

**Compendium of Methods  
for the Determination of  
Toxic Organic Compounds  
in Ambient Air**

**Second Edition**

**Compendium Method TO-13A**

**Determination of Polycyclic Aromatic  
Hydrocarbons (PAHs) in Ambient Air Using Gas  
Chromatography/Mass Spectrometry (GC/MS)**

**Center for Environmental Research Information  
Office of Research and Development  
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***This Compendium has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.***

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## METHOD TO-13A

### Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)

#### TABLE OF CONTENTS

	<u>Page</u>
1. Scope .....	13A-1
2. Summary of Method .....	13A-2
3. Significance .....	13A-3
4. Applicable Documents .....	13A-3
4.1 ASTM Standards .....	13A-3
4.2 EPA Documents .....	13A-3
4.3 Other Documents .....	13A-4
5. Definitions .....	13A-4
6. Limitations and Interferences .....	13A-5
6.1 Limitations .....	13A-5
6.2 Interferences .....	13A-6
7. Safety .....	13A-6
8. Apparatus .....	13A-7
8.1 Sampling .....	13A-7
8.2 Sample Clean-Up and Concentration .....	13A-8
8.3 Sample Analysis .....	13A-9
9. Equipment and Materials .....	13A-10
9.1 Materials for Sample Collection .....	13A-10
9.2 Sample Clean-up and Concentration .....	13A-11
9.3 GC/MS Sample Analysis .....	13A-11
10. Preparation of PUF Sampling Cartridge .....	13A-12
10.1 Summary of Method .....	13A-12
10.2 Preparation of Sampling Cartridge .....	13A-12
10.3 Procedure for Certification of PUF Cartridge Assembly .....	13A-13
10.4 Deployment of Cartridges for Field Sampling .....	13A-14
11. Assembly, Calibration, and Collection Using Sampling System .....	13A-15
11.1 Sampling Apparatus .....	13A-15
11.2 Calibration of Sampling System .....	13A-15
11.3 Sample Collection .....	13A-22

## TABLE OF CONTENTS, CONTINUED

	<u>Page</u>
12. Sample Extraction, Concentration, and Cleanup .....	13A-23
12.1 Sample Identification .....	13A-23
12.2 Soxhlet Extraction and Concentration .....	13A-24
12.3 Sample Cleanup .....	13A-25
13. Gas Chromatography with Mass Spectrometry Detection .....	13A-26
13.1 General .....	13A-26
13.2 Calibration of GC/MS/DS .....	13A-26
13.3 GC/MS Instrument Operating Conditions .....	13A-29
13.4 Sample Analysis by GC/MS .....	13A-37
14. Quality Assurance/Quality Control (QA/QC) .....	13A-41
14.1 General System QA/QC .....	13A-41
14.2 Process, Field, and Solvent Blanks .....	13A-42
15. References .....	13A-42

## METHOD TO-13A

### Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)

#### 1. Scope

**1.1** 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, reliable sampling and analytical methods are necessary. This document describes a sampling and analysis procedure for common PAHs involving the use of a combination of quartz filter and sorbent cartridge with subsequent analysis by gas chromatography with mass spectrometry (GC/MS) detection. The analytical methods are modifications of EPA Test Method 610 and 625, *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater*, and Methods 8000, 8270, and 8310, *Test Methods for Evaluation of Solid Waste*.

**1.2** Fluorescence methods were among the very first methods used for detection of B[a]P and other PAHs as carcinogenic constituents of coal tar (1-7). Fluorescence methods are capable of measuring subnanogram quantities of PAHs, but tend to be fairly non-selective. The normal spectra obtained are often intense and lack resolution. Efforts to overcome this difficulty led to the use of ultraviolet (UV) absorption spectroscopy (8) as the detection method coupled with pre-speciated techniques involving liquid chromatography (LC) and thin layer chromatography (TLC) to isolate specific PAHs, particularly B[a]P. As with fluorescence spectroscopy, the individual spectra for various PAHs are unique, although portions of spectra for different compounds may be the same. As with fluorescence techniques, the possibility of spectral overlap requires complete separation of sample components to ensure accurate measurement of component levels. Hence, the use of UV absorption coupled with pre-speciation involving LC and TLC and fluorescence spectroscopy declined and was replaced with the more sensitive high performance liquid chromatography (HPLC) with UV/fluorescence detection (9) or highly sensitive and specific gas chromatography/mass spectrometry (GC/MS) for detection (10-11).

**1.3** The choice of GC/MS as the recommended procedure for analysis of B[a]P and other PAHs was influenced by its sensitivity and selectivity, along with its ability to analyze complex samples.

**1.4** The analytical methodology has consequently been defined, but the sampling procedures can reduce the validity of the analytical results. Recent studies (12-17) have indicated that non-volatile PAHs (vapor 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 sorbent. A wide variety of sorbents such as Tenax®, XAD-2® and polyurethane foam (PUF) have been used to sample common PAHs. All sorbents have demonstrated high collection efficiency for B[a]P in particular. In general, XAD-2® resin has a higher collection efficiency (18-21) for volatile PAHs than PUF, as well as a higher retention efficiency. PUF cartridges, however, are easier to handle in the field and maintain better flow characteristics during sampling. Likewise, PUF has demonstrated (22) its capability in sampling organochlorine pesticides, polychlorinated biphenyls (22), and polychlorinated dibenzo-p-dioxins (23). PUF also has demonstrated a lower recovery efficiency and storage capability for naphthalene than XAD-2®. There have been no significant losses of PAHs up to 30 days of storage at room temperature (23 °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 includes the utilization of PUF as the primary sorbent.

**1.5** This method includes the qualitative and quantitative analysis of the following PAHs (see Figure 1) specifically by utilizing PUF as the sorbent followed by GC/MS analysis:

Acenaphthene (low collection efficiency; see Section 6.1.3)	Coronene
Acenaphthylene (low collection efficiency; see Section 6.1.3)	Dibenz(a,h)anthracene
Anthracene	Fluoranthene
Benz(a)anthracene	Fluorene
Benzo(a)pyrene	Benzo(b)fluoranthene
Benzo(e)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(g,h,i)perylene	Naphthalene (low collection efficiency; see Section 6.1.3)
Benzo(k)fluoranthene	Phenanthrene
Chrysene	Pyrene
	Perylene

The GC/MS method is applicable to the determination of PAHs compounds involving three member rings or higher. Naphthalene, acenaphthylene, and acenaphthene have only ~35 percent recovery when using PUF as the sorbent. Nitro-PAHs have *not* been fully evaluated using this procedure; therefore, they are not included in this method.

**1.6** With optimization to reagent purity and analytical conditions, the detection limits for the GC/MS method range from 1 ng to 10 pg based on field experience.

## 2. Summary of Method

**2.1** Filters and sorbent cartridges (containing PUF or XAD-2®) are cleaned in solvents and vacuum dried. The filters and sorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on the sampler.

**2.2** Approximately 300 m<sup>3</sup> of air is drawn through the filter and sorbent cartridge using a high-volume flow rate air sampler or equivalent.

**2.3** The amount of air sampled through the filter and sorbent cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with blank filter and sorbent cartridges to the analytical laboratory for analysis.

**2.4** The filters and sorbent cartridge are extracted by Soxhlet extraction with appropriate solvent. The extract is concentrated by Kuderna-Danish (K-D) evaporator, followed by silica gel cleanup using column chromatography to remove potential interferences prior to analysis by GC/MS.

**2.5** The eluent is further concentrated by K-D evaporation, then analyzed by GC/MS. The analytical system is verified to be operating properly and calibrated with five concentration calibration solutions.



**2.6** A preliminary analysis of the sample extract is performed to check the system performance and to ensure that the samples are within the calibration range of the instrument. If the preliminary analysis indicates non-performance, then recalibrate the instrument, adjust the amount of the sample injected, adjust the calibration solution concentration, and adjust the data processing system to reflect observed retention times, etc.

**2.7** The samples and the blanks are analyzed and used (along with the amount of air sampled) to calculate the concentration of PAHs in the air sample.

### 3. Significance

**3.1** As discussed in Section 1, several documents have been published that describe sampling and analytical approaches for common PAHs. The attractive features of these methods have been combined in this procedure. Although this method has been validated in the laboratory, one must use caution when employing it for specific applications.

**3.2** Because of the relatively low levels of common PAHs in the environment, the methodology suggest the use of high volume (0.22 m<sup>3</sup>/min) sampling technique to acquire sufficient sample for analysis. However, the volatility of certain PAHs prevents efficient collection on filter media alone. Consequently, this method utilizes both a filter and a backup sorbent cartridge, which provides for efficient collection of most PAHs involving three member rings or higher.

### 4. Applicable Documents

#### 4.1 ASTM Standards

- **Method D1356** *Definitions of Terms Relating to Atmospheric Sampling and Analysis.*
- **Method 4861-94** *Standard Practice for Sampling and Analysis of Pesticides and Polychlorinated Biphenyl in Air*
- **Method E260** *Recommended Practice for General Gas Chromatography Procedures.*
- **Method E355** *Practice for Gas Chromatography Terms and Relationships.*
- **Method E682** *Practice for Liquid Chromatography Terms and Relationships.*

#### 4.2 EPA Documents

- *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA-600/4-83-027, June 1983.
- *Quality Assurance Handbook for Air Pollution Measurement Systems*, U. S. Environmental Protection Agency, EPA-600/R-94-038b, May 1994.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-13, Second Supplement*, U. S. Environmental Protection Agency, EPA-600/4-89-018, March 1989.

### 4.3 Other Documents

- Existing Procedures (24-32).
- Ambient Air Studies (33-50).
- General Metal Works, Inc., "Operating Procedures for Model PS-1 Sampler," Village of Cleves, OH 45002 (800-543-7412).
- Illinois Environmental Protection Agency, Division of Air Quality, "Chicago Air Quality: PCB Air Monitoring Plan (Phase 2)," Chicago, IL, IEAP/APC/86/011, April 1986.
- Thermo Environmental, Inc. (formerly Wedding and Associates), "Operating Procedures for the Thermo Environmental Semi-Volatile Sampler," 8 West Forge Parkway, Franklin, MA 02038 (508-520-0430).
- American Chemical Society (ACS), "Sampling for Organic Chemicals in Air," *ACS Professional Book*, ACS, Washington, D.C., 1996.
- International Organization for Standardization (ISO), "Determination of Gas and Particle-Phase Polynuclear Aromatic Hydrocarbons in Ambient Air - Collected on Sorbent-Backed Filters with Gas Chromatographic/Mass Spectrometric Analysis," ISO/TC 146/SC 3/WG 17N, Case Postale 56, CH-1211, Genève 20, Switzerland.

### 5. Definitions

*[Note: Definitions used in this document and in any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, E260, and E255. All abbreviations and symbols are defined within this document at point of use.]*

**5.1 Retention time (RT)**-time to elute a specific chemical from a chromatographic column. For a specific carrier gas flow rate, RT is measured from the time the chemical is injected into the gas stream until it appears at the detector.

**5.2 Sampling efficiency (SE)**-ability of the sampler to trap and retain PAHs. The %SE is the percentage of the analyte of interest collected and retained by the sampling medium when it is introduced into the air sampler and the sampler is operated under normal conditions for a period of time equal to or greater than that required for the intended use.

**5.3 Dynamic retention efficiency**-ability of the sampling medium to retain a given PAH that has been added to the sorbent trap in a spiking solution when air is drawn through the sampler under normal conditions for a period of time equal to or greater than that required for the intended use.

**5.4 Polycyclic aromatic hydrocarbons (PAHs)**-two or more fused aromatic rings.

**5.5 Method detection limit (MDL)**-the minimum concentration of a substance that can be measured and reported with confidence and that the value is above zero.

**5.6 Kuderna-Danish apparatus**-the Kuderna-Danish (K-D) apparatus is a system for concentrating materials dissolved in volatile solvents.

**5.7 MS-SCAN**-the GC is coupled to a mass spectrometer where the instrument is programmed to acquire all ion data.

**5.8 Sublimation**-the direct passage of a substance from the solid state to the gaseous state and back into the solid form without at any time appearing in the liquid state. Also applied to the conversion of solid to vapor without the later return to solid state, and to a conversion directly from the vapor phase to the solid state.

**5.9 Surrogate standard**-a chemically inert compound (not expected to occur in the environmental sample) that is added to each sample, blank, and matrix-spiked sample before extraction and analysis. 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 acceptable limits.

**5.10 CAL**-calibration standards are defined as five levels of calibration: CAL 1, CAL 2, CAL 3, CAL 4, and CAL 5. CAL 1 is the lowest concentration and CAL 5 is the highest concentration. CAL 3, which is the mid-level standard, is designated as the solution to be used for continuing calibrations.

**5.11 Continuing calibration check**-a solution of method analytes used to evaluate the mass spectrometer response over a period of time. A continuing calibration check (CCC) is performed once each 12-hour period. The CCC solution (CAL 3) is the standard of the calibration curve.

**5.12 GC Response ( $A_x$ )**-the peak area or height of analyte, x.

**5.13 Internal standard (IS)**-a compound added to a sample extract in known amounts and used to calibrate concentration measurements of other compounds that are sample components. The internal standard must be a compound that is not a sample component.

## 6. Limitations and Interferences

### 6.1 Limitations

**6.1.1** PAHs span a broad spectrum of vapor pressures (e.g., from  $1.1 \times 10^{-2}$  kPa for naphthalene to  $2 \times 10^{-13}$  kPa for coronene at  $25^\circ\text{C}$ ). PAHs that are frequently found in ambient air are listed in Table 1. Those with vapor pressures above approximately  $10^{-8}$  kPa will be present in the ambient air substantially distributed between the gas and particulate phases. This method will permit the collection of both phases.

**6.1.2** Particulate-phase PAHs will tend to be lost from the particle filter during sampling due to volatilization. Therefore, separate analysis of the filter will not reflect the concentrations of the PAHs originally associated with particles, nor will analysis of the sorbent provide an accurate measure of the gas phase. Consequently, this method calls for *extraction of the filter and sorbent together* to permit accurate measurement of total PAH air concentrations.

**6.1.3** Naphthalene, acenaphthylene, and acenaphthene possess relatively high vapor pressures and may not be efficiently trapped by this method when using PUF as the sorbent. The sampling efficiency for naphthalene has been determined to be about 35 percent for PUF. The user is encouraged to use XAD-2® as the sorbent if these analytes are part of the target compound list (TCL).

### 6.2 Interferences

**6.2.1** 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.

**6.2.2** Glassware must be scrupulously cleaned (51). All glassware should be cleaned as soon as possible after use by rinsing with the last solvent used in it and then high-purity acetone and hexane. These rinses should be followed by detergent washing with hot water and rinsing with copious amounts of tap water and several portions of reagent water. The glassware should then be drained dry and heated in a muffle furnace at 400°C for four hours. Volumetric glassware must not be heated in a muffle furnace; rather it should be solvent rinsed with acetone and spectrographic grade hexane. After drying and rinsing, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Glassware should be stored inverted or capped with aluminum foil.

*[Note: The glassware may be further cleaned by placing in a muffle furnace at 450°C for 8 hours to remove trace organics.]*

**6.2.3** 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.

**6.2.4** Matrix interferences may be caused by contaminants that are coextracted from the sample. Additional clean-up by column chromatography may be required (see Section 12.3).

**6.2.5** During sample transport and analysis, heat, ozone, NO<sub>2</sub>, and ultraviolet (UV) light may cause sample degradation. Incandescent or UV-shielded fluorescent lighting in the laboratory should be used during analysis.

**6.2.6** The extent of interferences that may be encountered using GC/MS techniques has not been fully assessed. Although GC conditions described allow for unique resolution of the specific PAH compounds covered by this method, other PAH compounds may interfere. The use of column chromatography for sample clean-up prior to GC analysis will eliminate most of these interferences. The analytical system must, however, be routinely demonstrated to be free of internal contaminants such as contaminated solvents, glassware, or other reagents which may lead to method interferences. A laboratory reagent blank should be analyzed for each reagent used to determine if reagents are contaminant-free.

**6.2.7** Concern about sample degradation during sample transport and analysis was mentioned above. Heat, ozone, NO<sub>2</sub>, and ultraviolet (UV) light also may cause sample degradation. These problems should be addressed as part of the user-prepared standard operating procedure (SOP) manual. Where possible, incandescent or UV-shielded fluorescent lighting should be used during analysis. During transport, field samples should be shipped back to the laboratory chilled (~4°C) using blue ice/dry ice.

## 7. Safety

**7.1** 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 Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and are included in the reference list (52-54).

**7.2** B[a]P 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 whomever uses this method 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 (see Table 1 and Figure 1).

**7.3** All PAHs should be treated as carcinogens. Neat compounds should be weighed in a glove box. Spent samples and unused standards are toxic waste and should be disposed according to regulations. Counter tops and equipment should be regularly checked with "black light" for fluorescence as an indicator of contamination.

**7.4** The sampling configuration (filter and backup sorbent) and collection efficiency for target PAHs has been demonstrated to be greater than 95 percent (except for naphthalene, acenaphthylene and acenaphthene). Therefore, no field recovery evaluation will be required as part of this procedure.

*[Note: Naphthalene, acenaphthylene and acenaphthene have demonstrated significant breakthrough using PUF cartridges, especially at summer ambient temperatures. If naphthalene, acenaphthylene and acenaphthene are target PAHs, the user may want to consider replacing the PUF with XAD-2® in order to minimize breakthrough during sampling.]*

## 8. Apparatus

*[Note: This method was developed using the PS-1 semi-volatile sampler provided by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in the use of this equipment during various field-monitoring programs over the last several years. Other manufacturers' equipment should work as well; however, modifications to these procedures may be necessary if another commercially available sampler is selected.]*

### 8.1 Sampling

**8.1.1** High-volume sampler (see Figure 2). Capable of pulling ambient air through the filter/sorbent cartridge at a flow rate of approximately 8 standard cubic feet per minute (scfm) (0.225 std m<sup>3</sup>/min) to obtain a total sample volume of greater than 300 m<sup>3</sup> over a 24-hour period. Major manufacturers are:

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

Recent EPA studies have concluded that sample volumes *less than* 300 m<sup>3</sup> still collect enough PAHs on the filter/PUF for quantitation. The user is encouraged to investigate appropriate sample volume needed to meet project specific data quality objectives.

**8.1.2** Sampling module (see Figure 3). Metal filter holder (Part 2) capable of holding a 102-mm circular particle filter supported by a 16-mesh stainless-steel screen and attaching to a metal cylinder (Part 1) capable of holding a 65-mm O.D. (60-mm I.D.) x 125-mm borosilicate glass sorbent cartridge containing PUF or XAD-2®. The filter holder is equipped with inert sealing gaskets (e.g., polytetrafluorethylene) placed on either side of the

filter. Likewise, inert, pliable gaskets (e.g., silicone rubber) are used to provide an air-tight seal at each end of the glass sorbent cartridge. The glass sorbent cartridge is indented 20 mm from the lower end to provide a support for a 16-mesh stainless-steel screen that holds the sorbent. The glass sorbent cartridge fits into Part 1, which is screwed onto Part 2 until the sorbent cartridge is sealed between the silicone gaskets. Major manufacturers are:

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

**8.1.3 High-volume sampler calibrator.** Capable of providing multipoint resistance for the high-volume sampler. Major manufacturers are:

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

**8.1.4 Ice chest.** To hold samples at 4°C or below during shipment to the laboratory after collection.

**8.1.5 Data sheets.** Used for each sample to record the location and sample time, duration of sample, starting time, and volume of air sampled.

## 8.2 Sample Clean-Up and Concentration (see Figure 4).

**8.2.1 Soxhlet apparatus extractor (see Figure 4a).** Capable of extracting filter and sorbent cartridges (5.75-cm x 12.5-cm length), 1,000 mL flask, and condenser, best source.

**8.2.2 Pyrex glass tube furnace system.** For activating silica gel at 180°C under purified nitrogen gas purge for an hour, with capability of raising temperature gradually, best source.

**8.2.3 Glass vial.** 40 mL, best source.

**8.2.4 Erlenmeyer flask.** 50 mL, best source.

*[Note: Reuse of glassware should be minimized to avoid the risk of cross contamination. All glassware that is used must be scrupulously cleaned as soon as possible after use. 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 amounts of tap water and several portions of distilled water. Drain, dry, and heat in a muffle furnace at 400°C for 4 hours. Volumetric glassware must not be heated in a muffle furnace; rather, it should be rinsed with high-purity acetone and hexane. After the glassware is dry and cool, rinse it with hexane, and store it inverted or capped with solvent-rinsed aluminum foil in a clean environment.]*

**8.2.5 White cotton gloves.** For handling cartridges and filters, best source.

**8.2.6 Minivials.** 2 mL, borosilicate glass, with conical reservoir and screw caps lined with Teflon®-faced silicone disks, and a vial holder, best source.

**8.2.7 Teflon®-coated stainless steel spatulas and spoons.** Best source.

**8.2.8 Kuderna-Danish (K-D) apparatus (see Figure 4b).** 500 mL evaporation flask (Kontes K-570001-500 or equivalent), 10 mL graduated concentrator tubes (Kontes K570050-1025 or equivalent) with ground-glass stoppers, 1 mL calibrated K-D concentration tubes, and 3-ball macro Snyder Column (Kontes K-570010500, K-50300-0121, and K-569001-219, or equivalent), best source.

**8.2.9 Adsorption column for column chromatography (see Figure 4c).** 1-cm x 10-cm with stands.

**8.2.10 Glove box.** For working with extremely toxic standards and reagents with explosion-proof hood for venting fumes from solvents, reagents, etc.

**8.2.11 Vacuum oven.** Vacuum drying oven system capable of maintaining a vacuum at 240 torr (flushed with nitrogen) overnight.

**8.2.12 Concentrator tubes and a nitrogen evaporation apparatus with variable flow rate.** Best source.

**8.2.13 Laboratory refrigerator.** Best source.

**8.2.14 Boiling chips.** Solvent extracted, 10/40 mesh silicon carbide or equivalent, best source.

**8.2.15 Water bath.** Heated, with concentric ring cover, capable of  $\pm 5^\circ\text{C}$  temperature control, best source.

**8.2.16 Nitrogen evaporation apparatus.** Best source.

**8.2.17 Glass wool.** High grade, best source.

### 8.3 Sample Analysis

**8.3.1 Gas Chromatography with Mass Spectrometry Detection Coupled with Data Processing System (GC/MS/DS).** The gas chromatograph must be equipped for temperature programming, and all required accessories must be available, including syringes, gases, and a capillary column. The gas chromatograph 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 2  $\mu\text{L}$  injection volume is used consistently to maximize auto sampler reproducibility. With some gas chromatograph injection ports, however, 1  $\mu\text{L}$  injections may produce some improvement in precision and chromatographic separation. A 1  $\mu\text{L}$  injection volume may be used if adequate sensitivity and precision can be achieved.

*[Note: If 1  $\mu\text{L}$  is used as the injection volume, the injection volumes for all extracts, blanks, calibration solutions and performance check samples must be 1  $\mu\text{L}$ .]*

All GC carrier gas lines must be constructed from stainless steel or copper tubing. Poly-tetrafluoroethylene (PTFE) thread sealants or flow controllers should only be used.

**8.3.2 Gas chromatograph-mass spectrometer interface.** The GC is usually coupled directly to the MS 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. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface components should be compatible with 320 $^\circ\text{C}$  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 gas chromatograph injection area since they may adsorb PAHs. Vespel<sup>®</sup> or equivalent ferrules are recommended.

**8.3.3 Mass spectrometer.** The MS should be operated in the full range data acquisition (SCAN) mode with a total cycle time (including voltage reset time) of one second or less (see Section 13.3.2). Operation of the MS in the SCAN mode allows monitoring of all ions, thus assisting with the identification of other PAHs beyond Compendium Method TO-13A target analyte list. In addition, operating in the SCAN mode assists the analyst with identification of possible interferences from non-target analytes due to accessibility of the complete mass spectrum in the investigative process. The MS must be capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact (EI) ionization mode. The mass spectrometer must be capable of producing a mass spectrum for a 50 ng injection of decafluorotriphenyl phosphine (DFTPP) which meets all of the response criteria (see Section 13.3.3). To ensure sufficient precision of mass spectral data, the MS scan rate must allow acquisition of at least five scans while a sample compound elutes from the GC. The

GC/MS system must be in a room with atmosphere demonstrated to be free of all potential contaminants which will interfere with the analysis. The instrument must be vented outside the facility or to a trapping system which prevents the release of contaminants into the instrument room.

**8.3.4 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. The computer should have software that allows searching the GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as Selected Ion Current Profile (SICP). The software used must allow integrating the abundance in any SICP between specified time or scan number limits. The data system should be capable of flagging all data files that have been edited manually by laboratory personnel.

**8.3.5 Gas chromatograph column.** A fused silica DB-5 column (30 m x 0.32 mm I.D.) crosslinked 5 percent phenyl methylsilicone, 1.0  $\mu\text{m}$  film thickness is utilized to separate individual PAHs. Other columns may be used for determination of PAHs. Minimum acceptance criteria must be determined as per Section 13.3. 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.

**8.3.6 Balance.** Mettler balance or equivalent.

**8.3.7 All required syringes, gases, and other pertinent supplies.** To operate the GC/MS system.

**8.3.8 Pipettes, micropipettes, syringes, burets, etc.** Used to make calibration and spiking solutions, dilute samples if necessary, etc., including syringes for accurately measuring volumes such as 25  $\mu\text{L}$  and 100  $\mu\text{L}$ .

## 9. Equipment and Materials

### 9.1 Materials for Sample Collection (see Figure 3)

**9.1.1 Quartz fiber filter.** 102 millimeter binderless quartz microfiber filter, Whatman Inc., 6 Just Road, Fairfield, NJ 07004, Filter Type QMA-4.

**9.1.2 Polyurethane foam (PUF) plugs (see Figure 5a).** 3-inch thick sheet stock polyurethane type (density .022  $\text{g}/\text{cm}^3$ ). The PUF should be of the polyether type used for furniture upholstery, pillows, and mattresses. The PUF cylinders (plugs) should be slightly larger in diameter than the internal diameter of the cartridge. Sources of equipment are Tisch Environmental, Village of Cleves, OH; University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC; Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA; Supelco, Supelco Park, Bellefonte, PA; and SKC Inc., 334 Valley View Road, Eighty Four, PA.

**9.1.3 XAD-2® resin (optional).** Supelco, Supelco Park, Bellefonte, PA.

**9.1.4 Teflon® end caps (see Figure 5a).** For sample cartridge; sources of equipment are Tisch Environmental, Village of Cleves, OH; and University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC.

**9.1.5 Sample cartridge aluminum shipping containers (see Figure 5b).** For sample cartridge shipping; sources of equipment are Tisch Environmental, Village of Cleves, OH; and University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC.



**9.1.6 Glass sample cartridge (see Figure 5a).** For sample collection; sources of equipment are Tisch Environmental, Village of Cleves, OH; Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA; and University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC.

**9.1.7 Aluminum foil.** Best source.

**9.1.8 Hexane, reagent grade.** Best source.

## 9.2 Sample Clean-up and Concentration

**9.2.1 Methylene chloride (extraction solvent for XAD-2®; optional).** Chromatographic grade, glass-distilled, best source.

**9.2.2 Sodium sulfate-anhydrous (ACS).** Granular (purified by washing with methylene chloride followed by heating at 400°C for 4 hours in a shallow tray).

**9.2.3 Boiling chips.** Solvent extracted or heated in a muffle furnace at 450°C for 2 hours, approximately 10/40 mesh (silicon carbide or equivalent).

**9.2.4 Nitrogen.** High purity grade, best source.

**9.2.5 Hexane.** Chromatographic grade, glass-distilled, best source (extraction solvent for PUF).

**9.2.6 Glass wool.** Silanized, extracted with methylene chloride and hexane, and dried.

**9.2.7 Diethyl ether.** High purity, glass distilled (extraction solvent for PUF).

**9.2.8 Pentane.** High purity, glass distilled.

**9.2.9 Silica gel.** High purity, type 60, 70-230 mesh.

## 9.3 GC/MS Sample Analysis

**9.3.1 Gas cylinder of helium.** Ultra high purity, best source.

**9.3.2 Chromatographic-grade stainless steel tubing and stainless steel fitting.** For interconnections, Alltech Applied Science, 2051 Waukegan Road, Deerfield, IL 60015, 312-948-8600, or equivalent.

*[Note: All such materials in contact with the sample, analyte, or support gases prior to analysis should be stainless steel or other inert metal. Do not use plastic or Teflon® tubing or fittings.]*

**9.3.3 Native and isotopically labeled PAH isomers for calibration and spiking standards.** Cambridge Isotopes, 20 Commerce Way, Woburn, MA 01801 (617-547-1818). Suggested isotopically labeled PAH isomers are: D<sub>10</sub>-fluoranthene, D<sub>2</sub>-benzo(a)pyrene, D<sub>10</sub>-fluorene, D<sub>10</sub>-pyrene, D<sub>12</sub>-perylene, D<sub>10</sub>-acenaphthene, D<sub>12</sub>-chrysene, D<sub>8</sub>-naphthalene and D<sub>10</sub>-phenanthrene.

**9.3.4 Decafluorotriphenylphosphine (DFTPP).** Used for tuning GC/MS, best source.

**9.3.5 Native stock pure standard PAH analytes.** For developing calibration curve for GC/MS analysis, best source.

## 10. Preparation of PUF Sampling Cartridge

*[Note: This method was developed using the PS-1 sample cartridge provider by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in use of this equipment during various field monitoring program over the last several years. Other manufacturers' equipment should work as well; however, modifications to these procedures may be necessary if another commercially available sampler is selected.]*

## 10.1 Summary of Method

**10.1.1** This part of the procedure discusses pertinent information regarding the preparation and cleaning of the filter, sorbent, and filter/sorbent cartridge assembly. The separate batches of filters and sorbents are extracted with the appropriate solvent.

**10.1.2** At least one PUF cartridge assembly and one filter from each batch, or 10 percent of the batch, whichever is greater, should be tested and certified before the batch is considered for field use.

**10.1.3** Prior to sampling, the cartridges are spiked with field surrogate compounds.

## 10.2 Preparation of Sampling Cartridge

**10.2.1** Bake the Whatman QMA-4 quartz filters at 400°C for 5 hours before use.

**10.2.2** Set aside the filters in a clean container for shipment to the field or prior to combining with the PUF glass cartridge assembly for certification prior to field deployment.

**10.2.3** The PUF plugs are 6.0-cm diameter cylindrical plugs cut from 3-inch sheet stock and should fit, with slight compression, in the glass cartridge, supported by the wire screen (see Figure 5a). During cutting, rotate the die at high speed (e.g., in a drill press) and continuously lubricate with deionized or distilled water. Pre-cleaned PUF plugs can be obtained from commercial sources (see Section 9.1.2).

**10.2.4** For initial cleanup, place the PUF plugs in a Soxhlet apparatus and extract with acetone for 16 hours at approximately 4 cycles per hour. When cartridges are reused, use diethyl ether/hexane (5 to 10 percent volume/volume [v/v]) as the cleanup solvent.

*[Note: A modified PUF cleanup procedure can be used to remove unknown interference components of the PUF blank. This method consists of rinsing 50 times with toluene, acetone, and diethyl ether/hexane (5 to 10 percent v/v), followed by Soxhlet extraction. The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2 to 4 hours (until no solvent odor is detected). The extract from the Soxhlet extraction procedure from each batch may be analyzed to determine initial cleanliness prior to certification.]*

**10.2.5** If using XAD-2® in the cartridge, initial cleanup of the resin is performed by placing approximately 50-60 grams in a Soxhlet apparatus and extracting with methylene chloride for 16 hours at approximately 4 cycles per hour. At the end of the initial Soxhlet extraction, the spent methylene chloride is discarded and replaced with a fresh reagent. The XAD-2® resin is once again extracted for 16 hours at approximately 4 cycles per hour. The XAD-2® resin is removed from the Soxhlet apparatus, placed in a vacuum oven connected to an ultra-pure nitrogen gas stream, and dried at room temperature for approximately 2-4 hours (until no solvent odor is detected).

**10.2.6** Fit a nickel or stainless steel screen (mesh size 200/200) to the bottom of a hexane-rinsed glass sampling cartridge to retain the PUF or XAD-2® sorbents, as illustrated in Figure 5a. If using XAD-2® alone, then place a small diameter (~1/4") PUF plug on top of the nickel or stainless steel screen to retain the XAD-2® in the glass cartridge. Place the Soxhlet-extracted, vacuum-dried PUF (2.5-cm thick by 6.5-cm diameter) on top of the screen in the glass sampling cartridge using polyester gloves. Place ~200 g of the clean XAD-2® inside the glass sampling cartridge on top of the small diameter PUF plug.

**10.2.7** Wrap the sampling cartridge with hexane-rinsed aluminum foil, cap with the Teflon® end caps (optional), place in a cleaned labeled aluminum shipping container, and seal with Teflon® tape. Analyze at least 1 cartridge from each batch of cartridges prepared using the procedure described in Section 10.3, before the batch is considered acceptable for field use.

The acceptance level of the cartridge is for each target PAH analyte to be less than or equal to the detection limit requirements to meet the project data quality objectives. It is generally not possible to eliminate the presence of naphthalene, but the amount detected on the cleaned PUF cartridge should be less than five times the concentration of the lowest calibration standard (~500 ng). This amount is insignificant compared to the amount collected from a typical air sample.

In general, the following guidelines are provided in determining whether a cartridge is clean for field use:

- Naphthalene <500 ng/cartridge
- Other PAHs <200 ng total/cartridge

### 10.3 Procedure for Certification of PUF Cartridge Assembly

*[Note: The following procedure outlines the certification of a filter and PUF cartridge assembly. If using XAD-2® as the sorbent, the procedure remains the same, except the solvent is methylene chloride rather than 10 percent diethyl ether/hexane.]*

**10.3.1** Extract one filter and PUF sorbent cartridge by Soxhlet extraction and concentrate using a K-D evaporator for each lot of filters and cartridges sent to the field.

**10.3.2** Assemble the Soxhlet apparatus. Charge the Soxhlet apparatus (see Figure 4a) with 700 mL of the extraction solvent (10 percent v/v diethyl ether/hexane) and reflux for 2 hours. Let the apparatus cool, disassemble it, and discard the used extraction solvent. Transfer the filter and PUF glass cartridge to the Soxhlet apparatus (the use of an extraction thimble is optional).

*[Note: The filter and sorbent assembly are tested together in order to reach detection limits, to minimize cost and to prevent misinterpretation of the data. Separate analyses of the filter and PUF would not yield useful information about the physical state of most of the PAHs at the time of sampling due to evaporative losses from the filter during sampling.]*

**10.3.3** Add between 300 and 350 mL of diethyl ether/hexane (10 percent v/v) to the Soxhlet apparatus. Reflux the sample for 18 hours at a rate of at least 3 cycles per hour. Allow to cool, then disassemble the apparatus.

**10.3.4** Assemble a K-D concentrator (see Figure 4b) by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

**10.3.5** Transfer the extract by pouring it through a drying column containing about 10 cm of anhydrous granular sodium sulfate (see Figure 4c) and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of 10 percent diethyl ether/hexane to complete the quantitative transfer.

**10.3.6** Add one or two clean boiling chips and attach a 3-ball Snyder column to the evaporative flask. Pre-wet the Snyder column by adding about 1 mL of the extraction solvent to the top of the column. Place the K-D apparatus on a hot water bath (~50°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 1 hour. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches approximately 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 5 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 5 mL of cyclohexane. A 1-mL syringe is recommended for this operation.

**10.3.7** Concentrate the extract to 5 mL and analyze using GC/MS.

**10.3.8** The acceptance level of the cartridge is for each target PAH analyte to be less than or equal to the detection limit requirements to meet the project data quality objectives. It is generally not possible to eliminate the presence of naphthalene, but the amount detected on the cleaned PUF cartridge should be less than five times the concentration of the lowest calibration standard (~500 ng). This amount is insignificant compared to the amount collected from a typical air sample.

In general, the following guidelines are provided in determining whether a cartridge is clean for field use:

- Naphthalene <500 ng/cartridge
- Other PAHs <200 ng total/cartridge

Cartridges are considered clean for up to 30 days from date of certification when sealed in their containers.

#### 10.4 Deployment of Cartridges for Field Sampling

**10.4.1** Immediately prior to field deployment, add surrogate compounds (i.e., chemically inert compounds not expected to occur in an environmental sample) to the center of the PUF cartridge, using a microsyringe. Spike 20  $\mu\text{L}$  of a 50  $\mu\text{g}/\text{mL}$  solution of the surrogates onto the center bed of the PUF trap to yield a final concentration of 1  $\mu\text{g}$ . The surrogate compounds must be added to each cartridge assembly. The following field surrogate compounds should be added to each PUF cartridge prior to field deployment to monitor matrix effects, breakthrough, etc.

<u>Field Surrogate Compound</u>	<u>Total Spiked Amount (<math>\mu\text{g}</math>)</u>
D <sub>10</sub> -Fluoranthene	1
D <sub>12</sub> -Benzo(a)pyrene	1

Fill out a "chain-of-custody" indicating cartridge number, surrogate concentration, date of cartridge certification, etc. The chain-of-custody must accompany the cartridge to the field and return to the laboratory.

**10.4.2** Use the recoveries of the surrogate compounds to monitor for unusual matrix effects and gross sample processing errors. Evaluate surrogate recovery for acceptance by determining whether the measured concentration falls within the acceptance limits of 60-120 percent.

**10.4.3** Cartridges are placed in their shipping containers and shipped to the field. Blank cartridges do not need to be chilled when shipping to the field until after exposure to ambient air.

### 11. Assembly, Calibration, and Collection Using Sampling System

*[Note: This method was developed using the PS-1 semi-volatile sampler provided by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in the use of this equipment during various field monitoring programs over the last several years. Other manufacturers' equipment should work as well; however, modifications to these procedures may be necessary if another commercially available sampler is selected.]*

## 11.1 Sampling Apparatus

The entire sampling system is diagrammed in Figure 2. This apparatus was developed to operate at a rate of 4 to 10 scfm (0.114 to 0.285 std m<sup>3</sup>/min) and is used by EPA for high-volume sampling of ambient air. The method write-up presents the use of this device.

The sampling module (see Figure 3) consists of a filter and a glass sampling cartridge containing the PUF utilized to concentrate PAHs from the air. A field portable unit has been developed by EPA (see Figure 6).

## 11.2 Calibration of Sampling System

Each sampler should be calibrated (1) when new, (2) after major repairs or maintenance, (3) whenever any audit point deviates from the calibration curve by more than 7 percent, (4) before/after each sampling event, and (5) when a different sample collection medium, other than that which the sampler was originally calibrated to, will be used for sampling.

**11.2.1** Calibration of Orifice Transfer Standard. Calibrate the modified high volume air sampler in the field using a calibrated orifice flow rate transfer standard. Certify the orifice transfer standard in the laboratory against a positive displacement rootsmeter (see Figure 7). Once certified, the recertification is performed rather infrequently if the orifice is protected from damage. Recertify the orifice transfer standard performed once per year utilizing a set of five multi-hole resistance plates.

*[Note: The set of five multihole resistance plates is used to change the flow through the orifice so that several points can be obtained for the orifice calibration curve. The following procedure outlines the steps to calibrate the orifice transfer standard in the laboratory.]*

**11.2.1.1** Record the room temperature ( $T_1$  in °C) and barometric pressure ( $P_b$  in mm Hg) on the Orifice Calibration Data Sheet (see Figure 8). Calculate the room temperature in K (absolute temperature) and record on Orifice Calibration Data Sheet.

$$T_1 \text{ in K} = 273^\circ + T_1 \text{ in } ^\circ\text{C}$$

**11.2.1.2** Set up laboratory orifice calibration equipment as illustrated in Figure 7. Check the oil level of the rootsmeter prior to starting. There are three oil level indicators, one at the clear plastic end, and two sight glasses, one at each end of the measuring chamber.

**11.2.1.3** Check for leaks by clamping both manometer lines, blocking the orifice with cellophane tape, turning on the high-volume motor, and noting any change in the rootsmeter's reading. If the rootsmeter's reading changes, there is a leak in the system. Eliminate the leak before proceeding. If the rootsmeter's reading remains constant, turn off the hi-vol motor, remove the cellophane tape, and unclamp both manometer lines.

**11.2.1.4** Install the 5-hole resistance plate between the orifice and the filter adapter.

**11.2.1.5** Turn manometer tubing connectors one turn counter-clockwise. Make sure all connectors are open.

**11.2.1.6** Adjust both manometer midpoints by sliding their movable scales until the zero point corresponds with the meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required for the water manometer, remove tubing connector and add clean water.)

**11.2.1.7** Turn on the high-volume motor and let it run for 5 minutes to set the motor brushes. Turn the motor off. Ensure manometers are set to zero. Turn the high-volume motor on.

**11.2.1.8** Record the time in minutes required to pass a known volume of air (approximately 5.6 to 8.4 m<sup>3</sup> of air for each resistance plate) through the rootsmeter by using the rootsmeter's digital volume dial and a stopwatch.

**11.2.1.9** Record both manometer readings [orifice water manometer ( $\Delta H$ ) and rootsmeter mercury manometer ( $\Delta P$ )] on Orifice Calibration Data Sheet (see Figure 8).

*[Note:  $\Delta H$  is the sum of the difference from zero (0) of the two column heights.]*

**11.2.1.10** Turn off the high-volume motor.

**11.2.1.11** Replace the 5-hole resistance plate with the 7-hole resistance plate.

**11.2.1.12** Repeat Sections 11.2.1.3 through 11.2.1.11.

**11.2.1.13** Repeat for each resistance plate. Note results on Orifice Calibration Data Sheet (see Figure 8). Only a minute is needed for warm-up of the motor. Be sure to tighten the orifice enough to eliminate any leaks. Also check the gaskets for cracks.

*[Note: The placement of the orifice prior to the rootsmeter causes the pressure at the inlet of the rootsmeter to be reduced below atmospheric conditions, thus causing the measured volume to be incorrect. The volume measured by the rootsmeter must be corrected.]*

**11.2.1.14** Correct the measured volumes on the Orifice Calibration Data Sheet:

$$V_{\text{std}} = V_{\text{m}} \left( \frac{P_{\text{a}} - \Delta P}{P_{\text{std}}} \right) \left( \frac{T_{\text{std}}}{T_{\text{a}}} \right)$$

where:

$V_{\text{std}}$  = standard volume, std m<sup>3</sup>

$V_{\text{m}}$  = actual volume measured by the rootsmeter, m<sup>3</sup>

$P_{\text{a}}$  = barometric pressure during calibration, mm Hg

$\Delta P$  = differential pressure at inlet to volume meter, mm Hg

$P_{\text{std}}$  = 760 mm Hg

$T_{\text{std}}$  = 298 K

$T_{\text{a}}$  = ambient temperature during calibration, K.

**11.2.1.15** Record standard volume on Orifice Calibration Data Sheet.

**11.2.1.16** The standard flow rate as measured by the rootsmeter can now be calculated using the following formula:

$$Q_{\text{std}} = \frac{V_{\text{std}}}{\theta}$$

where:

$Q_{\text{std}}$  = standard volumetric flow rate, std m<sup>3</sup>/min

$\theta$  = elapsed time, min

**11.2.1.17** Record the standard flow rates to the nearest 0.01 std m<sup>3</sup>/min.

**11.2.1.18** Calculate and record  $\sqrt{\Delta H (P_1/P_{std})(298/T_1)}$  value for each standard flow rate.

**11.2.1.19** Plot each  $\sqrt{\Delta H (P_1/P_{std})(298/T_1)}$  value (y-axis) versus its associated standard flow rate (x-axis) on arithmetic graph paper and draw a line of best fit between the individual plotted points.

[*Note: This graph will be used in the field to determine standard flow rate.*]

### **11.2.2 Calibration of the High-Volume Sampling System Utilizing Calibrated Orifice Transfer Standard**

For this calibration procedure, the following conditions are assumed in the field:

- The sampler is equipped with an valve to control sample flow rate.
- The sample flow rate is determined by measuring the orifice pressure differential using a Magnehelic gauge.
- The sampler is designed to operate at a standardized volumetric flow rate of 8 ft<sup>3</sup>/min (0.225 m<sup>3</sup>/min), with an acceptable flow rate range within 10 percent of this value.
- The transfer standard for the flow rate calibration is an orifice device. The flow rate through the orifice is determined by the pressure drop caused by the orifice and is measured using a "U" tube water manometer or equivalent.
- The sampler and the orifice transfer standard are calibrated to standard volumetric flow rate units (scfm or scmm).
- An orifice transfer standard with calibration traceable to NIST is used.
- A "U" tube water manometer or equivalent, with a 0- to 16-inch range and a maximum scale division of 0.1 inch, will be used to measure the pressure in the orifice transfer standard.
- A Magnehelic gauge or equivalent with a 9- to 100-inch range and a minimum scale division of 2 inches for measurements of the differential pressure across the sampler's orifice is used.
- A thermometer capable of measuring temperature over the range of 32° to 122°F (0° to 50°C) to ±2°F (±1°C) and referenced annually to a calibrated mercury thermometer is used.
- A portable aneroid barometer (or equivalent) capable of measuring ambient barometric pressure between 500 and 800 mm Hg (19.5 and 31.5 in. Hg) to the nearest mm Hg and referenced annually to a barometer of known accuracy is used.
- Miscellaneous handtools, calibration data sheets or station log book, and wide duct tape are available.

**11.2.2.1** Set up the calibration system as illustrated in Figure 9. Monitor the airflow through the sampling system with a venturi/Magnehelic assembly, as illustrated in Figure 9. Audit the field sampling system once per quarter using a flow rate transfer standard, as described in the EPA *High-Volume Sampling Method, 40 CFR 50, Appendix B*. Perform a single-point calibration before and after each sample collection, using the procedures described in Section 11.2.3.

**11.2.2.2** Prior to initial multi-point calibration, place an empty glass cartridge in the sampling head and activate the sampling motor. Fully open the flow control valve and adjust the voltage variator so that a sample flow rate corresponding to 110 percent of the desired flow rate (typically 0.20 to 0.28 m<sup>3</sup>/min) is indicated on the Magnehelic gauge (based on the previously obtained multipoint calibration curve). Allow the motor to warm up for 10 min and then adjust the flow control valve to achieve the desired flow rate. Turn off the sampler. Record the ambient temperature and barometric pressure on the Field Calibration Data Sheet (see Figure 10).

**11.2.2.3** Place the orifice transfer standard on the sampling head and attach a manometer to the tap on the transfer standard, as illustrated in Figure 9. Properly align the retaining rings with the filter holder and secure by tightening the three screw clamps. Connect the orifice transfer standard by way of the pressure tap to a

manometer using a length of tubing. Set the zero level of the manometer or Magnehelic. Attach the Magnehelic gauge to the sampler venturi quick release connections. Adjust the zero (if needed) using the zero adjust screw on face of the gauge.

**11.2.2.4** To leak test, block the orifice with a rubber stopper, wide duct tape, or other suitable means. Seal the pressure port with a rubber cap or similar device. Turn on the sampler.

*Caution: Avoid running the sampler for too long a time with the orifice blocked. This precaution will reduce the chance that the motor will be overheated due to the lack of cooling air. Such overheating can shorten the life of the motor.*

**11.2.2.5** Gently rock the orifice transfer standard and listen for a whistling sound that would indicate a leak in the system. A leak-free system will not produce an upscale response on the sampler's magnehelic. Leaks are usually caused either by damaged or missing gaskets, by cross-threading, and/or not screwing sample cartridge together tightly. All leaks must be eliminated before proceeding with the calibration. When the sample is determined to be leak-free, turn off the sampler and unblock the orifice. Now remove the rubber stopper or plug from the calibrator orifice.

**11.2.2.6** Turn the flow control valve to the fully open position and turn the sampler on. Adjust the flow control valve until a Magnehelic reading of approximately 70 in. is obtained. Allow the Magnehelic and manometer readings to stabilize and record these values on the orifice transfer Field Calibration Data Sheet (see Figure 10).

**11.2.2.7** Record the manometer reading under Y1 and the Magnehelic reading under Y2 on the Field Calibration Data Sheet. For the first reading, the Magnehelic should still be at 70 inches as set above.

**11.2.2.8** Set the Magnehelic to 60 inches by using the sampler's flow control valve. Record the manometer (Y1) and Magnehelic (Y2) readings on the Field Calibration Data Sheet (see Figure 10).

**11.2.2.9** Repeat the above steps using Magnehelic settings of 50, 40, 30, 20, and 10 inches.

**11.2.2.10** Turn the voltage variator to maximum power, open the flow control valve, and confirm that the Magnehelic reads at least 100 inches. Turn off the sampler and confirm that the Magnehelic reads zero.

**11.2.2.11** Read and record the following parameters on the Field Calibration Data Sheet. Record the following on the calibration data sheet:

- Data, job number, and operator's signature.
- Sampler serial number.
- Ambient barometric pressure.
- Ambient temperature.

**11.2.2.12** Remove the "dummy" cartridge and replace with a sample cartridge.

**11.2.2.13** Obtain the manufacturer high volume orifice calibration certificate.

**11.2.2.14** If not performed by the manufacturer, calculate values for each calibrator orifice static pressure (Column 6, inches of water) on the manufacturer's calibration certificate using the following equation:

$$\sqrt{\Delta H(P_a/760)[298/(T_a + 273)]}$$

where:

$P_a$  = the barometric pressure (mm Hg) at time of manufacturer calibration, mm Hg

$T_a$  = temperature at time of calibration, °C

**11.2.2.15** Perform a linear regression analysis using the values in Column 7 of the manufacturer's High Volume Orifice Calibration Certificate for flow rate ( $Q_{std}$ ) as the "X" values and the calculated values as the Y



values. From this relationship, determine the correlation (CC1), intercept (B1), and slope (M1) for the Orifice Transfer Standard.

**11.2.2.16** Record these values on the Field Calibration Data Sheet (see Figure 10).

**11.2.2.17** Using the Field Calibration Data Sheet values (see Figure 10), calculate the Orifice Manometer Calculated Values (Y3) for each orifice manometer reading using the following equation:

#### **Y3 Calculation**

$$Y3 = \{Y1(P_a/760)[298/(T_a + 273)]\}^{1/2}$$

**11.2.2.18** Record the values obtained in Column Y3 on the Field Calibration Data Sheet (see Figure 10).

**11.2.2.19** Calculate the Sampler Magnehelic Calculated Value (Y4) using the following equation:

#### **Y4 Calculation**

$$Y4 = \{Y2(P_a/760)[298/(T_a + 273)]\}^{1/2}$$

**11.2.2.20** Record the value obtained in Column Y4 on the Field Calibration Data Sheet (see Figure 10).

**11.2.2.21** Calculate the Orifice Flow Rate (X1) in scm using the following equation:

#### **X1 Calculation**

$$X1 = \frac{Y3 - B1}{M1}$$

**11.2.2.22** Record the values obtained in Column X1 on the Field Calibration Data Sheet (see Figure 10).

**11.2.2.23** Perform a linear regression of the values in Column X1 (as X) and the values in Column Y4 (as Y). Record the relationship for correlation (CC2), intercept (B2), and slope (M2) on the Field Calibration Data Sheet. The correlation coefficient must be 0.990 or greater.

**11.2.2.24** Using the following equation, calculate a set point (SP) for the manometer to represent a desired flow rate:

#### **Set Point**

$$\text{Set point (SP)} = [(\text{Expected } P_a)/(\text{Expected } T_a)(T_{\text{std}}/P_{\text{std}})][M2 (\text{Desired flow rate}) + B2]^2$$

where:

$P_a$  = Expected atmospheric pressure ( $P_a$ ), mm Hg

$T_a$  = Expected atmospheric temperature ( $T_a$ ), 273 + °C

M2 = Slope of developed relationship

B2 = Intercept of developed relationship

$T_{\text{std}}$  = Temperature standard, 273 + 25°C

$P_{\text{std}}$  = Pressure standard, 760 mm Hg

**11.2.2.25** During monitoring, calculate a flow rate from the observed Magnehelic reading using the following equations:

**Flow Rate**

$$Y5 = [\text{Average Magnehelic Reading } (\Delta H) (P_a/T_a)(T_{std}/P_{std})]^{1/2}$$

$$X2 = \frac{Y5 - B2}{M2}$$

where:

Y5 = Corrected average magnehelic reading  
X2 = Instant calculated flow rate, scfm

**11.2.2.26** The relationship in calibration of a sampling system between Orifice Transfer Standard and flow rate through the sampler is illustrated in Figure 11.

### **11.2.3 Single-Point Audit of the High Volume Sampling System Utilizing Calibrated Orifice Transfer Standard**

Single point calibration checks are required as follows:

- Prior to the start of each 24-hour test period.
- After each 24-hour test period. The post-test calibration check may serve as the pre-test calibration check for the next sampling period if the sampler is not moved.
- Prior to sampling after a sample is moved.

For samplers, perform a calibration check for the operational flow rate before each 24-hour sampling event and when required as outlined in the user quality assurance program. The purpose of this check is to track the sampler's calibration stability. Maintain a control chart presenting the percentage difference between a sampler's indicated and measured flow rates. This chart provides a quick reference of sampler flow-rate drift problems and is useful for tracking the performance of the sampler. Either the sampler log book or a data sheet will be used to document flow-check information. This information includes, but is not limited to, sampler and orifice transfer standard serial number, ambient temperature, pressure conditions, and collected flow-check data.

In this subsection, the following is assumed:

- The flow rate through a sampler is indicated by the orifice differential pressure;
- Samplers are designed to operate at an actual flow rate of 8 scfm, with a maximum acceptable flow-rate fluctuation range of  $\pm 10$  percent of this value;
- The transfer standard will be an orifice device equipped with a pressure tap. The pressure is measured using a manometer; and
- The orifice transfer standard's calibration relationship is in terms of standard volumetric flow rate ( $Q_{std}$ ).

**11.2.3.1** Perform a single point flow audit check before and after each sampling period utilizing the Calibrated Orifice Transfer Standard (see Section 11.2.1).

**11.2.3.2** Prior to single point audit, place a "dummy" glass cartridge in the sampling head and activate the sampling motor. Fully open the flow control valve and adjust the voltage variator so that a sample flow rate corresponding to 110 percent of the desired flow rate (typically 0.19 to 0.28 m<sup>3</sup>/min) is indicated on the Magnehelic gauge (based on the previously obtained multipoint calibration curve). Allow the motor to warm up for 10 minutes and then adjust the flow control valve to achieve the desired flow rate. Turn off the sampler. Record the ambient temperature and barometric pressure on the Field Test Data Sheet (see Figure 12).

**11.2.3.3** Place the flow rate transfer standard on the sampling head.

**11.2.3.4** Properly align the retaining rings with the filter holder and secure by tightening the three screw clamps. Connect the flow rate transfer standard to the manometer using a length of tubing.

**11.2.3.5** Using tubing, attach one manometer connector to the pressure tap of the transfer standard. Leave the other connector open to the atmosphere.

**11.2.3.6** Adjust the manometer midpoint by sliding the movable scale until the zero point corresponds with the water meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required, remove tubing connector and add clean water.)

**11.2.3.7** Turn on the high-volume motor and let run for 5 minutes.

**11.2.3.8** Record the pressure differential indicated,  $\Delta H$ , in inches of water, on the Field Test Data Sheet. Be sure a stable  $\Delta H$  has been established.

**11.2.3.9** Record the observed Magnehelic gauge reading in inches of water on the Field Test Data Sheet. Be sure stable  $\Delta M$  has been established.

**11.2.3.10** Using previous established Orifice Transfer Standard curve, calculate  $Q_{xs}$  (see Section 11.2.2.23).

**11.2.3.11** This flow should be within  $\pm 10$  percent of the sampler set point, normally, 0.224 m<sup>3</sup>. If not, perform a new multipoint calibration of the sampler.

**11.2.3.12** Remove flow rate transfer standard and dummy sorbent cartridge.

## 11.3 Sample Collection

### 11.3.1 General Requirements

**11.3.1.1** The sampler should be located in an unobstructed area, at least 2 meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sample head.

**11.3.1.2** All cleaning and sample module loading and unloading should be conducted in a controlled environment, to minimize any chance of potential contamination.

**11.3.1.3** When new or when using the sampler at a different location, all sample contact areas need to be cleaned. Use triple rinses of reagent grade hexane or methylene chloride contained in Teflon® rinse bottles. Allow the solvents to evaporate before loading the PUF modules.

### 11.3.2 Preparing Cartridge for Sampling

**11.3.2.1** Detach the lower chamber of the cleaned sample head. While wearing disposable, clean, lint-free nylon, or cotton gloves, remove a clean glass sorbent module from its shipping container. Remove the Teflon® end caps (if applicable). Replace the end caps in the sample container to be reused after the sample has been collected.

**11.3.2.2** Insert the glass module into the lower chamber and tightly reattach the lower chambers to the module.

**11.3.2.3** Using clean rinsed (with hexane) Teflon®-tipped forceps, carefully place a clean conditioned fiber filter atop the filter holder and secure in place by clamping the filter holder ring over the filter. Place the

aluminum protective cover on top of the cartridge head. Tighten the 3 screw clamps. Ensure that all module connections are tightly assembled. Place a small piece of aluminum foil on the ball-joint of the sample cartridge to protect from back-diffusion of semi-volatiles into the cartridge during transporting to the site.

*[Note: Failure to do so could expose the cartridge to contamination during transport.]*

**11.3.2.4** Place the cartridge in a carrying bag to take to the sampler.

### **11.3.3 Collection**

**11.3.3.1** After the sampling system has been assembled, perform a single point flow check as described in Sections 11.2.3.

**11.3.3.2** With the empty sample module removed from the sampler, rinse all sample contact areas using reagent grade hexane in a Teflon® squeeze bottle. Allow the hexane to evaporate from the module before loading the samples.

**11.3.3.3** With the sample cartridge removed from the sampler and the flow control valve fully open, turn the pump on and allow it to warm-up for approximately 5 minutes.

**11.3.3.4** Attach a "dummy" sampling cartridge loaded with the exact same type of filter and PUF media to be used for sample collection.

**11.3.3.5** Turn the sampler on and adjust the flow control valve to the desired flow as indicated by the Magnehelic gauge reading determined in Section 11.2.2.24. Once the flow is properly adjusted, take extreme care not to inadvertently alter its setting.

**11.3.3.6** Turn the sampler off and remove the "dummy" module. The sampler is now ready for field use.

**11.3.3.7** Check the zero reading of the sampler Magnehelic. Record the ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number, and PUF cartridge number on the Field Test Data Sheet (see Figure 12). Attach the loaded sampler cartridge assembly to the sampler.

**11.3.3.8** Place the voltage variator and flow control valve at the settings used in Section 11.3.2, and the power switch. Activate the elapsed time meter and record the start time. Adjust the flow (Magnehelic setting), if necessary, using the flow control valve.

**11.3.3.9** Record the Magnehelic reading every 6 hours during the sampling period. Use the calibration factors (see Section 11.2.2.24) to calculate the desired flow rate. Record the ambient temperature, barometric pressure, and Magnehelic reading at the beginning and during sampling period.

### **11.3.4 Sample Recovery**

**11.3.4.1** At the end of the desired sampling period, turn the power off. Carefully remove the sampling head containing the filter and sorbent cartridge. Place the protective "plate" over the filter to protect the cartridge during transport to a clean recovery area. Also, place a piece of aluminum foil around the bottom of the sampler cartridge assembly.

**11.3.4.2** Perform a final calculated sampler flow check using the calibration orifice, assembly, as described in Section 11.3.2. If calibration deviates by more than 10 percent from initial reading, mark the flow data for that sample as suspect and inspect and/or remove from service, record results on Field Test Data Sheet, Figure 12.

**11.3.4.3** Transport the sampler cartridge assembly to a clean recovery area.

**11.3.4.4** While wearing white cotton gloves, remove the PUF glass cartridge from the lower module chamber and lay it on the retained aluminum foil in which the sample was originally wrapped.

**11.3.4.5** Carefully remove the quartz fiber filter from the upper chamber using clean Teflon®-tipped forceps.

**11.3.4.6** Fold the filter in half twice (sample side inward) and place it in the glass cartridge atop the PUF.

**11.3.4.7** Wrap the combined samples in the original hexane-rinsed aluminum foil, attach Teflon® end caps (if applicable) and place them in their *original* aluminum shipping container. Complete a sample label and affix it to the aluminum shipping container.

**11.3.4.8** Chain-of-custody should be maintained for all samples. Store the containers under blue ice or dry ice and protect from UV light to prevent possibly photo-decomposition of collected analytes. If the time span between sample collection and laboratory analysis is to exceed 24 hours, refrigerate sample at 4°C.

**11.3.4.9** Return at least one field blank filter/PUF cartridge to the laboratory with each group of samples. Treat a field blank exactly as the sample except that air is not drawn through the filter/sorbent cartridge assembly.

**11.3.4.10** Ship and store field samples chilled (<4°C) using blue ice until receipt at the analytical laboratory, after which samples should be refrigerated at less than or equal to 4°C for up to 7 days prior to extraction; extracts should be analyzed within 40 days of extraction.

## 12. Sample Extraction, Concentration, and Cleanup

*[Note: The following sample extraction, concentration, solvent exchange and analysis procedures are outlined for user convenience in Figure 13.]*

### 12.1 Sample Identification

**12.1.1** The chilled (<4°C) samples are returned in the aluminum shipping container (containing the filter and sorbents) to the laboratory for analysis. The "chain-of-custody" should be completed.

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

**12.1.3** If the time span between sample registration and analysis is greater than 24-hours, then the sample must be kept refrigerated at <4°C. Minimize exposure of samples to fluorescent light. All samples should be extracted within one week (7 days) after sampling.

### 12.2 Soxhlet Extraction and Concentration

*[Note: If PUF is the sorbent, the extraction solvent is 10 percent diethyl ether in hexane. If XAD-2® resin is the sorbent, the extraction solvent is methylene chloride.]*

**12.2.1** Assemble the Soxhlet apparatus (see Figure 4a). Immediately before use, charge the Soxhlet apparatus with 700 to 750 mL of 10 percent diethyl ether in hexane and reflux for 2 hours. Let the apparatus cool, disassemble it, transfer the diethyl ether in hexane to a clean glass container, and retain it as a blank for later analysis, if required. Place the sorbent and filter together in the Soxhlet apparatus (the use of an extraction thimble is optional).

*[Note: The filter and sorbent are analyzed together in order to reach detection limits, avoid questionable interpretation of the data, and minimize cost.]*

**12.2.1.1** Prior to extraction, add appropriate laboratory surrogate standards to the Soxhlet solvent. A surrogate standard (i.e., a chemically compound not expected to occur in an environmental sample) should be added to each sample, blank, and matrix spike sample just prior to extraction or processing. The recovery of the laboratory surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measure concentration falls within the acceptance limits. Spike 20 µL of a 50 µg/mL solution of the surrogates onto the PUF cartridge, prior to Soxhlet extraction, to yield a final concentration of 1 µg. The following laboratory surrogate standards have been

successfully utilized in determining Soxhlet extraction effects, sample process errors, etc., for GC/MS/DS analysis.

<b>Laboratory Surrogate Standard</b>	<b>Total Spiked Amount (<math>\mu\text{g}</math>)</b>
D <sub>10</sub> -Fluorene	1
D <sub>10</sub> -Pyrene	1

Section 13.2 outlines preparation of the laboratory surrogates. Add the laboratory surrogate compounds to the PUF cartridge. Add 700 mL of 10 percent diethyl ether in hexane to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour. Allow to cool, then disassemble the apparatus.

**12.2.1.2** Dry the extract from the Soxhlet extraction by passing it through a drying column containing about 10 grams of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator assembly. Wash the extractor flask and sodium sulfate column with 100-125 mL of 10 percent diethyl ether/hexane to complete the quantitative transfer.

**12.2.2** Assemble a K-D concentrator (see Figure 4b) by attaching a 10 mL concentrator tube to a 500 mL evaporative flask.

*[Note: Other concentration devices (vortex evaporator) or techniques may be used in place of the K-D as long as qualitative and quantitative recovery can be demonstrated.]*

**12.2.2.1** Add two boiling chips, attach a three-ball macro-Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65 °C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in one hour. At the proper rate of distillation, the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an approximate volume of 5 mL, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 minutes while cooling.

**12.2.2.2** Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 5 mL of cyclohexane. A 5 mL syringe is recommended for this operation. The extract is now ready for further concentration to 1.0 mL by nitrogen blowdown.

**12.2.2.3** Place the 1 mL calibrated K-D concentrator tube with an open micro-Snyder attachment in a warm water bath (30 to 35 °C) and evaporate the solvent volume to just below 1 mL by blowing a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon) above the extract.

**12.2.2.4** The internal wall of the concentrator tube must be rinsed down several times with hexane during the operation.

**12.2.2.5** During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.

**12.2.2.6** Bring the final volume back to 1.0 mL with hexane. Transfer the extract to a Teflon®-sealed screw-cap amber vial, label the vial, and store at 4 °C ( $\pm 2$  °C).

*[Note: It is not necessary to bring the volume to exactly 1.0 mL if the extract will be cleaned up by solid phase extraction cleanup methods. Final volume is brought to 1.0 mL after cleanup.]*

### 12.3 Sample Cleanup

**12.3.1** If the extract is cloudy, impurities may be removed from the extract by solid phase extraction using activated silica gel. Clean-up procedures may not be needed for relatively clean matrix samples.

**12.3.2** Approximately 10 grams of silica gel, type 60 (70-230 mesh), are extracted in a Soxhlet extractor with 10 percent diethyl ether for 6 hours (minimum rate, 3 cycles/hr) and then activated by heating in a foil-covered glass container for 16 hours at 150°C.

**12.3.3** Using a disposable Pasteur pipette (7.5-mm x 14.6-cm), place a small piece of glass wool in the neck of the pipette. Prepare a slurry of activated silica gel in 10 percent diethyl ether. Place 10 grams of the activated silica gel slurry into the column using additional 10 percent diethyl ether. Finally, 1 gram of anhydrous sodium sulfate is added to the top of the silica gel. Prior to use, the column is rinsed with 10 percent diethyl ether at 1 mL/min for 1 hour to remove any trace of contaminants. It is then pre-eluted with 40 mL of pentane and the eluate discarded.

**12.3.4** While the pentane pre-elutant covers the top of the column, 1 mL of the sample extract is transferred to the column, and washed on with 2 mL of *n*-hexane to complete the transfer. Allow to elute through the column. Immediately prior to exposure of the sodium sulfate layer the air, add 25 mL of pentane and continue the elution process. The pentane eluate is discarded.

**12.3.5** The column is finally eluted at 2 mL/min with 25 mL of 10 percent diethyl ether in pentane (4:6 v/v) and collected in a 50 mL K-D flask equipped with a 5 mL concentrator tube for concentration to less than 5 mL. The concentrate is further concentrated to 1.0 mL under a gentle stream of nitrogen as previously described.

**12.3.6** The extract is now ready for GC/MS analysis. Spike the extract with internal standards (ISs) before analysis. The following internal standards (ISs) have been successfully used in PAH analysis by GC/MS.

<b>Internal Standard (IS)</b>	<b>Total Spiked Amount (µg)</b>
D <sub>8</sub> -Naphthalene	0.5
D <sub>10</sub> -Acenaphthene	0.5
D <sub>10</sub> -Phenanthrene	0.5
D <sub>12</sub> -Chrysene	0.5
D <sub>12</sub> -Perylene	0.5

Section 13.2 outlines preparation of the ISs.

## 13. Gas Chromatography with Mass Spectrometry Detection

### 13.1 General

**13.1.1** The analysis of the extracted sample for benzo[a]pyrene and other PAHs is accomplished by an electron ionization gas chromatograph/mass spectrometer (EI GC/MS) in the mode with a total cycle time (including voltage reset time) of 1 second or less. The GC is equipped with an DB-5 fused silica capillary column (30-m x 0.32-mm I.D.) with the helium carrier gas for analyte separation. The GC column is temperature controlled and interfaced directly to the MS ion source.

**13.1.2** The laboratory must document that the EI GC/MS system is properly maintained through periodic calibration checks. The GC/MS system should be operated in accordance with specifications outlined in Table 2.

**13.1.3** The GC/MS is tuned using a 50 ng/µL solution of decafluorotriphenylphosphine (DFTPP). The DFTPP permits the user to tune the mass spectrometer on a daily basis. If properly tuned, the DFTPP key ions and ion abundance criteria should be met as outlined in Table 3.

**13.1.4** The GC/MS operating conditions are outlined in Table 2. The GC/MS system should be calibrated using the internal standard technique. Figure 14 outlines the following sequence involving the GC/MS calibration.

## 13.2 Calibration of GC/MS/DS

### 13.2.1 Standard Preparation

#### *Stock PAH Standards Including Surrogate Compounds*

**13.2.1.1** Prepare stock standards of B[a]P and other PAHs. The stock standard solution of B[a]P (2.0 µg/µL) and other PAHs can be user prepared from pure standard materials or can be purchased commercially.

**13.2.1.2** Place 0.2000 grams of native B[a]P and other PAHs on a tared aluminum weighing disk and weigh on a Mettler balance.

**13.2.1.3** Quantitatively transfer the material to a 100 mL volumetric flask. Rinse the weighing disk with several small portions of 10 percent diethyl ether/hexane. Ensure all material has been transferred.

**13.2.1.4** Dilute to mark with 10 percent diethyl ether/hexane.

**13.2.1.5** The concentration of the stock standard solution of B[a]P or other PAHs in the flask is 2.0 µg/µL.

*[Note: Commercially prepared stock PAH standards may be used at any concentration if they are certified by the manufacturer or by an independent source.]*

**13.2.1.6** 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 from them.

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

#### *Mix Internal Standard (IS) Solution*

**13.2.1.8** For PAH analysis, deuterated internal standards are selected that are similar in analytical behavior to the compound of interest. The following internal standards are suggested for PAH analysis:

#### D<sub>12</sub>-Perylene

Benzo(e)pyrene  
Benzo(a)pyrene  
Benzo(k)fluoranthene

#### D<sub>10</sub>-Acenaphthene

Acenaphthene (if using XAD-2® as the sorbent)  
Acenaphthylene (if using XAD-2® as the sorbent)  
Fluorene  
Benzo(g,h,i)perylene  
Dibenz(a,h)anthracene  
Indeno(1,2,3-cd)pyrene  
Perylene  
Benzo(b)fluoranthene  
Coronene

#### D<sub>12</sub>-Chrysene

Benz(a)anthracene  
Chrysene  
Pyrene

#### D<sub>8</sub>-Naphthalene

Naphthalene (if using XAD-2® as the sorbent)

#### D<sub>10</sub>-Phenanthrene

Anthracene  
Fluoranthene  
Phenanthrene



**13.2.1.9** Purchase a mix IS solution containing specific IS needed for quantitation at a concentration of 2,000 ng/μL.

***Mixed Stock PAH Standard Including Surrogate Compounds***

**13.2.1.10** Prepare a mixed stock PAH standard by taking 125 μL of the stock PAH standard(s) and diluting to mark with hexane in a 10-mL volumetric flask. The concentration of the mixed stock PAH standard(s) is 25 ng/μL.

***Calibration PAH Standards Including Surrogate Compounds***

**13.2.1.11** Calibration PAH standards can be generated from the stock PAH standard using serial dilution utilizing the following equation:

$$C_1 V_1 = C_2 V_2$$

where:

$C_1$  = Concentration of stock PAH standards, ng/μL

$V_1$  = Volume of stock PAH standard solution taken to make calibration PAH standards, μL

$V_2$  = Final volume diluted to generate calibration PAH standards, μL

$C_2$  = Final concentration of calibration PAH standards, ng/μL

**13.2.1.12** Using the above equation, prepare a series of calibration PAH standards which include the surrogate compounds (i.e., 2.50 ng/μL, 1.25 ng/μL, 0.50 ng/μL, 0.25 ng/μL, and 0.10 ng/μL) according to the scheme illustrated in Table 4 and described below.

- For CAL 5, transfer 1.00 mL of the mixed PAH stock standard in a 10-mL volumetric flask and dilute to 10.0 mL with hexane. The resulting concentration is 2.5 ng/μL for the PAH analytes.
- To prepare CAL 4, transfer 500 μL of the mixed PAH stock standard solution to a 10-mL volumetric flask and dilute to 10.0 mL with hexane. The resulting concentration is 1.25 ng/μL for PAH analytes.
- To prepare CAL 3, transfer 200 μL of the mixed PAH stock solution to a 10-mL volumetric flask and dilute to 10-mL with hexane. The resulting concentration is 0.50 ng/μL for PAH analytes.
- To prepare CAL 2, transfer 100 μL of the mixed PAH stock solution to a 10-mL volumetric flask and dilute to 10-mL with hexane. The resulting concentration is 0.25 ng/μL for PAH analytes.
- To prepare CAL 1, transfer 40 μL of the mixed PAH stock solution to a 10-mL volumetric flask and dilute to 10-mL with hexane. The resulting concentration is 0.10 ng/μL for PAH analytes.

**13.2.2 Internal Standard Spiking**

**13.2.2.1** Prior to GC/MS analysis, each 1 mL aliquot of the five calibration standards is spiked with internal standard to a final concentration of 0.5 ng/μL. To do this, first prepare a 1:40 dilution of the 2,000 ng/μL mixed internal standard solution by diluting 250 μL to a volume of 10 mL to yield a concentration of 50 ng/μL.

**13.2.2.2** Each 1.0-mL portion of calibration standard and sample extract is then spiked with 10 μL of the internal standard solution prior to analysis by GC/MS/DS operated in the SCAN mode.

**13.2.3 Storage, Handling, and Retention of Standards**

**13.2.3.1** Store the stock and mixed standard solutions at 4 °C (±2 °C) in Teflon®-lined screw-cap amber bottles. Store the working standard solutions at 4 °C (±2 °C) in Teflon®-lined screw-cap amber bottles.

**13.2.3.2** Protect all standards from light. Samples, sample extracts, and standards must be stored separately.

**13.2.3.3** Stock standard solutions must be replaced every 12 months, or sooner, if comparison with quality control check samples indicates a problem. Diluted working standards are usable for 6 months. Analysis difficulties, which warrant investigation, may require preparation of new standards. All standards are securely stored at  $\sim 4^{\circ}\text{C}$  ( $\pm 2^{\circ}\text{C}$ ) but above freezing. The concentration, preparation and expiration date, and solvent are identified on standard vial labels. Each standard is uniquely identified with its laboratory notebook number and a prefix. This procedure helps provide traceability to standard preparation.

**13.2.3.4** Take care to maintain the integrity of each standard. The solvent, hexane, is volatile and can easily evaporate. Make sure each vial is sealed after use, and mark the solvent level on the side of the vial. When retrieving a vial for use, if the solvent level does not match the mark, dispose of the standard and obtain a new one.

### 13.3 GC/MS Instrument Operating Conditions

**13.3.1 Gas Chromatograph (GC).** The following are the recommended GC analytical conditions, as also outlined in Table 3, to optimize conditions for compound separation and sensitivity.

Carrier Gas:	Helium
Linear Velocity:	28-29 cm <sup>3</sup> /sec
Injector Temperature:	250-300°C
Injector:	Grob-type, splitless, 2 $\mu\text{L}$
Temperature Program:	Initial Temperature: 70°C
Initial Hold Time:	4.0 $\pm$ 0.1 min.
Ramp Rate:	10°C/min to 300°C, hold for 10 min
Final Temperature:	300°C
Final Hold Time:	10 min (or until all compounds of interest have eluted).
Analytical Time:	Approximately 50 min.

**13.3.2 Mass Spectrometer. Following are the required mass spectrometer conditions for scan data acquisition:**

Transfer Line Temperature:	290°C
Source Temperature:	According to manufacturer's specifications
Electron Energy:	70 volts (nominal)
Ionization Mode:	EI
Mass Range:	35 to 500 amu, SCAN data acquisition
Scan Time:	At least 5 scans per peak, not to exceed 1 second per scan

#### 13.3.3 Instrument Performance Check for GC/MS.

**13.3.3.1 Summary.** It is necessary to establish that the GC/MS meet tuning and standard mass spectral abundance criteria prior to initiating any on-going data collection, as illustrated in Figure 14. This is accomplished through the analysis of decafluorotriphenylphosphine (DFTPP).

**13.3.3.2 Frequency.** The instrument performance check solution of DFTPP will be analyzed initially and once per 12-hour time period of operation. Also, whenever the laboratory takes corrective action which may change or affect the mass spectral criteria (e.g., ion source cleaning or repair, column replacement, etc.), the instrument performance check must be verified irrespective of the 12-hour laboratory requirement. The 12-hour

time period for GC/MS analysis begins at the injection of the DFTPP, which the laboratory submits as documentation of a compliance tune. The time period ends after 12 hours have elapsed. To meet instrument performance check requirements, samples, blanks, and standards must be injected within 12 hours of the DFTPP injection.

**13.3.3.3 Procedure.** Inject 50 ng of DFTPP into the GC/MS system. DFTPP may be analyzed separately or as part of the calibration standard.

**13.3.3.4 Technical Acceptance Criteria.** The following criteria have been established in order to generate accurate data:

- Prior to the analysis of any samples, blanks, or calibration standards, the laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing DFTPP.
- The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibrant. The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution.
- The abundance criteria listed in Table 3 must be met for a 50 ng injection of DFTPP. The mass spectrum of DFTPP must be acquired by averaging three scans (the peak apex scan and the scans immediately preceding and following the apex). Background subtraction is required, and must be accomplished using a single scan prior to the elution of DFTPP.

*[Note: All ion abundance **MUST** be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z 442 may be up to 110 percent of m/z 198.]*

- The above criteria are based on adherence to the acquisition specifications identified in Table 4 and were developed for the specific target compound list associated with this document. The criteria are based on performance characteristics of instruments currently utilized in routine support of ambient air program activities. These specifications, in conjunction with relative response factor criteria for target analytes, are designed to control and monitor instrument performance associated with the requirements of this document. As they are performance-based criteria for these specific analytical requirements, they may not be optimal for additional target compounds.
- If the mass spectrometer has the ability for autotuning, then the user may utilize this function following manufacturer's specifications. Autotune automatically adjusts ion source parameters within the detector using FC-43 (Heptacos). Mass peaks at m/z 69, 219, and 502 are used for tuning. After the tuning is completed, the FC-43 abundances at m/z 50, 69, 131, 219, 414, 502, and 614 are further adjusted such that their relative intensities match the selected masses of DFTPP.

**13.3.3.5 Corrective Action.** If the DFTPP acceptance criteria are not met, the MS must be retuned. It may be necessary to clean the ion source, or quadrupoles, or take other actions to achieve the acceptance criteria. DFTPP acceptance criteria **MUST** be met before any standards, or required blanks, are analyzed. Any standards, field samples, or required blanks analyzed when tuning criteria have not been met will require reanalysis.

#### **13.3.4 Initial Calibration for GC/MS.**

**13.3.4.1 Summary.** Prior to the analysis of samples and required blanks, and after tuning criteria (instrument performance check) have been met, each GC/MS system will be initially calibrated at a minimum of five concentrations to determine instrument sensitivity and the linearity of GC/MS response for the analyte compounds and the surrogates.

**13.3.4.2 Frequency.** Each GC/MS system must be initially calibrated whenever the laboratory takes corrective action, which may change or affect the initial calibration criteria (e.g., ion source cleaning or repair,

column replacement, etc.), or if the continuing calibration acceptance criteria have not been met. If time still remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. It is not necessary to analyze a continuing calibration standard within the 12-hour time period if the initial calibration standard (CAL 3) is the same concentration as the continuing calibration standard and both meet the continuing calibration technical acceptance criteria. Quantify all sample results using the mean of the relative response factors ( $\overline{\text{RRFs}}$ ) from the initial calibration.

**13.3.4.3 Procedure.** Perform the following activities to generate quantitative data:

- Set up the GC/MS system.
- Warm all standard/spiking solutions, sample extracts, and blanks to ambient temperature (~1 hour) before analysis.
- Tune the GC/MS system to meet the technical acceptance criteria (see Section 13.3.3).
- Prepare five calibration standards containing the target compounds, internal standards, and surrogate compounds at the concentrations outlined in Table 4.
- Calibrate the GC/MS by injecting 2.0  $\mu\text{L}$  of each standard. If a compound saturates when the CAL 5 standard is injected, and the system is calibrated to achieve a detection sensitivity of no less than the MDL for each compound, the laboratory must document it and attach a quantitation report and chromatogram. In this instance, the laboratory must calculate the results based on a four-point initial calibration for the *specific compound* that saturates. Secondary ion quantitation is only allowed when there are sample interferences with the primary quantitation ion. If secondary ion quantitation is used, calculate a relative response factor using the area response from the most intense secondary ion which is free of interferences and document the reasons for the use of the secondary ion.
- Record a mass spectrum of each target compound. Figure 15(a) through 15(q) documents the mass spectrum for each of the 16 target PAHs discussed in Compendium Method TO-13A. Judge the acceptability of recorded spectra by comparing them to spectra in libraries. If an acceptable spectrum of a calibration standard component is not acquired, take necessary actions to correct GC/MS performance. If performance cannot be corrected, report sample extract data for the particular compound(s), but document the affected compound(s) and the nature of the problem.

**13.3.4.4 Calculations.** Perform the following calculations to generate quantitative data:

[*Note: In the following calculations, the area response is that of the primary quantitation ion unless otherwise stated.*]

- **Relative Response Factors (RRFs).** Calculate RRFs for each analyte target compound and surrogate using the following equation with the appropriate internal standard. Table 5 outlines characteristic ions for the surrogate compounds and internal standards. Table 6 outlines primary quantitation ions for each PAH. Use the following equation for RRF calculation.

$$\text{RRF} = \frac{A_x C_{is}}{A_{is} C_x}$$

where:

$A_x$  = area of the primary quantitation ion for the compound to be measured, counts

$A_{is}$  = area of the primary quantitation ion for the internal standard, counts

$C_{is}$  = concentration or amount of the internal standard, ng/ $\mu\text{L}$

$C_x$  = concentration or amount of the compound to be measured, ng/ $\mu$ L

- **Percent Relative Standard Deviation (%RSD).** Using the RRFs from the initial calibration, calculate the %RSD for all target compounds and surrogates using the following equations:

$$\%RSD = \frac{SD_{RRF}}{\bar{x}} \times 100$$

and

$$SD_{RRF} = \sqrt{\sum_{i=1}^N \frac{(x_i - \bar{x})^2}{N - 1}}$$

where:

- $SD_{RRF}$  = standard deviation of initial response factors (per compound)
- $\bar{x}$  = mean of initial relative response factors (per compound)
- $X_i$  =  $i$ th RRF
- $N$  = number of determinations

- **Relative Retention Times (RRT).** Calculate the RRTs for each target compound and surrogate over the initial calibration range using the following equation:

$$RRT = \frac{RT_c}{RT_{is}}$$

where:

- $RT_c$  = retention time of the target compound, minutes
- $RT_{is}$  = retention time of the internal standard, minutes

- **Mean of the Relative Retention Times ( $\overline{RRT}$ ).** Calculate the mean of the relative retention times ( $\overline{RRT}$ ) for each analyte target compound and surrogate over the initial calibration range using the following equation:

$$\overline{RRT} = \sum_{i=1}^n \frac{RRT_i}{n}$$

where:

- $\overline{RRT}$  = mean relative retention time for the target compound or surrogate for each initial calibration standard, minutes
- $RRT$  = relative retention time for the target compound or surrogate for each initial calibration standard, minutes

- **Mean Area Response ( $\bar{Y}$ ) for Internal Standard.** Calculate the area response (Y) mean for primary quantitation ion each internal standard compound over the initial calibration range using the following equation:

$$\bar{Y} = \sum_{i=1}^n \frac{Y_i}{n}$$

where:

$\bar{Y}$  = mean area response, counts

$Y_i$  = area response for the primary quantitation ion for the internal standard for each calibration standard, counts

- **Mean of the Retention Time ( $\bar{RT}$ ) For Internal Standard.** Calculate the mean of the retention times ( $\bar{RT}$ ) for each internal standard over the initial calibration range using the following equation:

$$\bar{RT} = \sum_{i=1}^n \frac{RT_i}{n}$$

where:

$\bar{RT}$  = mean retention time, minutes

$RT$  = retention time for the internal standard for each initial calibration standard, minutes

**13.3.4.5 Technical Acceptance Criteria.** All initial calibration standards must be analyzed at the concentration levels at the frequency described in Section 13.3.3 on a GC/MS system meeting the DFTPP instrument performance check criteria.

- The relative response factor (RRF) at each calibration concentration for each target compound and surrogate that has a required minimum response factor value must be greater than or equal to the minimum acceptable relative response factor (see Table 7) of the compound.
- The percent relative standard deviation (%RSD) over the initial calibration range for each target compound and surrogate that has a required maximum %RSD must be less than or equal to the required maximum value (see Table 7). For all the other target compounds, the value for %RSD must be less than or equal to 30 percent. When the value for %RSD exceeds 30 percent, analyze additional aliquots of appropriate CALs to obtain an acceptable %RSD of RRFs over the entire concentration range, or take action to improve GC/MS performance.
- The relative retention time for each of the target compounds and surrogates at each calibration level must be within  $\pm 0.06$  relative retention time units of the mean relative retention time for the compound.
- The retention time shift for each of the internal standards at each calibration level must be within  $\pm 20.0$  seconds compared to the mean retention time ( $\bar{RT}$ ) over the initial calibration range for each internal standard.
- The compounds must meet the minimum RRF and maximum %RSD criteria for the initial calibration.

**13.3.4.6 Corrective Action.** If the technical acceptance criteria for initial calibration are not met, the system should be inspected for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the acceptance criteria. Initial calibration technical acceptance criteria MUST

be met before any samples or required blanks are analyzed in a 12-hour time period for an initial calibration analytical sequence.

### 13.3.5 Continuing Calibration.

**13.3.5.1 Summary.** Prior to the analysis of samples and required blanks and after tuning criteria have been met, the initial calibration of each GC/MS system must be routinely checked by analyzing a continuing calibration standard (see Table 4, CAL 3) to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the method. The continuing calibration standard (CAL 3) shall contain the appropriate target compounds, surrogates, and internal standards.

**13.3.5.2 Frequency.** Each GC/MS used for analysis must be calibrated once every time period of operation. The 12-hour time period begins with injection of DFTPP. If time still remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. It is not necessary to analyze a continuing calibration standard within this 12-hour time period, if the initial calibration standard that is the same concentration as the continuing calibration standard meets the continuing calibration technical acceptance criteria.

**13.3.5.3 Procedure.** The following activities should be performed for continuing calibration:

- Set up the GC/MS system as specified by the manufacturer.
- Tune the GC/MS system to meet the technical acceptance criteria (see Section 13.3.3).
- Analyze the CAL 3 standard solution containing all the target analytes, surrogate compounds, and internal standards using the procedure listed for the initial calibration.
- Allow all standard/spiking solutions and blanks to warm to ambient temperature (approximately 1 hour) before preparation or analysis.
- Start the analysis of the continuing calibration by injecting 2.0  $\mu\text{L}$  of the CAL 3 standard solution.

**13.3.5.4 Calculations.** The following calculations should be performed:

- **Relative Response Factor (RRF).** Calculate a relative response factor (RRF) for each target compound and surrogate.
- **Percent Difference (%D).** Calculate the percent difference between the mean relative response factor ( $\overline{\text{RRF}}$ ) from the most recent initial calibration and the continuing calibration RRF for each analyte target compound and surrogate using the following equation:

$$\%D_{\text{RRF}} = \frac{\text{RRF}_c - \overline{\text{RRF}}_i}{\overline{\text{RRF}}_i} \times 100$$

where:

$\%D_{\text{RRF}}$  = percent difference between relative response factors

$\overline{\text{RRF}}_i$  = average relative response factor from the most recent initial calibration

$\text{RRF}_c$  = relative response factor from the continuing calibration standard

**13.3.5.5 Technical Acceptance Criteria.** The continuing calibration standard must be analyzed for the compounds listed in concentration levels at the frequency described and on a GC/MS system meeting the DFTPP instrument performance check and the initial calibration technical acceptance criteria. The relative response factor for each target analyte and surrogate that has a required minimum relative response factor value must be greater than or equal to the compound's minimum acceptable relative response factor. For an acceptable

continuing calibration, the %D between the measured RRF for each target/surrogate compound of the CAL 3 standard and the mean value calculated during initial calibration must be within  $\pm 30$  percent. If the criteria for %D are not met for the target or surrogate compounds, remedial action must be taken and recalibration may be necessary.

**13.3.5.6 Corrective Action.** If the continuing calibration technical acceptance criteria are not met, recalibrate the GC/MS instrument. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the acceptance criteria. Continuing calibration technical acceptance criteria *MUST* be met before any samples or required blanks are analyzed in a 12-hour continuing calibration analytical sequence. Any samples or required blanks analyzed when continuing calibration criteria were not met will require reanalysis. Remedial actions, which include but are not limited to the following, must be taken if criteria are not met:

- Check and adjust GC and/or MS operating conditions.
- Clean or replace injector liner.
- Flush column with solvent according to manufacturers instructions.
- Break off a short portion (approximately 0.33 cm) of the column.
- Replace the GC column (performance of all initial calibration procedures are then required).
- Adjust MS for greater or lesser resolution.
- Calibrate MS mass scale.
- Prepare and analyze new continuing calibration.
- Prepare a new initial calibration curve.

### 13.3.6 Laboratory Method Blank (LMB).

**13.3.6.1 Summary.** The purpose of the LMB is to monitor for possible laboratory contamination. Perform all steps in the analytical procedure using all reagents, standards, surrogate compounds, equipment, apparatus, glassware, and solvents that would be used for a sample analysis. An LMB is an unused, certified filter/cartridge assembly which is carried through the same extraction procedure as a field sample. The LMB extract must contain the same amount of surrogate compounds and internal standards that is added to each sample. All field samples must be extracted and analyzed with an associated LMB.

**13.3.6.2 Frequency.** Analyze an LMB along with each batch of  $\leq 20$  samples through the entire extraction, concentration, and analysis process. The laboratory may also analyze a laboratory reagent blanks which is the same as an LMB except that no surrogate compounds or internal standards are added. This demonstrates that reagents contain no impurities producing an ion current above the level of background noise for quantitation ions for those compounds.

**13.3.6.3 Procedure.** Extract and analyze a clean, unused filter and glass cartridge assembly.

**13.3.6.4 Technical Acceptance Criteria.** Following are the technical criteria for the LMB:

- All blanks must be analyzed on a GC/MS system meeting the DFTPP instrument performance check and initial calibration or continuing calibration technical acceptance criteria.
- The percent recovery for each of the surrogates in the blank must be within the acceptance windows.
- The area response change for each of the internal standards for the blank must be within -50 percent and +100 percent compared to the internal standards in the most recent continuing calibration analysis.
- The retention time for each of the internal standards must be within  $\pm 20.0$  seconds between the blank and the most recent CAL 3 analysis.
- The LMB must not contain any target analyte at a concentration greater than the MDL and must not contain additional compounds with elution characteristics and mass spectral features that would interfere



with identification and measurement of a method analyte at its MDL. If the LMB that was extracted along with a batch of samples is contaminated, the entire batch of samples must be flagged.

**13.3.6.5 Corrective Action.** Perform the following if the LCBs exceed criteria:

- If the blanks do not meet the technical acceptance criteria, the analyst must consider the analytical system to be out of control. It is the analyst's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measure *MUST* be taken and documented before further sample analysis proceeds.
- All samples processed with a method blank that is out of control (i.e., contaminated) will require data qualifiers to be attached to the analytical results.

**13.3.7 Laboratory Control Spike (LCS).**

**13.3.7.1 Summary.** The purpose of the LCS is to monitor the extraction efficiency of Compendium Method TO-13A target analytes from a clean, uncontaminated PUF cartridge. An LCS is an unused, certified PUF that is spiked with the target analytes (1  $\mu\text{g}$ ) and carried through the same extraction procedures as the field samples. The LCS must contain the same amount of surrogate compounds and internal standards that is added to each sample. All field samples must be extracted and analyzed with an associated LCS. All steps in the analytical procedure must use the same reagents, standards, surrogate compounds, equipment, apparatus, glassware, and solvents that would be used for a sample analysis.

**13.3.7.2 Frequency.** Analyze an LCS along with each of  $\leq 20$  samples through the entire extraction, concentration, and analysis. (The laboratory may also analyze a laboratory reagent blank which is the same as an LMB except that no surrogate compounds or internal standards are added. This demonstrates that reagents contain no impurities producing an ion current above the level of background noise for quantitation ions of those compounds.)

**13.3.7.3 Procedure.** Extract and analyze a clean, unused certified PUF cartridge assembly.

**13.3.7.4 Technical Acceptance Criteria.** Technical criteria for the LCS are:

- All LCSs must be analyzed on a GC/MS system meeting the DFTPP instrument performance check and initial calibration or continuing calibration technical acceptance criteria.
- The percent recovery for each of the surrogates in the LCS must be within the acceptance windows.
- The area response change for each of the internal standards for the LCS must be within -50 percent and +100 percent compared to the internal standards in the most recent continuing calibration analysis.
- The retention time for each of the internal standards must be within  $\pm 20.0$  seconds between the LCS and the most recent CAL 3 analysis.
- All target analytes spiked on the certified PUF cartridge must meet a percent recovery between 60-120 to be acceptable.

**13.3.7.5 Corrective Action.** Perform the following if the LCS exceed criteria:

- If the LCS do not meet the technical acceptance criteria, the analyst must consider the analytical system to be out of control. It is the analyst's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measure *MUST* be taken and documented before further sample analysis proceeds.

- All samples processed with a LCS that is out of control (i.e., contaminated) will require re-analysis or data qualifiers to be attached to the analytical results.

### 13.4 Sample Analysis by GC/MS

**13.4.1 Summary.** The sample extract is analyzed by GC/MS and quantitated by the internal standard method.

**13.4.2 Frequency.** Before samples can be analyzed, the instrument must meet the GC/MS tuning and initial calibration or continuing calibration technical acceptance criteria. If there is time remaining in the 12-hour time period with a valid initial calibration or continuing calibration, samples may be analyzed in the GC/MS system that meet the instrument performance check criteria.

**13.4.3 Procedure.** For sample analysis, perform the following:

- Set up the GC/MS system.
- All sample extracts must be allowed to warm to ambient temperature (~1 hour) before analysis. All sample extracts must be analyzed under the same instrumental conditions as the calibration standards.
- Add the internal standard spiking solution to the 1.0 mL extract. For sample dilutions, add an appropriate amount of the internal standard spiking solution to maintain the concentration of the internal standards at 2 ng/ $\mu$ L in the diluted extract.
- Inject 2.0  $\mu$ L of sample extract into the GC/MS, and start data acquisition.
- When all semi-volatile target compounds have eluted from the GC, terminate the MS data acquisition and store data files on the data system storage device. Use appropriate data output software to display full range mass spectra and SICPs. The sample analysis using the GC/MS is based on a combination of retention times and relative abundances of selected ions (see Table 6). These qualifiers should be stored on the 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 acceptance level for relative abundance is determined to be  $\pm 15\%$  of the expected abundance. Three ions are measured for most of the PAH compounds. When compound identification is made by the computer, any peak that fails any of the qualifying tests is flagged (e.g., with an \*). 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. Although this step 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.

**13.4.4 Dilutions.** The following section provides guidance when an analyte exceeds the calibration curve.

- When a sample extract is analyzed that has an analyte target compound concentration greater than the upper limit of the initial calibration range or saturated ions from a compound (excluding the compound peaks in the solvent front), the extract must be diluted and reanalyzed. Secondary ion quantitation is *only* allowed when there are sample interferences with the primary quantitation ion. If secondary ion quantitation is used, calculate a relative response factor using the area response for the most intense secondary ion which is free of sample interferences, and document the reasons for the use of the secondary ion.
- Calculate the sample dilution necessary to keep the semi-volatile target compounds that required dilution within the upper half of the initial calibration range so that no compound has saturated ions (excluding the compound peaks in the solvent front). Dilute the sample in hexane in a volumetric flask. Analyze the sample dilution.

- The dilution factor chosen should keep the response of the largest peak for a *target compound* in the upper half of the initial calibration range of the instrument.
- If the on-column concentration of any target compound in any sample exceeds the initial calibration range, that sample must be diluted, the internal standard concentration readjusted, and the sample extract reanalyzed.
- Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

#### 13.4.5 Quantitation. This section provides guidance for quantitating PAH analytes.

- Target components identified shall be quantified by the internal standard method. The internal standards used for the target compounds are the ones nearest the retention time of a given analyte.
- The relative response factor (RRF) from the daily continuing calibration standard analysis (or RRF of CAL 3) if the sample is analyzed in the same 12-hour sequence as the initial calibration) is used to calculate the concentration in the sample. Secondary ion quantitation is allowed *only* when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reasons. The area of a secondary ion cannot be substituted for the area of a primary ion unless a relative response factor is calculated using the secondary ion.
- A retention time window is calculated for each single component analyte and surrogate. Windows are established as  $\pm 0.01$  RRT units of the retention time for the analyte in CAL 3 of the initial calibration or the continuing calibration.

#### 13.4.6 Calculations. Perform the following calculations:

**13.4.6.1 Calculation of Concentration.** Calculate target compound concentrations using the following equation:

$$\text{Concentration, (ng/std m}^3\text{)} = \frac{A_x I_s V_t D_f}{A_{is} V_i \overline{\text{RRF}}}$$

where:

$A_x$  = area response for the compound to be measured, counts

$A_{is}$  = area response for the internal standard, counts

$I_s$  = amount of internal standard, ng/ $\mu$ L

$\overline{\text{RRF}}$  = the mean RRF from the most recent initial calibration, dimensionless

$V_i$  = volume of air sampled, std  $\text{m}^3$

$V_t$  = volume of final extract,  $\mu$ L

$D_f$  = dilution factor for the extract. If there was no dilution,  $D_f$  equals 1. If the sample was diluted, the  $D_f$  is greater than 1.

The concentrations calculated can be converted to  $\text{ppb}_v$  for general reference. The analyte concentration can be converted to  $\text{ppb}_v$  using the following equation:

$$C_A(\text{ppb}_v) = C_A(\text{ng/m}^3) \times 24.4/\text{MW}_A$$

where:

- $C_A$  = concentration of analyte calculated, ng/std. m<sup>3</sup>  
 $MW_A$  = molecular weight of analyte, g/g-mole  
 24.4 = molar volume occupied by ideal gas at standard temperature and pressure (25°C and 760 mm Hg), L/mole.

**13.4.6.2 Estimated Concentration.** The equation in Section 13.4.6.1 is also used for calculating the concentrations of the non-target compounds. Total area counts (or peak heights) from the total ion chromatogram generated by the mass spectrometer for Compendium Method TO-13A PAHs (see Figure 16) are to be used for both the non-target compound to be measured ( $A_x$ ) and the internal standard ( $A_{is}$ ). Associate the nearest internal standard free of interferences with the non-target compound to be measured. A relative response factor (RRF) of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated ("J") (estimated, due to lack of a compound-specific response factor) and "N" (presumptive evidence of presence), indicating the quantitative and qualitative uncertainties associated with this non-target component. An estimated concentration should be calculated for all tentatively identified compounds (TICs) as well as those identified as unknowns.

**13.4.6.3 Surrogate Percent Recovery (%R).** Calculate the surrogate percent recovery using the following equation:

$$\%R = \frac{Q_d}{Q_a} \times 100$$

where:

- $Q_d$  = Quantity determined by analysis, ng  
 $Q_a$  = Quantity added to sample/blank, ng

The surrogate percent recovery must fall between 60-120% to be acceptable.

**13.4.6.4 Percent Area Response Change (%ARC).** Calculate the percent area response change (%ARC) for the sample/blank analysis compared to the most recent CAL 3 analysis for each of the internal standard compounds using the following equation:

$$\%ARC = \frac{A_s - A_x}{A_x} \times 100$$

where:

- $\%ARC$  = percent area response change, %  
 $A_s$  = area response of the internal standard in the sample/blank analysis, counts  
 $A_x$  = area response of the internal standard in the most recent CAL 3 analysis, counts

The area change for the internal standard must not exceed -50 to +100 percent.

**13.4.6.5 Internal Standard Retention Time Shift (RTS).** Calculate the retention time shift (RTS) between the sample/blank analysis and the most recent CAL 3 analysis for each of the internal standards using the following equation:

$$RTS = RT_s - RT_x$$

where:

$RT_s$  = retention time of the IS in the sample

$RT_x$  = retention time of the IS in the most recent CAL 3 analysis.

**13.4.7 Technical Acceptance Criteria.** The following guideline is provided as technical acceptance criteria.

**13.4.7.1** All target compound concentrations must not exceed the upper limit of the initial calibration range and no compound ion (excluding the compound peaks in the solvent front) may saturate the detector.

**13.4.7.2** Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 20 seconds from the latest continuing calibration standard or CAL 3 if samples are analyzed in the same 12-hour sequence as the initial calibration, the chromatographic system must be inspected for malfunctions, and corrections made as required. The SICP of the internal standards must be monitored and evaluated for each field and QC sample. If the SICP area for any internal standard changes by more than a factor of -50 to +100 percent, the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. If the analysis of a subsequent sample or standard indicates that the system is functioning properly, then corrections may not be required.

**13.4.7.3** When target compounds are below the low standard, but the spectrum meets the identification criteria, report the concentration/amount with a "J." For example, if the low standard corresponds to  $0.1\mu\text{g}$  and an amount of  $0.05\mu\text{g}$  is calculated, report as "0.05J."

**13.4.8 Corrective Action.** The following section provides guidance if analyte exceeds the technical criteria.

- If the sample technical acceptance criteria for the surrogates and internal standards are not met, check calculations, surrogate and internal standard solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the surrogate and internal standard technical acceptance criteria.
- Sample analysis technical acceptance criteria *must* be met before data are reported. Samples contaminated from laboratory sources, or associated with a contaminated method blank, or any samples analyzed that are not meet the technical acceptance criteria will require reanalysis.
- The samples or standards with SICP areas outside the limits must be reanalyzed. If corrections are made, then the laboratory must demonstrate that the mass spectrometric system is functioning properly. This must be accomplished by the analysis of a standard or sample that meets the SICP criteria. After corrections are made, the reanalysis of samples analyzed while the system was malfunctioning is required.
- If after reanalysis, the SICP areas for all internal standards are inside the technical acceptance limits (-50 to +100 percent), then the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, submit *only* data from the analysis with SICPs within the technical acceptance limits. This is considered the *initial* analysis and must be reported as such on all data deliverables.
- If the reanalysis of the sample does not solve the problem (i.e., the SICP areas are outside the technical acceptance limits for both analyses) then the laboratory must submit the SICP data and sample data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables, using the sample suffixes specified.
- Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window.
- If sample peaks are not detected, or all are less than full-scale deflection, the undiluted extract is acceptable for GC/MS analysis. If any sample ions are greater than the 120 percent of the initial calibration curve range, calculate the dilution necessary to reduce the major ion to between half- and full-range response.

## 14. Quality Assurance/Quality Control (QA/QC)

### 14.1 General System QA/QC

**14.1.1** Each laboratory that uses Compendium Method TO-13A must 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 a typical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

**14.1.2** 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.

**14.1.3** 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.

**14.1.4** The experience of the analyst performing GC/MS 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: Do the peaks look normal? Are the response windows 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.

### 14.2 Process, Field, and Solvent Blanks

**14.2.1** One PUF cartridge and filter from each batch of approximately 20 should be analyzed without shipment to the field for the compounds of interest to serve as a process blank. A blank level specified in Section 10.2 for each cartridge/filter assembly is considered to be acceptable.

**14.2.2** During each sampling episode, at least one cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.

**14.2.3** 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 those specified in Section 10.2 for single components to be acceptable.

**14.2.4** Because the sampling configuration (filter and backup sorbent) has been tested for targeted PAHs in the laboratory in relationship to collection efficiency and has been demonstrated to be greater than 95 percent for targeted PAHs (except naphthalene, acenaphthylene, and acenaphthene), no field recovery evaluation is required as part of the QA/QC program outlined in this section.

## 15. References

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TABLE 1. FORMULAE AND PHYSICAL PROPERTIES OF SELECTED PAHs

Compound	Formula	Molecular Weight	Melting Point, °C	Boiling Point, °C	Vapor Pressure, kPa	CAS RN #
Naphthalene	C <sub>10</sub> H <sub>8</sub>	128.18	80.2	218	1.1x10	91-20-3
Acenaphthylene	C <sub>12</sub> H <sub>8</sub>	152.20	92-93	265-280	3.9x10	208-96-8
Acenaphthene	C <sub>12</sub> H <sub>10</sub>	154.20	90-96	278-279	2.1x10	83-32-9
Fluorene	C <sub>13</sub> H <sub>10</sub>	166.23	116-118	293-295	8.7x10	86-73-7
Anthracene	C <sub>14</sub> H <sub>10</sub>	178.24	216-219	340	36x10	120-12-7
Phenanthrene	C <sub>14</sub> H <sub>10</sub>	178.24	96-101	339-340	2.3x10	85-01-8
Fluoranthene	C <sub>15</sub> H <sub>10</sub>	202.26	107-111	375-393	6.5x10	206-44-0
Pyrene	C <sub>16</sub> H <sub>10</sub>	202.26	150-156	360-404	3.1x10	129-00-0
Benz(a)anthracene	C <sub>18</sub> H <sub>12</sub>	228.30	157-167	435	1.5x10	56-55-3
Chrysene	C <sub>18</sub> H <sub>12</sub>	228.30	252-256	441-448	5.7x10	218-01-9
Benzo(b)fluoranthene	C <sub>20</sub> H <sub>12</sub>	252.32	167-168	481	6.7x10	205-99-2
Benzo(k)fluoranthene	C <sub>20</sub> H <sub>12</sub>	252.32	198-217	480-471	2.1x10	207-08-9
Perylene	C <sub>20</sub> H <sub>12</sub>	252.32	273-278	500-503	7.0x10	198-55-8
Benzo(a)pyrene	C <sub>20</sub> H <sub>12</sub>	252.32	177-179	493-496	7.3x10	50-32-8
Benzo(e)pyrene	C <sub>20</sub> H <sub>12</sub>	252.32	178-179	493	7.4x10	192-92-2
Benzo(g,h,i)perylene	C <sub>22</sub> H <sub>14</sub>	276.34	275-278	525	1.3x10	191-24-2
Indeno(1,2,3-cd)pyrene	C <sub>27</sub> H <sub>18</sub>	276.34	162-163	--	ca.10	193-39-5
Dibenz(a,h)anthracene	C <sub>28</sub> H <sub>18</sub>	278.35	266-270	524	1.3x10	53-70-3
Coronene	C <sub>24</sub> H <sub>14</sub>	300.36	438-440	525	2.0x10	191-07-1

Many of these compounds sublime.

TABLE 2. GC-MS OPERATING CONDITIONS

Activity	Conditions
<b><u>Gas Chromatography</u></b>	
Column	J&W Scientific, DB-5 crosslinked 5% phenylmethyl silicone (30 m x 0.32 mm, 1.0 µm film thickness) or equivalent
Carrier Gas	Helium, velocity between 28-30 cm <sup>3</sup> /sec at 250°C
Injection Volume	2 µL, Grob-type, splitless
Injector Temperature	290°C
<b><u>Temperature Program</u></b>	
Initial Column Temperature	70°C
Initial Hold Time	4 ± 0.1 min.
Program	10°C/min to 300°C and hold 10 min.
Final Temperature	300°C
Final Hold Time	10 min. or until all compounds of interest have eluted
<b><u>Mass Spectrometer</u></b>	
Transfer Line Temperature	290°C or According to Manufacturer's Specification
Source Temperature	According to Manufacturer's Specifications
Electron Energy	70 volts (nominal)
Ionization Mode	EI
Mass Range	35 to 500 amu, full range data acquisition (SCAN) mode
Scan Time	At least 5 scans per peak, not to exceed 1 second per scan.

TABLE 3. DFTPP KEY IONS &amp; ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30 to 60% of mass 198
68 70	Less than 2% of mass 69 Less than 2% of mass 69
127	40 to 60% of mass 198
197 198 199	Less than 2% of mass 198 Base peak, 100% relative abundance 5 to 9% of mass 198
275	10 to 30% of mass 198
365	Greater than 1.0% of mass 198
441 442 443	Present but less than mass 443 40% of mass 198 17 to 23% of mass 442

TABLE 4. COMPOSITION AND APPROXIMATE CONCENTRATION OF CALIBRATION SOLUTIONS

Target Compound	Concentration, ng/ $\mu$ L				
	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
<b>PAHs</b>	0.10	0.25	0.50	1.25	2.50
Acenaphthene	0.10	0.25	0.50	1.25	2.50
Acenaphthylene	0.10	0.25	0.50	1.25	2.50
Anthracene	0.10	0.25	0.50	1.25	2.50
Benz(a)anthracene	0.10	0.25	0.50	1.25	2.50
Benzo(a)pyrene	0.10	0.25	0.50	1.25	2.50
Benzo(b)fluoranthene	0.10	0.25	0.50	1.25	2.50
Benzo(e)pyrene	0.10	0.25	0.50	1.25	2.50
Benzo(g,h,i)perylene	0.10	0.25	0.50	1.25	2.50
Benzo(k)fluoranthene	0.10	0.25	0.50	1.25	2.50
Chrysene	0.10	0.25	0.50	1.25	2.50
Perylene	0.10	0.25	0.50	1.25	2.50
Dibenz(a,h)anthracene	0.10	0.25	0.50	1.25	2.50
Fluoranthene	0.10	0.25	0.50	1.25	2.50
Fluorene	0.10	0.25	0.50	1.25	2.50
Indeno(1,2,3-c,d)pyrene	0.10	0.25	0.50	1.25	2.50
Naphthalene	0.10	0.25	0.50	1.25	2.50
Coronene	0.10	0.25	0.50	1.25	2.50
Phenanthrene	0.10	0.25	0.50	1.25	2.50
Pyrene	0.10	0.25	0.50	1.25	2.50

TABLE 4. (Continued)

Target Compound	Concentration, ng/ $\mu$ L				
	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
<b>SUGGESTED INTERNAL STANDARDS</b>					
D <sub>8</sub> -Naphthalene	0.5	0.5	0.5	0.5	0.5
D <sub>10</sub> -Acenaphthene	0.5	0.5	0.5	0.5	0.5
D <sub>10</sub> -Phenanthrene	0.5	0.5	0.5	0.5	0.5
D <sub>12</sub> -Chrysene	0.5	0.5	0.5	0.5	0.5
D <sub>12</sub> -Perylene	0.5	0.5	0.5	0.5	0.5
<b>SUGGESTED SURROGATE COMPOUNDS</b>					
D <sub>10</sub> -Fluoranthene (field)	0.10	0.25	0.50	1.25	2.50
D <sub>12</sub> -Benzo[a]pyrene (field)	0.10	0.25	0.50	1.25	2.50
D <sub>10</sub> -Fluorene (lab)	0.10	0.25	0.50	1.25	2.50
D <sub>10</sub> -Pyrene (lab)	0.10	0.25	0.50	1.25	2.50

TABLE 5. CHARACTERISTIC IONS FOR SURROGATE SUGGESTED STANDARDS

Classification	Primary Ion	Secondary Ion
<b><u>Internal Standards</u></b>		
D <sub>8</sub> -Naphthalene	136	68,137
D <sub>10</sub> -Acenaphthene	164	162,165
D <sub>10</sub> -Phenanthrene	188	94,189
D <sub>12</sub> -Chrysene	240	120,241
D <sub>12</sub> -Perylene	264	260,265
<b><u>Laboratory Surrogates</u></b>		
D <sub>10</sub> -Fluorene	176	88,177
D <sub>10</sub> -Pyrene	212	106,213
<b><u>Field Surrogates</u></b>		
D <sub>10</sub> -Fluoranthene	212	106,213
D <sub>12</sub> -Benzo(a)pyrene	264	132,265



TABLE 6. EXAMPLE OF CHARACTERISTIC IONS FOR COMMON PAHs

Analyte	Primary Ion	Secondary Ion(s)
Pyrene	202	101,203
Benz(a)anthracene	228	229,226
Chrysene	228	226,229
Benzo(a)pyrene	252	253,126
Benzo(b)fluoranthene	252	253,126
Benzo(k)fluoranthene	252	253,126
Benzo(g,h,i)perylene	276	138,277
Dibenz(a,h)anthracene	278	139,279
Anthracene	178	179,176
Phenanthrene	178	179,176
Acenaphthene	154	153,152
Acenaphthylene	152	151,153
Benzo(e)pyrene	252	253,126
Fluoranthene	202	101,203
Fluorene	166	165,167
Ideno(1,2,3-cd)pyrene	276	138,227
Naphthalene	128	129,127
Perylene	252	253,126
Coronene	300	150,301

TABLE 7. EXAMPLE OF RELATIVE RESPONSE FACTOR CRITERIA  
FOR INITIAL AND CONTINUING CALIBRATION OF  
COMMON SEMI-VOLATILE COMPOUNDS

Semi-volatile Compounds	Minimum RRF	Maximum %RSD	Maximum %Difference
Naphthalene	0.700	30	30
Acenaphthylene	1.300	30	30
Acenaphthene	0.800	30	30
Fluorene	0.900	30	30
Phenanthrene	0.700	30	30
Anthracene	0.700	30	30
Fluoranthene	0.600	30	30
Pyrene	0.600	30	30
Benzo(a)anthracene	0.800	30	30
Chrysene	0.700	30	30
Benzo(b)fluoranthene	0.700	30	30
Benzo(k)fluoranthene	0.700	30	30
Benzo(a)pyrene	0.700	30	30
Indeno(1,2,3-cd)pyrene	0.500	30	30
Dibenz(a,h)anthracene	0.400	30	30
Benzo(g,h,i)perylene	0.500	30	30
Perylene	0.500	30	30
Coronene	0.700	30	30

TABLE 8. MINIMUM SAMPLING EQUIPMENT CALIBRATION AND ACCURACY REQUIREMENTS

Equipment	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Sampler</u>	Indicated flow rate = true flow rate, $\pm 10\%$ .	Calibrate with certified transfer standard on receipt, after maintenance on sampler, and any time audits or flow checks deviate more than $\pm 10\%$ from the indicated flow rate or $\pm 10\%$ from the design flow rate.	Recalibrate
<u>Associated equipment</u>			
Sampler on/off timer	$\pm 30$ min/24 hour	Check at purchase and routinely on sample-recovery days	Adjust or replace
Elapsed-time meter	$\pm 30$ min/24 hour	Compare with a standard time-piece of known accuracy at receipt and at 6-month intervals	Adjust or replace
Flowrate transfer standard (orifice device)	Check at receipt for visual damage	Recalibrate annually against positive displacement standard volume meter	Adopt new calibration curve

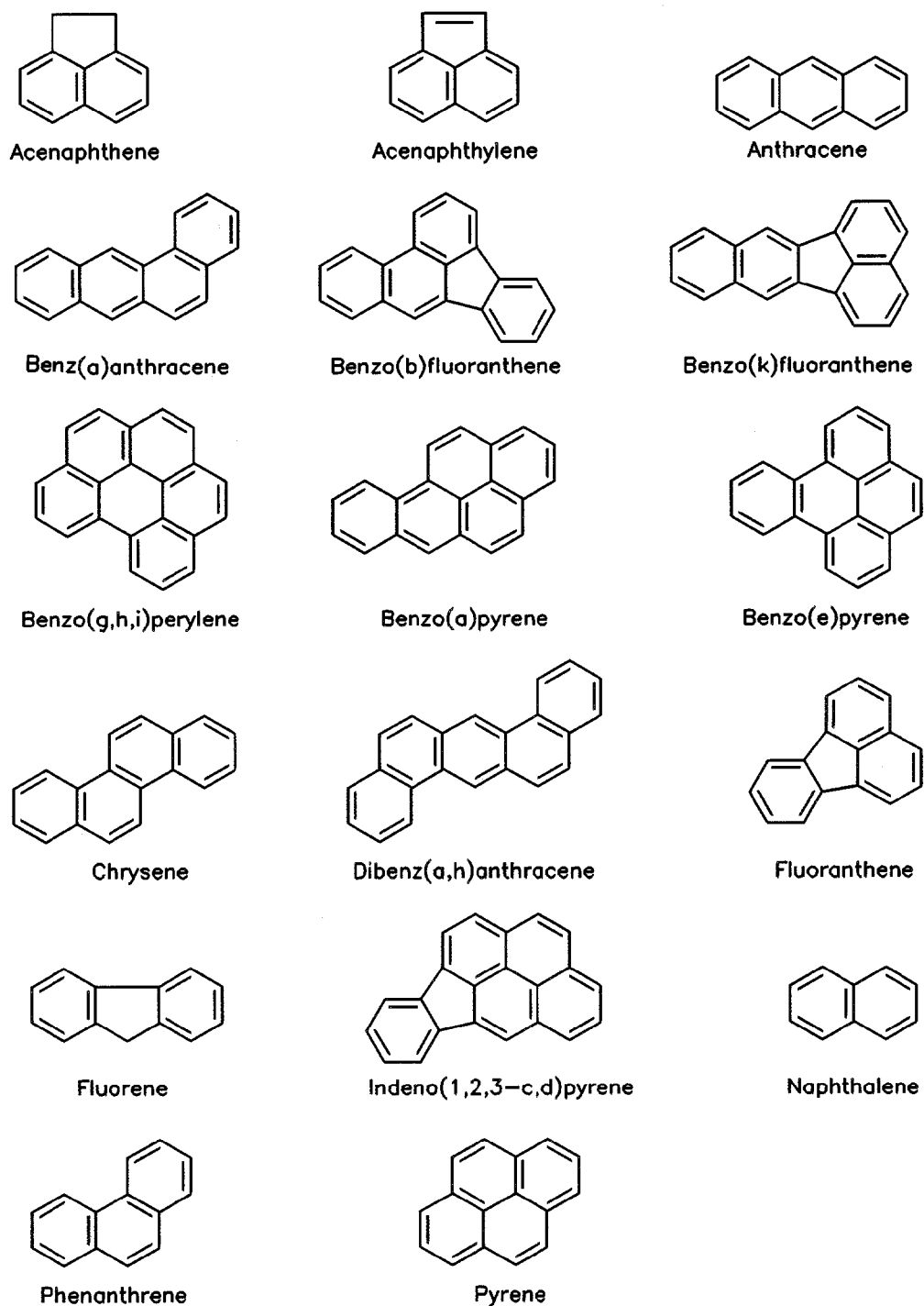


Figure 1. Ring structure of common PAHs.

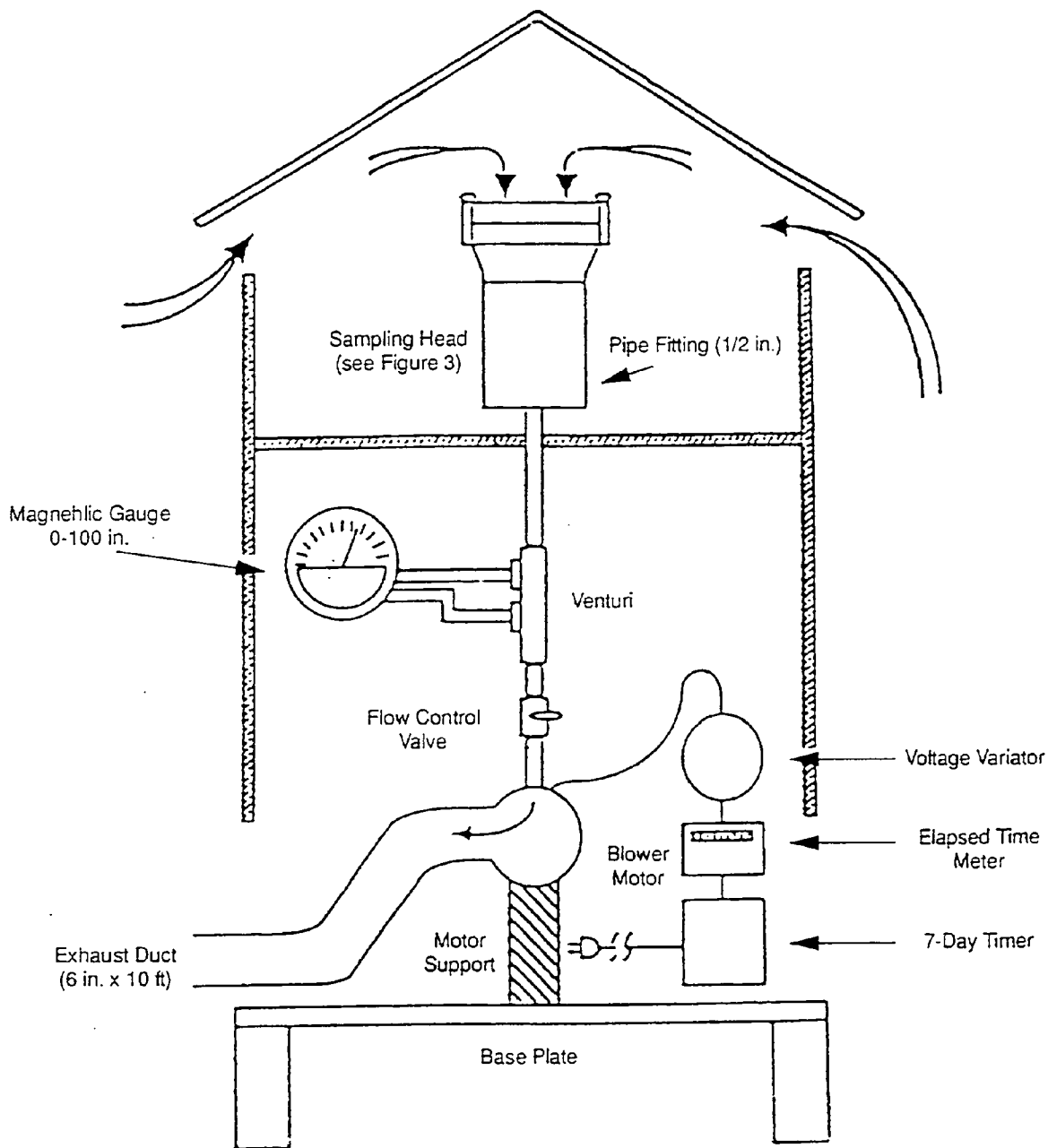


Figure 2. Typical high volume air sampler for PAHs.

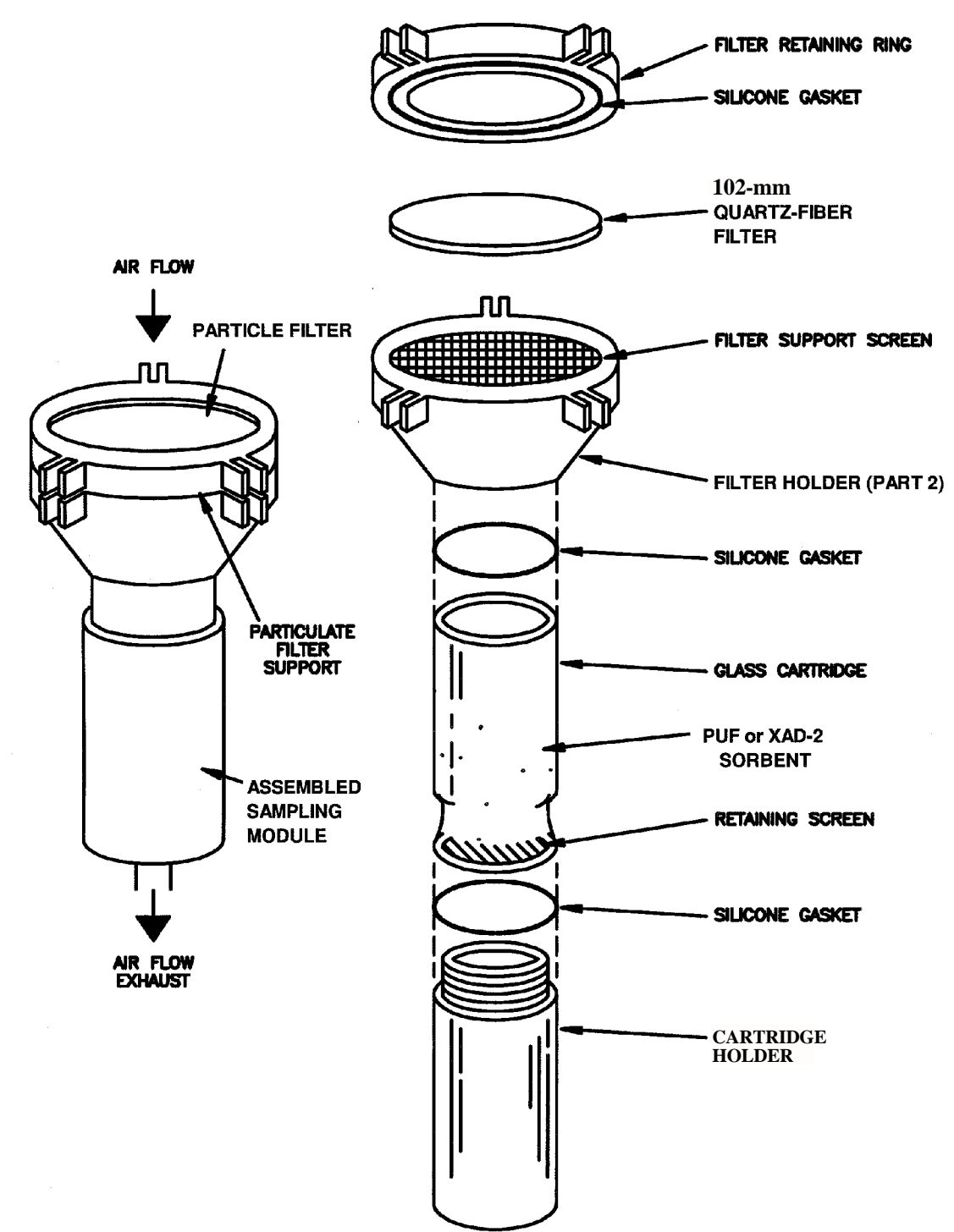


Figure 3. Typical absorbent cartridge assembly for sampling PAHs.

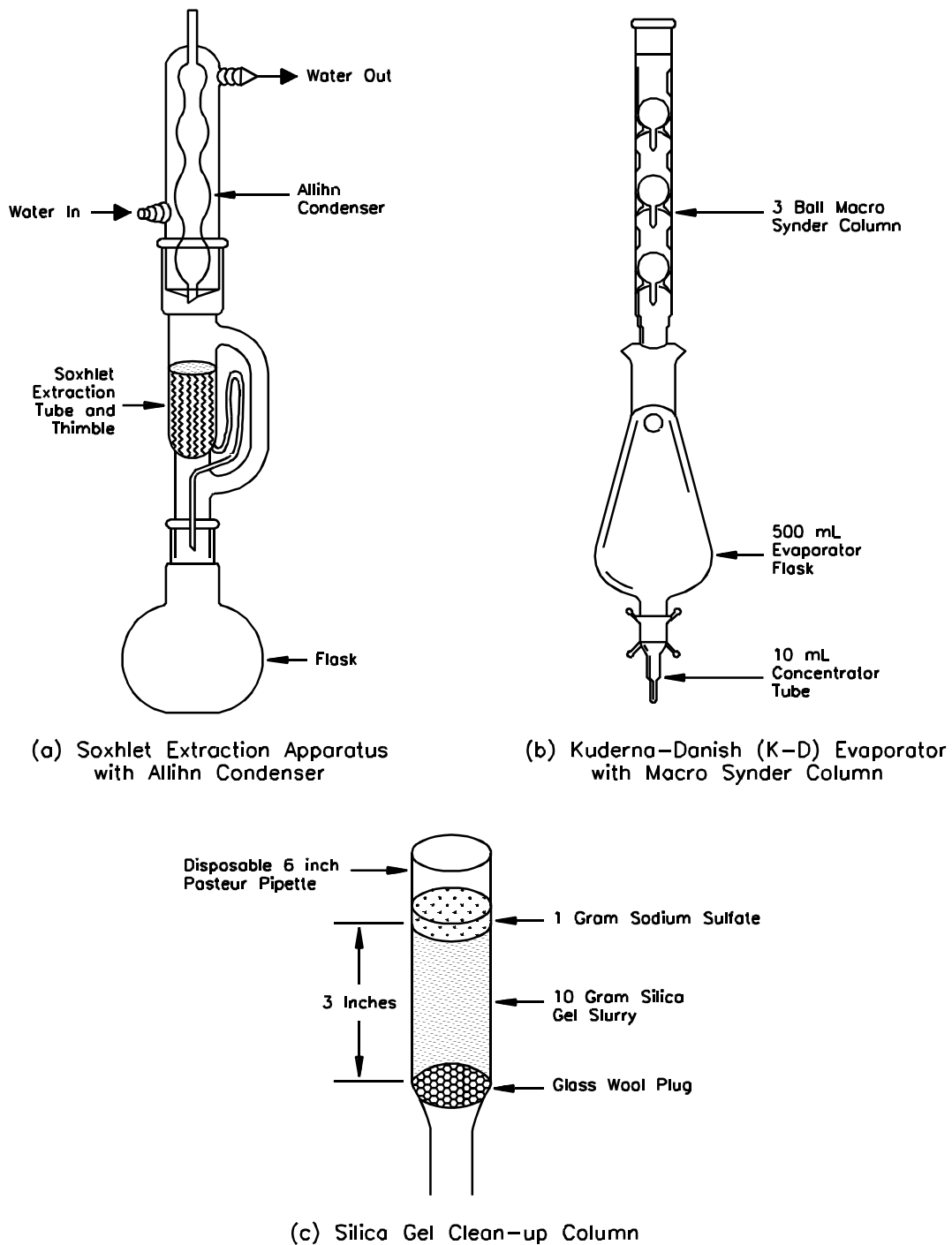
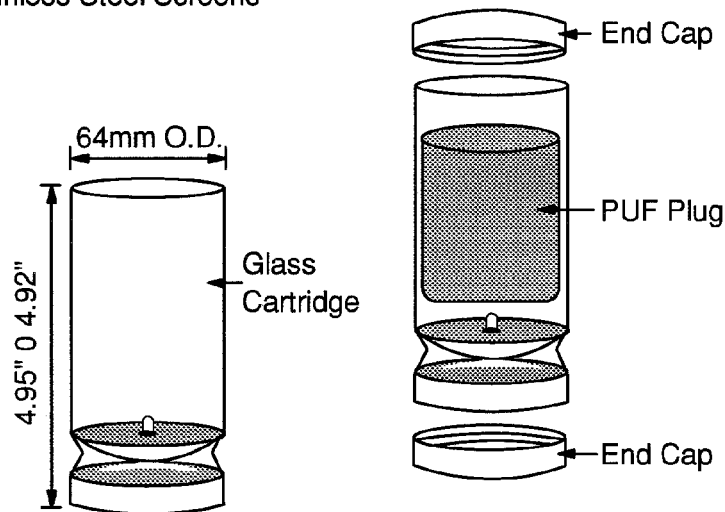
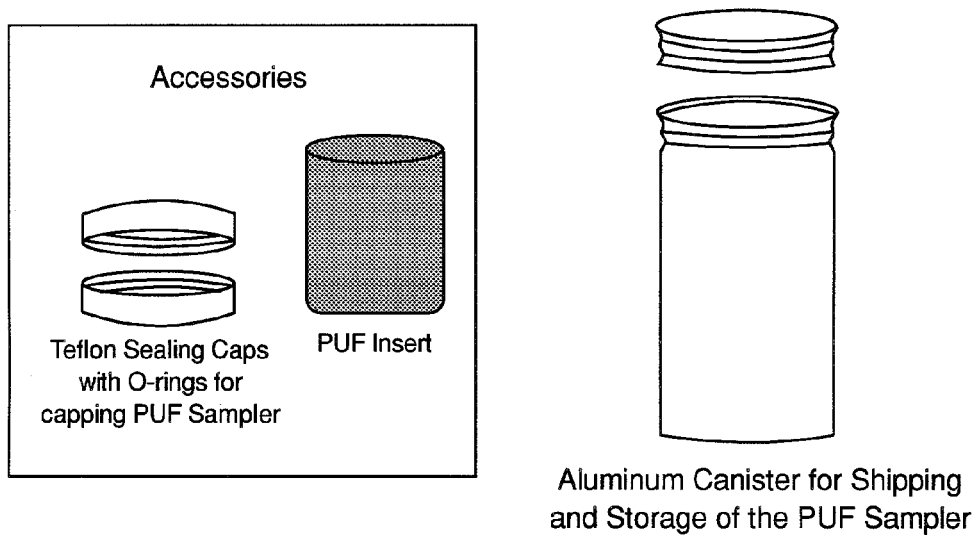


Figure 4. Apparatus used for sample clean-up and extraction.

Glass PUF Cartridge with  
Stainless Steel Screens



5a. Glass PUF cartridge, plug, and end caps.



5b. PUF shipping container.

Figure 5. Glass PUF cartridge (5a) and shipping container (5b) for use with Compendium Method TO-13A.



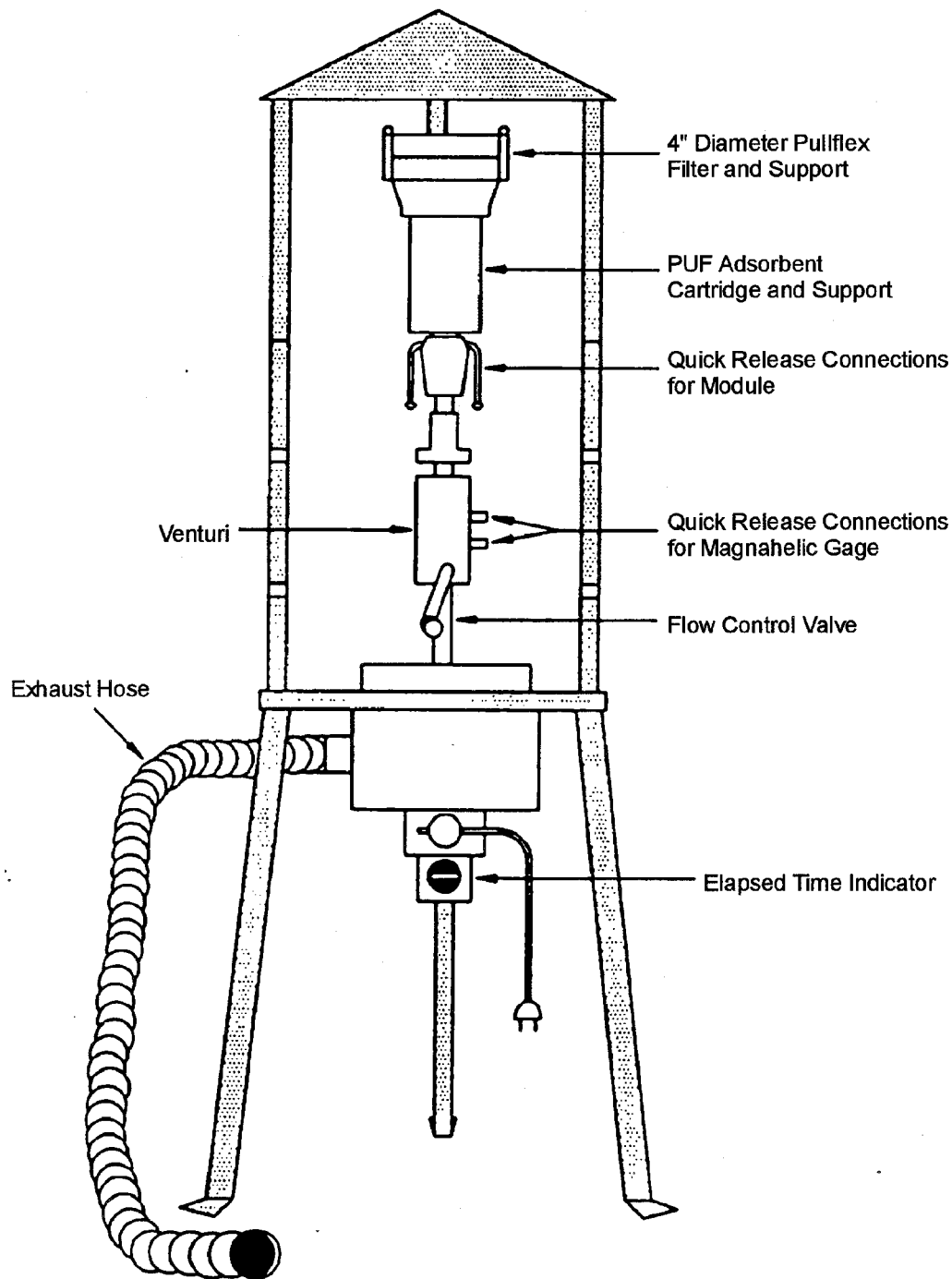


Figure 6. Example of a field portable high volume air sampler for sampling PAHs developed by EPA.

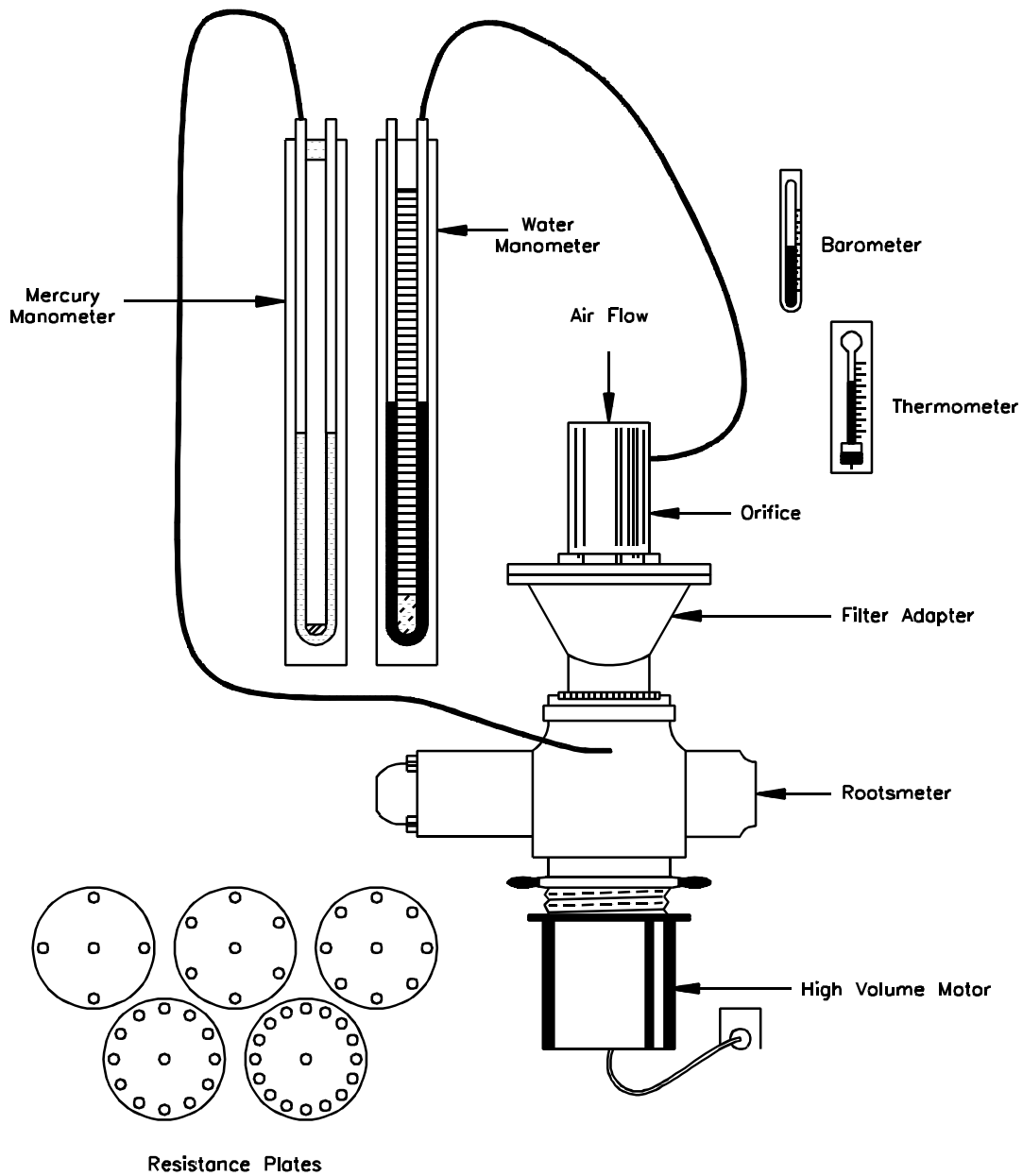


Figure 7. Positive displacement rootsmeter used to calibrate orifice transfer standard used in Compendium Method TO-13A.

COMPENDIUM METHOD TO-13A  
ORIFICE CALIBRATION DATA SHEET

T<sub>1</sub> \_\_\_\_\_ Name \_\_\_\_\_  
 P<sub>1</sub> \_\_\_\_\_ mmHg Date \_\_\_\_\_  
 Orifice No. \_\_\_\_\_  
 Rootsmeater No. \_\_\_\_\_

Resistance Plants (No. of holes)	Air Volume Measured by Rootsmeater V <sub>m</sub>		Standard Volume, V <sub>std</sub> (std m <sup>3</sup> )	Time for Air Volume to Pass Through Rootsmeater, θ (min)	Rootsmeater Pressure Differential, ΔP (mm Hg)	Pressure Drop Across Orifice, ΔH (in. H <sub>2</sub> O)	x-Axis Standard Flowrate, Q <sub>std</sub> (std m <sup>3</sup> /min)
	(R <sup>3</sup> )	(m <sup>3</sup> )					
5	200	5.66					
7	200	5.66					
10	300	8.50					
13	300	8.50					
18	300	8.50					

Factors:  $(R^3)(0.02832 \frac{m^3}{R^3}) = m^3$  and  $(in. Hg) 25.4 (\frac{mm Hg}{in. Hg}) = mm Hg$

Calculation Equations:

$$1. V_{std} = V_m \left( \frac{P_1 - \Delta P}{P_{std}} \right) \left( \frac{T_{std}}{T_1} \right)$$

where:

$$T_{std} = 296^\circ K$$

$$P_{std} = 760.0 \text{ mm Hg}$$

$$2. Q_{std} = \frac{V_{std}}{\theta}$$

Figure 8. Example of a high-volume orifice calibration data sheet for Compendium Method TO-13A.

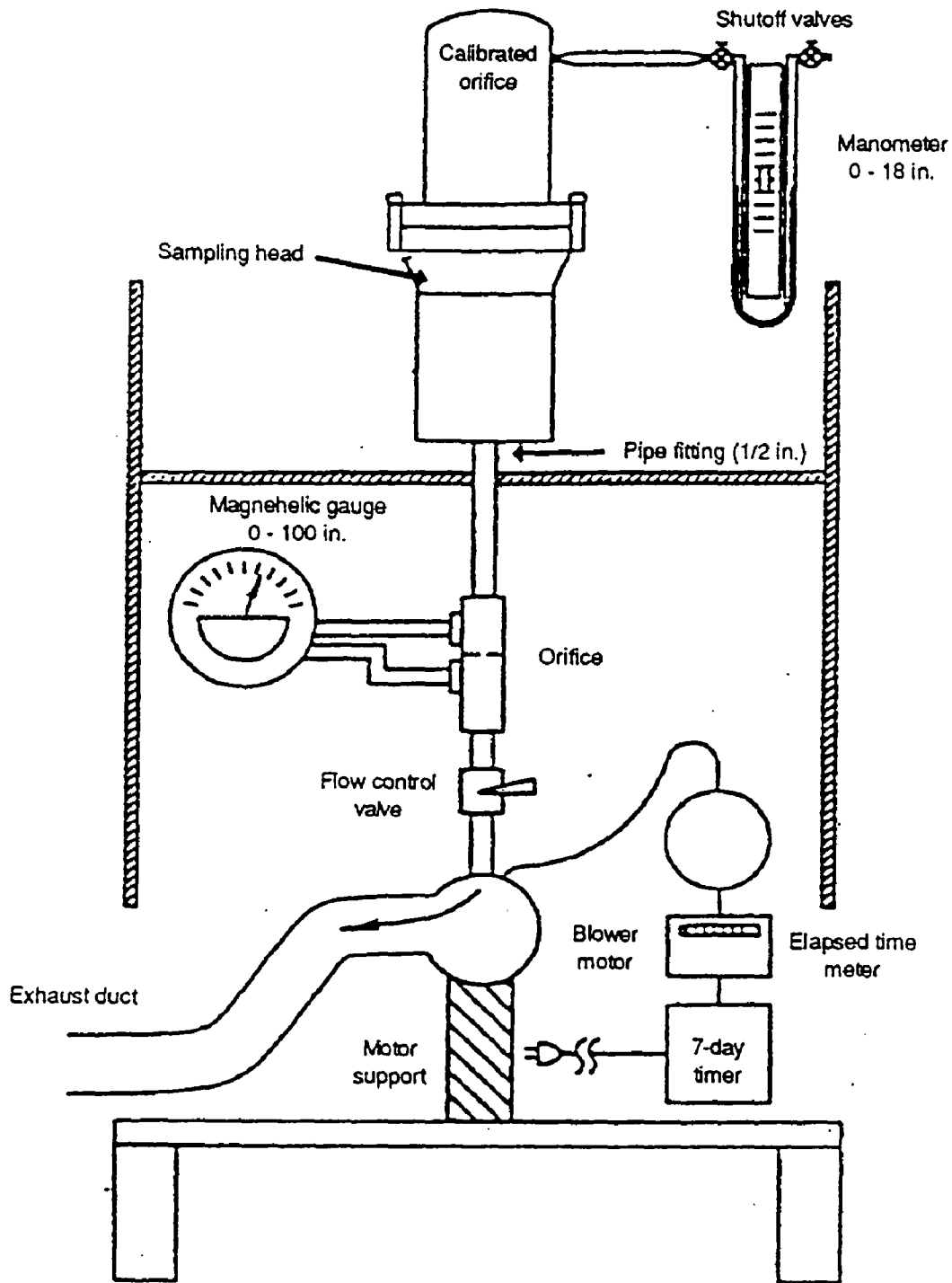


Figure 9. Typical field calibration configuration for Compendium Method TO-13A sampler.

FIELD CALIBRATION DATA SHEET FOR COMPENDIUM METHOD TO-13A PAH  
SAMPLER CALIBRATION

Sampler ID: \_\_\_\_\_

Sampler Location: \_\_\_\_\_

Calibration Orifice ID: \_\_\_\_\_

Job No.: \_\_\_\_\_

High Volume Transfer Orifice Data:

Correlation Coefficient (CC1): \_\_\_\_\_

Slope (M1): \_\_\_\_\_

(CC2): \_\_\_\_\_

(M2): \_\_\_\_\_

Intercept (B1): \_\_\_\_\_

(B2): \_\_\_\_\_

Calibration Date: \_\_\_\_ Time: \_\_\_\_\_

Calibration Ambient Temperature: \_\_\_\_ °F \_\_\_\_ °C CALIBRATOR'S SIGNATURE \_\_\_\_\_

Calibration Ambient Barometric Pressure: \_\_\_\_ "Hg \_\_\_\_ mm Hg \_\_\_\_\_

Calibration set point (SP): \_\_\_\_\_

SAMPLER CALIBRATION

Actual values from calibration		Calibrated values		
Orifice manometer, inches (Y1)	Monitor magnehelic, inches (Y2)	Orifice manometer (Y3)	Monitor magnehelic (Y4)	Calculated value orifice flow, scm (X1)
	70			
	60			
	50			
	40			
	30			
	20			
	10			

Definitions

Y1 = Calibration orifice reading, in. H<sub>2</sub>OY2 = Monitor magnehelic reading, in. H<sub>2</sub>OP<sub>a</sub> = Barometric pressure actual, mm Hg

B1 = Manufacturer's Calibration orifice Intercept

M1 = Manufacturer's Calibration orifice manometer slope

Y3 = Calculated value for orifice manometer  
= {Y1(Pa/760)[298/(Ta + 273)]<sup>1/2</sup>}

Y4 = Calculated value for magnehelic

= {Y2(Pa/760)[298/(Ta + 273)]<sup>1/2</sup>}

X1 = Calculated value orifice flow, scm

= (Y3 - B1)/M1

P<sub>std</sub> = Barometric pressure standard, 760 mm HgT<sub>a</sub> = Temperature actual, °CT<sub>std</sub> = Temperature standard, 25°C

Figure 10. Typical orifice transfer field calibration data sheet for Compendium Method TO-13A.

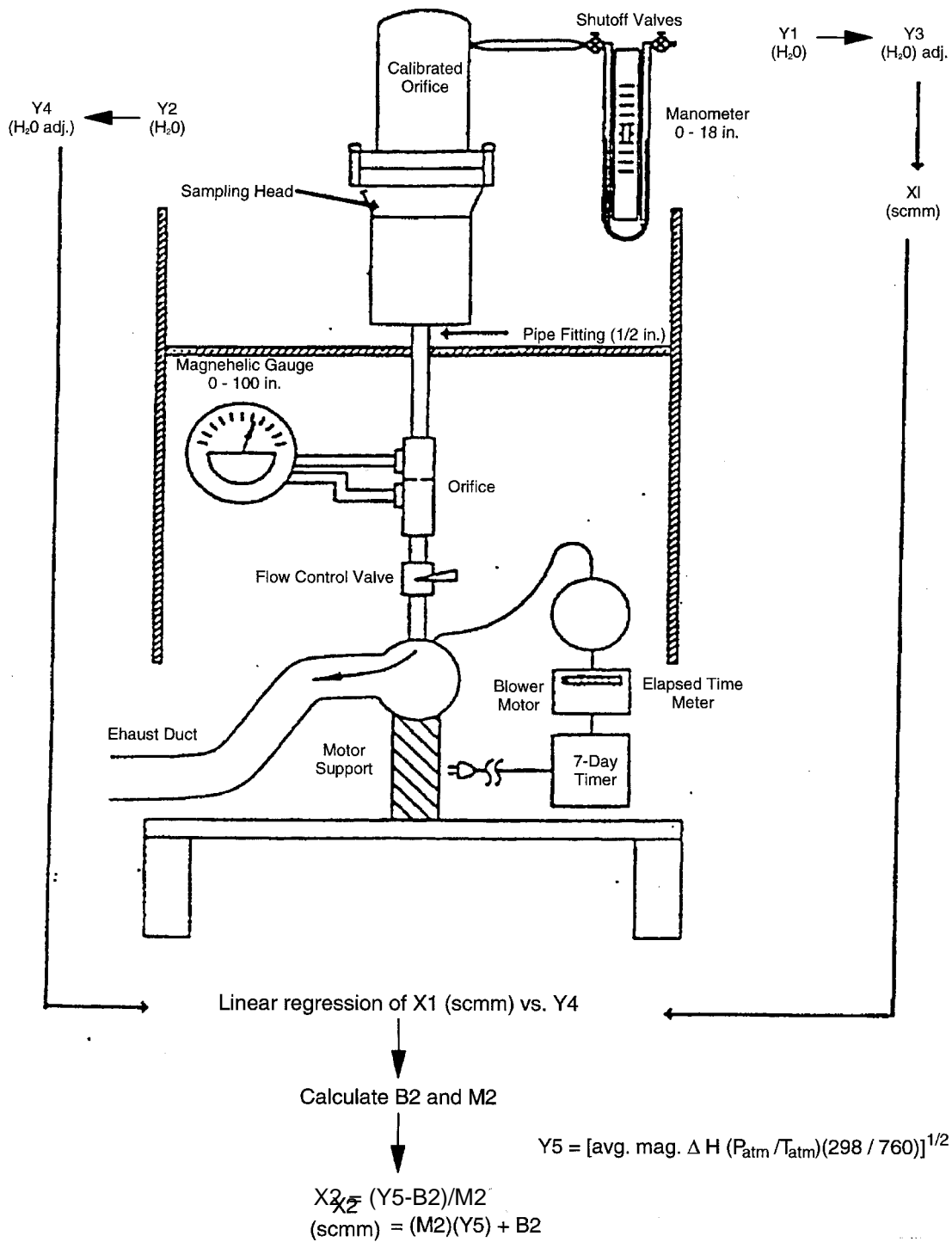


Figure 11. Example of relationship between orifice transfer standard and flow rate through Compendium Method TO-13A sampler.

**COMPENDIUM METHOD TO-13A  
FIELD TEST DATA SHEET  
GENERAL INFORMATION**

Sampler I.D. No.: \_\_\_\_\_  
 Lab PUF Sample No.: \_\_\_\_\_  
 Sample location: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

Operator: \_\_\_\_\_  
 Other: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

PUF Cartridge Certification Date: \_\_\_\_\_  
 Date/Time PUF Cartridge Installed: \_\_\_\_\_  
 Elapsed Timer: \_\_\_\_\_  
     Start \_\_\_\_\_  
     Stop \_\_\_\_\_  
     Diff. \_\_\_\_\_  
 Sampling  
     M1 \_\_\_\_\_      B1 \_\_\_\_\_  
     M2 \_\_\_\_\_      B2 \_\_\_\_\_

	Start	Stop
Barometric pressure ("Hg)	_____	_____
Ambient Temperature (°F)	_____	_____
Rain	Yes _____	Yes _____
	No _____	No _____
Sampling time		
Start	_____	
Stop	_____	
Diff.	_____	

Audit flow check within ±10 of set point  
 \_\_\_\_\_ Yes  
 \_\_\_\_\_ No

TIME	TEMP	BAROMETRIC PRESSURE	MAGNEHELIC READING	CALCULATED FLOW RATE (std. m <sup>3</sup> )	READ BY
Avg.					

Comments

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

Figure 12. Example of typical Compendium Method TO-13A field test data sheet (FTDS).

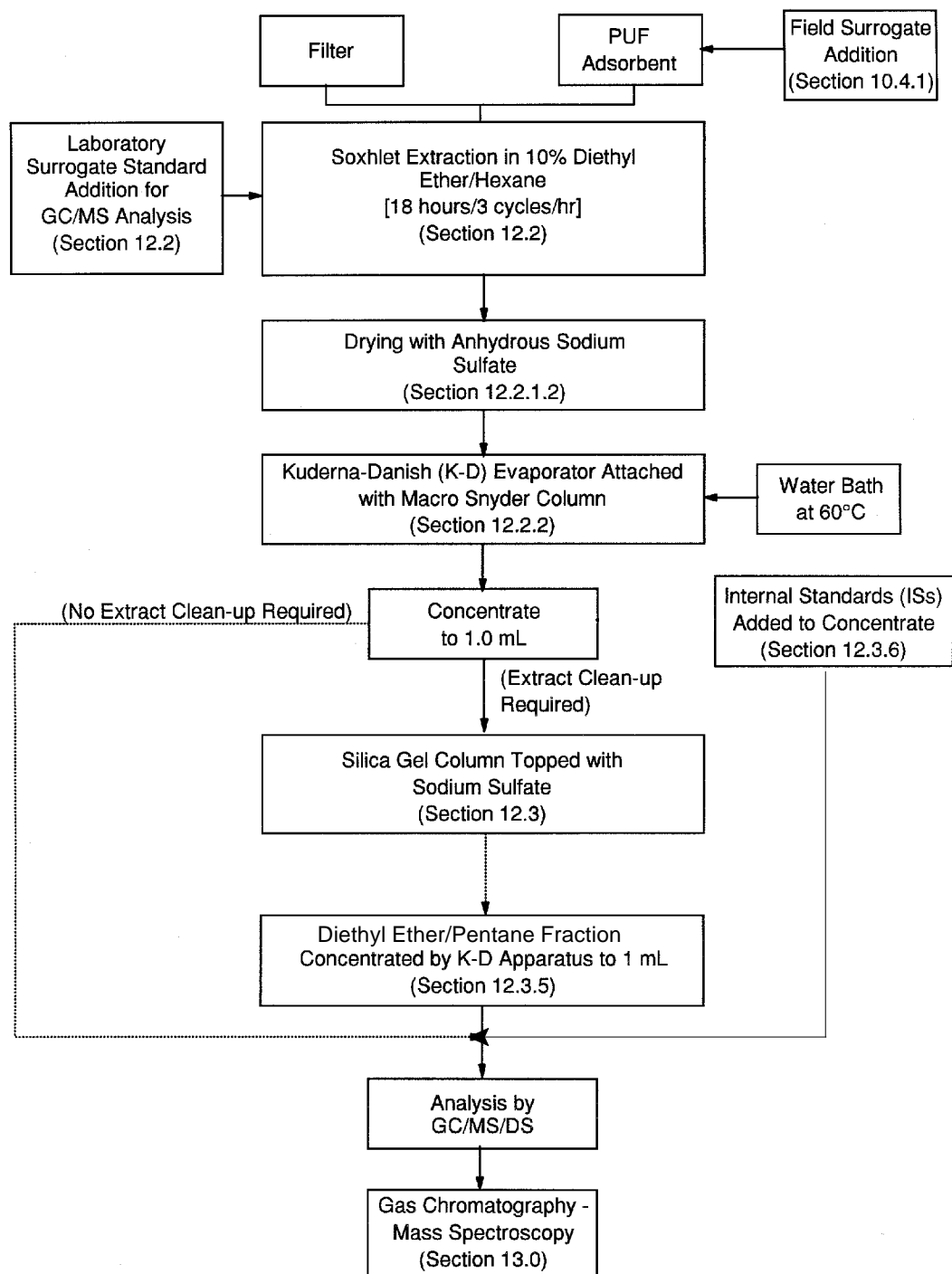


Figure 13. Sample clean-up, concentration, separation and analysis sequence for common PAHs.  
 [Note: XAD-2 sequence is similar to PUF except methylene chloride is the solvent.]



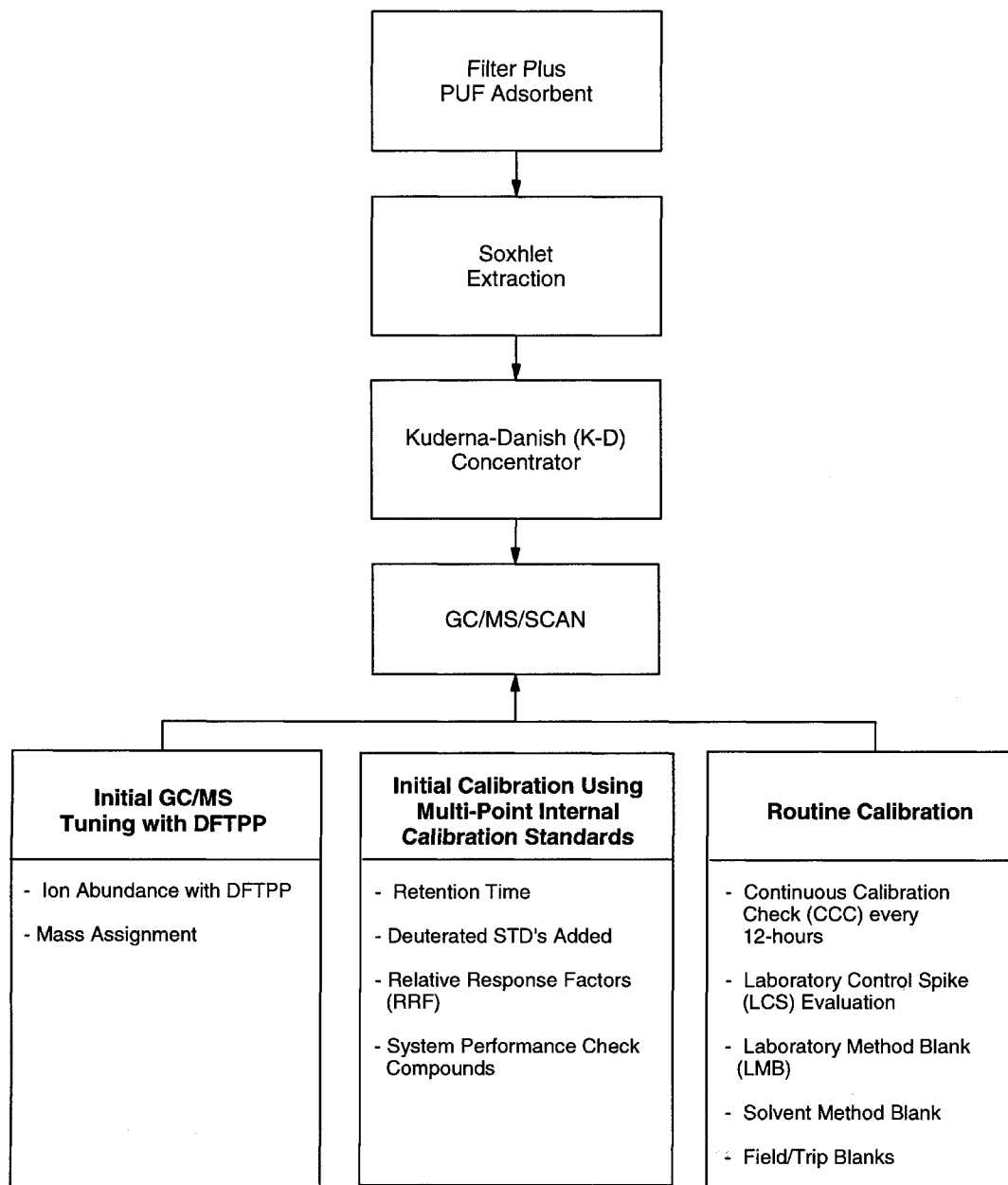


Figure 14. Typical quality assurance specifications for GC/MS/DS operation.

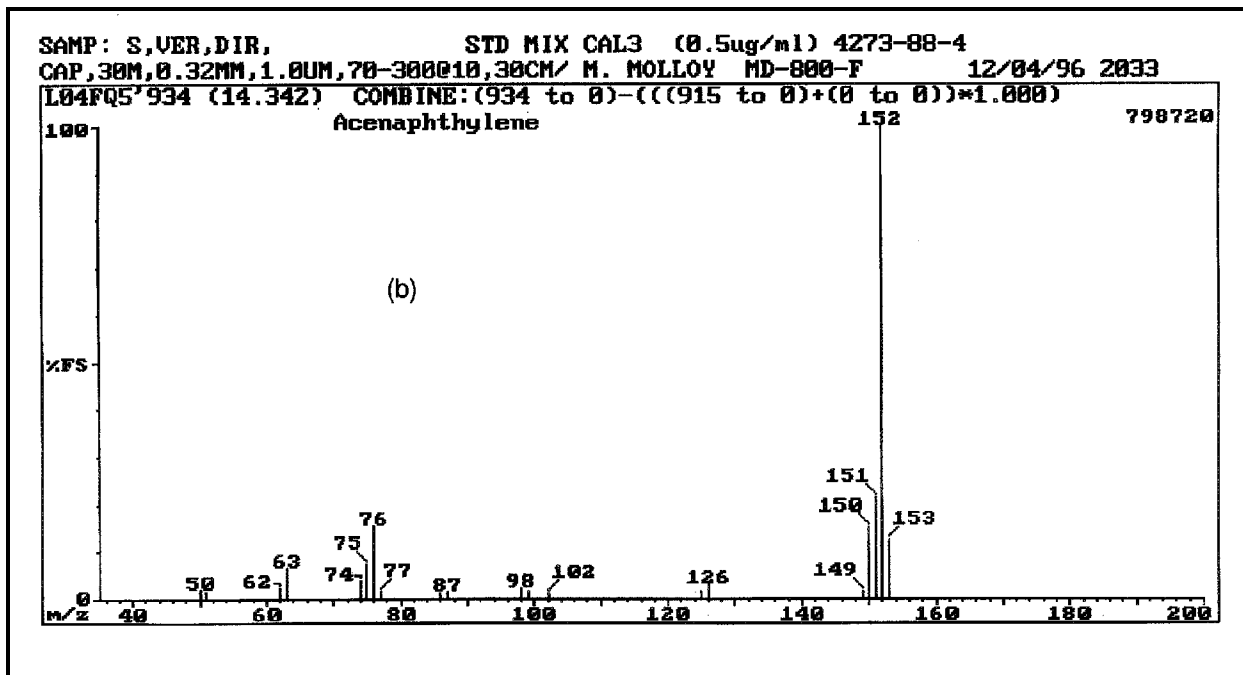
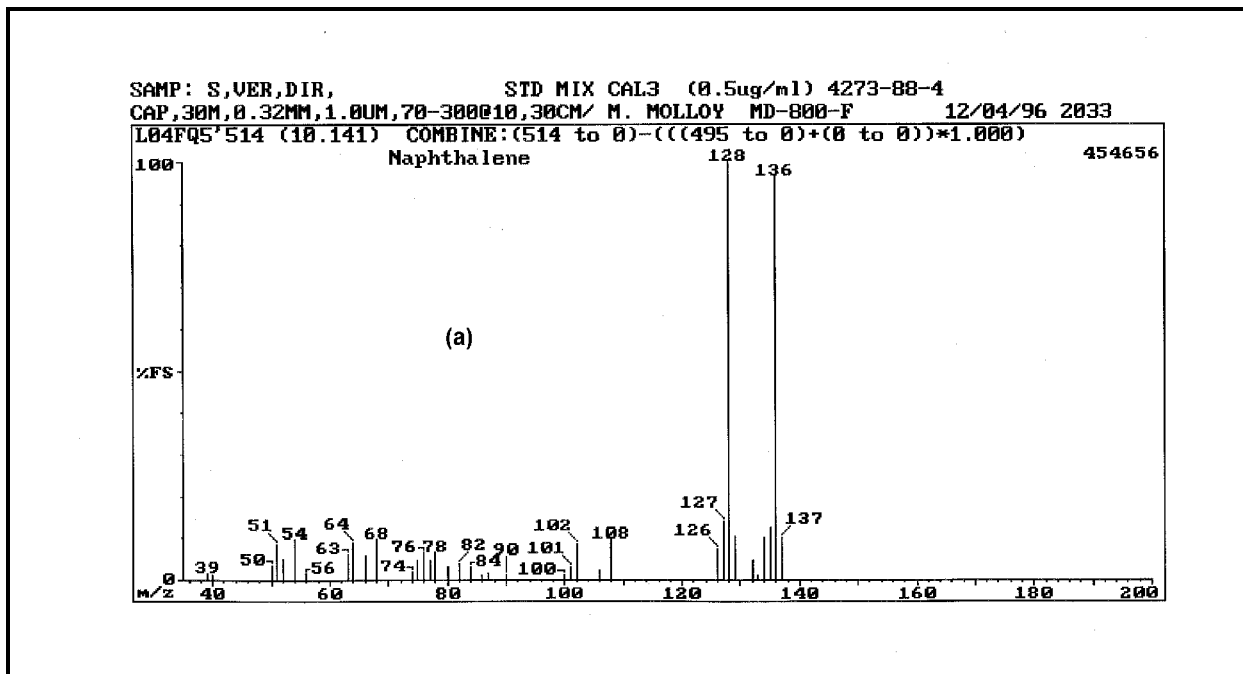


Figure 15. Mass spectra of Compendium Method TO-13A compounds for (a) naphthalene and (b) acenaphthylene.

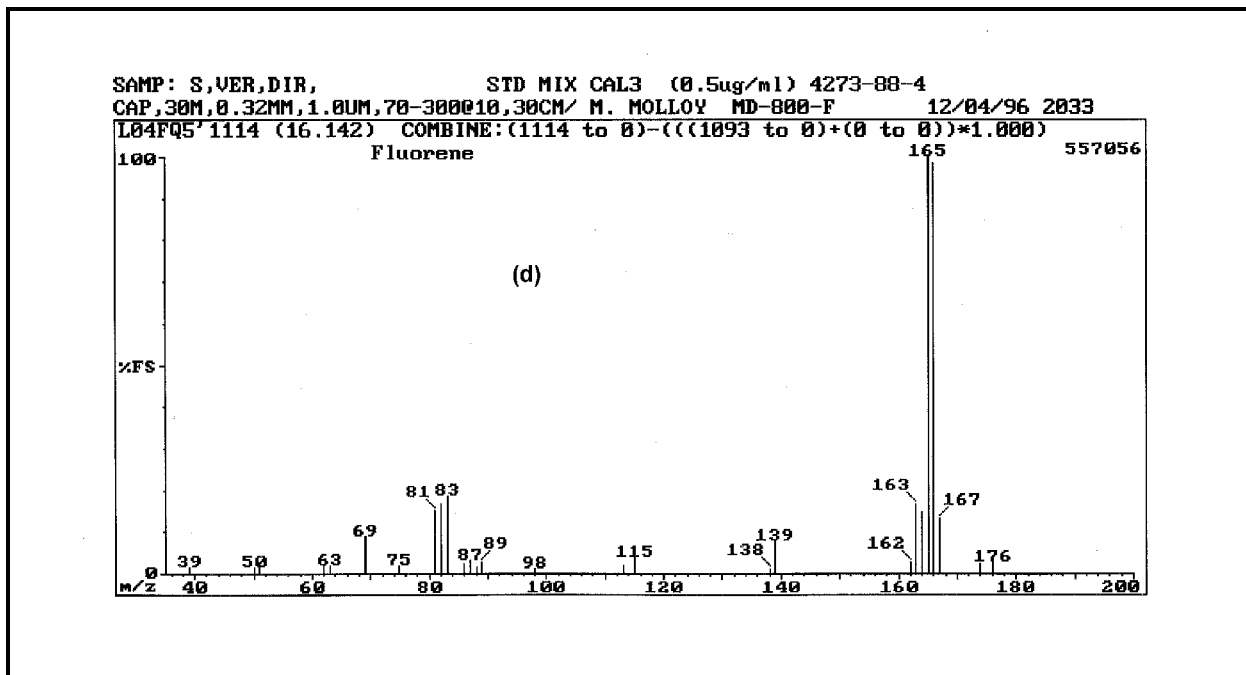
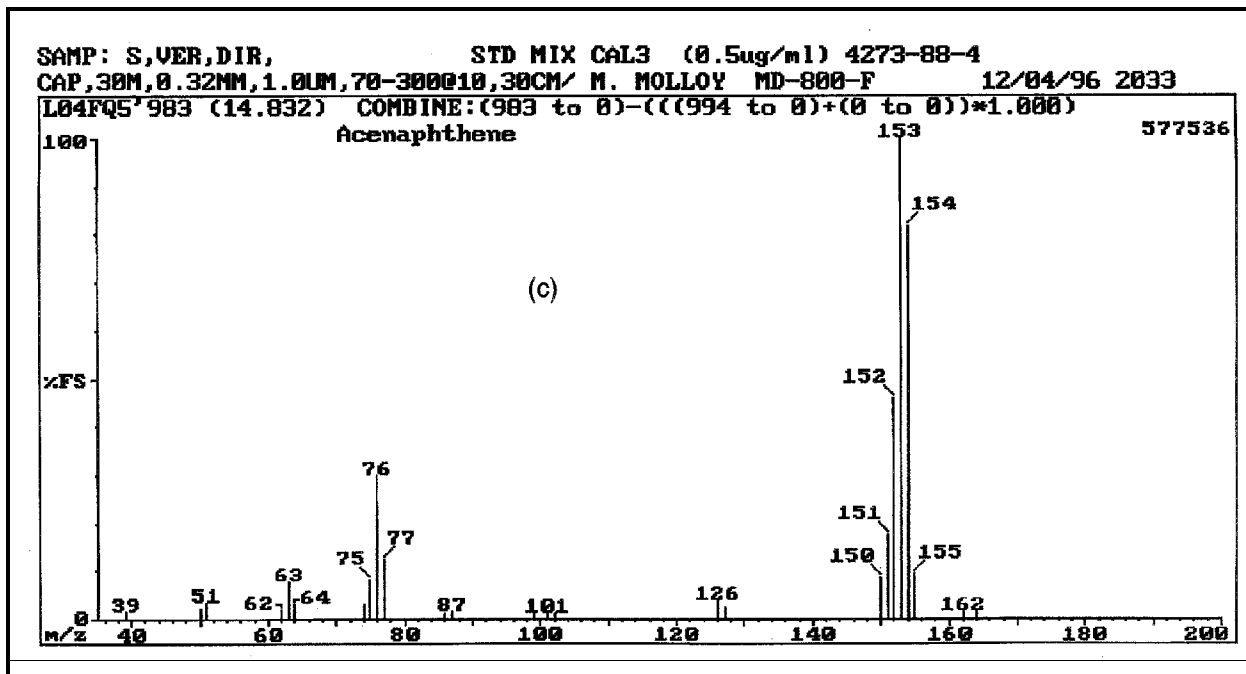


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (c) acenaphthene and (d) fluorene.

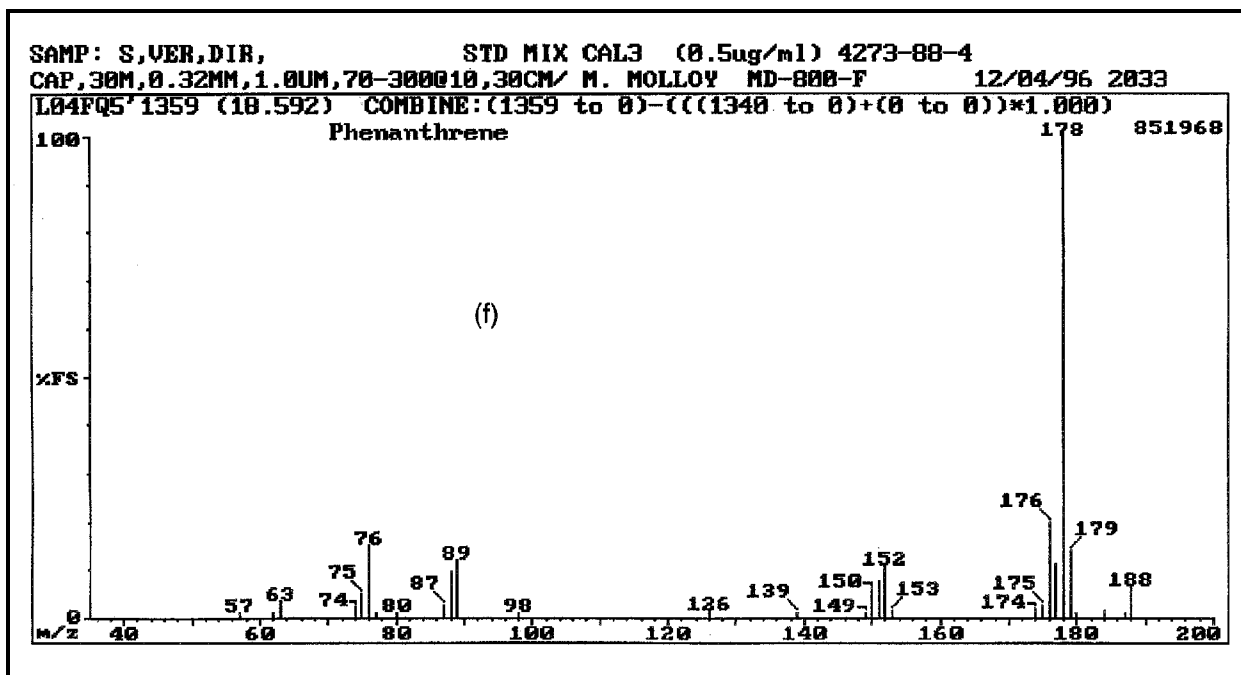
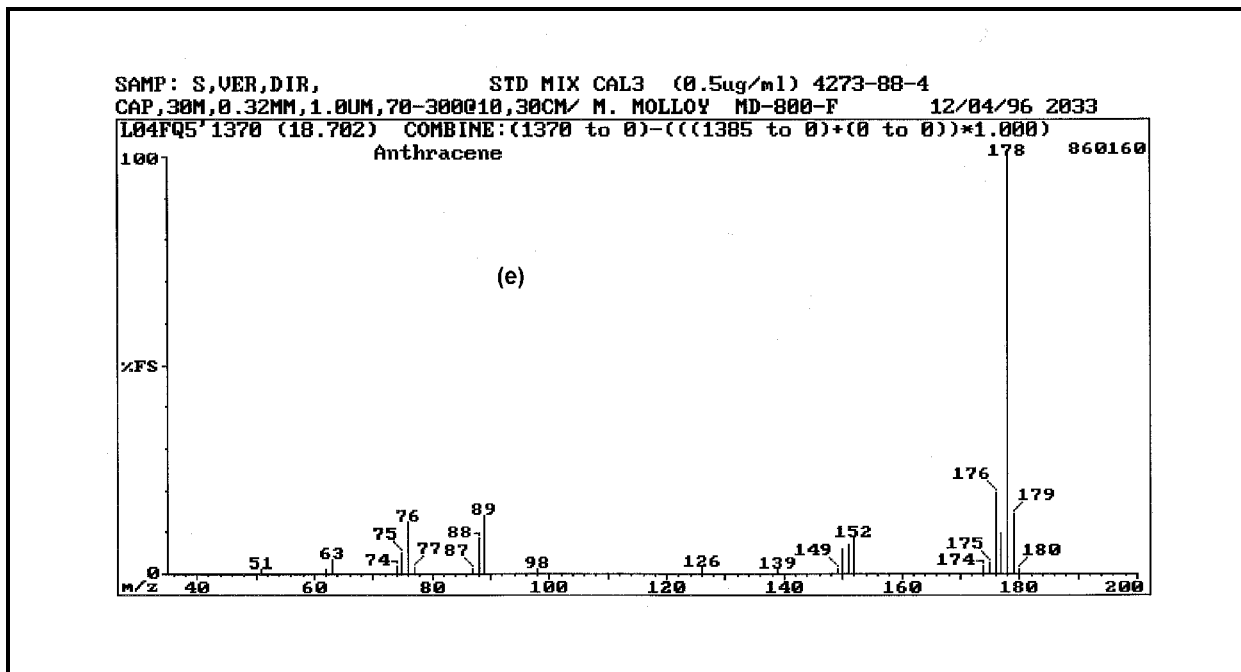


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (e) anthracene and (f) phenanthrene.

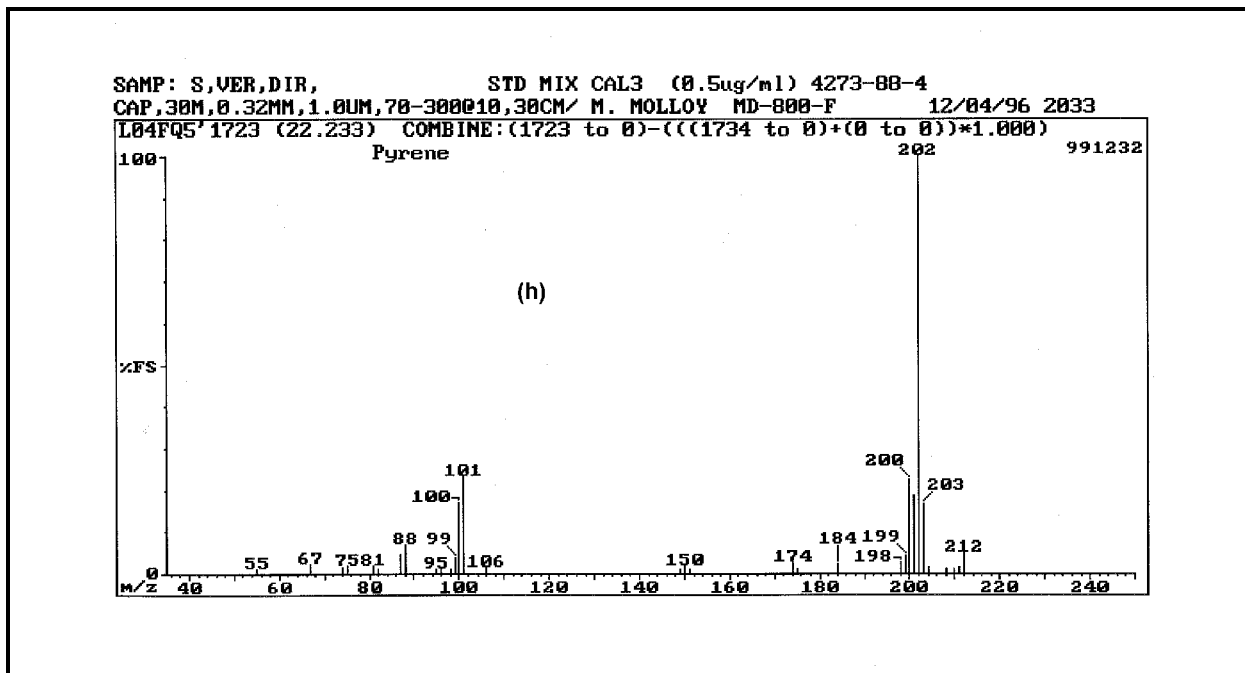
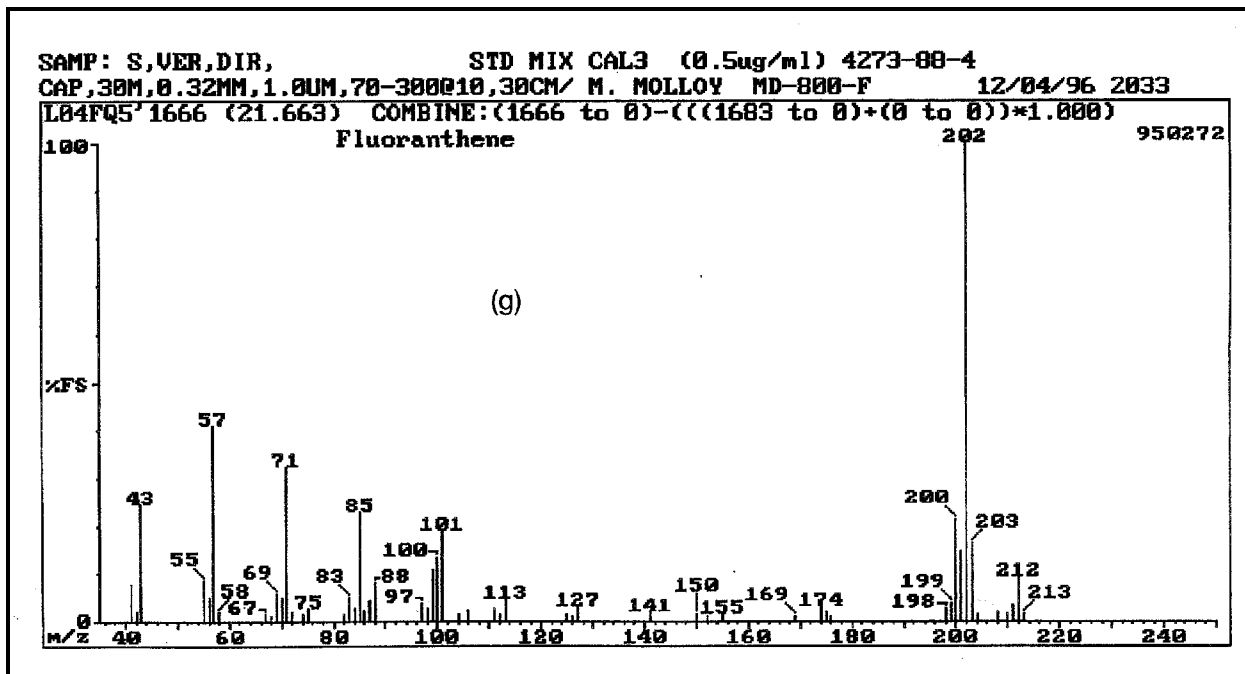


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (g) fluoranthene and (h) pyrene.

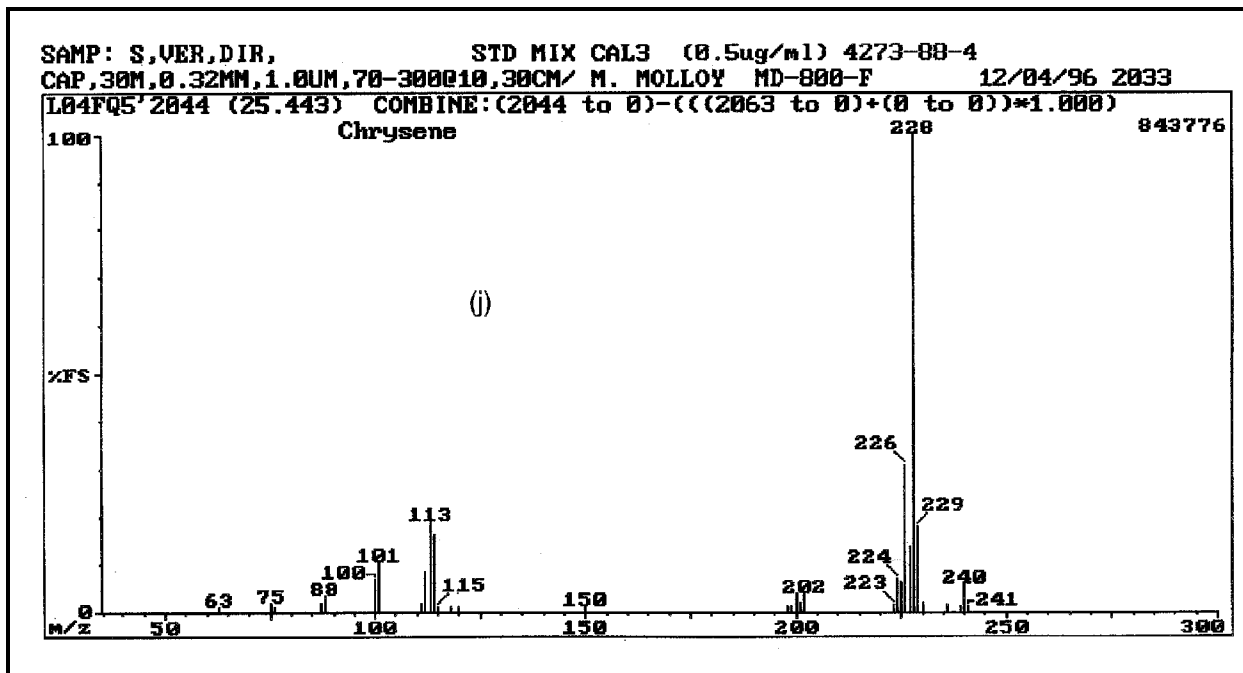
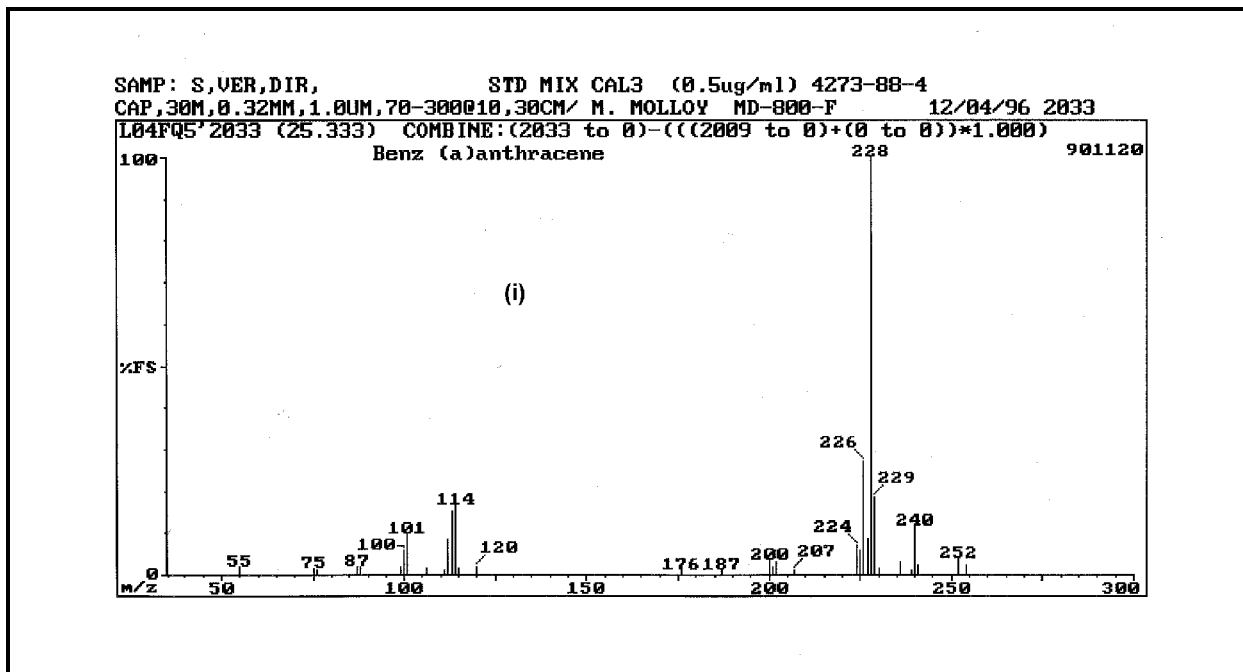


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (i) benz(a)anthracene and (j) chrysene.

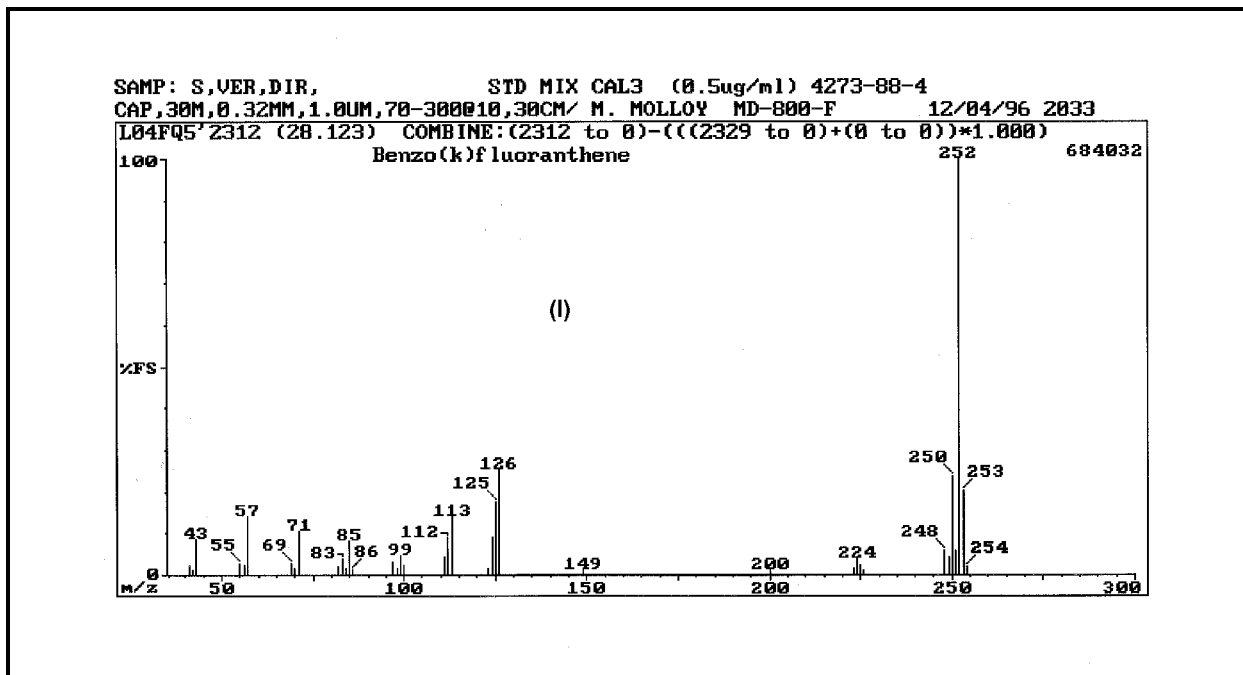
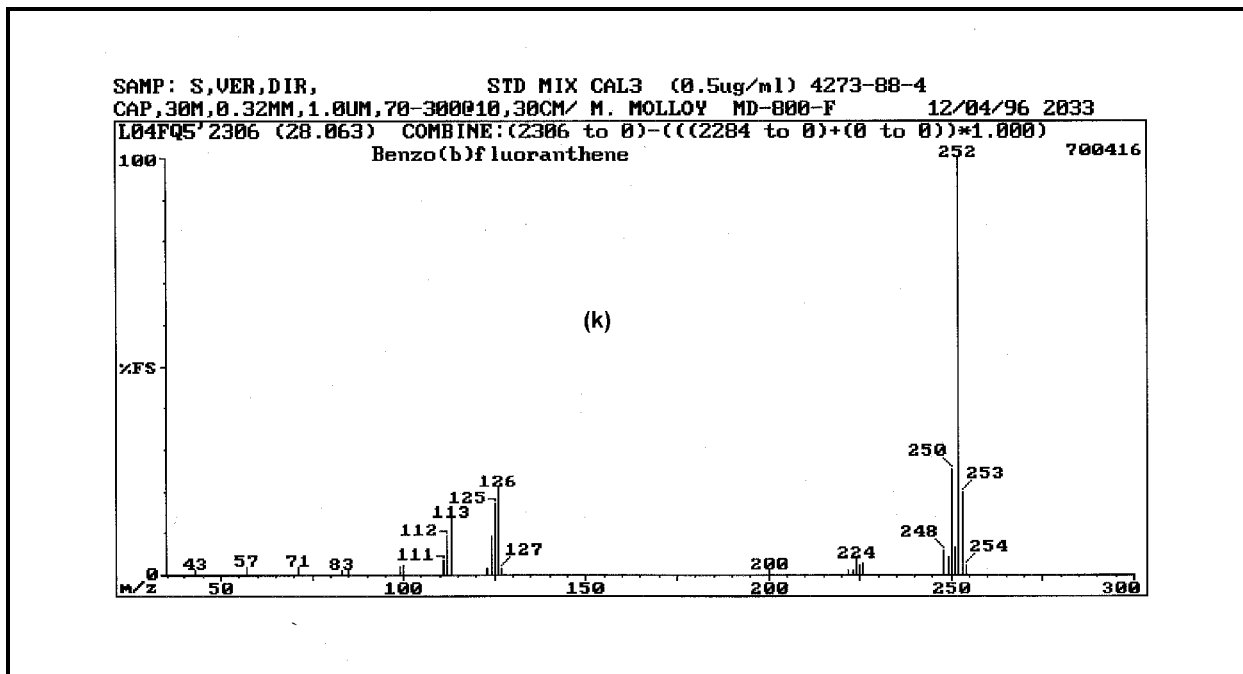


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (k) benzo(b)fluoranthene and (l) benzo(k)fluoranthene.

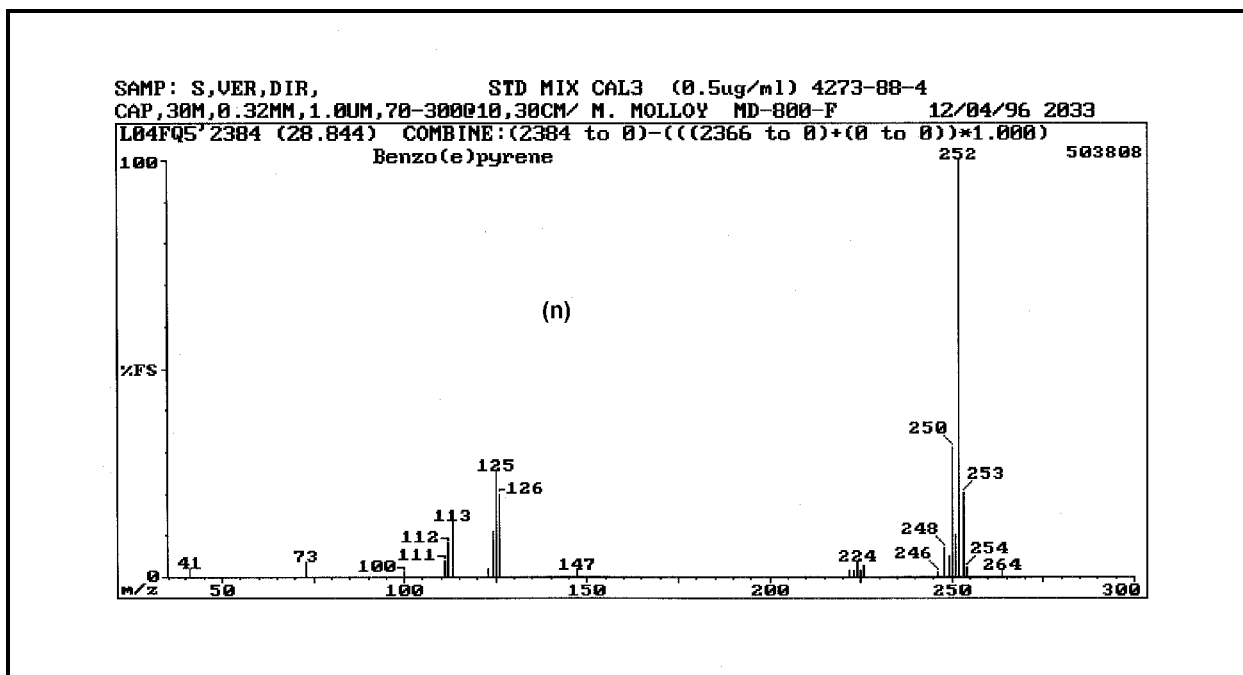
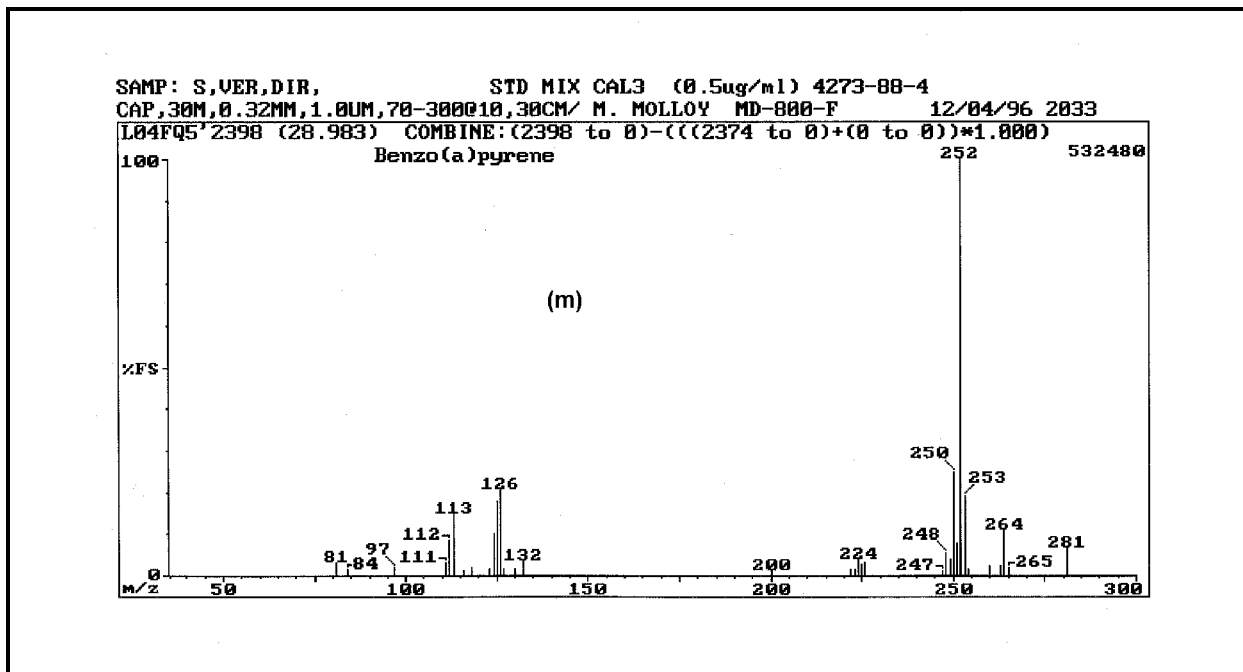


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (m) benzo(a)pyrene and (n) benzo(e)pyrene.



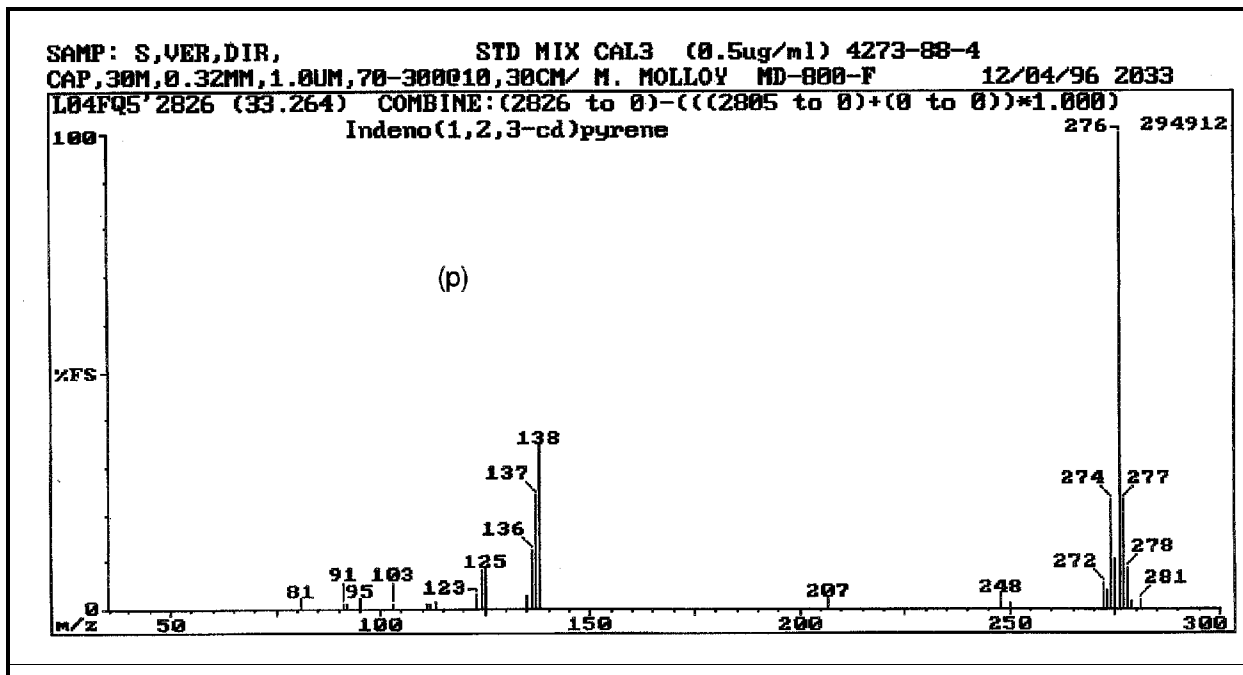
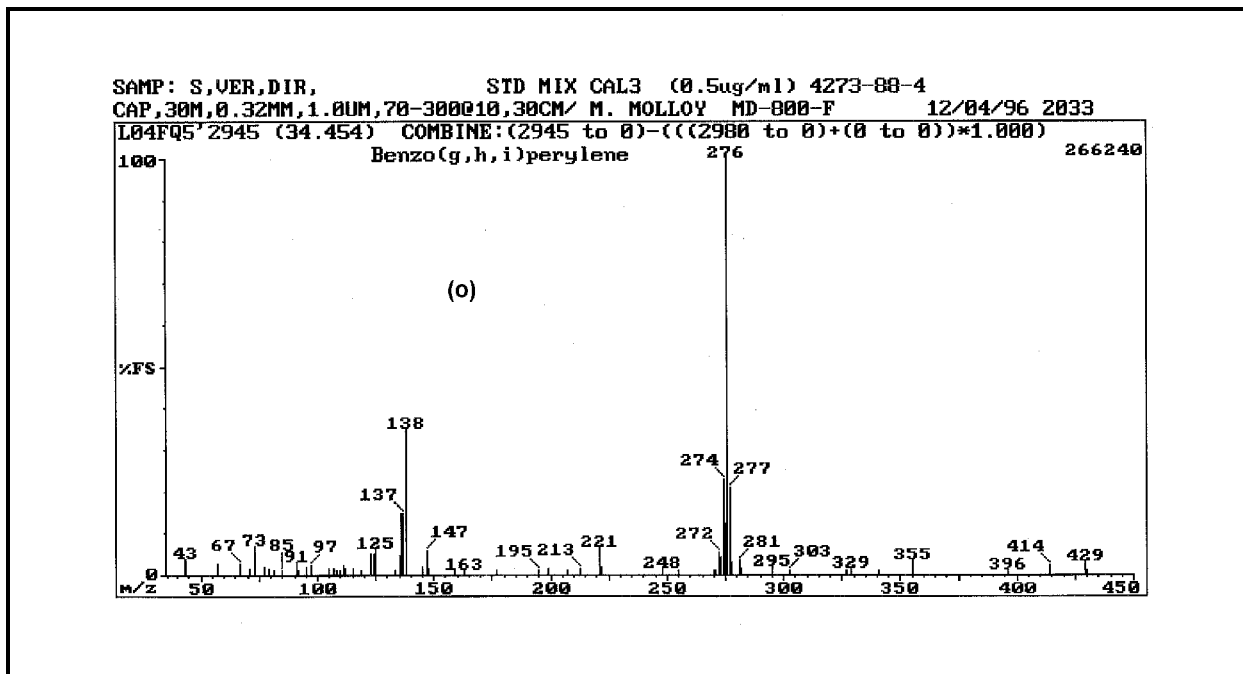


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (o) benzo(g,h,i)perylene and (p) indeno(1,2,3-cd)pyrene.

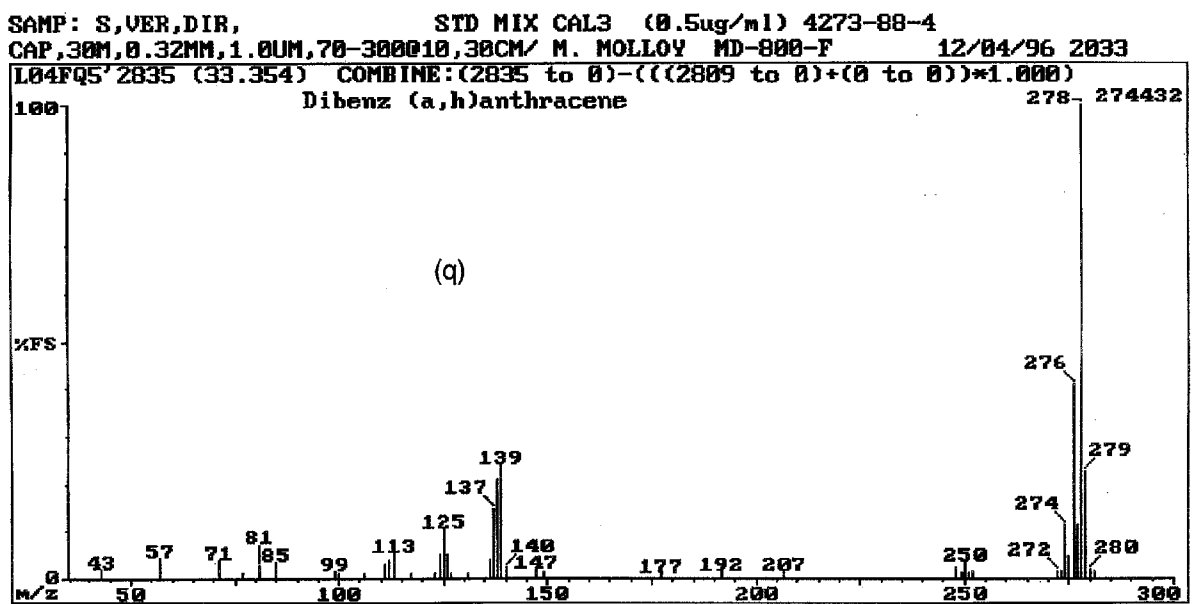


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (q) dibenz(a,h)anthracene.

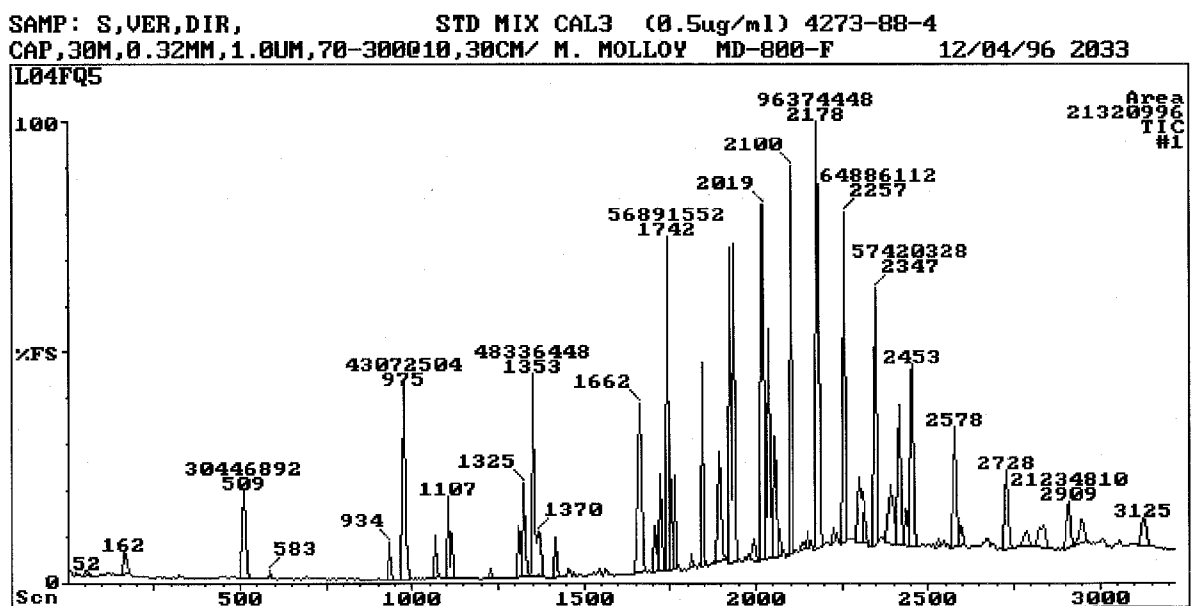


Figure 16. Total ion chromatogram (TIC) of Compendium Method TO-13A target PAHs.

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