National Human Exposure Assessment Survey (NHEXAS)

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The University of Arizona
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Standard Operating Procedure **SOP-BCO-L-17.1**

Title: Analysis of Volatile Organic Compounds Collected with a Passive Sampler

Source: The University of Arizona

U.S. Environmental Protection Agency
Office of Research and Development
Human Exposure & Atmospheric Sciences Division
Human Exposure Research Branch

Analysis of Volatile Organic Compounds Collected with a Passive Sampler

1.0 Purpose and Applicability

This standard operating procedure (SOP) describes methodology used for the analysis of the 3M OVM 3500 Organic Vapor Monitors for volatile organic compounds (VOCs), using solvent extraction and standard gas chromatograph/mass spectrometer (GC/MS) analysis procedures.

2.0 Definitions

2.1 Diffusional (passive) sampler: collects contaminant based on the principle of diffusion; no pump is used to collect the sample.

2.2 Sampling (uptake) rate: the mass of a diffusing chemical divided by the product of its concentration and the sampling period (in units of volume per unit time).

3.0 References

3.1 3M Organic Vapor Monitors #3500/3510 Instructions for Use, Occupational Health and Safety Products Division/3M, 1993.

3.2 3M Organic Vapor Monitor Sampling and Analysis Guide for Organic Vapor Monitors 3500/3510 and Organic Vapor Monitors 3520/3530, 1993.

3.3 H.C. Shields and C.J. Weschler, "Analysis of Ambient Concentrations of Organic Vapors with a Passive Sampler," JAPCA, **37**, 1039-1045 (1987).

3.4 R. Otson, P. Fellin, and S.E. Barnett, "Field Testing of a Passive Monitor for Airborne VOCs," paper 92-80.07, 85th A&WMA Annual Meeting, June 1992.

3.5 R. Otson, P. Fellin, and Q. Tran, "VOCs in Representative Canadian Residences," Atmos. Environ. **28**, 3563-3569 (1994).

3.6 P. Fellin and R. Otson, "Assessment of the Influence of Climatic Factors on Concentration Levels of Volatile Organic Compounds (VOCs) in Canadian Homes," Atmos. Environ. **28**, 3581-3586 (1994).

3.7 "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, Annual Book of ASTM Standards, 1989.

3.8 "Sampling Workplace Atmospheres to Collect Organic Gases or Vapors with Activated Charcoal Diffusional Samplers," Standard D 4597, American Society for Testing and Materials, Philadelphia, Annual Book of ASTM Standards, 1992.

3.9 Hewlett-Packard 5890 GC Operator's Manual, June 1993.

3.10 Hewlett-Packard 7673A Automatic Sampler Operating and Service Manual, 1995.

3.11 Finnigan MAT Ion Trap Mass Spectrometer System ITMS™ Operator's Guide, P/N 94099-97002, Rev. A, January 1989.

3.12 Finnigan MAT Ion Trap Detector™ Operation Manual, P/N 94011-98025, Rev. G, January 1989.

4.0 Discussion

4.1 The OVM 3500 Organic Vapor Monitor badges used to sample the target VOCs (according to the procedure described in SOP UA-F-12.1) are extracted with carbon disulfide. Organic compounds present in the extract are separated and identified using standard gas chromatography/mass spectrometry (GC/MS) analysis procedures. Specifically, a small aliquot of the extract (~1 μL) is injected into the hot injector of the GC. Analytes and solvent vapors are swept onto the GC column by the helium carrier gas. The GC column temperature is then increased uniformly (temperature programmed) and the components eluting from the column are identified and quantified by MS in the full scan mode. Component identification is normally accomplished on the basis of the GC retention time and mass spectral fragmentation pattern. The method is not suitable for the VOC 1,3-butadiene. The collection efficiency of the low boiling 1,3-butadiene by the OVM 3500 badge is generally poor, and instead, this compound is sampled and analyzed using actively-pumped carbon-based multisorbent tubes, as described in SOPs UA-F-11.1 and BCO-L-22.1.

4.2 Interferences resulting from the analytes having similar retention times during GC analysis are resolved by MS selection. Both the range and limit of detection depend strongly on the properties of the individual compounds of interest. According to Otson et al. (Refs. 3.5 and 3.6), the OVM 3500 badges provide reliable measurements of selected airborne VOCs at concentrations ranging from about 2 to 6,000 $\mu g/m^3$ for a 24-h to 7 day sampling period. For the compounds of interest, detection limits are in the range 1.6-5.9 $\mu g/m^3$ based upon GC/MS/

SIM analysis and extraction recoveries are: 95.0% for benzene, 97.6% for toluene, and 96.4% for trichloroethene.

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-12.1.

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 will 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 OVM 3500 Organic Vapor Monitors (Occupational Health and Safety Products Division, 3M).

6.1.2 2 mL conical vials (cone begins at 0.5 mL, 48 mm from base of cone to lip of vial, 8 mm ID).

6.1.3 1 µL, 10 µL Hamilton syringes; gas-tight microsyringes (10-2,500 µL)

6.1.4 Class A volumetric flasks, 10 mL.

6.1.5 Capillary pipettes, 50 µL.

6.1.6 Pasteur pipettes.

6.1.7 Combined Hewlett-Packard 5890 gas chromatograph/Finnigan MAT Ion Trap Mass Spectrometer (GC/ITMS or GC/MS). The GC is equipped with a split/splitless injector and a Hewlett-Packard 7673A autosampler. The GC oven contains a 60 m x 0.32 mm id. DB-5 poly(diphenyl/dimethyl siloxane) fused silica capillary column. Optimum analytical results are achieved by temperature programming the GC oven from -50 °C to 200 °C at 8 °/min. The MS is operated in the full-scan mode. In this mode, the ITMS scans all masses repeatedly during the GC run between a lower and an upper mass limit. This mode thus 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. For quantitation purposes, a characteristic ion mass is selected for each target compound and the peak area of the selected ion is used to determine the amount of material present in thje sample extract.

6.1.8 Helium carrier gas (purity ≥99.995%).

6.1.9 Low velocity laboratory fume hood.

6.1.10 Refrigerator.

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

6.1.12 Liquid microliter syringes, 10 µL, Hamilton (or equivalent), for injection of standards and sample extracts into GC/MS system.

6.2 Reagents

6.2.1 Carbon disulfide, 99.9+% ("benzene-free"), HPLC or Gold Label grade (Aldrich Chemical Co.), as specified in Ref. 3.3.

6.2.2 Benzene, A.R.G. (Aldrich Chemical Co.)

6.2.3 Toluene, A.R.G. (Aldrich Chemical Co.)

6.2.4 Trichloroethene, A.R.G. (Aldrich Chemical Co.)

6.2.5 m-Dichlorobenzene, A.R.G. (Aldrich Chemical Co.)

6.2.6 Styrene, A.R.G. (Aldrich Chemical Co.)

6.2.7 Tetrachloroethene, A.R.G. (Aldrich Chemical Co.)

6.2.8 1,1,2-Trichloroethane, A.R.G. (Aldrich Chemical Co.)

6.2.9 p-Xylene, A.R.G. (Aldrich Chemical Co.)

6.2.10 1,1,1-Trichloroethane, A.R.G. (Aldrich Chemical Co.)

6.2.11 Distilled water

6.2.12 Perfluorotributyl amine (FC-43) for MS mass-scale standardization.

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 - Badge/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 Primary Standard Solution

7.1.1.1 Prepare a stock solution at an equivalent air concentration of ~20 ppbv for each of the nine analytes listed below.

7.1.1.2 Using a 10 µL Hamilton syringe, add 2.50 µL of each compound to 50 mL carbon disulfide solvent in a 100 mL volumetric flask. Shake gently to mix and make up to mark with CS_2.

7.1.1.3 Stopper the 100-mL volumetric flask. Label with the laboratory notebook number, analytes and concentrations, solvent used, preparer's initials, and date.

7.1.1.4 Place flask in refrigerator.

7.1.1.5 The primary standard solution remains fresh for up to 6 months.

7.1.1.6 The actual equivalent concentrations of the analytes are summarized in the table:

Compound	µL Added per 100 mL	Density (g/mL)	Amount (mg) in 100 mL	Equivalent Concn (ng/µL)	Assumed Amount (µg) on Badge	Equiv Concn (ppbv)*
Benzene	2.50	0.874	2.185	21.85	32.78	30.2
Toluene	2.50	0.867	2.168	21.68	32.51	27.3
Trichloroethene	2.50	1.464	3.660	36.60	54.90	32.9
m-Dichlorobenzene	2.50	1.288	3.220	32.20	48.30	33.0
Styrene	2.50	.909	2.273	22.73	34.09	36.1
Tetrachloroethene	2.50	1.623	4.058	40.58	60.86	30.1
1,1,2-Trichloro-ethane	2.50	1.435	3.588	35.88	53.81	34.7
p-Xylene	2.50	0.866	2.165	21.65	32.48	28.0
1,1,1-Trichloro-ethane	2.50	1.338	3.345	33.45	50.18	28.7

* Calculated from equation in Section 7.6.4.

7.1.2 Preparation of Calibration Standards

7.1.2.1 Prepare five solutions to be used for the GC calibration curve in five 10-mL volumetric flasks, according to the following matrix.

Compound	Primary Standard (mL)				
	10	5	2.5	1.25	0.5
	Calibration Concentration (ng/µL)				
Benzene	21.9	10.9	5.46	2.73	1.09
Toluene	21.7	10.8	5.42	2.71	1.08
Trichloroethene	36.6	18.3	9.15	4.58	1.83
m-Dichlorobenzene	32.2	16.1	8.05	4.03	1.61
Styrene	22.7	11.4	5.68	2.84	1.14
Tetrachloroethene	40.6	20.3	10.1	5.07	2.03
1,1,2-Trichloroethane	35.9	17.9	8.97	4.48	1.79
p-Xylene	21.7	10.8	5.41	2.71	1.08
1,1,1-Trichloroethane	33.5	16.7	8.36	4.18	1.67

7.1.2.2 Using gloves and a fume hood, add ~1 mL of carbon disulfide to four of the five volumetric flasks. (The fifth flask is not diluted).

7.1.2.3 Transfer aliquots of each of the primary standard volumes into their respective volumetric flasks using volumetric pipettes.

7.1.2.4 Stopper the flasks and invert several times to mix thoroughly. Dilute to volume with carbon disulfide.

7.1.2.5 Label the flasks as Instrument Calibration Standards with the corresponding concentration level. Include the date of preparation, preparer's initials, and the page of the notebook where all the information was recorded.

7.1.2.6 Transfer aliquots from each of the volumetric flasks to individual 2-mL screw-cap vials with silicone septa. Label the vials as per Section 7.1.2.5.

7.1.2.7 Store all standard solutions in a refrigerator at 4 °C.

7.1.2.8 Switch to new vials of the calibration solution every six weeks and discard the previous solutions.

7.1.2.9 Use the concentrated stock solution to prepare fresh solutions or other dilutions for up to six months.

7.1.3 Preparation of Spiked Laboratory and Field Controls

7.1.3.1 Spiked controls are used to verify recoveries of the target compounds, since techniques and the presence of multiple contaminants can affect recovery efficiencies.

7.1.3.2 To prepare a spiked control, remove a monitor from its aluminum container.

7.1.3.3 Remove the white film and plastic ring from the monitor.

7.1.3.4 Place a 2.5 cm diameter filter paper on the spacer plate.

7.1.3.5 Snap the closure cap on the monitor.

7.1.3.6 The spiking standard is prepared as follows:

7.1.3.6.1 Using a volumetric pipette, add 30 µL each of benzene and toluene and 20 µL of trichloroethene to 25 mL carbon disulfide solvent in a 50 mL volumetric flask. Shake gently to mix and make up to mark with CS_2.

7.1.3.6.2 Stopper the 50-mL volumetric flask. Label as "Spiking Standard" and include the laboratory notebook number, analytes and concentrations, solvent used, preparer's initials, and date. The spiking standard solution remains fresh for up to 6 months. Store flask in refrigerator.

7.1.3.6.3 Assuming a 10-µL aliquot of the spiking standard is injected onto the badge, the actual equivalent concentrations of the analytes are:

Compound	m (µg)	K_0 (cm^3/min)	DE	t (min)	C_a^* (µg/m^3)	C_a^* (ppbv)
Benzene	5.24	35.5	0.95	10,080	15.41	4.83
Toluene	5.20	31.4	1.00	10,080	16.44	4.37
Trichloroethene	5.86	31.1	0.99	10,080	18.87	3.55

* Calculated from equation in Section 7.6.4.2: $C_a = m / (K_0.DE.t)$.

7.1.3.7 Using a Hamilton syringe, withdraw a suitable volume of liquid from the volumetric flask (e.g., 5 - 20 µL) and inject the solution onto the filter paper through the center port.

7.1.3.8 Allow the monitor to sit for 16-24 hours to allow total transfer of the compounds from the filter paper to the sorbent.

7.1.3.9 Remove the filter paper from the monitor.

7.2.1 GC/MS Instrument Set-Up

7.2.1.1. The helium sweep flow (across the GC injector septum) and carrier gas flow are set at approximately 3-5 mL/min and 1-2 mL/min, respectively.

7.2.1.2 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.

7.2.1.3 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 7.2.3. (Steps taken to validate the operation of the data system are described in the Appendix).

7.2.1.4 The injector module of the HP 7673A autosampler is positioned onto the injection port of the GC. It houses the syringe holder and a "turret"-type sample tray with space for 5 vials (one to three samples, one wash and one waste bottle), and associated electronics to perform the injection sequence. A tray module, which can position any one of 100 vials (sample extracts) into the injector, is located adjacent to the injector module. The turret tray rotates the 5 vials into position directly below the syringe. Settings for the sample volume (1 - 5 µL), number of injections per sample (1 - 4), number of sample pre-washes (0 - 10), and number of solvent post-washes (0 - 10) are selected through the front panel of the controller unit. Samples are loaded into the tray module in the order in which they are to be analyzed.

7.2.2 Daily GC/MS Tuning and Standardization

7.2.2.1 Once daily, the GC/MS system must be tuned according to manufacturer's instructions, to verify that acceptable performance criteria are achieved.

7.2.2.2 To tune the GC/MS, FC-43 is introduced directly into the ion trap via the molecular leak and the automatic calibration procedure is used to calibrate the ITMS, using seven peaks of the calibration compound: m/z 69, 131, 219, 264, 414, 502, and 614. If any of the calibration peaks are not found, especially at the higher masses, a slope value is calculated between the closest two peaks that are found. If necessary, instrumental parameters are adjusted to give documented, standard relative abundances as well as acceptable resolution and peak shape (see Section 7.7). If the instrument fails to tune under auto-tune conditions, the instrument must be retuned. If the criteria cannot be met, even

after retuning the mass spectrometer, the ion trap may require cleaning as per the manufacturer's instructions. The performance criteria must be achieved before any blanks, standards, or samples are analyzed.

7.2.2.3 After tuning is complete, output one spectrum of FC-43 from the calibration analyses and store this spectrum in the instrument calibration file folder in the MS laboratory.

7.2.3 Initial Calibration of the GC/MS System

7.2.3.1 Before analyzing a sample set on a new column, or after the instrument has been vented for cleaning or maintenance, calibration runs are performed with the Calibration Standards, under the same conditions used to analyze the field samples.

7.2.3.2 Calibration standards encompass four levels, plus a zero level, that bracket the expected concentration range of interest.

7.2.3.3 For the present purposes, a linear response corresponds to a correlation coefficient >0.98 for a linear least squares fit of the concentration versus relative response (peak area of the target ion of the analyte divided by the peak area of the target ion of the IS; A_S/A_{IS}) data.

7.2.3.4 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.

7.2.3.5 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.

7.2.3.6 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.

7.2.3.7 Generate the calibration curve, as described in Section 7.6.1.

7.2.3.8 Once the initial calibration curve has been established, the GC/MS system is checked on a daily basis with a one-point calibration.

7.2.3.9 After the single-point calibration, the analytical system is challenged with neat carbon disulfide to ensure the cleanliness of the system (i.e., levels of target VOCs must be <0.2 ppbv).

7.3 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.

7.3.1 Preparation of OVM 3500 Organic Vapor Monitor Samplers

7.3.1.1 Arrange the OVM 3500 samplers in sets of 5 in the order that the samplers are recorded in the Sample Custodian's sample logbook.

7.3.1.2 Inspect each sampler. Check, especially, that:
(a) The closure cap is firmly snapped to the monitor body
(b) The closure cap plugs are firmly seated in the cap ports.

7.3.1.3 If any defects are observed, note them in the "Comments" column of the Sample Laboratory Data Sheet (Figure 1).

7.3.1.4 If the sampler or seal is broken so that air may have entered the sampler, the sample is voided and marked "NOT ANALYZED" in the Sample Laboratory Data Sheet.

7.3.2 Extraction of OVM 3500 Badges

7.3.2.1 Open the center port of the badge and inject 1.5 mL of carbon disulfide. The rim port can be open to allow venting.

7.3.2.2 Reseal both ports.

7.3.2.3 Let badge stand with the charcoal pad of the badge in contact with the solvent for at least 45 minutes, with occasional mild agitation by hand.

7.3.2.4 Open both ports. Carefully transfer the solvent through the rim port to a 2-mL conical sampler vial.

7.3.2.5 Label, seal, and store the vial in the freezer until ready for GC/MS analysis.

7.4 Preparation of Samples for Analysis

7.4.1 Arrange the sample vials in sets of 20 samples with five standards (one standard vial from each concentration level) in the following order: standard, 8 samples, standard, 8 samples, etc, until all are used.

7.4.2 Inspect each vial. If any defects, such as low volume with respect to the marked volume line are observed, note them in the "Comments" column of the Data Sheet.

7.5 Analysis of OVM 3500 Sampler Extracts

7.5.1 Separate and quantify the target compounds present in the extract using standard GC/MS full-scan mode procedures.

7.5.2 Sample analysis is accomplished using a 60 m x 0.32 mm id DB-5 fused silica capillary 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 injection port is held at 240 °C.

7.5.3 Helium carrier gas flow through the column ranges from 3 to 5 cm^3/min.

7.5.4 Cool the GC oven to its set point.

7.5.5 Using a clean microliter syringe, withdraw a 1 or 2 µL aliquot of the sample extract from the vial and inject it into the GC.

7.5.6 Start the GC oven control program and the ITMS data acquisition ('ACQ') program.

7.5.7 After the final target compound elutes from the column, terminate the acquisition.

7.5.8 Once a stable baseline has been achieved, the system may be readied for the next analysis.

7.5.9 For sample extracts where target compound levels exceed the calibration range of standards, prepare dilutions with CS_2 at 1:10 and 1:100 for reanalysis.

7.5.10 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 selected characteristic ion and comparing the value to that of the calibration standard.

7.5.11. The characteristic ions selected post-acquisition from the full-scan run for each analyte include the "target ion", which is used for quantification, and the "qualifier ion", which is used to verify detection on the basis of correct intensity relative to the target ion intensity. These diagnostic ions are listed below with their respective relative intensities.

Compound	Target Ion	Qualifier Ion
Benzene	78	79
Toluene	91	92
Trichloroethene	130	95
m-Dichlorobenzene	146	148
p-Dichlorobenzene	146	148
o-Dichlorobenzene	146	148
Ethylbenzene	91	106
Styrene	104	103
Tetrachloroethane	166	164
1,1,2-Trichloroethane	97	99
m+p-Xylene	91	106
o-Xylene	91	106
1,1,1-Trichloroethane	97	99

7.5.12 Place all laboratory-related worksheets in the current analysis folder in preparation for report generation.

7.6 Calculations

7.6.1 Calibration Curve

7.6.1.1 Using the calibration standards data (from Section 7.2.3), perform a least-squares linear regression analysis, using a

standard personal computer program and an equation of the form

$A = a + bC$, where

A = MS peak area (in area units, AU)
C = level of the target compound standard (µg)
a = intercept, and
b = slope (AU/µg).

7.6.1.2 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.

7.6.2 Calculation of Target Compound Content of Blank Samplers

7.6.2.1 The target compound content of unexposed (blank) samplers or control samples m_{bl} must be calculated using the calibration coefficients from Section 7.6.1.1 and the measured peak areas of the sample A_{bl} for each compound of interest:

$$m_{bl} = \frac{\left(A_{bl} - a\right)}{b} \ (\mu g)$$

7.6.2.2 Calculate the average amount for the unexposed samplers from the same batch.

7.6.3 Calculation of Target Compound Content of Exposed Samplers

7.6.3.1 Use the calibration coefficients from Section 7.6.1.1 and the measured peak areas of the exposed sampler A_{exp}, for each compound of interest and correct for the content of unexposed samplers:

$$m_{\exp} = \frac{\left(A_{\exp} - a\right)}{b} - m_{bl} \ (\mu g)$$

where m_{exp} is the target compound content of the exposed sampler.

7.6.4 Calculation of Passive Sampler Target Compound Concentration

7.6.4.1 The behavior of the OVM 3500 sampler can be described by Fick's first law of diffusion (see Ref. 3.6), in terms of which the flux is proportional to the concentration gradient, i.e.,

$$\frac{m}{t\left(C_a - C_f\right)} = \frac{m}{t\,C_a} = D\left(\frac{A}{l}\right) \qquad (7\text{-}1)$$

where m = mass of compound adsorbed by the sampler (μg); t = sampling interval (s); A = cross-sectional area through which diffusion occurs (7.07 cm^2 for the OVM 3500 sampler); D = diffusion coefficient (cm^2/s); C_a = gas-phase concentration of compound ($\mu g/cm^3$); C_f = concentration of compound just above sorbent pad (=0); and l = path over which diffusion occurs (1.0 cm for the OVM 3500 sampler).

7.6.4.2 The quantity m/tC_a in Equation (7-1) defines the sampling (uptake) rate for diffusive samplers, which is a constant provided the amount of material collected is much less than the capacity of the sorbent material used in the device. If the sampling rate for a compound is known, it can be used to calculate the concentration C_a of that compound from the equation:

$$C_a = \frac{m}{K_0\,(DE)\,t} \qquad (7\text{-}2)$$

where K_0 = uptake rate, as defined in Equation (7-1); and DE = recovery (desorption) coefficient, a factor used to adjust for incomplete extraction of a substance from the OVM 3500 sorbent pad.

7.6.4.3 The sampling rates, recovery efficiencies, and capacity limits for the target compounds are as follows(see Ref. 3.2):

Compound	Sampling Rate (cm^3/min)	Recovery Coefficient	Capacity (mg)
Benzene	35.5±0.6	0.95	22
Toluene	31.4±0.6	1.00	>25
Trichloroethylene	31.1±0.2	0.99	>25
m-Dichlorobenzene	27.8±0.6	0.87	>25
p-Dichlorobenzene	27.8±0.6	0.87	>25
o-Dichlorobenzene	27.8±0.6	0.87	>25
Ethylbenzene	27.3	0.96	24
Styrene	26.8±0.8	0.82	>25
Tetrachloroethylene	31.1±0.2	0.95	>25
1,1,2-Trichloroethane	29.7±0.6	0.95	>25
m+p-Xylene	27.3±0.5	0.97	>25
o-Xylene	27.3±0.5	0.97	>25
1,1,1-Trichloroethane	30.9±0.3	1.03	22

7.6.4.4 To calculate the concentration in parts per million (ppm) at 25 °C and 760 mm Hg, use the value in mg/m^3 determined in Step 7.6.4.2 in the following equation:

$$C\,(\text{ppmv}) = C(\text{mg}/\text{m}^3)\ \text{x}\ \frac{24.45}{MW}$$

where MW = molecular weight of target compound (in g/mole).

7.6.4.5 If the sampling temperature is significantly different from 25 °C, then the temperature-corrected concentration C_0 is obtained from:

$$C_0 = C(\text{mg}/\text{m}^3)\ \text{x}\ \sqrt{\frac{298^0 K}{T_s}}$$

or

$$C_0 = C(\text{ppmv})\ \text{x}\ \sqrt{\frac{298^0 K}{T_s}}$$

where T_s = temperature recorded at the sample site (in °K). This correction eliminates an error of about 1% for every 10°F (5.6 °C) increment above or below 77°F (25°C) (see Ref. 3.2).

7.7 Quality Control

7.7.1 Solvent Purity, Spiked Controls, Blanks, and Duplicates

7.7.1.1 Each lot of HPLC or Gold Label Grade carbon disulfide must be analyzed before use to ensure that it contains no more than trace levels of benzene (see Ref. 3.3).

7.7.1.2 The overall performance of the monitoring method is evaluated using spiked controls, blanks, and duplicates.

7.7.1.3 Given the small amounts of material that are collected with the OVM 3500 badges, it is important that samplers used as spikes, blanks, duplicates, and field samplers come from the same lot number, since the background compounds present on unexposed samplers may vary significantly from lot to lot

7.7.1.4 At least one sampler should be prepared for analysis as a field spike, one sampler each presented for analysis as a field blank and an unexposed blank, and one field duplicate sampler taken with every 20 field samples.

7.7.1.5 Method Accuracy: Prior to conducting a study with OVM 3500 badges, blank badges are spiked with the compounds of interest and analyzed to determine the level of recovery of each compound. Percent relative accuracy is given by:

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

where X = expected level of target compound; and Y = measured level of target compound recovered in analysis.

7.7.1.6 Blank Badges: Blank badges are analyzed to determine inadvertent contamination. Of the analytes of interest in this SOP, benzene is one of the principal compounds detected in OVM 3500 blanks, and occurs typically at ~0.3 µg/badge. Most other VOCs should be present at ≤0.02 µg/badge.

7.7.2 Precision, Bias, and Detection Limit

7.7.2.1 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.

7.7.2.2 When the errors involving determination of desorption efficiency, sampling, and analysis are combined, a relative precision of ±15% is indicated.

7.7.2.3 Recovery efficiencies for the target compounds are between 95 and 100%.

7.7.2.4 The method detection limit MDL for a target compound is obtained from the above data. It is defined as:

$$MDL = A + 3.3\sigma$$

where A = intercept (coefficient) from the least squares fit to the calibration curve; and s = standard deviation of the lowest concentration measurements. The method detection limit for the 3M OVM 3500 passive monitor is about 2 $\mu g/m^3$, with a practical quantitation limit of about 8 $\mu g/m^3$. Field tests have also shown that these monitors provide reliable measurements of selected airborne VOCs at concentrations ranging from about 2 to 6,000 $\mu g/m^3$.

7.7.3 Instrument Tuning and Standardization

7.7.3.1 Refer to Section 7.2.2. These procedures provide a means of monitoring MS performance characteristics over time, and permanent records of the information are kept in the laboratory.

7.7.4 Calibration for Quantitative Analysis

7.7.4.1 Refer to the quantitative analysis calibration procedures. 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 trap should be cleaned or the first 0.5 m of the column should be removed.

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

7.7.5 Storage Stability

7.7.5.1 The shelf life of the OVM 3500 monitor prior to exposure is 18 months when stored in cool, dry conditions which do not exceed 90 °F for extended periods of time.

7.7.5.2 The shelf life of the OVM 3500 monitor after exposure is 1 month when stored in a refrigerator at 4 °C.

7.7.6 **Corrective Actions**

7.7.6.1 Before beginning any analytical sequence, insert a fresh septum into the injection port of the GC. Replace the septum daily or when necessary. Septum failure is probably the most frequent cause of inconsistent detector response for a given standard or sample.

7.7.6.2 Changes in the retention times of the target compounds may indicate a leak in the GC system or deterioration of the GC column. If this is accompanied by loss of column resolution, the column should be replaced.

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 OVM 3500 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, the exposure time (in minutes), and the dilution factor (default is 1).

8.3.3 Enter the amounts obtained (in μg) for the field sample and the blank.

8.4 All data files are stored on floppy 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 - Badge/VOCs"

ITEM:	PARAMETER:
Date	
Analyst	
Standard Curve Number	
Primary Std.: Benzene Lot No.	
Date Approved	
Primary Std.: Toluene Lot No.	
Date Approved	
Primary Std.: Trichloroethene Lot No.	
Date Approved	
Primary Std.: m-Dichlorobenzene Lot No.	
Date Approved	
Primary Std.: Styrene Lot No.	
Date Approved	
Primary Std.: Tetrachloroethene Lot No.	
Date Approved	
Primary Std.: 1,1,2-Trichloroethane Lot No	
Date Approved	
Primary Std.: p-Xylene Lot No	
Date Approved	
Primary Std.: 1,1,1-Trichloroethane Lot No	
Date Approved	
Solvent: Carbon Disulfide Lot No.	
Date Approved	
Carbon Disulfide Blank Check	Benzene at trace level
Helium Gas Cylinder ID No.	
Date Approved	

Figure 1: Continued

ITEM		PARAMETER
GC Column ID No.	_____	DB-5, 60 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
Autosampler Settings	_____	# of injections/sample; injection volume (µL); # of syringe pre-rinses; # of syringe post-rinses
MS (SIM): Filament Currrent	_____	80 µA
EM Voltage	_____	1.8 - 2.0 kV
Standard Curve	Data attached	
No. of Badges Analyzed	_____	
No. of Badges Recorded	_____	SAME AS ANALYZED

COMMENTS: _____

Figure 2: OVM 3500 Sampler Analysis Data Sheet
VOCs in Air

Sample ID: _____ **Analysis Date:** _____

HHID: _____ **Analyst:** _____

Exposure Time, t = _____ **min** **Dilution Factor:** _____

Compound	K_0 (cm^3/min)	DE	m_{bl}* (µg)	m_{exp}** (µg)
Benzene	35.5	0.95		
Toluene	31.4	1.00		
Trichloroethene	31.1	0.99		
m-Dichlorobenzene	27.8	0.87		
p-Dichlorobenzene	27.8	0.87		
o-Dichlorobenzene	27.8	0.87		
Ethylbenzene	27.3	0.96		
Styrene	26.8	0.82		
Tetrachloroethene	31.1	0.95		
1,1,2-Trichloroethane	29.7	0.95		
m+p-Xylene	27.3	0.97		
o-Xylene	27.3	0.97		
1,1,1-Trichloroethane	30.9	1.03		

* Calculated from equation in Sections 7.6.2.

** Calculated from equation in Sections 7.6.3.

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 extracts of 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 solutions 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 solution and calculating the standard deviation of the area responses.

After satisfactory linearity and precision data are obtained, a standard solution 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.