Section H

AIR and VAPOUR CONSTITUENTS — ORGANIC

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PAH - Polycyclic Aromatic Hydrocarbons

Parameter Polycyclic Aromatic Hydrocarbons (see list below).

Analytical Method
a) Puff GC/MS
b) XAD2: GC/MS

EMS Codes:

Parameter Name	Puff GC/MS	XAD2 GC/MS
Acenaphthene	PA01 PAH1	PA01 PAH2
Acenaphthylene	PA02 PAH1	PA02 PAH2
Anthracene	PA03 PAH1	PA03 PAH2
Benzo(a)anthracene*	PA04 PAH1	PA04 PAH2
Benzo(a)pyrene	PA05 PAH1	PA05 PAH2
Benzo(b)fluoranthene	PA06 PAH1	—
Benzo(g,h,i)perylene	PA07 PAH1	PA07 PAH2
Benzo(k)fluoranthene	PA08 PAH1	—
Benzo(b+j)fluoranthene	PA17 PAH1	PA17 PAH2
Chrysene	PA09 PAH1	PA09 PAH2
Dibenz(a,h)anthracene	PA10 PAH1	PA10 PAH2
Fluoranthene	PA11 PAH1	PA11 PAH2
Fluorene	PA12 PAH1	PA12 PAH2
Indeno(1,2,3-cd)pyrene	PA13 PAH1	PA13 PAH2
Naphthalene	PA14 PAH1	—
Phenanthrene	PA15 PAH1	PA15 PAH2
Pyrene	PA16 PAH1	PA16 PAH2

* synonymous to Benz(a)anthracene

EMS Codes for Surrogates

(Surrogates are reported as Percent Recovery with units of "%".)

Surrogate	Puff GC/MS	XAD2 GC/MS
Acenaphthalene-d_{10}	ACEN PAH1	ACEN PAH2
Chrysene-d_{12}	CHRY PAH1	CHRY PAH2
Fluorene-d_{10}	FLUO PAH1	FLUO PAH2
Naphthalene-d_8	NAPH PAH1	NAPH PAH2
Perylene-d_{12}	PERY PAH1	PERY PAH2
Phenanthrene-d_{10}	PHEN PAH1	PHEN PAH2

Introduction

Polycyclic aromatic hydrocarbons (PAHs) have received increased attention in recent years in air pollution studies because some of these compounds are highly carcinogenic or mutagenic. In particular, benzo[a]pyrene (B[a]P) has been identified as being highly carcinogenic. To understand the extent of human exposure to B[a]P, and other PAHs, a reliable sampling and analytical method has been established. This document describes a sampling and analysis procedure for B[a]P and other PAHs involving a combination quartz fibre filter/adsorbent cartridge with subsequent extraction and analysis by gas chromatography (GC) with mass spectrometry (MS) detection (GC/MS). The analytical methods are a modification of EPA Test

Method 625, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, and Methods 8270, Test Methods for Evaluation of Solid Waste.

The analytical methodology is well defined, but the sampling procedures can reduce the validity of the analytical results. Recent studies have indicated that non-volatile PAHs (vapour pressure $<10^{-8}$ mm Hg) may be trapped on the filter, but post-collection volatilization problems may distribute the PAHs downstream of the filter to the back-up adsorbent. A wide variety of adsorbents such as Tenax GC, XAD-2 resin and polyurethane foam (PUF) have been used to sample B[a]P and other PAH vapours. All adsorbents have demonstrated high collection efficiency for B[a]P in particular. In general, XAD-2 resin has a higher collection efficiency for volatile PAHs than PUF, as well as a higher retention efficiency. However, PUF cartridges are easier to handle in the field and maintain better flow characteristics during sampling. Likewise, PUF has demonstrated its capability in sampling organochlorine pesticides and polychlorinated biphenyls. PUF has demonstrated a lower recovery efficiency and storage capability for naphthalene and B[a]P, respectively, than XAD-2. In addition, XAD2 has a higher naphthalene blank than PUF; therefore, PUF is better when naphthalene is to be determined.

There have been no significant losses of PAHs, up to 30 days of storage at 0°C, using XAD-2. It also appears that XAD-2 resin has a higher collection efficiency for volatile PAHs than PUF, as well as a higher retention efficiency for both volatile and reactive PAHs. Consequently, while the literature cites weaknesses and strengths of using either XAD-2 or PUF, this method covers the utilization of both XAD-2 and PUF as the adsorbent to address post-collection volatilization problems associated with B[a]P and other reactive PAHs.

Method Summary

a) Filters and adsorbent cartridges (containing XAD-2 and/or PUF) are cleaned in solvents and dried. The filters and adsorbent cartridges are wrapped in clean aluminum foil and stored in two separate sealed heavy plastic bags. The cartridge and bags are then inserted into a cardboard mailer tube with fitted end caps. The end tubes are taped to exclude all light.
Note: Ensure that the cleaned filters and the adsorbent cartridges have all traces of solvent removed.
PUF by itself is used for PAHs. PUF plus XAD-2 is used for the broader range semi-volatiles.

b) Approximately 325 m^3 of ambient air is drawn through the filter and adsorbent cartridge using a calibrated General Metal Works Model PS-1 Sampler, or equivalent (breakthrough has not shown to be a problem with sampling volumes of 325 m^3).

c) The amount of air sampled through the sampling head is recorded against the label on the sampling head. The sampling head is resealed with the aluminum plate cover, hexane rinsed aluminum foil and plastic bag, then returned to the field laboratory for removal of the filter paper, adsorbent cartridge and placement into the shipping container (double wrapped plastic bag and cardboard mailer tube). The sample must be stored in a deep freeze while awaiting shipping. The cardboard mailer, containing the sample head and filter paper, along with

any blank filter and adsorbent cartridge is shipped in a cooler containing dry ice to the analytical laboratory for analysis.

d) The filters and adsorbent cartridge are extracted by Soxhlet extraction with dichloromethane. The extract is concentrated by rotary evaporator, followed by silica gel clean-up using column chromatography to remove potential interferences prior to analysis by GC/MS.
Note: cleanup may not be necessary for most indoor air samples by GC-MS.

e) The eluent is further concentrated by evaporation, then analyzed by gas chromatography with MS detection. The analytical system is verified to be operating properly and calibrated with three to five concentrations of calibration solutions. On-going calibration checks a mid-point standard. This response must be within 20% of the original response line, otherwise a five-point calibration must be repeated.

f) The sample is injected into the GC-MS system. If all the components are within the linear range, the data is accepted and reported. If the sample is above the linear range, an appropriate dilution is made, and the sample is re-run.

g) The samples and the blanks are analyzed and used (along with the amount of air sampled) to calculate the concentration of PAH in ambient air.

MDL

This method covers the determination of PAHs specifically by GC/MS and enables qualitative and quantitative analysis. The PAHs are:

Parameter Name	**MDL**	**Units**
Acenaphthene	50	pg/m³
Acenaphthylene	50	pg/m³
Anthracene	50	pg/m³
Benzo(a)anthracene*	50	pg/m³
Benzo(a)pyrene	50	pg/m³
Benzo(b)fluoranthene	50	pg/m³
Benzo(g,h,i)perylene	100	pg/m³
Benzo(k)fluoranthene	50	pg/m³
Benzo(b+j)fluoranthene	50	pg/m³
Chrysene	50	pg/m³
Dibenz(a,h)anthracene	100	pg/m³
Fluoranthene	50	pg/m³
Fluorene	50	pg/m³
Indeno(1,2,3-cd)pyrene	100	pg/m³
Naphthalene	50	pg/m³
Phenanthrene	50	pg/m³
Pyrene	50	pg/m³

*synonymous to Benz(a)anthracene

To obtain these detection limits at least 100 m³ of air must be sampled.

Matrix Interferences and Precautions

Ambient Air

a) Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that result in discrete artifacts and/or elevated baselines in the detector profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.
b) Glassware must be scrupulously cleaned.
c) The use of high purity water, reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.
d) Matrix interferences may be caused by contaminants that are coextracted from the sample. Additional clean-up by column chromatography may be required.

Sample Handling and Preservation

Conditions during sample transport and analysis should be considered. Heat, ozone, NO_2 and ultraviolet (UV) light may cause sample degradation. Where possible, incandescent or UV-shielded fluorescent lighting should be used during analysis.

Stability

Samples should be extracted within 2 weeks of receipt in laboratory. XAD2 exposed cartridges have been shown to be stable for 30 days at 0°C. PUF samples have a hold time of 20 days.

Safety

a) The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of MSDS information.
b) Benzo[a]pyrene has been tentatively classified as a known or suspected, human or mammalian carcinogen. Many of the other PAHs have been classified as carcinogens. Care must be exercised when working with these substances. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. The user should be thoroughly familiar with the chemical and physical properties of targeted substances (EPA TO-13 Table 1.0 and Figure 1.0).
c) Treat all polycyclic aromatic hydrocarbons as carcinogens. Neat compounds should be weighed in a glove box. Spent samples and unused standards are toxic waste and should be disposed of according to regulations. Regularly check counter tops and equipment with "black light" for fluorescence as an indicator of contamination.
d) Because the sampling configuration (filter and backup adsorbent) has demonstrated greater than 95% collection efficiency for target PAHs, no field recovery evaluation will occur as part of this procedure.

Note: Naphthalene, an exception, has demonstrated significant breakthrough using PUF cartridges, especially at summer ambient temperatures.

Principle or Procedure

Apparatus

Sample Collection:

a) General Metal Works (GMW) Model PS-1 Sampler, or equivalent [General Metal Works, Inc., 145 South Miami Ave., Village of Cleves, Ohio, 45002, (800-543-7412)].
b) At least two Model PS-1 sample cartridges with a filter, PUF and XAD-2 adsorbent material.
c) GMW Model PS-1 calibrator and associated equipment - General Metal Works, Inc, Model GMW-40, 145 South Miami Ave., Village of Cleves, Ohio, 45002, (800-542-7412).
d) Data sheets for each sample for recording the location and sampling time, duration of sample, starting time, and volume of air sampled.
e) Clean white cotton (freshly laundered) gloves, tweezers, heavy plastic zip-lock plastic bags, cardboard mailer tube with end covers (sized for a snug fit), aluminum foil and hexane for rinsing the foil and tweezers.
f) Disposable polyethylene [powder free] gloves for handling the sampling heads in the field, aluminum foil and plastic bags. To be used when installing/ removing the sampling head in the Model PS-1 sampler.
g) Dry-ice maker requiring a liquid CO_2 cylinder equipped with a siphon, kryo-gloves for handling the ice blocks and specially designed transportation cooler for handling dry-ice and samples.

Sample Clean-up and Concentration:

a) Soxhlet extractors capable of containing the GMW Model PS-1 filter and adsorbent cartridges (2.3" x 5" length), fitted with a 500 mL reservoir.
b) Oven for heating silica gel.
c) Glass vial lined with Teflon-faced silicone disk seal, 40 mL.
d) Erlenmeyer flask, 50 mL. [Glassware cleaning: Rinse glassware with the last solvent used in it and then with high-purity acetone and hexane. Wash with hot water containing detergent. Rinse with copious amount of tap water and several portions of de-ionized water. Drain, dry, and heat in an oven at 325°C for 8 hours. After the glassware is dry and cool, store it inverted or capped with solvent-rinsed aluminum foil in a clean environment.]
e) Clean white cotton gloves for handling (loading) cartridges and filters.
f) Minivials — 2 mL, borosilicate glass, with caps lined with Teflon-faced silicone disks, and a vial holder.
g) Stainless-steel spatulas and spoons.
h) Rotary evaporator.
i) Adsorption columns for column chromatography - 1 cm x 10 cm with stands.
j) Glove box for working with extremely toxic standards and reagents with explosion-proof hood for venting fumes from solvents, reagents, etc.
k) Concentrator tubes and a nitrogen evaporation apparatus with variable flow rate.

l) Laboratory refrigerator with chambers operating at 0°C and 4°C.
m) Boiling chips - solvent extracted, 10/40 mesh silicon carbide or equivalent.

Reagents

Sample Collection:

a) Acid-washed quartz glass fibre filter, 105 mm, micro quartz fibre binderless filter, General Metal Works, Inc., Cat. No. GMW QMA-4, 145 South Miami Ave., Village of Cleves, OH, 45002, 800-543-7412, or Supelco Park, Bellefonte, PA, 16823-0048.
b) Polyurethane foam (PUF) — 3-inch thick sheet stock, polyether type (density 0.022 g/cm³) used in furniture upholstering (General Metal Works, Inc., Cat. No PS-1-16, 145 South Miami Ave., Village of Cleves, Ohio, 45002 [800-543-7412] or Supelco Inc., Cat. No. 1-63, Supelco Park, Bellefonte, PA, 16823-0048).
c) XAD-2 resin - Supelco Inc., Cat. No. 2-02-79, Supelco Park, Bellefonte, PA, 16823-0048.
d) Hexane-rinsed aluminum foil - best source.
e) Hexane-reagent grade, best source.

Sample Clean-up and Concentration:

a) Dichloromethane - chromatographic grade, glass-distilled, best source.
b) Sodium sulfate, anhydrous - (ACS) granular anhydrous (purified by heating at 350°C for 8 hrs in a shallow tray).
c) Boiling chips - solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).
d) Nitrogen - high purity grade, best source.
e) Hexane - chromatographic grade, glass-distilled, best source.

Column Clean-up:

a) Silica gel - high purity grade, type 60, 70-230 mesh; cleaned and activated by heating in a foil-covered glass container for 12 hours at 325°C.
b) Sodium sulfate, anhydrous - (ACS) granular anhydrous (See #7).
c) Pentane - chromatographic grade, glass-distilled, best source.

Sample Analysis - Gas Chromatography Detection:

a) Gas cylinders of helium - ultra high purity, best source.
b) Combustion air - ultra high purity, best source.
c) Native and isotopically labelled PAHs isomers for calibration and spiking standards - [Cambridge Isotopes, 20 Commerce Way, Woburn, MA, 01801 (617-547-1818)].
Suggested isotopically labelled PAH isomers are:
- perylene-d_{12}
- chrysene-d_{12}
- acenaphthene-d_{10}
- naphthalene-d_8
- phenanthrene-d_{10}

d) Decafluorotriphenylphosphine (DFTPP) - best source, used for tuning GC/MS.
e) Gas Chromatograph with Mass Spectroscopy Detection (EPA TO-13 Figure 7) Coupled with Data Processing System (GC/MS/DS).
f) The GC must be equipped for temperature programming, and all required accessories must be available, including syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On-column injection techniques can be used but they may severely reduce column lifetime for nonchemically

bonded columns. In this protocol, a 1-3 µL injection volume is used consistently. With some GC injection ports, however, 1µL injections may produce some improvement in precision and chromatographic separation. A 1 µL injection volume may be used if adequate sensitivity and precision can be achieved. [Note: If 1 µL is used as the injection volume, the injection volumes for all extracts, blanks, calibration solutions and performance check samples must be 1µL.]

g) Gas Chromatograph-Mass Spectrometer Interface. The gas chromatograph is usually coupled directly to the mass spectrometer source. The interface may include a diverter valve for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass or glass-lined stainless-steel. The interface components should be compatible with 320°C temperatures. Cold spots and/or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the MS source. Graphite ferrules should be avoided in the GC injection area since they may adsorb PAHs. Vespel® or equivalent ferrules are recommended.

h) Mass Spectrometer. The mass spectrometer should be operated in the selected ion mode (SIM) with a total cycle time (including voltage reset time) of one second or less (EPA TO-13 Section 14.2).

i) Mass Spectrometer. Capable of scanning from 35 to 500 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria (EPA TO-13 Section 14.5.1).

j) Data System. A dedicated computer data system is employed to control the rapid multiple ion monitoring process and to acquire the data. Quantification data (peak areas or peak heights) and multi-ion detector (MID) traces (displays of intensities of each m/z being monitored as a function of time) must be acquired during the analyses. Quantifications may be reported based upon computer-generated peak areas or upon measured peak heights (chart recording). The detector zero setting must allow peak-to-peak measurement of the noise on the baseline.

k) GC Column. A fused silica column (30 m x 0.25 mm I.D.) DB-5 crosslinked 5% phenyl methylsilicone, 0.25 µm film thickness (Alltech Associates, 2051 Waukegan Rd, Deerfield, IL, 60015, 312-948-9600) is utilized to separate individual PAHs. Other columns may be used for determination of PAHs. For separation of (b+k) fluroanthene a DB5- EPA625 column is used. Minimum acceptance criteria must be determined as per EPA TO-13 Section 14.2. At the beginning of each 12-hour period (after mass resolution has been demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples.

l) Analytical Balance.

m) Pipettes, micropipettes, syringes, burets, etc. to make calibration and spiking solutions, dilute samples if necessary, etc., including

syringes for accurately measuring volumes such as 25 µL and 100 µL.

Sampling Preparation

Sampling Head Configuration:

a) The sampling head consist of a filter holder compartment followed by a glass cartridge for retaining the adsorbent. The present method is written to facilitate using the standard GMW PS-1 sampling head. However, Battelle-Columbus Laboratory has investigated the use of a smaller sampling head. The basic difference is that the Batelle head uses a 47 mm filter followed by the adsorbent. Approximately the same amount of XAD-2 (50 - 60 grams) is used in both sampling heads. The reason for going to a smaller head was to reduce the size of the Soxhlet extraction apparatus, consequently the volume of solvent used from 500mL to 200mL during the extraction procedure. All preparation steps for cleaning the filters and adsorbents are the same, regardless of size filter used.

b) Before field use, both the filter and adsorbent must be cleaned to <10 ng/apparatus of PAHs.
Note: recent studies have determined that naphthalene levels may be greater than 10 ng per apparatus even after successive cleaning procedures.

Glass Fiber Filter Preparation:

a) The glass fiber filters are baked at 600°C for five hours before use. To verify acceptable blanks, they are extracted with dichloromethane in a Soxhlet apparatus, similar to the cleaning of the XAD-2 resin.

b) The extract is concentrated and analyzed by GC. A filter blank of <10 ng/filter of PAHs is considered acceptable for field use.

c) The filter is placed in a transportation dish with an identification number marked on the outside.

XAD-2/PUF Adsorbent Preparation:

a) For initial cleanup of the XAD-2, a batch of XAD-2 (approximately 60 grams) is placed in a Soxhlet apparatus and extracted with dichloromethane for 16 hours at approximately 4 cycles per hour. For preparation of the PUF sandwich in this section refer to PUF Cartridge Preparation.

b) At the end of the initial Soxhlet extraction, the spent dichloromethane is discarded and replaced with fresh reagent. The XAD-2 resin is once again extracted for 16 hours at approximately 4 cycles per hour.

c) A nickel or stainless-steel screen (mesh size 200/200) is fitted to the bottom of a hexane-rinsed glass cartridge to retain a 2.54 mm PUF plug prior to adding the XAD-2 resin.

d) The Soxhlet extracted dried XAD-2 resin is placed (using clean white cotton gloves) into the sampling cartridge sandwiched between two 2.54 mm PUF plugs to a depth of approximately 2 inches. This should require between 50 and 60 grams of adsorbent. An alternate method for cleaning XAD-2 resin is summarized as follows: in a 600 g batch, XAD-2 resin is Soxhlet-extracted with dichloromethane for 16 hours. After extracting, the resin is transferred to a clean drying column. Then the resin is dried with high-purity nitrogen using Teflon® tubing from the nitrogen

cylinder with a charcoal tube in line. As a test for total system breakthrough of sampled compound a surrogate compound is injected at this time midway into the centre of the upper PUF plug. Select one or more surrogate to use at this point in the procedure. The following surrogate standards are suggested for use at the 100 µg level:

- Naphthalene-d_8
- Acenaphthene-d_{10}
- Phenanthrene-d_{10}
- Chrysene-d_{12}
- Perylene-d_{12}

(Recovery level 40 - 130%).

e) The glass module containing the PUF/XAD-2 adsorbent is wrapped with hexane-rinsed aluminum foil, placed in a labeled plastic bag (zip-lock) and tightly sealed with Teflon® tape. This is repeated with a second plastic bag. Be sure to extract all excess air remaining in the bag before they are sealed. Load the glass module, in plastic bags, into a cardboard shipping container fitted with end caps. Note: The aluminum foil must be baked in an oven overnight at 325°C, after rinsing with hexane to ensure no residuals remain.

f) At least one assembled cartridge from each batch must be analyzed, as a laboratory blank, using the procedure for samples described below, before the batch is considered acceptable for field use. A blank of <10 ng/cartridge of PAHs is considered acceptable.

PUF Sampling Cartridge Preparation:

a) The PUF adsorbent is a polyether-type polyurethane foam (density No. 3014 or 0.0225 g/cm³) used for furniture upholstery.

b) The PUF inserts are 6.0-cm diameter cylindrical plugs cut from 5 cm (3 inch) sheet stock and should fit, with slight compression, in the glass cartridge, supported by the wire screen. During cutting, the die is rotated at high speed (e.g., in a drill press) and continuously lubricated with water.

c) For initial cleanup, the PUF plug is placed in a Soxhlet apparatus and extracted with dichloromethane for 14-24 hours at approximately 4 cycles per hour. When cartridges are reused, DCM is used as the cleanup solvent.

d) The extracted PUF is dried at room temperature until no solvent odour is detected.

e) The PUF is placed into the glass sampling cartridge using clean white cotton gloves. The cartridge is wrapped with hexane-rinsed aluminum foil, placed in a labeled zip-lock plastic bag and tightly sealed with Teflon® tape. A second bag is used to protect the first making sure any excess air is removed from the bags before they are sealed. The PUF sampling cartridge and wrappings are loaded into a cardboard mailing tube with end caps while awaiting shipment into the field.

f) At least one assembled cartridge from each batch must be analyzed, as a laboratory blank, before the batch is considered acceptable for field use. A blank level of <10 ng/plug for single compounds is acceptable.

Sample Clean-up and Concentration

a) Samples are stored at 0°C in an ice chest until receipt at the analytical laboratory.

b) When the sample(s) arrive at the analytical laboratory the inside temperature of the cooler is immediately recorded and noted on the FIELD TEST DATA SHEET. The samples are then stored at 0°C if analysis is not scheduled to occur within two hours. If the analysis is scheduled to occur within two hours the samples are stored at 4°C.

Sample Identification:

a) The samples in the glass sample containers containing the filter and adsorbent are returned to the analyzing laboratory in the special transportation coolers containing dry ice.

b) The samples are logged in the laboratory logbook according to sample location, filter and adsorbent cartridge number identification and total air volume sampled (uncorrected).

c) If the time span between sample registration and analysis is greater than 24 hrs., then the samples must be kept below 0°C. Minimize exposure of samples to fluorescent light. All samples must be extracted within one week, after receiving the sample at the analytical laboratory.

Soxhlet Extraction and Concentration:

a) Place the adsorbent and filter together in the Soxhlet apparatus (use of an extraction thimble is optional) if using XAD-2 adsorbent in the sampling module. [Note: The filter and adsorbent are analyzed together to reach detection limits, avoid questionable interpretation of the data, and minimize cost.] The adsorbent is Soxhlet extracted overnight with dichloromethane.

b) A surrogate standard (i.e., a chemically inert compound not expected to occur in an environment sample) should be added to each sample, blank, and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits. The following surrogate standards have been successfully utilized in GC/MS analysis:

<u>Surrogate Standard</u>

- Naphthalene-d_8
- Acenaphthene-d_{10}
- Phenanthrene-d_{10}
- Chrysene-d_{12}
- Perylene-d_{12}

Note: The deuterated standards will be added (see Calibration Techniques, Internal Standard Calibration Procedure a). Add the surrogate standard to the Soxhlet solvent at the current step.

c) For the XAD-2 and filter extracted together, add 300 mL of dichloromethane to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.

d) For the PUF extraction the same procedure is used as for XAD-2.

e) For the filter extraction, add 300 mL of dichloromethane to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.

f) Concentrate the extract to a volume of about 2 mL in rotary evaporator.

Sample Cleanup:

Cleanup procedures may not be needed for relatively clean matrix samples.

Instrumental Analysis

a) The analysis of the extracted sample for PAHs is accomplished by an electron impact gas chromatography/mass spectrometry (EI GC/MS) in the selected ion monitoring (SIM) mode with a total cycle time (including voltage reset time) of one second or less. The gas chromatograph is equipped with a DB-5 fused silica capillary column (30m x 0.25 mm ID) with helium carrier gas for analyte separation. The gas chromatograph column is temperature controlled and interfaced directly to the MS ion source.

b) Ion Used for Mass spectrometry:

Parameter Name	Quantitation Ion	Confirming Ion
Acenaphthylene	152	153
Acenaphthene	154	152
Fluorene	166	167
Phenanthrene	178	179
Anthracene	178	179
Fluoranthene	202	203
Pyrene	202	203
Benzo(a)anthracene	228	229
Chrysene	228	229
Benzo(b+j)fluoranthene	252	253
Benzo(k)fluoranthene	252	250
Benzo(a)pyrene	252	250
Indeno(1,2,3-c,d)pyrene	276	277
Dibenz(a,h)anthracene	278	279
Benzo(g,h,i)perylene	276	277
Acenaphthene-d_{10}	164	160
Phenanthrene-d_{10}	188	189
Anthracene-d_{10}	188	189
Chrysene-d_{12}	240	241
Perylene-d_{12}	264	265.

c) The laboratory must document that the EI GC/MS system is properly maintained through periodic calibration checks.

d) The GC/MS system should have the following specifications:

Mass range:	35-500 amu.
Scan time:	1 sec/scan.
Column:	30 m x 0.25 mm ID, DB-5 crosslinked 5% phenyl methyl silicone, 0.25 µm film thickness capillary or equivalent.
Initial column temp. and hold time:	50°C for 1 min.
Column temperature program:	50-300°C at 10°C/min.
Final column temperature hold:	300°C for 19 minutes.
Injector temperature:	250°C
Transfer line temperature:	250°C
Source temperature:	300°C
Injector:	split, splitless
EI Condition:	70 eV
Mass Scan:	follow manufacturer instruction for select ion monitoring (SIM) mode.
Sample volume:	1 µL on-column injection
Carrier gas:	helium at 30 cm/sec.

e) The GC/MS is tuned using a 1 ng/µL solution of decafluorotriphenylphosphine (DFTPP). The DFTPP permits the user to tune the mass spectrometer daily.

Calibration Techniques

Note: The typical GC/MS operating conditions are outlined above. The GC/MS system can be calibrated using the external standard technique or the internal standard technique.

External Standard Calibration Procedure:

a) Prepare calibration standard of PAHs at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with dichloromethane. The stock standard solution of PAHs (0.1 µg/µL) must be prepared from pure standard materials or purchased as certified solutions.

b) Place 0.01 grams of native PAHs on a tared aluminum weighing disk and weigh on an analytical balance.

c) Quantitatively, transfer to a 100 mL volumetric flask. Rinse the weighing disk with several small portions of dichloromethane. Ensure all material has been transferred.

d) Dilute to mark with dichloromethane.

e) The concentration of the stock standard solution of PAHs in the flask is 0.1 µg/µL. Note: commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

f) Transfer the stock standard solutions into Teflon®-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards.

g) Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

h) Calibration standards at a minimum of five concentration levels should be prepared. Accurately pipette 1.0 mL of the stock solution (0.1 µg/µL) into 10 mL volumetric flask, dilute to mark with dichloromethane. This daughter solution contains 10 ng/µL of PAHs.

Note: One of the calibration standards should be at a concentration near, but above the method detection limit; the others should correspond to the range of concentrations found in the sample but should not exceed the working range of the GC/MS system.

i) Prepare a set of standard solutions by appropriately diluting, with dichloromethane, accurately measured volumes of the daughter solution (1 ng/µL).

j) Accurately pipette 30 µL, 100 µL, 300 µL, 1000 µL and 3000 µL of the daughter solution (10 ng/µL) into each 10 mL volumetric flask, respectively. To each of these flasks, add an internal deuterated standard to give a final concentration of 1 ng/µL of the internal deuterated standard (see Internal Standard Calibration Procedures a). Dilute to mark with dichloromethane.

k) The concentration of PAHs in each flask is 0.03 ng/µL, 0.1 ng/µL, 0.3 ng/µL, 1.0 ng/µL, and 3.0 ng/µL, respectively. All standards should be stored at -20°C, protected from fluorescent light and should be freshly prepared once a week or sooner if standards check indicates a problem.

l) Analyze a constant volume (1-3 µL) of each calibration standard by observing retention time and tabulate the area responses of the primary characteristic ion of each standard against the mass injected. The results may be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<20% relative standard deviation, RSD), linearity through the origin may be assumed and the average ratio or calibration factor may be used in place of a calibration curve.

m) The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 20%, the rest must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

Internal Standard Calibration Procedure:

a) To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. For analysis of B[a]P, the analyst should use perylene-d_{12}. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. The following internal standards are suggested at a concentration of 1 ng/µL for specific PAHs:

Benzo(a)pyrene-d_{12} is an appropriate surrogate for:

- Benzo(a)pyrene
- Benzo(k)fluoranthene
- Benzo(g,h,i)perylene
- Dibenzo(a,h)anthracene
- Indeno(1,2,3-cd)pyrene

Benzo(a)anthracene
Chrysene

Anthracene-d_{10} is an appropriate surrogate for:

Acenaphthene
Acenaphthylene
Fluorene
Pyrene
Naphthalene
Anthracene
Fluoranthene
Phenanthrene.

b) A mixture of the above deuterated compounds in the appropriate concentration range is commercially available.

c) Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next two most intense ions as the secondary ions. Note: PAHs have double charged ions that can also be used as secondary ions. The internal standard is added to all calibration standards and all sample extracts analyzed by GC/MS. Retention time standards, column performance standards, and a mass spectrometer tuning standard may be included in the internal standard solution used.

d) Prepare calibration standards at a minimum of three concentration level for each parameter of interest by adding appropriate volumes of one or more stock mixture, add a known constant amount of one or more of the internal deuterated standards to yield a resulting concentration of 1 ng/µL of internal standard and dilute to volume with dichloromethane. One of the calibration standards should be at a concentration near, but above, the minimum detection limit (MDL) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

e) Analyze constant amount (1-3 µL) of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound and internal standard, and calculate the response factor (RF) for each analyte using the following equation:

$$RF = (A_s C_{is}) / (A_{is} C_s)$$

where:

A_s = Area of the characteristic ion for the analyte to be measured, counts.

A_{is} = Area of the characteristic ion for the internal standard, counts.

C_{is} = Concentration of the internal standard, ng/µL.

C_s = Concentration of the analyte to be measured, ng/µL.

If the RF value over the working range is a constant (<20% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF. The Table (under Analysis b) outlines key ions for selected internal deuterated standards.

f) The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared.

g) The relative retention times for each compound in each calibration run should agree within 0.06 relative retention time units.

Sample Analysis:

a) Analyze the 1 mL extract by GC/MS. The recommended GC/MS operating conditions to be used are given above (under Analysis d).

b) If the response for any quantification ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 1 ng/µL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

c) Perform all qualitative and quantitative measurements as described in the section on calibration techniques. The typical characteristic ions for selective PAHs are outlined in that section. Store the extracts at 20°C, protected from light in screw-cap vials equipped with unpierced Teflon™-liner, for future analysis.

d) The sample analysis using the GC-MS-SIM is based on a combination of retention times and relative abundances of the selected ions. These qualifiers are stored on hard disk of the GC-MS data computer and are applied for identification of each chromatographic peak. The retention time qualifier is determined to be ± 0.10 minute of the library retention time of the compound. The accepted level for relative abundance is determined to be ± 20% of the expected abundance. Three ions are measured for most of the PAH compounds. When compound identification is made by a computer, any peak that fails any of the qualifying tests is flagged as questionable. The data should be manually examined by the analyst to determine the reason for the flag and whether the compound should be reported as found. While this adds some subjective judgment to the analysis, computer generated identification problems can be clarified by an experienced operator. Manual inspection of the quantitative results should also be performed to verify concentrations outside the expected range.

e) Determine the concentration of each analyte in the sample according to the methods described below (Sample Volume and Sample Concentration).

GC/MS Performance Tests:

a) Daily DFTPP Tuning - At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved when challenged with a 1 µL injection volume containing 1 ng of decafluorotriphenylphosphine (DFTPP). Analysis should not begin until all those criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or

instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Obtain a background correction mass spectra of DFTPP and check that all key ions criteria are met. If the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved.

The performance criteria must be achieved before any samples, blanks or standards are analyzed. If any key ion abundance observed for the daily DFTPP mass tuning check differs by more than 10% absolute abundance from that observed during the previous daily tuning, the instrument must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

b) Daily 1-point Initial Calibration Check: - At the beginning of each workday, a daily 1-point calibration check is performed by re-evaluating the midscale calibration standard. This is the same check that is applied during the initial calibration, but one instead of five working standards are evaluated. Analyze the one working standards under the same conditions the initial calibration curve was evaluated. Analyze 1 µL of each of the mid-scale calibration standard and tabulate the area response of the primary characteristic ion against mass injected. Calculate the percent difference using the following equation:

Percent Difference = (RF_C - RF_I) / RF_I X 100

where:

RFI = average response factor from initial calibration using mid-scale standard.

RFc = response factor from current verification check using mid-scale standard.

If the percent difference for the mid-scale level is greater than 10%, the laboratory should consider this a warning limit. If the percent difference for the mid-scale standard is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (>20% difference,), then corrective action MUST be taken. Note: Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration MUST be generated. This criterion MUST be met before sample analysis begins.

c) 12-hour Calibration Verification - A calibration standard at mid-level concentration containing B[a]P or other PAHs must be performed every twelve continuous hours of analysis. Compare the standard every 12-hours with the average response factor from the initial calibration. If the % difference for the response factor (see GC/MS Performance Tests, b) is less than 20%, then the GC/MS system is operative within initial calibration values. If the criteria is not met (>20% difference), then the source of the problem must be determined and a new five-point curve MUST be generated.

d) Surrogate Recovery - Additional validation of the GC system performance is determined by the surrogate standard recovery. If the recovery of the surrogate standard fall between 40 to 130%, then the sample extraction, concentration, clean-up and analysis is certified. If it lies outside of this range, then determine the cause of the problem and correct.

Calculations

Sample Volume

a) Retrieve the data logger and download to the computer. Note: all volumetric flows have should have been corrected to standard conditions.

b) The total sample volume (V_m) is calculated from the periodic flow readings (Magnehelic readings taken in the field) using the following equation:

$$V_m = (Q_1 + Q_2,... Q_n / N) \times T / 1000$$

where:

Vs = total sample volume at STP conditions, m³.
Q1,Q2….Qn = flow rates determined at the beginning, end, and intermediate points during sampling, L/minute.
N = number of data points.
T = elapsed sampling time, minutes.

c) The volume of air sampled can be converted to standard conditions (760 mm Hg pressure and 25°C) using the following equation:

$$V_s = V_m \times (pA / 760) \times 298 / (273 + tA)$$

where:

V_s = total sample volume (m³) at standard temperature and pressure (25°C and 760 mm Hg pressure).
V_m = total sample flow under ambient conditions (m³).
pA = ambient pressure (mm Hg).
tA = ambient temperature (°C).

Sample Concentration:

a) When an analyte has been identified, the quantification of that analyte will be based on the integrated abundance of the primary characteristic ion. Quantification will utilize the internal standard technique. The internal standard used shall be the one nearest the retention time of the given analyte.

b) Calculate the concentration of each identified analyte in the sample as follows:

$$\text{Concentration, ng/m}^3 = [(A_x) (I_s)] / [(A_{is}) (RF) (V_s)]$$

where:

A_x = area of characteristic ion(s) for analyte being measured, counts.
I_s = amount of internal standard injected, ng.
A_{is} = area of characteristic ion(s) for internal standard, counts.
RF = response factor for analyte being measured.
V_s = total sample volume at standard temperature and pressure (25°C and 760 mm Hg), m³.

c) The analyte concentration can be converted to ppb_v using the following equation:

C_A (ppbv) = C_A (ng/m³) x (22.4 / MW_A)

where:

C_A = concentration of analyte calculated above in ng/m³.
MW_A = molecular weight of analyte, g/g-mol.

General System QA/QC:

a) The laboratory is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

b) Before processing any samples, the analyst should demonstrate, through the analysis of a reagent solvent blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent solvent blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

c) For each analytical batch (up to 20 samples), a reagent blank, matrix spike and deuterated/surrogate samples must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

d) The experience of the analyst performing gas chromatography is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: a) do the peaks look normal?; and b) is the response window obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., column changed), recalibration of the system must take place.

Process, Field, and Solvent Blanks:

a) One cartridge (XAD-2 or PUF) and filter from each batch of approximately twenty should be analyzed, without shipment to the field, for the compounds of interest to serve as a process blank. A blank level of less than 10 ng per cartridge/filter assembly for single PAH component is considered to be acceptable.

b) During each sampling episode, a minimum of one sampling head per episode, or one sample head every two months (whichever is

more frequent) must be treated as a field blank. A field blank is a sample head that has had the wrappings removed and the cartridge loaded into the sample head. The sample head is transported to the field then returned to the field laboratory without being exposed in the sampler. The field blank is then removed from the sample head and re-wrapped and returned to the analytical laboratory for routine processing. The field blank is to serve as a control for contamination introduced in the field handling process. A sampling episode is defined as a group of samples obtained from one location over a period of time.

c) During each sample episode, a minimum of one split sample, or one split sample every two months, should be obtained. Split sample pairs must be run simultaneously in samplers that are located no more than three metres apart and no less than 2 metres apart. The exposed heads are processed routinely after exposure.

d) During the analysis of each batch of samples at least one solvent process blank (all steps conducted but no cartridge or filter included) should be carried through the procedure and analyzed. Blank levels should be less than 10 ng/sample for single components to be acceptable.

e) Because the sampling configuration (filter and backup adsorbent) has been tested for targeted PAHs in the laboratory in relationship to collection efficiency and has been demonstrated to be greater than 95% for targeted PAHs except naphthalene, no field recovery evaluation will occur as part of the QA/QC program outlined in this section.

Breakthrough Criteria:

a) The mass spectrometer be tuned daily with DFTPP and meet relative ion abundance requirements.

b) A minimum of five concentration levels of each analyte (plus deuterated internal standards) be prepared to establish a calibration factor to illustrate <20% variance over the linear working range of the calibration curve.

c) The verification of the working curve each working day (if using the external standard technique) by the measurement of one or more calibration standards. The predicted response must not vary by more than ±20%.

d) The initial calibration curve is to be verified each working day (if using the internal standard technique) by the measurement of one or more calibration standards. If the response varies by more than ±20% of predicted response, a fresh calibration curve (five point) must be established.

e) The sample analysis using the GC-MS-SIM is based on a combination of retention times and relative abundances of selected ions.

f) The initial calibration curve is to be verified every twelve continuous hours of analysis by a mid-level calibration standard. The response must be less than 20% different from the initial response.

g) The surrogate standard recovery must not deviate from 100% by more than 20%.

References

a) EPA Method TO-13 "The Determination of Benzo(a)pyrene and other polycyclic aromatic hydrocarbons (PAHs) in ambient air using GC/MS", June 1988. Note reference numbers in text are from this document.

Revision History

April 26, 1996:	Initial Draft.
October 29, 1996:	Procedure vetted by private sector laboratories.
January 14, 1998:	Minor editing; EMS codes added and confirmed. Randy Englar of PESC confirmed benz(a)anthracene is synonymous to benzo(a)anthrecene and dibenz(a,h)anthracene is synonymous to dibenzo(a,h)anthracene.
March 20, 1998:	Table of EMS codes for surrogates added.
December 31, 2000:	Merged into main Laboratory Manual; main edit changes to first page only.

Formaldehyde

Parameter Formaldehyde

Analytical Method Trap formaldehyde on DNPH cartridge, analyze by HPLC.

EMS Code **FO10 DNPA**

Introduction This is a method for the determination of formaldehyde in ambient air utilizing solid adsorbent followed by high performance liquid chromatography (HPLC). Formaldehyde has been found to be a major promoter in the formation of photochemical ozone. Short term exposure to formaldehyde is known to cause irritation of the eyes, skin and mucous membranes of the upper respiratory tract.

Method Summary Ambient air is drawn through a pre-packed silica gel cartridge coated with acidified 2,4-dinitrophenylhydrazine (DNPH) reagent, at a sampling rate of 500 - 1200 mL/min. Aldehydes and ketones readily form a stable derivative with DNPH reagent. These derivatives are analyzed using HPLC. This method uses a coated adsorbent for sampling formaldehyde. The reaction of organic carbonyl compounds (aldehydes and ketones) with DNPH-coated cartridges in the presence of acid, forms a stable derivative. The sampling method gives a time weighted average and can be used for a 1-24 hours ambient air sampling time where the concentration of formaldehyde is in the low ppb (1-20 v/v) range or for short term (5-60 min) of source-impacted atmosphere where the concentration is in the ppm range. Sampling flow rate is limited to 1.5 L/min because of the high pressure drop across the DNPH-coated silica gel cartridges. This procedure is therefore not compatible with pumps used in personal sampling equipment.

Cartridges can be user prepared from Sep-PAK chromatographic grade silica gel cartridges to which acidified DNPH is applied in situ or commercially prepared DNPH cartridges. Three randomly selected cartridges should be taken from each production lot to determine formaldehyde background levels. Cartridges in glass culture tubes with polypropylene caps should be kept in the cold when not in use.

MDL 0.03 µg per cartridge

Matrix Air (ambient)

Units µg / m³

Interferences and Precautions It has been recently shown that ozone can react with the formaldehyde- DNPH derivative in the cartridge. This can lead to a lowering of the apparent formaldehyde concentration in the air sample. It is recommended that the sample be draw through a 3 foot length copper tube coated with potassium iodide. Any ozone present in the air will be scrubbed out in the copper tubing. (See 'Apparatus' under Procedure heading below for preparation of scrubber). Certain isomeric aldehydes or ketones that are unresolved by HPLC may interfere. Organic compounds with the same retention time and significant absorption at 360 nm will interfere. Interferences may be eliminated by altering the HPLC columns or mobile phase.

Sample Handling and Preservation

a) After charging, DNPH cartridges should be sealed at their ends with Teflon tape.

b) The cartridge should then be placed in a 40 mL amber glass vial containing a DNPH soaked filter paper, and sealed with a Teflon lined cap or in the aluminum packing bag used by commercial suppliers.

c) The vial is then placed in an individual Zip-Lock bag containing a second DNPH soaked filter.

d) The cartridges should be stored at 4°C.

e) Cartridges should be used within one month of preparation. Label each vial with date of preparation and expiry date. Polyethylene gloves should be worn while handling the cartridges.

f) After sampling the cartridges should be sealed and packaged as described above and stored at 4°C.

g) The cartridges should be shipped to and from the lab in a box, not a cooler since the cooler may contain formaldehyde. Refrigeration during transit is not necessary because this time is short.

Stability

Samples should be analyzed within 2 weeks of return to laboratory.

Procedure

Apparatus

a) HPLC system with UV detector.

b) Sep-PAK C-18 Cartridges (Waters Associates, MA, part # 51910) for in situ charging with DNPH or Sep-Pak for Solid Phase Extraction (DPNH on Silica gel) (Waters Associates, part # 37500).

Ozone Scrubber Construction:

a) Form a coil form a 3-foot, 0.18 inch ID (1 meter, 0.46 mm ID) copper tube.

b) Fill the coil with a potassium iodide solution (dilute a saturated aqueous solution of potassium iodide 1:1 with deionized water) for 5–10 minutes. One g potassium iodide dissolves in 0.7 mL of water at 25°C.

c) Drain the coil and dry it completely by-passing nitrogen through the coil.

d) This device removes ozone at a concentration of 700 ppbv ozone in air at a flow rate of 2 L/min for up to 80 hours.

Reagents

Note: the following procedure describes the in situ charging of cartridges with DPNH. It is not necessary if commercial DNPH charged cartridges are used.

a) DNPH reagent: 0.3 g of DNPH and 0.5 g of ortho-phosphoric acid (H3PO4) in 50 mL of acetonitrile that has been glass distilled. Both the DNPH and H3PO4 must be re-crystallized to eliminate hydrazone blank levels. This is sufficient to prepare ~80 cartridges (4 batches).

b) DNPH cartridges are best prepared in batches of 20. Fill each cartridge with ~1 mL of clean acetonitrile. Rinse slowly (drop by

drop) with a further 2 mL of acetonitrile and blow off the excess with aldehyde free Nitrogen (DNPH scrubbed). Slowly fill each cartridge with 0.4 mL of DNPH reagent. Blot the excess with a piece of Whatman filter paper and blow off with a stream (~1/L per minute) of nitrogen for ~30 seconds. The cartridge ends are then closed with Teflon tape.

c) After all twenty are prepared, number each cartridge and place it in a screw cap 40 mL amber glass vial containing a piece of DNPH soaked filter paper. Store in refrigerator. Analyze one in twenty cartridges to check for clean background (< 0.1 µg of formaldehyde).

Resume normal procedure here.

d) Prepare stock solutions of hydrazone standards in methanol at about 10 mg/100 mL. The standards are synthesized by reacting the formaldehyde with DNPH and then by recrystallizing in methanol to chromatographic purity. Commercial standards are available from Radian Corporation.

Note: standards are prepared using hydrazones, the amount of formaldehyde in the standard must be corrected by molecular weight ratios: 10 mg/L of formaldehyde dinitrophenyl hydrazone is equivalent to 1.423 mg/L formaldehyde. [MW formaldehyde = 30, MW dinitrophenylhydrzine = 198, MW formaldehyde dinitrophenyl hydrazone = 210, loss of 1 Oxygen and 2 Hydrogen's on reaction].

e) Synthesis of formaldehyde hydrazone: 1-2 g of DNPH is recrystallized using hot ethanol (150 mL) or a mixture of 60:40 acetonitrile: H2O. Allow the solution to cool slowly to yield large crystals. Do not induce crystallization. Store crystals in dark in refrigerator for 2 days while the crystallization takes place.

f) 2 mL of concentrated sulphuric acid is added to 0.4 g of DNPH in an Erlenmeyer flask. 3 mL of HPLC water is added dropwise to the solution while stirring and swirling the flask until solution is complete. Caution: the solution becomes HOT. 10 mL of HPLC grade 95% ethanol is added to the solution.

g) 0.5 g of formaldehyde is dissolved in 20 mL of 95% ethanol. The freshly prepared DNPH solution (15 mL) is added and the resulting solution is allowed to stand at room temperature. Crystallization of the 2,4-dinitrophenylhydrazone usually occurs within 5-10 minutes; however it may be necessary to allows the mixture to crystallize overnight.

h) Recrystallize the hydrazone precipitate by dissolving in 30 mL of hot ethanol (heated on a steam cone or a hot plate). If the precipitate dissolves immediately HPLC water is added slowly until the cloud point or until a maximum of 5 mL of HPLC water has been added. If the hydrazone does not dissolve, add ethyl acetate slowly to the hot solution, until solution is attained. Gravity filter the hot solution through fluted filter paper, and allow to stand at rooms temperature until crystallization is complete (~12 hours). Suction filter using glass fibre filter and wash crystals with cold ethanol. Store dried crystals in the dark in the refrigerator.

Procedure

a) Sample preparation: Uncap the cartridge and place it in a small test tube holder with short stem up. Add 200 µL of internal standard solution. Let stand 5-10 minutes, but no longer. Reverse the cartridge (short stem down) and elute with 2 mL of acetonitrile into a 2 mL septum vial. Cap the vial and write the cartridge number on both the side and bottom using permanent ink. If a fibrous material is visible, centrifuge the sample. Transfer the clean supernatant to a second vial and renumber it.

b) Working standards: Dilute stock standards to obtain working standards in the range 1 to 20 µg/mL. Higher concentrations may be necessary if concentrations during air sampling exceed 20 ppb. At least three working standards bracketing the sample concentrations should be used.

c) Pipet 1 mL of working standard and 200 µL of internal standard into a septum vial. Mix the contents. Repeat this step to produce the required range of working standards (1, 4, 10, 20 µg, etc.).

d) Set up the HPLC for the following conditions:
Isocratic Elution
Solvent: 65% acetonitrile, 35% water
Flow rate: 1.5 mL/min
Column: A 4.6 x 250 mm C18 (eg. Ultrasphere ODS -Altex)
Detector: Variable wavelength UV set at 360 nm
Optional Gradient elution
42% acetonitrile, 58% water for 20 min
linear increase to
70% acetonitrile, 30% water over 12 min
hold at
40% acetonitrile, 60% water for 2 minutes.
Allow 5 minutes between each run so column can re-equilibrate to initial conditions.

Calculation:
The amount of formaldehyde in the cartridge is calculated as follows:

$M = (A \times 2) / (Rf \times 7)$

where:
M = amount of formaldehyde in µg
Rf = response factor for the Formaldehyde-DNPH derivative.

The concentration of formaldehyde in air is calculated as follows:

$C = (M \times 24.25 \times 1000) / (V \times Mo)$

Where:
C = concentration in ppb
M = amount of formaldehyde determined in µg
V = volume of air sampled in Litres
Mo = mol wt of the formaldehyde

Since $V = F \times t = (F_o + F_1 \times t) / 2$

Where:
F = average sampling flow, L/min
F_o = initial sampling flow, L/min
F_1 = final sampling flow, L/min

t = duration of sampling in minutes

Substitution for V yields:

$C = M \times 48900 / [(Fo + F1) \times t \times Mo]$

which is concentration (ppb) of formaldehyde in the air.

Precision Ten DNPH cartridges spiked at midrange level (2.74 µg) gave coefficient of variation of 5%.

Accuracy Ten DNPH cartridges spiked at midrange level (2.74 µg) gave recovery of 94%.

Quality Control One in fourteen DNPH cartridges should be run as blanks. Limits are <0.1 µg/cartridge.

Field blanks should be shipped and returned for analysis for each batch of DNPH cartridges sent to a sampling site.

After the initial calibration a single standard should be re-run every ten samples throughout the run. Duplicates standards should have a relative standard deviation of ≤ 10%.

One in fourteen samples should be run in duplicate. These duplicates should be within 15% of each other for concentrations > 5 x MDL.

Every fourteen samples spike a DNPH blank cartridges (BMS) with 200 µL of 250 ppm formaldehyde. Spike recovery should be in the range 80 - 120%.

Documentation of QC Laboratory and field blanks, and standard and sample duplicates will be recorded in an ongoing database. Control chart on duplicates will be prepared when sufficient data (~20 pairs > MDL) is accumulated.

Data Analysis See calculations above.

Safety This method may involve hazardous materials, operations and equipment. It is the responsibility of the user to consult appropriate safety information.

Disposal In accordance with procedures recommended by Safety committee.

References

a) U.S. EPA Method TO-11,"Determination of Formaldehyde in Ambient Air Using Absorbent Cartridge followed by High Performance Liquid Chromatography", May 1988. [Note field techniques can be found in this reference].

b) ENSR Consulting and Engineering, Camarillo, California, "Standard Operating Procedure for Analysis of Carbonyl Compounds in Air Samples Collected on DNPH-Impregnated Cartridges", 1990.

c) B. G. Oliver, Zenon Laboratories (BC), "A study of the Stability of 2,4-Dinitrophenylhydrazine (DNPH) Cartridges for Analysis of Ambient Air Concentrations of Formaldehyde: Recommended Storage and Handling Procedures", 1992.

d) A. Sirju and P. Shepson, "Laboratory and Field Investigation of DNPH Cartridge Technique for the Measurement of Atmospheric Carbonyl Compounds." Environ. Sci. Technol, 1995, volume 29, 384–392.

Revision History: December 13, 1994: Initial draft.

April 1, 1996: Ozone Scrubber added.

October 29, 1996: Procedure vetted by private sector laboratories.

January 14, 1998: EMS codes added and confirmed.

December 31, 2000: Merged into main Laboratory Manual. Minor edit changes; units added.

Volatile Organic Compounds in Air-Vapour by Canister Sampling / GCMS — PBM

Parameter	Volatile Organic Compounds (VOCs) in air-vapour.
Analytical Method	Canister sampling, GC/MS analysis (GC/FID optional for VHv_{6-13}).
Introduction	This method is applicable to the quantitative determination of volatile organic compounds in air, when appropriately sampled and collected in stainless-steel canisters.
Method Summary	Ambient air or soil gas samples are collected by introduction of air into an evacuated passivated stainless-steel canister through a calibrated sampling valve. Specialized calibrated sampling heads allow samples to be collected at selected flow rates and durations. Pressurized sampling is also possible. Small volumes of an air sample may then be analyzed by GC/MS after being pre-focused on a cryogenic or adsorbent trap. Samples are then introduced to the GC/MS by thermal desorption. This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.
Parameter Applicability, MDLs	The Appendix to this method lists parameters from Schedule 11 of the BC CSR for which this method may be applied. For these parameters, the Appendix lists the following physical properties and information: CAS# (Chemical Abstract Services number). Boiling Point (°C). Vapour Pressure at 25°C. Molecular Weight (grams / mole). Applicability notes regarding this method. Satisfactory performance using this method has not been verified for all listed compounds. Some parameters may require validation and/or the use of heated canister techniques. MDLs are not listed for each compound. Most discrete compounds amenable to this method can be determined to an approximate MDL of 1 ug/m³, sometimes lower in Selected Ion Monitoring (SIM) mode. Sensitivity is affected by instrument configuration choices. Where appropriate, the method may be used for other compounds not listed in the Appendix if performance requirements and Quality Control requirements can be met.
Matrix	Air (ambient) / Soil Gas

Interferences and Precautions

Interferences may result from residual contaminants in canisters, or from the laboratory's sample introduction system, internal standard system, or dilution gases. The entire analysis system must be monitored daily using Method Blanks and must be demonstrated to be free of interferences under the conditions of the analysis.

The most common and most significant source of interferences for this method is residual contamination in canisters, resulting from the incomplete cleanout of highly contaminated samples that may have previously occupied a canister. Scrupulous pre-cleaning and batch-proofing protocols are necessary to ensure canisters are reliably cleaned before use.

Sample Handling and Preservation

Container: Samples are collected in specially prepared stainless-steel canisters, ranging in volume from 400mL to 6L. Appropriate sampling heads that have been pre-calibrated to deliver the desired sampling rate are also required.

Preservation: Not applicable.

Stability

Holding Time: Air samples in canisters may be stored for up to 30 days before instrumental analysis.

Storage: Storage of canisters at ambient temperatures is recommended.

Procedure

Canister Preparation: Rigorous canister pre-cleaning, tracking, and proofing protocols are essential to the application of this method. Refer to Method TO15 for recommended cleaning and batch-proofing protocols.

The precise usage history of every canister must be recorded to provide audit trail in the event of suspected sample contamination.

Sampling Guidelines: Detailed field sampling guidelines for canisters are beyond the scope of this method. For information please refer to EPA Method TO15, and to the BC SAB document "Guidance on Site Characterization for Evaluation of Soil Vapour Intrusion Into Buildings".

Consensus among sampling experts is that soil gas samples should be collected at flow rates not exceeding 200 mL/min, to permit sufficient recharge and to help prevent short-circuiting.

Instrumental Analysis: Detailed instrumental procedures are not provided in this method. Refer to the EPA Compendium Method TO15 (see references) for detailed guidance on instrumental analysis.

The method requires the use of either cryogenic or adsorbent based analyte trapping and focusing techniques. GC/MS must be used for target compound analysis. Selective ion monitoring (SIM) mode may be utilized where necessary to achieve lower detection limits. In SIM mode, one quantitation ion and two qualifier ions per analyte should be monitored where possible. GC/FID may be used for VHv_{6-13}.

For target compounds, a five-point initial calibration over the desired working range is required (four-point minimum in extenuating circumstances). Calibration standards must be introduced to canisters in the gas phase. Only calibrated parameters may be reported under this method; it is not intended for semi-quantitative applications.

The use of internal standards is required, unless sample interferences preclude accurate assessment of internal standard areas. Internal standards must not introduce significant interferences on test analytes or surrogates. Internal standard areas must be monitored throughout each run, and should not vary by more than +/-50% from the initial calibration or CCV.

Under normal circumstances, this method is limited to compounds with vapour pressures of >0.05 Torr. With the use of canister heating devices, the upper range of the method may be extended (subject to validation, and to meeting stated performance requirements).

Reporting: Labs must clearly specify the units of reported air concentrations. Recommended reporting units for CSR purposes are ug/m³.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 Lab Control Samples must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 1-2 years).

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Average accuracy must be between 80-120% for all routinely reported parameters.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Precision must be ≤20% relative standard deviation (%RSD) for all routinely reported parameters.

Where the laboratory's method does not meet these accuracy or precision requirements for specific parameters, the method may still be used, but reports must indicate that results are semi-quantitative or qualitative, and the established performance should be provided.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Internal Standard Area Checks	All samples and QC	Within 50% of initial calibration or last CCV
Method Blank (MB)	1 per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS) / Calibration Verification Standard (CVS)	1 per batch (max 20 samples)	60-140% recovery
Lab Duplicates	≥ 5%	≤ 40% RPD
Field Duplicates	Recommended	Not specified
Continuing Calibration Verification (CCV)	Every 24 hours (max 20 samples), and at end of each batch.	70-130% recovery for mid-level standards.

* Minimum DQOs apply to individual QC samples, not averages, at levels above 10x MDL. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

QC Details

Method Blank: Method Blanks must be prepared from randomly selected canisters. Use of dedicated canisters for Method Blanks is not permitted.

Lab Duplicates: Minimum frequency 5%.

Field Duplicates: Recommended. Field duplicates are normally accomplished by sampling in parallel (distributed volume pairs).

Laboratory Control Sample (LCS) / Calibration Verification Standard (CVS): A second source must be utilized for the LCS/CVS to confirm the integrity of the calibration standards and the accuracy of the calibration. All calibrated and reported parameters must be included in the LCS / CVS.

Continuing Calibration Verification (CCV): Calibration standards (typically a mid-point standard, e.g. 10ppbv) must be re-analyzed periodically throughout the instrument run to monitor calibration drift. Run a CCV at least every 24 hours (at least every 20 samples), and at the end of each batch. An LCS may serve the same purpose if the CCV DQOs are met.

Prescribed Elements

The following components of this method are mandatory:

Sample holding times must be adhered to. Samples analyzed beyond the stated holding time must be qualified.

All target compound analysis must be by GC/MS.

Initial GC/MS calibrations must be five points or more (four-point minimum in extenuating circumstances). Internal standards must be used. Continuing calibrations may be employed while Calibration Verification Standards meet acceptance criteria for all reported compounds.

Calibration standards must be introduced to canisters in the gas phase. All reported compounds must be represented in calibration standards.

Samples that exceed the calibration range must be diluted and re-analyzed, or reported as estimated or minimum values.

Usage history of each canister must be recorded to enable tracking of suspected contamination.

All canisters must be batch-proofed prior to use.

All stated Performance Requirements and Quality Control requirements must be met.

This method may not be utilized for analysis of compounds listed as not appropriate by this technique, in the table that follows.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

i) Method TO-15, Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters And Analyzed by Gas Chromatography / Mass Spectrometry (GC/MS), from the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Center for Environmental Research Information, Office of Research and Development, US EPA, Cincinnati, OH, January 1999.

ii) Method TO-14A, Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially-Prepared Canisters With Subsequent Analysis By Gas Chromatography, from the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Center for Environmental Research Information, Office of Research and Development, US EPA, Cincinnati, OH, January 1999.

Revision History

June 19, 2009: First draft of BC Lab Manual method.

Table 1: VOCs in Air by Canister Sampling — Method Applicability & Physical Constants						
Schedule 11 Substance	**CAS #**	**BP (°C)**	**VP, 25C (Torr)**	**MW (g/mol)**	**Henry's Law atm-m³/mol**	**Method Applicability**
acetaldehyde	75-07-0	20.1	902	44.05	6.7E-05	✓
acetone	67-64-1	55.5	231	58.08	4.0E-05	✓
acetone cyanohydrin	75-86-5	171	0.341	85.11	1.3E-05	VR*
acetonitrile	75-05-8	59.6	88.8	41.05	3.4E-05	✓*
acrolein (2-propenal)	107-02-8	52.6	274	56.06	1.2E-04	✓
acrylonitrile (2-propenenitrile)	107-13-1	77.3	109	53.06	1.4E-04	✓
ammonia	7664-41-7	-33.3	7508	17.03	1.6E-05	X
benzene	71-43-2	80	94.8	78.11	5.6E-03	✓
benzyl chloride (a-chlorotoluene)	100-44-7	179	1.23	126.59	4.1E-04	✓
bis(2-chloroethyl)ether	111-44-4	178.5	1.55	143.01	1.7E-05	VR*
bis(2-chloroisopropyl)ether	39638-32-9	124.9	12.6	171.07	3.3E-04	VR*
bis(2-chloromethyl)ether	542-88-1	106	29.4	114.96	2.1E-04	VR*
bis(2-chloro-1-methylethyl)ether	108-60-1	187	0.56	171.07	1.1E-04	VR*
bromobenzene	108-86-1	156	4.18	157.01	2.7E-03	✓
bromodichloromethane (BDCM)	75-27-4	90	57.4	163.83	2.1E-03	✓
bromoform (tribromomethane)	75-25-2	149.1	5.4	252.73	2.2E-02	✓
bromomethane (methyl bromide)	74-83-9	3.5	1620	94.94	6.2E-03	✓
1,3-butadiene	106-99-0	-4.4	2110	54.09	7.4E-02	✓
carbon disulfide	75-15-0	46	359	76.13	1.4E-02	✓
carbon tetrachloride (tetrachloromethane)	56-23-5	76.8	115	153.82	2.8E-02	✓
chlorine	7782-50-5	-34.0	5854	70.91	1.2E-02	X
chlorobenzene (monochlorobenzene)	108-90-7	131.7	12	112.56	3.1E-03	✓
4-chlorobenzotrifluoride	98-56-6	138.5	7.63	180.56	3.5E-02	✓*
2-chloro-1,3-butadiene	126-99-6	59.4	215	88.54	5.6E-02	✓*
1-chlorobutane	109-69-3	78.6	101	92.57	1.7E-02	✓*
1-chloro-1,1-difluoroethane (HCFC-142b)	75-68-3	-9.7	2540	100.5	5.9E-02	✓*
chlorodifluoromethane	75-45-6	-40.7	7250	86.47	4.1E-02	✓
chloroethane (ethyl chloride)	75-00-3	12.3	1010	64.52	1.1E-02	✓
chloroform (trichloromethane)	67-66-3	61.1	197	119.38	3.7E-03	✓
chloromethane (methyl chloride)	74-87-3	-24	4300	50.49	8.8E-03	✓
4-chloronitrobenzene	100-00-5	242	0.022	157.55	4.9E-06	✓
2-chlorophenol	95-57-8	174.9	2.53	128.56	1.1E-05	VR*
2-chloropropane	75-29-6	35.7	515	78.54	1.7E-02	✓*
3-chloropropene (allyl chloride)	107-05-1	45.1	368	76.53	1.1E-02	✓*
2-chlorotoluene	95-49-8	159	3.43	126.59	3.6E-03	✓*
crotonaldehyde	123-73-9	104	30	70.09	1.9E-05	VR*
cyanogen	460-19-5	-21.1	4300	52.04	5.3E-03	VR*
cyanogen bromide	506-68-3	61.5	122	105.92	n/a	VR*
cyanogen chloride	506-77-4	13	1230	61.47	1.9E-03	VR*
n-decane	124-18-5	174.1	1.32	142.29	4.7E+00	✓
1,4-dibromobenzene	106-37-6	220	0.0575	235.91	3.7E-02	✓
1,2-dibromoethane (ethylene dibromide, EDB)	106-93-4	131.6	11.2	187.86	6.7E-04	✓
dibromochloromethane (DBCM)	124-48-1	120	15.6	208.28	3.2E-02	✓
1,2-dibromo-3-chloropropane (DBCP)	96-12-8	196	0.58	236.33	6.0E-03	✓*
dibromomethane (methylene bromide)	74-95-3	97	44.4	173.84	8.2E-04	✓*
1,2-dichlorobenzene	95-50-1	180	1.47	147.01	7.9E-02	✓
1,3-dichlorobenzene	541-73-1	173	2.15	147.01	2.6E-03	✓
1,4-dichlorobenzene	106-46-7	174	1.74	147.01	2.4E-03	✓
1,4-dichloro-2-butene, cis + trans	7364-41-0	152.5	4.09	125.00	8.5E-03	✓*
dichlorodifluoromethane (freon 12)	75-71-8	-29.8	4850	120.91	3.4E-01	✓
1,1-dichloroethane	75-34-3	57.4	227	98.96	5.6E-03	✓

Table 1: VOCs in Air by Canister Sampling — Method Applicability & Physical Constants						
Schedule 11 Substance	**CAS #**	**BP (°C)**	**VP, 25C (Torr)**	**MW (g/mol)**	**Henry's Law atm-m³/mol**	**Method Applicability**
1,2-dichloroethane	107-06-2	83.5	78.9	98.96	1.2E-03	✓
1,1-dichloroethene (1,1-dichloroethylene)	75-35-4	31.6	634	96.94	2.6E-02	✓
1,2-dichloroethene, cis (1,2-dichloroethylene, cis)	156-59-2	55	201	96.94	4.1E-03	✓
1,2-dichloroethene, trans (1,2-dichloroethylene, trans)	156-60-5	55	201	96.94	9.4E-03	✓
1,2-dichloropropane (propylene dichloride)	78-87-5	95.5	53.3	112.99	2.8E-03	✓
1,3-dichloropropane	142-28-9	120.9	18.2	112.99	9.8E-04	✓*
1,3-dichloropropene (mixed isomers)	542-75-6	112	34	110.97	3.5E-03	✓
1,3-dichloropropene, cis	10061-01-5	112	34	110.97	3.5E-03	✓
1,3-dichloropropene, trans	10061-02-6	112	34	110.97	3.5E-03	✓
dicyclopentadiene	77-73-6	170	2.29	132.21	6.3E-02	✓*
diethyl ether (ethyl ether)	60-29-7	34.5	538	74.12	1.2E-03	✓
diisopropyl methylphosphonate (DIMP)	1445-75-6	209.8	0.277	180.19	4.4E-05	VR*
dimethylamine	124-40-3	6.9	1520	45.08	9.1E-05	VR
n,n-dimethylaniline	121-69-7	193.5	0.7	121.18	5.7E-05	VR*
epichlorohydrin (chloromethyl-ethylene oxide)	106-89-8	117	16.4	92.53	3.0E-05	✓
1,2-epoxybutane	106-88-7	63.3	180	72.11	1.8E-04	VR*
ethyl acetate	141-78-6	77.1	93.2	88.11	1.3E-04	✓
ethyl acrylate	140-88-5	99.4	38.6	100.12	3.4E-04	✓*
ethylbenzene	100-41-4	136.1	9.6	106.17	7.9E-03	✓
ethyl methacrylate (ethyl 2-methyl-2-propenoate)	97-63-2	117	20.6	114.15	5.7E-04	VR
ethylene oxide	75-21-8	10.6	1310	44.05	1.5E-04	✓
furan	110-00-9	31.5	600	68.08	5.4E-03	✓*
1,3-hexachlorobutadiene	87-68-3	215	0.22	260.76	4.2E-01	✓
hexachlorocyclopentadiene	77-47-4	239	0.06	272.77	1.1E+00	✓
hexachloroethane	67-72-1	154.5	0.21	236.74	1.6E-01	✓
hexane (n-)	110-54-3	68.7	151	86.18	1.8E+00	✓
hydrogen cyanide (cyanide)	74-90-8	25.7	741.9	27.03	1.3E-04	X
isopropylbenzene (cumene)	98-82-8	152.4	4.5	120.19	1.1E-02	✓*
methacrylonitrile (2-methylprop-2-enenitrile)	126-98-7	90.3	71.2	67.09	2.5E-04	✓*
methyl acetate	79-20-9	92	216	74.08	1.1E-04	✓
methyl acrylate	96-33-3	80.2	86.6	86.09	2.0E-04	✓
methylcyclohexane	108-87-2	100.9	46	98.19	4.3E-01	✓
methylene chloride (dichloromethane)	75-09-2	40	435	84.93	3.3E-03	✓
methyl ethyl ketone (2-butanone)	78-93-3	79.5	90.6	72.11	5.7E-05	✓
methyl isobutyl ketone (4-methyl-2-pentanone)	108-10-1	116.5	19.9	100.16	1.4E-04	✓
methyl mercaptan (methanethiol)	74-93-1	5.9	1510	48.11	3.1E-03	✓
methyl methacrylate	80-62-6	100.5	38.5	100.12	3.4E-04	✓
a-methylstyrene (1-methyl-1-phenylethylene)	98-83-9	165.4	1.9	118.18	2.5E-03	✓*
methyl styrene, m+p (vinyl toluene, m+p)	25013-15-4	165.4	1.5	118.18	7.9E-03	✓*
methyl tert-butyl ether (MTBE)	1634-04-4	55.2	250	88.15	5.9E-04	✓
naphthalene	91-20-3	217.9	0.085	128.18	4.4E-04	✓
nitrobenzene	98-95-3	210.8	0.245	123.11	2.4E-05	✓
2-nitrotoluene	88-72-2	222	0.188	137.14	5.1E-04	VR
phosphine	7803-51-2	-87.8	29300	34.00	2.4E-02	X
propylene oxide	75-56-9	35	538	58.08	7.0E-05	✓
pyridine	110-86-1	115.2	20.6	79.10	1.1E-05	VR
styrene	100-42-5	145	6.4	104.15	2.7E-03	✓
1,1,1,2-tetrachloroethane	630-20-6	130.5	12	167.85	2.4E-03	✓
1,1,2,2-tetrachloroethane	79-34-5	156.5	13.3	167.85	3.7E-04	✓

Table 1: VOCs in Air by Canister Sampling — Method Applicability & Physical Constants						
Schedule 11 Substance	**CAS #**	**BP (°C)**	**VP, 25C (Torr)**	**MW (g/mol)**	**Henry's Law atm-m³/mol**	**Method Applicability**
tetrachloroethylene (PCE, PERC)	127-18-4	121.3	18.5	165.83	1.8E-02	✓
tetrahydrofuran	109-99-9	66	162	72.11	7.1E-05	✓*
toluene	108-88-3	110.6	28.4	92.14	6.6E-03	✓
1,2,4-trichlorobenzene	120-82-1	213.5	0.46	181.45	5.8E-02	✓
1,1,1-trichloroethane	71-55-6	74	124	133.41	1.7E-02	✓
1,1,2-trichloroethane	79-00-5	113.8	23	133.41	8.2E-04	✓
trichloroethylene (TCE)	79-01-6	87.2	69	131.39	9.9E-03	✓
1,1,2-trichloro-1,2,2-trifluoroethane (freon 113)	76-13-1	47.7	363	187.38	2.2E+01	✓
trichlorofluoromethane (freon 11)	75-69-4	23.7	803	137.37	9.7E-02	✓
1,1,2-trichloropropane	598-77-6	132	3.1	147.43	3.2E-04	✓*
1,2,3-trichloropropane	96-18-4	157	3.69	147.43	3.4E-04	✓*
1,2,3-trichloropropene	96-19-5	142	4.4	145.42	1.8E-02	✓*
a,a,a-trichlorotoluene (benzotrichloride)	98-07-7	220.6	0.414	195.48	0.0106	✓*
triethylamine	121-44-8	89	57.1	101.19	1.5E-04	VR
1,2,4-trimethylbenzene	95-63-6	169.3	2.1	120.19	6.2E-03	✓
1,3,5-trimethylbenzene	108-67-8	164.7	2.1	120.19	8.8E-03	✓
vinyl acetate (ethenyl acetate)	108-05-4	72.5	90.2	86.09	5.1E-04	✓
vinyl bromide (bromoethene)	593-60-2	15.8	1030	106.95	1.2E-02	✓
vinyl chloride (chloroethene)	75-01-4	-13.3	2980	62.50	2.8E-02	✓
VHv_{6-13} / VPHv	n/a	n/a	n/a	n/a	n/a	✓
xylenes (o-xylene + m,p-xylenes)	1330-20-7	138.5	7.99	106.17	6.6E-03	✓
Key:						
✓ Technique is appropriate for this substance						
X Technique is not appropriate for this substance						
VR Validation Required (technique may be appropriate for this substance)						
* Gas-phase reference standards may not be commercially available for this compound but can be prepared in-house.						

Volatile Organic Compounds & Other Volatile Substances in Air-Vapour by Charcoal Tubes and Miscellaneous Collection Media — PBM

Parameter	Volatile Organic Compounds (VOCs) and other Volatile Substances in air-Vapour.
Analytical Method	Sampling and analysis of VOCs and other volatile substances in air by charcoal tubes and miscellaneous collection media.
Introduction	This method provides abbreviated guidance for the sampling and analysis of volatile substances in air by charcoal tubes and a wide variety of miscellaneous collection media. It provides endorsed references to a collection of published reference methods, as opposed to a single technique. These techniques are applicable to the quantitative determination of VOCs and some volatile inorganic substances in air, when appropriately sampled and collected on suitable collection media.
Method Summary	Ambient air or soil gas samples are collected by introduction of air onto a suitable collection medium using a calibrated sampling pump. Samples are collected at a fixed pump flow rate (typically 10-200mL/min) for a pre-determined duration. Referenced collection media include: charcoal tubes (coconut shell, petroleum charcoal, beaded carbon, and carbon molecular sieve), silica gel (coated and uncoated), XAD (coated and uncoated), impingers and bubblers, coated filters, and other miscellaneous adsorbents. Most collection media referenced within this method are solvent desorbed, with the solvent extract analyzed by gas chromatography with GC/MS, GC/FID, GC/ECD, GC/NPD, GC/ELCD, GC/FPD, or HPLC-UV. Some methods utilize IC or Ion Selective Electrodes. This method is performance-based and provides only guidance and boundaries within which laboratories must operate when utilizing these techniques. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.
Parameter Applicability, MDLs	Table 1 lists parameters from Schedule 11 of the BC CSR for which this method may be applied. For these parameters, the following physical properties and information are provided: CAS# (Chemical Abstract Services number). Boiling Point (°C). Vapour Pressure at 25°C. Molecular Weight (grams / mole).

	Applicability notes regarding this method. Satisfactory performance using this method has not been verified for all listed compounds. Some parameters may require the use of alternative techniques. MDLs are not listed for each compound because they vary by technique, and with the sampling and analytical options selected. Laboratory MDLs for this method are determined in absolute amount units (e.g. µg), so air concentration MDLs are a function of sampling volume. Where appropriate, the techniques described herein may be used for other VOCs not listed in Table 1, if performance requirements and Quality Control requirements can be met.
Matrix	Air (ambient) Soil Gas
Interferences and Precautions	Interferences may result from residual contaminants in the collection media, from media decomposition products, or from contaminants introduced during sampling or at the laboratory. Diligent use of Field Blanks is strongly recommended. The analytical system must be monitored daily using Method Blanks and must be demonstrated to be free of interferences under the conditions of the analysis. Breakthrough, caused by high concentration of analyte(s) or excess sampling volumes can result in a low bias for the analytes of interest. High humidity, as is common with soil gas sampling, can increase the likelihood of breakthrough. Water condensation can occur inside sampling tubes when collecting soil vapour samples. The effects of excessive water on the sample integrity and/or on desorption efficiency are not well understood and may vary with different media types. Most sources of carbon disulfide contain detectable levels of benzene. Reagent blank subtraction, combined with careful control of carbon disulfide sources and lots may be necessary to minimize benzene detection limits.
Sample Handling and Preservation	**Container**: Samples are collected on specially prepared collection media, which may be in the form of solid sorbent tubes, filters, cartridges, impingers, or bubblers (refer to appropriate method reference). Optimal sample collection volumes vary by technique and detection limit requirements. **Preservation**: Normally none required (refer to reference methods).
Stability	**Holding Time:** VOCs and other Volatile Substances collected as described within this method may be stored up to 30 days before instrumental analysis. This holding time is based on a general review of stability data and studies published by NIOSH and OSHA for the listed techniques (see Table 2 and reference methods). Few, if any, analytes exhibited any statistically significant degradation over the studied storage durations. **Storage:** Store at ≤ 10°C during transport, and at ≤ 6°C at the laboratory. Alternatively, the guidance provided within the applicable reference method from Table 1 may be used.

Some referenced methods state a requirement to store samples in darkness. For these methods, this requirement must be met.

Method Selection

Detailed procedures are not directly provided in this method. Pertinent information regarding recommended and endorsed methodologies may be found within the applicable reference methods listed *by substance* in Table 1, and summarized *by method* in Table 2.

Methods listed as "Validation Required" are believed to be suitable for the indicated parameter, but the analyte has not been specifically listed within the reference method. These references have been included due to chemical similarities with

analytes listed within the referenced method(s), or based on the prior experience of BC laboratories.

Select an appropriate collection medium based on one of the reference methods in Tables 1 and 2. Only those collection media listed within these tables as appropriate for a particular target analyte may be used (or equivalent, in the case of commercial brand names).

Media Information

Most sample collection media listed within this method are disposable, for one-time use, and are readily available from commercial suppliers (e.g. Supelco, SKC).

For charcoal tube and other solid sorbent tube methods, different size tubes are commercially available, each containing separate front and back sections. Commonly available sizes for charcoal tubes (front/back) are: 100mg/50mg, and 400/200mg. In most cases, the larger capacity tubes are recommended to maximize capacities.

Field Sampling Guidelines

Detailed sampling guidelines are beyond the scope of this method. For information please refer to the applicable reference method(s) from Table 1, and to the BC SAB document "Guidance on Site Characterization for Evaluation of Soil Vapour Intrusion Into Buildings" (see References).

Samplers should consult the laboratory for recommended maximum sampling flow rates and Safe Sampling Volumes (SSVs) for the applicable analytes and collection media, where known. This information may originate either from published reference information, or from laboratory or field validation studies (see Performance Requirements).

When sampling is undertaken outside the boundaries of referenced or validated maximum flow rates and/or SSVs, samples must be collected using two collection media in series (e.g. front and back media sections, or two independent collection devices), to permit evaluation of breakthrough and to verify effective sample collection.

Consensus among sampling experts is that soil gas samples should be collected at flow rates not exceeding 200 mL/min, to permit sufficient recharge and to help prevent short-circuiting.

The intent of this method is to sample vapours as opposed to particulate-bound substances. At sampling locations where particulate sources of target analytes in air are likely, a non-adsorptive pre-filter may be used to exclude particulates. Analyte specific reference methods may offer more guidance.

Some target analytes are particularly prone to breakthrough. For such analytes, samples may be taken using two collection media in series, to improve retention capacity and increase safe sampling volumes.

Analysis Procedure

Sample Preparation: Follow the sample preparation instructions from the relevant reference method. Minor validated changes to the reference methods are permitted, if validation and ongoing QC demonstrates that performance requirements are met. For example, referenced desorption solvents, solvent volumes, or desorption times may be varied if validated.

For collection media that include separate front and back sections, it is highly recommended for both sections to be analyzed separately, as per standard industrial

hygiene practice. This provides a definitive check for breakthrough on every sample, and can identify samples that may have been collected in the reverse direction.

Instrumental Analysis: For detailed guidance on instrumental analysis techniques pertinent to this method refer to the applicable reference method(s) from Table 1, or to EPA SW846.

Instrumental analysis techniques may be varied if performance requirements are met. Most NIOSH and OSHA methods specify the use of inexpensive selective or non-selective detectors. In many cases, GC/MS may be used instead of the recommended detector, and may generate more sensitive and/or more conclusive results (especially in the case of GC/FID).

If GC/MS is used, Selective Ion Monitoring (SIM) mode may be utilized where necessary to achieve lower detection limits. In SIM mode, one quantitation ion and two qualifier ions per analyte should be monitored where possible.

For target compounds, a five-point initial calibration over the desired working range is required (four-point minimum in extenuating circumstances). Only calibrated parameters may be reported under this method; it is not intended for semi-quantitative applications.

For all routinely conducted GC/MS tests, The use of internal standards is required, unless sample interferences preclude accurate assessment of internal standard areas. Internal standards must not introduce significant interferences on test analytes or surrogates. Internal standard areas must be monitored throughout each run and should not vary by more than +/- 50% from the last calibration or CCV.

Reporting: Labs must clearly specify the units of reported air concentrations. Recommended reporting units for CSR purposes are $\mu g/m^3$.

Where front and back media sections are analyzed separately, laboratories should report results for each section separately. Where the amount on the back section is less than 25% of the front section, data users should be advised to sum the two results. Where the amount on the back section is equal to or greater than 25% of the front section (for any given compound), the tube is considered to have been saturated (OSHA 07), and results should be qualified (e.g. report as minimum values).

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 Lab Control Samples must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 1-2 years).

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Average accuracy must be between 80-120% for all routinely reported parameters.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Precision must be ≤ 20% relative standard deviation (%RSD) for all routinely reported parameters.

Where the laboratory's method does not meet these accuracy or precision requirements for specific parameters, the method may still be used, but reports must indicate that results are semi-quantitative or qualitative, and the established performance should be provided.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Safe Sampling Volumes (SSVs): Most collection media have a finite capacity. Where known, SSVs must not be exceeded. For a given analyte / media combination, SSVs are a function of analyte concentration, sampling flow rate, and air humidity, among other factors. If referenceable SSV information is not readily available for the analytes being tested on the selected media, then SSVs must be validated in the laboratory, or in the field. The following test is recommended:

Place two sample collection media in series (or use a collection medium with separate front and back sections). Introduce known amounts of high concentration gas phase standard(s) onto the first media section. The spiked concentration should be at least 200 times the MDL. Then pass a volume of inert humidified air or nitrogen through both sections, equal to the desired maximum sampling volume. Introduce ~60-80% humidified air or nitrogen at the maximum sampling flow rate to be validated. A dynamic humidified air or nitrogen stream may be generated using an impinger/bubbler.

If the amount of spiked analyte detected on the 2nd media section is less than 1% of the amount on the 1st media section, then the air volume tested may be considered to be below the SSV for the analyte in question, at the evaluated flow rate. If the amount of spiked analyte

detected on the 2nd media section is between 1-5% of the amount on the 1st media section, calculate the SSV as 80% of the sampling volume

used (OSHA Evaluation Guidelines for Air Sampling Methods Using Chromatographic Analysis). Repeat the study with a lower sampling volume and/or lower flow rate if breakthrough exceeds 5%.

In the absence of laboratory validated data, a field test may be used to assess breakthrough, if sample concentrations are sufficiently high. Collect samples using multiple collection media or media sections in series and follow the same principles as above.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Method Blank (MB)	1 per batch (max 20 samples)	Less than reported DL
Field Blank (FB)	Recommended (1 per sampling event)	Less than reported DL
Lab Control Sample (LCS) / Calibration Verification Standard (CVS)	1 per batch (max 20 samples)	60-140% recovery
Lab Duplicates	Generally not possible	n/a
Field Duplicates	Recommended	Not specified
Continuing Calibration Verification (CCV)	At least every 12 hours, and at end of each batch.	70-130% recovery for mid-level standards.

* Minimum DQOs apply to individual QC samples, not averages, at levels above 10x MDL. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected. These are minimum standards applied to a wide variety of analytes and techniques. Laboratories are encouraged to set higher acceptance criteria for more precise techniques.

QC Details

Method Blank: Method Blanks must be prepared from randomly selected collection media that are comparable to the samples being analyzed. Where possible, they must be prepared from the same media lot numbers as samples.

Field Blank: Recommended. May constitute a blank collection medium that is opened and handled in the field.

Field Duplicates: Recommended. Field duplicates are normally accomplished by sampling in parallel (distributed volume pairs).

Lab Control Sample (LCS) / Calibration Verification Standard (CVS): A second source must be utilized for the LCS/CVS to confirm the integrity of the calibration standards and the accuracy of the calibration. All calibrated and reported parameters must be included in the LCS / CVS.

Continuing Calibration Verification (CCV): Calibration standards (typically a mid-point standard) must be re-analyzed periodically throughout the instrument run to monitor calibration drift. Run a CCV at least every 12 hours, and at the end of each batch. An LCS may serve the same purpose if the CCV DQOs are met.

Prescribed Elements

The following components of this method are mandatory:

Sample holding times must be adhered to. Samples analyzed beyond the stated holding time must be qualified.

Initial calibrations must be five points or more (four points in extenuating circumstances). Internal standards must be used for routinely conducted GC/MS tests.

All reported compounds must be represented in calibration standards.

Samples that exceed the calibration range must be diluted and re-analyzed or reported as estimated or minimum values.

All stated Performance Requirements and Quality Control requirements must be met.

Collection media must be equivalent in type to one of the references listed in Table 1 for each applicable analyte.

Active (pump-based) sampling must be used. Passive or diffusive samplers are generally only appropriate for industrial hygiene applications, where continued airflow above the sample media can be guaranteed.

Samples must be collected within the boundaries of referenceable or validated Safe Sampling Volumes and Flow Rates for the specific collection medium, or they must be sampled using two or more independent collection media in series (e.g. front and back sections of solid sorbent tubes), following the reporting guidelines described in the Reporting section.

Data must be qualified if samples have been collected beyond the boundaries of referenceable or validated Safe Sampling Volumes and Flow Rates for the specific collection medium. If the concentration of the parameter(s) of interest is sufficiently high, Safe Sampling Volumes and Flow Rates may be validated in the field using two or more independent collection media in series (e.g. front and back sections of sorbent tubes - see Safe Sampling Volumes section).

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

NIOSH Manual of Analytical Methods, National Institute for Occupational Health and Safety. http://www.cdc.gov/niosh/nmam/

OSHA Index of Sampling and Analytical Methods, Occupational Safety and Health Administration, US Dept. of Labor. http://www.osha.gov/dts/sltc/methods/toc_b.html

OSHA Chemical Sampling Information (CSI). Salt Lake Technical Center, Occupational Safety and Health Administration, US Dept. of Labor. http://www.osha.gov/dts/chemicalsampling/toc/toc_chemsamp.html

OSHA Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, Occupational Safety and Health Administration, US Dept. of Labor. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.html

US EPA Air Toxics Methods, Technology Transfer Network, Ambient Monitoring Technology Information Center.

http://www.epa.gov/ttnamti1/airtox.html

CARB 430, Ashland Modification. Ashland Specialty Chemical Company Modified Impinger Method for Acrolein in Air. http://www.arb.ca.gov/ei/acrolein/modified.doc

Revision History June 19, 2009: First draft of BC Lab Manual method.

Table 1: Method References & Physical Constants for VOCs and Other Volatile Substances by Miscellaneous Collection Media

Schedule 11 Substance	CAS #	BP (°C)	VP, 25C (Torr)	MW (g/mol)	Henry's Law atm-m³/mol	References for Charcoal Tube and Misc Collection Media*
acetaldehyde	75-07-0	20.1	902	44.05	6.7E-05	NIOSH 2018, 2538, 2539, EPA TO5/TO11
acetone	67-64-1	55.5	231	58.08	4.0E-05	NIOSH 1600, 1300, 2555; OSHA 69
acetone cyanohydrin	75-86-5	171	0.341	85.11	1.3E-05	NIOSH 2506
acetonitrile	75-05-8	59.6	88.8	41.05	3.4E-05	NIOSH 1606
acrolein (2-propenal)	107-02-8	52.6	274	56.06	1.2E-04	NIOSH 2501, 2539; OSHA 52, EPA TO5 / O11, CARB 430 (Ashland modification)
acrylonitrile (2-propenenitrile)	107-13-1	77.3	109	53.06	1.4E-04	NIOSH 1604
ammonia	7664-41-7	-33.3	7508	17.03	1.6E-05	NIOSH 6015, 6016
benzene	71-43-2	80	94.8	78.11	5.6E-03	NIOSH 1501, 1500
benzyl chloride (a-chlorotoluene)	100-44-7	179	1.23	126.59	4.1E-04	NIOSH 1003
bis(2-chloroethyl)ether	111-44-4	178.5	1.55	143.01	1.7E-05	NIOSH 1004 (VR)
bis(2-chloroisopropyl)ether	39638-32-9	124.9	12.6	171.07	3.3E-04	NIOSH 1004 (VR)
bis(2-chloromethyl)ether	542-88-1	106	29.4	114.96	2.1E-04	OSHA 10
bis(2-chloro-1-methylethyl)ether	108-60-1	187	0.56	171.07	1.1E-04	NIOSH 1004 (VR)
bromobenzene	108-86-1	156	4.18	157.01	2.7E-03	NIOSH 1003 (VR)
bromodichloromethane (BDCM)	75-27-4	90	57.4	163.83	2.1E-03	NIOSH 1003 (VR)
bromoform (tribromomethane)	75-25-2	149.1	5.4	252.73	2.2E-02	NIOSH 1003
bromomethane (methyl bromide)	74-83-9	3.5	1620	94.94	6.2E-03	NIOSH 2520
1,3-butadiene	106-99-0	-4.4	2110	54.09	7.4E-02	NIOSH 1024; OSHA 56
carbon disulfide	75-15-0	46	359	76.13	1.4E-02	NIOSH 1600
carbon tetrachloride (tetrachloromethane)	56-23-5	76.8	115	153.82	2.8E-02	NIOSH 1003
chlorine	7782-50-5	-34.0	5854	70.91	1.2E-02	OSHA ID101; NIOSH 6011
chlorobenzene (monochlorobenzene)	108-90-7	131.7	12	112.56	3.1E-03	NIOSH 1003
4-chlorobenzotrifluoride	98-56-6	138.5	7.63	180.56	3.5E-02	NIOSH 1026
2-chloro-1,3-butadiene	126-99-6	59.4	215	88.54	5.6E-02	NIOSH 1002; OSHA 112
1-chlorobutane	109-69-3	78.6	101	92.57	1.7E-02	NIOSH 1003 (VR)
1-chloro-1,1-difluoroethane (HCFC-142b)	75-68-3	-9.7	2540	100.5	5.9E-02	NIOSH 1026
chlorodifluoromethane	75-45-6	-40.7	7250	86.47	4.1E-02	NIOSH 1018, 1026
chloroethane (ethyl chloride)	75-00-3	12.3	1010	64.52	1.1E-02	NIOSH 2519
chloroform (trichloromethane)	67-66-3	61.1	197	119.38	3.7E-03	NIOSH 1003
chloromethane (methyl chloride)	74-87-3	-24	4300	50.49	8.8E-03	NIOSH 1001
4-chloronitrobenzene	100-00-5	242	0.022	157.55	4.9E-06	NIOSH 2005
2-chlorophenol	95-57-8	174.9	2.53	128.56	1.1E-05	NIOSH 2014
2-chloropropane	75-29-6	35.7	515	78.54	1.7E-02	NIOSH 1003 (VR)
3-chloropropene (allyl chloride)	107-05-1	45.1	368	76.53	1.1E-02	NIOSH 1000, 1002 (VR); OSHA 07
2-chlorotoluene	95-49-8	159	3.43	126.59	3.6E-03	NIOSH 1003 (VR)
crotonaldehyde	123-73-9	104	30	70.09	1.9E-05	EPA TO11; NIOSH 2539
cyanogen	460-19-5	-21.1	4300	52.04	5.3E-03	OSHA PV2104
cyanogen bromide	506-68-3	61.5	122	105.92	n/a	no reference methods (see cyanogen chloride)
cyanogen chloride	506-77-4	13	1230	61.47	1.9E-03	OSHA CSI

Table 1: Method References & Physical Constants for VOCs and Other Volatile Substances by Miscellaneous Collection Media

Schedule 11 Substance	CAS #	BP (°C)	VP, 25C (Torr)	MW (g/mol)	Henry's Law atm-m³/mol	References for Charcoal Tube and Misc Collection Media*
n-decane	124-18-5	174.1	1.32	142.29	4.7E+00	NIOSH 1500
1,4-dibromobenzene	106-37-6	220	0.0575	235.91	3.7E-02	NIOSH 1003 (VR)
1,2-dibromoethane (ethylene dibromide, EDB)	106-93-4	131.6	11.2	187.86	6.7E-04	NIOSH 1008
dibromochloromethane (DBCM)	124-48-1	120	15.6	208.28	3.2E-02	NIOSH 1003 (VR)
1,2-dibromo-3-chloropropane (DBCP)	96-12-8	196	0.58	236.33	6.0E-03	NIOSH 1003 (VR), OSHA CSI
dibromomethane (methylene bromide)	74-95-3	97	44.4	173.84	8.2E-04	NIOSH 1003 (VR)
1,2-dichlorobenzene	95-50-1	180	1.47	147.01	7.9E-02	NIOSH 1003
1,3-dichlorobenzene	541-73-1	173	2.15	147.01	2.6E-03	NIOSH 1003
1,4-dichlorobenzene	106-46-7	174	1.74	147.01	2.4E-03	NIOSH 1003
1,4-dichloro-2-butene, cis + trans	7364-41-0	152.5	4.09	125.00	8.5E-03	NIOSH 1003 (VR)
dichlorodifluoromethane (freon 12)	75-71-8	-29.8	4850	120.91	3.4E-01	NIOSH 2516
1,1-dichloroethane	75-34-3	57.4	227	98.96	5.6E-03	NIOSH 1003
1,2-dichloroethane	107-06-2	83.5	78.9	98.96	1.2E-03	NIOSH 1003
1,1-dichloroethene (1,1-dichloroethylene)	75-35-4	31.6	634	96.94	2.6E-02	NIOSH 1003
1,2-dichloroethene, cis (1,2-dichloroethylene, cis)	156-59-2	55	201	96.94	4.1E-03	NIOSH 1003
1,2-dichloroethene, trans (1,2-dichloroethylene, trans)	156-60-5	55	201	96.94	9.4E-03	NIOSH 1003
1,2-dichloropropane (propylene dichloride)	78-87-5	95.5	53.3	112.99	2.8E-03	NIOSH 1013
1,3-dichloropropane	142-28-9	120.9	18.2	112.99	9.8E-04	NIOSH 1013
1,3-dichloropropene (mixed isomers)	542-75-6	112	34	110.97	3.5E-03	NIOSH 1013
1,3-dichloropropene, cis	10061-01-5	112	34	110.97	3.5E-03	NIOSH 1013
1,3-dichloropropene, trans	10061-02-6	112	34	110.97	3.5E-03	NIOSH 1013
dicyclopentadiene	77-73-6	170	2.29	132.21	6.3E-02	OSHA PV 2098
diethyl ether (ethyl ether)	60-29-7	34.5	538	74.12	1.2E-03	NIOSH 1610
diisopropyl methylphosphonate (DIMP)	1445-75-6	209.8	0.277	180.19	4.4E-05	NIOSH 5600
dimethylamine	124-40-3	6.9	1520	45.08	9.1E-05	NIOSH 2010; OSHA 41
n,n-dimethylaniline	121-69-7	193.5	0.7	121.18	5.7E-05	NIOSH 2002; OSHA PV2064
epichlorohydrin (chloromethyl-ethylene oxide)	106-89-8	117	16.4	92.53	3.0E-05	NIOSH 1010
1,2-epoxybutane	106-88-7	63.3	180	72.11	1.8E-04	NIOSH 1612 (VR)
ethyl acetate	141-78-6	77.1	93.2	88.11	1.3E-04	NIOSH 1450, 1457
ethyl acrylate	140-88-5	99.4	38.6	100.12	3.4E-04	NIOSH 1450, 1457; OSHA 92
ethylbenzene	100-41-4	136.1	9.6	106.17	7.9E-03	NIOSH 1501
ethyl methacrylate (ethyl 2-methyl-2-propenoate)	97-63-2	117	20.6	114.15	5.7E-04	NIOSH 2537
ethylene oxide	75-21-8	10.6	1310	44.05	1.5E-04	OSHA 50; NIOSH 1614
furan	110-00-9	31.5	600	68.08	5.4E-03	NIOSH 1613 (VR)
1,3-hexachlorobutadiene	87-68-3	215	0.22	260.76	4.2E-01	NIOSH 2543
hexachlorocyclopentadiene	77-47-4	239	0.06	272.77	1.1E+00	NIOSH 2518, 2543
hexachloroethane	67-72-1	154.5	0.21	236.74	1.6E-01	NIOSH 1003
hexane (n-)	110-54-3	68.7	151	86.18	1.8E+00	NIOSH 1500

Table 1: Method References & Physical Constants for VOCs and Other Volatile Substances by Miscellaneous Collection Media

Schedule 11 Substance	CAS #	BP (°C)	VP, 25C (Torr)	MW (g/mol)	Henry's Law atm-m³/mol	References for Charcoal Tube and Misc Collection Media*
hydrogen cyanide (cyanide)	74-90-8	25.7	741.9	27.03	1.3E-04	NIOSH 6010, 6017, 7904
isopropylbenzene (cumene)	98-82-8	152.4	4.5	120.19	1.1E-02	NIOSH 1501
methacrylonitrile (2-methylprop-2-enenitrile)	126-98-7	90.3	71.2	67.09	2.5E-04	NIOSH 1604; OSHA 37
methyl acetate	79-20-9	92	216	74.08	1.1E-04	NIOSH 1450, 1457, 1458
methyl acrylate	96-33-3	80.2	86.6	86.09	2.0E-04	NIOSH 1457, 1459, 2552, 2537; OSHA 92
methylcyclohexane	108-87-2	100.9	46	98.19	4.3E-01	NIOSH 1500
methylene chloride (dichloromethane)	75-09-2	40	435	84.93	3.3E-03	NIOSH 1005
methyl ethyl ketone (2-butanone)	78-93-3	79.5	90.6	72.11	5.7E-05	NIOSH 1300, 2500, 2555; OSHA 84
methyl isobutyl ketone (4-methyl-2-pentanone)	108-10-1	116.5	19.9	100.16	1.4E-04	NIOSH 1300, 2555; OSHA 84
methyl mercaptan (methanethiol)	74-93-1	5.9	1510	48.11	3.1E-03	NIOSH 2542
methyl methacrylate	80-62-6	100.5	38.5	100.12	3.4E-04	NIOSH 2537
a-methylstyrene (1-methyl-1-phenylethylene)	98-83-9	165.4	1.9	118.18	2.5E-03	NIOSH 1501
methyl styrene, m+p (vinyl toluene, m+p)	25013-15-4	165.4	1.5	118.18	7.9E-03	NIOSH 1501
methyl tert-butyl ether (MTBE)	1634-04-4	55.2	250	88.15	5.9E-04	NIOSH 1615
naphthalene	91-20-3	217.9	0.085	128.18	4.4E-04	NIOSH 1501, 5515
nitrobenzene	98-95-3	210.8	0.245	123.11	2.4E-05	NIOSH 2005
2-nitrotoluene	88-72-2	222	0.188	137.14	5.1E-04	NIOSH 2005
phosphine	7803-51-2	-87.8	29300	34.00	2.4E-02	NIOSH 6002
propylene oxide	75-56-9	35	538	58.08	7.0E-05	NIOSH 1612
pyridine	110-86-1	115.2	20.6	79.10	1.1E-05	NIOSH 1613
styrene	100-42-5	145	6.4	104.15	2.7E-03	OSHA 89
1,1,1,2-tetrachloroethane	630-20-6	130.5	12	167.85	2.4E-03	NIOSH 1019 (VR)
1,1,2,2-tetrachloroethane	79-34-5	156.5	13.3	167.85	3.7E-04	NIOSH 1019
tetrachloroethylene (PCE, PERC)	127-18-4	121.3	18.5	165.83	1.8E-02	NIOSH 1003
tetrahydrofuran	109-99-9	66	162	72.11	7.1E-05	NIOSH 1609
toluene	108-88-3	110.6	28.4	92.14	6.6E-03	NIOSH 1501, 1500
1,2,4-trichlorobenzene	120-82-1	213.5	0.46	181.45	5.8E-02	NIOSH 5517
1,1,1-trichloroethane	71-55-6	74	124	133.41	1.7E-02	NIOSH 1003
1,1,2-trichloroethane	79-00-5	113.8	23	133.41	8.2E-04	NIOSH 1003
trichloroethylene (TCE)	79-01-6	87.2	69	131.39	9.9E-03	NIOSH 1003, 1022
1,1,2-trichloro-1,2,2-trifluoroethane (freon 113)	76-13-1	47.7	363	187.38	2.2E+01	NIOSH 1020
trichlorofluoromethane (freon 11)	75-69-4	23.7	803	137.37	9.7E-02	NIOSH 1006
1,1,2-trichloropropane	598-77-6	132	3.1	147.43	3.2E-04	NIOSH 1003
1,2,3-trichloropropane	96-18-4	157	3.69	147.43	3.4E-04	NIOSH 1003
1,2,3-trichloropropene	96-19-5	142	4.4	145.42	1.8E-02	NIOSH 1003 (VR)
a,a,a-trichlorotoluene (benzotrichloride)	98-07-7	220.6	0.414	195.48	0.0106	OSHA CSI, NIOSH 1003 (VR)
triethylamine	121-44-8	89	57.1	101.19	1.5E-04	OSHA PV2060; NIOSH 2010
1,2,4-trimethylbenzene	95-63-6	169.3	2.1	120.19	6.2E-03	NIOSH 1501
1,3,5-trimethylbenzene	108-67-8	164.7	2.1	120.19	8.8E-03	NIOSH 1501

Table 1: Method References & Physical Constants for VOCs and Other Volatile Substances by Miscellaneous Collection Media

Schedule 11 Substance	CAS #	BP (°C)	VP, 25C (Torr)	MW (g/mol)	Henry's Law atm-m³/mol	References for Charcoal Tube and Misc Collection Media*
vinyl acetate (ethenyl acetate)	108-05-4	72.5	90.2	86.09	5.1E-04	NIOSH 1453
vinyl bromide (bromoethene)	593-60-2	15.8	1030	106.95	1.2E-02	NIOSH 1009
vinyl chloride (chloroethene)	75-01-4	-13.3	2980	62.50	2.8E-02	NIOSH 1003, 1007
VHv_{6-13} / VPHv	n/a	n/a	n/a	n/a	n/a	NIOSH 1500/1501 + VHv and VPHv Lab Manual Methods
xylenes (o-xylene + m,p-xylenes)	1330-20-7	138.5	7.99	106.17	6.6E-03	NIOSH 1501

Notes:

VR Validation required. Technique may be appropriate for this substance. Reference method does not list this analyte but includes chemically similar compounds.

* Not all techniques will be sufficiently sensitive to meet the lowest Schedule 11 numerical vapour standards.

Table 2: Reference Method Summaries for VOCs and Other Volatile Substances by Miscellaneous Collection Media				
Reference Method	**Method Title**	**Media / Description**	**Analysis**	**Referenced Stability**
NIOSH 1000	Allyl Chloride	Charcoal, coconut shell; benzene desorption (30 min)	GC/FID**	>6 weeks / 25°C
NIOSH 1001	Methyl Chloride	Charcoal, coconut shell; DCM desorption	GC/FID**	>7 days / 25°C
NIOSH 1002	Beta-Chloroprene	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	>8 days / 25°C
NIOSH 1003	Hydrocarbons, Halogenated	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	30 days
NIOSH 1004	Dichloroethyl Ether	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	>7 days / 25°C
NIOSH 1005	Methylene Chloride	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	30 days / 5°C
NIOSH 1006	Fluorotrichloromethane	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	8 days / 4°C
NIOSH 1007	Vinyl Chloride	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	10 days / 25°C
NIOSH 1008	Ethylene Dibromide	Charcoal, coconut shell; desorption with 99:1 v/v benzene/methanol (1 hr)	GC/ECD	2 weeks / -25°C
NIOSH 1009	Vinyl Bromide	Charcoal, coconut shell; Ethanol desorption (ultrasonic, 30 min)	GC/FID**	>14 days / 25°C
NIOSH 1010	Epichlorohydrin	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	>14 days / 25°C
NIOSH 1013	Propylene Dichloride	Charcoal, petroleum; desorption with 15% (v/v) acetone in cyclohexane (ultrasonic, 30 min)	GC/ELCD (HALL)	>26 days / 25°C
NIOSH 1018	Dichlorodifluoromethane	Charcoal, coconut shell; DCM desorption	GC/FID**	>7 days / -10°C
NIOSH 1019	1,1,2,2-Tetrachloroethane	Charcoal, petroleum; CS_2 desorption (30 min)	GC/FID**	not determined
NIOSH 1020	1,1,2-Trichloro-1,2,2-Trifluoroethane	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	not determined
NIOSH 1022	Trichloroethylene	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	not determined
NIOSH 1024	1,3-Butadiene	Charcoal, coconut shell; DCM desorption (30 min)	GC/FID**	>2 mths / -4°C
NIOSH 1026	p-Chlorobenzotrifluoride	Charcoal, coconut shell; desorption with 99:1 (v/v) CS_2:methanol (30 min)	GC/FID**	7 days @ 25°C 30 days @ 5°C
NIOSH 1300	Ketones I	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	not determined
NIOSH 1450	Esters I	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	>30 days @ 4°C
NIOSH 1453	Vinyl Acetate	Carbon molecular sieve (ORBO-92 or equiv); desorption with 95:5 DCM:methanol (30 min)	GC/FID**	>30 days @ 5°C
NIOSH 1457	Ethyl Acetate	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	6 days @ 5°C
NIOSH 1458	Methyl Acetate	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	>6 days @ 5°C
NIOSH 1459	Methyl Acrylate	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	not determined
NIOSH 1500	Hydrocarbons, BP 36°-216°C	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	30 days @ 4°C
NIOSH 1501	Hydrocarbons, Aromatic	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	30 days @ 4°C
NIOSH 1600	Carbon Disulfide	Charcoal, coconut shell + drying tube (sodium sulfate); toluene desorption (30 min)	GC/Sulfur FPD	1 week @ 25°C 6 weeks @ 0°C
NIOSH 1604	Acrylonitrile	Charcoal, coconut shell; desorption with 2% acetone in CS_2 (30 min)	GC/FID**	>7 days @ 25°C
NIOSH 1606	Acetonitrile	Charcoal, coconut shell; desorption with 85:15 (v/v) DCM:methanol (45 min)	GC/FID**	>30 days @ 5°C

Table 2: Reference Method Summaries for VOCs and Other Volatile Substances by Miscellaneous Collection Media				
Reference Method	**Method Title**	**Media / Description**	**Analysis**	**Referenced Stability**
NIOSH 1609	Tetrahydrofuran	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	not determined
NIOSH 1610	Ethyl Ether	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	14 days @ 5°C
NIOSH 1612	Propylene Oxide	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	not determined
NIOSH 1613	Pyridine	Charcoal, coconut shell; DCM desorption (30 min)	GC/FID**	not determined
NIOSH 1614	Ethylene Oxide	Charcoal, petroleum, HBr-coated; DMF desorption (5 min)	GC/ECD	>17 days @ 25C
NIOSH 1615	Methyl tert-Butyl Ether	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	>5 days @ 25°C 3 weeks @ -7°C
NIOSH 2002	Amines, Aromatic	Silica gel; desorption with 95% ethanol, non-denatured (ultrasonic, 1 hour)	GC/FID**	>7 days (see method)
NIOSH 2005	Nitroaromatic Compounds	Silica gel; methanol desorption (ultrasonic, 30 min)	GC/FID**	30 days @ 5°C
NIOSH 2010	Amines, Aliphatic	Silica gel; desorption with 0.1M H_2SO4 in 10% (v/v) aqueous methanol (3 hours)	GC/FID**	not determined
NIOSH 2014	p-Chlorophenol	Silica gel; acetonitrile desorption (30 min)	HPLC/UV	7 days @ 25°C >29 days @ 0°C
NIOSH 2018	Aliphatic Aldehydes	Silica gel, coated with acidified DNPH, desorption with carbonyl-free acetonitile	HPLC/UV	>30 days @ 5°C
NIOSH 2500	Methyl Ethyl Ketone	Carbon, beaded; CS_2 desorption (30 min)	GC/FID**	>90 days @ -5°C
NIOSH 2501	Acrolein	2-HMP on XAD-2 (Supelco ORBO-23 or equiv); toluene desorption (ultrasonic, 30 min)	GC/NPD	>4 weeks @ 25°C
NIOSH 2506	Acetone Cyanohydrin	Poropak QS; ethyl acetate desorption (ultrasonic, 60 min)	GC/NPD	>5 days @ 0°C
NIOSH 2516	Dichlorofluoromethane	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	>7 days @ 25°C
NIOSH 2518	Hexachloro-1,3-cyclopentadiene	Poropak T; hexane desorption (ultrasonic, 1 hour)	GC/ECD	>7 days @ 25°C >28 days @ 0°C
NIOSH 2519	Ethyl Chloride	Charcoal, coconut shell; CS_2 desorption (30 min)	GC/FID**	>7 days @ 25°C
NIOSH 2520	Methyl Bromide	Charcoal, petroleum; DCM desorption (30 min)	GC/AED	6 days @ -10°C
NIOSH 2537	Methyl and Ethyl Methacrylate	XAD-2; CS_2 desorption (ultrasonic, 30 min)	GC/FID**	7 days @ 20°C 31 days @ 5°C
NIOSH 2538	Acetaldehyde by GC	2-HMP on XAD-2 (Supelco ORBO-25 or equiv); toluene desorption (ultrasonic, 60 min)	GC/FID**	>21 days @ 0°C
NIOSH 2539	Aldehydes, Screening	10% 2-HMP on XAD-2 (Supelco ORBO-23 or equiv); toluene desorption (ultrasonic, 60 min)	GC/FID** & GC/MS	>7 days @ 25°C
NIOSH 2542	Mercaptans, Methyl-, Ethyl-, and n-Butyl-	Filter, 37mm glass fiber, impregnated with mercuric acetate; desorption with 25% HCl and 1,2-dichloroethane (separatory funnel, 2 min)	GC/Sulfur FPD	>3 weeks @ 25°C
NIOSH 2543	Hexachlorobutadiene	XAD-2; hexane desorption (ultrasonic, 1 hour)	GC/ECD	7 days @ 25°C 28 days @ 0°C
NIOSH 2552	Methyl Acrylate	Anasorb Carbon Molecular Sieve; CS_2 desorption (30 min)	GC/FID**	30 days @ 5°C
NIOSH 2555	Ketones I	Anasorb Carbon Molecular Sieve; CS_2 desorption (30 min)	GC/FID**	30 days @ 5°C
NIOSH 5515	Polynuclear Aromatic Hydrocarbons by GC	PTFE Filter + XAD-2, desorb with appropriate solvent (refer to method)	GC/FID**	not determined
NIOSH 5517	Polychlorobenzenes	PTFE Filter + XAD-2, desorb with appropriate solvent (refer to method)	GC/ECD	>13 days @ 25°C

Table 2: Reference Method Summaries for VOCs and Other Volatile Substances by Miscellaneous Collection Media

Reference Method	Method Title	Media / Description	Analysis	Referenced Stability
NIOSH 5600	Organophosphorus Pesticides	Quartz Filter + XAD-2 (OVS-2), desorption with 90:10 (v/v) toluene:acetone (ultrasonic, 30 min)	GC/FPD	>10 days @ 25°C >30days @ 0°C
NIOSH 6002	Phosphine	Silica gel, coated with $Hg(CN)_2$; desorption with hot acidic permanganate reagent solution (see method)	UV-VIS	7 days @ 25°C
NIOSH 6010	Hydrogen Cyanide	Soda lime sorbent tube; desorption with deionized water (60 min)	UV-VIS	>2 weeks @ 25°C
NIOSH 6011	Chlorine and Bromine	PTFE pre-filter (0.5um) + silver membrane filter (25mm, 0.45um); desorption in darkness with 6mM $Na_2S_2O_3$ (10 min)	IC-Conductivity	>30 days @ 25°C
NIOSH 6015	Ammonia	Silica gel, sulfuric acid treated; desorption with deionized water (45 min)	UV-VIS	See NIOSH 6016
NIOSH 6016	Ammonia	Silica gel, sulfuric acid treated; desorption with deionized water (45 min)	IC-Conductivity	>35 days @ 5°C
NIOSH 6017	Hydrogen Cyanide	Soda lime sorbent tube + glass fiber filter; desorption with deionized water (60 min)	IC-DC Amperometry	>2 weeks @ 25°C
NIOSH 7904	Cyanides, aerosol and gas	Filter + Bubbler, PVC membrane filter + 0.1N KOH; desorption of filter with 0.1N KOH (30 min)	Ion Specific Electrode	5 days
OSHA 07	Organic Vapors	Charcoal, coconut shell; CS_2 desorption (alternate solvents listed by analyte in OSHA CSI)	GC/FID**	not specified
OSHA 10	Chloromethyl Methyl Ether, bis-Chloromethyl Ether	2 fritted glass bubblers in series, each containing sodium methoxide derivatizing reagent; derivatives are extracted with hexane.	GC/ECD	>15 days @ 22°C
OSHA 37	Acrylonitrile	Charcoal, coconut shell; acetone desorption (1 hour)	GC/NPD	>15 days @ 22°C
OSHA 41	Diethylamine	XAD-7 coated with 10% NBD chloride; desorption with 5% (w/v) NBD chloride in tetrahydrofuran with sodium bicarbonate (2.5 hours @ 60°C)	HPLC-Fluorescence or Visible	>15 days @ 22°C >15 days @ 0°C
OSHA 50	Ethylene Oxide	Charcoal, petroleum, coated with 24% HBr; DMF desorption (5 min), HFBI derivatization	GC/ECD	>17 days @ 22°C >17 days @ 5°C
OSHA 52	Acrolein and/or Formaldehyde	10% 2-HMP on XAD-2; toluene desorption (1 hour)	GC/NPD	>19 days @ 22°C >15 days @ -20°C
OSHA 56	1,3-Butadiene	Charcoal, coconut, coated with 4-tert-butylcatechol; CS_2 desorption (1 hour)	GC/FID**	17 days @ 22°C >18 days @ -25°C
OSHA 69	Acetone	Carbosieve S-III molecular sieve; desorption with 1% DMF in CS_2 with magnesium sulfate (mechanical shaker, 15 min)	GC/FID**	>17 days @ 22°C >17 days @ 5°C
OSHA 84	2-Butanone	Carbosieve S-III molecular sieve; desorption with 1% DMF in CS_2 with sodium sulfate (30 min)	GC/FID**	>17 days @ 22°C >17 days @ -20°C
OSHA 89	Divinylbenzene, Ethylvinylbenzene, Styrene	Charcoal, coconut, coated with 4-tert-butylcatechol; toluene desorption (30 min)	GC/FID**	>17 days @ 22°C >17 days @ -20°C
OSHA 92	Ethyl Acrylate, Methyl Acrylate	Charcoal, coconut, coated with 4-tert-butylcatechol; CS_2 desorption (30 min)	GC/FID**	>16 days @ 22°C >16 days @ 12°C
OSHA 112	Beta Chloroprene	Chromosorb 106; toluene desorption	GC/ECD	>15 days @ 22°C >15 days @ 5°C
OSHA CSI	Benzotrichloride (OSHA in-house, not validated)	Tenax GC tube; carbon tetrachloride desorption	GC/FID**	not determined
OSHA CSI	Cyanogen chloride (OSHA in-house, not validated)	XAD-2 coated with 2-HMP; toluene desorption	GC/NPD	not determined
OSHA CSI	12-Dibromo-3-chloro-propane (OSHA in-house, partially validated)	Charcoal, petroleum	GC/ECD	not determined

Table 2: Reference Method Summaries for VOCs and Other Volatile Substances by Miscellaneous Collection Media				
Reference Method	**Method Title**	**Media / Description**	**Analysis**	**Referenced Stability**
OSHA ID101	Chlorine in Workplace Atmospheres	Fritted glass bubbler containing 0.1% sulfamic acid solution; aliquot of solution is added to buffered potassium iodide	Residual Chlorine ISE	>30 days @ 22°C (in darkness)
OSHA PV2060	Triethylamine (Partially Validated)	XAD-7 coated with 10% phosphoric acid; desorption with 1:1 methanol:deionized water (30 min)	GC/FID**	>14 days @ 22°C
OSHA PV2064	N,N-Dimethylaniline (Partially Validated)	XAD-7 coated with 10% phosphoric acid; desorption with 0.2N ammonium hydroxide	GC/FID or GC/MS	>14 days @ 22°C >14 days @ 5°C
OSHA PV2104	Cyanogen (Partially Validated)	XAD-2 coated with 2-HMP; toluene desorption [note: cyanogen reacts with water to form HCN and cyanate].	GC/NPD	>13 days @ 22°C
EPA TO5	Method for the Determination of Aldehydes and Ketones in Ambient Air using HPLC	Midget impinger sampler with 10 mL 2N HCl / 0.05% DNPH / 10 mL iso-octane. Aqueous layer is extracted with 70:30 hexane:DCM, which is combined with the iso-octane phase.	HPLC-UV	not determined
EPA TO11	Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by HPLC	Silica gel cartridge coated with DNPH, with ozone scrubber (KI denuder); acetonitrile desorption	HPLC-UV	2 weeks @ 4°C
CARB 430 (Ashland modification)	Ashland Specialty Chemical Company Modified Impinger Method for Acrolein in Air	3 midget impingers in series, each containing 10 mL deionized water, 2 mL toluene, and 2 mL DNPH-HCl acidic solution. Analyze toluene layer.	GC-NPD	>2 weeks @ 22°C

** Reference method utilizes GC/FID. GC/MS is recommended for additional sensitivity and selectivity. GC/FID is appropriate only where necessary detection limits can be met, and in the absence of interferences.

Volatile Organic Compounds in Air by Thermal Desorption Tube / GCMS — PBM

Parameter

Volatile Organic Compounds (VOCs) in air.

Analytical Method

Thermal desorption tube sampling, GC/MS analysis (GC/FID optional for VHv_{6-13}).

Introduction

This method is applicable to the quantitative determination of volatile organic compounds in air, when appropriately sampled and collected in suitable thermal desorption tubes.

Method Summary

Ambient air or soil gas samples are collected by introduction of air onto a multi-bed thermal desorption (TD) tube using a calibrated sampling pump. Samples are collected at a fixed pump flow rate (i.e. 10-200mL/min) for a pre-determined duration.

Thermal desorption tubes may be analyzed by GC/MS either by direct thermal desorption, or after being pre-focused on a secondary cryogenic or adsorbent trap. Samples are then introduced to the GC/MS by thermal desorption.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

Parameter Applicability, MDLs

The Appendix to this method lists parameters from Schedule 11 of the BC CSR for which this method may be applied. For these parameters, the Appendix lists the following physical properties and information:

- CAS# (Chemical Abstract Services number).
- Boiling Point (°C).
- Vapour Pressure at 25°C.
- Molecular Weight (grams / mole).
- Applicability notes regarding this method. Satisfactory performance using this method has not been verified for all listed compounds. Some parameters may require the use of alternative techniques.
- MDLs are not listed for each compound. Most discrete compounds amenable to this method can be determined to an approximate MDL of 1 ug/m³, sometimes lower in Selected Ion Monitoring (SIM) mode. Sensitivity is affected by instrument configuration choices. Laboratory MDLs for this method are expressed in absolute amount units (e.g. ug), so air concentration MDLs are a function of sampling volume.

Where appropriate, the method may be used for other compounds not listed in the Appendix if performance requirements and Quality Control requirements can be met.

Matrix

Air (ambient)
Soil Gas

Interferences and Precautions

Interferences may result from residual contaminants in TD tubes, or from the laboratory's sample introduction system. The entire system must be monitored daily using Method Blanks and must be demonstrated to be free of interferences under the conditions of the analysis.

Breakthrough (caused by high concentration of analyte(s) or excess sample volume) and high humidity during sampling can result in a low bias for the analytes of interest. The sampler must have a good understanding of the site conditions and required criteria level to keep the amount of air sampled to a minimum. Good communication between the sampler and laboratory is important to ensure the TD tubes are handled in accordance with the sampling conditions (i.e., tubes are pre-purged with nitrogen to reduce interference from sample moisture).

Sample Handling and Preservation

Container: Samples are collected in specially prepared multi-bed thermal desorption tubes. The adsorbent material(s) in the tube may be specifically tailored to the types of compounds expected at the site. The optimal volume of air sample required is 1-10L (or more), depending on the detection limits required to achieve the regulatory limits, safe sampling volumes specific to the analyte and adsorbent material, as well as the humidity of the sampling environment.

Preservation: None required.

Stability

Holding Time: VOCs collected on TD tubes may be stored up to 30 days before instrumental analysis.

Storage: Store at ≤10°C during transport, and ≤ 6°C at the laboratory.

Media Preparation

Rigorous TD tube pre-cleaning, tracking, and proofing protocols are essential to the application of this method. Note that the high temperature (> 300C) bake cycle of the thermal desorber is normally sufficient to remove residual contaminants. Refer to Method TO17 for recommended cleaning and batch-proofing protocols.

The precise usage history of every TD tube must be recorded to provide audit trail in the event of suspected sample contamination.

Sampling Procedure

Detailed field sampling guidelines are beyond the scope of this method. For more information, please refer to Method TO17, and to the BC SAB document "Guidance on Site Characterization for Evaluation of Soil Vapour Intrusion Into Buildings".

Samplers should consult the laboratory for recommended maximum sampling flow rates and Safe Sampling Volumes (SSVs) for the applicable analytes and collection media, where known. This information may originate either from published reference information, or from laboratory or field validation studies (see Performance Requirements).

When sampling is undertaken outside the boundaries of referenced or validated maximum flow rates and/or SSVs, samples must be collected using two thermal desorption tubes in series, to permit evaluation of breakthrough and to verify effective sample collection.

Consensus among sampling experts is that soil gas samples should be collected at flow rates not exceeding 200 mL/min, to permit sufficient recharge and to help prevent short-circuiting.

The intent of this method is to sample vapours as opposed to particulate-bound VOCs. At sampling locations where particulate sources of target analytes in air are likely, a non-adsorptive pre-filter may be used to exclude particulates. Analyte specific procedures may offer more guidance.

Analysis Procedure

Instrumental Analysis: Detailed instrumental procedures are not provided in this method. Refer to the EPA Compendium Method TO15 and TO17 for detailed guidance on instrumental analysis.

The method recommends the use of either cryogenic or adsorbent based analyte trapping/focusing techniques, but neither is required if adequate resolution and sensitivity of the target VOCs can be achieved. GC/MS must be used for target compound analysis. Selective ion monitoring (SIM) mode may be utilized where necessary to achieve lower detection limits. In SIM mode, one quantitation ion and two qualifier ions per analyte should be monitored. GC/FID may be used for VHv_{6-13}.

For target compounds, a five-point initial calibration over the desired working range is required (four-point minimum in extenuating circumstances). Calibration standards must be introduced to TD tubes in the gas phase (gas phase standards may be generated by evaporation at time of use, e.g. using gas bombs or a GC inlet or similar device). Only calibrated parameters may be reported under this method; it is not intended for semi-quantitative applications.

The use of internal standards is required, unless sample interferences preclude accurate assessment of internal standard areas. Internal standards must not introduce significant interferences on test analytes or surrogates. Internal standard areas must be monitored throughout each run and should not vary by more than +/-50% from the last calibration or CCV.

According to EPA TO-17, thermal desorption analysis techniques may be suitable for the analysis of most compounds that are less volatile than eicosane (nC20; BP 343C, Vapour Pressure 4.6E-6 Torr @ 25C). The actual volatility limit of any TD analytical system will depend on the characteristics of the media employed and the temperatures and inertness of the sample flow pathway.

Reporting: Labs must clearly specify the units of reported air concentrations. Recommended reporting units for CSR purposes are ug/m³.

If two independent TD tubes are collected in series for a single sample, laboratories should report results for each tube separately. Where the amount on the back section is < 25% of the front section, data users should be advised to sum the two results. Where the amount on the back section is ≥ 25% of the front section (for any given compound), the tube is considered to have been saturated, and results should be qualified (e.g. report as minimum values).

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 Lab Control Samples must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations

(performance reviews) should assess QC data encompassing longer timeframes (e.g. 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Average accuracy must be between 80-120% for all routinely reported parameters.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of Lab Control Samples at concentrations above ten times the MDL. Precision must be ≤ 20% relative standard deviation (%RSD) for all routinely reported parameters.

Where the laboratory's method does not meet these accuracy or precision requirements for specific parameters, the method may still be used, but reports must indicate that results are semi-quantitative or qualitative, and the established performance should be provided.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Safe Sampling Volumes (SSVs): All adsorbent media have a finite capacity. Where known, SSVs must not be exceeded. For a given analyte / media combination, SSVs are a function of analyte concentration, sampling flow rate, and air humidity, among other factors. If referenceable SSV information is not readily available for the analytes being tested on the selected media, then SSVs must be validated in the laboratory, or in the field. The following test is recommended:

Place two sample thermal desorption tubes in series. Introduce known amounts of high concentration gas phase VOC standard(s) onto the first tube. If practical, the spiked concentration should be > 200 times the MDL, but must be at least 20 times the MDL. Then pass a volume of inert humidified air or nitrogen through both sections, equal to the desired maximum sampling volume. Introduce ~60-80% humidified air or nitrogen at the maximum sampling flow rate to be validated. A dynamic humidified air or nitrogen stream may be generated using an impinger/bubbler.

If the amount of spiked analyte detected on the 2nd media section is less than 1% of the amount on the 1st media section, then the air volume tested may be considered to be below the SSV for the analyte in question, at the evaluated flow rate. If the amount of spiked analyte detected on the 2nd media section is between 1-5% of the amount on the 1st media section, calculate the SSV as 2/3 of the sampling volume used (EPA TO17). Repeat the study with a lower sampling volume and/or lower flow rate if breakthrough exceeds 5%.

In the absence of laboratory validated data, a field test may be used to assess breakthrough, if sample concentrations are sufficiently high (i.e. > 20x

the laboratory's MDL). Collect samples with two thermal desorption tubes in series, and follow the same principles as above.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Internal Standard Area Checks	All samples and QC	Within 50% of initial calibration or last CCV.
Method Blank (MB)	1 per batch (max 20 samples)	Less than reported DL
Field Blank (FB)	Recommended	Less than reported DL
Lab Control Sample (LCS) / Calibration Verification Standard (CVS)	1 per batch (max 20 samples)	60-140% recovery
Lab Duplicates	≥ 5%	≤ 40% RPD
Field Duplicates	Recommended	Not specified
Continuing Calibration Verification (CCV)	At least every 24 hours (max 20 samples), and at end of each batch.	70-130% recovery for mid-level standards.

* Minimum DQOs apply to individual QC samples, not averages, at levels above 10x MDL. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

QC Details

Method Blank: Method Blanks must be prepared from randomly selected TD tubes. Use of dedicated TD tubes for Method Blanks is not permitted.

Field Blank: Recommended. May constitute a blank collection medium that is opened and handled in the field.

Lab Duplicates: Recommended. This can only be accomplished with systems equipped with sample recollection capability.

Field Duplicates: Recommended. This is normally accomplished by sampling TD tubes in parallel (distributed volume pairs). Determine suitable frequencies in consultation with clients.

Laboratory Control Sample (LCS) / Calibration Verification Standard (CVS): A second source must be utilized for the LCS/CVS to confirm the integrity of the calibration standards and the accuracy of the calibration. All calibrated and reported parameters must be included in the LCS / CVS.

Continuing Calibration Verification (CCV): Calibration standards (typically a mid-point standard, e.g. 100ng) must be re-analyzed periodically throughout the instrument run to monitor calibration drift. Run a CCV at least every 24 hours (maximum 20 samples), and at the end of each batch. An LCS may serve the same purpose if the CCV DQOs are met.

Prescribed Elements

The following components of this method are mandatory:

a) Sample holding times must be adhered to. Samples analyzed beyond the stated holding time must be qualified.

b) All target compound analysis must be by GC/MS.

c) Initial GC/MS calibrations must be five points or more (four-point minimum in extenuating circumstances). Internal standards must be used. Continuing calibrations may be employed while Calibration Verification Standards meet acceptance criteria for all reported compounds.

d) Calibration standards must be introduced onto blank TD tubes in the gas phase. All reported compounds must be represented in calibration standards.

e) Samples that exceed the calibration range must be diluted and re-analyzed, or reported as estimated or minimum values.

f) Usage history of each TD tube must be recorded to enable tracking of suspected contamination.

g) All TD tubes must be batch proofed prior to use.

h) All stated Performance Requirements and Quality Control requirements must be met.

i) This method may not be utilized for analysis of compounds listed as not appropriate by this technique in the table that follows.

j) Data must be qualified if samples have been collected beyond the boundaries of referenceable or validated Safe Sampling Volumes and Flow Rates for the specific collection medium. If the concentration of the parameter(s) of interest is sufficiently high, Safe Sampling Volumes and Flow Rates may be validated in the field using two or more TD tubes in series (see Safe Sampling Volumes section).

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

i) Method TO-15, Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters And Analyzed by Gas Chromatography / Mass Spectrometry (GC/MS), from the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Center for Environmental Research Information, Office of Research and Development, US EPA, Cincinnati, OH, January 1999.

ii) Method TO-17, Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Active Sampling onto Sorbent Tubes with Subsequent Analysis By Gas Chromatography, from the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Center for Environmental Research Information, Office of Research and Development, US EPA, Cincinnati, OH, January 1999.

Revision History

June 19, 2009: First draft of BC Lab Manual method.

Table 1: VOCs in Air by Thermal Desorption: Method Applicability & Physical Constants						
Schedule 11 Substance	**CAS #**	**BP (°C)**	**VP, 25C (Torr)**	**MW (g/mol)**	**Henry's Law atm-m³/mol**	**Method Applicability**
acetaldehyde	75-07-0	20.1	902	44.05	6.7E-05	✓
acetone	67-64-1	55.5	231	58.08	4.0E-05	✓
acetone cyanohydrin	75-86-5	171	0.341	85.11	1.3E-05	VR
acetonitrile	75-05-8	59.6	88.8	41.05	3.4E-05	✓
acrolein (2-propenal)	107-02-8	52.6	274	56.06	1.2E-04	✓
acrylonitrile (2-propenenitrile)	107-13-1	77.3	109	53.06	1.4E-04	✓
ammonia	7664-41-7	-33.3	7508	17.03	1.6E-05	X
benzene	71-43-2	80	94.8	78.11	5.6E-03	✓
benzyl chloride (a-chlorotoluene)	100-44-7	179	1.23	126.59	4.1E-04	✓
bis(2-chloroethyl)ether	111-44-4	178.5	1.55	143.01	1.7E-05	✓
bis(2-chloroisopropyl)ether	39638-32-9	124.9	12.6	171.07	3.3E-04	✓
bis(2-chloromethyl)ether	542-88-1	106	29.4	114.96	2.1E-04	✓
bis(2-chloro-1-methylethyl)ether	108-60-1	187	0.56	171.07	1.1E-04	✓
bromobenzene	108-86-1	156	4.18	157.01	2.7E-03	✓
bromodichloromethane (BDCM)	75-27-4	90	57.4	163.83	2.1E-03	✓
bromoform (tribromomethane)	75-25-2	149.1	5.4	252.73	2.2E-02	✓
bromomethane (methyl bromide)	74-83-9	3.5	1620	94.94	6.2E-03	✓
1,3-butadiene	106-99-0	-4.4	2110	54.09	7.4E-02	✓
carbon disulfide	75-15-0	46	359	76.13	1.4E-02	✓
carbon tetrachloride (tetrachloromethane)	56-23-5	76.8	115	153.82	2.8E-02	✓
chlorine	7782-50-5	-34.0	5854	70.91	1.2E-02	X
chlorobenzene (monochlorobenzene)	108-90-7	131.7	12	112.56	3.1E-03	✓
4-chlorobenzotrifluoride	98-56-6	138.5	7.63	180.56	3.5E-02	✓
2-chloro-1,3-butadiene	126-99-6	59.4	215	88.54	5.6E-02	✓
1-chlorobutane	109-69-3	78.6	101	92.57	1.7E-02	✓
1-chloro-1,1-difluoroethane (HCFC-142b)	75-68-3	-9.7	2540	100.5	5.9E-02	✓
chlorodifluoromethane	75-45-6	-40.7	7250	86.47	4.1E-02	✓
chloroethane (ethyl chloride)	75-00-3	12.3	1010	64.52	1.1E-02	✓
chloroform (trichloromethane)	67-66-3	61.1	197	119.38	3.7E-03	✓
chloromethane (methyl chloride)	74-87-3	-24	4300	50.49	8.8E-03	✓
4-chloronitrobenzene	100-00-5	242	0.022	157.55	4.9E-06	✓
2-chlorophenol	95-57-8	174.9	2.53	128.56	1.1E-05	✓
2-chloropropane	75-29-6	35.7	515	78.54	1.7E-02	✓
3-chloropropene (allyl chloride)	107-05-1	45.1	368	76.53	1.1E-02	✓
2-chlorotoluene	95-49-8	159	3.43	126.59	3.6E-03	✓
crotonaldehyde	123-73-9	104	30	70.09	1.9E-05	✓
cyanogen	460-19-5	-21.1	4300	52.04	5.3E-03	✓
cyanogen bromide	506-68-3	61.5	122	105.92	n/a	✓
cyanogen chloride	506-77-4	13	1230	61.47	1.9E-03	✓
n-decane	124-18-5	174.1	1.32	142.29	4.7E+00	✓
1,4-dibromobenzene	106-37-6	220	0.0575	235.91	3.7E-02	✓
1,2-dibromoethane (ethylene dibromide, EDB)	106-93-4	131.6	11.2	187.86	6.7E-04	✓
dibromochloromethane (DBCM)	124-48-1	120	15.6	208.28	3.2E-02	✓
1,2-dibromo-3-chloropropane (DBCP)	96-12-8	196	0.58	236.33	6.0E-03	✓
dibromomethane (methylene bromide)	74-95-3	97	44.4	173.84	8.2E-04	✓

Table 1: VOCs in Air by Thermal Desorption: Method Applicability & Physical Constants						
Schedule 11 Substance	**CAS #**	**BP (°C)**	**VP, 25C (Torr)**	**MW (g/mol)**	**Henry's Law atm-m³/mol**	**Method Applicability**
1,2-dichlorobenzene	95-50-1	180	1.47	147.01	7.9E-02	✓
1,3-dichlorobenzene	541-73-1	173	2.15	147.01	2.6E-03	✓
1,4-dichlorobenzene	106-46-7	174	1.74	147.01	2.4E-03	✓
1,4-dichloro-2-butene, cis + trans	7364-41-0	152.5	4.09	125.00	8.5E-03	✓
dichlorodifluoromethane (freon 12)	75-71-8	-29.8	4850	120.91	3.4E-01	✓
1,1-dichloroethane	75-34-3	57.4	227	98.96	5.6E-03	✓
1,2-dichloroethane	107-06-2	83.5	78.9	98.96	1.2E-03	✓
1,1-dichloroethene (1,1-dichloroethylene)	75-35-4	31.6	634	96.94	2.6E-02	✓
1,2-dichloroethene, cis (1,2-dichloroethylene, cis)	156-59-2	55	201	96.94	4.1E-03	✓
1,2-dichloroethene, trans (1,2-dichloroethylene, trans)	156-60-5	55	201	96.94	9.4E-03	✓
1,2-dichloropropane (propylene dichloride)	78-87-5	95.5	53.3	112.99	2.8E-03	✓
1,3-dichloropropane	142-28-9	120.9	18.2	112.99	9.8E-04	✓
1,3-dichloropropene (mixed isomers)	542-75-6	112	34	110.97	3.5E-03	✓
1,3-dichloropropene, cis	10061-01-5	112	34	110.97	3.5E-03	✓
1,3-dichloropropene, trans	10061-02-6	112	34	110.97	3.5E-03	✓
dicyclopentadiene	77-73-6	170	2.29	132.21	6.3E-02	✓
diethyl ether (ethyl ether)	60-29-7	34.5	538	74.12	1.2E-03	✓
diisopropyl methylphosphonate (DIMP)	1445-75-6	209.8	0.277	180.19	4.4E-05	✓
dimethylamine	124-40-3	6.9	1520	45.08	9.1E-05	✓
n,n-dimethylaniline	121-69-7	193.5	0.7	121.18	5.7E-05	✓
epichlorohydrin (chloromethyl-ethylene oxide)	106-89-8	117	16.4	92.53	3.0E-05	✓
1,2-epoxybutane	106-88-7	63.3	180	72.11	1.8E-04	✓
ethyl acetate	141-78-6	77.1	93.2	88.11	1.3E-04	✓
ethyl acrylate	140-88-5	99.4	38.6	100.12	3.4E-04	✓
ethylbenzene	100-41-4	136.1	9.6	106.17	7.9E-03	✓
ethyl methacrylate (ethyl 2-methyl-2-propenoate)	97-63-2	117	20.6	114.15	5.7E-04	✓
ethylene oxide	75-21-8	10.6	1310	44.05	1.5E-04	✓
furan	110-00-9	31.5	600	68.08	5.4E-03	✓
1,3-hexachlorobutadiene	87-68-3	215	0.22	260.76	4.2E-01	✓
hexachlorocyclopentadiene	77-47-4	239	0.06	272.77	1.1E+00	✓
hexachloroethane	67-72-1	154.5	0.21	236.74	1.6E-01	✓
hexane (n-)	110-54-3	68.7	151	86.18	1.8E+00	✓
hydrogen cyanide (cyanide)	74-90-8	25.7	741.9	27.03	1.3E-04	X
isopropylbenzene (cumene)	98-82-8	152.4	4.5	120.19	1.1E-02	✓
methacrylonitrile (2-methylprop-2-enenitrile)	126-98-7	90.3	71.2	67.09	2.5E-04	✓
methyl acetate	79-20-9	92	216	74.08	1.1E-04	✓
methyl acrylate	96-33-3	80.2	86.6	86.09	2.0E-04	✓
methylcyclohexane	108-87-2	100.9	46	98.19	4.3E-01	✓
methylene chloride (dichloromethane)	75-09-2	40	435	84.93	3.3E-03	✓
methyl ethyl ketone (2-butanone)	78-93-3	79.5	90.6	72.11	5.7E-05	✓
methyl isobutyl ketone (4-methyl-2-pentanone)	108-10-1	116.5	19.9	100.16	1.4E-04	✓
methyl mercaptan (methanethiol)	74-93-1	5.9	1510	48.11	3.1E-03	✓
methyl methacrylate	80-62-6	100.5	38.5	100.12	3.4E-04	✓
a-methylstyrene (1-methyl-1-phenylethylene)	98-83-9	165.4	1.9	118.18	2.5E-03	✓

Table 1: VOCs in Air by Thermal Desorption: Method Applicability & Physical Constants						
Schedule 11 Substance	**CAS #**	**BP (°C)**	**VP, 25C (Torr)**	**MW (g/mol)**	**Henry's Law atm-m³/mol**	**Method Applicability**
methyl styrene, m+p (vinyl toluene, m+p)	25013-15-4	165.4	1.5	118.18	7.9E-03	✓
methyl tert-butyl ether (MTBE)	1634-04-4	55.2	250	88.15	5.9E-04	✓
naphthalene	91-20-3	217.9	0.085	128.18	4.4E-04	✓
nitrobenzene	98-95-3	210.8	0.245	123.11	2.4E-05	✓
2-nitrotoluene	88-72-2	222	0.188	137.14	5.1E-04	✓
phosphine	7803-51-2	-87.8	29300	34.00	2.4E-02	X
propylene oxide	75-56-9	35	538	58.08	7.0E-05	✓
pyridine	110-86-1	115.2	20.6	79.10	1.1E-05	✓
styrene	100-42-5	145	6.4	104.15	2.7E-03	✓
1,1,1,2-tetrachloroethane	630-20-6	130.5	12	167.85	2.4E-03	✓
1,1,2,2-tetrachloroethane	79-34-5	156.5	13.3	167.85	3.7E-04	✓
tetrachloroethylene (PCE, PERC)	127-18-4	121.3	18.5	165.83	1.8E-02	✓
tetrahydrofuran	109-99-9	66	162	72.11	7.1E-05	✓
toluene	108-88-3	110.6	28.4	92.14	6.6E-03	✓
1,2,4-trichlorobenzene	120-82-1	213.5	0.46	181.45	5.8E-02	✓
1,1,1-trichloroethane	71-55-6	74	124	133.41	1.7E-02	✓
1,1,2-trichloroethane	79-00-5	113.8	23	133.41	8.2E-04	✓
trichloroethylene (TCE)	79-01-6	87.2	69	131.39	9.9E-03	✓
1,1,2-trichloro-1,2,2-trifluoroethane (freon 113)	76-13-1	47.7	363	187.38	2.2E+01	✓
trichlorofluoromethane (freon 11)	75-69-4	23.7	803	137.37	9.7E-02	✓
1,1,2-trichloropropane	598-77-6	132	3.1	147.43	3.2E-04	✓
1,2,3-trichloropropane	96-18-4	157	3.69	147.43	3.4E-04	✓
1,2,3-trichloropropene	96-19-5	142	4.4	145.42	1.8E-02	✓
a,a,a-trichlorotoluene (benzotrichloride)	98-07-7	220.6	0.414	195.48	0.0106	✓
triethylamine	121-44-8	89	57.1	101.19	1.5E-04	✓
1,2,4-trimethylbenzene	95-63-6	169.3	2.1	120.19	6.2E-03	✓
1,3,5-trimethylbenzene	108-67-8	164.7	2.1	120.19	8.8E-03	✓
vinyl acetate (ethenyl acetate)	108-05-4	72.5	90.2	86.09	5.1E-04	✓
vinyl bromide (bromoethene)	593-60-2	15.8	1030	106.95	1.2E-02	✓
vinyl chloride (chloroethene)	75-01-4	-13.3	2980	62.50	2.8E-02	✓
VHv_{6-13} / VPHv	n/a	n/a	n/a	n/a	n/a	✓
xylenes (o-xylene + m,p-xylenes)	1330-20-7	138.5	7.99	106.17	6.6E-03	✓
Key:						
✓ Technique is appropriate for this substance						
X Technique is not appropriate for this substance						
VR Validation Required (technique may be appropriate for this substance)						

Volatile Hydrocarbons in Air-Vapour by GC-FID / GC-MS

Parameter

Volatile Hydrocarbons (vapours) in air (VHv_{6-13}).

Analytical Method

Sampling by thermal desorption tube, coconut charcoal tube, or canister. Analysis by GC/FID or GC/MS.

Introduction

This method is applicable to the quantitative determination of volatile hydrocarbons (vapours) in air, when appropriately sampled and collected on suitable sorbent tubes (thermal desorption or charcoal), or in stainless-steel canisters.

VHv_{6-13} measures the aggregate concentration of Volatile Hydrocarbons in air, quantitated against toluene and n-dodecane. VHv_{6-13} measures hydrocarbons and other VOCs between the range of n-hexane (nC_6) and n-tridecane (nC_{13}). VHv_{6-13} encompasses a vapour pressure range of approximately 0.05–150 Torr (at 25°C), or a boiling point range of approximately 69°C to 234°C.

Volatile Hydrocarbons (VHv_{6-13}) is the precursor to Volatile Petroleum Hydrocarbons (VPHv), a calculated parameter regulated under Schedule 11 of the BC CSR.

Method Summary

Ambient air or soil gas samples for VHv_{6-13} are collected using stainless-steel canisters, or with appropriate sorbent tubes. VHv_{6-13} is analyzed by GC/FID or by GC/MS in scan mode and is quantified in two ranges; the nC_6–nC_{10} range is quantitated against toluene, and the nC_{10}–nC_{13} range is quantitated against n-dodecane (nC_{12}), using 3-point (minimum) linear calibrations.

This method describes analytical requirements for VHv_{6-13} but does not provide general details about sample collection or instrumental configurations of the canister, thermal desorption, or charcoal tube methods, except where applicable only to VHv_{6-13}. For detailed information and requirements applicable to each of these techniques, refer to the following BC Lab Manual methods:

- Volatile Organic Compounds in Air by Canister / GCMS
- Volatile Organic Compounds in Air by Thermal Desorption Tube / GCMS
- Volatile Organic Compounds and Other Volatile Substances in Air by Charcoal Tubes & Miscellaneous Collection Media

This is a prescriptive method that describes options and requirements for the analysis of VHv_{6-13}. However, detailed method conditions are not provided, so laboratories may customize their approach within the confines described.

MDLs

Sampling Technique	Typical Air Volumes	Typical MDL
Thermal Desorption	1–10 L (total sample volume)	100 ug/m³
Canister	200–400 mL (sub-sample analyzed)	100 ug/m³
Charcoal (400mg tubes)	10–50 L (total sample volume)	500 ug/m³

Laboratory MDLs for this method are expressed in absolute amount units (e.g., µg), so air concentration MDLs are a function of sampling volume.

VPHv is calculated by subtracting BTEX, nC_6, and nC_{10} from VHv_{6-13}. Refer to the BC Lab Manual Method for VPH for more information.

Matrix

Air (ambient)
Soil Gas

Interferences and Precautions

Interferences may result from residual contaminants in the collection media, or from contaminants introduced during sample collection or at the laboratory. The analytical system must be monitored daily using Method Blanks and must be demonstrated to be free of interferences under the conditions of the analysis.

Because the thermal desorption and canister techniques employ re-usable sample collection media, both require rigorous pre-cleaning and proofing procedures to prevent carryover from high samples.

Excessive moisture or condensation inside the collection medium can reduce the capacities of thermal desorption and charcoal tubes. This is an important consideration when sampling soil gases, which generally have humidities of near 100%.

For the thermal desorption and canister methods, excessive or poorly managed moisture can cause GC/MS signal depression, resulting in low biased results. Use of a volatile internal standard helps to monitor this problem. GC/FID flame-out can also occur due to excessive moisture.

For most sample types (including hydrocarbon-contaminated samples), quantitative results by the GC/MS and GC/FID methods will be similar. For some unique sample types, differences between MS and FID quantitation may be encountered. Notably, VHv_{6-13} results for samples containing only perchlorinated solvents may be lower by GC/FID (however, VHv_{6-13} would not normally be a contaminant of concern at such sites).

Sampling, Handling and Preservation

Detailed field sampling guidelines are beyond the scope of this method. For information, please refer to the BC Lab Manual methods for the sampling techniques listed below, and to the BC Science Advisory Board document "Guidance on Site Characterization for Evaluation of Soil Vapour Intrusion Into Buildings".

Thermal Desorption Tubes: Samples are collected in specially prepared thermal desorption tubes, which typically have multiple (2-3) sorbent beds to permit analysis of a broad range of VOCs. Carbotrap B is typically used to capture nC_5-nC_{12} hydrocarbons. Carbotrap C can extend the range to C_{13} and beyond. Selected TD media must be appropriate for aliphatics and aromatics within the nC_6 to nC_{13} range. Typical sample collection volumes range from 0.2-10L, depending on required detection limits, analyte

requirements, and sample humidity. Thermal desorption tubes must be capped tightly when not in use, e.g. using Swagelok fittings with PTFE ferrules.

Coconut Shell Charcoal Tubes: Samples are collected onto disposable single-use coconut shell charcoal tubes. Each tube has both a front and back section. Back sections are normally analyzed separately to permit identification of breakthrough. 400/200mg tubes are strongly recommended to maximize adsorptive capacity and to minimize breakthrough. Typical sample collection volumes range from 10-50L, depending on the detection limits required. Tubes must be capped securely after collection.

Canisters: Samples are collected in specially prepared stainless-steel canisters, ranging in volume from 400mL to 6L. Appropriate sampling heads that have been pre-calibrated to deliver the desired sampling rate are also required.

Preservation: None

Stability

Holding Time:

Canisters: 30 days prior to analysis

TD: 30 days prior to analysis

Charcoal: 30 days prior to analysis

Storage: Protect collection media against intrusion of ambient vapours before and after sampling. Store thermal desorption and charcoal tubes at ≤ 10°C during transport, and at ≤ 6°C at the laboratory. Canisters should not be refrigerated.

Instrument Configuration

Detailed instrumental procedures are not provided in this method. For detailed guidance on instrumental analysis conditions, refer to EPA Compendium Methods TO15 (Canister Method) or TO17 (TD Method), or to NIOSH Methods 1500 or 1501 (Charcoal Method).

The reference column for this method is a 30-60 meter, 0.32mm ID capillary column with a 1.5 um coating of 100% dimethyl siloxane (e.g. DB-1, HP-1, RTX-1 or equivalent). The stationary phase type may not be modified. The phase thickness and column length may be modified, provided adequate resolution can be demonstrated.

Either a Mass Spectrometer (MS) or a Flame Ionization Detector (FID) must be used for VHv_{6-13}, provided the prescribed performance criteria are met. With GC/MS, scan mode must be used, with a scan range of 35-260 amu.

GC Analysis and Calibration Procedures

VHv_{6-13} Calibration Overview: TIC or GC/FID areas are integrated in two ranges: C6-10, and C10-13. The C6-10 range is calibrated against toluene, and the C10-13 range is calibrated against n-dodecane. Calculations are based on linear response factors for toluene and n-dodecane that are determined from 3-point (minimum) calibration curves that must span at least 2 orders of magnitude. Internal standard calibration is utilized for GC/MS determinations, using a separate internal standard for each range. Samples where the maximum peak height exceeds the highest peak height of the upper calibration level must be diluted or appropriately qualified. VHv_{6-13} is the sum of the C6-10 and C10-13 fraction concentrations.

Calibration Standards: Calibration Standards must contain (at minimum) n-hexane (nC_6), n-decane (nC_{10}), toluene, n-dodecane (nC_{12}), and n-tridecane (nC_{13}).

For the thermal desorption and canister methods, calibration standards must be introduced to the TD media or canister system using gas phase reference standards (which may be generated by evaporation at time of use, e.g. using gas bombs or a GC inlet or similar device). For the charcoal method, calibration standards are prepared in carbon disulfide.

A second source Calibration Verification Standard (CVS) is required to confirm the integrity of the toluene and nC_{12} calibration standards.

System Performance Check Requirements (Instrument + Media):
Whenever a Calibration Standard or Verification Standard is analyzed, perform the following checks:

a) Measure and control the relative response factors of nC_6 and nC_{12} versus toluene,

b) Determine retention time windows for VHv_{6-13} integration ranges,

c) Confirm resolution of n-hexane (nC_6) from the solvent peak or other potential interferences.

For both nC_6 and nC_{12}, determine the relative response factor (RRF) versus toluene by MS TIC or FID peak area. For the initial calibration, use the average RRFs from all levels of the initial calibration. RRFs must also be verified with each CCV. RRFs must be determined based on absolute mass (e.g. µg) or weight / volume concentrations in air, but cannot be determined from volume / volume concentrations. For both nC_6 and nC_{12}, the acceptance criteria for RRFs vs toluene is 0.60 - 1.40. Calculate RRFs as follows:

Relative Response Factors for thermal desorption and canister methods:

Avg RRF nC_6 / toluene = Avg-RF nC_6 (µg-1) / Avg-RF toluene (μg^{-1})

Avg RRF nC_{12} / toluene = Avg-RF nC_{12} (µg-1) / Avg-RF toluene (μg^{-1})

Relative Response Factors for charcoal tube methods:

RRF nC_6 / toluene = Avg-RF nC_6 (mL/µg) / Avg-RF toluene (mL/µg)

RRF nC_{12} / toluene = Avg-RF nC_{12} (mL/µg) / Avg-RF toluene (mL/µg)

See initial calibration section for Response Factor equations.

Internal Standards: For VHv_{6-13} by GC/MS, the use of internal standards (one per calibration range) is required, except where precluded due to sample-specific interferences. Internal standards normalize variations in system response, and provide an additional degree of quality control for each sample. Each Internal standard should elute within (or near) their respective hydrocarbon ranges. The C6-10 fraction internal standard should elute in the C6-C7 range, to enable identification of signal suppression due to excess sample moisture. Fluorobenzene or 1,4-Difluorobenzene are recommended for the C6-10 internal standard. 3,4-Dichlorotoluene, d4-1,2-Dichlorobenzene, or 4-Bromofluorobenzene are recommended for the C10-13 internal standard. Internal standard areas must be monitored for all samples and must not vary by more than +/-50% from initial calibration or CCV.

Initial Calibration: Analyze the toluene and n-dodecane Calibration Standards at the beginning of each new analytical batch (or verify an existing calibration with a CCV).

Linear averaged response factor calibration must be used for this method, using 3 concentration levels (minimum) that span at least 2 orders of magnitude. Calibration linearity is acceptable if the RSD of the response factors for toluene and n-dodecane are ≤ 20%.

For each calibration level, calculate the Response Factors (RFs) for toluene and n-dodecane. Then calculate the average response factor for the 3 or more calibration levels. Response Factors for the TD and canister methods are based on the total mass of analyte transferred from the sample media to the analytical system (e.g. in µg). Response factors for the charcoal tube method are based on the concentrations of calibration standards (e.g. in µg/mL):

Response Factor expressions for thermal desorption and canister methods:

Avg-$RF_{toluene}$ (μg^{-1}) = Average Response Factor for toluene standards (μg^{-1})

Avg-$RFnC_{12}$ (μg^{-1}) = Average Response Factor for n-dodecane standards (μg^{-1})

$RF_{toluene}$ (μg^{-1}) per level = Toluene area / Toluene amount (µg in TD tube or canister aliquot)

$RFnC_{12}$ (µg-1) per level = nC_{12} area / nC_{12} amount (µg in TD tube or canister aliquot)

Response Factor expressions for charcoal tube method:

Avg-$RF_{toluene}$ (mL/µg)= Average Response Factor for toluene standards (mL / µg)

Avg-$RFnC_{12}$ (mL/µg) = Average Response Factor for n-dodecane standards (mL / µg)

$RF_{toluene}$ (mL/µg) per level = Toluene area / Toluene concentration (µg/mL in CS_2 standards)

$RFnC_{12}$ (mL/µg) per level = nC_{12} area / nC_{12} concentration (µg/mL in CS_2 standards)

Calibration Verification Standard (CVS): A second source Calibration Verification Standard must be analyzed with each initial calibration. The CVS must contain toluene and n-dodecane. The CVS should be prepared at a level near the mid-point of the calibration range and must be recovered within 15% of its expected concentration.

Continuing Calibration Verification (CCV): After initial calibration, the Response Factors (RF-toluene and RF-nC_{12}) must be verified, at minimum, after every 24 hours of continuous operation (at least every 20 samples). The calibration must also be verified at the end of each analysis batch.

Use a Calibration Standard as a CCV. If either Response Factor changes by more than 20% from the Avg-RF of the initial calibration, then corrective action must be taken, and samples analyzed after the last acceptable standard must be re-run or qualified.

System Performance Checks must be successfully conducted with each CCV.

Integration of Total Areas for VHv_{6-13}: VHv_{6-13} is quantitated by summing the results for two sub-ranges within the nC_6-nC_{13} range. The first VH sub-range falls between the retention times of n-hexane and n-decane. The second VH sub-range falls between the retention times of decane and n-tridecane. Each sub-range is integrated and quantitated separately, and VHv_{6-13} is calculated by summing the two results.

Note: Calculating VH using two sub-ranges reduces the impact of relative response biases which can exist between higher and lower volatility VH components with some sample collection media.

Determine the total integrated peak area of each VH sub-range, where:

a) The VHv_{6-10} range begins at the *beginning of the n-hexane peak* and ends at the *apex of the decane peak* (hexane must be included in VHv_{6-13}, as it is subtracted to determine VPHv).

b) The VHv_{10-13} range begins at the *apex of the n-decane peak* and ends at the *apex of the n-tridecane peak*.

Retention times of the marker compounds must be updated or verified with each analysis batch and should be established using marker compound concentrations that do not overload the liquid phase of the GC column.

Peak integration must include all peaks, whether resolved or not, that are above the chromatographic baseline, as established by instrument blanks within the analysis batch. Automated software integrations of VH areas must be visually verified and must be manually corrected where potential error may exceed 2%.

VHv_{6-13} Calculations: VHv_{6-13} is the sum of the calculated concentrations for VHv_{6-10} and VHv_{10-13}.

If VHv-range Surrogate or Internal Standards are added to samples, their contribution to VHv must be subtracted. Because discrete compounds frequently experience FID / MS-TIC interference, it is practical to subtract the actual spiked concentrations of surrogate and internal standard compounds from calculated VHv concentrations. If this approach is used (rather than subtraction of actual peak areas), the total amount of surrogate and internal standard compounds that lie within the VH-range should be less than the Reported Detection Limit for VHv_{6-13}.

Use the following equations to calculate VHv_{6-13}:

VHv_{6-13} (µg/m³) = VHv_{6-13} (µg) / air volume sampled (m³)

VHv_{6-13} (µg) = VHv_{6-10} (µg) + VHv_{10-13} (µg)

VHv Sub-fraction Calculations for TD and Canisters (external calculations shown):

VHv_{6-10} (µg) = $A_{(6-10)}$ x DF / Avg-$RF_{toluene}$ (μg^{-1})

VHv_{10-13} (µg) = $A_{(10-13)}$ x DF / Avg-$RFnC_{12}$ (μg^{-1})

VHv Sub-fraction Calculations for Charcoal tubes (external calculations shown):

VHv_{6-10} (µg) = $A_{(6-10)}$ x DF x (Desorption Solvent Volume) / Avg-$RF_{toluene}$ (mL/µg)

VHv_{10-13} (µg) = $A_{(10-13)}$ x DF x (Desorption Solvent Volume) / Avg-$RFnC_{12}$ (mL/µg)

where:

$A_{(6-10)}$ = Total area between nC_6 and nC_{10} from the sample chromatogram *

$A_{(10-13)}$ = Total area between nC_{10} and nC_{13} from the sample chromatogram *

DF = Dilution Factor

* Subtract areas of any Surrogates and Internal Standards that elute within the VHv_{6-13} range.

To convert results to µg/m³ (the units of the regulatory limits), divide the µg results by the volume of sample passed through the sorbent tube or sub-sampled from the canister.

Diluting High Level Samples: Where sample results exceed the calibrated linear range of the system (i.e. where any sample component exceeds the maximum peak height of calibration standards), they must be diluted and re-analyzed at a more appropriate concentration, or must be clearly qualified as semi-quantitative (estimated) values. Reported Detection Limits for diluted samples must be adjusted accordingly.

Reporting: Labs must clearly specify the units of reported air concentrations. Recommended reporting units for CSR purposes are µg/m³. VHv_{6-13} results may also be expressed using absolute mass units (e.g. µg per tube), but cannot be expressed in volume / volume units (e.g. ppbv, ppmv).

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
System Performance QC		
Initial Calibration Linearity Criteria	Each initial calibration	RSD of RFs must be < 20% for toluene and nC_{12}
System Performance Check	Each initial calibration and CCV	Avg RRF for nC_6 and nC_{12} vs toluene must be 0.6-1.4
Calibration QC and Verification	**Minimum Frequency**	**Minimum Data Quality Objectives***
Calibration Verification Standard (CVS)	1 per batch (max 20 samples)	Within 15% of expected concentration
Continuing Calibration Verification (CCV) Standard	Every 24 hrs (max 20 samples) and at end of each batch	Within 20% of initial calibration
Internal Standard Area Checks	All samples and QC	Within 50% of initial calibration or last CCV

Method QC	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank (MB)	1 per batch (max 20 samples)	Less than reported DL
Field Blank (FB)	Recommended	Less than reported DL
Laboratory Control Sample (LCS)	1 per batch (max 20 samples)	70–130% of target
Lab Duplicates	≥ 5% (where possible)	≤ 40% RPD
Field Duplicates	Recommended	None specified
Internal Standards (GC/MS only)	Required for GC/MS — All samples	Areas must be within ±50% of Initial Calibration IS values
Surrogates	Recommended where possible	None specified

* Minimum DQOs apply to individual QC samples, not averages, at levels above 10x MDL. Laboratories must report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

QCDetails

Method Blank: Method Blanks must be prepared from randomly selected media that are representative of the preparation and storage of samples. Use of dedicated media for Method Blanks is not permitted.

Field Blank: Recommended. May constitute a blank collection medium that is opened and handled in the field. Not normally applicable for the canister sampling technique, unless pre-filled with clean air at the laboratory, as a check on canister cleanliness.

Laboratory Control Sample (LCS): Prepare an LCS using an appropriate petroleum reference standard (e.g. mineral spirits, deodourized kerosene, or artificially weathered gasoline; see Method Validation section). The expected target for VHv_{6-13} should be within ±20% of the nominal (gravimetric) concentration of the product. Concentrations above 10x the MDL are recommended. The LCS must be prepared using the appropriate sample collection media, preferably in the gas phase.

Lab Duplicates: Recommended. For thermal desorption tubes, this can only be accomplished with systems equipped with sample recollection capability. For canisters, analyze a separate aliquot of an equal amount of the air sample. Lab duplicates are not possible for charcoal tubes.

Field Duplicates: Recommended. Normally accomplished by simultaneous parallel collection of samples from one location onto two independent collection media (distributed volume pairs).

Calibration Verification Standard (CVS): A second source standard containing toluene and nC_{12} must be utilized to confirm the integrity of the calibration standards and the accuracy of the calibration.

Continuing Calibration Verification (CCV): Calibration standards (typically a mid-point standard) must be re-analyzed periodically throughout the instrument run to monitor calibration drift. Run a CCV at least every 24 hours (maximum 20 samples), and at the end of each batch.

Method Validation Requirements

Initial Method Validation requirements as outlined below must be completed before this method may be used to generate VHv_{6-13} results for

unknown samples. Separate validations must be performed for each media type and for each detector type.

Initial Verification of Relative Response Requirements: Verify that the method meets relative response requirements for nC_6 and nC_{12} versus toluene by performing a System Performance Check. For the charcoal method, a Media Relative Response Check is also required at least once per lot of charcoal media as a component of method validation (i.e. check relative response factors from a calibration standard that has been spiked onto a charcoal tube).

Establish System Calibration Range: Prepare and analyze a series of concentrations of the toluene and n-dodecane calibration standards to determine the calibration range for the instrument system. The calibration range of the method must span at least 2 orders of magnitude. The upper calibrated range is capped by the peak height of the highest calibration standards.

Selection of a Petroleum Reference Standard and Determination of Reference Values: This method requires the use of a petroleum reference standard for validation and routine QC purposes. Ideal petroleum products for this purpose are those where all or most components lie within the C_{6-13} range. Recommended petroleum reference products include mineral spirits (also known as Stoddard solvent), deodourized (distilled) kerosene, or artificially weathered gasoline. Artificial weathering by evaporation can be used to selectively remove the <C6 fraction to increase the fraction of VHv_{6-13} in the material.

If a Petroleum Reference Standard is available where >95% of its composition has been confirmed to lie within the C_{6-13} range, the nominal (gravimetric) petroleum product concentration may be used as the reference concentration for VHv_{6-13}.

Alternatively, the VHv_{6-13} concentration of the petroleum product reference solution may be determined by direct injection GC/FID or GC/MS techniques, as follows:

a) Prepare a solution of the petroleum reference standard in methanol or carbon disulfide at a high concentration (at least 50x the estimated Instrument Detection Limit for VHv_{6-13}).

b) Analyze the petroleum reference standard solution by direct injection (splitless or on-column), using appropriate conditions for VHv_{6-13}. This procedure requires that all volatile components within the reference standard (i.e. those <C6) are resolved from the solvent peak.

c) Integrate the total peak area that lies before C6, within the C_{6-13} range, and after C_{13}. Use peak areas to calculate the percentage of reference standard that lies within the C_{6-13} range.

d) Use the percentage value determined above to calculate reference VHv_{6-13} concentrations for any prepared concentrations of the same product.

Establish Linear Range for VHv_{6-13} and Estimate MDL: Establish the linear working range of the instrument system for VHv_{6-13} using a series of dilutions of the selected Petroleum Reference Standard, prepared on the appropriate sample collection media.

Analyze Petroleum Reference Standard concentrations ranging from below the estimated MDL to above the maximum calibration range concentration in 2-5x increments. Plot *Calculated VHv_{6-13} Results* (y-axis) versus *Reference VHv_{6-13} Concentrations* (x-axis) to confirm the linear working range of VHV_{6-13}.

Estimate the MDL. Accuracy at the MDL must be at least 50-150%, and the chromatographic fingerprint must resemble chromatograms of higher concentrations of the same reference standard.

Initial Demonstration of Accuracy and Precision: Use a Petroleum Reference Standard with known VHv_{6-13} reference concentration to prepare at least 7 spike samples at a concentration that exceeds 10x the MDL. Average accuracy, relative to the expected VHv_{6-13} target, must be at least 80-120%. Precision must be <15% RSD.

Establish Method Detection Limit: Determine the Method Detection Limit (MDL) for VHv_{6-13}. Use a Petroleum Reference Standard with known VHv_{6-13} reference concentration to prepare at least 7 method spikes at approximately the level of the estimated MDL. Analyze for VHv_{6-13} and calculate the MDL as described in the BC Lab Manual. The MDL should be determined in absolute amount units (e.g. µg); the MDL in concentration units is a function of sampling volume and/or of the aliquot volume analyzed.

Average recoveries of the MDL Method Spikes for VHv_{6-13} must be between 50–150%, where recovery is defined as: [average VHv_{6-13} result] / [reference VHv_{6-13} concentration], where the reference concentration is determined as above. If this condition is not met, repeat the MDL determination at a higher spike level.

Determine Safe Sampling Volumes (SSVs): Thermal desorption tubes and charcoal tubes have finite adsorptive capacities, and SSVs must not be exceeded. SSVs are normally determined for discrete compounds and are more critical for highly volatile compounds than for aggregate hydrocarbons. For VHv_{6-13} by TD or charcoal methods, determine the SSV using a suitable Petroleum Reference Standard, or use the lowest SSV for BTEX, n-hexane, or n-decane. Refer to the BC Lab Manual methods for Thermal Desorption and Charcoal methods for further information.

Reported Detection Limits: Detection Limits reported for VHv_{6-13} must be greater than or equal to the MDL as determined above. To meet CSR requirements, calculated MDLs and Reporting Detection Limits must be below the applicable Schedule 11 standards (note however that MDLs are a function of sampling volume, and will vary from sample to sample).

References

Volatile Organic Compounds in Air by Canister Sampling / GCMS — PBM, BC Environmental Lab Manual.

Volatile Organic Compounds in Air by Thermal Desorption Tube / GCMS — PBM, BC Environmental Lab Manual.

Volatile Organic Compounds and Other Volatile Substances in Air by Charcoal Tubes and Miscellaneous Collection Media — PBM, BC Environmental Lab Manual.

Method TO-15, Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters And Analyzed by Gas Chromatography / Mass Spectrometry (GC/MS), from the Compendium of

Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Center for Environmental Research Information, Office of Research and Development, US EPA, Cincinnati, OH, January 1999.

Method TO-17, Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Active Sampling onto Sorbent Tubes with Subsequent Analysis By Gas Chromatography, from the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Center for Environmental Research Information, Office of Research and Development, US EPA, Cincinnati, OH, January 1999.

NIOSH Method 2549, Volatile Organic Compounds (Screening Method), NIOSH Manual of Analytical Methods (NMAM), Issue 3, March 15 2003.

Method 1500, Hydrocarbons BP 36° - 216°C, NIOSH Manual of Analytical Methods (NMAM), Issue 3, March 15 2003.

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Revision History June 26, 2009: First draft of BC Lab Manual method.