

## **Section H**

# **AIR CONSTITUENTS - ORGANIC**

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## SECTION H

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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:**

	<b>Puff GC/MS</b>	<b>XAD2 GC/MS</b>
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+k)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 "%".)

	<b>Puff GC/MS</b>	<b>XAD2 GC/MS</b>
Acenaphthalene d10	ACEN PAH1	ACEN PAH2
Chrysene d12	CHRY PAH1	CHRY PAH2
Fluorene d10	FLUO PAH1	FLUO PAH2
Naphthalene d8	NAPH PAH1	NAPH PAH2
Perylene d12	PERY PAH1	PERY PAH2
Phenanthrene d10	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 down stream 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:** Insure 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<sup>3</sup> 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<sup>3</sup>).
- 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:

Acenaphthene	50	pg/m <sup>3</sup>
Acenaphthylene	50	pg/m <sup>3</sup>
Anthracene	50	pg/m <sup>3</sup>
Benzo(a)anthracene*	50	pg/m <sup>3</sup>
Benzo(a)pyrene	50	pg/m <sup>3</sup>
Benzo(b)fluoranthene	50	pg/m <sup>3</sup>
Benzo(g,h,i)perylene	100	pg/m <sup>3</sup>
Benzo(k)fluoranthene	50	pg/m <sup>3</sup>
Benzo(b+k)fluoranthene	50	pg/m <sup>3</sup>
Chrysene	50	pg/m <sup>3</sup>
Dibenz(a,h)anthracene	100	pg/m <sup>3</sup>
Fluoranthene	50	pg/m <sup>3</sup>
Fluorene	50	pg/m <sup>3</sup>
Indeno(1,2,3-cd)pyrene	100	pg/m <sup>3</sup>
Naphthalene	50	pg/m <sup>3</sup>
Phenanthrene	50	pg/m <sup>3</sup>
Pyrene	50	pg/m <sup>3</sup>

\*synonymous to Benz(a)anthracene

To obtain these detection limits at least 100 m<sup>3</sup> 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<sub>2</sub> 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).
- d) 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.
- e) 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<sub>2</sub> 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/cm<sup>3</sup>) used in furniture upholstery (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:
  - o perylene - d<sub>12</sub>
  - o naphthalene - d<sub>8</sub>
  - o chrysene - d<sub>12</sub>
  - o phenanthrene - d<sub>10</sub>
  - o acenaphthene - d<sub>10</sub>
- 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 uL injection volume is used consistently. With some GC injection ports, however, 1 uL injections

may produce some improvement in precision and chromatographic separation. A 1 uL injection volume may be used if adequate sensitivity and precision can be achieved. [Note: If 1 uL is used as the injection volume, the injection volumes for all extracts, blanks, calibration solutions and performance check samples must be 1 uL.]

- 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 um 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) fluoroanthene 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 uL and 100 uL.

## Sampling Preparation

### Sampling Head Configuration:

- a) The sampling head consists 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 Battelle 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<sub>8</sub>  
Acenaphthene d<sub>10</sub>  
Phenanthrene d<sub>10</sub>  
Chrysene d<sub>12</sub>  
Perylene d<sub>12</sub>

(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/cm<sup>3</sup>) 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 considered to be 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 in order 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:

#### Surrogate Standard

Naphthalene d<sub>8</sub>  
Acenaphthene d<sub>10</sub>  
Phenanthrene d<sub>10</sub>  
Chrysene d<sub>12</sub>  
Perylene d<sub>12</sub>

**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.

**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:

<u>Parameter Name</u>	<u>Quantitation Ion</u>	<u>Confirming Ion</u>
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)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 d10	164	160
Phenanthrene d10	188	189
Anthracene d10	188	189
Chrysene d12	240	241
Perylene d12	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 $\mu\text{m}$ 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.
El Condition:	70 eV.
Mass Scan:	follow manufacturer instruction for select ion monitoring (SIM) mode.
Sample volume:	1 $\mu\text{L}$ on-column injection
Carrier gas:	helium at 30 cm/sec.

- e) The GC/MS is tuned using a 1 ng/ $\mu\text{L}$  solution of decafluorotriphenylphosphine (DFTPP). The DFTPP permits the user to tune the mass spectrometer on a daily basis.

### 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:

- 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  $\mu\text{g}/\mu\text{L}$ ) must be prepared from pure standard materials or purchased as certified solutions.
- Place 0.01 grams of native PAHs on a tared aluminum weighing disk and weigh on an analytical balance.
- Quantitatively, transfer to a 100 mL volumetric flask. Rinse the weighing disk with several small portions of dichloromethane. Ensure all material has been transferred.
- Dilute to mark with dichloromethane.
- The concentration of the stock standard solution of PAHs in the flask is 0.1  $\mu\text{g}/\mu\text{L}$ . Note: commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.
- Transfer the stock standard solutions into Teflon<sup>®</sup>-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.
- Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.
- 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<sub>12</sub>. 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<sub>12</sub> 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<sub>10</sub> 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:  
$$RF = (A_{sCis}) / (A_{iCs}),$$

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  $\pm 20\%$ , 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/ $\mu\text{L}$  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  $\pm 0.10$  minute of the library retention time of the compound. The accepted level for relative abundance is determined to be  $\pm 20\%$  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  $\mu\text{L}$  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 work day, 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  $\mu$ L 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:

$$\text{Percent Difference} = (RF_C - RF_I) / RF_I \times 100,$$

where:

RF<sub>I</sub> = average response factor from initial calibration using mid-scale standard,

RF<sub>C</sub> = 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

- Retrieve the data logger and download to the computer. Note: all volumetric flows have should have been corrected to standard conditions.
- The total sample volume ( $V_m$ ) is calculated from the periodic flow readings (Magnehelic readings taken in the field) using the following equation:

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

where:

$V_s$  = total sample volume at STP conditions,  $M^3$ ,  
 $Q_1, Q_2 \dots Q_n$  = flow rates determined at the beginning, end, and intermediate points during sampling, L/minute,  
 $N$  = number of data points,  
 $T$  = elapsed sampling time, minutes.

- 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 ( $m^3$ ) at standard temperature and pressure (25°C and 760 mm Hg pressure),  
 $V_m$  = total sample flow under ambient conditions ( $m^3$ ),  
 $pA$  = ambient pressure (mm Hg),  
 $tA$  = ambient temperature (°C).

### Sample Concentration:

- 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.
- 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), m<sup>3</sup>.

- c) The analyte concentration can be converted to ppb<sub>v</sub> using the following equation:

$$C_A (\text{ppbv}) = C_A (\text{ng/m}^3) \times (22.4 / MW_A)$$

where:

$C_A$  = concentration of analyte calculated above in ng/m<sup>3</sup>,  
 $MW_A$  = 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  $\pm 20\%$ .
- 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  $\pm 20\%$  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 hour of analysis by a mid-level calibration standard. The response must be less than 20% different from the initial response.

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)anthracene 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** Ambient Air

**Units** µg / m<sup>3</sup>

**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 (DNPH on Silica gel) (Waters Associates, part # 37500).

#### Ozone Scrubber Construction:

- a) Form a coil from 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 DNPH. 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 (H<sub>3</sub>PO<sub>4</sub>) in 50 mL of acetonitrile that has been glass distilled. Both the

DNPH and H<sub>3</sub>PO<sub>4</sub> 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 dinitrophenylhydrazine = 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: H<sub>2</sub>O. 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 allow 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 room 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  $\mu\text{L}$  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  $\mu\text{g}/\text{mL}$ . 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  $\mu\text{L}$  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  $\mu\text{g}$ , 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:

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

where: M = amount of formaldehyde in  $\mu\text{g}$

$R_f$  = response factor for the Formaldehyde-DNPH derivative.

The concentration of formaldehyde in air is calculated as follows:

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

where C = concentration in ppb

M = amount of formaldehyde determined in  $\mu\text{g}$ .

V = volume of air sampled in Litres

$M_o$  = 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:

$$C = M \times 48900 / [(F_o + F_1) \times t \times M_o]$$

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

<b>Precision</b>	Ten DNPH cartridges spiked at midrange level (2.74 $\mu\text{g}$ ) gave coefficient of variation of 5%.
<b>Accuracy</b>	Ten DNPH cartridges spiked at midrange level (2.74 $\mu\text{g}$ ) gave recovery of 94%.
<b>Quality Control</b>	<p>One in fourteen DNPH cartridges should be run as blanks. Limits are &lt;0.1 <math>\mu\text{g}</math>/cartridge.</p> <p>Field blanks should be shipped and returned for analysis for each batch of DNPH cartridges sent to a sampling site.</p> <p>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 <math>\leq 10\%</math>.</p> <p>One in fourteen samples should be run in duplicate. These duplicates should be within 15% of each other for concentrations <math>&gt; 5 \times \text{MDL}</math>.</p> <p>Every fourteen samples spike a DNPH blank cartridges (BMS) with 200 <math>\mu\text{L}</math> of 250 ppm formaldehyde. Spike recovery should be in the range 80 - 120%.</p>
<b>Documentation of QC</b>	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 ( $\sim 20$ pairs $> \text{MDL}$ ) is accumulated.
<b>Data Analysis</b>	See calculations above.
<b>Safety</b>	This method may involve hazardous materials, operations and equipment. It is the responsibility of the user to consult appropriate safety information.
<b>Disposal</b>	In accordance with procedures recommended by Safety committee.
<b>References</b>	<ol style="list-style-type: none"><li>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].</li><li>ENSR Consulting and Engineering, Camarillo, California, "Standard Operating Procedure for Analysis of Carbonyl Compounds in Air Samples Collected on DNPH-Impregnated Cartridges", 1990.</li></ol>

- 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.