" column of the Sampler Analysis Data Sheet.
- 7.2.1.3 If the 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 200 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 Varian 3600 GC with FID. A controller on the Varian GC 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 sorbent material Carbotrap B and Carbosieve S-III (Supelco). Target compounds are chromatographically resolved with a 50 m x 0.32 mm id fused silica PLOT column coated with  $\text{Al}_2\text{O}_3/\text{NaSO}_4$ . Optimum analytical results are achieved with this column by holding the temperature at  $-50^\circ\text{C}$  for two min, then temperature-programming the GC oven from  $-50^\circ\text{C}$  to  $60^\circ\text{C}$  at  $20^\circ/\text{min}$ , holding the temperature at  $60^\circ\text{C}$  for one min, then temperature-programming to  $200^\circ\text{C}$  at  $10^\circ/\text{min}$ . The column exit flow is directed to the FID.
- 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 then is attached to the heated transfer line (165°C) from the automated GC/FID system.
- 7.3.4 Prior to desorbing the sorbent tubes, the cryogenic preconcentrator on the GC/FID system is cooled to -40°C when a sorbent-based preconcentration trap is used. The GC column is cooled to -50°C.
- 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 flow purging 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 then is heated to between 150°C and 250°C while flushing the trap with helium. The trapped compounds then are transferred to the Al<sub>2</sub>O<sub>3</sub>/NaSO<sub>4</sub> PLOT column, and the GC oven temperature program is started along with the FID data acquisition system.
- 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 quantification of each identified component by integrating the peak area of a target compound and comparing the value to that of the calibration standard.
- 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 are 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. FID Peak area. (In general, quantities of a component greater than 1,000 ng should not be injected because of the potential for 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:

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

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

## 7.5 Quality Control

### 7.5.1 Calibration for Quantitative Analysis

7.5.1.1 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 should be cleaned or the first 0.5 m of the column should be removed.

7.5.1.2 Those samples which were analyzed during the period when low level standards were not detected will be reanalyzed.

### 7.5.3 Precision, Bias, and Detection Limit

7.5.3.1 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.

7.5.3.2 Precision also depends greatly on the chemical; for thermal desorption introduction, repeatability is typically  $\pm 20\%$  at a 300 ng level.

7.5.3.3 Method Accuracy: Prior to conducting a study with the Carbotrap 200 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%.



- 7.5.3.4 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  $\sigma$  = 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.

- 7.5.3.5 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/FID in the instrument log book, including the date of data acquisition, project number, instrument conditions, file name, and removable diskette identification.
- 8.3 All analytical results are logged in specific project books and entered on the Carbotrap 200 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  $\mu\text{g}$ ) 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 generated 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.

**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   | <b>ON BACK</b>   |
| Helium Gas Cylinder ID No.        | _____  |
| Date Approved                     | _____  |
| Nitrogen Gas Cylinder ID No.      | _____  |
| Date Approved                     | _____  |
| GC Column ID No.                  | Al <sub>2</sub> O <sub>3</sub> /NaSO <sub>4</sub> , 50 m x 0.32 mm                             |
| Date Installed                    | _____  |
| GC Carrier Gas Flow Rate          | 1.0 - 1.2 cm <sup>3</sup> /min   |
| GC Temperature Program            | -50°C hold for 2 min, -50°C - 60°C at 20°/min, hold at 60°C for 1 min, 60°C - 200°C at 10°/min |
| Thermal Desorber Cycle            | 320°C for 10 min with pre-concentrator at -40°C and 36 mL/min He purge                         |
| Standard Curve Slope Value        | XXX - XXY  |
| Intercept                         | YYY - YYZ  |
| Regression R <sup>2</sup>         | >0.98  |
| No. of Cartridges Analyzed        | _____  |
| No. of Monitors Recorded          | SAME AS ANALYZED   |
| COMMENTS:                         | _____  |

**Figure 1. Example of Sample Laboratory Data Sheet - Multisorbent/VOCs.**

**Sample Laboratory Data Sheet - Multisorbent/VOCs (continued)**

| <b>COMPOUND</b> | <b>LOT NO.</b> | <b>DATE APPROVED</b> | <b>MANUFACTURER</b> |
|-----------------|----------------|----------------------|---------------------|
| Acetylene       |                |                      |                     |
| Ethylene        |                |                      |                     |
| Propene         |                |                      |                     |
| Propane         |                |                      |                     |
| Isobutane       |                |                      |                     |
| 1-Butene        |                |                      |                     |
| n-Butane        |                |                      |                     |

**Carbotrap 200 Sampler Analysis Data Sheet**

**Sample ID:** \_\_\_\_\_

**Date:** \_\_\_\_\_

**Active Sampling Time:** \_\_\_\_\_ min

**Sample Volume, V =** \_\_\_\_\_ L

| <b>Compound</b> | <b>Amount, <math>\mu\text{g}</math></b> | <b>MDL, <math>\mu\text{g}</math></b> |
|-----------------|---|--------------------------------------|
| Acetylene       |   |                                      |
| Ethylene        |   |                                      |
| Propene         |   |                                      |
| Propane         |   |                                      |
| Isobutane       |   |                                      |
| 1-Butene        |   |                                      |
| n-Butane        |   |                                      |

**Figure 2. Example of Carbotrap 200 Sampler Analysis Data Sheet.**

## **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-FID 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 identifying the peak retention times for the target 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.