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PART 2 OF 2

COMPENDIUM OF METHODS FOR THE DETERMINATION OF AIR POLLUTANTS IN INDOOR AIR

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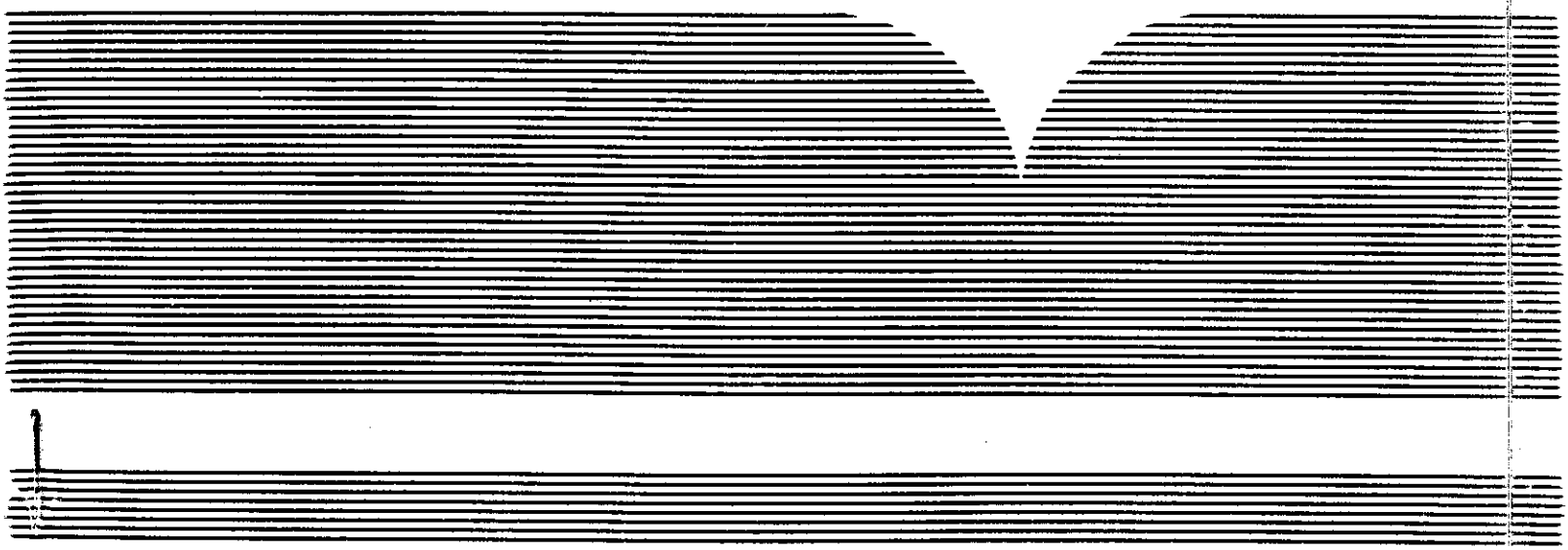

U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
NTIS

Method IP-5B

DETERMINATION OF NITROGEN DIOXIDE (NO_2) IN INDOOR AIR USING PALMES DIFFUSION TUBES

Method IP-5B

DETERMINATION OF NITROGEN DIOXIDE (NO_2) IN INDOOR AIR USING PALMES DIFFUSION TUBES

1. Scope

1.1 In order to perform sampling and analysis of indoor air pollutants it is necessary to develop highly sensitive, lightweight and affordable instrumentation. The technology and methods for sampling and analysis of nitrogen dioxide (NO_2) use both passive and active samplers and an array of analytical systems.

1.2 Among the methods for determining NO_2 is the Palmes tube (1). This is a passive sampler which employs sorption for NO_2 collection and spectrophotometry for detection.

1.3 The Palmes tube is based on sorption of NO_2 gas onto a surface coated with triethanolamine. The coated surface is then extracted with a mixture of sulfanilamide reagent and N-1-napthylethylene-diamine-dihydrochloride (NEDA) reagent.

1.4 The method gives a time-weighted average and can be used for 8 hour as well as week long sampling periods for personal exposure or area concentrations. This method stands out as the most sensitive method used at low levels of NO_2 around the 0.1 ppm level, but has some variance at higher levels above approximately 5 ppm.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definitions of Terms Related to Atmospheric Sampling
E275 Recommended Practice for Describing and Measuring Spectrophotometers

2.2 Other Documents

U.S. Environmental Protection Agency Technical Assistance Document (2) Laboratory Studies (3-7)

3. Summary of Method

3.1 The Palmes diffusion tube consists of a hollow acrylic tube with one end permanently sealed and the other equipped with a top which can be removed and replaced. At the sealed end of the tube are three stainless steel mesh screens previously coated with a solution of triethanolamine. The diffusion tube has a cross sectional area to length ratio of 0.1 cm. A typical Palmes Tube is shown in Figure 1.

3.2 The principle of sample collection is based on Ficks First Law of Diffusion. For analysis, a color reagent is added to the tube, mixed, and allowed time to develop. Within the period between 20 and 30 min. after the reagent is added, the absorbance of the diazo coupling of the NO_2 and N-1-napthylethylene-diamine dihydrochloride (NEDA) in the color reagent is measured spectrophotometrically at 540 nm. The concentration of NO_2 in the

sampled atmosphere is calculated from the nanomoles of nitrite measured, the exposure time, the diffusion coefficient of NO_2 through air, and the sampler's diffusion characteristics.

3.3 To commence sampling, the end of the tube is opened. Air is free to flow through the tube to the absorbent on the interior screens. When the collection period is through, the tube is recapped and stored until analysis is performed.

3.4 For analysis, a color reagent is added to the tube, mixed, and allowed time to develop. Within the period between 20 and 30 minutes after the reagent is added, the absorbance of the diazo coupling of the NO_2 and N-1-napthylethylene-diamine-dihydrochloride (NEDA) in the color reagent is measure spectrophotometrically at 540 nm. The concentration of NO_2 in the sampled atmosphere is calculated form the nanomoles of nitrite measure, the exposure time, the diffusion coefficient of NO_2 through air, and the sampler's diffusion characteristics.

3.5 This standard may involve hazardous materials, operations, and equipment. This does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitation prior to use.

4. Significance

4.1 Personal exposure to indoor air pollutants is becoming more of an industrial concern with the formation of OSHA and other groups, but indoor air pollutants have become a general public concern as well. Of particular concern are domestic and non-industrial areas such as homes, public offices, theaters, etc. where many air pollutants have been found in excess of ambient levels. So, it has become imperative to have personal and indoor sampling devices to accurately measure indoor public, industrial and domestic areas for air pollutants.

4.2 Nitrogen dioxide is a reactive gas product of combustion. Household combustion sources include gas stoves, gas heating, wood burning stoves, furnaces and fireplaces. Indoors, NO_2 may result form infiltration of outdoor air containing NO_2, use of combustion appliances, and from processes involving nitric acid, nitrates, use of explosives, and welding in industrial workplace environments.

4.3 Concentrations as low as five parts per million (ppm) can cause respiratory distress; approximately 50 ppm can cause chronic lung disease and above 150 ppm is lethal.

4.4 Historically, NO_2 has been determined by colorimetric methods and chemiluminescence methods using catalytic oxidation which converts the NO_2 to NO. In turn, NO reacts with ozone and causes measurable chemiluminescence. Consequently, NO interferes with the NO_2 analysis.

5. Definitions

Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356. All abbreviations and symbols are defined with this document at the point of use.

5.1 Absorbent - material on which absorption occurs.

5.2 Spectrophotometry - a method for identifying substances by determining their concentration by measuring light transmittance in different parts of the spectrum.

5.3 Molecular diffusion - a process of spontaneous intermixing of different substances, attributable to molecular motion and tending to produce uniformity of concentration.

5.4 Colorimetry - the science of color measurement (spectrophotometry).

5.5 Transmittance - that fraction of the incident light of a given wavelength which is not reflected or absorbed, but passes through a substance.

6. Interferences

6.1 Sampling times under 15 minutes when NO_2 level is 0.5 ppm or lower.

6.2 At levels of NO_2 above 5 ppm precision of the method decreases.

6.3 Temperatures that vary from 70°F will effect the theoretical calculated value of the diffusion coefficient, thereby effecting the calculated quantity of NO_2 gas transferred from the air to the TEA substrate, as illustrated by the following equation:

$$D \propto T^{3/2}/P$$

where:
D = diffusion coefficient, cm^2/s
T = absolute temperature, °K
P = atmospheric pressure, mm Hg

The diffusion coefficient (D) changes proportionately to $T^{3/2}$, and P changes inversely proportionately to T. Overall, P then is proportional to the square root of T.
Note: Studies show that a 1% per 10°F over or below 70°F correction factor can be used for temperature changes during sampling. For most applications no adjustment is needed.

6.4 Collection efficiency of NO_2 by the diffusion tube is affected by temperature. Triethanolamine has a liquid-solid phase transition at 21°C. In laboratory tests, collection efficiency was found to decrease by 15% when the temperature decreased from 27°C to 15°C (4). If the temperature history is known for the exposure period, correction factors may be applied (4).

6.5 Collection efficiency of NO_2 by the diffusion tube is affected by humidity. Collection efficiency decreased by approximately 20% in controlled tests when humidity was decreased

from 85% to 5% (5). If the humidity history is known for the exposure period, correction factors may be applied (5).

6.6 Collection efficiency of NO_2 by the diffusion tube is affected by the air velocity at the open end of the tube. Collection efficiency increases with increasing wind velocity (1). In controlled tests, collection efficiency increased by an average of 12% when windspeed increased from 52 to 262 cm/s (1). The diffusion tube will not yield accurate results in an essentially stagnant atmosphere. Sampler starvation may occur at very low air velocities. Correction for the theoretical sampling efficiency caused by low face velocity can be applied using available equations (4,6) if the air velocity history is known for the exposure period.

6.7 Peroxyacetyl nitrate (PAN) and some nitroso compounds may be positive interferences in this method, but no applicable experimental data exist.

6.8 In very dusty environments, particles may deposit in the samplers and be resuspended in the analytical reagent, resulting in a positive bias in the spectrophotometric reading.

7. Apparatus

7.1 Palmes sampling tubes - a diffusion device used for collecting NO_2 samples. Palmes tubes and their modification are available from numerous commercial vendors.

7.2 Spectrophotometer - capable of measuring adsorbance at 540 nm.

7.3 Volumetric flasks - 100 mL for making combined reagent and standard solutions.

7.4 Pipettes - 50 mL, 5 mL for preparing NEDA reagent and standard solutions.

7.5 Graduated cylinders - 50 mL, 5 mL for preparing NEDA reagent and combined reagent.

7.6 Tared measuring dishes, best source.

8. Reagents

Note: Reagent-grade chemicals should be used in all tests. Unless otherwise indicated, all reagents should conform to the specifications of the Committee on Analytical reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.1 Sulfanilamide - reagent grade used to extract NO_2 from TEA coated filters, best source.

8.2 N-1-napthylethylene-diamine-dihydrochloride (NEDA) -reagent grade - used to extract NO_2 from the TEA coated filters, best source.

8.3 Phosphoric acid - concentrated - used in sulfanilamide reagent, best source.

8.4 Water - reagent grade - preparing standard solutions and extract, best source.

8.5 $NaNO_2$ - reagent grade used as a source of NO_2 in preparing standard solutions, best source.

9. Sampling System

9.1 System Description

9.1.1 Commercially available tubes

9.1.1.1 The diffusion tube (see Figure 1) consists of commercial acrylic tubing with outside dimensions of approximately 1.27 cm (0.5 in.) and inside dimensions of 0.95 cm (0.37 in.) cut to a length of approximately 7.1 cm (2.8 in.) to yield a cross-sectional area (A) to length (L) ratio of 0.2 cm (0.04 in.). It is permanently sealed on one end and has a removable cap on the other end. The unsealed end is exposed to the air when the cap is removed. A Palmes tube is shown in Figure 1.

9.1.1.2 Inside the tube are three stainless steel wire mesh screens coated with a substrate of triethanolamine (TEA). These are permanently affixed in the interior of the tube at the sealed end of the tube. The metal screens are approximately 1.11 cm (0.438 in.) in diameter 0.025 cm (0.010 in.) wire size, 40 x 40 mesh, 316 stainless steel (approximately 120 mg per three screens).

9.1.1.3 Commercial tubes may be wrapped in a label which serves two functions. The label is used for identification purposes, and with a clip attached serves as the holder for the sampling device.

9.1.1.4 The tube should be clipped to an individual clothing when sampling or individual exposure or appropriately placed in an area to sample indoor environments.

9.1.1.5 The sampler should be situated vertically with the open end down to avoid moisture or dust from entering the tube.

9.1.2 User prepared tubes

9.1.2.1 Acquire commercial acrylic tubing (O.D. 1.27 cm, I.D. 0.95 cm) to an area to length ratio of 0.2 cm specification from a local vendor.

9.1.2.2 Measure the inside diameter and the length of the tubes to determine if the area-to-length (A/L) are within a tolerance of + 5% of the 0.2 cm specification. If the tubes are outside these predetermined quality control limits, then the tubing should be recut or rejected.

9.1.2.3 Clean the acrylic tubes and end closures with TEA-free detergent. Rinse with tap water three or more times to remove all detergent solution. Rinse a minimum of three times with reagent water. Dry overnight at temperature below 40°C. Store in sealed plastic bags or plastic tubs.

9.1.2.4 Clean screens with detergent solution in ultrasonic bath for 10 minutes. Rinse with tap water to remove all detergent solution. Rinse once with reagent water. Immerse screens in 3 N HCl and allow to stand for 2 hours. Rinse the screens at least three times with reagent water. Then clean the screens in reagent water in an ultrasonic bath for 5 minutes. Rinse the screens with reagent water. Dry overnight at 110°C.

9.1.2.5 The triethanolamine (TEA) solution used to coat the screens is prepared by mixing TEA with acetone in a ratio of TEA:acetone of 1:7 (v/v). Keep reagent covered when not in use to minimize contact with air. A fresh solution must be prepared each day screens are coated.

9.1.2.6 Prepare an area for drying coated screens by placing several layers of paper towels on a flat surface.

9.1.2.7 Pour a portion of the TEA solution into a container that can be capped when not being used.

9.1.2.8 Using clean stainless steel or TeflonR-coated forceps, immerse screens into the solution in batches of 50 or fewer at one time. As an alternative, screens may be dipped into the solution individually. (Immersion time is not critical; screens may be dipped and removed immediately or left immersed indefinitely.)

9.1.2.9 Remove screens one at a time and place on paper towels to dry. Allow to dry no fewer than 2 nor more than 5 minutes, to minimize contamination of the screens.

9.1.2.10 Place three screens into a bottom cap; insert acrylic tube into the bottom cap; then place top (flanged) cap on the other end for final assembly.

9.1.2.11 Select approximately 5% of the tubes for analysis as production blanks. (If absorbance of any of the production blanks exceeds 0.025, additional blanks should be analyzed. If absorbance of any additional blanks exceed 0.030, the production batch should be rejected.)

9.1.2.12 Store assembled diffusion tubes in heat-sealed foil bags or in sealed plastic bags. Tubes can be stored in well-sealed containers for periods up to 6 months after preparation and before use and for 6 months after exposure and before analysis.

9.2 Sampling Procedures

9.2.1 Take the tube out of its well-sealed container and label properly the start date, time and sampling location identification.

9.2.2 Place the tube in the appropriate area to be sampled.

Note: Representative sampling must be considered, therefore, placement of a sampling tube should be determined with considerable planning.

9.2.3 Appropriate time and placement of the tube should follow the following guidelines.

9.2.3.1 Avoid sampling when seasonal alterations in insulation or building lightness are occurring or will occur during the sampling period.

9.2.3.2 Avoid sampling if remodeling or redecorating is occurring. During the sampling period there should be no changes in furnishings or appliances such as: carpeting, stoves, HVAC systems, etc.

9.2.3.3 Open and close doors in a usual manner and keep windows closed if possible.

9.2.3.4 Ventilation should not be altered in any way during sampling.

9.2.3.5 Air conditioning and heating should not be altered from normal use.

9.2.3.6 Humidifiers and dehumidifiers should not be used where sampling is being performed.

9.2.3.7 Normal occupancy and activity should continue.

9.2.3.8 The placement of the sampler should not obstruct normal occupancy or activity.

9.2.3.9 Avoid locations near sinks, tubs, showers, washers.

9.2.3.10 Avoid locations near heating elements such as: direct sunlight, furnaces, electric lights or electrically operated devices.

9.2.3.11 Avoid locations where a known draft or pressure differential occurs or areas near furnace vents, HVAC intake/exhaust, compacter cooling fans and appliance fans.

9.2.4 Placement of the sampler should ideally be at least 8 inches below the ceiling 20 inches above the floor and 6 inches from a wall.

Note: Outside walls should not be used, and suspension from the ceiling may be suitable.

9.2.5 Remove the cap from the unsealed end of the tube. Sampling commences immediately.

Note: The sampling tube should be oriented with the open end facing downward to minimize contamination by particulate matter.

9.2.6 Re-cap the tube when the sampling time is complete.

9.2.7 Record the time and date that finishes on the label, and store the tube at room temperature until analysis is performed.

10. Analysis

10.1 Reagent Preparation

Note: Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of ASTM Specification D 1193.

10.1.1 Preparation of sulfanilamide reagents (1%) - combine 10 g sulfanilamide and 25 mL concentrated (85%) H3PO4 in a 1000 mL volumetric flask. Dilute to 1000 mL with water.

10.1.2 Preparation of N-1-napthylethylene-diamine-dihydrochloride (NEDA) Reagent (0.14%) - weigh 70 mg NEDA in a beaker. Dissolve in 50 mL of deionized distilled water.

10.1.3 Combined reagent preparation - mix 50 mL of the NEDA solution and 1000 mL of the sulfanilamide solution. Check solution for pinkish color or immediately measure the reagent on the spectrophotometer at 540 nm to verify that the reagent is free of contamination. If the adsorbance is greater than 0.015 adsorption units, discard the reagent and prepare a new reagent.

Note: The reagent will be stable for 1 to 2 months if kept well-stoppered in an amber glass bottle in the refrigerator.

10.1.4 Preparation of sodium nitrite standard stock solution (1.725 g/L) - dissolve 0.1725 g of previously dried and assayed sodium nitrite ($NaNO_2$) in water and make up to 100 mL in a volumetric flask. This solution (25 mM NO_2) is used to prepare working standards.

10.1.5 Preparation of Working Standards

10.1.5.1 Pipette different volumes of $NaNO_2$ Standard Stock solution into seven 50 mL volumetric flasks.

Note: A good range of standards range from 0 to 40 nanomoles and the following additions are advised: 0.0 mL, 0.5 mL, 1.0 mL, 1.5 mL, 2.0 mL, 3.0 mL, and 4.0 mL.

10.1.5.2 Bring to the 50-mL mark with deionized distilled water.

10.2 Construction Calibration Curve

10.2.1 Add 2.0 mL of the color reagent to each of seven test tubes. Prepare calibration standards of approximately 0, 5, 10, 15, 20, 30, and 40 nanomoles of NO_2 by adding 20 uL of the appropriate working standard to the respective labeled tube for the calibration standard. Vortex briefly.

Note: Prepare calibration standards daily.

10.2.2 Allow color to develop for a period of approximately 10-15 minutes. A water bath may be used if room temperature cannot be controlled adequately during the analysis session.

10.2.3 Transfer the solution to a cuvette and read absorbance, not lapsing 20 minutes from the beginning of color development, at 540 nm after zeroing spectrophotometer with a reference cell containing reagent water.

10.2.4 Plot absorbance versus nanomoles of NO_2 per tube. The absorbance follows Beer's Law and the slope should be approximately 40+ nmol per absorbance unit.

Note: Reagent volumes may be adjusted for different curvette sizes; maintain the ratios of reagent volumes specified above. Automated methods may be used to conduct the analysis. Ratios of reagent volumes specified above should be maintained.

10.3 Sample Analysis

10.3.1 Remove the top (flanged) cap and pipet 2.0 mL of the color reagent directly into each tube to be analyzed. Re-cap and mix contents of tube well.

10.3.2 Allow 20 to 30 minutes for color development. Volume of the color reagent should be the same as that used for calibration (see Section 10.1).

10.3.3 Transfer the solution to a curvette and read absorbance at 540 nm in a spectrophotometer previously zeroed with a reference cell containing reagent water.

10.3.4 If the absorbance is greater than the 40 nmol calibration standard, dilute the sample by adding 1.0 mL of the sample to 2.0 mL of color reagent. Mix and allow 20 to 30 minutes for color development. Record the dilution factor.

10.3.5 If automated methods are used, reagent volumes for analysis should be the same as those used for calibration.

10.3.6 For each analytical session, a number of laboratory or field blanks should be analyzed as prescribed in internal procedures for quality control.

11. Calculations

11.1 In this method the volume of the calibration standards is 2.02 mL (2 mL color reagent plus 20 μL of working standard, as documented in Section 10) but the volume of the

samples is only 2.0 mL (only color reagent). Therefore, to simplify calculations, the calibration standard concentration is corrected to correspond to the 2.0 mL sample volume by multiplying by 2.0/2.02 (0.99) to yield nanomoles of NO_2 per 2.0 mL. If the standard stock solution is 25 nmol NO_2, the standard concentrations are 0, 4.95, 9.90, 14.85, 19.80, 29.70, and 39.60 nmol NO_2. Plot absorbances of the standards against standard concentrations (nmol NO_2).

11.2 Perform a least-squares linear regression analysis on the date [absorbance (y-axis) vs. nitrogen dioxide concentration (x-axis)] to derive a standard curve slope, calculated intercept, and correlation coefficient. Though absolute values are somewhat dependent upon the specific spectrophotometer used, values and standard deviations similar to intercept = 0.0158 + 0.0301 slope = 0.0230 + 0.0023, and R squared greater than 0.999 should be obtained.

11.3 Calculate the number of nanomoles of nitrogen dioxide collected for each passive monitor using the standard curve parameters and measured absorbances at 540 nm by the following equation:

$$F = (A_{540} - a)/b$$

where:
F = nanomoles of nitrogen dioxide eluted into 1.0 mL
A = absorbance of the sample at 540 nm
a = standard curve calculated intercept, AU
b = standard curve slope, AUmL/nanomole

11.4 Calculate the concentration of nitrogen dioxide in the sampled atmosphere as follows:

$$\text{ppm } NO_2 = (F - B)/(2.3 \times t)$$

where:
F = NO_2 collected, nanomoles
B = NO_2 blank, nanomoles
t = exposure time, hours
Note: The concentration of NO_2 in the monitored air is computed based on diffusion coefficient of 0.154 cm2/s (1). When sampled with a tube having a cross-sectional area (A) to length (L) ratio of exactly 0.1 cm, the following formula is used:

$$\text{ppb } NO_2 = (\text{nmol } NO_2 \times 1000)/(2.3 \times t_{hr}) = (435 \times \text{nmol } NO_2)/[(A/L) \times t_{hr}]$$

For tubes having an A/L ratio different than 0.1 cm, the following formula should be used:

$$\text{ppb } NO_2 = (\text{nmol } NO_2 \times 1000)/[2.3 \times (A/L) \times 10 \times t_{hr}] = (43.5 \times \text{nmol } NO_2)/[(A/L) \times t_{hr}]$$

11.5 To calculate the concentration of NO_2 in micrograms per cubic meter at 25°C, multiply the ppb NO_2 by the conversion factor of 1.88 μg/m3/ppb.

12. Performance Criteria and Quality Assurance

12.1 Standard Operating Procedures (SOPs)

12.1.1 Users should generate SOPs describing and documenting the following activities in their laboratory: 1) assembly, calibration, leak check, and operation of the specific sampling system and equipment used, 2) preparation, storage, shipment, and handling of samples, 3) assembly, calibration, and operation of the analytical system, addressing the specific equipment used, 4) sampler storage, and transport 5) all aspects of data recording and processing, including lists of computer hardware and software used.

12.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

12.2 Method Sensitivity, Linearity, and Reproducibility

12.2.1 Sensitivity - the sensitivity of the method has a limit of detection of 0.1 ppm (188 μg/m3) for an 8 hour sampling period and 0.005 ppm (9.4 μg/m3) for a one week sampling period.

12.2.2 Linearity - the method is linear from 0.005 ppm to 10 ppm and is dependent upon the dilution used in the analytical scheme.

12.2.3 Reproducibility (Single Analyst) - precision estimates of 1.68 μg/m3 have been reported for pairs of diffusion tubes located in outdoor, bedroom, and kitchen locations. Precision estimates of 1.0 μg/m3 for 93 replicate pairs and 1.32 μg/m3 for 81 replicate pairs have also been reported for week-long samples in residential dwellings and outdoors (9). In a laboratory study with exposure periods of 15 minutes to 8 hours (10 to 79,000 ppb.hr), the coefficient of variation for triplicate tubes ranged form 0.8% to 10% (10). In reported interlaboratory comparisons, the difference between means for two laboratories was 1.16 μg/m3 or 3.3% for one set of samples and 3.29 μg/m3 or 6.51% for a second set of samples (9).

12.3 Method Bias

12.3.1 Bias was evaluated in a laboratory study by exposing diffusion tubes to concentrations of NO_2 of 0.5 ppm, 5 ppm, or 10 ppm for periods of 15 minutes to 8 hours.

12.3.2 The determined recovery with the diffusion tubes differed from that measured with an NO_2 chemiluminescent analyzer by between -13.6% to +16.7% (10). An accuracy within 10% for preparation and analysis procedures nearly identical to those of this method has been reported (11-12).

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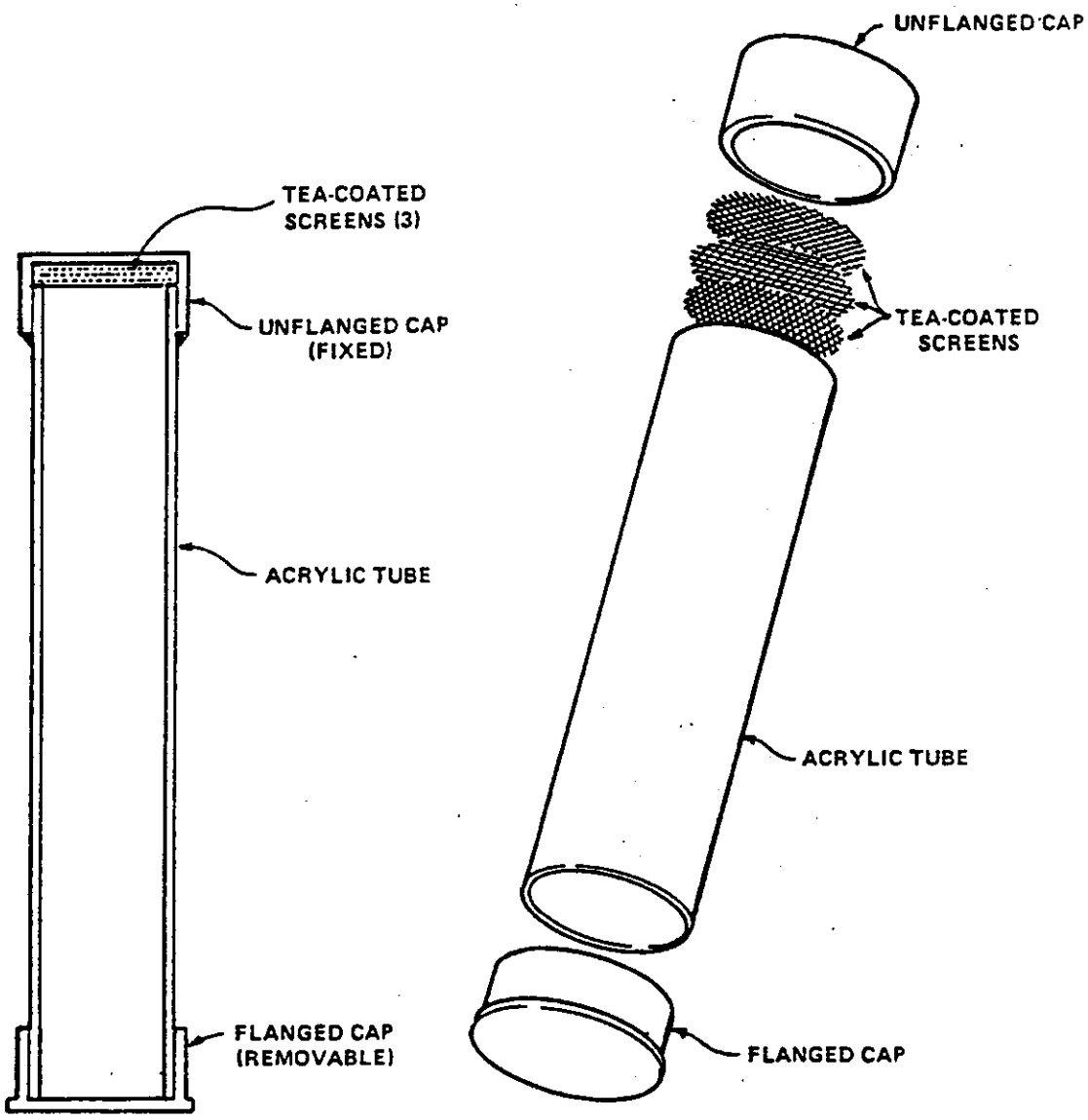

Figure 1. Assembled View (Left) and Exploded View (Right) of Palmes NO_2 Diffusion Tube Sampler

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Method IP-5C

DETERMINATION OF NITROGEN DIOXIDE (NO_2) IN INDOOR AIR USING PASSIVE SAMPLING DEVICE

Method IP-5C

DETERMINATION OF NITROGEN DIOXIDE (NO_2) IN INDOOR AIR USING PASSIVE SAMPLING DEVICE

1. Scope

1.1 In the past, active sampling devices have been the method of choice for collection of NO_2 from indoor air. More specifically, Compendium Method IP-5A uses a real-time, direct measurement monitor for characterizing NO_2 involving the detection of fluorescent energy emitted from the reaction of NO_2 with a Luminol solution (5-amino-2,3-dihydro-1,4 phthalazine dione). Active sampling systems utilizing a pump have been successfully used for occupational exposure assessment both inside and outside of the workplace (1,2).

1.2 As illustrated, real-time, direct measurement monitors are active sampling devices that require a mechanical pump to move the sample to the collection medium. Consequently, the sampling devices require some form of power to drive the pump and are usually heavy and bulky in appearance.

1.3 In recent years, interest has been increasing in the use of diffusion-based passive sampling devices (PSDs) for the collection of NO_2 in indoor air.

1.4 PSDs are more attractive for indoor air because of their characteristics of small size, quiet operation (no pump), and low unit cost.

1.5 Real-time monitors have been used more at fixed monitoring stations, thus not always reflecting the actual concentration of pollutant that people come in contact with in their daily lives.

1.6 Since the PSD is lighter and smaller than the real-time monitors, they can be worn by the person or in close proximity to where people spend most of their time, thus enabling epidemiologists to better attribute health effects of NO_2 to indoor air concentrations.

1.7 Application of the diffusion technique has been successful in monitoring NO_2 in indoor air utilizing the Palmes tube (3). Compendium Method IP-5B has standardized this sampling approach and variations of the device are commercially available. However, the Palmes tube lacks the sensitivity needed to obtain 8 to 24 hour time weighted average (TWA). With a sampling rate of ~1.0 cm^3/min, the sensitivity of the Palmes tube is 300 ppbv-hr when spectrophotometrically analyzed. Therefore, to determine a lower level of NO_2, a 5- to 7-day exposure is required.

1.8 To address the need for a 8 to 24 hour TWA PSD, the EPA funded several projects (4-8) in developing a PSD for monitoring a variety of indoor pollutants.

1.9 Initial studies centered around the application of the PSD to monitoring volatile organic compounds (VOCs) in indoor air (9-12). Both activated charcoal and Tenax® solid adsorbents were investigated as possible constituents of the PSD.

1.10 Such problems as sorbent contamination (4), atmospheric humidity (5), air velocity (6, 5, 10) and reverse sorption (6) were studied extensively in development of the VOC

PSD. A commercial version of the VOC PSD has subsequently become available (Scientific Instrumentation Specialists, Moscow, ID).

1.11 In the commercial version, a granular sorbent (activated carbon, Tenax®) was used to collect the compounds of interest from air. To address the application of monitoring NO_2 in indoor air, a modification of the VOC PSD was evaluated (13) by replacing the granular sorbent with filter paper treated with specific reagent to trap NO_2.

2. Applicable Documents

2.1 ASTM Standards

D 1356 Standard Definitions of Terms Relating to Atmospheric Sampling and Analysis
D 3609 Standard Practice for Calibration Techniques Using Permeation Tubes
D 1357 Practice for Planning the Sampling of the Ambient Atmosphere
D 1605 Recommended Practices for Sampling Atmospheres for Analysis of Gases and Vapors

2.2 Other Documents

Existing Procedures (14-16)
US EPA Technical Assistance Document (17)

3. Summary

3.1 The passive sampling method involves placing triethanolamine-coated glass fiber filters behind sets of diffusion barriers on each side of a containment cavity of a PSD and locating the PSD in the sampling area.

3.2 NO_2 in the indoor air specifically reacts with the triethanolamine-coated glass fiber filters according to Fick's First Law of Diffusion.

$$M = D(A/L)(C_\infty - C_o)$$

where:
M = mass flow, cm^3/min
D = diffusion coefficient, cm^2/min
A = cross sectional area of diffusion channel, cm^2
L = length of diffusion channel, cm
C_∞ = concentration of NO_2 in surrounding PSD
C_o = concentration of NO_2 at surface of treated filter (generally zero)

3.3 After sampling is complete, the PSD sampler is capped, returned to the laboratory, dissembled, extracted with 10 mL of distilled-deionized water and analyzed by ion chromatography.

3.4 Evaluation of the NO_2 PSD sampler utilizing an exposure chamber found it to be linear from 10.6 ppb (~20 $\mu g/m^3$) to 244.8 ppb (~460 $\mu g/m^3$) while sensing standard gas test atmospheres (14). Correlation coefficient was 0.9955 over this range. Under these

test conditions, it was found that 91 $\mu g/m^3$ of nitric oxide and a relative humidity of 57% had no deleterious effect on the efficiency of the PSD.

3.5 The use of triethanolamine-coated glass fiber filters as part of a PSD sampler coupled with ion chromatography analysis has a minimum detectable quantity (MDQ) of 30 ppb-hr for an 8 to 24 hour time weighted average.

4. Significance

4.1 The monitoring of NO_2 at sub-ppm and low-ppb levels is of primary concern in indoor, nonindustrial locations such as the home. The trends toward much more airtight homes which began during the energy crisis of the early 1970s has caused concern among health experts about increase levels of NO_2 indoors.

4.2 Nitrogen dioxide is a combustion product found in houses mostly due to gas or wood burning stoves, heaters and/or fireplaces. Hazardous concentrations can occur in closed environments such as kitchens and family rooms where ventilation is minimal.

4.3 Most health effects associated with nitrogen oxides (NO_x) have been attributed to nitrogen dioxide (NO_2). Levels of NO_2 above 282 mg/m^3 (150 ppm) can be lethal while concentrations in the range of 94-282 mg/m^3 (50-150 ppm) can produce chronic lung disease (18). The earliest response to NO_2 occurs in the sense organs. Odor can be perceived at 0.23 mg/m^3 (0.12 ppm) and reversible changes in dark adaptation at exposures of 0.14 - 0.50 mg/m^3 (0.075 - 0.26 ppm) (19). Animal studies have suggested that reduced resistance to respiratory infection is the most sensitive indicator of respiratory damage. Recent studies show a small but apparently higher incidence of respiratory symptoms and disease for children living with gas stoves (an NO_x source) versus those in homes with electric stoves. When indoor concentrations were measured, the levels were much lower than were previously thought to contribute to lung function changes or disease effect. These effects were not observed in adults living in the same or similar environments.

5. Limitations

5.1 The effects of indoor temperature and pressure fluctuations on the diffusion coefficient or sampling rate of a PSD may be estimated from the equation:

$$D \propto T^{3/2}/P$$

where:
D = diffusion coefficient, cm^2/min
T = absolute temperature, °K, and
P = atmospheric pressure, mm Hg

The theoretical temperature coefficient was found to be −0.6% per °C and the pressure coefficient −0.1% per mm Hg.

5.2 Humidity effects are less predictable, but may be pronounced for hydrophilic collectors or sorbents. During evaluation (13) of the EPA PSD, no interferences were observed at 57% and 80% relative humidity.

5.3 Sampling rates are affected by the velocity of air movement over the face of the device, particularly if there are protrusions around the channel openings or if one side of a two-sided badge is obstructed. Protrusions can contribute to the formation of secondary layers of stagnant air, which reduces the uptake rates. For chemicals that are weakly sorbed, significant equilibrium vapor pressures may exist at the face of the sorbent, which effectively reduce sampling rates according to Fick's law (i.e., $C_o > O$). Theoretical predictions suggest that the magnitude of this decrease will depend on air concentrations. Since most passive samplers have relatively large time constants and since the rates of migration into the sorbent bed are slow compared to the time constant, diffusional samplers may not respond accurately to rapidly fluctuating air concentrations. However, such fluctuations are not usually characteristic of pollutant levels in indoor air.

6. Apparatus Description

6.1 Passive Sampling Device (PSD)

6.1.1 Passive air monitors may be either permeation or diffusion controlled. In operation, a collector or sorbent material is separated from the external environment by a physical barrier that determines the sampling characteristics of the device.

6.1.2 Permeation-limited devices employ a membrane in which the test compounds are soluble. Because of this solubility requirement, it is possible to achieve some selectivity with permeation devices by choice of the membrane material.

6.1.3 With diffusion-limited devices (see Figure 1), the collector is isolated from the environment by a porous barrier containing a well defined series of channels or pores. The purpose of these channels is to provide a geometrically well-defined zone of essentially quiescent space through which mass transport is achieved solely by diffusion.

6.1.4 As a general criterion for this condition, the length/diameter ratio (L/d) of the pores should be at least three. Under such conditions, the mass flow rate to the collector is given by Fick's first law.

$$M = D(A/L)(C_\infty - C_o)$$

where:
M = mass flow, cm^3/min
D = diffusion coefficient, cm^2/min
A = cross sectional area of diffusion channel, cm^2
L = length of diffusion channel, cm
C_∞ = concentration of NO_2 in surrounding PSD
C_o = concentration of NO_2 at surface of treated filter (generally zero)

The component D(A/L) is in units of volume/time or sampling rate.

6.1.5 For most commercial diffusion-controlled devices, the effective sampling rate varies from 1 to 150 cm^3/min depending on the molecular species. Pump-based personal monitors may sample at rates up to 8,000 cm^3/min. Consequently, longer exposure times are often required for passive monitors in order to achieve equivalent sensitivities to pump-based personal monitors.

6.1.6 Figure 2 illustrates an exploded view of the current design of the EPA PSD.

6.1.7 Using the current design of the EPA PSD, the effective sampling rate of the EPA PSD was calculated from Fick's First Law of Diffusion to be 154 cm^3/min.

6.2 Analytical System

6.2.1 Ion chromatography (IC) is a technique which employs ion exchange, eluent suppression, and conductometric detection to quantify levels of strong acid anions such as sulfate, nitrate and chloride.

6.2.2 The basic components of a commercially available ion chromatographic instrument are illustrated in Figure 3. The instrument uses three (3) columns to protect, separate and detect the anions. In operation, the sample first enters the guard column which is used primarily to protect the main analytical column. The guard column filters particulate matter from the eluent and prevents poisoning by strongly present ions of the analytical column.

6.2.3 The sample stream now enters the analytical column which provides high efficiency separation of anions through competition of the anions and the eluent (0.0018 M Na_2CO_3 and 0.0017 M $NaHCO_3$) for active sites on the column. The degree of species separation and retention time depends on the relative affinities of different ions for the active sites, eluent strength and eluent flow rate.

6.2.4 After separation the eluent plus sample stream passes through a suppressor column which converts the eluent from a high conductivity form to a low conductivity form (H_2CO_3).

6.2.5 The anions of strong acids remain dissociated and are detected by means of their electrical conductivity.

6.2.6 The basic components of the IC with supporting reagents are:

- Guard Column — HPIC AG4A
- Analytical Column — HPIC AS4A
- Suppressor Column — AMMSI Anion micro membrane
- Eluent — 0.0018 M $NaCO_3$
0.0017 M NH_3CO_3
- Regenerant — 0.025 M H_2SO_4

7. Equipment

7.1 Sampling

7.1.1 Passive sampling device (PSD) - Scientific Instrumentation Specialists, P.O. Box 8941, Moscow, ID, 83843.

7.1.2 Glass fiber filters - 37 mm, Whatman GF/B Glass Microfibre, Whatman Inc., 9 Bridgewell Place, Clifton, NJ, 07014, 800-922-0361.

7.2 Analysis

7.2.1 The Dionex Model 14 or Model 4000 may be used for this procedure. The procedure addresses the use of the Model 14. The master components of this system are listed below.

7.2.1.1 Guard column - 3 x 150 mm anion column which serves to guard the separator column from reactive ions and particulate matter. Guard columns are used primarily to protect analytical columns. The guard column is normally a shorter version of the analytical column. It filters particulate matter from the eluent and the sample aliquot. In addition, strongly retained ions which could lead to "poisoning" of the analytical column are trapped within the guard column.

Note: Guard columns have a finite lifetime and when expended, the contaminants will reach the more critical analytical column. There are no general rules for estimating the effective life of a guard column since the life is very dependent upon the matrix being injected. However, they need to be cleaned or replaced on a periodic basis.

7.2.1.2 Analytical column - 3 x 250 mm anion column (HPIC AS4A) containing the resin on which the ion separation occurs. The analytical column is the heart of ion chromatography (IC). In all cases, the IC separation is due to difference in the equilibrium distribution of sample component between the mobile phase and the analytical column (stationary phase). High performance Ion Chromatography (HPIC) involves the use of low capacity pellicular ion exchange materials in a separation mode dominated by ion exchange. The ion exchange material is a resin base consisted of polystyrene.

7.2.1.3 Micromembrane suppressor column - column (AMMSI) containing a resin which converts anions to their hydrogen forms. This column has limited capacity and must be frequently refreshed with a regeneration process. The most popular mode of detection in IC is conductivity. However, the conductivity of the eluent used in IC is usually high. Therefore, a micromembrane suppressor column is used to chemically suppress (lower) the eluent prior to detection by conductivity. The suppressor column is a micromembrane fiber device that is placed downstream of the analytical column (see Figure 3). The suppressor column (anion exchange technique) changes the concentration of highly conductive eluent ions (carbonate) to species which are significantly less conductive (carbonic acid). In addition, solute ions are converted to their corresponding acids or hydroxides as they pass through the suppressor column, which are more conductive.

Note: As with the guard column, the micromembrane suppressor column can be periodically regenerated with 0.025 N H_2SO_4.

7.2.1.4 Conductivity cell - a 6 microliter volume cell in which the electrical conductivity of the eluent stream is measured.

7.2.1.5 Pumps - Milton Roy positive displacement pumps are used to pump the required liquids at pressures up to about 1000 psi. Flow rates are continuously adjustable from 0 to 400 mL/hour.

7.2.2 Valve system - a complex array of air-actuated valves controls the liquid flow through the system. Valves and columns are interconnected with Teflon® tubing (1/32 inch i.d. by 1/16 inch o.d.).

7.2.3 Integrator - a Hewlett-Packard Model 3385A Integrator or similar instrument is used to produce a strip chart recording of the chromatogram and may also be used to measure the areas under specified peaks of the chromatogram. This system also generates valve switching signals for automatic control of the ion chromatograph.

7.2.4 Pressurized air system - a continuous supply of 80 psi compressed air is required for valve actuation. Either a house air supply or compressed air cylinders with regulators may be used.

8. Reagents and Materials

8.1 Triethanolamine (TEA) - absorbing solution (1.68 M) used to coat filters used in the EPA PSD, best source.

8.2 Glove box - used to provide preparation area to assemble and disassemble PSDs, best source.

8.3 Nitrogen - used to condition glove box during filter preparation and PSD assembly/disassembly, NO_2 free, best source.

8.4 Syringes - used to apply TEA to filters, best source.

8.5 Plastic Petri dishes or watch glasses - used to contain filters during TEA application, best source.

8.6 Metal cans - used to transport PSDs, 0.5 pt and 1.0 gallon, best source

8.7 Activated charcoal - used to place in bottom of 1.0 gallon metal can to protect PSDs during transport, best source.

8.8 Gelman Acrodisc® - used to filter extracted PSD solution prior to injection into the ion chromatograph, Gelman Sciences, 600 S. Wagner Rd., Ann Arbor, MI 48106 (800-521-1520).

8.9 Sodium carbonate (0.0018 M) - used as part of the IC eluent, best source.

8.10 Ammonium bicarbonate (0.0017 M) - used as part of the IC eluent, best source.

8.11 Sulfuric acid (0.025 M) - used to regenerate IC columns, best source.

8.12 Guard column - used to protect analytical column from poisoning and particulate matter, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086, (408-737-0700), Model HPIC AG4A.

8.13 Analytical column - used to separate ions from the eluent, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086, (408-737-0700), Model HPIC AS4A.

8.14 Micromembrane suppressor column - used to chemically suppress the eluent prior to detection by conductivity.

8.15 Calcium sulfate - used in the desiccator during drying of filters, best source.

8.16 Desiccator - used to store filters prior to application of TEA, best source.

8.17 Vacuum oven - used to dry filters during preparation, best source.

8.18 35 mL screen-capped polpropylene bottle - used to extract exposed filters with deionized water.

8.19 Sonification bath - used to assist in the filter extraction process, best source.

8.20 Potassium nitrate - used to prepare calibration standards, best source.

8.21 Volumetric flasks (100, 200 and 1000 mL) - used to prepare calibration standards.

8.22 Pipettes (1, 2, 3, 4, 5, 10, 20 mL) - used to prepare calibration standards.

9. Preparation and Application of the Personal Sampling Device

9.1 Filter Preparation

9.1.1 Unpack the 37 mm filters from their shipping container. Insure that the filters are separated without tearing.

9.1.2 Observe filter construction to note any tears or holes in the material or soiling and abrasions.

9.1.3 Place the filters on a piece of cardboard. Using a wooden mallet and a 33 mm circular diameter stainless steel die, cut the number of filters needed for completion of the project objectives.

9.1.4 To prepare the filters for treatment, place five at a time in a Buchner funnel and rinse with five 100 mL volumes of charcoal-filtered deionized water.

9.1.5 Remove the filters from the funnel and place in a vacuum oven at 60°C for 1 hour.

9.1.6 After drying, remove the filters from the oven and store in a desiccator containing anhydrous calcium sulfate until cooled to room temperature.

9.2 Filter Treatment

9.2.1 Remove five clean filters from the desiccator and place on a watch glass in a glove box under a nitrogen atmosphere.

9.2.2 Using a syringe, add 0.5 mL of 1.68 M solution of TEA in acetone to the center of each filter and allow it to disperse.

9.2.3 Allow to equilibrate in the nitrogen atmosphere for ~80 minutes. This will allow the solution to diffuse completely throughout the filter.

Note: One may need to apply solution to the edges of the filter to insure complete application.

9.3 PSD Assembly

9.3.1 The PSD is a dual-faced sampler made up from a series of diffusion barriers placed on either side of a cavity, as illustrated in Figure 2. The PSD is 3.8 cm in diameter, 1.2 cm in depth and weighs 36 grams.

9.3.2 With the aid of a glove box under a nitrogen blanket, remove the treated TEA filter papers from the watch glass and place behind each set of the diffusion barriers of the PSD.

9.3.3 Reassemble the PSD, attach the protective caps and place in small (0.5 pt) can while still in the glove box. For further protection from exposure, place the small cans into a large (1 gal) can containing activated charcoal when removing from glove box for field application.

10. Placement of the PSD

10.1 Take the PSD out of its protective shipping can and complete Field Test Data Sheet (see Figure 4) with the start date, time and sampling location identification.

10.2 Place the PSD in the appropriate area to be sampled.
Note: Representative sampling must be considered, therefore, placement of a PSD should be determined with considerable planning.

10.3 Guidelines for the appropriate time and placement of passive monitors are found below and in Appendix C-3 of this Compendium.

10.3.1 Avoid sampling when seasonal alterations in insulation or building tightness are occurring or will occur during the sampling period.

10.3.2 Avoid sampling if remodeling or redecorating is occurring. During the sampling period there should be no changes in furnishings or appliances such as: carpeting, stoves, HVAC systems, etc.

10.3.3 Open and close doors in a usual manner and keep windows closed if possible.

10.3.4 Ventilation should not be altered in any way during sampling.

10.3.5 Air conditioning and heating should not be altered from normal use.

10.3.6 Humidifiers and dehumidifiers should not be used where sampling is being performed.

10.3.7 Normal occupancy and activity should continue.

10.3.8 The placement of the sampler should not obstruct normal occupancy or activity.

10.3.9 Avoid locations near sinks, tubs, showers,and washers.

10.3.10 Avoid locations near heating elements such as: direct sunlight, furnaces, electric lights or electrically operated devices.

10.3.11 Avoid locations where a known draft or pressure differential occurs or areas near furnace vents, HVAC intake/exhaust, computer cooling fans and appliance fans.

10.4 Placement of the PSD should ideally be at least 8 inches below the ceiling, 20 inches above the floor and 6 inches from a wall.
Note: Outside walls should not be used, and suspension from the ceiling may be suitable.

10.5 Remove the protective caps from the PSD. Sampling commences immediately. Place samples at predetermined location.

10.6 Complete information on the Field Test Data Sheet (see Figure 4).

10.7 Recap the PSD when the sampling time is complete.

10.8 Record the time and date that sampling finishes on the Field Test Data Sheet and store the PSD in the 0.5 pt can which will be stored in the larger can containing activated charcoal until analysis.

11. Analysis of PSD

11.1 Sample Preparation

11.1.1 After exposure, the PSDs are returned to the lab in the large cans containing activated charcoal. Remove the small returned (0.5 pt) can from the larger paint can. Log sample I.D. into laboratory notebook.

11.1.2 Under a nitrogen blanket in a glove box, remove the PSD from the smaller can and disassemble the filter cassette.

11.1.3 Place the exposed filters in a 35 mL screw-capped polypropylene bottle.

11.1.4 Add 10 mL of deionized water to the bottle, tightly cap and place in a sonification bath at room temperature for 30 minutes.

11.1.5 At the end of 30 minutes, remove the polypropylene bottle from the sonification bath. Filter the anion extract through a Gelman Acrodisc® disposable filter assembly by attaching the Acrodisc® to the IC syringe and drawing the solution through the Acrodisc® into the cavity of the syringe.

Note: The use of the Acrodisc® removes extraneous fibers from the anion solution as a result of the filter.

11.2 Preparation of Analytical Reagents

11.2.1 Nitrate Standard Solutions

11.2.1.1 Nitrate Stock Standard, 1000 mg/L - dry a few grams of ACS reagent grade crystals in an air oven at 100°C for 1 hour. Store the dried crystals in a desiccator over silica gel until use. Dissolve 1.629 gm of dry sodium nitrate in about 600 mL of distilled water. Dilute to 1 liter and mix thoroughly.

11.2.1.2 Nitrate Intermediate Standards, 100 mg/L - make a 100 mg/L standard solution by pipetting 10.0 mL of the nitrate stock standard into a 100 mL volumetric flask. Dilute to volume with distilled water and mix thoroughly. Keep refrigerated. Stable for 1 month.

11.2.1.3 Working Standards - prepare the working standard by pipetting aliquots of the nitrate intermediate standards into each 100 mL volumetric flask, according to the following table:

Std	Std (µg/mL)	Aliquot	Conc (µg/mL)	Flask Conc (µg/mL)
A	100	25.0	25.0	0.25
B	100	20.0	20.0	0.20
C	100	15.0	15.0	0.15
D	100	10.0	10.0*	0.10
E	100	5.0	5.0*	0.05
F	100	3.0	3.0*	0.03
G	100	1.5	1.5*	0.015
H	100	0.5	0.5*	0.005

*Normal Working Range

Mix thoroughly. Prepare daily and keep refrigerated.

11.2.2 Ion Chromatograph Operating Solutions

The following produces the IC eluent. Preparation of these solutions need only be accurate to several percent:

- Sodium carbonate solution - Prepare 0.0018 M sodium carbonate solution by dissolving 0.7631 g into 4 liters of deionized water. Mix thoroughly.
- Ammonium bicarbonate solution - Prepare 0.0017 M ammonium bicarbonate by dissolving 0.5712 g into 4 liters of deionized water. Mix thoroughly.
- Regenerant solution - Prepare the regenerant solution by adding 3 mL of concentrated H_2SO_4 to 4 liters of deionized water. Mix thoroughly.

11.3 Ion Chromatograph Operation

The following procedures address the Dionex Model 14 ion chromatographic system.

11.3.1 Start-up

11.3.1.1 Ascertain that there are sufficient levels of eluent, regenerate and deionized water in the IC reservoirs. Refill if necessary.

11.3.1.2 If not already on, turn on main power to IC. If the red "Ready" lamp does not glow, depress the red "Reset" button.

11.3.1.3 Flip toggle switch on front panel for pump 1 to "On". The pressure gauge should indicate 50 psi or higher. If not, the pump has probably lost prime and the following procedure should apply: Slide pump tray out; with 3/8 inch wrench, loosen the stainless steel fitting for the exit side of the eluent pump (upper fitting). Allow the pump to run until only fluid is being pumped (no escaping air bubbles). Retighten the fitting.

11.3.1.4 Flip toggle switch to Eluent 1 position.

11.3.1.5 Switch "Analyt" and "Suppress" toggle up respectively.

11.3.1.6 Allow approximately 30 minutes for system equilibration.

11.3.1.7 Check all column and valve fittings for leaks.

11.3.1.8 Turn Mode switch for the detector to "Lin" position and select the proper operating range for the detector - 3 is the usual position.

11.3.1.9 Using the offset adjustments, adjust the specific conductance to approximately 0.1 on the linear scale. This allows for some baseline drift downward during the course of analysis.

11.3.2 Analysis

Note: Samples may be injected either automatically with the autosampler or manually.

11.3.2.1 Analysis preparation - prepare working standards in a range to bracket the sample concentration expected. Include extraction blanks, quality control samples and replicate standards.

11.3.2.2 For the Model 14 Autosampler, use clean disposable 13 x 100 mm test tubes to contain the unknowns. Prepare a list which sequentially lists the unknown samples and quality control solutions which will be analyzed. A suggested "Run Sequence" is outlined below. Load the autosampler tray with the samples in sequence. Enter an identification number on the HP 3385 strip chart recording and press "Start Run". As analysis proceeds, label the chromatogram according to the sequence.

Test Tube Number	Sample Type
1	D.I. Water
2-7	Six Calibrants from High to Low
8	Extraction Blank
9	External Standard (High)
10	External Standard (Low)
11-30	20 Filter Samples
31	Internal Standard (Medium)
32-52	20 Filter Samples
53-58	Repeat Six Calibrants High to Low
59	Repeat of Extraction Blank
60	Internal Standard (Medium)
61	Internal Standard (Low)

11.3.2.3 For a manual injection draw 5 mL of the desired solution through the Acrodisc® into a 5 mL disposable pipet. Remove air bubbles from the syringe by lightly tapping with the tip pointed upward. Push the plunger in until liquid starts to run out. Attach syringe to injection port. Set Inject/Load toggle to the Load position and inject the aliquot. Enter the ID number in the Hewlett-Packard and press "Start Run". After 45 seconds, move the Inject/Load toggle back to the Load position.

11.3.3.4 Figure 5 illustrates a typical Dionex Model 14 chromatogram.

11.3.3 Shutdown

11.3.3.1 Turn "Pumps" switch to OFF.

11.3.3.2 Turn "Analyt" toggle switch. Turn Suppressor/Bypass/Rgn to Bypass/Rgn (Suppress down on Model 14) down.

11.3.3.3 Ascertain that there is a 3:1 rinse ratio programmed into the regeneration program, e.g., 30 minutes regenerate and 90 minutes rinse.

11.3.3.4 Turn detector to "Zero" position.

11.3.3.5 Push button for regeneration.

11.4 Calculation

11.4.1 Peak Height Measurement

11.4.1.1 An engineer's fully divided scale (using the 50 scale) is used for measurement of peak heights and drawing of baselines. Measured peak heights should be indicated on the strip chart recording.

11.4.1.2 Sample concentrations may be calculated on the basis of the following formula:

Sample concentration = sample peak ht. x calibration concentration/calibration peak ht.

Example: A 10.0 neq/mL sulfate standard gave a peak height of 42 units. An unknown had a peak height of 37 units. The concentration of the unknown was:

$$37 \times (10 \text{ neq/mL})/42 = 8.8 \text{ neq/mL}$$

11.4.2 Sample Analysis by Area Measurement

11.4.2.1 The Hewlett-Packard Integrator calculates the area under specified peaks.

11.4.2.2 Unknown concentrations are determined by comparing the peak area to that of a standard.

Sample concentration = sample area x calibration concentration/calibration area

12. Standard Operating Procedures (SOPs)

12.1 Users should generate SOPs describing and documenting the following activities in their laboratory: 1) assembly, calibration, leak check, and operation of the specific sampling system and equipment used, 2) preparation, storage, shipment, and handling of samples, 3) assembly, calibration, and operation of the analytical system, addressing the specific equipment used, 4) sampler storage and transport, and 5) all aspects of data recording and processing, including lists of computer hardware and software used.

12.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

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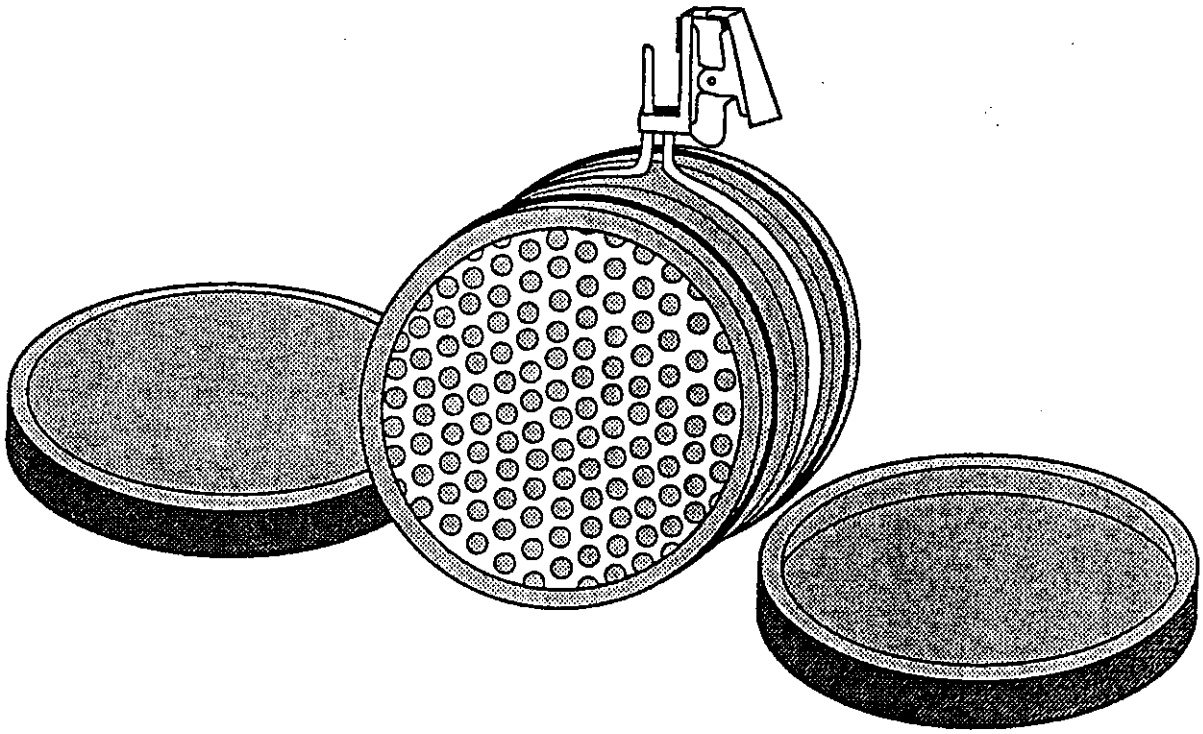

Figure 1. Commercially Available NO_2 Passive Sampling Device

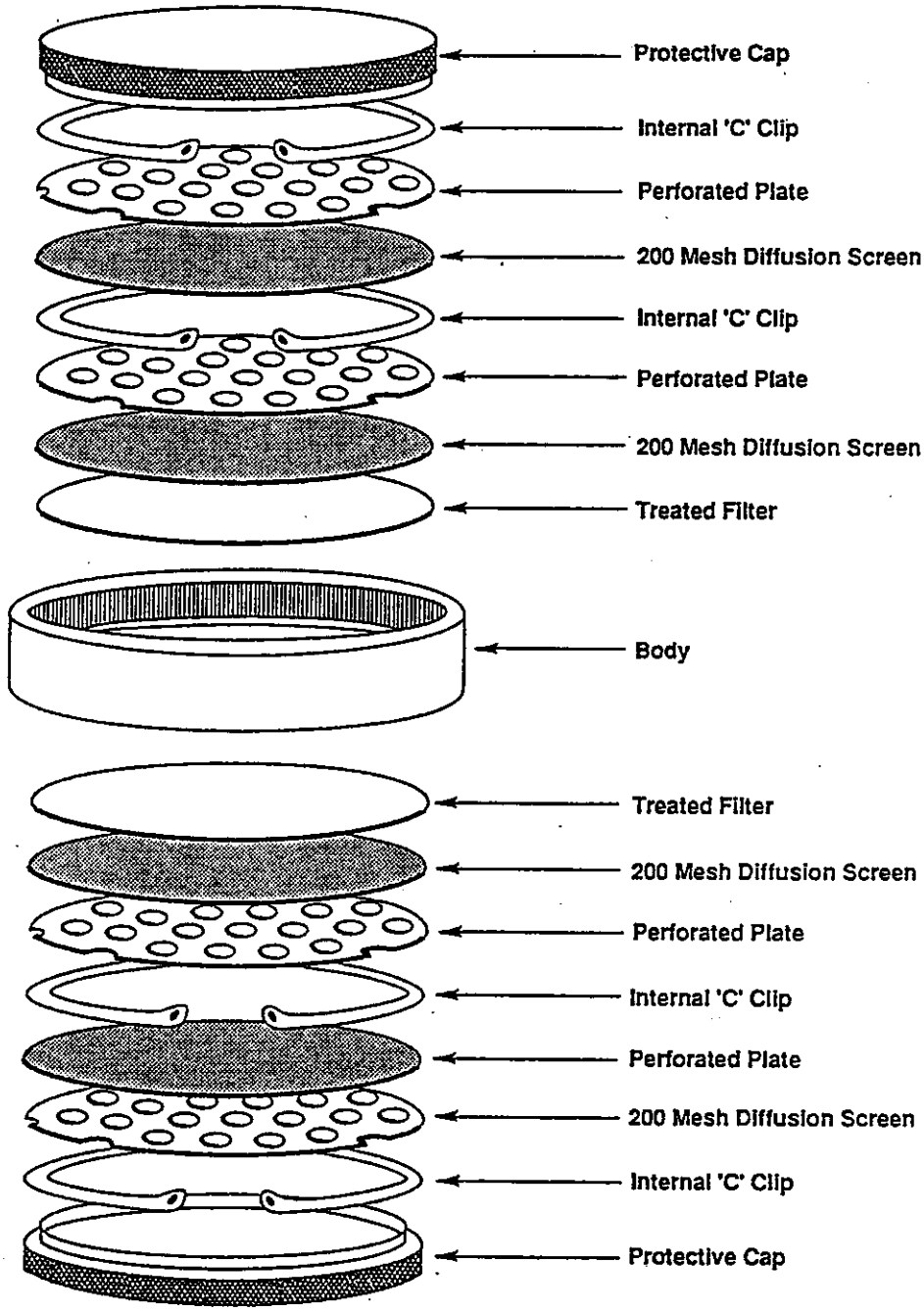

Figure 2. Exploded View of a Commercially Available Passive Sampling Device

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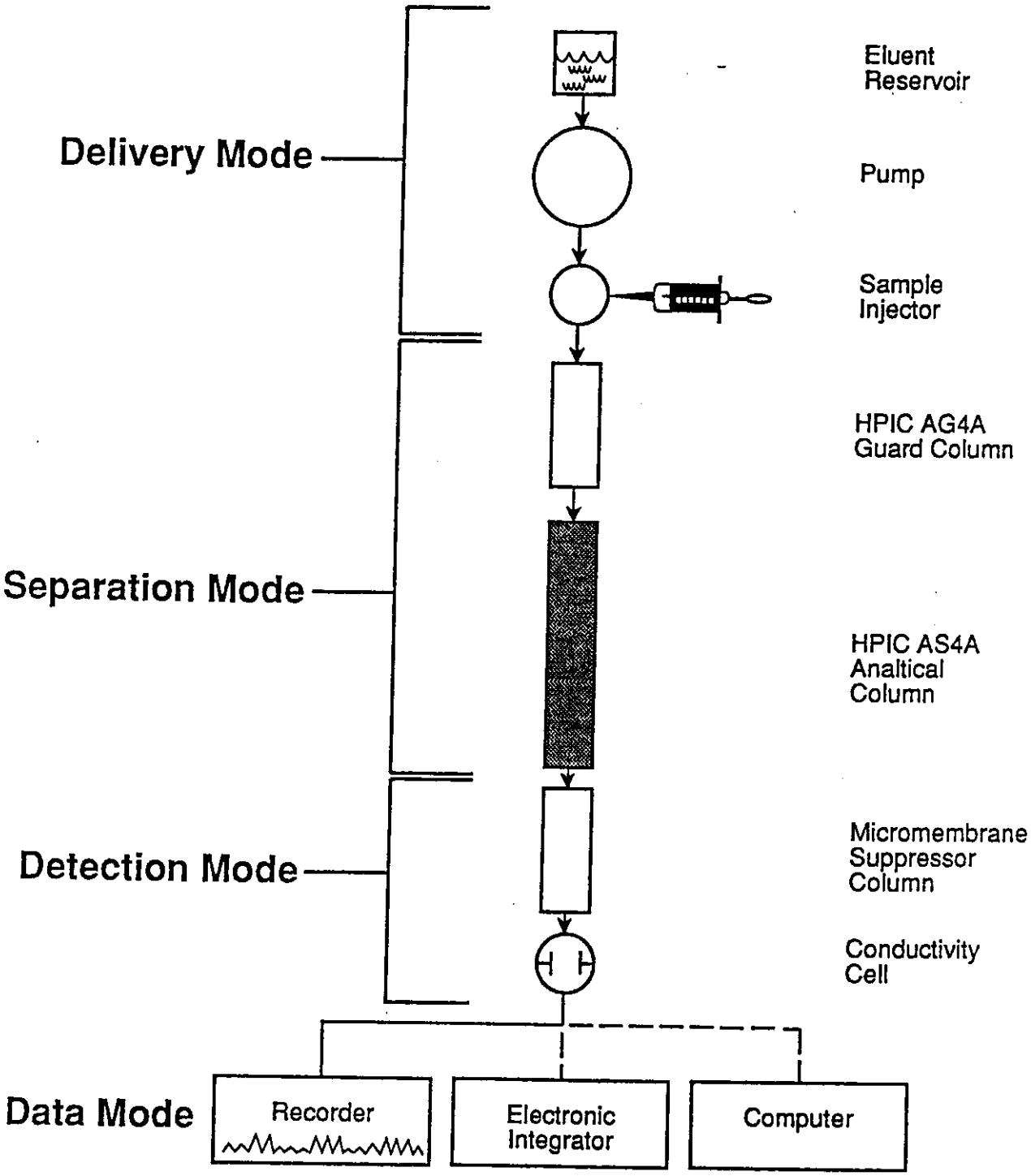

Figure 3. Major Components of a Commercially Available Ion Chromatograph

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FIELD TEST DATA SHEET
(One Sample per Data Sheet)

PROJECT: _____ DATE(S) _____

SITE: _____ TIME PERIOD SAMPLED: _____

LOCATION: _____ OPERATOR: _____

_____

_____

SAMPLER INFORMATION:

Type: _____ Serial Number: _____

Adsorbent: _____ Sample Number: _____

SAMPLING DATA:

Start Time: _____ Stop Time: _____

Start Temperature: _____ Stop Temperature: _____

Start RH(%): _____ Stop RH(%): _____

Calculated Sampling Rate: _____

SAMPLING LOCATION:

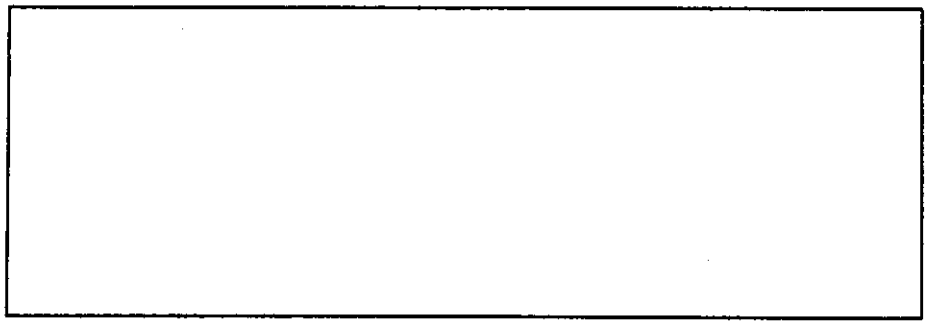

Figure 4. Field Test Data Sheet for PSD

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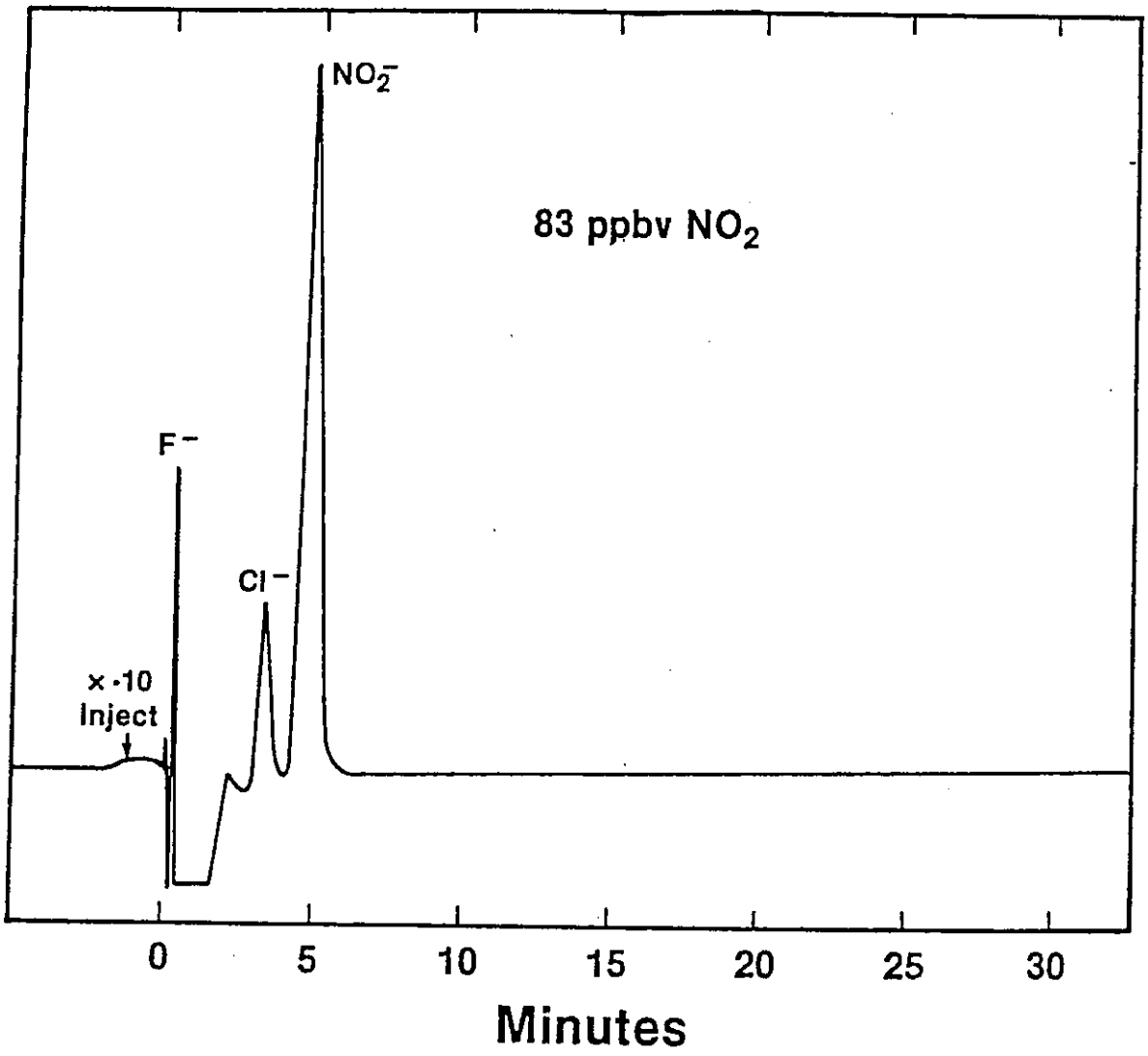

Figure 5. Typical Dionex Model 14 Chromatogram

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Chapter IP-6

DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES IN INDOOR AIR

- **Method IP-6A - Solid Adsorbent Cartridge**
- **Method IP-6B - Continuous Colorimetric Analyzer**
- **Method IP-6C - Passive Sampling Device**

1. Scope

This document describes three methods for determination of formaldehyde in indoor air. The first method (IP-6A) utilizes solid adsorbent sampling followed by high performance liquid chromatographic analysis (HPLC). The second method (IP-6B) for formaldehyde determination employs a commercially available continuous colorimetric gas analyzer. The analyzer operates on the principle of monitoring the amount of color change produced when the air sample is scrubbed with liquid reagents. Finally, the third method (IP-6C) utilizes a passive technique wherein 2,4-dinitrophenylhydrazine (DNPH) is loaded on glass fiber filters and placed behind diffusion screens of a personal sampling device (PSD). Formaldehyde and other aldehydes diffuse to the PSD sampler and react specifically with the DNPH treated filters. For analysis, the filters are extracted with acetonitrile and analyzed by HPLC.

2. Significance

2.1 Indoor air quality has become a significant environmental health issue because generally people spend most of their time indoors, as well as concerns with improved insulation and new materials issues. As with outdoor and occupational air quality, monitoring indoor air pollutant concentrations is an essential part of evaluating potential health threats and identifying abatement approaches.

2.2 Short term exposure to formaldehyde and other specific aldehydes (i.e., acetaldehyde, acrolein, crotonaldehyde) is known to cause irritation of the eyes, skin, and mucous membranes of the upper respiratory tract. Animal studies indicate that high concentrations can injure the lungs and other organs of the body. Formaldehyde may contribute to eye irritation and unpleasant odors that are common annoyances in polluted atmospheres.

2.3 Indoor sources of formaldehyde include particleboard, plywood, hardwood paneling, furniture, urea-formaldehyde foam insulation, tobacco smoke, and gas combustion. Some of the highest concentrations, exceeding 0.1 ppm, have been found in tightly constructed mobile homes where internal volumes are small compared with surface areas of formaldehyde-containing materials. Formaldehyde emissions increase with increasing temperature and humidity.

2.4 The procedures described herein provide the user with a choice of methodologies and instrumentation for sampling and analysis of formaldehyde in indoor air. All sampling systems can be set up in domestic, industrial, or office environments for monitoring indoor air atmospheres.

Method IP-6A

DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES IN INDOOR AIR USING A SOLID ADSORBENT CARTRIDGE

Method IP-6A

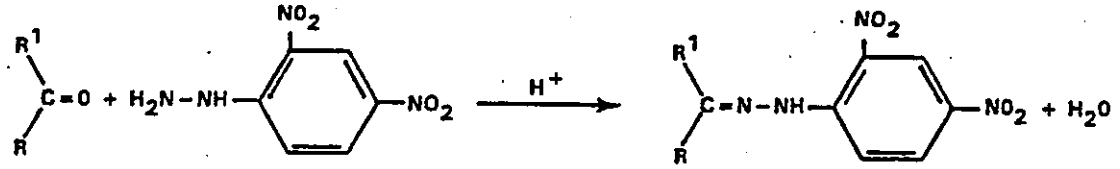
DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES IN INDOOR AIR USING A SOLID ADSORBENT CARTRIDGE

1. Scope

1.1 This method describes a procedure for determination of formaldehyde (HCHO) and other aldehydes in indoor air. The method is specific for formaldehyde, but with modification, fourteen other aldehydes can be detected.

1.2 Method TO-5, "Method For the Determination of Aldehydes and Ketones in Ambient Air Using High Performance Liquid Chromatography (HPLC)" of the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (1) involves drawing ambient air through a midget impinger sampling train containing 10 mL of 2N HCl/0.05% 2,4-dinitrophenylhydrazine (DNPH) reagent. Aldehydes and ketones readily form a stable derivative with the DNPH reagent. The DNPH derivative is analyzed for aldehydes and ketones utilizing HPLC. The solid sorbent sampling procedure in Method IP-6 modifies the sampling procedures outlined in Method TO-5 by introducing a coated adsorbent (instead of the impinger) for sampling formaldehyde in indoor air.

1.3 This current method is based on the specific reaction of carbonyl compounds (aldehydes and ketones) with DNPH-coated cartridges in the presence of an acid to form stable derivatives according to the following equation (2):



CARBONYL GROUP (ALDEHYDES AND KETONES) | 2,4-DINITROPHENYLHYDRAZINE (DNPH) | DNPH-DERIVATIVE | WATER

where R and R^1 are alkyl or aromatic groups (ketones) or either substituent is a hydrogen (aldehydes). The determination of formaldehyde from the DNPH-formaldehyde derivative is similar to Method TO5 in incorporating HPLC. The detection limits have been extended and other aldehydes and ketones can be determined as outlined in Section 14. The method can determine formaldehyde concentrations in the low ppb (v/v) or higher ppm (v/v) levels.

1.4 The sampling method gives a time-weighted average (TWA) sample. It can be used for long-term (1-24 hr) or short-term (5-60 min) sampling of indoor air for formaldehyde.

1.5 The sampling flow rate, as described in this document, is presently limited to about 1.5 L/min. This limitation is principally due to the high pressure drop (>30 inches of water at 1.0 L/min) across the DNPH-coated silica gel cartridges. Because the pumps are not adequate, the procedure is not compatible with pumps used in personal sampling equipment.

1.6 The method instructs the user to purchase Sep-PAK® chromatographic grade silica gel cartridges (Waters Associates, 34 Maple St., Milford, MA 01757) and apply acidified DNPH in situ to each cartridge as part of the user-prepared quality assurance program (2,3). Commercially precoated cartridges are also available. Thermosorb/F cartridges (Thermedics, Inc., 470 Wildwood St., P.O. Box 2999, Woburn, MA 01888-1799, or equivalent) can be purchased prepacked. The cartridges are 1.5 cm I.D. x 2 cm long polyethylene tubes with Luer® type fittings on each end. The adsorbent is composed of 60/80-mesh Florisil (magnesium silicate) coated with DNPH. The adsorbent is held in place with 100 mesh stainless steel screens at each end. The precoated cartridges are used as received and are discarded after use. The cartridges are stored in glass culture tubes with polypropylene caps and placed in cold storage when not in use. [Caution: Recent studies have indicated abnormally high formaldehyde background levels in commercially prepacked cartridges. Three cartridges randomly selected from each production lot should be analyzed for formaldehyde before use to determine if background formaldehyde levels are acceptable.]

1.7 Similarly, ORBO®-24 cartridges (Supelco, Inc., Supelco Park, Bellefonte, PA, 16923-0048) are also available. ORBO®-24 tubes (4 mm x 10 cm) were developed by the Organic Method Evaluation Branch of the Occupational Safety and Health Administration (OSHA) for collection and solvent desorption of formaldehyde and acrolein. ORBO-24 tubes contain either 150 mg or 75 mg adsorbent beds of 10% 2-(hydroxymethyl)piperidine coated and Supelpak® 20N, allowing sampling up to 24 liters of indoor air for more accurate time-weighted average values. The advantage of the ORBO®-24 cartridges is that they allow the use of a personal sampling pump, having only a 4 inches water pressure drop at a flow rate of 200 mL/min, whereas the user prepared DNPH-coated silica gel cartridges requires the use of a laboratory type Thomas pump which is able to maintain a flow of 1 L/min at a pressure drop of greater than 30 inches of water. DNPH coated silica gel cartridges with a sufficiently large gel matrix (20/40 mesh) to greatly reduce the pressure drop, allowing for the use of personal sampling pumps, have been custom ordered through Supelco. However, validation tests to determine if cartridges of this type will exhibit break through when high volumes of air are drawn and tests to determine recovery efficiencies have not been completed. In addition the background level of formaldehyde in the Supelco cartridges, which are precoated with DNPH, may be high. Because the user can certify the low level concentration of formaldehyde in the DNPH, the method instructs the user to use the Sep-PAK® cartridges over other available techniques.

1.8 This method may involve hazardous materials, operations, and equipment. This method does not purport to address all the safety problems associated with its use. It is the user's responsibility to develop and implement appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific precautions are outlined in Section 9.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definition of Terms Relating to Atmospheric Sampling and Analysis
E682 Practice for Liquid Chromatography Terms and Relationships

2.2 Other Documents

Existing Procedures (3-5)
Ambient Air Studies (6-8)
U.S. EPA Technical Assistance Document (9)
Indoor Air Studies (10-11)

3. Summary of Method

3.1 A known volume of indoor air is drawn through a prepacked silica gel cartridge coated with acidified DNPH at a sampling rate of 500-1200 mL/min for an appropriate period of time. Sampling rate and time are dependent upon carbonyl concentrations in the test atmosphere.

3.2 After sampling, the sample cartridges are capped and placed in borosilicate glass culture tubes with polypropylene caps. The capped tubes are then placed in a friction-top can containing a pouch of charcoal and returned to the laboratory for analysis. Alternatively, the sample vials can be placed in a styrofoam box with appropriate padding for shipment to the laboratory. The cartridges may either be placed in cold storage until analysis or immediately washed by gravity feed elution of 6 mL of acetonitrile from a plastic syringe reservoir to a graduated test tube or a 5-mL volumetric flask. The eluate is then topped to a known volume and refrigerated until analysis.

3.3 The DNPH-formaldehyde derivative is determined using isocratic reverse phase HPLC with an ultraviolet (UV) absorption detector operated at 360 nm.

3.4 A cartridge blank is likewise desorbed and analyzed as per Section 3.3.

3.5 Formaldehyde and other carbonyl compounds in the sample are identified and quantified by comparison of their retention times and peak heights or peak areas with those of standard solutions.

4. Significance

4.1 This method uses an active sampling system, requiring a pump to move sample air through the DNPH coated cartridge. The cartridge is coated by the user in order to avoid the high background levels often encountered in commercially prepared cartridges. The portable sampling system allows for flexible employment of this sampling technique in close proximity to people within their work and living environment. Appendix C-3 of this Compendium, Placement of Stationary Active Samplers in Indoor Environments, discusses factors regarding monitor placement.

4.2 Subsequent HPLC analysis provides a very accurate measure of indoor formaldehyde concentrations.

5. Definitions

Note: Definitions used in this document and any user-prepared SOPs should be consistent with ASTM Methods D1356 and E682. All pertinent abbreviations and symbols are defined within this document at point of use. Additional definitions, symbols, and abbreviations are provided in Appendices A-1 and B-2 of this Compendium.

6. Interferences

6.1 The solid sorbent sampling procedure is specific for sampling and analysis of formaldehyde. Interferences in the method are certain isomeric aldehydes or ketones that may be unresolved by the HPLC system when analyzing for other aldehydes and ketones. Organic compounds that have the same retention time and significant adsorbance at 360 nm as the DNPH derivative of formaldehyde will interfere. Such interferences can often be overcome by altering the separation conditions (e.g., using alternative HPLC columns or mobile phase compositions). Other aldehydes and ketones can be detected with a modification of the basic procedure. In particular, chromatographic conditions can be optimized to separate acrolein, acetone, and propionaldehyde and the following higher molecular weight aldehydes and ketones (within an analysis time of about one hour) by utilizing two Zorbax ODS columns in series under a linear gradient program.

formaldehyde	crotonaldehyde	o-tolualdehyde
acetaldehyde	butyraldehyde	m-tolualdehyde
acrolein	benzaldehyde	p-tolualdehyde
acetone	isovaleraldehyde	hexanaldehyde
propionaldehyde	valeraldehyde	2,5-dimethylbenzaldehyde

The linear gradient program varies the mobile phase composition periodically to achieve maximum resolution of the C-3, C-4, and benzaldehyde region of the chromatogram. The following gradient program was found to be adequate to achieve this goal: upon sample injection, linear gradient from 60-75% acetonitrile/40-25% water in 30 minutes, linear gradient from 75-100% acetonitrile/25-0% water in 20 minutes, hold at 100% acetonitrile for 5 minutes, reverse gradient to 60% acetonitrile/40% water in 1 minute, and maintain isocratic at 60% acetonitrile/40% water for 15 minutes.

6.2 Formaldehyde contamination of the DNPH reagent is a frequently encountered problem. The DNPH must be purified by multiple recrystallizations in UV grade acetonitrile. Recrystallization is accomplished at 40-60°C by slow evaporation of the solvent to maximize crystal size. The purified DNPH crystals are stored under UV grade acetonitrile until use. Impurity levels of carbonyl compounds in the DNPH are determined by HPLC prior to use and should be less than 0.025 μg/mL.

6.3 Ozone has been shown to interfere negatively by reacting with both DNPH and its hydrazone derivatives in the cartridge (15). Ozone emission factors can be in the 0-546 μg/min range for electrostatic air cleaners installed in central air conditioning units and the 2-158 μg/copy range (at a typical copy rate of 5/min) for photocopying machines (16,17). The presence of high indoor ozone concentrations may be very site specific. The user must determine whether ozone interference will be significant to the sample location. The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds during samping. The presence of ozone in the sample stream is readily inferred from the appearance of new compounds with retention times shorter than that of the hydrazone of formaldehyde. Figure 1 shows chromatographs of cartridge samples of a formaldehyde spiked air stream with and without ozone (15). Ozone interference can be removed by selectively scrubbing the ozone from the sample stream before it reaches the cartridge. A simple denuder (scrubber) device has been developed and tested to accomplish this. The denuder is made by coiling a copper tubing (3 ft x 1/4 in O.D. x 4.6 mm I.D.) and coating the inside surface with potassium iodide (KI). The copper-KI ozone denuder is connected to the sampling cartridge by a short piece of silicone or Tygon tubing. For in-depth information regarding this method of removal of ozone interference, see Section 15, reference 15.

7. Apparatus

7.1 Sampling system - capable of accurately and precisely sampling 100-1500 mL/min of indoor air (see Figures 2, 3 and 4). The dry test meter in Figure 3(b) may not be accurate at flows below 500 mL/min, and should then be replaced by recorded flow readings at the start, finish, and hourly intervals during the collection. The sample pump consists of a diaphragm or metal bellows pump capable of extracting an air sample between 500-1200 mL/min.

Note: A normal pressure drop through the sample cartridge approaches 14 cm Hg at a sampling rate of 1.5 L/min.

7.2 Isocratic HPLC system - consisting of a mobile phase reservoir; a high pressure pump; an injection valve (automatic sampler with an optional 25-μL loop injector); a Zorbax ODS (DuPont Instruments, Wilmington, DE), or equivalent C-18, reverse phase (RP) column, or equivalent (25 cm x 4.6 mm ID); a variable wavelength UV detector operating at 360 nm; and a data system or strip chart recorder (see Figure 5).

7.3 Stopwatch.

7.4 Friction-top metal can (e.g., 1-gallon paint can) or a styrofoam box with polyethlyene air bubble padding - to hold sample vials.

7.5 Thermometer - to record indoor temperature.

7.6 Barometer (optional).

7.7 Suction filtration apparatus - for filtering HPLC mobile phase.

7.8 Volumetric flasks - various sizes, 5-2000 mL.

7.9 Pipets - various sizes, 1-50 mL.

7.10 Helium purge line (optional) - for degassing HPLC mobile phase.

7.11 Erlenmeyer flask - 1 L, for preparing HPLC mobile phase.

7.12 Graduated cylinder - 1 L, for preparing HPLC mobile phase.

7.13 Syringes - 100-250 μL, for HPLC injection.

7.14 Sample vials.

7.15 Melting point apparatus.

7.16 Rotameters.

7.17 Calibrated syringes.

7.18 Mass flowmeters and mass flow controllers - for metering/setting air flow rate of 500-1200 mL/min through sample cartridge.
Note: The mass flow controllers are necessary because cartridges have a high pressure drop and at maximum flow rates, the cartridge behaves like a "critical orifice." Recent studies have shown that critical flow orifices may be used for 24-hour sampling periods at a maximum rate of 1 L/min for atmospheres not heavily loaded with particulates without any problems. Flow drop of less than 5% of the initial flow was generally observed for a 24-hour sampling episode.

7.19 Positive displacement, repetitive dispensing pipets (Lab-Industries, or equivalent) - 0-10 mL range.

7.20 Cartridge drying manifold with multiple standard male Luer® connectors.

7.21 Liquid syringes (polypropylene syringes are adequate) - 10 mL, used to prepare DNPH-coated cartridges.

7.22 Syringe rack - made of an aluminum plate (0.16 x 36 x 53 cm) with adjustable legs on four corners. A matrix (5 x 9) of circular holes of diameter slightly larger than the diameter of the 10-mL syringes was symmetrically drilled from the center of the plate to enable batch processing of 45 cartridges for cleaning, coating, and/or sample elution (see Figure 6).

7.23 Luer® fittings/plugs - to connect cartridges to sampling system and to cap prepared cartridges.

7.24 Hot plates, beakers, flasks, measuring and disposable pipets, volumetric flasks, etc. used in the purification of DNPH.

7.25 Borosilicate glass culture tubes (20 mm x 125 mm) with polypropylene screw caps - used to transport Sep-PAK® coated cartridges (Fisher Scientific, Pittsburgh, PA, or equivalent).

7.26 Heated probe - necessary when temperature of sampled air is below 60°F, to insure effective collection of formaldehyde as a hydrazone.

7.27 Cartridge sampler - prepacked silica gel cartridge, Sep-PAK® (Waters Associates, Milford, MA 01757, or equivalent) coated in situ with DNPH according to Section 9.

7.28 Polyethylene gloves - used to handle Sep-PAK® silica gel cartridges, best source.

8. Reagents and Materials

8.1 2,4-Dinitrophenylhydrazine (DNPH) - Aldrich Chemical or J.T. Baker, reagent grade or equivalent. Recrystallize at least twice with UV grade acetonitrile before use.

8.2 Acetonitrile - UV grade, Burdick and Jackson "distilled-in-glass," or equivalent.

8.3 Deionized-distilled water - charcoal filtered.

8.4 Perchloric acid - analytical grade, best source.

8.5 Hydrochloric acid - analytical grade, best source.

8.6 Formaldehyde - analytical grade, best source.

8.7 Aldehydes and ketones - analytical grade, best source, used for preparation of DNPH derivative standards (optional).

8.8 Ethanol or methanol - analytical grade, best source.

8.9 Sep-PAK® silia gel cartridges - Waters Associates, 34 Maple St., Milford, MA 01757, or equivalent.

8.10 Nitrogen - high purity grade, best source.

8.11 Charcoal - granular, best source.

8.12 Helium - high purity grade, best source.

8.13 ORBO®-24 cartridges -Supelco, Inc., Supelco Park, Bellefonte, PA, 16823-0048 (optional).

9. Preparation of Reagents and Cartridges

9.1 Purification of 2,4-Dinitrophenylhydrazine (DNPH)

Note: This procedure should be performed under a properly ventilated hood.

9.1.1 Prepare a supersaturated solution of DNPH by boiling excess DNPH in 200 mL of acetonitrile for approximately one hour.

9.1.2 After one hour, remove and transfer the supernatant to a covered beaker on a hot plate and allow gradual cooling to 40-60°C.

9.1.3 Maintain the solution at this temperature (40°C) until 95% of solvent has evaporated.

9.1.4 Decant solution to waste, and rinse crystals twice with three times their apparent volume of acetonitrile.

Note: Various health effects result from the inhalation of acetonitrile. At 500 ppm in air, brief inhalation has produced nose and throat irritation. At 160 ppm, inhalation for 4 hours has caused flushing of the face (2 hour delay after exposure) and bronchial tightness (5 hour delay). Heavier exposures have produced systemic effects with symptoms ranging from headache, nausea, and lassitude to vomiting, chest or abdominal pain, respiratory depression, extreme weakness, stupor, convulsions and death (dependent upon concentration and time).

9.1.5 Transfer crystals to another clean beaker, add 200 mL of acetonitrile, heat to boiling, and again let crystals grow slowly at 40-60°C until 95% of the solvent has evaporated.

9.1.6 Repeat rinsing process as described in Section 9.1.4.

9.1.7 Take an aliquot of the second rinse, dilute 10 times with acetonitrile, acidify with 1 mL of 3.8 M perchloric acid per 100 mL of DNPH solution, and analyze by HPLC.

9.1.8 The chromatogram illustrated in Figure 7 represents an acceptable impurity level of <0.025 μg/mL of formaldehyde in recrystallized DNPH reagent. An acceptable impurity level for an intended sampling application may be defined as the mass of the analyte (e.g., DNPH-formaldehyde derivative) in a unit volume of the reagent solution equivalent to less than one tenth (0.1) the mass of the corresponding analyte from a volume of an air sample when the carbonyl (e.g., formaldehyde) is collected as DNPH derivative in an equal unit volume of the reagent solution. An impurity level unacceptable for a typical 10-L sample volume may be acceptable if sample volume is increased to 100 L. The impurity level of DNPH should be below the sensitivity (ppb, v/v) level indicated in Table 1 for the anticipated sample volume. If the impurity level is not acceptable for intended sampling application, repeat recrystallization.

9.1.9 Transfer the purified crystals to an all-glass reagent bottle, add 200 mL of acetonitrile, stopper, shake gently, and let stand overnight. Analyze supernatant by HPLC according to Section 11. The impurity level should be comparable to that shown in Figure 7.

9.1.10 If the impurity level is not satisfactory, pipet off the solution to waste, then add 25 mL of acetonitrile to the purified crystals. Rinsing should be repeated with 20 mL portions of acetonitrile until a satisfactorily low impurity level in the supernatant is

confirmed by HPLC analysis. An impurity level of <0.025 μg/mL formaldehyde should be achieved, as illustrated in Figure 7.

9.1.11 If the impurity level is satisfactory, add another 25 mL of acetonitrile, stopper and shake the reagent bottle, then set aside. The saturated solution above the purified crystals is the stock DNPH reagent.

9.1.12 Maintain only a minimum volume of saturated solution adequate for day to day operation. This will minimize waste of purified reagent should it ever become necessary to rerinse the crystals to decrease the level of impurity for applications requiring more stringent purity specifications.

9.1.13 Use clean pipets when removing saturated DNPH stock solution for any analytical applications. Do not pour the stock solution from the reagent bottle.

9.2 Preparation of DNPH-Formaldehyde Derivative

9.2.1 Titrate a saturated solution of DNPH in 2N HCl with formaldehyde (other aldehydes or ketones may be used if their detection is desired).

9.2.2 Filter the colored precipitate, wash with 2N HCl and water, and allow precipitate to air dry.

9.2.3 Check the purity of the DNPH-formaldehyde derivative by melting point determination or HPLC analysis. If the impurity level is not acceptable, recrystallize the derivative in ethanol. Repeat purity check and recrystallization as necessary until acceptable level of purity (e.g., 99%) is achieved.

9.3 Preparation of DNPH-Formaldehyde Standards

9.3.1 Prepare a standard stock solution of the DNPH-formaldehyde derivative by dissolving accurately weighed amounts in acetonitrile.

9.3.2 Prepare a working calibration standard mix from the standard stock solution. The concentration of the DNPH-formaldehyde compound in the standard mix solutions should be adjusted to reflect relative distribution in a real sample.

Note: Individual stock solutions of approximately 100 mg/L are prepared by dissolving 10 mg of the solid derivative in 100 mL of acetonitrile. The individual solution is used to prepare calibration standards containing the derivative of interest at concentrations of 0.5-20 μg/L, which spans the concentration of interest for most indoor air work.

9.3.3 Store all standard solutions in a refrigerator. They should be stable for several months.

9.4 Preparation of DNPH-Coated Sep-PAK® Cartridges

Note: This procedure must be performed in an atmosphere with a very low aldehyde background. All glassware and plasticware must be scrupulously cleaned and rinsed with deionized water and aldehyde free acetonitrile. Contact of reagents with laboratory air must be minimized. Polyethylene gloves must be worn when handling the cartridges.

9.4.1 DNPH Coating Solution

9.4.1.1 Pipet 30 mL of saturated DNPH stock solution to a 1000 mL volumetric flask, then add 500 mL acetonitrile.

9.4.1.2 Acidify with 1.0 mL of concentrated HCl.

Note: The atmosphere above the acidified solution should preferably be filtered through a DNPH-coated silica gel cartridge to minimize contamination from laboratory air. Shake solution, then make up to volume with acetonitrile. Stopper the flask, invert and shake several times until the solution is homogeneous. Transfer the acidified solution to a reagent bottle equipped with a 0-10 mL range positive displacement dispenser.

9.4.1.3 Prime the dispenser and slowly dispense 10-20 mL to waste.

9.4.1.4 Dispense an aliquot solution to a sample vial, and check the impurity level of the acidified solution by HPLC according to Section 9.1.

9.4.1.5 The impurity level should be <0.025 μg/mL formaldehyde, similar to that in the DNPH stock solution.

9.4.2 Coating of Sep-PAK® Cartridges

9.4.2.1 Open the Sep-PAK® package, connect the short end to a 10-mL syringe, and place it in the syringe rack. The syringe rack for coating and drying the sample cartridges is illustrated in Figures 6(a) and 6(b).

9.4.2.2 Using a positive displacement repetitive pipet, add 10 mL of acetonitrile to each of the syringes.

9.4.2.3 Let liquid drain to waste by gravity.

Note: Remove any air bubbles that may be trapped between the syringe and the silica cartridge by displacing them with the acetonitrile in the syringe.

9.4.2.4 Set the repetitive dispenser containing the acidified DNPH coating solution to dispense 7 mL into the cartridges.

9.4.2.5 Once the effluent flow at the outlet of the cartridge has stopped, dispense 7 mL of the coating reagent into each of the syringes.

9.4.2.6 Let the coating reagent drain by gravity through the cartridge until flow at the other end of the cartridge stops.

9.4.2.7 Wipe the excess liquid at the outlet of each of the cartridges with clean tissue paper.

9.4.2.8 Assemble a drying manifold with a scrubber or "guard cartridge" connected to each of the exit ports. These "guard cartridges" are DNPH-coated and serve to remove any trace of formaldehyde in the nitrogen gas supply. This process is illustrated in Figure 6(b).

9.4.2.9 Remove the cartridges from the syringes and connect the short ends to the exit end of the scrubber cartridge.

9.4.2.10 Pass nitrogen through each of the cartridges at about 300-400 mL/min for 5-10 minutes.

9.4.2.11 Within 10 minutes of the drying process, rinse the exterior surfaces and outlet ends of the cartridges with acetonitrile using a Pasteur pipet.

9.4.2.12 Stop the flow of nitrogen after 15 minutes and insert cartridge connectors (flared at both ends, 0.25 O.D. x 1 in Teflon® FEP tubing with I.D. slightly smaller than the O.D. of the cartridge port) to the long end of the scrubber cartridges.

9.4.2.13 Connect the short ends of a batch of the coated cartridges to the scrubbers and pass nitrogen through at about 300-400 mL/min.

9.4.2.14 Follow procedure in Section 9.4.2.11.

9.4.2.15 After 15 minutes, stop the flow of nitrogen, remove the dried cartridges and wipe the cartridge exterior free of rinse acetonitrile.

9.4.2.16 Plug both ends of the coated cartridge with standard polypropylene Luer® male plugs and place the plugged cartridge in a borosilicate glass culture tube with polypropylene screw caps.

9.4.2.17 Put a serial number and a lot number label on each of the individual cartridge glass storage containers and refrigerate the prepared lot until use.

9.4.2.18 Store cartridges in an all-glass stoppered reagent bottle in a refrigerator until use.

Note: Plugged cartridges could also be placed in screw-capped glass culture tubes and placed in a refrigerator until use. Cartridges will maintain their integrity for up to 90 days stored in refrigerated, capped culture tubes, and can remain in refrigerated storage for much longer provided the background level is acceptable.

9.4.2.19 Before transport, remove the glass-stoppered reagent bottles (or screw-capped glass culture tubes) containing the adsorbent tubes from the refrigerator and place the tubes individually in labeled glass culture tubes. Place culture tubes in a friction-top metal can containing 1-2 inches of charcoal for shipment to sampling location.

9.4.2.20 As an alternative to friction-top cans for transporting sample cartridges, the coated cartridges could be shipped in their individual glass containers. A big batch of coated cartridges in individual glass containers may be packed in a styrofoam box for shipment to the sampling location. The box should be padded with clean tissue paper or polyethylene air bubble padding. Do not use polyurethane foam or newspaper as padding material.

9.4.2.21 The cartridges should be immediately stored in a refrigerator upon arrival to the sampling site.

10. Sample Collection

10.1 The sampling system is assembled and should be similar to that shown in Figures 2, 3 or 4.

Note: Figure 3a illustrates a three tube/one pump configuration. The tester should ensure that the pump is capable of constant flow rate throughout the sampling period. The coated cartridges can be used as direct probes and traps for sampling indoor air when the temperature is above freezing.

Note: For sampling indoor air below freezing, a short length (30-60 cm) of heated (50-60°C) stainless steel tubing must be added to condition the air sample before collection on adsorbent tubes. Two types of sampling systems are shown in Figure 2. For purposes of discussion, the following procedure assumes use of a dry test meter.

Note: The dry test meter may not be accurate at flows below 500 mL/min and should be backed up by recorded flow readings at the start, finish, and hourly intervals during sample collection.

10.2 Before sample collection, the system is checked for leaks. Plug the input end of the cartridge so no flow is indicated at the output end of the pump. The mass flowmeter should not indicate any air flow through the sampling apparatus.

10.3 The entire assembly (including a dummy cartridge not to be used for sampling) is installed and the flow rate checked at a value near the desired rate. In general, flow rates of 500-1200 mL/min should be employed. The total moles of carbonyl in the volume of air sampled should not exceed that of the DNPH concentration (2 mg/cartridge). In general, a safe estimate of the sample size should be approximately 75% of the DNPH loading of the cartridge (~200 μg as CH_2O). Generally, calibration is accomplished using a soap bubble flowmeter or calibrated wet test meter connected to the flow exit, assuming the system is sealed.
Note: ASTM Method 3686 describes an appropriate calibration scheme that does not require a sealed flow system downstream of the pump.

10.4 Ideally, a dry gas meter is included in the system to record total flow. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling period exceeds two hours, the flow rate should be measured at intermediate points during the sampling period. A rotameter is included to allow observation of the flow rate without interruption of the sampling process.

10.5 Before sampling, remove the glass culture tube from the friction-top metal can or styrofoam box. Let the cartridge warm to room temperature in the glass tube before connecting it to the sample train.

10.6 Using polyethylene gloves, remove the coated cartridge from the glass tube and connect it to the sampling system with a Luer® adapter fitting. Seal the glass tube for later use, and connect the cartridge to the sampling train so that the short end becomes the sample inlet. Record the following parameters on the sampling data sheet (Figure 8): date, sampling location, time, room temperature, barometric pressure (if available), relative humidity (if available), flow rate, rotameter setting, and cartridge batch number.

10.7 The sampler is turned on and the flow is adjusted to the desired rate. A typical flow rate through one cartridge is 1.0 L/min and 0.8 L/min for two cartridges in tandem.

10.8 The sampler is operated for the desired period, with periodic recording of the variables listed above.

10.9 At the end of the sampling period, the parameters listed in Section 10.6 are recorded and the sample flow is stopped. If a dry gas meter is not used, the flow rate must be checked at the end of the sampling interval. If the flow rates at the beginning and end of the sampling period differ by more than 15%, the sample should be marked as suspect.

10.10 Immediately after sampling, remove the cartridge (using polyethylene gloves) from the sampling system, cap with Luer® end plugs, and place it back in the original labeled glass culture tube. Cap the culture tube, seal it with Teflon® tape, and place it in a friction-top can containing 1-2 inches of granular charcoal or styrofoam box with appropriate padding. Refrigerate the culture tubes until analysis. Refrigeration period of exposed cartridges prior to analysis should not exceed 90 days.
Note: If samples are to be shipped to a central laboratory for analysis, the duration of the non-refrigerated period should be kept to a minimum, preferably less than two days.

10.11 If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate must be calculated according to the following equation:

$$Q_A = (Q_1 + Q_2 + \ldots + Q_N)/N$$

where:
Q_A = average flow rate, mL/min
$Q_1, Q_2, \ldots Q_N$ = flow rates determined at beginning, end and intermediate points during sampling
N = number of points averaged

10.12 The total flow is then calculated using the following equation:

$$V_m = [(T_2 - T_1) \times Q_A]/1000$$

where:
V_m = total volume sampled at measured temperature and pressure, L
T_2 = stop time, min
T_1 = start time, min
$T_2 - T_1$ = total sampling time, min
Q_A = average flow rate, mL/min

10.13 The total volume (V_s) at standard conditions, 25°C and 760 mm Hg, is calculated from the following equation:

$$V_s = V_m \times (P_A/760) \times [298/(273 + t_A)]$$

where:
V_s = total sample volume at 25°C and 760 mm Hg pressure, L
V_m = total sample volume at measured temperature and pressure, L
P_A = average indoor pressure, mm Hg
t_A = average indoor temperature, °C

11. Sample Analysis

11.1 Sample Preparation

The samples are returned to the laboratory in a friction-top can containing 1-2 inches of granular charcoal and stored in a refrigerator until analysis. Alternatively, the samples may

also be stored alone in their individual glass containers. The time between sampling and analysis should not exceed 30 days.

11.2 Sample Desorption

11.2.1 Remove the sample cartridge from the labeled culture tube. Connect the sample cartridge (outlet end during sampling) to a clean syringe.
Note: The liquid flow during desorption should be in the reverse direction of air flow during sample collection.

11.2.2 Place the cartridge/syringe in the syringe rack.

11.2.3 Backflush the cartridge (gravity feed) by passing 6 mL of acetonitrile from the syringe through the cartridge to a graduated test tube or to a 5-mL volumetric flask.
Note: A dry cartridge has an acetonitrile holdup volume slightly greater than 1 mL. The eluate flow may stop before the acetonitrile in the syringe is completely drained into the cartridge because of air trapped between the cartridge filter and the syringe Luer® tip. If this happens, displace the trapped air with the acetonitrile in the syringe using a long-tip disposable Pasteur pipet.

11.2.4 Dilute to the 5-mL mark with acetonitrile. Label the flask with sample identification. Pipet two aliquots into sample vials with Teflon®-lined septa. Analyze the first aliquot for the derivative carbonyls by HPLC. Store the second aliquot in the refrigerator until the results of the analysis of the first aliquot are complete and validated. The second aliquot should be used for confirmatory analysis, if necessary.

11.3 HPLC Analysis

11.3.1 The HPLC system is assembled and calibrated as described in Section 11.4 and as illustrated in Figure 5. Before each analysis, the detector baseline is checked to ensure stable conditions. The operating parameters are as follows:

Column - Zorbax ODS (4.6 mm inner diameter x 25 cm, or equivalent)
Mobile Phase - 60% acetonitrile/40% water, isocratic
Detector - ultraviolet, operating at 360 nm
Flow Rate - 1.0 mL/min
Retention Time - 7 minutes for formaldehyde with one Zorbax ODS column.
13 minutes for formaldehyde with two Zorbax ODS columns.
Sample Injection Volume - 25 µL.

11.3.2 The HPLC mobile phase is prepared by mixing 600 mL of acetonitrile and 400 mL of water. This mixture is filtered through a 0.22-um polyester membrane filter in an all-glass and Teflon® suction filtration apparatus. The filtered mobile phase is degassed by purging with helium for 10-15 minutes (100 mL/min) or by heating to 60°C for 5-10 minutes in an Erlenmeyer flask covered with a watch glass. A constant back pressure restrictor (350 kPa) or short length (15-30 cm) of 0.25 mm (0.01 inch) inner diameter Teflon® tubing should be placed after the detector to eliminate further mobile phase outgassing.

11.3.3 The mobile phase is placed in the HPLC solvent reservoir and the pump is set at a flow rate of 1.0 mL/min and allowed to pump for 20-30 minutes before the first analy-

sis. The detector is switched on at least 30 minutes before the first analysis, and the detector output is displayed on a strip chart recorder or similar output device.

11.3.4 A 100 µL aliquot of the sample is drawn into a clean HPLC injection syringe. The sample injection loop (25 µL) is loaded and an injection is made. The data system, if available, is activated simultaneously with the injection, and the point of injection is marked on the strip chart recorder.

11.3.5 After approximately one minute, the injection valve is returned to the "inject" position and the syringe and valve are rinsed or flushed with acetonitrile/water mixture in preparation for the next sample analysis.

Note: The flush/rinse solvent should not pass through the sample loop during flushing. The loop is clean while the valve is in the "inject" mode.

11.3.6 After elution of the DNPH-formaldehyde derivative (see Figure 9), data acquisition is terminated and the component concentrations are calculated as described in Section 12.

11.3.7 After a stable baseline is achieved, the system can be used for further sample analyses as described above.

Note: After several cartridge analyses, buildup on the column may be removed by flushing with several column volumes of 100% acetonitrile.

11.3.8 If the concentration of analyte exceeds the linear range of the instrument, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

11.3.9 If the retention time is not duplicated (± 10%), as determined by the calibration curve, the acetonitrile/water ratio may be increased or decreased to obtain the correct elution time. If the elution time is too long, increase the ratio; if it is too short, decrease the ratio.

Note: The chromatographic conditions described here have been optimized for the detection of formaldehyde. Analysts are advised to experiment with their HPLC system to optimize chromatographic conditions for their particular analytical needs.

11.4 HPLC Calibration

11.4.1 Calibration standards are prepared in acetonitrile from the DNPH-formaldehyde derivative. Individual stock solutions of 100 mg/L are prepared by dissolving 10 mg of solid derivative in 100 mL of mobile phase. These individual solutions are used to prepare calibration standards at concentrations spanning the range of interest.

11.4.2 Each calibration standard (at least five levels) is analyzed three times and area response is tabulated against mass injected (see Figure 10). All calibration runs are performed as described for sample analyses in Section 11.3. Using the UV detector, a linear response range of approximately 0.05-20 µg/mL should be achieved for 25-µL injection volumes. The results may be used to prepare a calibration curve, as illustrated in Figure 11. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (concentration versus area response) is obtained. The retention times for each analyte should agree within 2%.

11.4.3 Once linear response has been documented, an intermediate concentration standard near the anticipated levels of each component, but at least 10 times the detection limit, should be chosen for daily calibration. The day to day response for the various components should be within 10% for analyte concentrations of 1 μg/mL or greater and within 15-20% for analyte concentrations near 0.5 μg/mL. If greater variability is observed, recalibration may be required or a new calibration curve must be developed from fresh standards.

12. Calculations

12.1 The total mass of analyte (DNPH-formaldehyde) is calculated for each sample using the following equation:

$$W_d = W_s - W_b$$

where:

W_d = total analyte mass from volume of sampled air, μg
W_s = analyte mass in the sample cartridge, μg
= $A_s \times (C_{std}/A_{std}) \times v_s \times d_s$
W_b = analyte mass in the blank cartridge, μg
= $A_b \times (C_{std}/A_{std}) \times v_b \times d_b$
A_s = area counts, sample cartridge
A_b = area counts, blank cartridge
A_{std} = area counts, standard
C_{std} = concentration of analyte in the daily calibration standard, μg/mL
v_s = total volume of the sample cartridge eluate, mL
v_b = total volume of the blank cartridge eluate, mL
d_s = dilution factor for the sample cartridge eluate
= 1 if sample was not rediluted
= v_d/v_a if sample was rediluted to bring detector response within linear range
v_d = redilution volume
v_a = aliquot used for redilution
d_b = dilution factor for the blank cartridge eluate
= 1

12.2 The concentration of aldehyde (formaldehyde) in the original sample is calculated from the following equation:

$$C_A = W_d \times (MW_{ald}/MW_{der}) \times 1000/V_m \text{ (or } V_s)$$

where:

C_A = concentration of aldehyde (formaldehyde) in the original sample, ng/L
W_d = weight of the aldehyde (formaldehyde) derivative collected on the sample cartridge, from Section 11.4, blank corrected, μg
Vm = total sample volume under indoor conditions, from Section 10.13, L
V_s = total sample volume at 25°C and 760 mm Hg, from Section 10.13, L

MW_{ald} = molecular weight of aldehyde (formaldehyde), g/g-mole
MW_{der} = molecular weight of the DNPH derivative of the aldehyde (formaldehyde), g/g-mole

The aldehyde (formaldehyde) concentrations can be converted to ppbv using the following equation:

$$C_A(ppbv) = C_A(ng/L) \times (24.4/MW_{ald})$$

where:
$C_A(ppbv)$ = concentration of aldehyde (formaldehyde) by volume, ppb
C_A = concentration of aldehyde (formaldehyde) in the original sample, calculated using V_s, ng/L
MW_{ald} = molecular weight of the aldehyde (formaldehyde), g/g-mole

13. Performance Criteria and Quality Assurance

This section summarizes required quality assurance measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

13.1 Standard Operating Procedures (SOPs)

13.1.1 Users should generate SOPs describing the following activities in their laboratory: 1) assembly, calibration, and operation of the sampling system, with make and model of equipment used, 2) preparation, purification, storage, and handling of sampling reagent and samples, 3) assembly, calibration, and operation of the HPLC system, with make and model of equipment used, and 4) all aspects of data recording and processing, including lists of computer hardware and software used.

13.1.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

13.2 HPLC System Performance

13.2.1 The general appearance of the HPLC system should be similar to that illustrated in Figure 5.

13.2.2 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54(t_r^2/W_{1/2})$$

where:
N = column efficiency (theoretical plates)
t_r = retention time of analyte, seconds
$W_{1/2}$ = width of component peak at half height, seconds

A column efficiency of >5,000 theoretical plates should be obtained.

13.2.3 Precision of response for replicate HPLC injections should be ±10% or less, day to day, for analyte calibration standards at 1 µg/mL or greater levels. At the 0.5 µg/mL level and below, precision of replicate analyses could vary up to 25%. Precision of retention times should be ±2% on a given day.

13.3 Process Blanks

At least one field blank or 10% of the field samples, whichever is larger, should be shipped and analyzed with each group of samples. The number of samples within a group and/or time frame should be recorded so that a specified percentage of blanks is obtained for a given number of indoor air samples. The field blank is treated identically to the samples except that no air is drawn through the cartridge. The performance criteria described in Section 9.1 should be met for process blanks.

13.4 Method Precision and Accuracy

13.4.1 At least one duplicate sample or 10% of the field samples, whichever is larger, should be collected during each sampling episode. Precision for field replication should be ±20% or better.

13.4.2 Precision for replicate HPLC injections should be ±10% or better, day to day, for calibration standards.

13.4.3 At least one sample spike with analyte of interest or 10% of the field samples, whichever is larger, should be collected.

13.4.4 Before initial use of the method, each laboratory should generate triplicate spiked samples at a minimum of three concentration levels, bracketing the range of interest for each compound. Triplicate nonspiked samples must also be processed. Spike recoveries of >80 ± 10% and blank levels as outlined in Section 9.1 should be achieved.

14. Detection of Other Aldehydes and Ketones

Note: The procedure outlined above has been written specifically for the sampling and analysis of formaldehyde in indoor air using an adsorbent cartridge and HPLC. Indoor air contains other aldehydes and ketones. Optimizing chromatographic conditions by using two Zorbax ODS columns in series and varying the mobile phase composition through a gradient program will enable the analysis of other aldehydes and ketones in indoor air.

14.1 Sampling Procedures

The sampling procedures for other aldehydes and ketones are the same as in Section 10.

14.2 HPLC Analysis

14.2.1 The HPLC system is assembled and calibrated as described in Section 11. The operating parameters are as follows:

Column - Zorbax ODS, two columns in series
Mobile Phase - Acetonitrile/water, linear gradient
Detector - Ultraviolet, operating at 360 nm
Flow Rate - 1.0 mL/min
Sample Injection Volume - 25 µL
Step 1 - 60-75% acetonitrile/40-25% water in 30 minutes
Step 2 - 75-100% acetonitrile/25-0% water in 20 minutes
Step 3 - 100% acetonitrile for 5 minutes

Step 4 - 60% acetonitrile/40% water reverse gradient in 1 minute
Step 5 - 60% acetonitrile/40% water, isocratic, for 15 minutes

14.2.2 The gradient program allows for optimization of chromatographic conditions to separate acrolein, acetone, propionaldehyde, and other higher molecular weight aldehydes and ketones in an analysis time of about one hour. Table 1 illustrates the sensitivity for selected aldehydes and ketones in ambient air that have been identified using two Zorbax ODS columns in series.

14.2.3 The chromatographic conditions described herein have been optimized for a gradient HPLC (Varian Model 5000, or equivalent) system equipped with a UV detector (ISCO Model 1840 variable wavelength, or equivalent), an automatic sampler with a 25-μL loop injector and two DuPont Zorbax ODS columns (4.6 x 250 mm), a recorder, and an electronic integrator. Analysts are advised to experiment with their HPLC systems to optimize chromatographic conditions for their particular analytical needs. Highest chromatographic resolution and sensitivity are desirable but may not be achieved. The separation of acrolein, acetone, and propionaldehyde should be a minimum goal of the optimization.

14.2.4 The carbonyl compounds in the sample are identified and quantified by comparing their retention times and area counts with those of standard DNPH derivatives. Formaldehyde, acetaldehyde, acetone, propionaldehyde, crotonaldehyde, benzaldehyde and o-, m-, p-tolualdehydes can be identified with a high degree of confidence. The identification of butyraldehyde is less certain because it coelutes with isobutyraldehyde and methyl ethyl ketone under the stated chromatographic conditions. Figure 12 illustrates a typical chromatogram obtained with the gradient HPLC system.

14.2.5 The concentrations of individual carbonyl compounds are determined as outlined in Section 12.

14.2.6 Performance criteria and quality assurance activities should meet those requirements outlined in Section 13.

15. References

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Table 1. Sensitivity (ppb, v/v) of Sampling/Analysis Using Adsorbent Cartridge Followed by HPLC

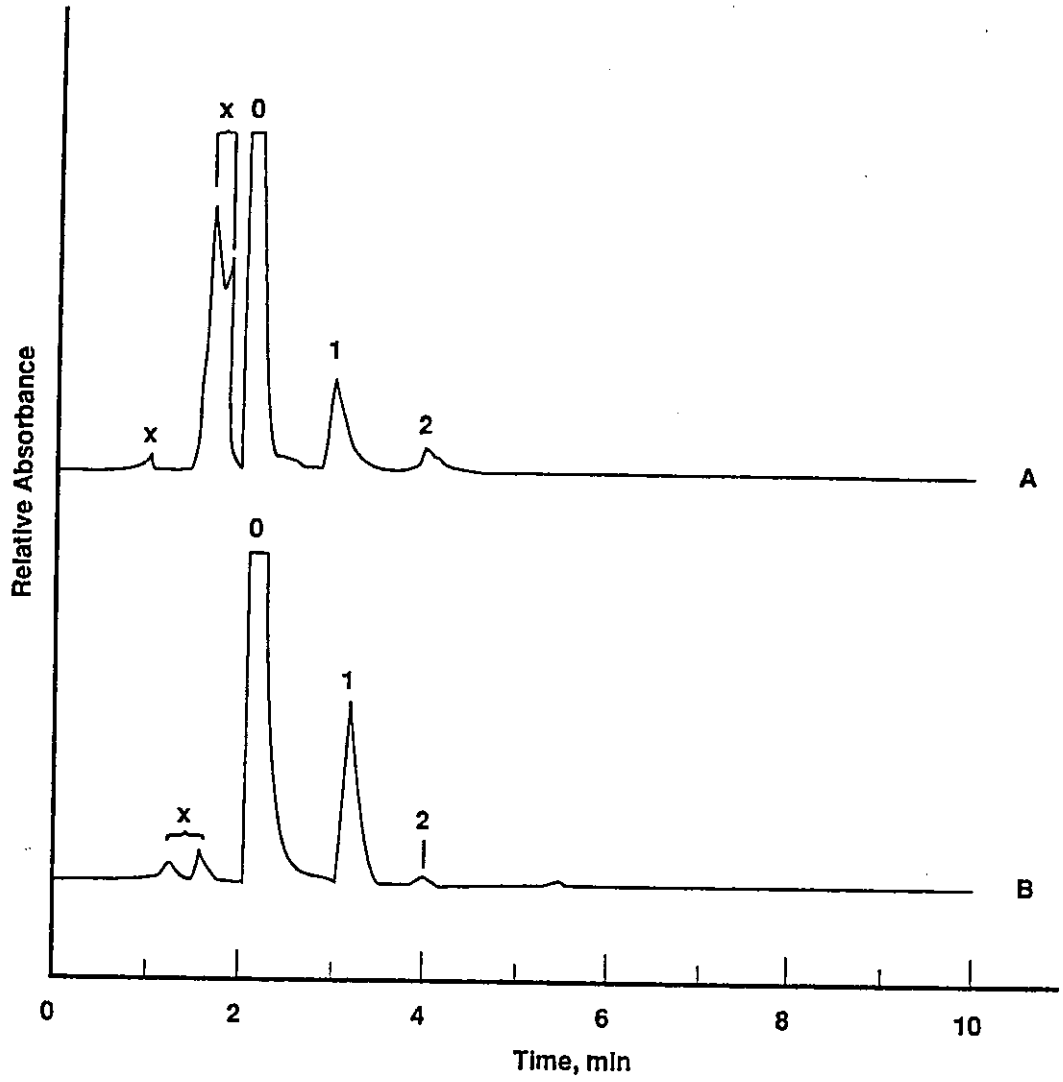
	Sample Volume, L										
Compound	10	20	30	40	50	100	200	300	400	500	1000
Formaldehyde	1.45	0.73	0.48	0.36	0.29	0.15	0.07	0.05	0.04	0.03	0.01
Acetaldehyde	1.36	0.68	0.45	0.34	0.27	0.14	0.07	0.05	0.03	0.03	0.01
Acrolein	1.29	0.65	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03	0.01
Acetone	1.28	0.64	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03	0.01
Propionaldehyde	1.28	0.64	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03	0.01
Crotonaldehyde	1.22	0.61	0.41	0.31	0.24	0.12	0.06	0.04	0.03	0.02	0.01
Butyraldehyde	1.21	0.61	0.40	0.30	0.24	0.12	0.06	0.04	0.03	0.02	0.01
Benzaldehyde	1.07	0.53	0.36	0.27	0.21	0.11	0.05	0.04	0.03	0.02	0.01
Isovaleraldehyde	1.15	0.57	0.38	0.29	0.23	0.11	0.06	0.04	0.03	0.02	0.01
Valeraldehyde	1.15	0.57	0.38	0.29	0.23	0.11	0.06	0.04	0.03	0.02	0.01
o-tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02	0.01
m-tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02	0.01
p-tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02	0.01
Hexanaldehyde	1.09	0.55	0.36	0.27	0.22	0.11	0.05	0.04	0.03	0.02	0.01
2,5-dimethylbenzaldehyde	0.97	0.49	0.32	0.24	0.19	0.10	0.05	0.03	0.02	0.02	0.01

Note: ppb values are measured at 1 atm and 25°C; sample cartridge is eluted with 5 mL acetonitrile, and 25 mL are injected onto HPLC column.

Note: Maximum sampling flow through a DNPH-coated Sep-PAK® cartridge is about 1.5 L per minute.

Table 2. Typical Performance Specifications for Formaldehyde Analyzer

Standard Range:	0-5 ppm (adjustable from 0-0.25 up to 0-10 ppm full scale)
Low Level Range:	0-250 ppb
Reproducibility:	1%
Minimum Detection:	0.003 ppm (3 ppb) at 0-0.25 ppm full scale or 1% of full scale
Nonlinearity:	Less than 2% up to 2.5 ppm
Zero Drift:	Less than 2% per 24 hours
Span Drift:	Less than 2% per 24 hours
Airflow Drift:	Less than 1% per 24 hours
Zero Noise:	±0.3%
Lag Time:	4-1/2 minutes (8 1/2 minutes with double coil)
Rise Time:	(90%) 4-1/2 minutes
Fall Time:	(90%) 4-1/2 minutes
Air Sample Flow Rate:	0.5 liters per minute
Optimum Temperature Range:	60° to 80°F. Useable at 40° to 120°F.
Relative Humidity Range:	5 to 95%



x = unknown
0 = DNPH
1 = formaldehyde
2 = acetaldehyde

Figure 1. Cartridge Samples of a Formaldehyde Air Stream with (A) and without (B) Ozone

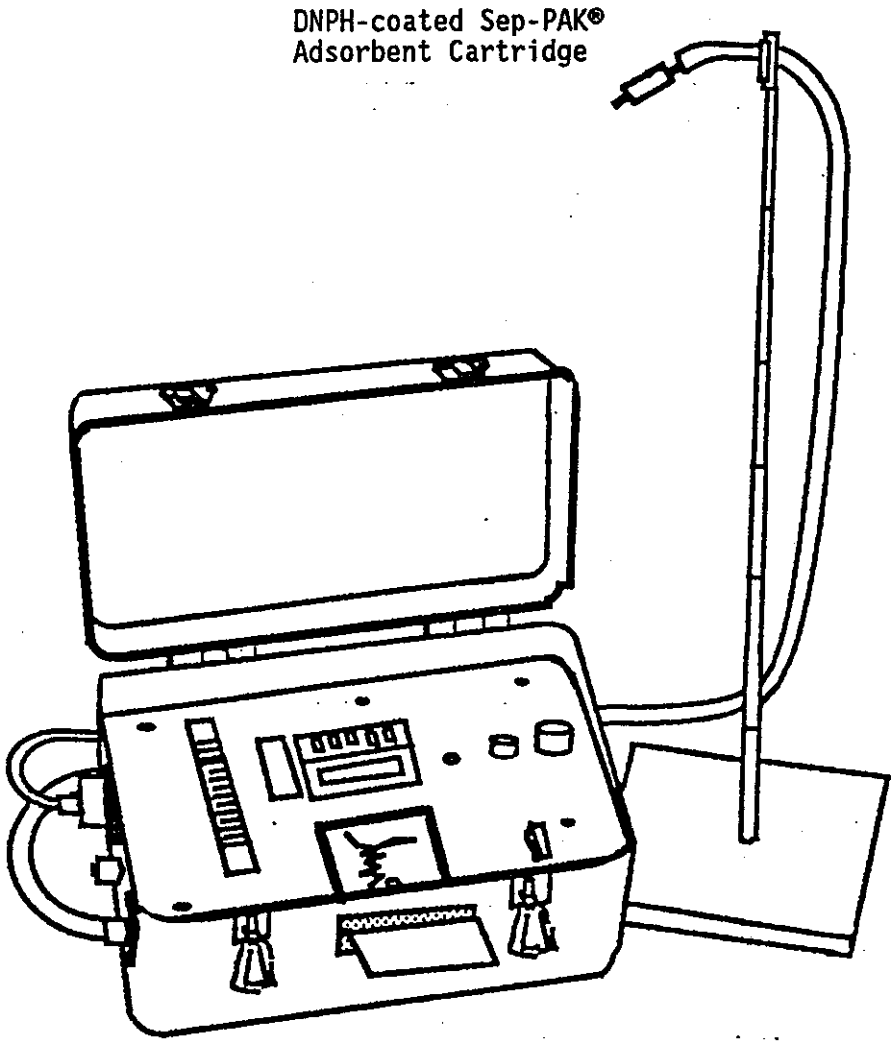


Figure 2. Portable Sampling System for Adsorbent Cartridges

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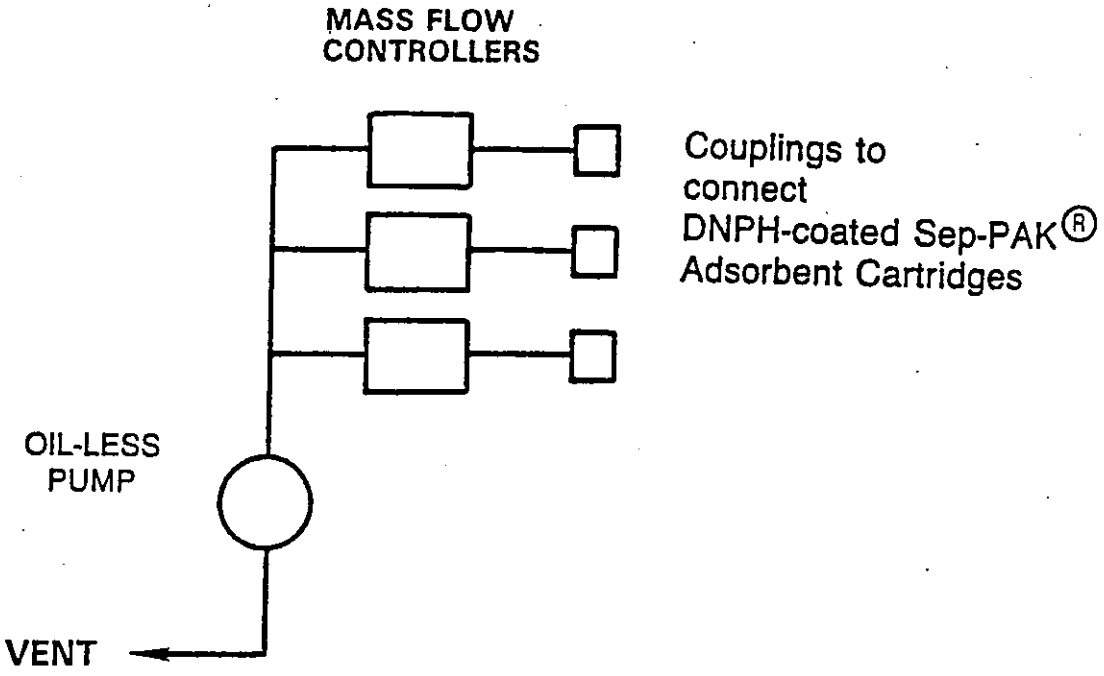
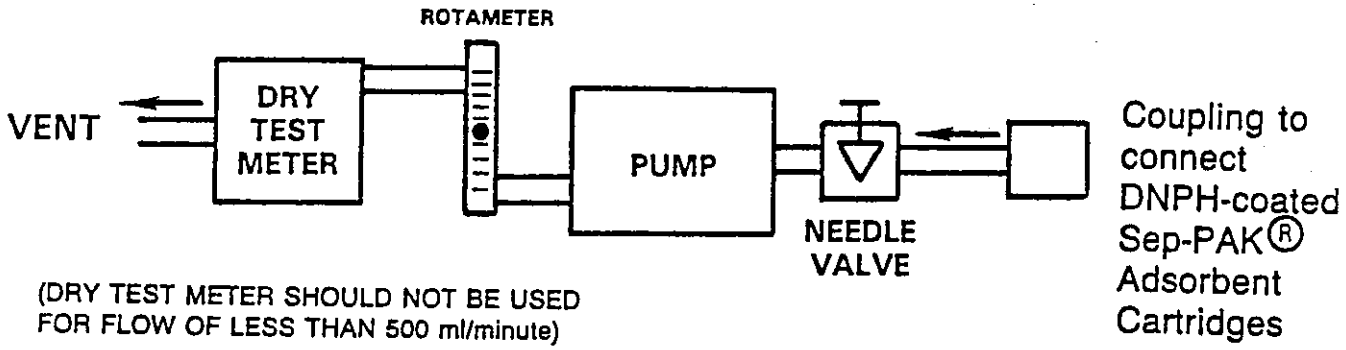


(a) MASS FLOW CONTROL



(b) NEEDLE VALVE/DRY TEST METER

Figure 3. Typical Sampling System Configurations

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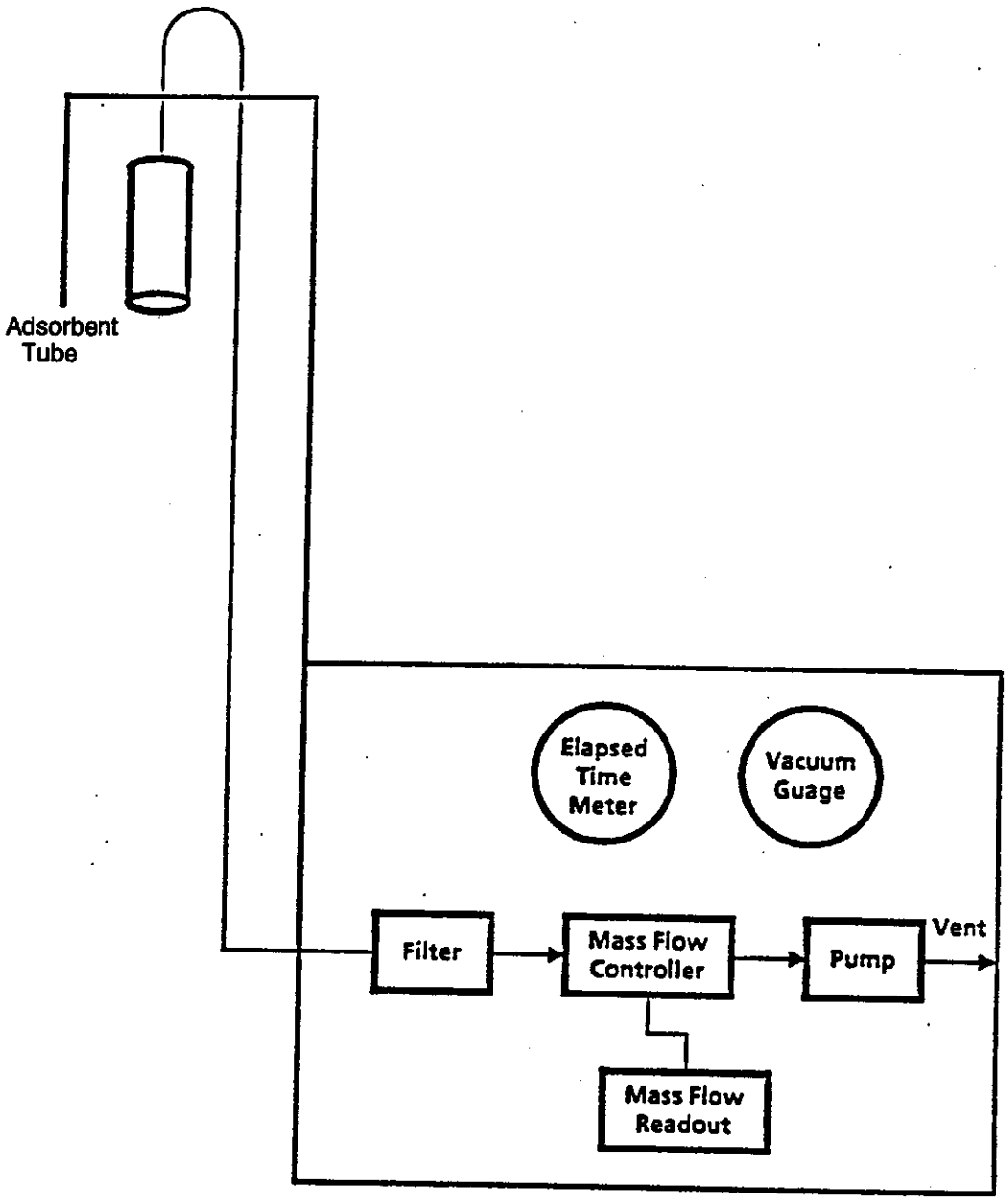


Figure 4. Diagram of Adsorbent Sampling Device for Airborne Aldehydes

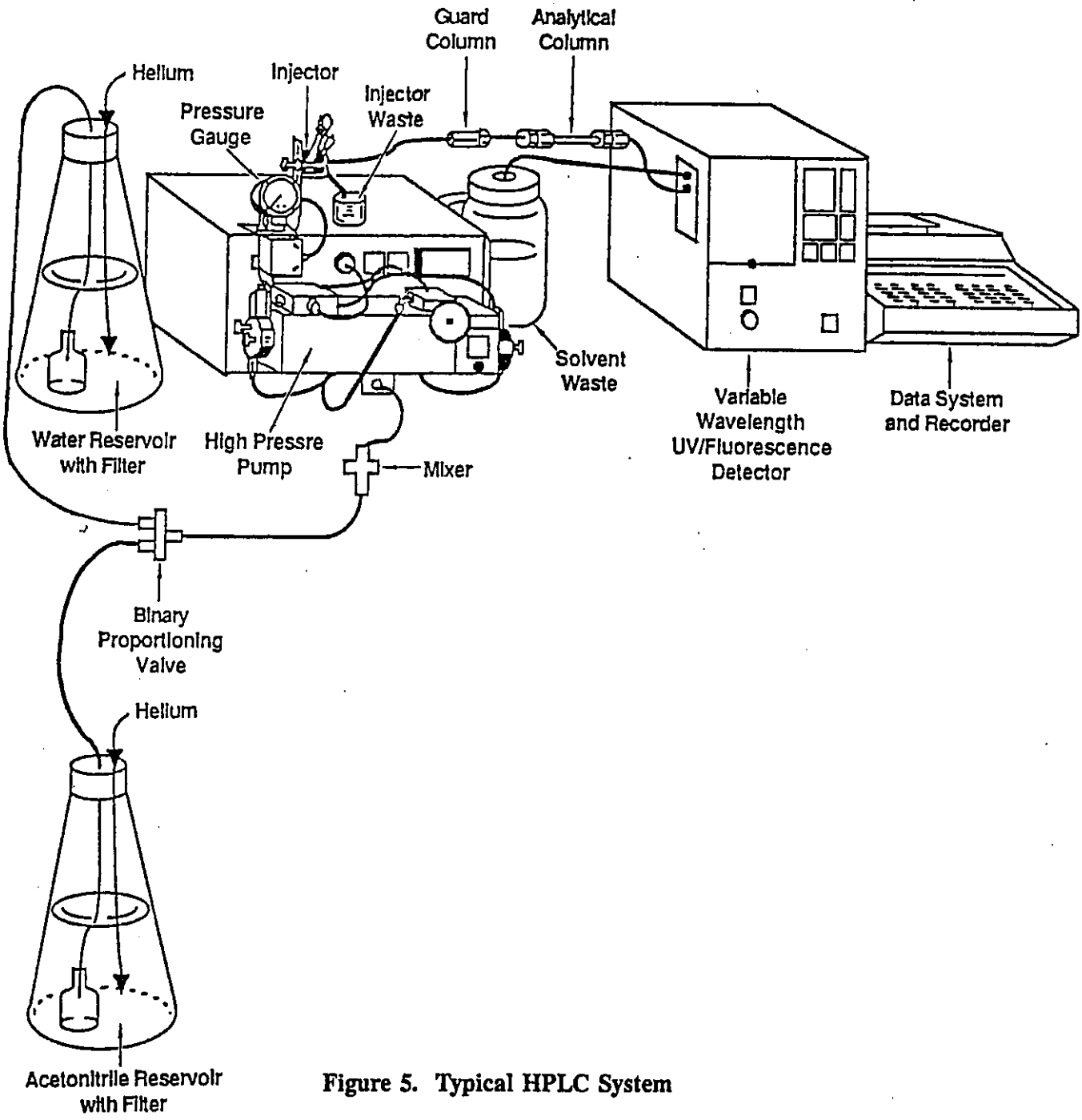
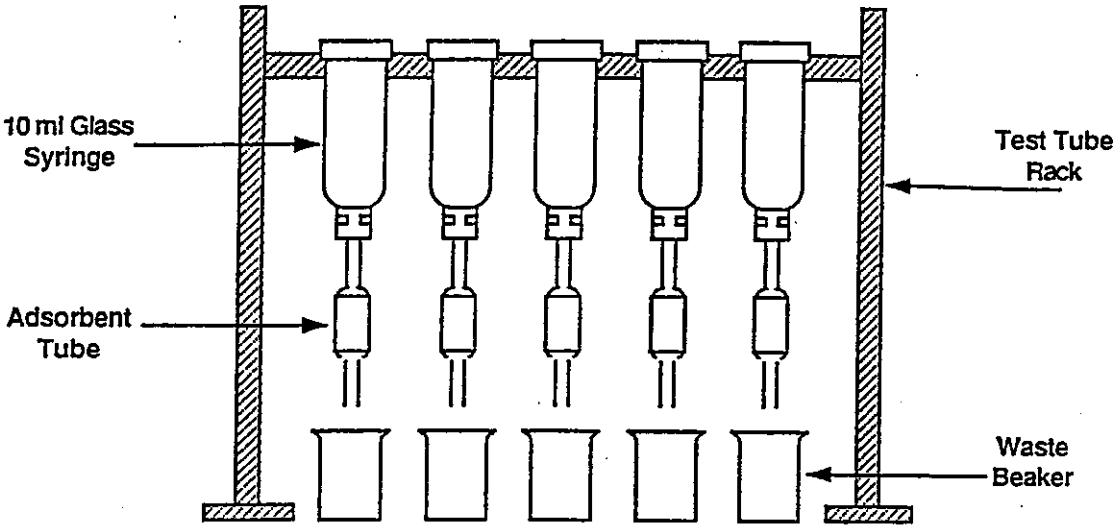
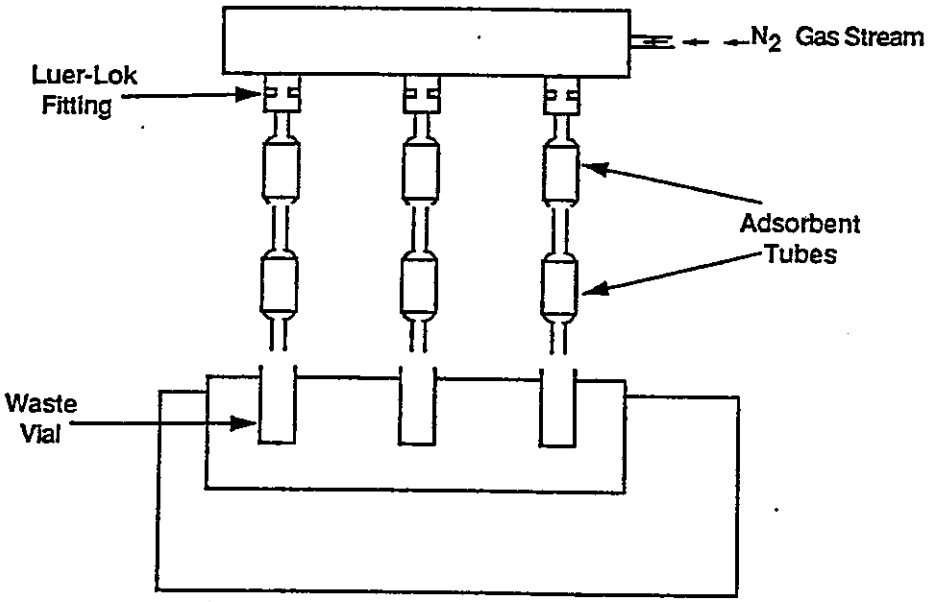


Figure 5. Typical HPLC System

508



(a) RACK FOR COATING CARTRIDGES



(b) RACK FOR DRYING DNPH-COATED CARTRIDGES

Figure 6. Syringe Rack for Coating and Drying Sample Cartridges

509

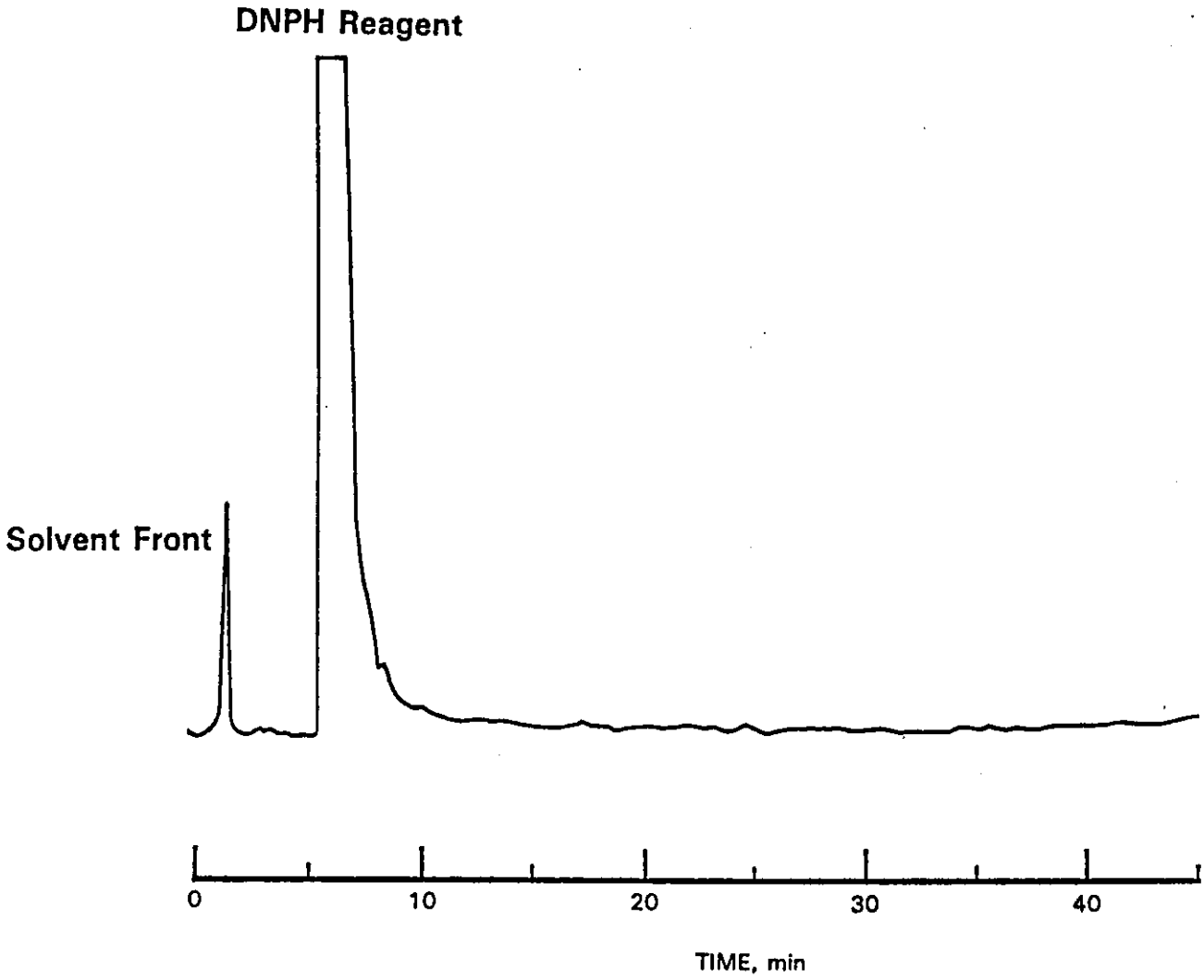


Figure 7. Impurity Level of DNPH after Recrystallization

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SAMPLING DATA SHEET
(One Sample per Data Sheet)

PROJECT:_____ DATE(S) SAMPLED:_____
SITE:_____ TIME PERIOD SAMPLED:_____
LOCATION:_____ OPERATOR:_____
INSTRUMENT MODEL NO:_____ CALIBRATED BY:_____
PUMP SERIAL NO:_____

ADSORBENT CARTRIDGE INFORMATION:
Type:_____ Serial Number:_____
Adsorbent:_____ Sample Number:_____

SAMPLING DATA:
Start Time:_____ Stop Time:_____

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate (Q)*, mL/min	Indoor Temperature, °C	Barometric Pressure, mm Hg	Relative Humidity,%	Comments
Avg.							

* Flow rate from rotameter or soap bubble calibrator (specify which)
Total Volume Data (V_m) (use data from dry gas meter, if available)

V_m = (Final - Initial) Dry Gas Meter Reading, or = _____ Liters

$$V_m = \frac{Q_1 + Q_2 + Q_3 \cdot \cdot \cdot Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \_\_\_\_\_ \text{ Liters}$$

Figure 8. Example Sampling Data Sheet

OPERATING PARAMETERS
HPLC

Column: Zorbax ODS or C-18 RP
Mobile Phase: 60% Acetonitrile/40% Water
Detector: Ultraviolet, operating at 360 nm
Flow Rate: 1 mL/min.
Retention Time: ~ 7 minutes for formaldehyde
Sample Injection Volume: 25 uL

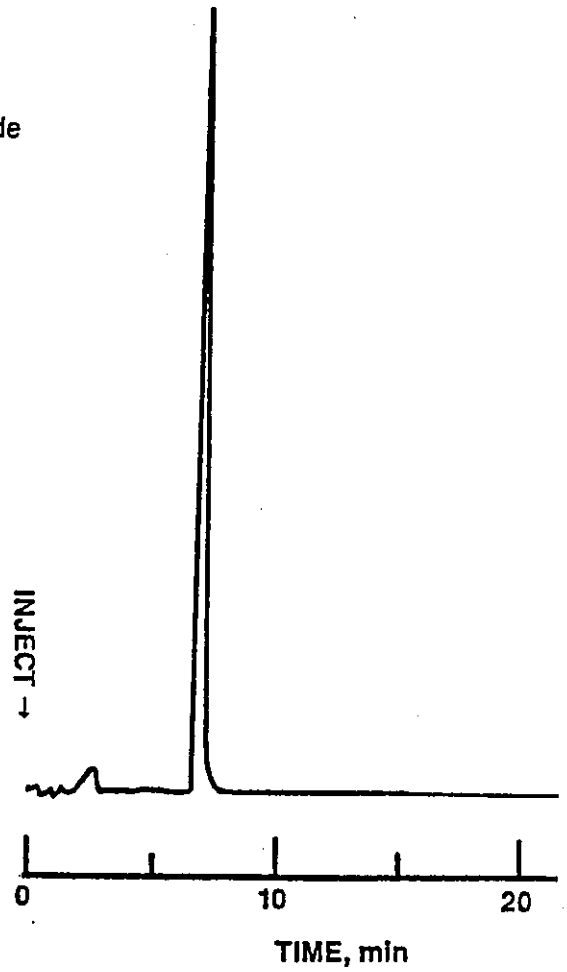
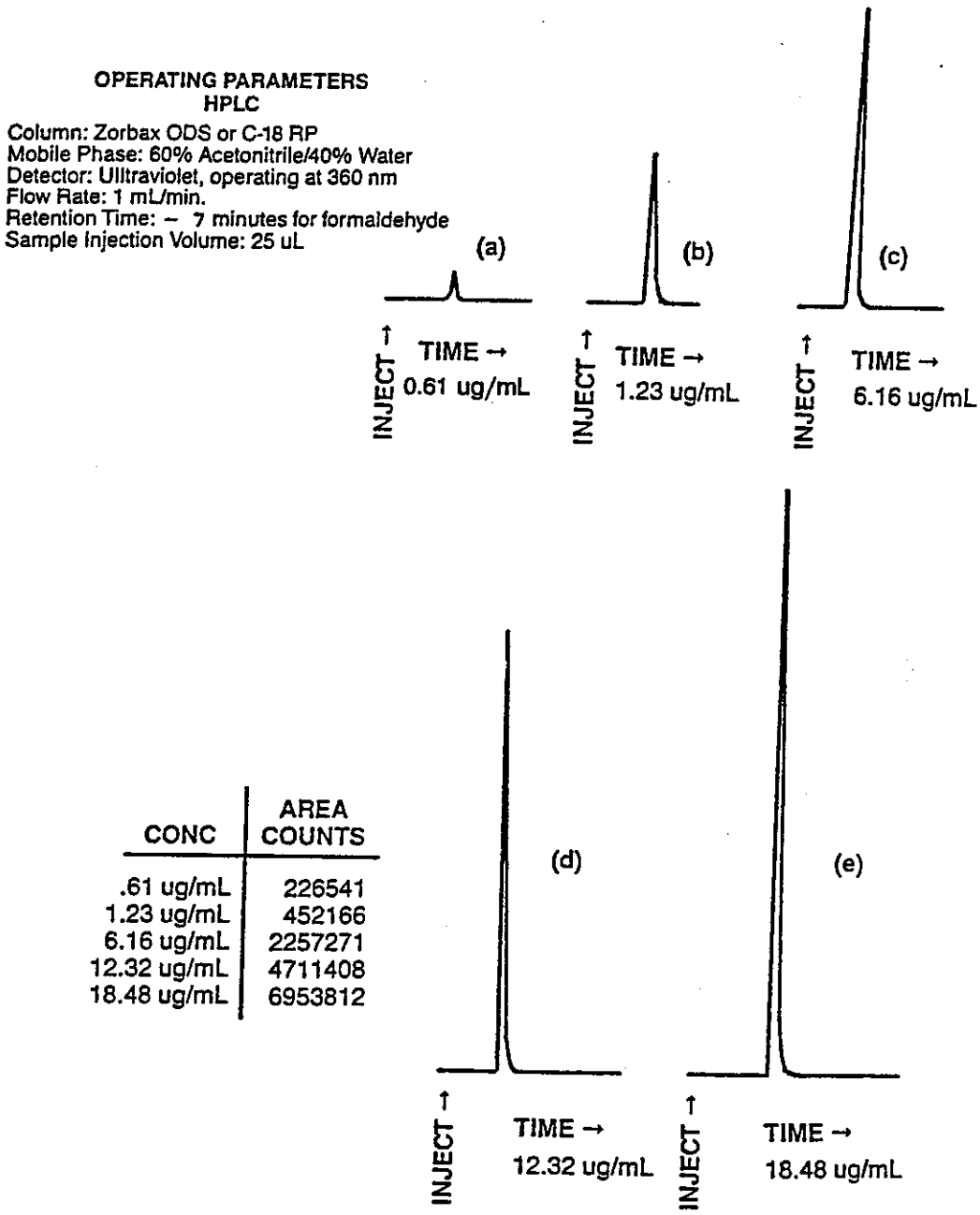


Figure 9. Chromatogram of DNPH-Formaldehyde Derivative

512



CONC	AREA COUNTS
.61 ug/mL	226541
1.23 ug/mL	452166
6.16 ug/mL	2257271
12.32 ug/mL	4711408
18.48 ug/mL	6953812

Figure 10. HPLC Chromatogram of Varying Concentrations of DNPH-Formaldehyde Derivative

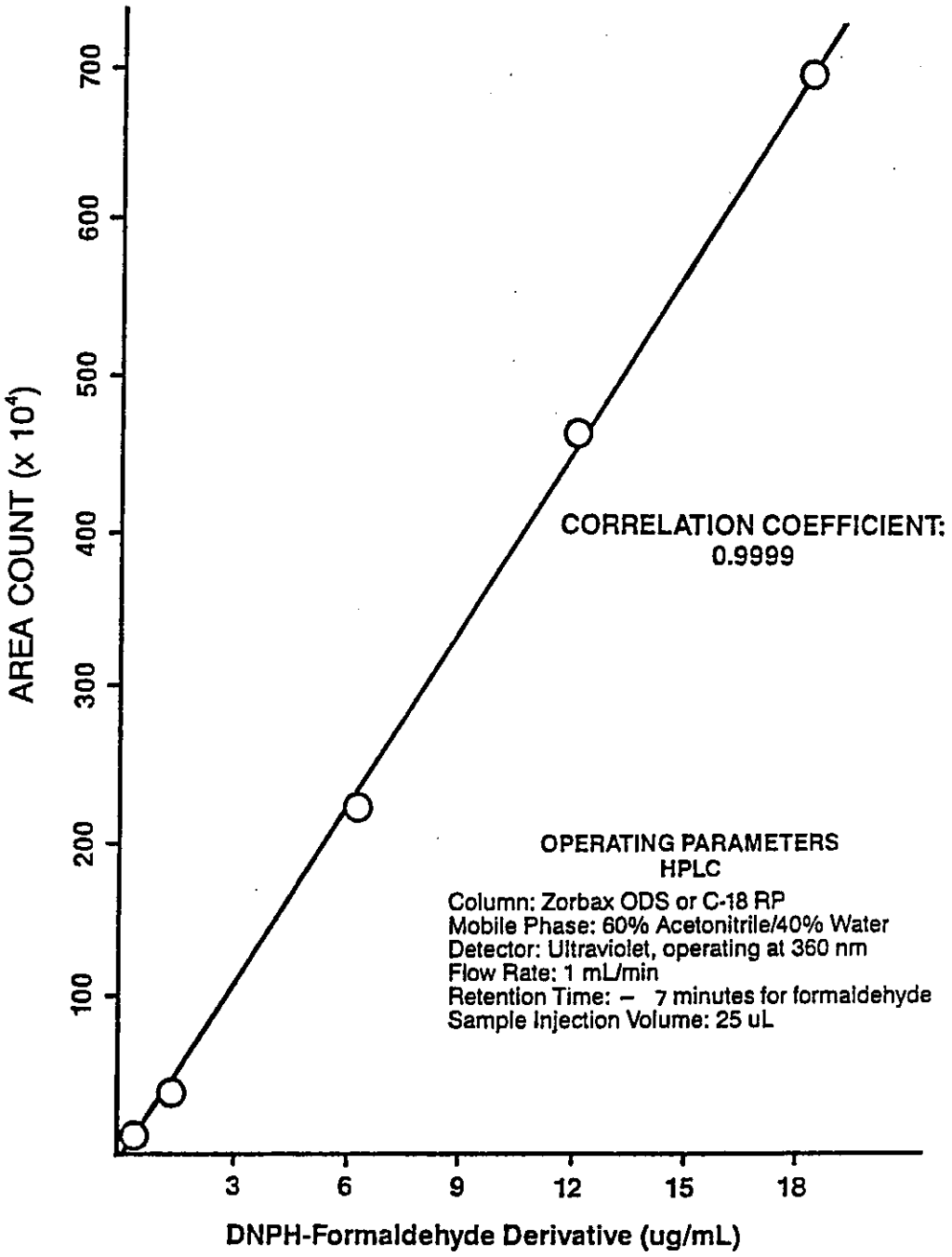


Figure 11. Typical Calibration Curve for Formaldehyde

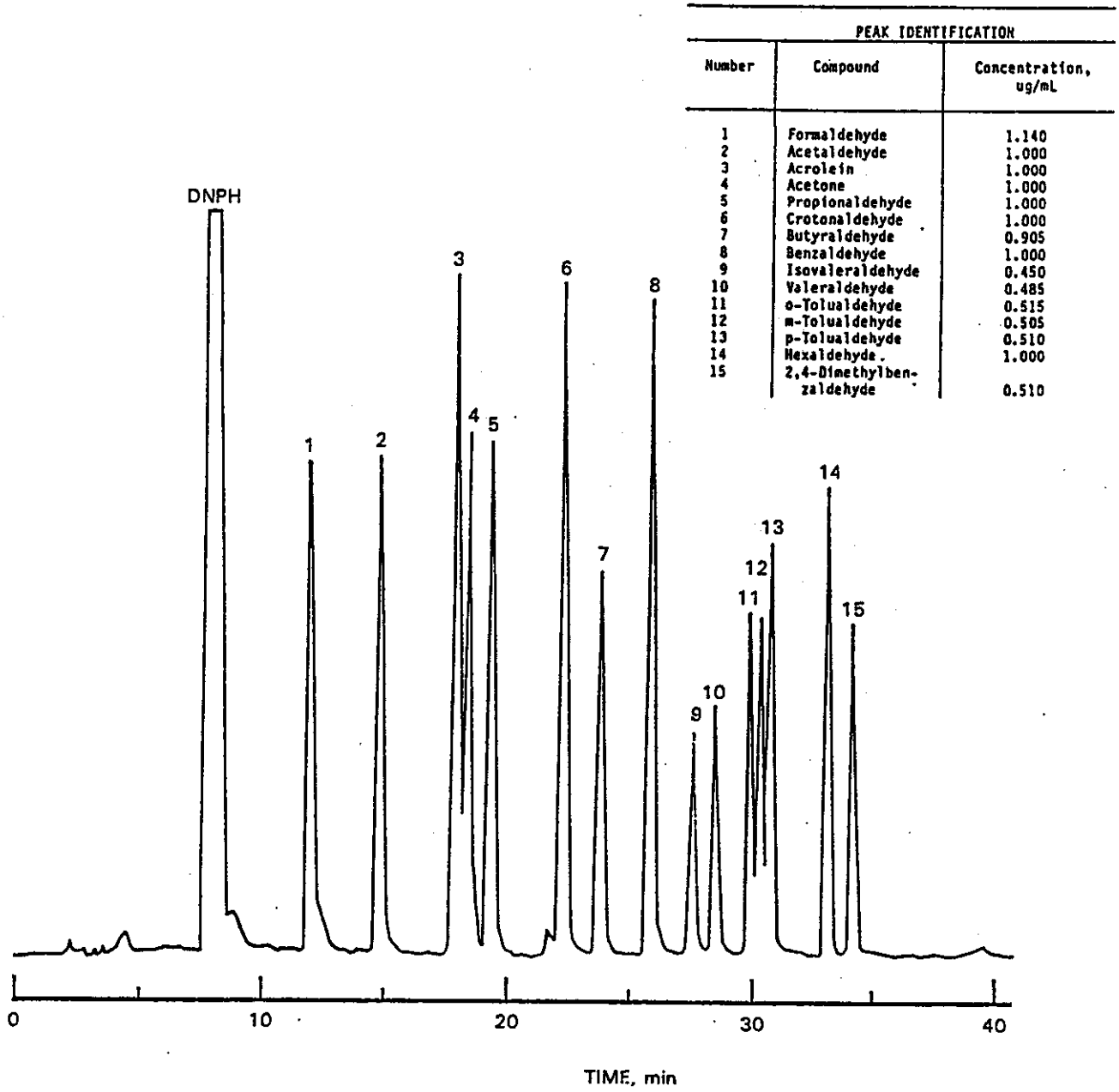


Figure 12. Chromatographic Separation of DNPH Derivatives of 15 Carbonyl Standards

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Method IP-6B

DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES IN INDOOR AIR USING A CONTINUOUS COLORIMETRIC ANALYZER

Method IP-6B

DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES IN INDOOR AIR USING A CONTINUOUS COLORIMETRIC ANALYZER

1. Scope

1.1 This method describes a procedure for indoor air sampling and analysis of formaldehyde. The procedure employs an automated wet-chemical colorimetric analyzer (CEA Instruments, Inc., 16 Chestnut St., P.O. Box 303, Emerson, NJ, 07630, Model TGM 555-FD, or equivalent) with a continuous signal output.

1.2 This analyzer is fully portable and can be placed on a tabletop or other appropriate surface for monitoring formaldehyde in indoor air. Both air and liquid formaldehyde standards can be analyzed.

2. Principle of Operation

2.1 General

2.1.1 The analyzer measures formaldehyde concentrations by monitoring the amount of color change produced when specific reagents are combined with the air sample. The air sample to be analyzed is continuously drawn into the monitor by an internal vacuum pump.

2.1.2 Any formaldehyde present in the sample is scrubbed with a sodium tetrachloromercurate (TCM) solution containing a fixed quantity of sodium sulfite. Acid-bleached pararosaniline is then added. The sampling lines and connecting tubing are made of stainless steel, glass, FEP Teflon® or PFA Teflon®. Tygon® tubing or TFE Teflon® should not be used. The air stream is transported to an absorber separator coil. For formaldehyde absorption, a two stage liquid/gas separator removes the scrubbed air stream which is then vented to the atmosphere through a vacuum pump.

2.1.3 All the glassware including the absorber coil and the liquid air separator are mounted in an analytical module which is diagrammed in Figure 1. Unreacted reagent is pumped through the reference cell of the dual beam colorimeter of the analyzer. The colored reaction product flows through the sample cell. The colorimeter measures electronically either the difference in color or light absorption of the reagent before and after the reaction with the gas, or the formation of the color from the addition of reagents.

2.1.4 Transmission of light through the flow cells is measured by a matched set of photodetectors at a wavelength of 550 nm. The intensity of the color is directly proportional to the concentration of the formaldehyde to be measured.

2.1.5 The electrical signal generated in the colorimeter is amplified and fed to a digital display, where it is read out as a percentage (%) of full scale.

2.2 Sample Collection and Analysis

2.2.1 Air flow - The sample air flow rate must be kept constant at 0.5 L/min for accurate results. A potentiometer controls the air pump voltage and hence the flow rate.

The air flow rate should be periodically checked using a flowmeter. When a long sample line is used, the flowmeter should be at the inlet of the sample line.

2.2.2 Drain system - Reacted solution is drained through a horizontal "tee" to an appropriate waste container either external or internal to the analyzer.

2.2.3 Liquid pump - The formaldehyde analyzer uses an integral peristaltic-type pump to transfer reagents to the scrubber and to the reaction and detection systems. The reagent pump can run "dry" with no damage to the analyzer occurring.

3. Significance

3.1 In the early 1960's, procedures for measuring formaldehyde were being developed. At a symposium in 1965, Yunghans and Munroe (1) discussed a modified Schiff procedure, utilizing pararosaniline, developed by Lyles, Downing, and Blanchard (2) as the method of choice for formaldehyde measurement. The chromotropic acid method of West and Sen (3) was rejected due to problems associated with the handling of sulfuric acid, as well as the MBTH procedure developed by Sawicki (4) and modified by Hauser (5) due to the time needed to complete a preliminary reaction prior to adding the oxidizing agent. The basic chemistry of the pararosaniline procedure is that formaldehyde is absorbed in a sodium tetrachloromercurate (II) solution containing a fixed quantity of sulfur dioxide. Acid bleached pararosaniline is added, and the intensity of the resultant purple dye, measured at 555 nanometers, is proportional to the formaldehyde present. In 1976, CEA Instruments (6) adapted this procedure to an automated wet chemical analyzer, to be known as the Model TGM 555-FD.

3.2 Recent research has ben conducted which builds on successive modifications of the pararosaniline method and the Model TGM-155-FD analyzer, eliminates the use of tetrachloromercurate, and uses only pararosaniline and sodium sulfate based working reagents. The recent modifications also use several additional time delay coils to increase the reactants residence time. The analytical module was modified with additional tubing and glassware and an additional debubbler was added to overcome the increased drag on the system. Because this method does not use the toxic mercury working reagent, the potential hazard of using this method in an indoor air testing environment is reduced. For additional information on the modified pararosaniline method see references 7, 8 and 9.

4. Interferences

The colorimeter measures a chemical reaction electronically. The chemical reaction is influenced by changes in atmospheric and operating conditions. The following are some interferences that have been observed during extensive tests of the colorimeter.

4.1 Changes in air pressure and temperature - The flowmeter is calibrated at standard atmospheric conditions. At low temperatures (40°-45°F) and high barometric pressures the meter will display a reading which is 3% to 4% lower than the reading at which the unit was calibrated. At temperatures between 60°F to 90°F, the unit will operate properly. At temperatures above 90°F, the sensitivity of the unit decreases. At about 90°F, the absorbing

solution becomes saturated. The manufacturer's specifications will provide instructions on operating the analyzer at temperatures above 90°F.

4.2 Changes in light conditions - If the monitor is operated with the cover removed, the sensing cells should be shielded from direct sunlight. A leakage of strong collimated light into the light paths can affect the reading. No effect with scattered light has been observed.

4.3 Optimum responses of the unit will be achieved after running the unit for approximately an hour. In particular, baseline and span noise will decrease significantly, as will baseline drift.

4.4 Air bubbles and precipitated colored reactants are responsible for the majority of the increases in noise and erratic response. Cleaning all lines and pump tubes when needed will reduce or eliminate these problems. Air bubbles and erratic fluid levels in the sample cell can be eliminated by flushing the unit with a suitable wetting agent (BRIJ 35 -Fisher CS-285-2, or equivalent) (5% solution).
Caution: Do not use this wetting agent in conjunction with the reagents! Flush the unit for half an hour with distilled water. Then flush with the diluted wetting agent solution for an additional half hour, followed by a minimum of 1 hour of flushing with distilled water. The unit can then be operated with the reagents.

4.5 The influence of atmospheric conditions on the chemical reaction cannot be changed. However, if the observer takes into consideration The above interferences and accounts for fluctuations that affect signal noise and baseline drift, the unit will give accurate results within these limitations.

5. Reagents and Materials

5.1 Pararosaniline (PRA) chloride - specially purified pararosaniline chloride, 0.2% 1 M hydrochloric acid must be used (CEA Instruments, Product No. CRP-61A Emerson, NJ or Eastman Kodak, Product No. A14051, or Fisher Scientific, Pittsburgh, PA, Product No. 14051-A, or equivalent).

5.2 Sodium sulfite - prepared fresh daily with distilled water (Fisher Scientific, Pittsburgh, PA, Product No. S-430, or equivalent).

5.3 Mercuric chloride - ACS grade, or equivalent.

5.4 Sodium chloride - ACS grade, or equivalent.

5.5 Hydrochloric acid - analytical grade, best source.

5.6 Distilled water - analytical grade, best source.

5.7 Permeation tube - permeation rate of approximately 750 ng/min per ppm of range desired. For example, if the unit is to be calibrated over a full scale range of 0-5 ppm, an output of about 3750 ng/min (i.e., 5 x 750) is required for proper calibration (Kin-Tek, Texas City, Texas, or equivalent).

5.8 Alpha-polyoxymethylene - for preparation of permeation tubes.

5.9 Formaldehyde - 37% by weight in water, analytical grade,or equivalent.

5.10 Zero gas filter.

5.11 Mohr pipet - 1-mL graduated.

6. Reagent Preparation

6.1 Reagent Preparation and Consumption

6.1.1 Reagent 1 - Reagent 1 is a sodium sulfite solution and is used as part of the working absorbing solution. This solution is prepared by dissolving 0.35 grams of sodium sulfite in one liter of distilled water. This reagent must be made fresh daily.

6.1.2 Reagent 2 - Reagent 2 is a sodium tetrachloromercurate solution and is combined with a fixed quantity of Reagent 1 to form the working absorbing solution. This is prepared by dissolving 1.36 grams of mercuric chloride and 0.58 grams sodium chloride in approximately 850 mL of distilled water. Make up to one liter with distilled water. Caution: This reagent solution is extremely toxic and is readily absorbed through the skin.

6.1.3 Reagent 3 - Reagent 3 is a modified pararosaniline (PRA) solution and is added to reagents 1 and 2 for color formation in the sample. This solution is prepared by diluting 50 mL of specially purified PRA to 250 mL with distilled water.

6.2 Reagent Consumption

This section provides nominal flow rates for reagents through the system.

6.2.1 Reagent 1 - The following flow rates for the reagent 1 solution (i.e., sodium sulfite solution) are recommended for successful operation of the analyzer: 20 mL per hour of continuous operation, 0.8 liters per 40 hours, and 3.4 liters per 168 hours.

6.2.2 Reagent 2 - The following flow rates for the reagent 2 solution (i.e., working TCM solution) are recommended for successful operation of the analyzer: 20 mL per hour of continuous operation, 0.8 liters per 40 hours, and 3.4 liters per 168 hours.

6.2.3 Reagent 3 - The following flow rates for the reagent 3 solution (i.e., working PRA solution) are recommended for successful operation of the analyzer: 20 mL per hour of continuous operation, 0.8 liters per 40 hours, and 3.4 liters per 168 hours.

7. Analyzer Calibration

The analyzer should undergo the following calibration procedures on a weekly basis, and additionally when the lamp assembly and pump tubing are replaced.

7.1 Gaseous Formaldehyde Standards

7.1.1 The most reliable means of calibrating the formaldehyde analyzer is with certified permeation tubes. Tubes prepared from alpha-polyoxymethylene should be used.
Note: The use of paraformaldehyde permeation tubes is not recommended due to their apparent unstability and lack of reproducibility.

7.1.2 For 0-5 ppm full scale using a gaseous standard of 2.5 ppm, adjust the analyzer to read 50%. A calibration curve should be prepared using concentrations of 1, 2, 3, 4 and 5 ppm. For ranges of 3 ppm or less, use standards equal to 0, 20, 40, 60, 80 and 100% of full scale. The calibration of the unit should be checked at least once a month.

7.1.3 If a suitable permeation tube is used in conjunction with an accurate controllable calibrator (CEA Instruments, SC-100, or equivalent), consistently accurate and reliable calibration of the analyzer for the analysis of HCHO can be achieved.

7.2 Liquid Formaldehyde Standards

7.2.1 As an alternate procedure, liquid standards can be prepared that can be correlated to gaseous standards.

Note: When calibrating with liquid standards, the zero gas filter must be connected. The exact weight and actual assay value of the formaldehyde solution, as well as the precise pump tube flow rate of reagent 2, must be used in all calculations.

7.2.2 The stock solution is prepared by diluting 2.4 grams of formaldehyde that is 37% by weight in water with one liter distilled water. The solution is approximately 888 mg/L. Dilute 10 mL of the stock solution to 100 mL with distilled water. Dilute 5 mL of the this solution to 100 mL with the working TCM solution. This dilution results in a liquid standard equivalent to approximately 3.6 μl (i.e., 1 μg HCHO = 0.815 μL) of formaldehyde.

Note: This solution is stable for at least three months.

7.2.3 Connect the zero gas filter to the air sample intake, and place reagent 2 line into the standard solution to be analyzed. At the 0-5 ppm range, the calibration curve is only linear up to approximately 3 ppm. The 2.5 ppm standard should be run and after equilibrium achieved, adjust the digital readout to 50% of full scale. Using the diluted stock standard solution without the TCM, dilute 8 mL to 100 mL with working TCM solution. Repeat using 10 mL. Run the above 4 and 5 ppm liquid standards and prepare a five point calibration curve using 0, 2.5, 4 and 5 ppm.

7.2.4 If the air sample flow rate (ASFR), absorption efficiency (AE), and liquid standards flow rates (LSFR) are known, a liquid standard value can be expressed in an equivalent gaseous standard for formaldehyde. The conversion formula is as follows under the stated conditions:

$$\text{Std. Concentration/ASFR} \times \text{LSFR/AE} = \text{ppm}$$

The liquid standard pump tube flow rate must be calibrated by placing a one mL Mohr pipet graduated in 0.1 mL divisions in the line between the reagent container and the pump. Lift the end of the reagent line out of solution, and allow an air bubble twice the diameter of the pipet bore to enter. Time the air bubble through the pipet and determine the exact flow rate, mL/min. Use this flow rate in calculating the equivalent gaseous standard for formaldehyde in air.

Note: Dilute standards are not stable longer than 12 hours, and should therefore be freshly prepared prior to use.

8. Using the Analyzer

Operation of the analyzer consists of the following three basic steps: 1) pumping working reagents through the system, 2) zeroing the unit, and 3) adjusting the span control. This section is provided to familiarize the operator with performing those functions.

8.1 Pumping Reagents Through System

8.1.1 Attach the zero gas filter to the sample air inlet. The filter removes interfering gases from the air and generates "zero air" for establishing a zero baseline.

8.1.2 Connect drain line to bottom of drain "tee." If desired, connect a suitable vent line from air pump.

8.1.3 Place pump tubes in position around reagent pump rollers.

8.1.4 Ensure that tubing between reagent pump, analytical module, and reagent containers is in accordance with the flow diagram provided in Figure 2.

8.1.5 Turn on power and activate air and reagent pumps. Place reagent feed lines one at a time into distilled water and observe the liquid flow within the unit. Water should not accumulate in the liquid air separator. Liquid should be pulled out of the separator faster than it is pumped into the absorber coil. Thus the tube leaving the separator should have slugs of liquid alternated with an air bubble. During start up, the liquid level in the sample cell may rise into the upper bulb portion. This is due to a blockage in the drain line from the sample cell. Pinch or clamp the tubing on top of the sample cell for a few moments and the liquid level will drop. Repeat as necessary. If the drain still fails to operate properly, check for kinks or blockages.

8.1.6 The liquid level in the sample cell should stabilize at the point where the square glass begins to flare out into the bulb portion. The level is determined by the vertical height of the drain "tee."

8.1.7 Once it is determined that all the liquid flows are normal (i.e., all pump tubes pumping, no leaks or build-ups and sample cell level is regulating), remove reagent lines from the distilled water and allow the reagent pump to pump out as much water as possible. Turn off the unit and slip the pump tubes off the pump brackets so the tubes will not kink.

8.2 Introducing Reagents and Zeroing The Unit

8.2.1 Prepare reagents 1, 2, and 3 according to Section 6.1. For convenience, reagent kits may be purchased from some manufacturers (CEA Instruments, or equivalent) that contain all necessary chemicals to prepare Reagents 1, 2, and 3.

8.2.2 If a recorder is used, zero it according to manufacturer's instructions, and attach it to the analyzer using the recorder cable supplied by the manufacturer.

8.2.3 For faster start-up, pump out as much distilled water from the system as possible. Drain any distilled water from the reference cell by removing tubing from bottom and top fittings of the cell. Allow the water to run into a paper towel or small beaker, replace tubing.

8.2.4 Perform Sections 7.2.1 to 7.2.4.

8.2.5 Place reagent feed lines into appropriate working reagents. Activate air and liquid pump(s).

8.2.6 Observe that liquid flows are normal as described in Section 6.2.

8.2.7 Attach air flowmeter and adjust flow rate according to methodology and/or calibration sheet supplied with the analyzer. Remove flowmeter and replace it with zero gas filter or other source of zero air.

8.2.8 Set span control, range, and damp switches to settings of last calibration.

8.2.9 Allow the monitor to operate on zero air for approximately 30 minutes. After the unit is stabilized, adjust zero control if necessary to give a readout of 000.

8.3 Adjusting Span Control With Gaseous Calibration Standards

8.3.1 Zero the unit as described in Section 8.2.

8.3.2 Attach source of known calibration gas to analyzer inlet.

8.3.3 The damp switch must be in the low (down) position.

8.3.4 After reading stabilizes, adjust span control to give appropriate digital readout. Adjust range switch to standard (up) position or low level range (down) position as required. Example: To calibrate the instrument for 0-2 ppm full scale with a calibration gas of 1.5 ppm, adjust the span so that the readout is 075 (i.e., 75% of full scale).

8.3.5 Remove the calibration gas and replace the zero gas filter. Unit will return to zero.

8.3.6 Return damp switch to normal operating position.

9. Formaldehyde Sampling and Analysis

9.1 Indoor Air Monitoring

After the unit has been zeroed and the span adjusted, remove the zero gas filter. The analyzer is now monitoring the indoor air for formaldehyde.

9.2 Range Changing

Details for changing the measurement range of the various gas parameters are provided with the manufacturer's operating instructions. Generally, there are two ways to change the range: 1) by recalibration with a different gas or liquid standard or 2) by changing the electronic sensitivity and/or sample air flow rate. This second method is useful for a quick range change.

9.3 Shutdown Procedure

9.3.1 Place all reagent lines into distilled water.

9.3.2 Operate monitor until liquid leaving via drain is clear (15-30 minutes). If necessary, flush out system with appropriate cleaning solution per manufacturer's instructions.

9.3.3 Remove all reagent lines from distilled water and run monitor until all possible liquid has been pumped out (15-30 minutes).

9.3.4 Set monitor power and pump power switches to off.

9.3.5 Slip pump tube fittings off the metal slots to relax the pump tubes.

9.3.6 If desired, disconnect electrical and pumping connections at monitor. (External 115-volt AC source should be left connected with DC power switch in "down" position if internal battery is to be recharged.)

10. Analyzer Maintenance

The analyzer is designed for continuous, long-term operation with a minimum of maintenance. Periodic inspection of sample cell and glassware for a build-up of foreign materials is necessary. Solutions should be replenished as required. Daily baseline and calibration indications should be noted and adjusted as necessary. If excessive variation occurs, consult the manufacturer's troubleshooting guide. Care must be taken not to scratch the glass surfaces of the cells, or spill liquid into the sensing block. Reagents must never be allowed to evaporate or dry out within the system. On any shutdown lasting more than a few hours, the unit must be flushed with distilled water. Typical performance specifications of the monitor are provided in Table 1.

10.1 Daily Maintenance

The following should be performed on a daily basis for successful operation of the monitor:

- check instrument air flow and adjust if necessary
- check zero baseline
- check reagent supply and replenish if necessary

10.2 Periodic Maintenance

The following should be performed on a periodic basis for continued proper operation of the monitor:

- perform optical zero per Section 8.2
- perform dynamic calibrations per Section 8.3
- replace peristaltic pump tubes after 30 days of use
- replace lamp assembly
- clean flow cells

10.3 Instrument Cleaning

To clean the analyzer, place all reagent lines in distilled water. Run monitor for at least 30 minutes. Replace distilled water with 1N nitric acid (i.e., conc. HNO_3 cut 10:1 with distilled water). Allow unit to run for one to two hours only. Flush unit for at least one hour with distilled water.

11. Performance Criteria and Quality Assurance

11.1 Users should generate Standard Operating Procedures (SOPs) describing the following activities in their laboratory: 1) assembly, calibration, and operation of the sampling system, with make, and model of equipment used, 2) preparation, purification, storage, and handling of sampling reagent and samples, 3) assembly, calibration, and operation of the HPLC

system, with make and model of equipment used, and 4) all aspects of data recording and processing, including lists of computer hardware and software used.

11.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

12. References

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Table 1. Typical Performance Specifications for Formaldehyde Analyzer

Standard Range:	0-5 ppm
Low Level Range:	0-250 ppb (adjustable from 0-0.25 ppm full scale or 1% of full scale)
Reproducibility:	1%
Minimum Detection:	0.003 ppm (3 ppb) at 0-0.25 ppm full scale or 1% of full scale
Nonlinearity:	Less than 2% up to 2.5 ppm
Zero Drift:	Less than 2% per 24 hours
Span Drift:	Less than 2% per 24 hours
Air Flow Drift:	Less than 1% per 24 hours
Zero Noise:	± 0.3%
Lag Time:	4-1/2 minutes (8-1/2 minutes with double coil)
Rise Time:	(90%) 4-1/2 minutes
Fall Time:	(90%) 4-1/2 minutes
Air Sample Flow Rate:	0.5 liters per minute
Optimum Temperature Range:	60° to 80°F. Usable at 40° to 120°F.
Relative Humidity Range:	5 to 95%

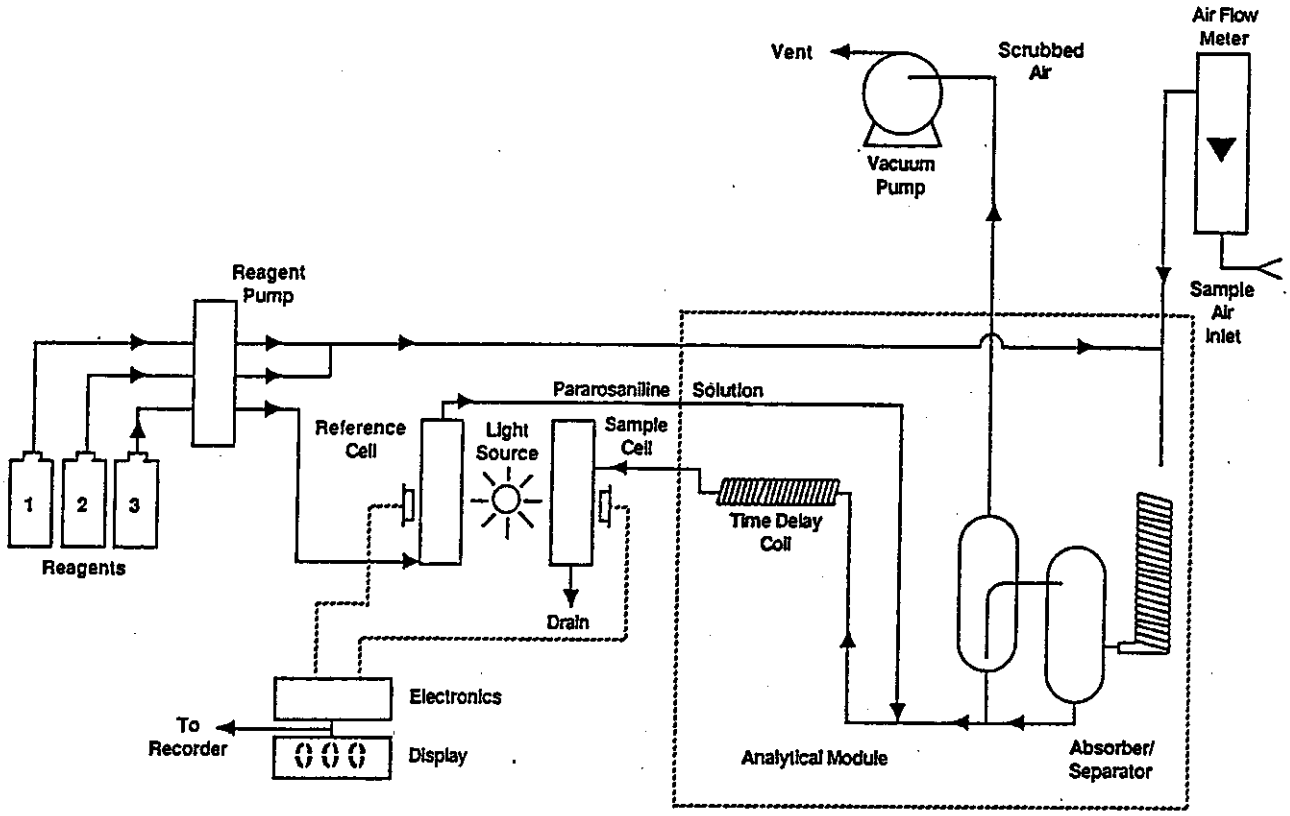

Figure 1. Flow Diagram of Formaldehyde Analyzer

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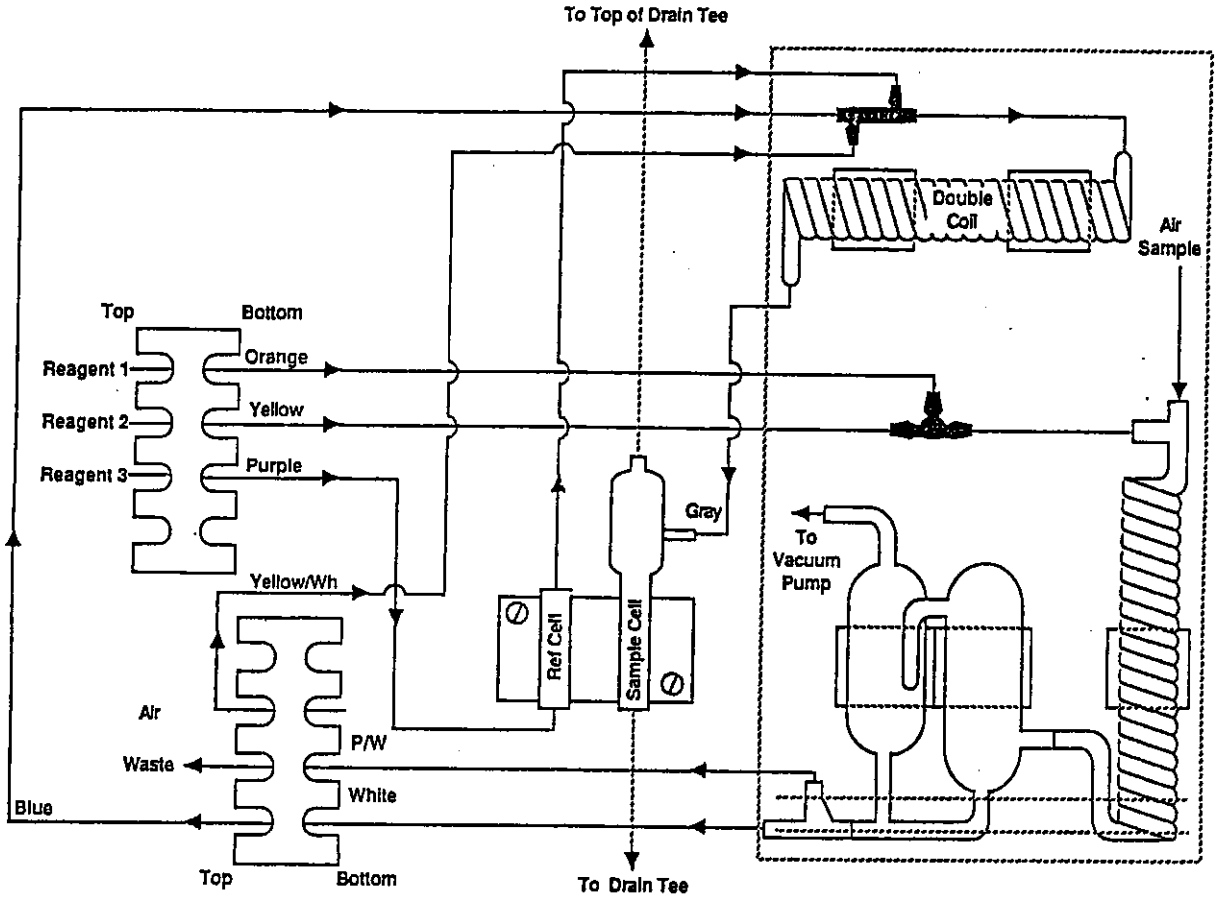

Figure 2. Flow Diagram of Reagents Through Analyzer

Method IP-6C

DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES IN INDOOR AIR USING PASSIVE SAMPLING DEVICE

Method IP-6C

DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES IN INDOOR AIR USING PASSIVE SAMPLING DEVICE

1. Scope

1.1 In the past, active sampling devices have been the method of choice for the collection of formaldehyde (CH_2O) in indoor air. Active sampling devices are flowthrough devices that require a mechanical means (pump) to move the sample to the collection medium. More specifically, Compendium Method IP-6A describes a solid adsorbent procedure wherein 2,4-dinitrophenylhydrazine (DNPH) is impregnated on commercially purchased Sep-PAK® silica gel cartridges to capture formaldehyde and other aldehydes during active sampling. After exposure to the indoor air, the cartridges are returned to the laboratory for analysis utilizing high performance liquid chromatography (HPLC) analysis. These solvent free sampling methods constitute a greater improvement over the impinger techniques (1-5). Likewise, Compendium Method IP-6B utilizes a real time monitor for detecting formaldehyde in indoor air.

1.2 In recent years (6-10) interest has been increasing in the use of diffusion-based passive sampling devices (PSDs) for the collection of formaldehyde in indoor air. PSDs are more attractive for indoor air because of their characteristics of small size, quiet operation (no pump), and low unit cost. Diffusion sampling has been recognized as an efficient alternative to pump based sampling.

1.3 Most importantly, epidemiologists believe that to determine health effects of aldehydes on humans, the sampler must be either worn by people or be in close proximity to where people spend most of their time indoors.

1.4 Since most people do not wish to carry noisy pump samplers on their person or have them near their work, sleep, eat or play areas, passive samplers are ideal for personal monitoring.

1.5 In recent years several diffusion samplers for formaldehyde have been extensively validated for occupational monitoring in the Threshold Limit Value (TLV) range (11). The DuPont Pro-TeK Badge (12), the 3-M (13) Formaldehyde Monitor 3750/51, the modified Palmes (14) tube and the Air Quality Research PF-20 passive workplace monitors have all been widely used in occupational monitoring. The National Institute of Occupational Health has recently completed studies involving a simplified diffusion sampler for detecting formaldehyde (15-16).

1.6 Since most diffusion samplers have low sampling rates, sampling times of five to ten days or more are needed to quantitatively detect formaldehyde below the 0.1 ppm level. Consequently, a more sensitive diffusion method is needed to measure formaldehyde levels over a shorter period, typically a few hours.

1.7 To address the sensitivity issue, the USEPA has developed a passive sampling device for monitoring indoor levels of formaldehyde (17).

2. Summary of Method

2.1 The passive sampling method involves loading 2,4-dinitrophenylhydrazine on glass fiber filters and placing them behind sets of diffusion barriers on each side of a containment cavity of a PSD.

2.2 Formaldehyde and other aldehydes diffuse to the PSD sampler and react specifically with the DNPH treated filters in the presence of an acid to form a stable DNPH-derivative according to Ficks first law of diffusion:

$$M = D\,(A/L)\,(C_\infty - C_0)$$

where:
M = mass flow, cm^3/min
D = diffusion coefficient, cm^2/min
A = cross sectional area of diffusion channel, cm^2
L = length of diffusion channel, cm
C_∞ = concentration of formaldehyde in air surrounding the PSD
C_0 = concentration of formaldehyde at surface of the treated filter

2.3 After sampling is complete, the PSD sampler is capped, returned to the laboratory, disassembled under a nitrogen blanket, extracted with acetonitrile and analyzed by high performance liquid chromatography (HPLC).

2.4 Recent field studies (17) involving "Sick Building Syndrome (SBS)" have compared the PSD method (Compendium IP-6C) with the established pump-based DNPH-coated Sep-Pak® method (Compendium IP-6A). The results of the collocated samplers are shown in Table 1. The agreement between the two sampling methods was shown to be good, and the PSDs were found to be more convenient to use and less obtrusive than the pumped-based samplers.

3. Significance and Use

3.1 Since the analysis of the indoor environment is influenced by many factors except the method of sampling, an effort should be made to minimize interfering factors and maintain air at normal conditions in the vicinity of the passive monitor.

3.2 Passive detection provides for time-integrated measurements. Passive monitors are usually placed in an indoor environment over a sampling period of from 3 days to 1 year. Due to the length of time involved with sampling, interfering factors should be anticipated and eliminated where possible.

3.3 Placement and recovery of the monitors can be performed by unskilled personnel with suitable instruction (even an occupant). Appendix C-3 of this compendium contains guidance on procedures for placement of stationary passive monitors in the indoor environment.

4. Equipment

4.1 Passive sampling device (PSD) - Scientific Instrumentation Specialists, P.O. Box 8941, Moscow, ID, 83843, (see Figure 1).

4.2 Treated glass fiber filters - Whatman GF/B Glass Microfibre®, Whatman Inc., 9 Bridgwell Place, Clifton, NJ, 07014.

5. Reagents and Materials

5.1 2,4-Dinitrophenylhydrazine (DNPH)- Aldrich Chemical or J.T. Baker, reagent grade or equivalent. Recrystallize at least twice with UV grade acetonitrile before use.

5.2 Acetonitrile - UV grade, Burdick and Jackson "distilled in glass," or equivalent.

5.3 Deionized-distilled water - charcoal filtered.

5.4 Perchloric Acid - analytical grade, best source.

5.5 Hydrochloric acid - analytical grade, best source.

5.6 Formaldehyde - analytical grade, best source.

5.7 Aldehydes and ketones - analytical grade, best source, used for preparation of DNPH derivative standards (optional).

5.8 Ethanol or methanol - analytical grade, best source.

5.9 Nitrogen - high purity grade, best source.

5.10 Charcoal - granular, best source.

5.11 Helium - high purity grade, best source.

6. Preparation, Purification and Application of Glass Fiber Filters

6.1 Filter Preparation

6.1.1 Upon receipt of the 8"x10" filter paper, inspect surfaces for soiling and abrasions.

6.1.2 Place the filter sheet on a marble slab.

6.1.3 Using a wooden mallet and a 33-mm circular diameter stainless steel die, cut the desired number of filters needed for completion of the project objectives.

Note: One can purchase commercially available 37 mm Whatman GF/B Microfibre filter and cut to the 33 mm size.

6.1.4 To prepare the filters for treatment, place five at a time in a Büchner funnel and rinse with five 100 mL volumes of charcoal-filtered deionized water.

6.1.5 Remove the filters from the funnel and place in a vacuum oven at 60°C for 1 hour.

6.1.6 After drying, remove from the oven and store in a desiccator containing anhydrous calcium sulfate until cooled to room temperature.

6.2 Filter Treatment

Note: Formaldehyde contamination of the DNPH reagent is a frequently encountered problem. The DNPH must be purified by multiple recrystallizations in UV grade acetonitrile. Recrystallization is accomplished at 40-60°C by slow evaporation of the solvent to maximize crystal size. The purified DNPH crystals are stored under UV grade acetonitrile until use. Impurity levels of carbonyl compounds in the DNPH are determined by HPLC prior to use and should be less than 0.025 mg/mL.

6.2.1 Remove five clean filters from the desiccator and place in a glove box under a nitrogen atmosphere.

6.2.2 Using a syringe add 0.5 mL of the purified (recrystallized) 2,4-dinitrophenylhydrazine to the center of each filter.

6.2.3 Allow to equilibrate in the nitrogen atmosphere for 40 minutes. This will allow the solution to diffuse completely throughout the filter.

6.2.4 After 40 minutes, remove from the glove box, place in a vacuum desiccator and dry at room temperature (23°C) and 0.5 kPa for an additional 40 minutes.

6.2.5 After vacuum drying, place the filters in a sealed glass Petrie dish and store under activated charcoal in metal cans with compression-sealed lids (paint cans) until use.

6.3 Purification of 2,4- Dinitrophenylhydrazine (DNPH)

Note: This procedure should be performed under a properly ventilated hood.

6.3.1 Prepare a supersaturated solution of DNPH by boiling excess DNPH in 200 mL of acetonitrile for approximately one hour.

6.3.2 After one hour, remove and transfer the supernatant to a covered beaker on a hot plate and allow gradual cooling to 40-60°C.

6.3.3 Maintain the solution at this temperature (40-60°C) until 95% of solvent has evaporated.

6.3.4 Decant solution to waste, and rinse crystals twice with three times their apparent volume of acetonitrile.

Note: Various health effects result from the inhalation of acetonitrile. At 500 ppm in air, brief inhalation has produced nose and throat irritation. At 160 ppm, inhalation for 4 hours has caused flushing of the face (2 hour delay after exposure) and bronchial tightness (5 hour delay). Heavier exposures have produced systemic effects with symptoms ranging from headache, nausea, and lassitude to vomiting, chest or abdominal pain, respiratory depression, extreme weakness, stupor, convulsions and death (dependent upon concentration and time).

6.3.5 Transfer crystals to another clean beaker, add 200 mL of acetonitrile, heat to boiling, and again let crystals grow slowly at 40-60°C until 95% of the solvent has evaporated.

6.3.6 Repeat rinsing process as described in Section 6.3.4.

6.3.7 Take an aliquot of the second rinse, dilute 10 times with acetonitrile, acidify with 1 mL of 3.8 M perchloric acid per 100 mL of DNPH solution,and analyze by HPLC.

6.3.8 The chromatogram illustrated in Figure 2 represents an acceptable impurity level of <0.025 μg/mL of formaldehyde in recrystallized DNPH reagent. If the impurity level is not acceptable for intended sampling application, repeat recrystallization.

6.3.9 Transfer the purified crystals to an all-glass reagent bottle, stopper, shake gently, and let stand overnight. Analyze supernatant by HPLC according to Section 9. The impurity level should be comparable to that shown in Figure 2.

6.3.10 If the impurity level is not satisfactory, pipet off the solution to waste, then add 25 mL of acetonitrile to the purified crystals. Rinsing should be repeated with 20 mL portions of acetonitrile until a satisfactorily low impurity level in the supernatant is confirmed by HPLC analysis. An impurity level of 40.025 mg/mL formaldehyde should be achieved, as illustrated in Figure 2.

6.3.11 If the impurity level is satisfactory, add another 25 mL of acetonitrile, stopper and shake the reagent bottle, then set aside. The saturated solution above the purified crystals is the stock DNPH reagent.

6.3.12 Maintain only a minimum volume of saturated solution adequate for day to day operation. This will minimize waste of purified reagent should it ever become necessary to re-rinse the crystals to decrease the level of impurity for applications requiring more stringent purity specifications.

6.3.13 Use clean pipets when removing saturated DNPH stock solution for any analytical applications. Do not pour the stock solution from the reagent bottle.

6.4 Preparation of DNPH-Formaldehyde Derivative

6.4.1 Titrate a saturated solution of DNPH in 2N HCl with formaldehyde (other aldehydes or ketones may be used if their detection is desired).

6.4.2 Filter the colored precipitate, wash with 2N HCl and water, and allow precipitate to air dry.

6.4.3 Check the purity of the DNPH-formaldehyde derivative by melting point determination or HPLC analysis. If the impurity level is not acceptable, recrystallize the derivative in ethanol. Repeat purity check and recrystallization as necessary until acceptable level of purity (e.g., 99%) is achieved.

6.5 Preparation of DNPH-Formaldehyde Standards

6.5.1 Prepare a standard stock solution of the DNPH-formaldehyde derivative by dissolving accurately weighed amounts in acetonitrile.

6.5.2 Prepare a working calibration standard mix from the standard stock solution. The concentration of the DNPH-formaldehyde compound in the standard mix solutions should be adjusted to reflect relative distribution in a real sample.

Note: Individual stock solutions of approximately 100 mg/L are prepared by dissolving 10 mg of the solid derivative in 100 mL of acetonitrile. The individual solution is used to prepare calibration standards containing the derivative of interest at concentrations of 0.5-20 ug/L, which spans the concentration of interest for most indoor air work.

6.5.3 Store all standard solutions in a refrigerator. They should be stable for several months.

7. Personal Sampling Device (PSD) Assembly

7.1 The PSD is a dual-faced sampler made up from a series of diffusion barriers placed on either side of a cavity, as illustrated in Figure 3. This PSD is 3.8 cm in diameter, 1.2 cm in depth and weighs 36 grams.

7.1.1 With the aid of a glove box with a flow of nitrogen, remove the treated 2,4-dinitrophenylhydrazine filter papers from the Petrie dish and place behind each set of diffusion barriers of the PSD.

7.1.2 Reassemble the PSD, attach the protecting caps and place in small (0.5 pt) can.

7.2 For further protection from exposure, place the small cans into a large (1 gal.) can containing activated charcoal until use.

8. Sampling Procedures

8.1 Take the PSD out of its protective shipping can and label properly with the start date, time and sampling location identification.

8.2 Place the PSD in the appropriate area to be sampled.
Note: Representative sampling must be considered; therefore, placement of the PSD should be determined with considerable planning.

8.3 Appropriate time and placement of the PSD should follow the following guidelines:

8.3.1 Avoid sampling when seasonal alterations in insulation or building tightness are occurring or will occur during the sampling period.

8.3.2 Avoid sampling if remodeling or redecorating is occurring. During the sampling period there should be no changes in furnishings or appliances such as: carpeting, stoves, HVAC systems, etc.

8.3.3 Open and close doors in a usual manner and keep windows closed if possible.

8.3.4 Ventilation should not be altered in any way during sampling.

8.3.5 Air Conditioning and heating should not be altered from normal use.

8.3.6 Humidifiers and dehumidifiers should not be used where sampling is being performed.

8.3.7 Normal occupancy and activity should continue.

8.3.8 The placement of the sampler should not obstruct normal occupancy or activity.

8.3.9 Avoid locations near sinks, tubs, showers, washers.

8.3.10 Avoid locations near heating elements such as: direct sunlight, furnaces, electric lights or electrically operated devices.

8.3.11 Avoid locations where a known draft or pressure differential occurs areas near furnace vents, HVAC intake/exhaust, computer cooling fans and appliance fans.

8.4 Placement of the sampler should ideally be at least 8 inches below the ceiling, 20 inches above the floor and 6 inches from a wall.
Note: Outside walls should not be used, and suspension from the ceiling may be suitable.

8.5 Remove the caps from the PSD. Sampling commences immediately. Place sampler at predetermined location. Fill out needed information on Field Test Data Sheet.

8.6 Re-cap the PSD when the sampling time is complete.

8.7 Record the final time and date on the PSD label and the Field Test Data Sheet. Store the PSD in a 1 gallon can containing activated charcoal at room temperature until analysis is performed.

9. Sample Analysis

9.1 Sample Preparation

9.1.1 After exposure, the PSDs are returned to the lab in the labeled cans containing activated charcoal.

9.1.2 Under a nitrogen blanket in a glove box, remove the PSD's from the can and disassemble the filter cassette.

9.1.3 Place the exposed filters in a 35 mL screw-capped polypropylene bottle.

9.1.4 Add 5 mL of acetonitrile to the bottle, tightly cap and place in a sonification bath at room temperature for 30 minutes.

9.1.5 At the end of 30 minutes, remove the polypropylene bottle from the sonification bath, filter the anion extract through a Gelman Acrodisc® disposable filter assembly into a 5 mL volumetric flask. Dilute to the 5 mL mark with acetonitrile. Label the flask with sample identification. Pipet two aliquots into sample vials with Teflon-lined septa. Analyze the first aliquot for the derivative carbonyls by HPLC. Store the second aliquot in the refrigerator until sample analysis.

9.2 High Pressure Liquid Chromotography (HPLC) Analysis

9.2.1 The HPLC system is assembled and calibrated as described in Section 11.3 of Compendium Method IP-6A. Before each analysis, the detector baseline is checked to ensure stable conditions. The operating parameters are as follows:

Column - Zorbax ODS (4.6 mm inner diameter 25 cm), or equivalent
Mobile Phase - 60% acetonitrile/40% water, isocratic
Detector - Ultraviolet, operating at 360 nm
Flow Rate - 1.0 mL/min
Retention Time - Seven minutes for formaldehyde with one Zorbax ODS column. Thirteen minutes for formaldehyde with two Zorbax ODS columns
Sample Injection Volume - 25 μL

9.2.2 The HPLC mobile phase is prepared according to Section 11.3.2 of Compendium Method IP-6A, pump-based Sep-PAK DNPH-coated cartridge procedure.

9.2.3 The mobile phase is placed in the HPLC solvent reservoir and the pump is set at a flow rate of 1.0 mL/min and allowed to pump for 20-30 minutes before the first analysis. The detector is switched on at least 30 minutes before the first analysis, and the detector output is displayed on a strip chart recorder or similar output device.

9.2.4 A 100-µL aliquot of the sample is drawn into a clean HPLC injection syringe. The sample injection loop (25 µL) is loaded and an injection is made. The data system, if available, is activated simultaneously with the injection, and the point of injection is marked on the strip chart recorder.

9.2.5 After approximately one minute, the injection valve is returned to the "inject" position and the syringe and valve are rinsed or flushed with acetonitrile/water mixture in preparation for the next sample analysis.

Note: The flush/rinse solvent should not pass through the sample loop during flushing. The loop is clean while the valve is in the "inject" mode.

9.2.6 After elution of the DNPH-formaldehyde derivative, data acquisition is terminated and the component concentrations are calculated as described in Section 10.

9.2.7 After a stable baseline is achieved, the system can be used for further sample as described above.

Note: After several PSD analyses, buildup on the column may be removed by flushing with several column volumes of 100% acetonitrile.

9.2.8 If the concentration of analyte exceeds the linear range of the instrument, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

9.2.9 If the retention time is not duplicated (±10%), as determined by the calibration curve, the acetonitrile/water ratio may be increased or decreased to obtain the correct elution time. If the elution time is too long, increase the ratio; if it is too short, decrease the ratio.

Note: The chromatographic conditions described here have been optimized for the detection of formaldehyde. Analysts are advised to experiment with their HPLC system to optimize chromatographic conditions for their particular analytical needs.

9.3 HPLC Calibration

9.3.1 Calibration standards are prepared in acetonitrile from the DNPH-formaldehyde derivative. Individual stock solutions of 100 mg/L are prepared by dissolving 10 mg of solid derivative in 100 mL of mobile phase. These individual solutions are used to prepare calibration standards at concentrations spanning the range of interest.

9.3.2 Each calibration standard (at least five levels) is analyzed three times and area response is tabulated against mass injected. All calibration runs are performed as described for sample analyses in Section 9.2. Using the UV detector, a linear response range of approximately 0.05-20 µg/L should be achieved for 25-µL injection volumes. The results may be used to prepare a calibration curve. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (concentration versus area response) is obtained. The retention times for each analyte should agree within 2%.

9.3.3 Once linear response has been documented, an intermediate concentration standard near the anticipated levels of each component, but at least 10 times the detection limit, should be chosen for daily calibration. The day to day response for the various components should be within 10% for analyte concentrations 1 µg/mL or greater and within

15-20% for analyte concentrations near 0.5 μg/mL. If greater variability is observed, recalibratiion may be required or a new calibration curve must be developed from fresh standards.

9.3.4 The response for each component in the daily calibration standard is used to calculate a response factor according to the following equation:

$$RF^c = (C_c \times V_I)/R_c$$

where:

RF_c = response factor (usually area counts) for the component of interest, nanogram injected/response unit
C_c = concentration of analyte in the daily calibration standard, mg/L
V_I = volume of calibration standard injected, μL
R_c = response for analyte in the calibration standard, area counts

10. Calculations

10.1 The total mass of analyte (DNPH-formaldehyde) is calculated for each sample using the following equation:

$$W_d = RF_c \times R_d \times (V_E/V_I)$$

where:

W_d = total quantity of analyte in the sample, μg
RF_c = response factor calculated in Section 9.3.4
R_d = response for analyte in sample extract, blank corrected, (area counts or other response units)
$= [(A_s)\ (V_D/V_A) - (A_b)(V_b/V_s)]$

where:

A_s = area counts, sample
A_b = area counts, blank
V_b = volume, blank, mL
V_s = volume, sample, mL
V_D = redilution volume (if sample was rediluted)
V_A = aliquot used for redilution (if sample was rediluted)
V_E = final volume of sample extract, mL
V_I = volume of extract injected into the HPLC system, μL

10.2 The concentration of formaldehyde in the original sample is calculated from the following equation:

$$C_A = W_d/[V_m \text{ (or } V_s)] \times 1000$$

where:

C_A = concentration of analyte in the original sample, ng/L
W_d = total quantity of analyte in sample, blank corrected, μg

V_m = total sample volume under ambient conditions*, L
V_s = total sample volume at 25°C and 760 mm Hg, L
* Based on sampling rate of 103 cm^3/min.
The analyte concentrations can be converted to ppbv using the following equation:

$$C_A \text{ (ppbv)} = C_A \text{ (ng/L)} \times (24.4/MW_A)$$

where:
C_A(ppbv) = concentration of analyte in parts per billion by volume. C_A (ng/L) is calculated using V_s.
MW_A = molecular weight of analyte

11. Performance Criteria and Quality Assurance

Note: This section summarizes required quality assurance measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

11.1 Standard Operating Procedures (SOPs)

11.1.1 Users should generate SOPs describing the following activities in their laboratory: 1) assembly, calibration and operation of the sampling system, with make and model of equipment used; 2) preparation, purification, storage, and handling of sampling reagent and samples; 3) assembly, calibration, and operation of the HPLC system, with make and model of equipment used; and 4) all aspects of data recording and processing, including lists of computer hardware and software used.

11.1.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

11.2 HPLC System Performance

11.2.1 The general appearance of the HPLC system should be similar to that illustrated in Figure 4.

11.2.2 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54 \, (t_r/W_{1/2})^2 \times 1000$$

where:
N = column efficiency (theoretical plates)
t_r = retention time of analyte, seconds
$W_{1/2}$ =width of component peak at half height, seconds. A column efficiency of >5,000 theoretical plates should be obtained.

11.2.3 Precision of response for replicate HPLC injections should be ±10% or less day to day, for analyte calibration standards at 1 µg/mL or greater levels. At 0.5 µg/mL level and below, precision of replicate analyses could vary up to 25%. Precision of retention times should be ±2% on a given day.

11.3 Process Blanks

11.3.1 At least one field blank or 10% of the field samples, whichever is larger, should be shipped and analyzed with each group of samples. The number of samples within a group and/or time frame should be recorded so that a specified percentage of blanks is obtained for a given number of field samples.

11.3.2 The field blank is not opened in the field, but is otherwise treated identically to the samples. The performance criteria described in Section 6.3 should be met for process blanks.

11.4 Method Precision and Accuracy

11.4.1 At least one duplicate sample or 10% of the field samples, whichever is larger, should be collected during each sampling episode. Precision for field replication should be ±20% or better.

11.4.2 Precision for replicate HPLC injections should be ±10% or better, day to day, for calibration standards.

11.4.3 At least one sample spike with analyte of interest or 10% of the field samples, whichever is larger, should be collected.

11.4.4 Before initial use of the method, each laboratory should generate triplicate spiked samples at a minimum of three concentration levels, bracketing the range of interest for each compound. Triplicate nonspiked samples must also be processed. Spike recoveries of >80 ± 10% and blank levels as outlined in Section 6.3 should be achieved.

12. Detection of other Aldehydes and Ketones

Note: The procedure outlined above has been written specifically for the sampling and analysis of formaldehyde in ambient air using PSDs followed by HPLC analysis. Indoor air contains other aldehydes and ketones. Optimizing chromatographic conditions by using two Zorbax ODS columns in series and varying the mobile phase composition through a gradient program will enable the analysis of other aldehydes and ketones. However, the extended analytical finish discussed here and as part of Compendium Method IP-6A, Section 14, has not been fully investigated using the PSD, but has using the Sep-Pak® adsorbent cartridge.

12.1 Sampling Procedures

The sampling procedure for other aldehydes and ketones is the same as in Section 8.

12.2 HPLC Analysis

12.2.1 The HPLC system is assembled and calibrated as described in Section 9.3. The operating parameters are as follows:

Column - Zorbax ODS, two columns in series
Mobile Phase - Acetonitrile/water, linear gradient
Detector - Ultraviolet, operating at 360 nm
Flow Rate - 1.0 mL/min

Sample Injection Vol. - 25 µL
Step 1 - 60-75% acetonitrile/40-25% water in 30 minutes
Step 2 - 75-100% acetonitrile/25-0% water in 20 minutes
Step 3 - 100% acetonitrile for 5 minutes
Step 4 - 60% acetonitrile/40% water reverse gradient in 1 minute
Step 5 - 60% acetonitrile/40% water, isocratic for 15 minutes

12.2.2 The gradient program allows for optimization of chromatographic conditions to separate acrolein, acetone, propionaldehyde, and other higher molecular weight aldehydes and ketones in an analysis time of about one hour.

12.2.3 The chromatographic conditions described herein have been optimized for a gradient HPLC (Varian Model 5000) system with a UV detector (ISCO Model 1840 variable wavelength), an automatic sampler with a 25-µL loop injector and two DuPont Zorbax ODS columns (4.6 x 250 mm), a recorder, and an electronic integrator. Analysts are advised to experiment with their HPLC systems to optimize chromatographic conditions for their particular analytical needs. Highest chromatographic resolution and sensitivity are desirable but may not be achieved. The separation of acrolein, acetone, and propionaldehyde should be a minimum goal of the optimization.

12.2.4 The carbonyl compounds in the sample are identified and quantified by comparing their retention times and area counts with those of standard DNPH derivatives. Formaldehyde, acetaldehyde, acetone, propionaldehyde, crotonaldehyde, and o-, m-, p-tolualdehydes can be identified with a high degree of confidence. The identification of butyraldehyde is less certain because it coelutes with isobutyraldehyde and methyl ethyl ketone under the stated chromatographic conditions. Figure 5 illustrates the chromatogram utilizing this system.

13. Evaluation of the Formaldehyde-PSD System

13.1 In a recent incident of "Sick Building Syndrome (SBS)," an indoor air quality study was completed for samples and analysis of formaldehyde. In the study, formaldehyde PSDs were placed next to the established Sep-PAK® DNPH-coated cartridges (17).

13.2 The results of the collected samples are illustrated in Table 1. The agreement between the two sampling methods was shown to be good, and the PSD were found to be more convenient than the pump-based Sep-PAK® DNPH-coated cartridges.
Note: Outdoor measurements are given for reference.

13.3 The formaldehyde levels determined were not atypical for older office buildings.

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Table 1. Comparative Study of the PSD Sampler With the Active Sep-PAK® Cartridge Sampler

Concentration[3], $\mu g/m^3$

		Day 1		Day 2	
Office	Method	0700- 1900	1900- 0700	0700- 1900	Mean
1	PSD[1]	21.2, 27.2[4]	38.4, 38.4	--	29.8
	Sep-PAK®[2]	32.8, 33.2	38.8, 41.0	28.7	33.7
2	PSD	22.0	28.6	22.0	24.2
	Sep-PAK®	24.5	31.8	19.9	25.4
3	PSD	25.5	29.1	30.8	28.5
	Sep-PAK®	26.6	31.8	30.6	29.2
4	PSD	20.4	30.6	22.4	24.4
	Sep-PAK®	28.2	--	26.2	27.2
Outdoors, roof	Sep-PAK®	4.2	4.9	1.8	3.6

[1] Compendium Method IP-6A
[2] Compendium Method IP-6C
[3] Average room temperature of 25°C
[4] Paired values represent collocated samples

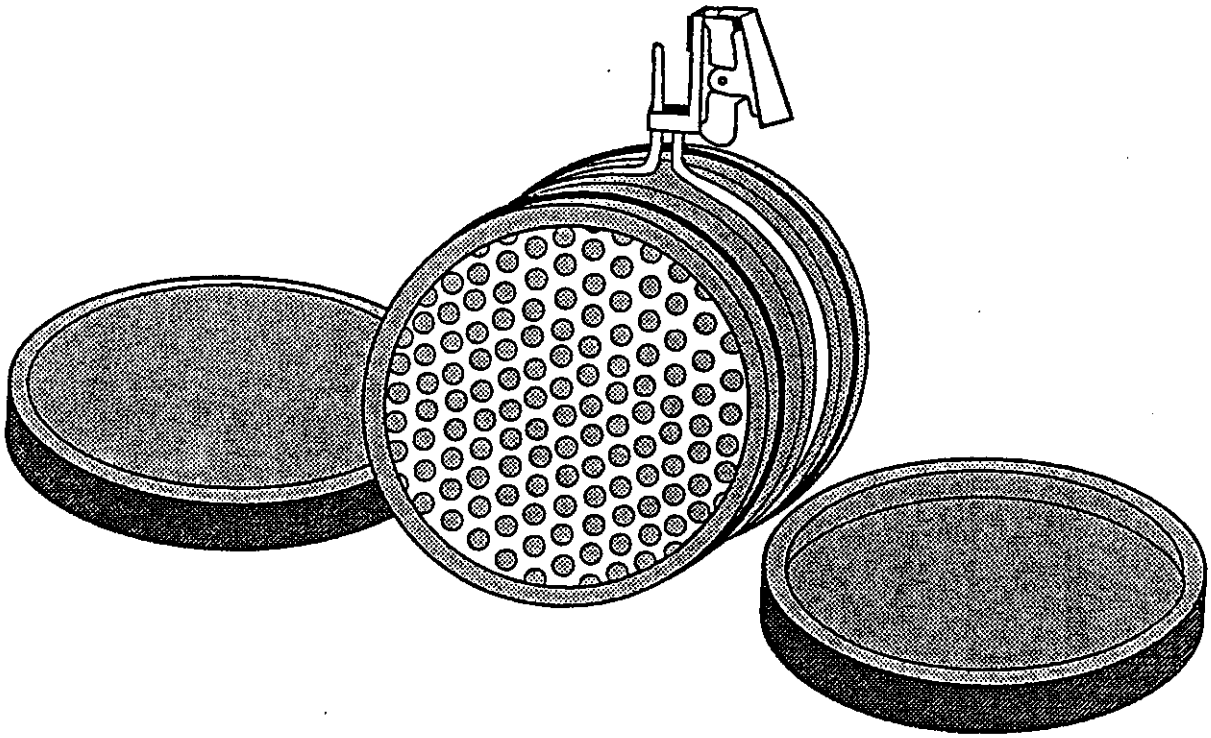

Figure 1. Passive Sampling Device (PSD) for Monitoring Formaldehyde

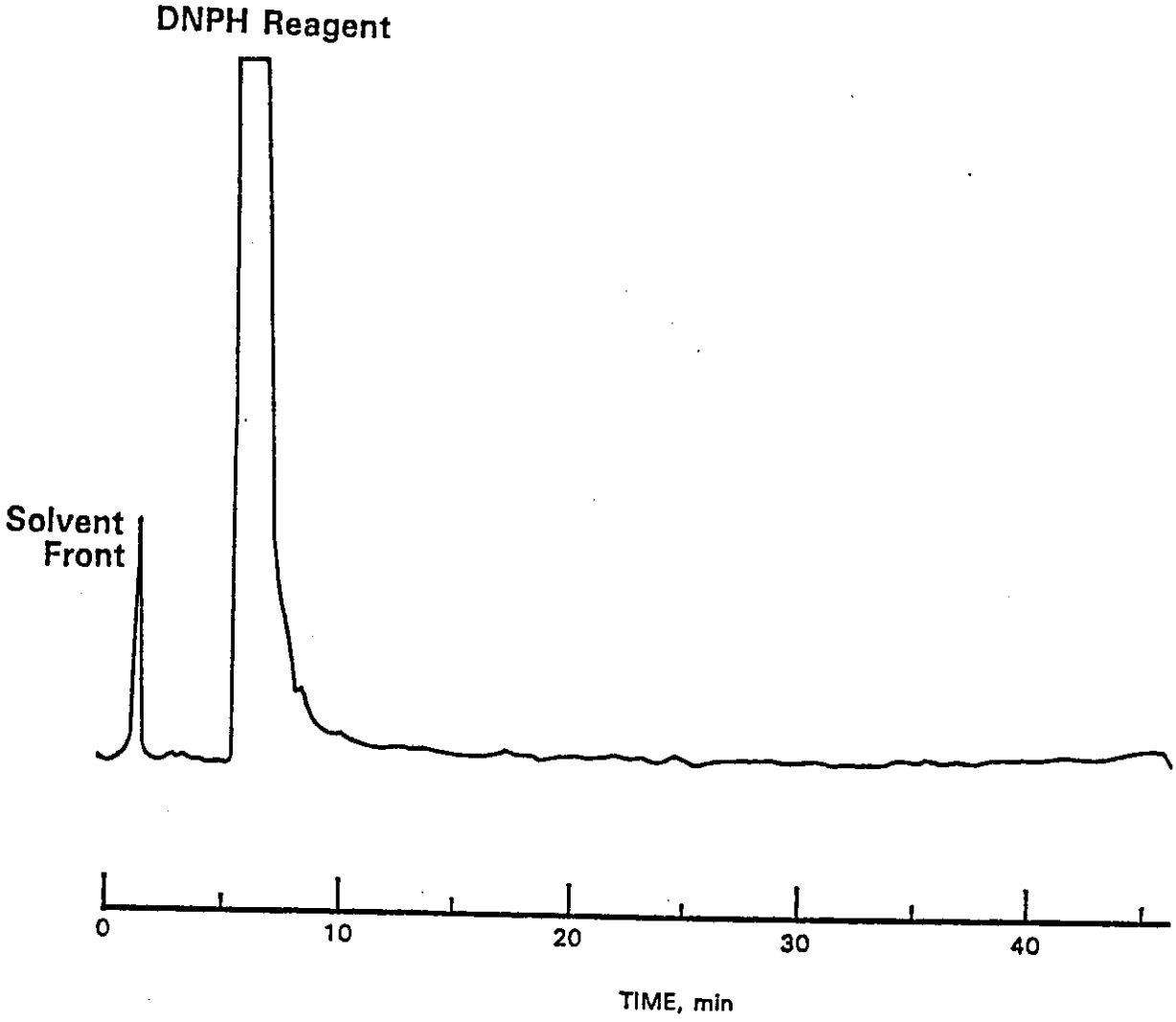

Figure 2. Impurity Level of DNPH After Recrystallization

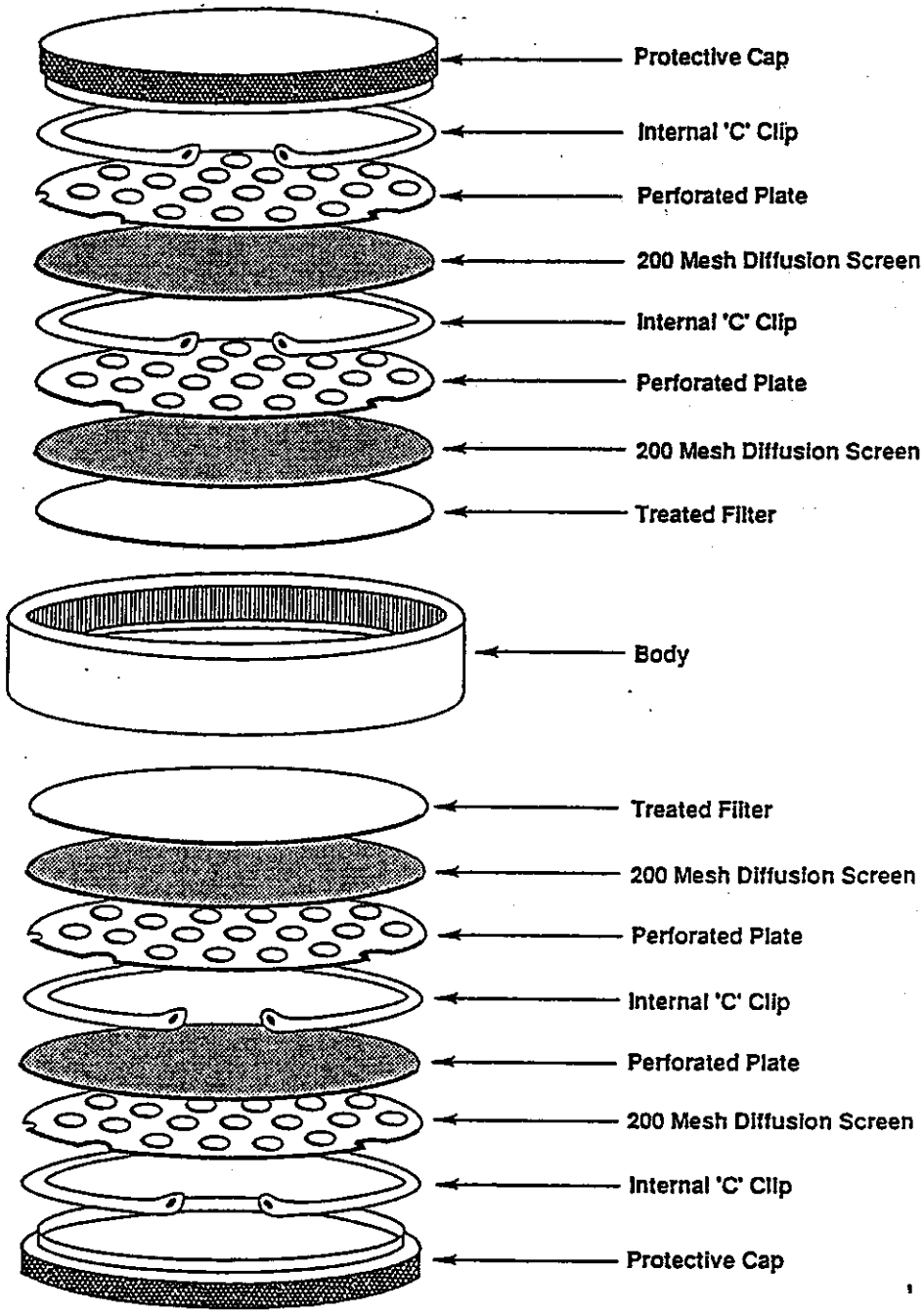

Figure 3. Exploded View of the Passive Sampling Device (PSD)

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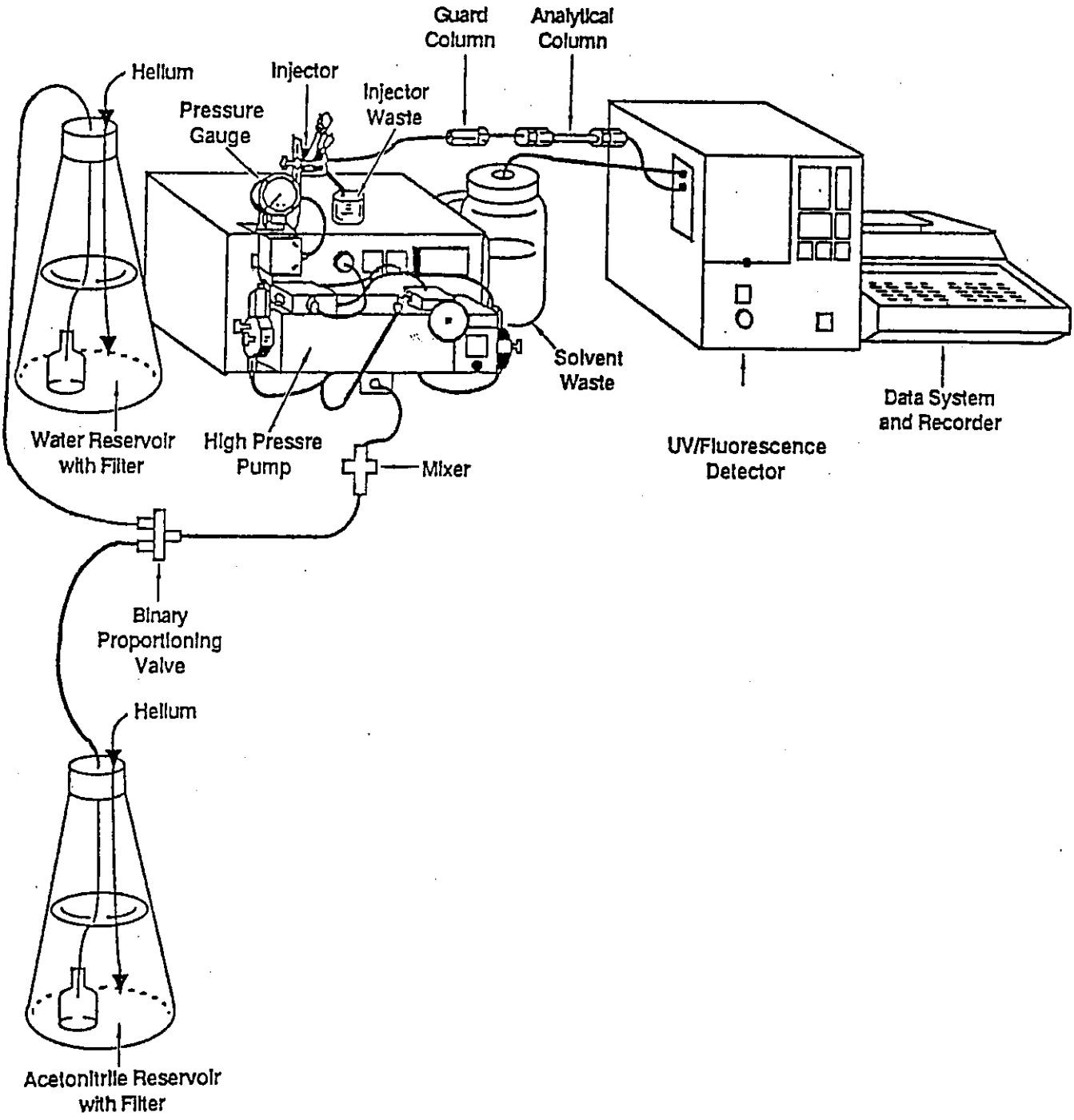

Figure 4. Typical Configuration Associated with a High Performance Liquid Chromatographic Analytical System

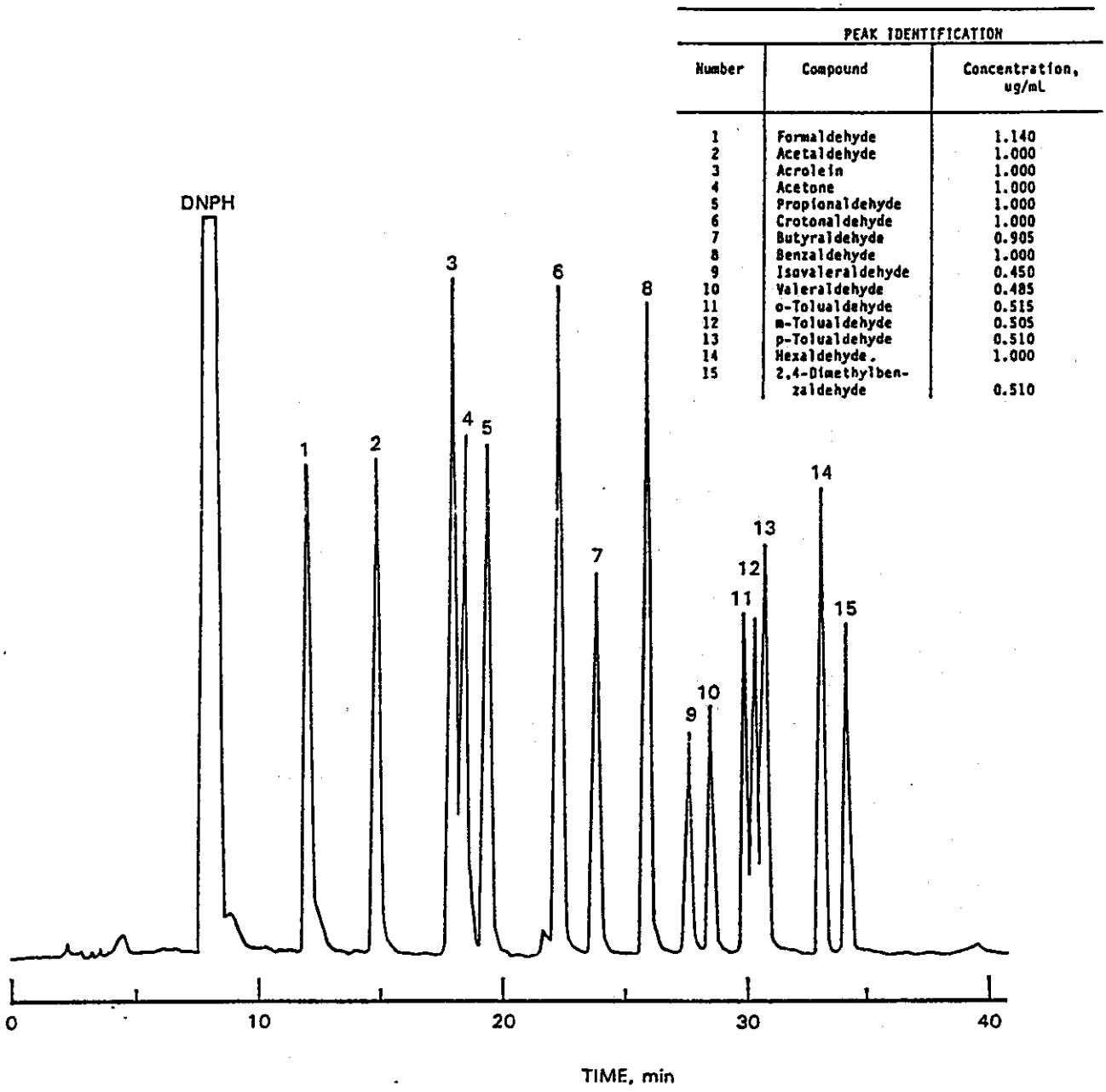

Figure 5. Chromatographic Separation of DNPH Derivatives of 15 Carbonyl Standards

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Chapter IP-7

DETERMINATION OF BENZO(a)PYRENE [B(a)P] AND OTHER POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN INDOOR AIR

1. Scope

1.1 Polynuclear aromatic hydrocarbons (PAHs) have received increased attention in recent years in indoor 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 B[a]P and other PAHs involving a combination quartz filter/adsorbent cartridge with subsequent analysis by gas chromatography (GC) with flame ionization (FI) and mass spectrometry (MS) detection (GC-FI and GC-MS) or high performance liquid chromatography (HPLC).

2. Significance

2.1 Only limited information is currently available on the quality of indoor air. Since most of the population spends a major part of each day indoors, the indoor air quality may be a more important component of the risk to which the public is subjected than is the outdoor air quality. Recent trends towards energy-efficient building construction typically result in significant reductions in the indoor-outdoor air exchange rate. This fact, coupled with the increasing use of alternative heating sources in homes, results in a potential for concentrations of PAHs to reach undesirable levels.

2.2 Many research and monitoring efforts have focused on assessing and improving the quality of indoor air. Several studies have demonstrated that some PAHs and nitrated PAH found in indoor air are potent carcinogens, mutagens, or both. Because people spend more than 80% of their time indoors, there is increasing concern over human exposure to these and other semivolatile organic compounds in homes, workplaces, and schools.

2.3 Historically, sampling techniques have been categorized according to sampling flow rates. Traditionally, these categories are:

Sampling Approach	Nominal Flow Rate, L/min	Compendium Method
High volume	> 100	IP-7
Medium volume	10 - 100	IP-9, IP-7
Low volume	< 10	IP-10, IP-8, IP-6, IP-5, IP-1, IP-2

Current sampling techniques for semivolatile organic compounds require a large volume of air to be sampled in order to reach needed detection limits. Traditionally this has been accomplished utilizing the high volume air sampler. The use of available high volume air samplers in occupied residences is not practicable due to the noise they emit, the very high flow rates they employ, and their size. Due to these and other limitations, a medium

volume air sampling system (20 Lpm) suitable for use in residential environments has been developed and evaluated. The flow rate achievable with this device is adequate for at least 24 hour time resolution of typical concentrations of most PAHs of interest. The system is quiet, transportable, and relatively unobtrusive, making it attractive for use in sampling in occupied residences or workplaces.

Method IP-7

DETERMINATION OF BENZO(a)PYRENE [B(a)P] AND OTHER POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) IN INDOOR AIR

Method IP-7

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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 spectra overlap requires complete separation of sample components to insure accurate measurement of component levels. Hence, the use of UV absorption coupled with pre-speciation involving LC and TLC and fluorescence spectroscopy has declined and is now being replaced with the more sensitive high performance liquid chromatography (9) with UV/fluorescence detection or highly sensitive and specific gas chromatography with either flame ionization or mass spectroscopy (10-11) detection.

1.3 The choice of GC and HPLC as the recommended procedures for analysis of B[a]P and other PAHs are influenced by their sensitivity and selectivity, along with their ability to analyze complex samples. This method provides for both GC and HPLC approaches to the determination of B[a]P and other PAHs in the extracted sample.

1.4 The analytical methodology is well defined, but the sampling procedures can reduce the validity of the analytical results. Recent studies (12-15) have indicated that nonvolatile 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 adsorbent. A wide variety of adsorbents such as Tenax®, XAD-2 and polyurethane foam (PUF) have been used to sample B[a]P and other PAH vapors. All adsorbents have demonstrated high collection efficiency for B[a]P in particular. In general, XAD-2 resin has

a higher collection efficiency (16-17) for volatile PAHs than PUF, as well as a higher retention efficiency. However, PUF cartridges are easier to handle in the field and maintain better flow characteristics during sampling. Likewise, PUF has demonstrated its capability in sampling organochlorine pesticides, polychlorinated biphenyls (18) and polychlorinated dibenzo-p-dioxins (19). However, PUF has demonstrated a lower recovery efficiency and storage capability for naphthalene and B[a]P, respectively, 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 covers both the utilization of XAD-2 and PUF as the adsorbent to address post collection volatilization problems associated with B[a]P and other reactive PAHs.

1.5 This method covers the determination of B[a]P specifically by both GC and HPLC and enables the qualitative and quantitative analysis of other PAHs (see Figure 1). They are:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene*
Benzo(e)pyrene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene*
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

* Not well resolved by GC. Typically the identified benzo(k)fluoranthene is a mixture of benzo(k)fluoranthene and benzofluoranthene.

The GC and HPLC methods are applicable to the determination of PAHs compounds involving two member rings or higher. Nitro-PAHs have <u>not</u> been fully evaluated using this procedure; therefore, they are not included in this method. When either of the methods is used to analyze unfamiliar samples for any or all of the compounds listed above, compound identification should be supported by both techniques.

1.6 With careful attention to reagent purity and optimized analytical conditions, the detection limits for GC and HPLC methods range from 1 ng to 10 pg which represents detection of B[a]P and other PAHs in filtered air at 120 pg/m^3.

2. Applicable Documents

2.1 ASTM Standards

2.1.1 Method D1356 - Definitions of Terms Relating to Atmospheric Sampling and Analysis.

2.1.2 Method E260 - Recommended Practice for General Gas Chromatography Procedures.
2.1.3 Method E355 - Practice for Gas Chromatography Terms and Relationships.
2.1.4 Method E682 - Practice for Liquid Chromatography Terms and Relationships.
2.1.5 Method D-1605-60 - Standard Recommended Practices for Sampling Atmospheres for Analysis of Gases and Vapors.

2.2 Other Documents

2.2.1 Existing Procedures (19-28).
2.2.2 Air Studies (29-31).
2.2.3 U.S. EPA Technical Assistance Document (32).
2.2.4 *General Metal Works Operating Procedures for Model PS 1 Sampler*, General Metal Works, Inc., Village of Cleves, Ohio.

3. Summary of Method

3.1 Filters and adsorbent cartridges (containing XAD-2 or PUF) are cleaned in solvents and vacuum dried. The filters and adsorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on the sampler.
Note: Insure that the cleaned filters and adsorbent cartridges have all traces of solvent removed. Specifically, residual dichloromethane has been a contributor to larger than expected indoor concentrations of dichloromethane due to residuals on the filter and adsorbent cartridges after cleaning.

3.2 Approximately 30 m^3 of indoor air is drawn through the filter and adsorbent cartridge using a medium flow rate indoor air sampler or equivalent (breakthrough of less than 10% of target compounds at a flow rate of 20 Lpm has not been a problem with a total sample volume of 30 m^3).

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

3.4 The filters and adsorbent 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 either GC-FID or HPLC.
Note: If GC-MS is the chosen analytical scheme, cleanup may not be necessary for most indoor air samples.

3.5 The eluent is further concentrated by K-D evaporation, then analyzed by either GC equipped with FI or MS detection or HPLC. The analytical system is verified to be operating properly and calibrated with five concentration calibration solutions, each analyzed in triplicate.

3.6 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 necessary, 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.

3.7 The samples and the blanks are analyzed and used (along with the amount of air sampled) to calculate the concentration of B[a]P in indoor air.

3.8 Other PAHs can be determined both qualitatively and quantitatively through optimization of the GC or HPLC procedures.

4. Significance

4.1 Only limited information is currently available on the quality of indoor air. Since most of the population spends a major part of each day indoors, the indoor air quality may be a more important component of the risk to which the public is subjected than is the outdoor air quality. Recent trends towards energy-efficient building construction typically result in significant reductions in the indoor-outdoor air exchange rate. This fact, coupled with the increasing use of alternative heating sources in homes, results in a potential for concentrations of PAHs to reach undesirable levels.

4.2 Many research and monitoring efforts have focused on assessing and improving the quality of indoor air. Several studies (33-41) have demonstrated that some PAH's and nitrated PAH found in indoor air are potent carcinogens, mutagens, or both. Because people spend more than 80% of their time indoors, there is increasing concern over human exposure to these and other semivolatile organic compounds in homes, workplaces, and schools.

4.3 Current sampling and analytical techniques for these semivolatile organic compounds require a large volume of air to be sampled in order to reach needed detection limits. Traditionally this has been accomplished utilizing the high volume (1400 Lpm) air sampler, as outlined in Compendium Method TO-13, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (18). The use of available high volume air samplers in occupied residences is not practicable due to the noise they emit, the very high flow rates they employ, and their size. Due to these and other limitations, a lower flow (224 Lpm) acoustically enclosed high volume sampling system (see Figure 2) suitable for use in residential environments has been developed and evaluated (42). The flow rate achievable with this device is adequate for at least eight hour time resolution of typical concentrations of most PAHs of interest. The system is quiet, transportable, and relatively unobtrusive. The acoustic insulation of the sampler allows it to meet a noise criterion of 35, roughly the sound level in a quiet conference room. Operation of the sampler with its exhaust both vented (see Figure 3) and not vented showed that the sampler itself does not contribute significantly to the levels of PAHs in indoor air, therefore making it unnecessary to vent the exhaust outdoors during indoor air sampling for these compounds. Thus, the effect of the sampler on the house air exchange rate is minimized.

The attractive features of this sampler are:

- PM-10 inlet - The sampler can be adapted with an optional PM-10 aerodynamic aerosol inlet cut-point design which is insensitive to small variations in sampling flow rate (see Figure 2).
- Annular denuder - The sampler can be adapted with an optional annular denuder system to assist in gaseous/particle separation studies (see Figure 2), as detailed in Compendium Method IP-9.
- Tripod sampling head - The sampler can be modified to incorporate the sampling head containing the filter and adsorbent on a tripod (see Figure 3) with meter box assembly, with the exhaust vented external or internal to the room.
- Sorbent bed - The sampler is capable of collecting adequate samples on the adsorbent bed for limited time resolution of species of interest at the design flow rate.
- Acoustic performance - Acoustic insulation of the sampler allows it to meet a noise criterion of 35, roughly the sound level in a quiet conference room.
- Sampler operation - Operation of the sampler in a house with its exhaust both vented and not vented showed that it does not contribute significantly to indoor levels of PAH's and has minimal affect on the air exchange rate.
- Biological testing - Operation of the sampler at 224 Lpm for a 24-hour test period enables sufficient quantity for bioassay analysis if biological screening is part of the sampling protocol.

However, if at these flowrates the sampler disturbs the air exchange in the indoor environment, then it becomes part of the test, not independent of it. Due to these and other limitations, a medium (20 Lpm) volume air sampling system (see Figure 4) was developed by Battelle-Columbus Laboratory. The amount of mass required for accurate chemical analysis is considerable smaller than that needed for bioassays, so the air volume which needs to be sampled for chemical analyses alone could be correspondingly smaller. This reduction in the sample volume permits significant reduction of the sampler size and weight and therefore permits use of a more portable and more easily produced sampler. Therefore, a sampler with a constant sample flow rate of approximately 20 Lpm, compatibility with filter and/or XAD sorbent bed sampling media as well as small-scale optional denuder, and operating noise level (<35 noise criteria) consistent with indoor use (see Figure 5), was developed.

4.4 The flow rate requirements for the indoor sampling system are determined primarily by the quantity of material needed for organic chemical analysis and/or bioassays. The system must collect sufficient sample so that organic pollutant levels prevalent in indoor air may be determined by chemical analysis GC, combined GC-MS, or HPLC. In addition, collection of an adequate-sized sample should be achieved over a time interval that permits resolution of pollutant levels originating from specific sources or activities such as cooking or fireplace use in a residence. On one hand, these requirements dictate that the sampling rate be as high as possible. Considerations such as noise level, size of the sampler, and effects on air exchange require a compromise in the sampler flow rate. The latter consideration is important since the sampling could affect the natural air flow between the outside and inside of a residence and between rooms within the dwelling, if the exhaust is

vented in a different location from collection. All of these considerations were taken into account in the development of the 20 Lpm medium volume sampler. However, in its present design, specific considerations should be noted. They are:

- If sampler is placed in a location that exceeds 85°F, the user may want to add a thermal protection cutoff switch to protect electrical components and to maintain integrity of data logger and other electrical components.
- If high particulate loading is anticipated, the user may want to add a filter in front of the pump for protection.
- The sampler has been evaluated in test homes, but not in areas where cigarette smoke was predominant. If using sampler for an extended test period (7-days), then cigarette smoke may enhance sample loss due to volatility and reaction of PAHs on the collection media.
- Losses, apparently due to reaction of anthracene, benzo[a]pyrene and acenaphthylene were observed during 7-day testing period.

Overall, the evaluation (42-43) of this sampler indicates that it is quiet, portable, relatively small and easy to operate, making it attractive for use in sampling in occupied residences or workplaces. Testing demonstrates the combination of filter and sorbent media is suitable for collection of semi-volatile organic compounds. Breakthrough volume of the target compounds (see Table 1) with the total sample volume of 28 m^3 was not significant (<10%), thus providing sufficient mass for chemical analysis of most of the target compounds.

5. Definitions

Note: Definitions used in this document and in any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, D1605-60, E260, and E255. All abbreviations and symbols are defined within this document at point of use.

5.1 Breakthrough volume (V_B) - Ability of the sampling medium to trap vapors of interest. $\%V_B$ 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.

5.2 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.

5.3 High performance liquid chromatography (HPLC) - An analytical method based on separation of compounds of a liquid mixture through a liquid chromatographic column and measurement of the separated components with a suitable detector.

5.4 Gradient elution - Defined as increasing the strength of the mobile phase during a HPLC analysis. The net effect of gradient elution is to shorten the retention time of compounds strongly retained on the analytical column. Gradient elution may be stepwise or continuous.

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 (KD) apparatus is a system for concentrating materials dissolved in volatile solvents.

5.7 Reverse phase liquid chromatography - Reverse phase liquid chromatography involves a nonpolar absorbent (C-18,ODS) coupled with a polar solvent to separate nonpolar compounds.

5.8 Guard column - Guard columns in HPLC are usually short (5 cm) columns attached after the injection port and before the analytical column to prevent particles and strongly retained compounds from accumulating on the analytical column. The guard column should always be the same stationary phase as the analytical column and is used to extend the life of the analytical column.

5.9 MS-SIM - The GC is coupled to a select ion mode (SIM) detector where the instrument is programmed to acquire data for only the target compounds and to disregard all others. This is performed using SIM coupled to retention time discriminators. The SIM analysis procedure provides quantitative results.

5.10 Sublimation - Sublimation is 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.

5.11 Surrogate standard - A surrogate standard is a chemically inert compound (not expected to occur in the environmental sample) which 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.

5.12 Retention time window - Retention time window is determined for each analyte of interest and is the time from injection to elution of a specific chemical from a chromatographic column. The window is determined by three injections of a single component standard over a 72 hour period as plus or minus three times the standard deviation of the absolute retention time for that analyte.

6. Interferences

6.1 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.

6.1.1 Glassware must be scrupulously cleaned (44). Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water and rinsing with tap water and reagent water. It should then be drained dry, 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.

6.1.2 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.

6.1.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. Additional clean-up by column chromatography may be required (see Section 12.4).

6.2 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although GC and HPLC 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 or HPLC 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 is run for each batch of reagents used to determine if reagents are contaminant-free.

6.3 Although HPLC separations have been improved by recent advances in column technology and instrumentation, problems may occur with baseline noise, baseline drift, peak resolution and changes in sensitivity. Problems affecting overall system performance can arise (45). The user is encouraged to develop a standard operating procedure (SOP) manual specific for his laboratory to minimize problems affecting overall system performance.

6.4 Concern during sample transport and analysis is mentioned. Heat, ozone, NO_2 and ultraviolet (UV) light may cause sample degradation. These problems should be addressed as part of the user-prepared SOP manual. Where possible, incandescent or UV-shielded fluorescent lighting should be used during analysis.

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 regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all

personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the analyst (46-48).

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 whoever 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 Treat all PAHs 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. Regularly check counter tops and equipment with "black light" for fluorescence as an indicator of contamination.

7.4 Because the sampling configuration (filter and backup adsorbent), the collection efficiency for treated PAHs has been demonstrated to be greater than 95% (except for naphthalene), no field recovery evaluation will occur as part of this procedure.
Note: Naphthalene has demonstrated significant breakthrough using PUF cartridges, especially at summer ambient temperatures.

8. Apparatus

8.1 Sample Collection (see Figure 4)

8.1.1 Acoustically enclosed sampling case - Cabbage Cases, Inc., 1166-C Steelwood Road, Columbus, OH, 43212-1356, 614-486-2495.

8.1.2 Vacuum pump - Gast Inc., P.O. Box 97, Benton Harbor, MI, 49022, 616-926-6171, Model 1531-107B-6288X.

8.1.3 Flow sensor - R. D. McMillan Co., 1301 Sparrow Trail, Copperas Cove, TX, 76522, 817-547-2555, Model 100-10.

8.1.4 Data logger with DOS-PRONTO program and supporting cables - Rustrak, Inc., Route 2 and Middle Road, East Greenwich, RI, 02818-0962, 401-884-6800, Rustrak Ranger Model RR-400, 0-5V.

8.1.5 Programmable timer, seven day - Micronta Inc., Radio Shack, a Division of Tandy Corp., Fort Worth, TX, 76102, Cat. No. 63-889.

8.1.6 Fan - McLean Fans, 70 K. Washington Road, Princeton Junction, NJ, 08550, 609-799-0100.

8.1.7 Tripod ring stand with sample cartridge and filter assembly - General Metal Works, Inc. (GMW), 145 South Miami Avenue, Village of Cleves, OH, 45002, Model PS-1 Assembly, 800-543-7412.

8.2 Sample Clean-up and Concentration (see Figure 6)

8.2.1 Soxhlet extractors capable of extracting GMW Model PS-1 filter and adsorbent cartridges (2.3" x 5" length), 500 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 crosscontamination. All glassware that is used, especially glassware that is reused, 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 amount 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 (KD) apparatus - 500 mL evaporation flask (Kontes K-570001-500 or equivalent), 10 mL graduated concentrator tubes (Kontes K-570050-1025 or equivalent) with ground-glass stoppers, and 3-ball macro Snyder Column (Kontes K-5700010500, K-50300-0121, and K-569001-219, or equivalent), best source.

8.2.9 Adsorption columns for column chromatography - 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 ± 5°C temperature control, best source.

8.2.16 Vortex evaporator (optional).

8.3 Sample Analysis

8.3.1 Gas Chromatography with Flame Ionization Detection (GC-FID)

8.3.1.1 Gas chromatography - Analytical system complete with gas chromatography suitable for on-column injections and all required accessories, including detectors, column

supplies, recorder, gases, and syringes (see Figure 7). A data system for measuring peak areas and/or peak heights is recommended.

8.3.1.2 Packed column - 1.8 m x 2 mm ID glass column packed with 3% OV-17 on Chromosorb W-AW-DMCS (100/120 mesh) or equivalent - Supelco Inc., Supelco Park, Bellefonte, PA, Supelco SPB-5.

8.3.1.3 Capillary column - 30 m x 0.25 mm ID fused silica DB-5 column coated with 0.25 μm thickness 5% phenyl, 90% methyl siloxane - Alltech Associates, 2051 Waukegan Road, Deerfield, IL, 60015, 312-948-8600.

8.3.1.4 Detector - Flame Ionization

8.3.2 Gas Chromatography with Mass Spectroscopy Detection (see Figure 7) Coupled with Data Processing System (GC-MS-DS)

8.3.2.1 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 1-3 μL injection volume is used consistently. With some gas chromatograph injection ports, however, 1 μL injections may produce some improvement in precision and chromatographic separation. A 1 μL injection volume may be used if adequate sensitivity and precision can be achieved.

Note: If 1 μL is used as the injection volume, the injection volumes for all extracts, blanks, calibration solutions and performance check samples must be 1 μL.

8.3.2.2 Gas chromatograph-mass spectrometer interface - The gas chromatograph 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. The interface components should be compatible with 320°C temperatures. Cold spots and/or active surfaces (adsorption sites) in the GC-MS interface can cause peak tailing and peak broadening. It is recommended that the gas chromatograph 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® or equivalent ferrules are recommended.

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

8.3.2.4 Mass spectrometer - Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenyl phosphine (DFTPP) which meets all of the criteria (see Section 14.5.1).

8.3.2.5 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.

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

8.3.2.7 Balance - Mettler balance or equivalent.

8.3.2.8 All required syringes, gases, and other pertinent supplies to operate the GC-MS system.

8.3.2.9 Pipettes, micropipettes, syringes, burets, etc., to make calibration and spiking solutions, dilute samples if necessary, etc., including syringes for accurately measuring volumes such as 25 μL and 100 μL.

8.3.3 High Performance Liquid Chromatography (HPLC) System (see Figure 8)

8.3.3.1 Gradient HPLC system - consisting of acetonitrile and water phase reservoirs; mixing chamber; a high pressure pump; an injection valve (automatic sampler with an optional 25 μL loop injector); a Vydac C-18-bonded reverse phase (RP) column, (The Separations Group, P.O. Box 867, Hesperia, CA, 92345) or equivalent (25 cm x 4.6 mm ID); an UV (λ = 254 nm) adsorbent detector (Spectro Physics 8440 or equivalent) and a data system or printer plotter.

8.3.3.2 Guard column - 5 cm guard column pack with Vydac reverse phase C-18 material.

8.3.3.3 Reverse phase analytical column - Vydac or equivalent, C-18 bonded RP column (The Separation Group, P.O. Box 867, Hesperia, CA, 92345), 4.6 mm x 25 cm, 5 micron particle diameter.

8.3.3.4 LS-4 fluorescence spectrometer, Perkin Elmer, separate excitation and emission, monochromator positioned by separate microprocessor-controlled flow cell and wavelength programming ability (optional).

8.3.3.5 UV/visible detector, Spectra Physics 8440, deuterium lamp, capable of programmable wavelengths (optional).

8.3.3.6 Dual channel, Spectra Physics 4200, computing integrator, measures peak areas and retention times from recorded chromatographs. IBM PC XT with Spectra Physics Labnet system for data collection and storage (optional).

8.4 Flow Calibration

8.4.1 Tripod ring stand with sample cartridge and filter assembly - General Metal Works, Inc. (GMW), 145 South Miami Avenue, Village of Cleves, OH, 45002, Model PS-1 Assembly, 800-543-7412.

8.4.2 Wet test meter - VWR Scientific, P.O. Box 7900, San Francisco, CA, 94120, 415-468-7150, Cat. No. 32598-063.

9. Reagents and Materials

9.1 Sample Collection

9.1.1 Acid-washed quartz fiber filter - 105 mm micro quartz fiber binderless filter, General Metal Works, Inc., Cat. No. GMW QMA-4, 145 South Miami Ave., Village of Cleves, OH, 45002, 800-543-7412, or Supelco Inc., Cat. No. 1-62, Supelco Park, Bellefonte, PA, 16823-0048.

9.1.2 Acid-washed quartz fiber filter - 37 mm micro quartz fiber binderless filter, best source.

9.1.3 Polyurethane foam (PUF) - 3 inch thick sheet stock, polyether type (density 0.022 g/cm^3) used in furniture upholstering, General Metal Works, Inc., Cat. No. PS-1-16, 145 South Miami Ave., Village of Cleves, OH, 45002, 800-543-7412, or Supelco Inc., Cat. No. 1-63, Supelco Park, Bellefonte, PA, 16823-0048.

9.1.4 XAD-2 resin - Supelco Inc., Cat. No. 2-02-79, Supelco Park, Bellefonte, PA, 16823-0048.

9.1.5 Aluminum foil, best source.

9.1.6 Hexane, reagent grade, best source.

9.2 Sample Clean-up and Concentration

9.2.1 Soxhlet Extraction

9.2.1.1 Methylene chloride - chromatographic grade, glass-distilled, best source.

9.2.1.2 Sodium sulfate-anhydrous (ACS), granular (purified by washing with methylene chloride followed by heating at 400°C for 4 hrs in a shallow tray).

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

9.2.1.4 Nitrogen - high purity grade, best source.

9.2.1.5 Ether - chromatographic grade, glass-distilled, best source.

9.2.1.6 Hexane - chromatographic grade, glass-distilled, best source.

9.2.1.7 Dibromobiphenyl - chromatographic grade, best source. Used for internal standard.

9.2.1.8 Decafluorobiphenyl - chromatographic grade, best source. Used for internal standard.

9.2.2 Solvent Exchange

9.2.2.1 Cyclohexane - chromatographic grade, glass-distilled, best source.

9.2.3 Column Clean-up

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9.2.3.1 Silica gel - high purity grade, type 60, 70-230 mesh; extracted in a Soxhlet apparatus with methylene chloride for 6 hours (minimum of 3 cycles per hour) and activated by heating in a foil-covered glass container for 24 hours at 130°C.

9.2.3.2 Sodium sulfate-anhydrous (ACS), granular (see Section 9.2.1.2).

Note: Put in an oven at 450°C for 8 hours prior to use to activate.

9.2.3.3 Pentane - chromatographic grade, glass-distilled, best source.

Lobar Prepacked Column

9.2.3.4 Silica gel Lobar prepacked column - E. Merck, Darmstadt, Germany [size A(240-10) Lichroprep Si (40-63 μm)].

9.2.3.5 Precolumn containing sodium sulfate - (ACS) granular anhydrous (purified by washing with methylene chloride followed by heating at 400°C for 4 hours in a shallow tray).

9.2.3.6 Hexane - chromatographic grade, glass-distilled, best source.

9.2.3.7 Methylene chloride - chromatographic grade, glass-distilled, best source.

9.2.3.8 Methanol - chromatographic grade, glass-distilled, best source.

9.3 Sample Analysis

9.3.1 Gas Chromatography Detection

9.3.1.1 Gas cylinders of hydrogen and helium - ultra high purity, best source.

9.3.1.2 Combustion air - ultra high purity, best source.

9.3.1.3 Zero air - Zero air may be obtained from a cylinder or zero-grade compressed air scrubbed with Drierite® or silica gel and 5A molecular sieve or activated charcoal, or by catalytic cleanup of ambient air. All zero air should be passed through a liquid argon cold trap for final cleanup.

9.3.1.4 Chromatographic-grade stainless steel tubing and stainless steel fittings - 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.

9.3.1.5 Native and isotopically labeled PAHs isomers for calibration and spiking standards, Cambridge Isotopes, 20 Commerce Way, Woburn, MA, 01801, 617-547-1818. Suggested isotopically labeled PAH isomers are:

- perylene-d_{12}, chrysene-d_{12}, acenaphthene-d_{10},
- naphthalene d_8, phenanthrene-d_{10}.

9.3.1.6 Decafluorotriphenylphosphine (DFTPP), best source (used for tuning GC-MS).

9.3.2 High Performance Liquid Chromatography Detection

9.3.2.1 Acetonitrile - chromatographic grade, glass-distilled, best source.

9.3.2.2 Boiling chips - solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

9.3.2.3 Water - HPLC grade. Water must not have an interference that is observed at the minimum detectable limit (MDL) of each parameter of interest.

9.3.2.4 Decafluorobiphenyl - HPLC grade, best source (used for internal standard).

10. Preparation of Sample Filter and Adsorbent

10.1 Sampling Head Configuration

10.1.1 The sampling head (see Figure 9) consists of a filter holder compartment followed by a glass cartridge for retaining the adsorbent. The present method is written using the standard GMW PS-1 sampling head. However, Battelle-Columbus Laboratory has investigated (43) the use of a smaller sampling head, as illustrated in Figure 10. The basic difference is that the Battelle head uses a 47 mm filter followed by the adsorbent. Approximately the same amount of XAD-2 (50 - 60 grams) is used in both sampling heads. The idea of going to a smaller head was to reduce the size of the Soxhlet extraction apparatus, consequently the volume of solvent used from 500 mL to 200 mL during the extraction procedure. All preparation steps for cleaning the filters and adsorbents are the same, no matter which size filter is used.

10.1.2 Before field use, both the filter and adsorbent must be cleaned to <10 ng/apparatus of B[a]P or other PAHs.

Note: Recent studies have determined that naphthalene levels may be greater than 10 ng per apparatus even after successive cleaning procedures.

10.2 Glass Fiber Filter Preparation

10.2.1 The quartz fiber filters are baked at 600°C for five hours before use. To insure acceptable filters, they are extracted with methylene chloride in a Soxhlet apparatus, similar to the cleaning of the XAD-2 resin (see Section 10.3).

10.2.2 The extract is concentrated and analyzed by either GC or HPLC. A filter blank of <10 ng/filter of B[a]P or other PAHs is considered acceptable for field use.

10.3 XAD-2 Adsorbent Preparation

10.3.1 For initial cleanup of the XAD-2, a batch of XAD-2 (approximately 50-60 grams) is placed in a Soxhlet apparatus [see Figure 6 (a)] and extracted with methylene chloride for 16 hours at approximately 4 cycles per hour.

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

10.3.3 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).

Note: Alternatively, the XAD-2 resin is placed in a Pyrex® column (10 cm x 600 cm), allowing sufficient space for fluidizing. The column is wrapped with heat tape, maintained at 40°C, during the drying process. High purity air, scrubbed through a charcoal trap, is

forced through the resin bed, fluidizing the bed while generating a minimum load at the exit of the column.

10.3.4 A nickel or stainless steel screen (mesh size 200/200) is fitted to the bottom and the top of a hexane-rinsed glass sampling cartridge to retain the XAD-2 resin.

10.3.5 The Soxhlet-extracted, vacuum dried XAD-2 resin is placed into the sampling cartridge (using clean white cotton gloves) to a depth of approximately 2 inches. This should require between 50 and 60 grams of adsorbent.

10.3.6 The glass module containing the XAD-2 adsorbent is wrapped with hexane-rinsed aluminum foil, placed in a labeled container and tightly sealed with Teflon® tape.

Note: The aluminum foil should be baked in an oven overnight at 500°C to insure no residuals remain after rinsing with hexane.

An alternative method for cleaning XAD-2 resin is summarized as follows:

- In a 600 g batch, XAD-2 resin is Soxhlet-extracted with dichloromethane for 16 hours.
- After extracting, the resin is transferred to a clean drying column. Then the resin is dried with high-purity nitrogen using Teflon® tubing from the nitrogen cylinder with a charcoal tube in the line.
- Approximately 60 g of dried resin is packed into each precleaned PS-1 glass sampling cartridge and held in place with stainless steel screens and glass wool.
- The packed cartridge is wrapped and placed in a wide-mouth screw-cap glass jar.

10.3.7 At least one assembled cartridge from each batch must be analyzed as a laboratory blank, using the procedures described in Section 13, before the batch is considered acceptable for field use. A blank of <10 ng of B[a]P or other PAHs is considered acceptable.

10.4 PUF Sampling Cartridge Preparation

10.4.1 The PUF adsorbent is a polyether-type polyurethane foam (density 0.0225 g/cm^3) used for furniture upholstery.

10.4.2 The PUF inserts 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 9). During cutting, the die is rotated at high speed (e.g.,in a drill press) and continuously lubricated with water.

10.4.3 For initial cleanup, the PUF plug is placed in a Soxhlet apparatus [see Figure 6(a)] and extracted with acetone for 14-24 hours at approximately 4 cycles per hour. When cartridges are reused, 5% diethyl ether in n-hexane can be used as the cleanup solvent.

Note: A modified PUF cleanup procedure can remove the unknown interference components and the mutagenicity of the PUF blank. This method consists of compressed rinsing 50 times with toluene, acetone and 5% diethyl ether/hexane and followed by Soxhlet extraction.

10.4.4 The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2-4 hours (until no solvent odor is detected).

10.4.5 The PUF is placed into the glass sampling cartridge using polyester gloves. The module is wrapped with hexane-rinsed aluminum foil, placed in a labeled container, and tightly sealed.

10.4.6 At least one assembled cartridge from each batch must be analyzed as a laboratory blank, using the procedures described in Section 13, before the batch is considered acceptable for field use. A blank level of <10 ng/plug for single compounds is considered to be acceptable.

11. Sample Collection

11.1 Description of Sampling Apparatus

11.1.1 Traditionally, the sampling of PAHs has been accomplished utilizing the high volume air sampler. The use of high volume air samplers in occupied residences, however, is not practicable due to the noises that they emit, the high flow rates that they employ and their size. To address these limitations, this method utilizes an acoustically insulated medium volume sampler (see Figure 4) meeting a noise criterion of 35 (see Figure 5). The flow rate achievable with this device is adequate for at least 24 hour time resolution of typical concentrations of most PAHs of interest.

11.1.2 The sampling module consists of a glass sampling cartridge and an air-tight metal cartridge holder, as outlined in Section 10.1. The adsorbent (XAD-2 or PUF) is retained in the glass sampling cartridge.

11.2 Calibration of Sampling System

Note: Each sampler is to 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%, 4) when a different sample collection media, other than that which the sampler was originally calibrated to, will be used for sampling, 5) at the frequency specified in the user Standard Operating Procedure (SOP) manual in which the samplers are utilized, and 6) before and after each test series.

11.2.1 Assemble the calibration system as illustrated in Figure 11.

11.2.2 Level the wet test meter. Adjust the meter until the bubble is exactly centered in the level [see Figure 11 (a)].

11.2.3 Fill the wet test meter with distilled water until the water just covers the pointer [see Figure 11 (b)].

11.2.4 Connect the wet test meter to the vacuum source. Attach one end of the hose to the wet test meter outlet, as identified on the meter casing. Attach the other hose to the outlet of the flow sensor and connect to the inlet of the wet test meter.

Note: Best results are obtained if the complete sampling system is calibrated as a system.

11.2.5 Connect the sampling cartridge containing a "dummy" filter/PUF assembly to the inlet of the flow sensor.

11.2.6 Insure the flow sensor and data logger are properly connected.

11.2.7 Turn the data logger on and insure 0 volts as sensed by the flow sensor. Adjust to zero if necessary as displayed by the data logger.

11.2.8 Turn the vacuum pump on and adjust to 2.0 volts as displayed by the data logger. Use the flow control needle valve to make this adjustment.

11.2.9 Allow the system to equilibrate from approximately 10 revolutions of the wet test meter's large pointer.

11.2.10 As the wet test meter pointer passes zero, begin timing with a precision stopwatch. As the wet test meter pointer passes the three-quarter revolution mark, read and record on Flow Sensor Calibration Data Sheet (see Figure 12) the displayed volts.

11.2.11 As the wet test meter pointer passes the starting point, stop the stopwatch and record elapsed time on the Flow Sensor Calibration Sheet.

11.2.12 Record the volume of air passed through the wet test meter in column headed by V_m.

11.2.13 Record wet test meter fluid temperature (T_m) in °K, barometric pressure (P_b) in mm Hg, and the vapor pressure of the wet test meter's water in mm Hg as acquired from a saturation vapor pressure over water table (Handbook of Chemistry and Physics).

11.2.14 Calculate actual volume (V_a):

$$V_a = V_m \times C.F.$$

where:
V_a = actual volume of wet test meter, L
V_m = volume of wet test meter, L
C.F. = wet test meter's correction factor, dimensionless

11.2.15 Calculate V_s from P_m, p_v. T_m and V_a and record on the Calibration Data Sheet.

$$V_s = (V_a) \times (P_m - p_v/P_s) \times (T_s/T_m)$$

where:
V_s = volume corrected to standard temperature and pressure, L
V_a = defined in Section 11.2.14
P_m = barometric pressure (P_b) corrected for internal meter pressure - Δp in mm Hg
= $P_b - \Delta p$
p_v = vapor pressure of wet test meter's water, mm Hg
P_s = standard pressure, 760 mm Hg
T_s = standard temperature, 25°C + 273.16, 298.16°K
T_m = temperature of meter, °C + 273.16, °K

11.2.16 Calculate standard flow rate (Q_s) from V_s and θ and record.

$$Q_s = V_s/\theta$$

where:
Q_s = volumetric flow rates corrected to standard temperature and pressure, L/min
θ = time, minutes

11.2.17 Convert Q_s (L/min) to Q_s (m^3/min) by multiplying by 1.00×10^{-3} to be used in Section 17.1.2.

11.2.18 Plot Q_s (L/min) versus mass flow meter readings on linear graph paper. Repeat Section 11.2.10 through Section 11.2.16 for three other flow rates within the range of the flow sensor.

11.2.19 Construct a best fit curve for the points generated and use this relationship for future work employing the flow sensor device.

11.2.20 Place calibration curve in sample for use in setting sampling flows during collection.

11.2.21 Retrieve the data logger and transport to a computer site while still under battery power. It is then cable-connected to the personal computer for the playback operational phase through a serial I/O port on the computer from the "output/recharge" port on the data logger. The playback menu permits you to transfer your recorded data from the data logger to your personal computer. Playback permits all recording sessions to be loaded into computer memory in the form of raw data for filing, review, analysis, and printout. The playback operation of the Rustrak Ranger is coordinated between the data logger and the personal computer, driven by the PRONTO application software.

11.2.22 You can now start playback. Use the SELECT and ENTER keys as required, and increment the menu as follows:

- Select PLAYBACK from the main menu; the readout shows a flashing PLAYBACK.
- Press ENTER key; the readout shows a steady-state PLAYBACK (stops flashing).
- When computer acknowledges data transmission, the display on the data logger begins to ripple, indicating that data is being transmitted.
- Display returns to READY upon completing playback.

You have now performed the procedure for sending the collected data in the data logger memory to the personal computer.

Note: If the computer is not connected, the data logger will stay in the "wait" condition (readout shows a steady-state PLAYBACK).

11.2.23 Retrieve volts for individual flow values correction to standard temperature and pressure (STP). Construct a calibration curve, as illustrated below:

Volts	Q_s, L/min	Volts	Q_s, L/min
0.5	10.86	1.5	17.50
0.7	12.16	:	:
0.9	13.46	:	:
1.1	14.86	2.0	22.50
1.3	16.24		

11.2.24 Also place calibration curve in sampler for use in setting flows during sample collection.

11.3 Sample Collection

11.3.1 Monitor Placement

Note: The sampler should be located at ground level on a soft surface (for noise absorption) if possible. One should take care to not restrict the air circulation vents to prevent overheating of the unit. The sampling line should be not more than 3 m in length,

and preferably shorter. The sampler inlet should be located in an area which can be considered part of the breathing zone of the building occupants. Avoid placing the inlet on the floor, in corners of rooms, or in the immediate vicinity of a possible source of the compounds being sampled.

11.3.1.1 After the sampling system has been assembled and flow checked as described in Section 11.1 and Section 11.2, it can be used to collect air samples, as described in Section 11.3.2.

11.3.1.2 The monitors should be placed at a minimum horizontal distance from an obstruction that is equivalent to one meter from the obstructing object. In addition, the sampler intake should be minimum of one meter above floor.

11.3.2 Sample Module Loading

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

11.3.2.2 Detach the lower chamber of the rinsed sampling module. While wearing disposable clean lint free nylon or powder-free surgical gloves, remove a clean glass cartridge/sorbent from its container (wide mouthed glass jar with a Teflon®-lined lid) and unwrap its aluminum foil covering. The foil should be replaced back in the sample container to be reused after the sample has been collected.

Note: Check glass for cracks prior to installation.

11.3.2.3 Insert the cartridge into the lower chamber and tightly reattach it to the module.

11.3.2.4 Using clean Teflon® tipped or metal forceps, carefully place a clean fiber filter atop the filter holder and secure in place by clamping the filter holder ring over the filter using the three screw clamps. Insure that all module connections are tightly assembled.

Note: Failure to do so could result in air flow leaks at poorly sealed locations which could affect sample representativeness. Ideally, sample module loading and unloading should be conducted in a controlled environment or at least a centralized sample processing area so that the sample-handling variables can be minimized.

11.3.2.5 With the module removed from the sampler and the flow control valve fully open, turn the pump on and allow it to warmup for approximately 5 minutes.

11.3.2.6 Attach a "dummy" sampling module loaded with the exact same type of filter and sorbent media as that which will be used for sample collection.

11.3.2.7 Turn the sampler on and adjust flow to 20 Lpm using the calibration curve and as indicated by the flow indicator.

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

11.3.2.9 Room temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number, and adsorbent sample number are recorded on the Field Test Data Sheet (see Figure 13). Attach the loaded sampler module to the sampler.

11.3.3 Powering Medium Volume Sampling Unit

11.3.3.1 With the master power switch (the red rocker switch on the 4" x 6" electrical box in the pump compartment) turned off, connect the 3-prong A.C. power line to the sampler and a suitable 110 V A.C. outlet.

11.3.3.2. Ensure that the timer is in the OFF mode--the word OFF will be displayed on the right hand side of LCD. The timer should be in the MANUAL position. The SET switch will toggle the power OFF/ON for the 110 V A.C. unit which operates the pump and cooling fan.

11.3.3.3 Turn on the master power switch, which should illuminate. This supplies 12 V D.C. power to the data logger, the flow transducer, and the timer.

Note: The timer and data logger do have internal battery backups, but it should be routine to keep power to them when feasible.

11.3.4 Data Logger Unit Start-up

11.3.4.1 After turning the data logger on, READY should flash on the LCD. If not, press SELECT (S) and ENTER (E) together. Pressing S and E together will always return the data logger to the start of the menu, as illustrated in Figure 14.

Note: S takes you down through the menu tree (or cycles you through available options). E moves you to the right through the tree (or accepts the displayed option), as illustrated in Figure 14. Press S to get to DEFINE, then E for SENSOR.

11.3.4.2 To indicate the type sensor in use (Type 13), at the SENSOR prompt press E, then S to cycle to I/P NO. 4. This assumes that you are connected to I/P Port 4 on the data logger, as illustrated in Figure 14.

11.3.4.3 Next, press S when the CALIBRATE prompt appears.

11.3.4.4 Return to DEFINE mode and define the recording time to be long enough to cover the entire period of interest. If, for example, you select 7 days, you need to specify 7 days, 00 hours, 00 minutes, 00 seconds to enable the data logger to function as you desire.

11.3.4.5 After the sensor and recording times are displayed, press S and E to obtain READY prompt, then S, S, to get to RECORD mode. Press E to obtain START prompt, then E again to begin recording. When data are being recorded the LCD will flash an R on the left side to the display, and the data will appear to the right.

11.3.4.6 During a recording session, press E at any time to place an event market in the recorded file. This is recommended when the sampling flow is started or interrupted for sample changing. Pressing S and E together terminates recording. (It can be restarted.)

11.3.4.7 When data have been recorded, asterisks will appear on left of the flashing READY. Do not turn the data logger power switch off until the data have been downloaded to a PC.

Note: Turning off the data logger will erase all stored data and functions programmed. The data logger is returned to a tabula rasa by means of the switch on its left side.

11.3.5 Sampling

11.3.5.1 After the logger is recording data, the timer can be used to turn on the pump and begin the sampling period.

11.3.5.2 The flow reading is recorded at the beginning, end and every six hours during the sampling period for sampling durations of 24 hours or longer. Room temperature, barometric pressure, and elapsed time readings are recorded at the beginning and end of the sampling period.

11.3.6 Sample Retrieval

11.3.6.1 At the end of the desired sampling period, the power is turned off. Carefully remove the sampling head containing the filter and adsorbent cartridge to a clean area.

11.3.6.2 While wearing disposable lint free cotton or surgical gloves, remove the sorbent cartridge from the lower module chamber and place it on the retained aluminum foil in which the sample was originally wrapped.

Note: Do not lay cartridge in a horizontal position if XAD-2 is used as the back-up adsorbent. Loss of adsorbent or contamination may occur.

11.3.6.3 Carefully remove the glass fiber filter from the upper chamber using clean Teflon® tipped forceps.

11.3.6.4 Fold the filter in half twice (sample side inward) and place it in the glass cartridge atop the sorbent.

Note: The filter may be separated from the PUF cartridge and placed in a glass watch glass or petri dish for shipment to the laboratory.

11.3.6.5 Wrap the combined samples in aluminum foil and place them in their original glass sample container. A sample label should be completed and affixed to the sample container. Chain-of-custody should be maintained for all samples.

11.3.6.6 The glass containers should be stored with dry ice packs or blue ice and protected from light to prevent possible photo decomposition of collected analytes. If the time span between sample collection and laboratory analysis is to exceed 24 hours, samples must be kept refrigerated.

Note: Recent studies (13,16) have indicated that during storage, PUF does not retain B[a]P as effectively as XAD-2. Therefore, sample holding time should not exceed 20 days.

11.3.6.7 A final sample flow check is performed using the dummy cartridge, as described in Section 11.3.2. If calibration deviates by more than 10% from the initial reading, the flow data for that sample must be marked as suspect and the sampler should be inspected and/or removed from service.

11.3.6.8 At least one field filter/adsorbent blank should be returned to the laboratory with each group of samples (~10 samples). A field blank is treated exactly as a sample except that no air is drawn through the filter/adsorbent cartridge assembly.

11.3..6.9 Samples should be stored with frozen ice until receipt at the analytical laboratory, after which they are refrigerated at 4°C.

Note: If ice is used to preserve collected samples, safeguards must be used to prevent water seepage into the sample jars.

12. Sample Clean-up and Concentration

Note: The following sample extraction, concentration, solvent exchange and analysis procedures are outlined for user convenience in Figure 15.

12.1 Sample Identification

12.1.1 The samples are returned to the laboratory with dry ice in the glass sample container containing the filter and adsorbent.

12.1.2 The samples are logged in the laboratory logbook according to sample location, filter and adsorbent 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 hrs., then the samples must be kept refrigerated. Minimize exposure of samples to fluorescent light. All samples should be extracted within one week after sampling.

12.2 Soxhlet Extraction and Concentration

12.2.1 Assemble the Soxhlet apparatus [see Figure 6(a)]. Immediately before use, charge the Soxhlet apparatus with 800 mL of methylene chloride and reflux for 2 hours. Let the apparatus cool, disassemble it, transfer the methylene chloride to a clean glass container, and retain it as a blank for later analysis, if required. Place the adsorbent and filter together in the Soxhlet apparatus (the use of an extraction thimble is optional) if using XAD-2 adsorbent in the sampling module.

Note: The filter and adsorbent are analyzed together in order to reach detection limits, avoid questionable interpretation of the data, and minimize cost. Since methylene chloride is not a suitable solvent for PUF, 10% ether in hexane is employed to extract the PAHs from the PUF resin bed separate from the methylene chloride extraction of the accompanying filter, rather than methylene chloride for the extraction of the XAD-2 cartridge.

12.2.1.1 Prior to extraction, add a surrogate standard to the Soxhlet solvent. A surrogate standard (i.e., a chemically inert 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 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 measured concentration falls within the acceptance limits. The following surrogate standards have been successfully utilized in determining matrix effects, sample process errors, etc. utilizing GC-FID, GC-MS or HPLC analysis.

Surrogate Standard	Concentration	Analytical Technique
Dibromobiphenyl	50 ng/μL	GC-FID
Dibromobiphenyl	50 ng/μL	GC-MS
Deuterated Standards	50 ng/μL	GC-MS
Decafluorobiphenyl	50 ng/μL	HPLC

Note: The deuterated standards will be added in Section 14.3.2. Deuterated analogs of selective PAHs cannot be used as surrogates for HPLC analysis due to coelution problems. Add the surrogate standard to the Soxhlet solvent.

12.2.1.2 For the XAD-2 and filter extracted together, add 800 mL of methylene chloride to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.

12.2.1.3 For the PUF extraction separate from the filter, add 800 mL of 10% ether in hexane to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.

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

12.2.2 Dry the extract from the Soxhlet extraction by passing it through a drying column containing about 10 grams of anhydrous sodium sulfate.

Note: If water is observed in the Soxhlet extract, the drying process is mandatory, especially if the Field Test Data Sheet indicates rain or snow during sampling period. Collect the dried extract in a Kuderna-Danish (K-D) concentrator assembly. Wash the extractor flask and sodium sulfate column with 100-125 mL of methylene chloride to complete the quantitative transfer.

12.2.3 Assemble a Kuderna-Danish concentrator [see Figure 6(b)] 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.

12.2.4 Add at least two boiling chips, attach a three-ball macro-Snyder column to the K-D flask, and concentrate the extract using a hot water bath at 60°C 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.

12.2.5 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 5 mL of cyclohexane.

12.3 Solvent Exchange

12.3.1 Replace the K-D apparatus equipped with a Snyder column back on the water bath.

12.3.2 Increase the temperature of the hot water bath to 95-100°C. Momentarily remove the Snyder column, add a new boiling chip, and attach a two-ball micro-Snyder column. Prewet the Snyder column, using 1 mL of cyclohexane. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 15-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

12.3.3 When the apparatus is cool, remove the micro-Snyder column and rinse its lower joint into the concentrator tube with about 0.2 mL of cyclohexane.

Note: A 5 mL syringe is recommended for this operation. Adjust the extract volume to exactly 1.0 mL with cyclohexane. Stopper the concentrator tube and store refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than 24 hours, it should be transferred to a Teflon®-sealed screw-cap vial.

12.4 Sample Cleanup by Solid Phase Exchange

Cleanup procedures may not be needed for relatively clean matrix samples. If the extract in Section 12.3.3 is clear, cleanup may not be necessary. If cleanup is not necessary, the cyclohexane extract (1 mL) can be analyzed directly by GC-FI detection, except the initial oven temperature begins at 30°C rather than 80°C for cleanup samples (see Section 13.3), or solvent exchange to acetonitrile for HPLC analysis. More specifically, if GC-MS is employed as the analytical finish, then clean-up is not necessary to determine PAHs. If cleanup is required, the procedures are presented using either a handpack silica gel column as outlined in Method 610 (20, 24), a Lobar prepacked silica gel column, or an aminosilane column for PAH concentration and separation. The user has the option to use any of the outlined solid phase exchange methods.
Note: The user may be wise to use an UV lamp during the chromatographic concentration and separation procedure to detect the eluting PAHs from the column.

12.4.1 Method 610 Cleanup Procedure [see Figure 6(c)]

12.4.1.1 Pack a 6 inch disposable Pasteur pipette (10 mm ID x 7 cm length) with a piece of glass wool. Push the wool to the neck of the disposable pipette. Add 10 grams of activated silica gel in methylene chloride slurry to the disposable pipette. Gently tap the column to settle the silica gel and elute the methylene chloride. Add 1 gram of anhydrous sodium sulfate to the top of the silica gel column.

12.4.1.2 Prior to initial use, rinse the column with methylene chloride at 1 mL/min for 1 hr to remove any trace of contaminants. Pre-elute the column with 40 mL of pentane. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 1 mL of the cyclohexane sample extract onto the column, using an additional 2 mL of cyclohexane to complete the transfer. Allow to elute through the column.

12.4.1.3 Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue elution of the column. Save the pentane eluate in case that the silica gel was not 100% activated and some PAHs may collect in this fraction.
Note: The pentane fraction contains the aliphatic hydrocarbons collected on the filter/adsorbent combination. If interested, this fraction may be analyzed for specific aliphatic organics. Elute the column with 25 mL of methylene chloride/pentane (4:6 v/v) and collect the eluate in a 500 mL K-D flask equipped with a 10 mL concentrator tube.
Note: This fraction contains the B[a]P and other moderately polar PAHs. The use of a UV lamp will assist in observing the PAHs as they elute from the mL/min.

12.4.1.4 Concentrate the collected fraction to less than 10 mL by the K-D technique, as illustrated in Section 12.3 using pentane to rinse the walls of the glassware. The extract is now ready for HPLC or GC analysis.

Note: An additional elution through the column with 25 mL of methanol will collect highly polar oxygenated PAHs with more than one functional group. This fraction may be analyzed for specific polar PAHs. However, additional cleanup by solid phase extraction may be required to obtain both qualitative and quantitative data due to complexity of the eluant.

12.4.2 Lobar Prepacked Column Procedure

12.4.2.1 The setup using the Lobar prepacked column consists of an injection port, septum, pump, pre-column containing sodium sulfate, Lobar prepacked column and solvent reservoir.

12.4.2.2 The column is cleaned and activated according to the following cleanup sequence:

Fraction	Solvent Composition	Volume (mL)
1	100% Hexane	20
2	80% Hexane/20% Methylene Chloride	10
3	50% Hexane/50% Methylene Chloride	10
4	100% Methylene Chloride	10
5	95% Methylene Chloride/5% Methanol	10
6	80% Methylene Chloride/20% Methanol	10

12.4.2.3 Reverse the sequence at the end of the run and run to the 100% hexane fraction in order to activate the column. Discard all fractions.

12.4.2.4 Pre-elute the column with 40 mL of hexane, which is also discharged.

12.4.2.5 Inject 1 mL of the cyclohexane sample extract, followed by 1 mL injection of blank cyclohexane.

12.4.2.6 Continue elution of the column with 20 mL of hexane, which is also discharged.

12.4.2.7 Now elute the column with 180 mL of a 40/60 mixture of methylene chloride/hexane respectively.

12.4.2.8 Collect approximately 180 mL of the 40/60 methylene chloride/hexane mixture in a K-D concentrator assembly.

12.4.2.9 Concentrate to less than 10 mL with the K-D assembly as discussed in Section 12.2.

12.4.2.10 The extract is now ready for either HPLC or GC analysis.

12.4.3 Aminosilane Column Procedure

12.4.3.1 While silica gel (Method 610) and Lobar prepacked columns have effectively fractionated PAHs into their respective groups, a μ Bondapak NH_2 (Waters Associates, Milford, MA) aminosilane column (300 x 8 mm ID) using 3% methylene chloride in hexane as the mobile phase, is also available.

12.4.3.2 Normal phase liquid chromatography is used in the μ Bondapak NH_2 fractionating scheme.

12.4.3.3 As with other techniques, a UV lamp is used to detect eluting PAHs to better identify characteristic PAHs.

13. Gas Chromatography Analysis with Flame Ionization Detection

13.1 Gas chromatography (GC) is a quantitative analytical technique useful for PAH identification. This method provides the user the flexibility of column selection (packed or capillary) and detector [flame ionization (FI) or mass spectrometer (MS)] selection. The mass spectrometer provides for specific identification of B(a)P; however, with system optimization, other PAHs may be qualitatively and quantitatively detected using MS (see Section 14.0). This procedure provides for common GC separation of the PAHs with subsequent detection by either FI or MS (see Figure 7). The following PAHs have been quantified by GC separation with either FI or MS detection:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene*
Benzo(e)pyrene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene*
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

* May not be completely resolved by GC

The packed column gas chromatographic method described here can not adequately resolve the following four pairs of compounds: anthracene and phenanthrene; chrysene and benzo(a)anthracene; benzo(b)fluoranthene and benzo(k)fluoranthene; and dibenzo(a,h) anthracene and indeno(1,2,3-cd)pyrene. The use of a capillary column instead of the packed column, also described in this method, should adequately resolve these PAHs. However, unless the purpose of the analysis can be served by reporting a quantitative sum for an unresolved PAH pair, either capillary GC-MS (see Section 14.0) or HPLC (see Section 15.0) should be used for these compounds. This section will address the use of GC-FI detection using packed or capillary columns.

13.2 To achieve maximum sensitivity with the GC-FI method, the extract must be concentrated to 1.0 mL, if not already concentrated to 1 mL. If not already concentrated to 1 mL, add a clean boiling chip to the methylene chloride extract in the concentrator tube. Concentrate the extract using a two-ball micro-Snyder column attached to a K-D apparatus according to Section 12.2.4. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus. Drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small volume of methylene chloride. Adjust the final volume to 1.0 mL and stopper the concentrator tube.

13.3 Assemble and establish the following operating parameters for the GC equipped with an FI detector:

	Capillary (A)	Capillary (B)	Packed
Identification	DB-5 fused silica capillary, 0.25 μm 5% phenyl, methyl siloxane bonded	SPB-5 fused silica capillary, 0.25 μm 5% phenyl, methyl siloxane bonded	Chromosorb W-AW-DMCS (100/120 mesh) coated with 3% OV-17
Dimensions	30 m x 0.25 mm ID	30 m x 0.25 mm ID	1.8 m x 2 mm ID
Carrier Gas	Helium	Helium	Nitrogen
Carrier Gas Flow Rate	28-30 cm/sec (1 cm/minute)	28-30 cm/sec (1 cm/minute)	30-40 cm/minute
Column Program	40°C for 1 min; program at 15°C/min to 200°C; program at 3°C/min to 300°C	80°C for 2 min; program at 8°C/min to 280°C and hold for 12 minutes	Hold at 100°C for 4 minutes; program at 8°C/min to 280°C and hold for 15 minutes
Detector	Flame Ionization	Flame Ionization	Flame Ionization

(A) Without column cleanup (see Section 12.4)
(B) With column cleanup (see Section 12.4.1)

13.4 Prepare and calibrate the chromatographic system using either the external standard technique (see Section 13.4.1) or the internal standard technique (see Section 13.4.2). Figure 16 outlines the following sequence involving GC calibration and retention time window determination.

13.4.1 External standard calibration procedure - For each analyte of interest, including surrogate compounds for spiking (if used) prepare calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with methylene chloride.
Note: All calibration standards of interest involving selected PAHs of the same concentration can be prepared in the same flask.

13.4.1.1 Prepare stock standard solutions at a concentration of 0.1 μg/μL by dissolving 0.0100 gram of assayed PAH material in methylene chloride and diluting to volume in a 100 mL volumetric flask.
Note: Larger volumes can be used at the convenience of the analyst.

13.4.1.2 When compound purity is assayed to be 98% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

Note: Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source. Transfer the stock standard solutions into Teflon®-sealed screw-cap bottles.

13.4.1.3 Store at -20°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

13.4.1.4 Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with methylene chloride. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC.
Note: Calibration solutions must be replaced after six months, or sooner if comparison with a check standard indicates a problem.

13.4.1.5 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g., 1- to 3-μL injections).
Note: The same amount must be injected each time.

13.4.1.6 Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each analyte.
Note: Alternatively, for samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration by the following equation:

$$\text{Calibration factor (CF)} = \frac{\text{Total Area of Peak}}{\text{Mass injected (in nanograms)}}$$

If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

13.4.1.7 The working calibration curve or calibration factor must be verified on each working day by the injection of one or more calibration standards. If the response for any analyte varies from the predicted response by more than $\pm$20%, a new calibration curve must be prepared for that analyte. Calculate the percent variance by the following equation:

$$\text{Percent variance} = (R_2 - R_1)/R_1 \times 100$$

where:
R_2 = calibration factor from succeeding analysis, and
R_1 = calibration factor from first analysis.

13.4.2 Internal standard calibration procedure - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.
Note: It is recommended that the internal standard approach be used only when the GC-MS procedure is employed due to coeluting species.

13.4.2.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask.

13.4.2.2 To each calibration standard, add a known constant amount of one or more internal standard and dilute to volume with methylene chloride.
Note: One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

13.4.2.3 Inject each calibration standard using the same introduction technique that will be applied to the actual samples (e.g., 1 to 3 μL injection).

13.4.2.4 Tabulate the peak height or area responses against the concentration of each compound and internal standard.

13.4.2.5 Calculate response factors (RF) for each compound as follows:

$$\text{Response Factor (RF)} = (A_s C_{is})/(A_{is} C_s)$$

where:
A_s = response for the analyte to be measured, area units or peak height
A_{is} = response for the internal standard, area units or peak height
C_{is} = concentration of the internal standard, μg/L
C_s = concentration of the analyte to be measured, μg/L

13.4.2.6 If the RF value over the working range is constant (<20% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculations.
Note: Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} versus RF.

13.4.2.7 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards.

13.4.2.8 If the response for any analyte varies from the predicted response by more than $\pm$20%, a new calibration curve must be prepared for that compound.

13.5 Retention Time Windows Determination

13.5.1 Before analysis can be performed, the retention time windows must be established for each analyte.

13.5.2 Make sure the GC system is within optimum operating conditions.

13.5.3 Make three injections of the standard containing all compounds for retention time window determination.

Note: The retention time window must be established for each analyte throughout the course of a 72 hr period.

13.5.4 The retention window is defined as plus or minus three times the standard deviation of the absolute retention times for each standard.

13.5.5 Calculate the standard deviation of the three absolute retention times for each single component standard. In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

13.5.6 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be noted and retained in a notebook by the laboratory as part of the user SOP and as a quality assurance check of the analytical system.

13.6 Sample Analysis

13.6.1 Inject 1 to 3 μL of the methylene chloride extract from Section 13.2 (however, the same amount each time) using the splitless injection technique when using capillary column. Note: Smaller (1.0 μL) volumes can be injected if automatic devices are employed.

13.6.2 Record the volume injected and the resulting peak size in area units or peak height.

13.6.3 Using either the internal or external calibration procedure, determine the identity and quantity of each component peak in the sample chromatogram through retention time window and established calibration curve. Table 2 outlines typical retention times for selected PAHs, using both the packed and capillary column technique coupled with FI detection, while Figure 17 illustrates typical chromatogram for the capillary column conditions outlined in Table 2.

13.6.3.1 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

13.6.3.2 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte from Section 13.5.4 as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 13.5.4.

13.6.3.3 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window.

Note: Confirmation may be required on a second GC column, or by GC-MS (if concentration permits) or by other recognized confirmation techniques if overlap of peaks occur.

13.6.3.4 Validation of GC system qualitative performance is performed through the use of the mid-level standards. If the mid-level standard falls outside its daily retention

time window, the system is out of control. Determine the cause of the problem and perform a new calibration sequence (see Section 13.4).

13.6.3.5 Additional validation of the GC system performance is determined by the surrogate standard recovery. If the recovery of the surrogate standard deviates from 100% by not more than 20%, then the sample extraction, concentration, clean-up and analysis is certified. If it exceeds this value, then determine the cause of the problem and correct.

13.6.4 Determine the concentration of each analyte in the sample according to Section 17.1 and Section 17.2.1.

14. Gas Chromatography with Mass Spectroscopy Detection

14.1 Analytical System

14.1.1 The analysis of the extracted sample for B[a]P and other PAHs is accomplished by an electron impact GC-MS (EI GC-MS) in the selected ion monitoring (SIM) mode with a total cycle time (including voltage reset time) of one second or less within each set of ions.

14.1.2 The gas chromatograph is equipped with a DB-5 fused silica capillary column (30 m x 0.25 mm ID) with helium carrier gas for analyte separation. The gas chromatograph column is temperature controlled and interfaced directly to the MS ion source.

14.2 Operation Parameters

14.2.1 The laboratory must document that the EI-GC-MS system is properly maintained through periodic calibration checks.

14.2.2 The GC-MS system should have the following specifications:

Mass range: 35-500 amu
Scan time: 1 sec/scan
Column: 30 m x 0.25 mm ID, DB-5 crosslinked 5% phenyl methyl silicone, 0.25 μm film thickness, capillary column or equivalent
Initial column temperature and hold time: 60°C for 1 min
Column temperature program: 60°C to 200°C at 15°C/min; 200°C to 310°C at 3°C/min
Final column temperature hold: 310°C for 15 min (until benzo[g,h,i] perylene has eluted)
Injector temperature: 250-300°C
Transfer line temperature: 250-300°C
Source temperature: According to manufacturer's specifications
Injector: Grob-type, splitless
EI Condition: 70 eV
Mass Scan: Follow manufacturer's instructions for selection monitoring (SIM) mode.
Sample volume: 1 μL on-column injection
Carrier gas: Helium at 30 cm/sec

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

14.2.4 If properly tuned, the DFTPP key ions and ion abundance criteria should be met as outlined in Table 3.

14.3 Calibration Techniques

Note: The typical GC-MS operating conditions are outlined in Table 4. The GC-MS system can be calibrated using the external standard technique (see Section 14.3.1) or the internal standard technique (see Section 14.3.2). Figure 18 outlines the following sequence involving the GC-MS calibration.

14.3.1 External Standard Calibration Procedure

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

14.3.1.2 Place 0.0100 grams of native B[a]P or other PAHs on a tared aluminum weighing disk and weigh on a Mettler balance.

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

14.3.1.4 Dilute to mark with methylene chloride.

14.3.1.5 The concentration of the stock standard solution of B[a]P or other PAHs in the flask is 0.1 μg/μL

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

14.3.1.6 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.

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

14.3.1.8 Calibration standards at a minimum of five concentration levels should be prepared. Accurately pipette 1.0 mL of the stock solution (0.1 μg/μL) into 10 mL volumetric flask, dilute to mark with methylene chloride. This daughter solution contains 10 ng/μL of B[a]P or other PAHs.

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

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

14.3.1.10 Accurately pipette 100 μL, 300 μL, 500 μL, 700 μL and 1000 μL of the daughter solution (10 ng/μL) into each 10 mL volumetric flask, respectively. To each of these flasks, add an internal deuterated standard to give a final concentration of 1 ng/μL of the internal deuterated standard (see Section 14.3.2.1). Dilute to mark with methylene chloride.

14.3.1.11 The concentration of B[a]P in each flask is 0.1 ng/μL, 0.3 ng/μL, 0.5 ng/μL, 0.7 ng/μL, and 1.0 ng/μL respectively. All standards should be stored at -20°C and protected from fluorescent light and should be freshly prepared once a week or sooner if standards check indicates a problem.

14.3.1.12 Analyze a constant volume (1-3 μL) of each calibration standard by observing retention time (see Table 5) and tabulate the area responses of the primary characteristic ion of each standard against the mass injected. The results may be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<20% relative standard deviation, RSD), linearity through the origin may be assumed and the average ratio or calibration factor may be used in place of a calibration curve. Figure 19 illustrates a typical chromatogram of selected PAHs under conditions outlined in Section 14.2.2.

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

14.3.2 Internal Standard Calibration Procedure

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

Perylene-d_{12}	Acenaphthene-d_{10}
Benzo(a)pyrene	Acenaphthene
Benzo(k)fluoranthene	Acenaphthylene
Benzo(g,h,i)perylene	Fluorene
Dibenzo(a,h)anthracene	
Indeno(1,2,3-cd)pyrene	Naphthalene-d_8
	Naphthalene
Chrysene-d_{12}	
Benzo(a)anthracene	Phenanthrene-d_{10}
Chrysene	Anthracene
Pyrene	Fluoranthene
	Phenanthrene

14.3.2.2 A mixture of the above deuterated compounds in the appropriate concentration range are commercially available (see Section 9.3.1.5).

14.3.2.3 Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next two most intense ions as the secondary ions.

Note: PAHs have double charge ions that can also be used as secondary ions. The internal standard is added to all calibration standards and all sample extracts analyzed by GC-MS. Retention time standards, column performance standards, and a mass spectrometer tuning standard may be included in the internal standard solution used.

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

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

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

where:
A_s = area of the characteristic ion for the analyte to be measured, counts
A_{is} = area of the characteristic ion for the internal standard, counts
C_{is} = concentration of the internal standard, ng/μL
C_s = concentration of the analyte to be measured, ng/μL

If the RF value over the working range is a constant (<20% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF. Table 6 outlines key ions for selected internal deuterated standards.

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

14.3.2.7 The relative retention times (see Table 5) for each compound in each calibration run should agree within 0.06 relative retention time units.

14.4 Sample Analysis

14.4.1 It is highly recommended that the extract be screened on a GC-FID or GC-PID using the same type of capillary column as in the GC-MS procedure. This will minimize contamination of the GC-MS system from unexpectedly high concentrations of organic compounds.

14.4.2 Analyze the 1 mL extract (see Section 13.2) by GC-MS. The recommended GC-MS operating conditions to be used are specified in Section 14.2. Typical chromatogram of selected PAHs by GC-MS is illustrated in Figure 19.

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

14.4.4 Perform all qualitative and quantitative measurements described in Section 14.3. The typical retention time and characteristic ions for selective PAHs are outlined in Table 6. Store the extracts at -20°C, protected from light in screw-cap vials equipped with unpierced Teflon® liner, for future analysis.

14.4.5 The sample analysis using the GC-MS-SIM is based on a combination of retention times and relative abundances of selected ions (see Table 5). These qualifiers are 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. While this adds some subjective judgment to the analysis, computer generated identification problems can be clarified by an experienced operator. Manual inspection of the quantitative results should also be performed to verify concentrations outside the expected range.

14.4.6 Determine the concentration of each analyte in the sample according to Section 17.1 and Section 17.2.2.

14.5 GC-MS Performance Tests

14.5.1 Daily DFTPP Tuning - At the beginning of each day that analyses are to be performed, the GC-MS system must be checked to see that acceptable performance criteria are achieved when challenged with a 1 μL injection volume containing 1 ng of decafluorotriphenylphosphine (DFTPP). The DFTPP key ions and ion abundance criteria that must be met are illustrated in Table 3. Analysis should not begin until all those criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC-MS tuning standard should also be used to assess GC column performance and injection port inertness. Obtain a background correction mass spectra of DFTPP and check that all key ions criteria are met. If the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed. If any key ion abundance observed for the daily DFTPP mass tuning check differs by more than 10% absolute abundance from that observed during the previous daily tuning, the instrument must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

14.5.2 Daily Single Point Initial Calibration Check - At the beginning of each work day, a daily 1-point calibration check is performed by re-evaluating the midscale calibration standard. This is the same check that is applied during the initial calibration, but one

instead of five working standards are evaluated. Analyze the one working standards under the same conditions the initial calibration curve was evaluated. Analyze 1 μL of each of the midscale calibration standard and tabulate the area response of the primary characteristic ion against mass injected. Calculate the percent difference using the following equation:

$$\% \text{ Difference} = (RF_C - \overline{RF}_I/\overline{RF}_I) \times 100$$

where:

$\overline{RF}_I$ = average response factor from initial calibration using mid-scale standard
RF_C = response factor from current verification check using mid-scale standard

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

14.5.3 12 hour Calibration Verification - A calibration standard at mid-level concentration containing B[a]P or other PAHs must be performed every twelve continuous hours of analysis. Compare the standard every 12 hours with the average response factor from the initial calibration. If the % difference for the response factor (see Section 14.5.2) is less than 20%, then the GC-MS system is operative within initial calibration values. If the criteria is not met (>20% difference), then the source of the problem must be determined and a new five point curve MUST be generated.

14.5.4 Surrogate Recovery - Additional validation of the GC system performance is determined by the surrogate standard recovery. If the recovery of the surrogate standard deviates from 100% by not more than 20%, then the sample extraction, concentration, clean-up and analysis is certified. If it exceeds this value, then determine the cause of the problem and correct.

15. High Performance Liquid Chromatography (HPLC) Detection

15.1 Introduction

15.1.1 While GC-FID and GC-MS have been used successfully to measure PAHs in ambient air, detection of B[a]P by HPLC has become a viable analytical tool in recent years. The HPLC technique is very sensitive and less expensive than the GC-MS technique. The use of synchronous fluorescence detection as part of the HPLC system offers several advantages in terms of improved sensitivity and specificity. Similar to the GC-FID and GC-MS techniques, the HPLC procedure using either UV and/or synchronous fluorescence

detection requires column cleanup before analysis. The procedure outlined below has been written specifically for analysis of B[a]P by HPLC using UV detection. Other PAHs may also be identified using UV detection but positive identification and quantitation may be difficult due to poor resolution of eluting peaks. However, optimizing chromatographic conditions through UV detection (λ = 254 nm), coupled with fluorescence detection with programmable wavelength to change the excitation and emission wavelengths during the chromatographic analysis will optimize selectivity and/or sensitivity for selective PAHs. The following PAHs have been quantified using the combined UV and programmable fluorescence detectors a part of the HPLC system:

Compound	Detector[1]	Compound	Detector[1]
Acenaphthene	UV	Benzo(k)fluoranthene	UV/FL
Acenaphthylene	UV	Dibenzo(a,h)anthracene	UV/FL
Anthracene	UV/FL	Fluoranthene	UV/FL
Benzo(a)anthracene	UV/FL	Fluorene	UV/FL
Benzo(a)pyrene	UV/FL	Indeno(1,2,3-cd)pyrene	UV/FL
Benzo(b)fluoranthene	UV/FL	Naphthalene	UV
Benzo(ghi)perylene	UV/FL	Phenanthrene	UV/FL

[1]UV= Ultraviolet, FL = Fluorescence

15.1.2 Through the use of column cleanup before HPLC analysis employing UV detection, B[a]P can be quantitatively identified along with other PAHs. However, it should be noted that HPLC analysis employing a single detector (UV) does not give unambiguous results.

15.1.3 For improved sensitivity and specificity, UV detection coupled with synchronous fluorescence detection allows the optimization of chromatographic conditions.

15.2 Solvent Exchange To Acetonitrile

15.2.1 To the extract in the concentrator tube, add 4 mL of acetonitrile and a new boiling chip; attach a micro-Snyder column to the apparatus.

15.2.2 Increase temperature of the hot water bath to 95 to 100°C.

15.2.3 Concentrate the solvent as in Section 12.3.

15.2.4 After cooling, remove the micro-Snyder column and rinse its lower sections into the concentration tube with approximately 0.2 mL acetonitrile.

15.2.5 To the cool extract, add an internal standard solution of 7-methylfluoranthene and/or perylene-d_{12}.

Note: The 7-methylfluoranthene can be obtained from the National Cancer Institute, Chemical Carcinogen Repository, IIT Research Institute, Chicago, Ill. and the perylened_{12} can be obtained from MSD Isotopes, Merck & Co., Rahway, N.J. With this approach, the most suitable internal standards for each isomeric family would be the predeuterated analogue of the isomer which elutes first, minimizing the possibility of coelution with alkyl-substituted PAHs within the specific isomeric group. Thus, the ideal internal standards would be the perdeuterated fluoranthene, benzo[a]pyrene and benzo[ghi]perylene.

15.2.6 After adding the internal standard, adjust the solution in the concentrator tube to 1.0 mL.

15.3 HPLC Assembly

15.3.1 The HPLC system is assembled, as illustrated in Figure 8.

15.3.2 The HPLC system is operated according to the following parameters:

HPLC Operating Parameters

Guard Column	VYDAC 201 GCCIOYT
Analytical Column	VYDAC 201 TP5415 C-18 RP (0.46 x 25 cm)
Column Temperature	27.0 ± 2°C
Mobile Phase	
Solvent Composition	Time (Minutes)
40% Acetonitrile/60% water	0
100% Acetonitrile	25
100% Acetonitrile	35
40% Acetonitrile/60% water	45

Linear gradient elution at 1.0 mL/min

Detector	Ultraviolet, operating at 254 nm
Flow Rate	1.0 mL/minute
Injection Volume	10 mL

Note: To prevent irreversible absorption due to "dirty" injections and premature loss of column efficiency, a guard column is installed between the injector and the analytical column. The guard column is generally packed with identical material as is found in the analytical column. The guard column is generally replaced with a fresh guard column after several injections (~50) or when separation between compounds becomes difficult. The analytical column specified in this procedure has been laboratory evaluated. Other analytical columns may be used as long as they meet procedure and separation requirements. Table 8 outlines other columns uses to determine PAHs by HPLC.

15.3.3 The mobile phases are placed in separate HPLC solvent reservoirs and the pumps are set to yield a total of 1.0 mL/minute and allowed to pump for 20-30 minutes before the first analysis.

Note: The chromatographic analysis involves an automated solvent program allowing unattended instrument operation. The solvent program consists of varying concentrations of acetonitrile in water with a constant flow rate, a constant column temperature, and a 10-minute equilibrium time. The detector is switched on at least 30 minutes before the first analysis. UV detection at 254 nm is generally preferred.

15.3.4 Before each analysis, the detector baseline is checked to ensure stable operation.

15.4 HPLC Calibration

15.4.1 Prepare stock standard solutions at PAH concentrations of 1.00 μg/μL by dissolving 0.0100 grams of assayed material in acetonitrile and diluting to volume in a 10 mL volumetric flask.

Note: Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 98% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

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

15.4.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

15.4.4 Prepare calibration standards at a minimum of five concentration levels ranging from 1 ng/μL to 10 ng/μL by first diluting the stock standard 10:1 with acetonitrile, giving a daughter solution of 0.1 μg/μL. Accurately pipette 100 μL, 300 μL, 500 μL, 700 μL and 1000 μL of the daughter solution (0.1 μg/μL) into each 10 mL volumetric flask, respectively. Dilute to mark with acetonitrile. One of the concentration levels should be at a concentration near, but above, the method detection limit (MDL). The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the HPLC.

Note: Calibration standards must be replaced after one year, or sooner if comparison with check standards indicates a problem.

15.4.5 Analyze each calibration standard (at least five levels) three times. Tabulate area response vs. mass injected. All calibration runs are performed as described for sample analysis in Section 15.5.1. Typical retention times for specific PAHs are illustrated in Table 8. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (concentration versus area response) is obtained. The retention times for each analyte should agree within ± 2%.

15.4.6 Once linear response has been documented, an intermediate concentration standard near the anticipated levels for each component, but at least 10 times the detection limit, should be chosen for a daily calibration check. The response for the various components should be within 15% day to day. If greater variability is observed, recalibration may be required or a new calibration curve must be developed from fresh standards.

15.4.7 The response for each component in the daily calibration standard is used to calculate a response factor according to the following equation:

$$RF_C = (C_C)\ (V_I)/R_C$$

where:
RF_C = response factor (usually area counts) for the component of interest, nanograms injected/response unit
C_C = concentration of analyte in the daily calibration standard, mg/L
V_I = volume of calibration standard injected, µL
R_C = response for analyte in the calibration standard, area counts

15.5 Sample Analysis

15.5.1 A 100 µL aliquot of the sample is drawn into a clean HPLC injection syringe. The sample injection loop (10 µL) is loaded and an injection is made. The data system, if available, is activated simultaneously with the injection and the point of injection is marked on the strip-chart recorded.

15.5.2 After approximately one minute, the injection valve is returned to the "load" position and the syringe and valve are flushed with acetonitrile/water solution (40/60) in preparation for the next sample analysis.

15.5.3 After elution of the last component of interest, concentrations are calculated as described in Section 16.2.3.

Note: Table 8 illustrates typical retention times associated with individual PAHs, while Figure 20 represents a typical chromatogram associated with UV detection.

15.5.4 After the last compound of interest has eluted, establish a stable baseline; the system can be now used for further sample analyses as described above.

Note: Table 9 illustrates retention time for selective PAHs using other chromatographic columns.

15.5.5 If the concentration of analyte exceeds the linear range of the instrument, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

15.5.6 Calculate surrogate standard recovery on all samples, blanks and spikes. Calculate the percent difference by the following equation:

$$\% \text{ difference} = [S_R - S_I/S_I] \times 100$$

where:
S_I = surrogate injected, ng
S_R = surrogate recovered, ng

15.5.7 Once a minimum of thirty samples of the same matrix has been analyzed, calculate the average percent recovery (%R) and standard deviation of the percent recovery (SD) for the surrogate.

15.5.8 For a given matrix, calculate the upper and lower control limit for method performance for the surrogate standard. This should be done as follows:

$$\text{Upper Control Limit (UCL)} = (\%R) + 3(SD)$$
$$\text{Lower Control Limit (LCL)} = (\%R) - 3(SD)$$

The surrogate recovery must fall within the control limits. If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solution, and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveals a problem.
- Re-extract and reanalyze the sample if none of the above is a problem or flag the data as "estimated concentration."

15.5.9 Determine the concentration of each analyte in the sample according to Section 17.1 and Section 17.2.3.

15.6 HPLC System Performance

15.6.1 The general appearance of the HPLC system should be similar to that illustrated in Figure 8.

15.6.2 HPLC system efficiency is calculated according to the following equation:

$$N = (5.54)\ (t_r)^2 / W_{1/2}$$

where:
N = column efficiency, theoretical plates
t_r = retention time of analyte, seconds
$W_{1/2}$ = width of component peak at half height, seconds

A column efficiency of >5,000 theoretical plates should be obtained.

15.6.3 Precision of response for replicate HPLC injections should be $\pm$10% or less, day to day, for analyte calibration standards at 1 µg/mL or greater levels. At 0.5 µg/mL level and below, precision of replicate analyses could vary up to 25%. Precision of retention times should be $\pm$2% on a given day.

15.6.4 From the calibration standards, area responses for each PAH compound can be used against the concentrations to establish working calibration curves. The calibration curve must be linear and have a correlation coefficient greater than 0.98 to be acceptable.

15.6.5 The working calibration curve should be checked daily with an analysis of one or more calibration standards. If the observed response (r_o) for any PAH varies by more than 15% from the predicted response (r_p), the test method must be repeated with new calibration standards. Alternately a new calibration curve must be prepared.
Note: If $r_o - r_p / r_p > 15\%$, recalibration is necessary.

15.7 HPLC Method Modification

15.7.1 The HPLC procedure has been automated by Acurex Corporation (9) as part of their "Standard Operating Procedure for Polynuclear Aromatic Hydrocarbon Analysis by High Performance Liquid Chromatography Methods".

15.7.2 The system consists of a Spectra Physics 8100 Liquid Chromatograph, a microprocessor-controlled HPLC, a ternary gradient generator, and an autosampler (10 µL injection loop).

15.7.3 The chromatographic analysis involves an automated solvent program allowing unattended instrument operation. The solvent program consists of four timed segments

using varying concentrations of acetonitrile in water with a constant flow rate, a constant column temperature, and a 10 minute equilibration time, as outlined below.

AUTOMATED HPLC WORKING PARAMETERS

Time	Solvent Composition	Temperature	Rate
10 minutes equilibration	40% Acetonitrile 60% Water	27.0 ± 2°C	1 mL/min
T=0	40% Acetonitrile 60% Water		
T=25	100% Acetonitrile		
T=35	100% Acetonitrile		
T=45	40% Acetonitrile 60% Water		

Table 9 outlines the associated PAHs with their minimum detection limits (MDL) which can be detected employing the automated HPLC methodology.

15.7.4 A Vydac or equivalent analytical column packed with a C18 bonded phase is used for PAH separation with a reverse phase guard column. The optical detection system consists of a Spectra Physics 8440 Ultraviolet (UV)/Visible (VIS) wavelength detector and a Perkin Elmer LS-4 Fluorescence Spectrometer. The UV/VIS detector, controlled by remote programmed commands, contains a deuterium lamp with wavelength selection between 150 and 600 nanometers. It is set at 254 nanometers with the time constant (detector response) at 1.0 seconds.

15.7.5 The LS-4 Fluorescence Spectrometer contains separate excitation and emission monochromators which are positioned by separate microprocessor-controlled stepper motors. It contains a Xenon discharge lamp, side-on photomultiplier and a 3 microliter illuminated volume flow cell. It is equipped with a wavelength programming facility to set the monochromators automatically to a given wavelength position. This greatly enhances selectivity by changing the fluorescence excitation and emission detection wavelengths to specific settings during the chromatographic separation in order to optimize the detection of each PAH. The timed excitation wavelengths range from 230 to 330 nanometers; the emission wavelengths range from 300 to 500 nanometers. The excitation and emission slits are both set at 10 nanometers nominal bandpass. The programmable fluorescence detector allows optimized selectivity and sensitivity for specific compounds. The excitation and emission wavelength conditions listed below do not necessarily correspond to the excitation and emission maxima for the PAHs. They were selected to achieve the most selective response for the analyte compound in the presence of known coeluting compounds. The program fluorescence detector follows the sequence:

Time, minutes	Excitation Wavelength, nm	Emission Wavelength, nm	PAH Quantitated
0.0	254	300	anthracene
19.2	270	380	benzo[a]anthracene dibenzo[a,h,]anthracene benzo[g,h,i]perylene
21.0	285	450	fluoranthene
23.2	330	385	pyrene
24.7	260	400	crysene
28.0	295	405	phenanthrene, benzo[k]fluoranthene, benzo[a]pyrene benzo[g,h,i]perylene
34.6	300	500	indeno[1,2,3-cd] pyrene

15.7.6 The UV detector is used for determining naphthalene, acenapthylene and acenapthene, and the fluorescence detector is used for the remaining PAHs. Table 10 outlines the detection techniques and minimum detection limit (MDL) employing this HPLC system. A Dual Channel Spectra Physics (SP) 4200 computing integrator, with a Labnet power supply, provides data analysis and a chromatogram. An IBM PC XT with a 10 megabyte hard disk provides data storage and reporting. Both the SP4200 and the IBM PC XT can control all functions of the instruments in the series through the Labnet system except for the LS-4, whose wavelength program is started with a signal from the High Performance Liquid Chromatograph autosampler when it injects. All data are transmitted to the XT and stored on the hard disk. Data files can later be transmitted to floppy disk storage.

16. Quality Assurance/Quality Control (QA/QC)

16.1 General System QA/QC

16.1.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate 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.

16.1.2 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.

16.1.3 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.

16.1.4 The experience of the analyst performing GC and HPLC 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.

16.2 Process, Field, and Solvent Blanks

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

16.2.2 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.

16.2.3 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 less than 10 ng/sample for single components to be acceptable.

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

16.3 Gas Chromatography with Flame Ionization Detection

16.3.1 Under the calibration procedures (internal and external), the % RSD of the calibration factor should be <20% over the linear working range of a five point calibration curve (see Section 13.4.1.6 and Section 13.4.2.6).

16.3.2 Under the calibration procedures (internal and external), the daily working calibration curve for each analyte should not vary from the predicted response by more than ±20% (see Section 13.4.1.7 and Section 13.4.2.8).

16.3.3 For each analyte, the retention time window must be established (see Section 13.5.1), verified on a daily basis (see Section 13.6.3.2) and established for each analyte throughout the course of a 72 hour period (see Section 13.5.3).

16.3.4 For each analyte, the mid level standard must fall within the retention time window on a daily basis as a qualitative performance evaluation of the GC system (see Section 13.6.3.4).

16.3.5 The surrogate standard recovery must not deviate from 100% by more than 20% (see Section 13.6.3.5).

16.4 Gas Chromatography with Mass Spectroscopy Detection

16.4.1 Section 14.5.1 requires the mass spectrometer be tuned daily with DFTPP and meet relative ion abundance requirements outlined in Table 3.

16.4.2 Section 14.3.1.1 requires a minimum of five concentration levels of each analyte (plus deuterated internal standards) be prepared to establish a calibration factor to illustrate <20% variance over the linear working range of the calibration curve.

16.4.3 Section 14.3.1.13 requires the verification of the working curve each working day (if using the external standard technique) by the measurement of one or more calibration standards. The predicted response must not vary by more than $\pm$20%.

16.4.4 Section 14.3.2.6 requires the initial calibration curve be verified each working day (if using the internal standard technique) by the measurement of one or more calibration standards. If the response varies by more than $\pm$20% of predicted response, a fresh calibration curve (five point) must be established.

16.4.5 Section 14.4.5 requires that for sample analysis, the comparison between the sample and reference spectrum illustrates: The sample analysis using the GC-MS-SIM is based on a combination of retention times and relative abundances of selected ions (see Table 5). These qualifiers are 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. While this adds some subjective judgment to the analysis, computer- generated identification problems can be clarified by an experienced operator. Manual inspection of the quantitative results should also be performed to verify concentrations outside the expected range.

16.4.6 Section 14.5.3 requires that initial calibration curve be verified every twelve continuous hours of analysis by a mid level calibration standard. The response must be less than 20% difference from the initial response.

16.4.7 The surrogate standard recovery must not deviate from 100% by more than 20% (see Section 14.5.4).

16.5 High Performance Liquid Chromatography Detection

16.5.1 Section 15.4.4 requires the preparation of calibration standards at a minimum of five concentration levels to establish correlation coefficient of at least 0.999 for a linear least-squares fit of the data.

16.5.2 Section 15.4.5 requires that the retention time for each analyte should agree within $\pm 2\%$.

16.5.3 A daily calibration check involving an intermediate standard of the initial five point calibration curve should be within $\pm 15\%$ from day to day.

16.5.4 Section 15.5.6 requires the calculation of percent difference of surrogate standard recovery in order to establish control limits:

$$\text{Upper Control Limit (UCL)} = (\%R) + 3\,(SD)$$
$$\text{Lower Control Limit (LCL)} = (\%R) - 3\,(SD)$$

The surrogate recovery must fall within the control limits.

17. Calculations

17.1 Sample Volume

17.1.1 Retrieve the data logger and download to a computer using the procedure outlined in Section 11.2.20.

Note: All volumetric flows have been corrected to STP as illustrated in Section 11.2.16.

17.1.2 The total sample volume (V_m) is calculated from the periodic flow readings using the following equation.

$$V_s = [(Q_1 + Q_2 \ldots + Q_n)/N] \times [T]$$

where:

V_s = total sample volume at STP conditions, m^3

$Q_1, Q_2, \ldots Q_n$ = flow rates determined at the beginning, end, and intermediate points during sampling, L/minute, see Section 11.2.2.6 and Section 11.2.2.7,

N = number of data points

T = elapsed sampling time, minutes

17.2 Sample Concentration

17.2.1 Gas Chromatography with Flame Ionization Detection

17.2.1.1 The concentration of each analyte in the sample may be determined from the external standard technique by calculating from the peak response, the amount of standard injected using the calibration curve or the calibration factor determined in Section 13.4.1.6.

17.2.1.2 The concentration of a specific analyte is calculated as follows:

$$\text{Concentration, ng/m}^3 = [(A_x)(V_t)(D)]/[(CF)(V_i)(V_s)]$$

where:
CF = calibration factor for chromatographic system, peak height or area response per mass injected, Section 13.4.1.6
A_x = response for the analyte in the sample, area counts or peak height
V_t = volume of total sample, μL
D = dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D=1, dimensionless
V_i = volume of sample injected, μL
V_s = total sample volume at standard temperature and pressure (25°C and 760 mm Hg), m^3, see Section 11.2.16 and Section 17.1.2.

17.2.2 Gas Chromatography-Mass Spectroscopy Detection

17.2.2.1 When an analyte has been identified, the quantification of that analyte will be based on the integrated abundance from the monitoring of the primary characteristic ion. Quantification will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (see Section 14.3.2.1).

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

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

where:
A_x = area of characteristic ion(s) for analyte being measured, counts
I_s = amount of internal standard injected, ng
V_t = volume of total sample, μL
D = dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless
A_{is} = area of characteristic ion(s) for internal standard, counts
RF = response factor for analyte being measured, see Section 14.3.2.5
V_i = volume of analyte injected, μL
V_s = total sample volume at standard temperature and pressure (25°C and 760 mm Hg), m^3, see Section 17.1

17.2.3 High Performance Liquid Chromatography Detection

17.2.3.1 The concentration of each analyte in the sample may be determined from the external standard technique by calculating response factor and peak response using the calibration curve.

17.2.3.2 The concentration of a specific analyte is calculated as follows:

$$\text{Concentration, ng/m}^3 = [(RF_c)(A_x)(V_t)(D)]/[(V_i)(V_s)]$$

where:
RF_c = response factor calculated in Section 15.4.7, ng/area counts
A_x = response for the analyte in the sample, area counts or peak height

V_t = volume of total sample, μL
D = dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless
V_i = volume of sample injected, μL
V_s = total sample volume at standard temperature and pressure (25°C and 760 mm Hg), m^3, see Section 17.1.3

17.3 Sample Concentration Conversion From ng/m^3 to ppb_v

17.3.1 The concentrations calculated in Section 17.2 can be converted to ppb_v for general reference.

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

$$C_A\ (ppb_v) = C_A\ (ng/m^3) \times 24.4/MW_A$$

where:
C_A = concentration of analyte calculated according to Section 17.2.1 through Section 17.2.3, ng/m^3
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

18. Acknowledgements

The determination of PAHs in ambient air is a complex task, primarily because of the wide variety of compounds of interest and the lack of standardized sampling and analysis procedures. Compendium Method IP-7 is an effort to address these difficulties.

While there are numerous procedures for sampling and analyzing PAHs in ambient air, this method draws upon the best aspects of each one and combine them into a standardized methodology. To that end, the following individuals contributed to the research, documentation and peer review of this manuscript.

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Table 1. Formulas and Physical Properties of Selective PAHs

	Formula	Molecular Weight	Melting Point (°C)*	Boiling Point(°C)	Case#
Acenaphthene	$C_{12}H_{10}$	154.21	96.2	279	83-32-9
Acenaphthylene	$C_{12}H_8$	152.20	92-93	265-275	208-96-8
Anthracene	$C_{14}H_{10}$	178.22	218	342	120-12-7
Benzo(a)anthracene	$C_{18}H_{12}$	228.29	158-159	-	56-55-3
Benzo(a)pyrene	$C_{20}H_{12}$	252.32	177	310-312	50-32-8
Benzo(b)fluoranthene	$C_{20}H_{12}$	252.32	168	-	205-99-2
Benzo(e)pyrene	$C_{20}H_{12}$	252.32	178-179	-	192-92-2
Benzo(g,h,i)perlene	$C_{22}H_{12}$	276.34	273	-	191-24-2
Benzo(k)fluoranthene	$C_{20}H_12$	252.32	217	480	207-08-9
Chrysene	$C_{18}H_12$	228.29	255-256	-	218-01-9
Dibenzo(a,h)anthracene	$C_{22}H_{14}$	278.35	261	-	53-70-3
Fluoranthene	$C_{16}H_{10}$	202.26	110	-	206-44-0
Fluorene	$C_{13}H_{10}$	166.22	116-117	293-295	86-73-7
Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276.34	161.5-163	-	193-39-5
Naphthalene	$C_{10}H_8$	128.16	80.2	217.9	91-20-3
Phenanthrene	$C_{14}H_{10}$	178.22	100	340	85-01-8
Pyrene	$C_{16}H_{10}$	202.26	156	399	129-00-0

*Many of these compounds sublime.

Table 2. Retention Times for Selective PAHs for Packed and Capillary Columns Using Flame Ionization Detector

Compound	Packed[1]	Capillary[2]
Acenaphthene	10.8	8.60
Acenaphthylene	10.4	11.38
Anthracene	15.9	11.65
Benzo(a)anthracene	20.6	12.60
Benzo(a)pyrene	29.4	14.82
Benzo(b)fluoranthene	28.0	15.00
Benzo(ghi)perylene	38.6	19.05
Benzo(k)fluoranthene	28.0	20.05
Chrysene	24.7	26.90
Dibenzo(a,h)anthracene	36.2	27.20
Fluoranthene	19.8	34.00
Fluorene	12.6	34.20
Indeno(1,2,3-cd)pyrene	36.2	35.98
Naphthalene	4.5	42.80
Phenanthrene	15.9	43.00
Pyrene	20.6	44.18

[1] GC conditions: Chromosorb W-AW-DMCS (100/120 mesh) coated with 3% OV-17,packed in a 1.8-m long x 2 mm ID glass column, with nitrogen carrier gas at a flow rate of 40 mL/min. Column temperature was held at 100°C for 4 min. then programmed at 8°/minute to a final hold at 280°C.

[2] Capillary GC conditions: 30 meter x 0.25 mm ID fused silica, DB-5 capillary column; on column injection; oven temperature held at 40°C for 1 minute; program at 15°C/min to 200°C; program at 3°C/min to 300°C (see Figure 17 for representative chromatogram under these conditions).

Table 3. DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

Table 4. GC and MS Operating Conditions

<u>Chromatography</u>	
Column	J & W Scientific, DB-5 crosslinked 5% phenylmethyl silicone (30 m x 0.25 mm, 0.25 μm film thickness) or equivalent
Carrier Gas	Helium velocity 20 cm^3/sec at 250°C
Injection Volume	1 μL
Injection Mode	On-column injection
<u>Temperature Program</u>	
Initial Column Temp.	60°C
Initial Hold Time	1 min
Program	60°C to 200°C at 15°C/min; 200°C to 310°C at 3°C/min
Final Hold Time	15 min until benzo(ghi)perylene eludes
<u>Mass Spectrometer</u>	
Detection Mode	Multiple ion detection, SIM mode

Table 5. Approximate Retention Time and Characteristic Ions From GC-MS Detection for Selected PAHs

Compound	Approximate[1] Retention Time (min)	Characteristic Ions Primary		Secondary	Double Charge Ions
Acenaphthene	10.57	154	153	152	77
Acenaphthylene	10.24	152	151	153	76
Anthracene	14.04	178	179	176	89
Benzo(a)anthracene	26.42	228	229	226	114
Benzo(a)pyrene	35.53	252	253	125	126
Benzo(b)fluoranthene	33.55	252	253	125	126
Benzo(ghi)perylene	43.70	276	138	277	138
Benzo(k)fluoranthene	33.72	252	253	125	226
Chrysene	26.66	228	226	229	114
Dibenzo(a,h)anthracene	42.62	278	139	279	139
Fluoranthene	18.36	202	101	203	101
Fluorene	11.56	166	165	167	83
Indeno(1,2,3-cd)pyrene	42.34	276	138	227	138
Naphthalene	7.10	128	129	127	64
Phenanthrene	13.84	178	179	176	89
Pyrene	19.37	202	200	203	101

[1] Capillary GC conditions: 30 m x 0.25 mm DB-5 fused silica capillary column; on-column injection; oven temperature held at 60°C for 1 minute; program at 15°C/min to 200°C; program at 3°C/min to 310°C (see Figure 19 for representative chromatogram under these conditions).

Table 6. Characteristic Ions From GC-MS Detection for Deuterated Internal Standards and Selected PAHs

Compound	M/Z
D_8-naphthalene	136
D_{10}-phenanthrene	188
Phenanthrene	178
Anthracene	178
Fluoranthene	202
D_{10}-pyrene	212
Pyrene	202
Cyclopenta[c,d]pyrene	226
Benzo[a]anthracene	228
D_{12}-chrysene	240
Benzo[e]pyrene	252
D_{12}-benzo[a]pyrene	264
Benzo[a]pyrene	252

Table 7. Commercially Available Columns for PAH Analysis Using HPLC

Company	Column Identification	Column Name
The Separation Group P.O. Box 867 Hesperia, California 92345	201-TP	VYDAC
Rainin Instrument Company Mack Road Wasurn, MA 01801-4626	Ultrasphere - ODS	ALEX
Supelco, Inc. Supelco Park Bellefonte, PA 16823-0048	LC-PAH	Supelcosil
DuPont Company Biotechnology Systems Barley Mill Plaza, P24 Wilmington, DE 19898	ODS	Zorbax
Perkin-Elmer Corp. Corporate Office Main Avenue Norwalk, CT 06856	HC-ODS	Sil-X
Waters Associates 34-T Maple St. Milford, MA 01757	μ-Bondapak	μ-Bondapak NH_2

Table 8. Typical Retention Time for Selective PAHs by HPLC Separation* and UV Detection

Compound	Retention Times (minutes)
Acenaphthene	18.0
Acenaphthylene	15.8
Anthracene	21.0
Benzo(a)anthracene	26.3
Benzo(a)pyrene	31.1
Benzo(b)fluoranthene	29.3
Benzo(ghi)perylene	33.9
Benzo(k)fluoranthene	30.2
Chrysene	26.7
Dibenzo(a,h)anthracene	32.7
Fluoranthene	22.5
Fluorene	18.5
Indeno(1,2,3-cd)pyrene	34.6
Naphthalene	14.0
Phenanthrene	19.9
Pyrene	23.4

* HPLC parameters: VYDAC 201 guard column, reverse phase VYDAC 201 TP 5415 analytical column. Isocratic elution for 10 minutes using acetonitrile/water (4:6)(v/v), then linear gradient elution to 100% acetonitrile within 15 minutes, then 100% acetonitrile for 10 minutes, then linear gradient to acetonitrile/water (4:6)(v/v) within 10 minutes. UV detector operating at 254 nm.

Table 9. Typical Retention Time for Selective PAHs by HPLC Separation and UV Detection

Compound	Method 8310[1]	Fluorescence[2]	Ultraviolet[2]
Acenaphthene	20.5	-	18.0
Acenaphthylene	18.5	-	15.8
Anthracene	23.4	21.0	21.0
Benzo(a)anthracene	28.5	26.3	26.3
Benzo(a)pyrene	33.9	31.1	31.1
Benzo(b)fluoranthene	31.6	29.3	29.3
Benzo(ghi)perylene	36.3	33.9	33.9
Benzo(k)fluoranthene	32.9	30.2	30.2
Chrysene	29.3	26.7	26.7
Dibenzo(a,h)anthracene	35.7	32.7	32.7
Fluoranthene	24.5	22.5	22.5
Fluorene	21.2	18.5	18.5
Indeno(1,2,3-cd)pyrene	37.4	34.6	34.6
Naphthalene	16.6	-	14.0
Phenanthrene	22.1	19.9	19.9
Pyrene	25.4	23.4	23.4

[1] Condition A HPLC Parameters: Reverse phase HC-ODS Si -X, 5 micron particle size, in a 250 mm x 2.6 mm ID stainless steel column. Isocratic elution for 5 min using acetonitrile/ water (4:6)(v/v), then linear gradient elution to 100% acetonitrile over 25 min at 0.5 mL/min flow rate.
Note: If columns having other internal diameters are used, the flow rate should be adjusted to maintain a linear velocity of 2 mm/sec. UV detector operating at 254 nm.

[2] Condition B HPLC Parameters: VYDAC 201 guard column, reverse phase VYDAC 201 TP 5415 analytical column. Isocratic elution for 10 minutes using acetonitrile/water (4:6)(v/v), then linear gradient elution to 100% acetonitrile within 15 minutes, then 100% acetonitrile for 10 minutes, then linear gradient to acetonitrile/water (4:6)(v/v) within 10 minutes. UV detector operating at 254 nm.

Table 10. Retention Times (RTs) and Minimum Detection Limits (MDLs) for Selected PAHs by HPLC Analysis* Using UV and Fluorescence Detection

	Ultraviolet Detector		Fluorescence Detector	
PAH	Retention Time	Detection Limit	Retention Time	Detection Limit
Naphthalene	14.0	250pg/μL	-	-
Acenaphthylene	15.85	250pg/μL	-	-
Acenaphthene	18.0	250pg/μL	-	-
Fluorene	18.5	50pg/μL	18.5	5pg/μL
Phenanthrene	19.9	50pg/μL	19.9	10pg/μL
Anthracene	21.0	50pg/μL	21.0	50pg/μL
Fluoranthene	22.5	50pg/μL	22.5	10pg/μL
Pyrene	23.4	50pg/μL	23.4	5pg/μL
Benzo(a)anthracene	26.3	50pg/μL	26.3	5pg/μL
Chrysene	26.7	50pg/μL	26.7	5pg/μL
Benzo(b)fluoranthene	29.3	50pg/μL	29.3	10pg/μL
Benzo(k)fluoranthene	30.2	50pg/μL	30.2	5pg/μL
Benzo(a)pyrene	31.1	50pg/μL	31.1	5pg/μL
Dibenzo(a,h)anthracene	32.7	50pg/μL	32.7	5pg/μL
Benzo(ghi)perylene	33.9	50pg/μL	33.9	5pg/μL
Indeno(1,2,3-cd)pyrene	34.6	50pg/μL	34.6	50pg/μL

* HPLC Conditions:

Guard Column: VYDAC 201 GCCIOYT

Analytical Column: VYDAC 201 TP5415 C-18 RP (0.46 x 25 cm)

Column Temperature: 27.0 ± 2°C

Mobile Phase:

Solvent Composition	Time (Minutes)
40% Acetonitrile/60% water	0
100% Acetonitrile	25
100% Acetonitrile	35
40% Acetonitrile/60% water	45

Flow Rate: 1.0 mL/minute

Injection Volume: 10 μL

Linear gradient elution at 1.0 mL/min

Detector: UV, operating at 254 nm

Fluorescence, programmable wavelength to set monochromators at:

Time	Fixed Scale	Excitation (nm)	Emission (nm)
0.0	0.5	254	300
19.2		270	380
21.9		285	450
23.2		330	385
24.7		260	400
28.0		295	405
34.6		300	500

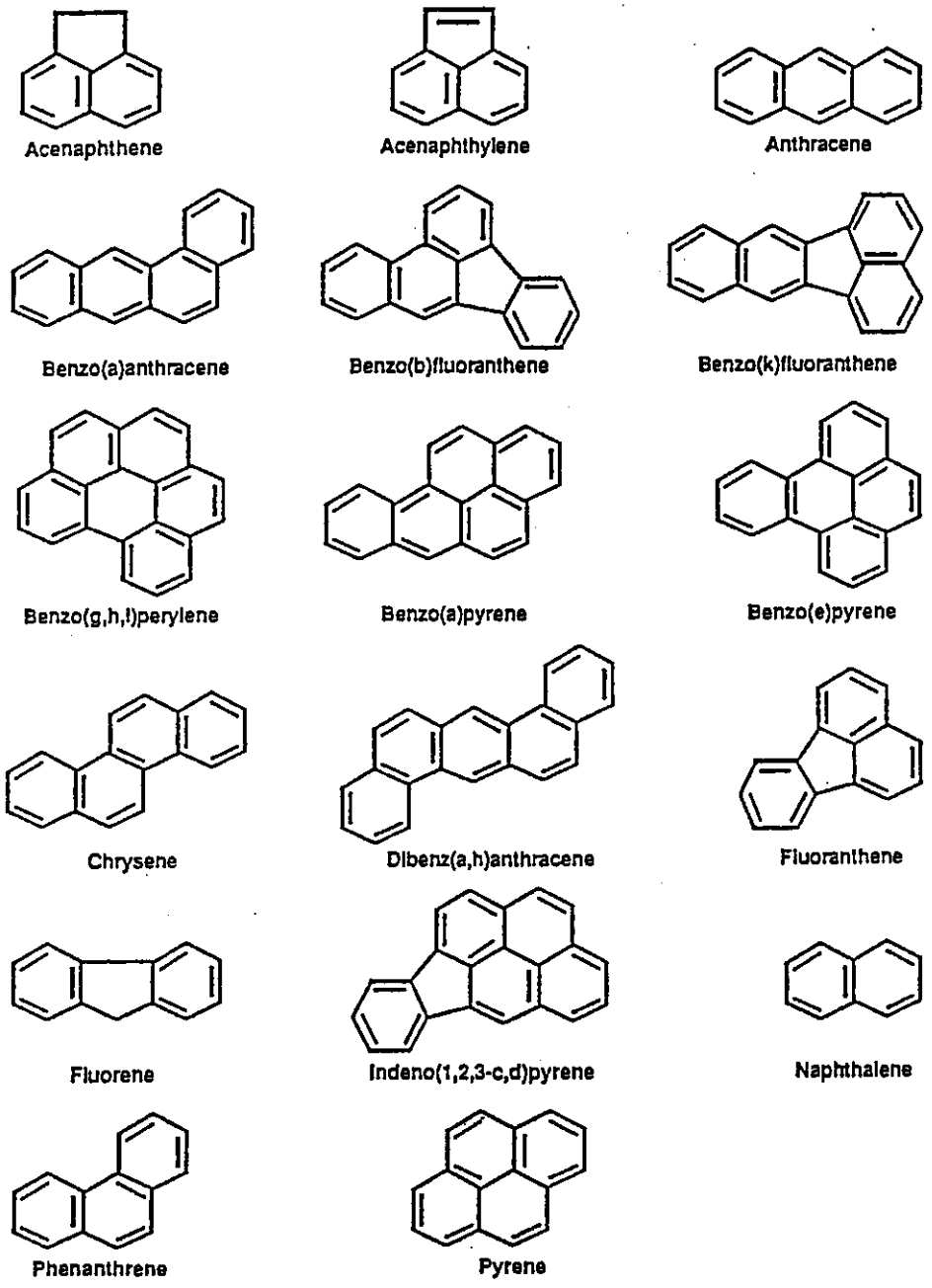

Figure 1. Ring Structure of Selected PAHs

620

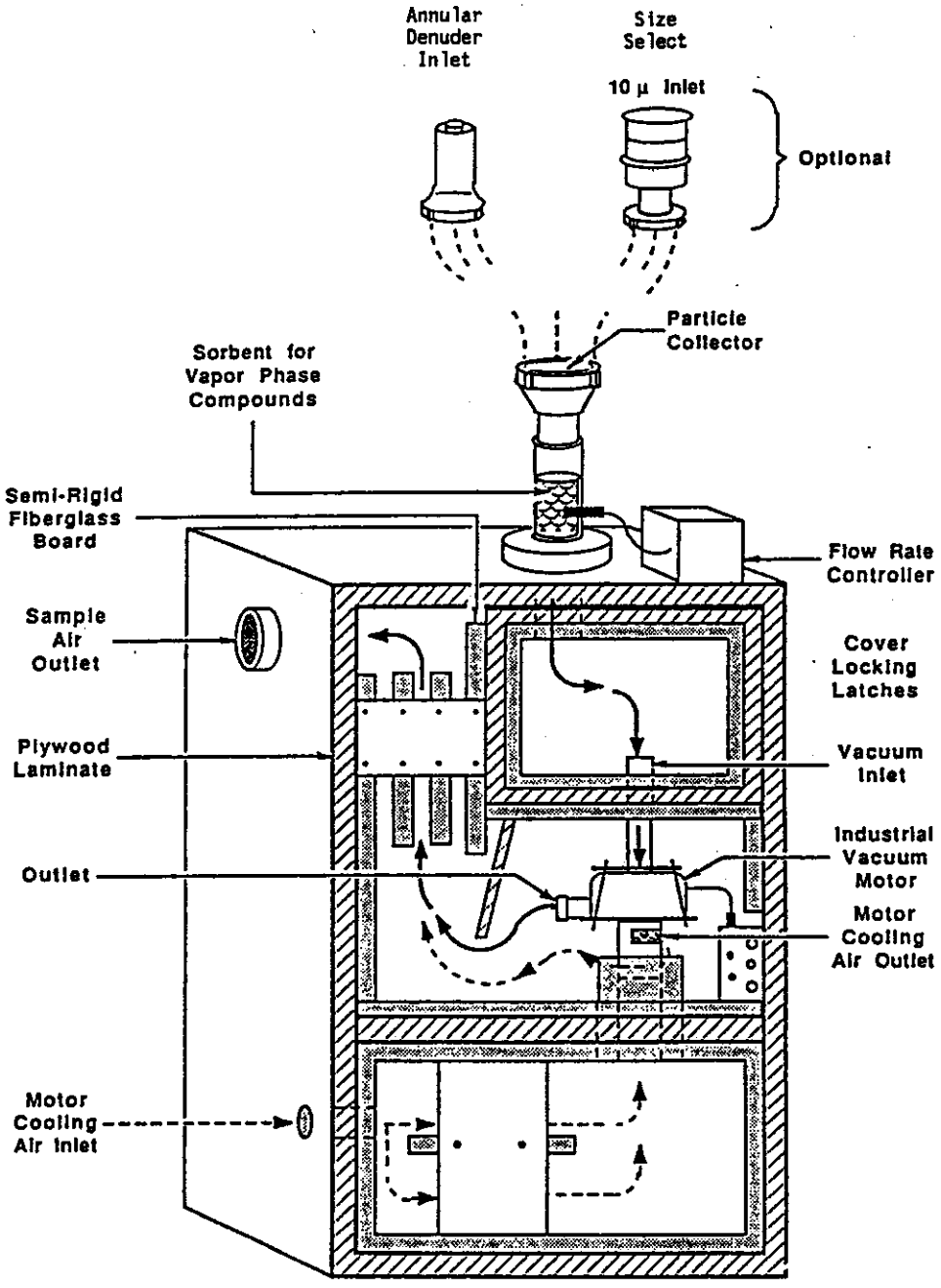

Figure 2. Acoustically Enclosed Medium Volume Sampler

621

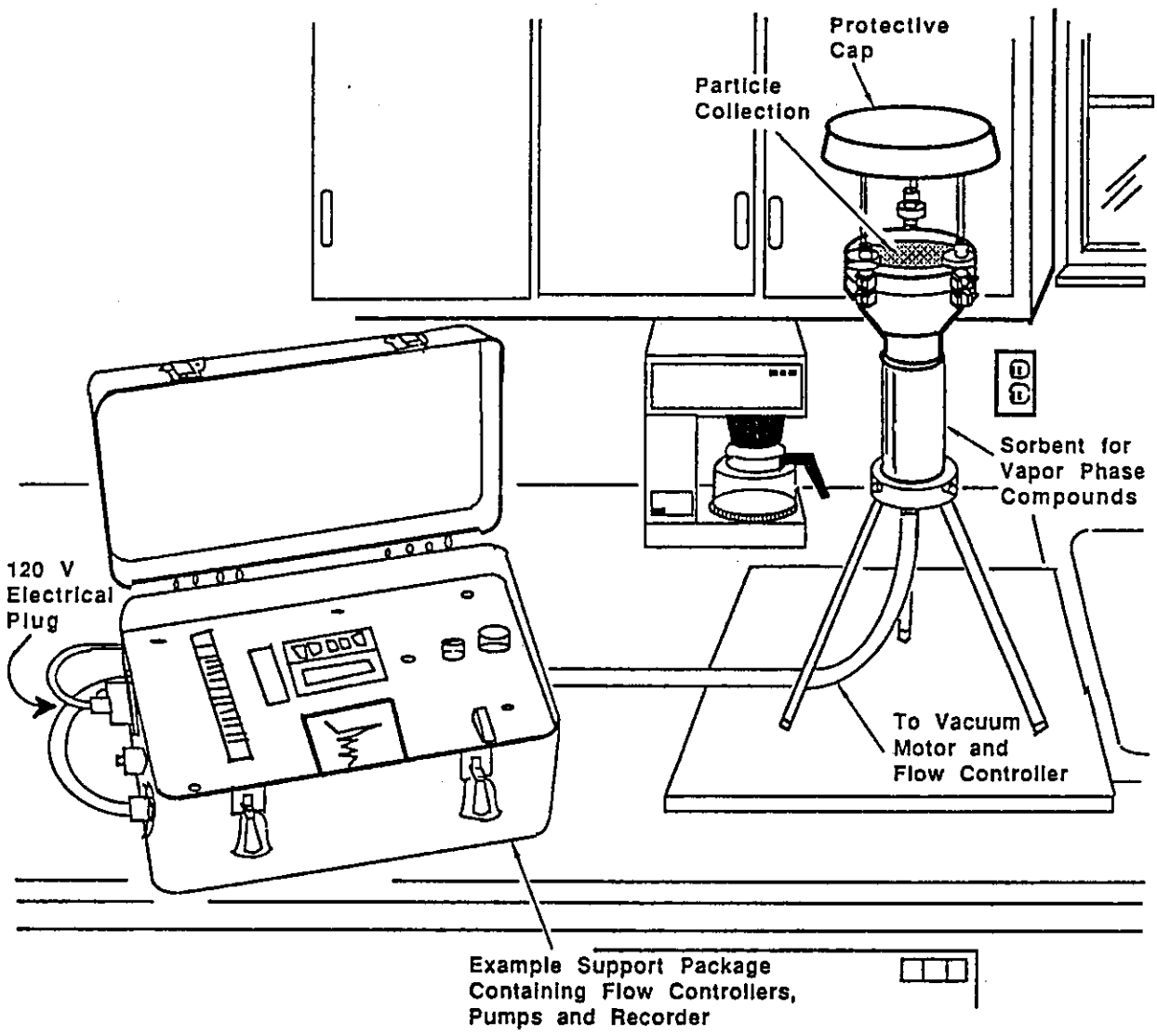

Figure 3. Tripod Sampler with Portable Meter Box Assembly

622

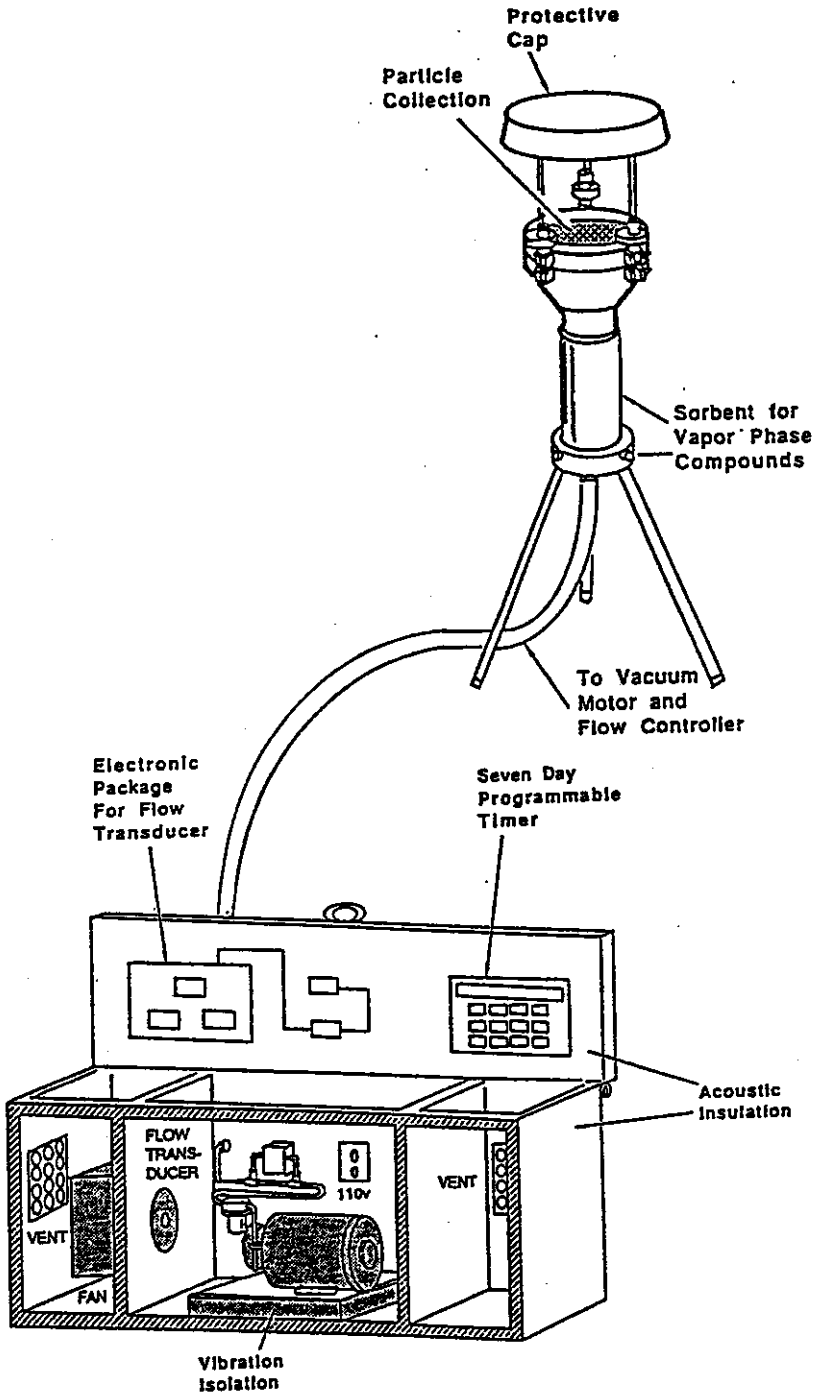

Figure 4. Battelle-Columbus Laboratory Medium Volume Air Sampler with Tripod Sampling Head

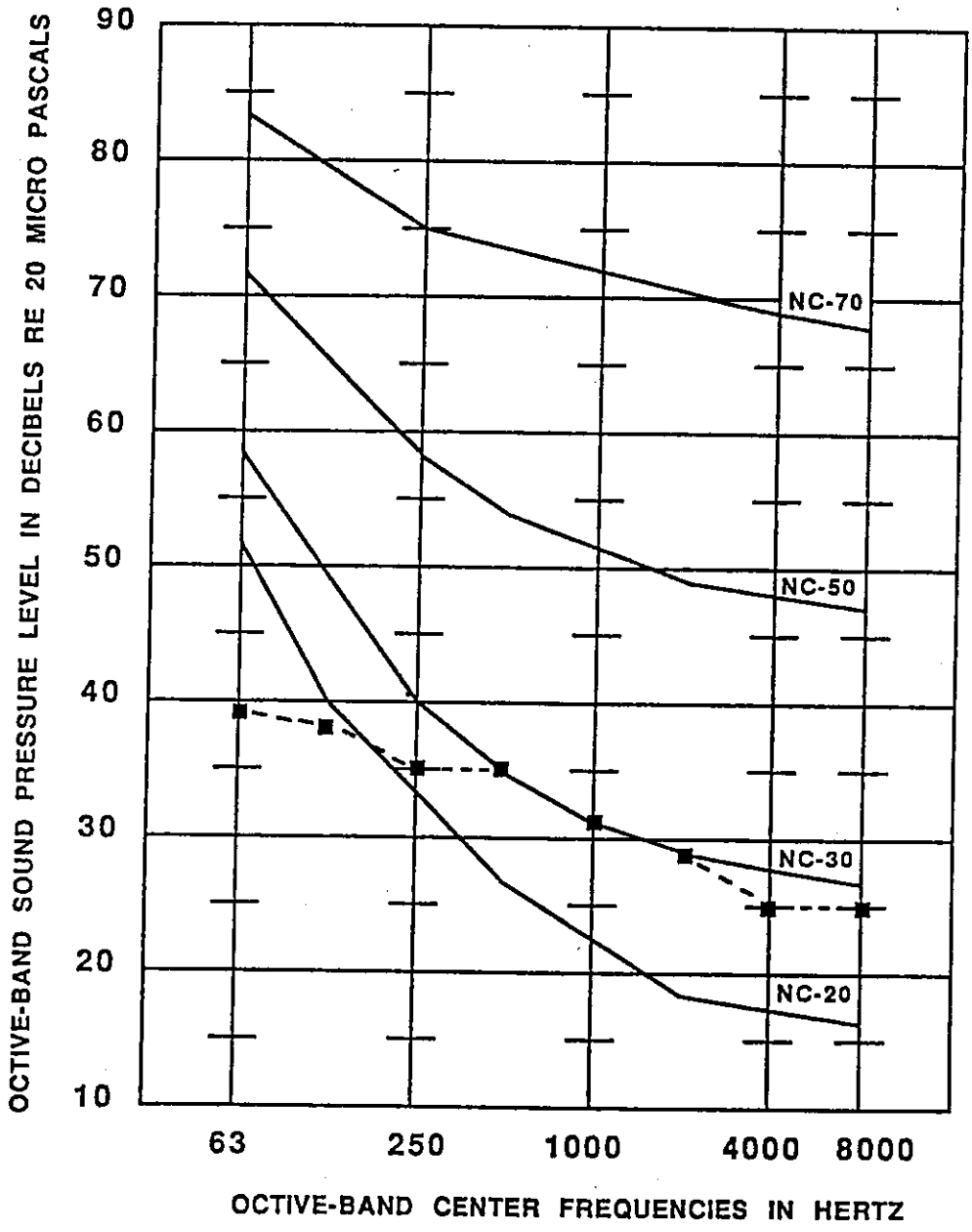

Figure 5. Noise Criterion for Indoor Air Sampler

624

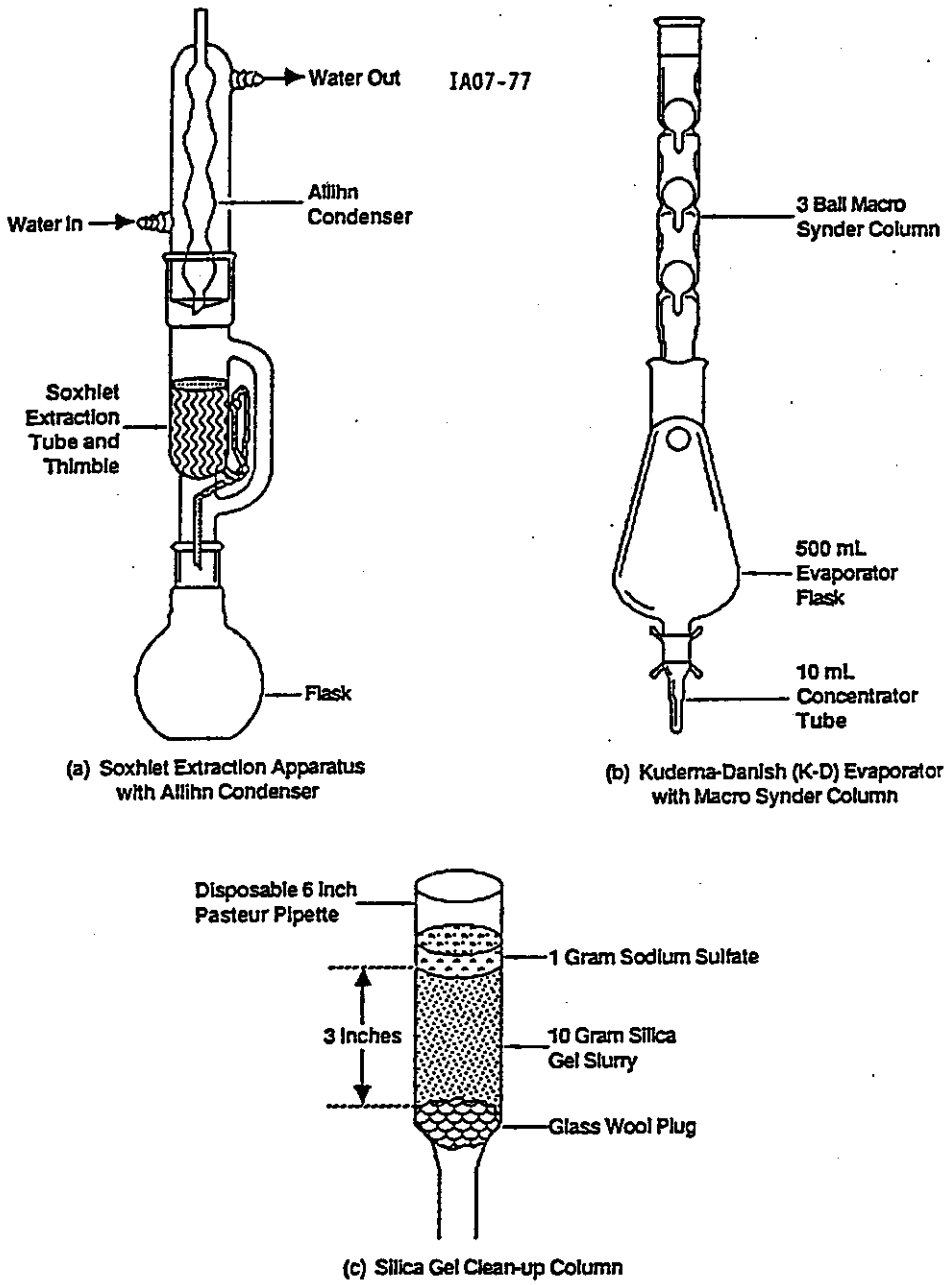

Figure 6. Apparatus Used in Sampling Analysis

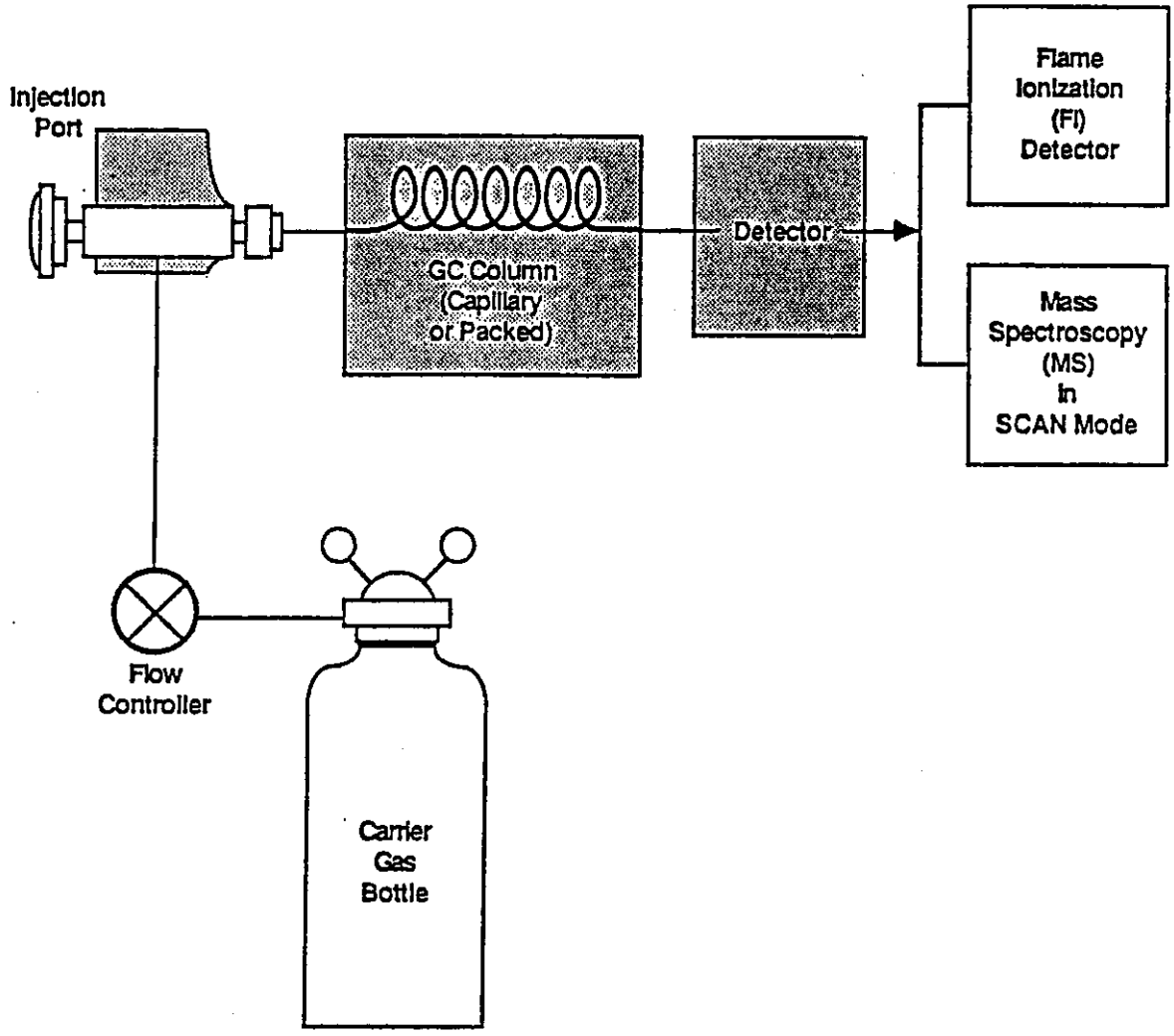

Figure 7. GC Separation with Subsequent Flame Ionization (FI) or Mass Spectroscopy (MS) Detection

626

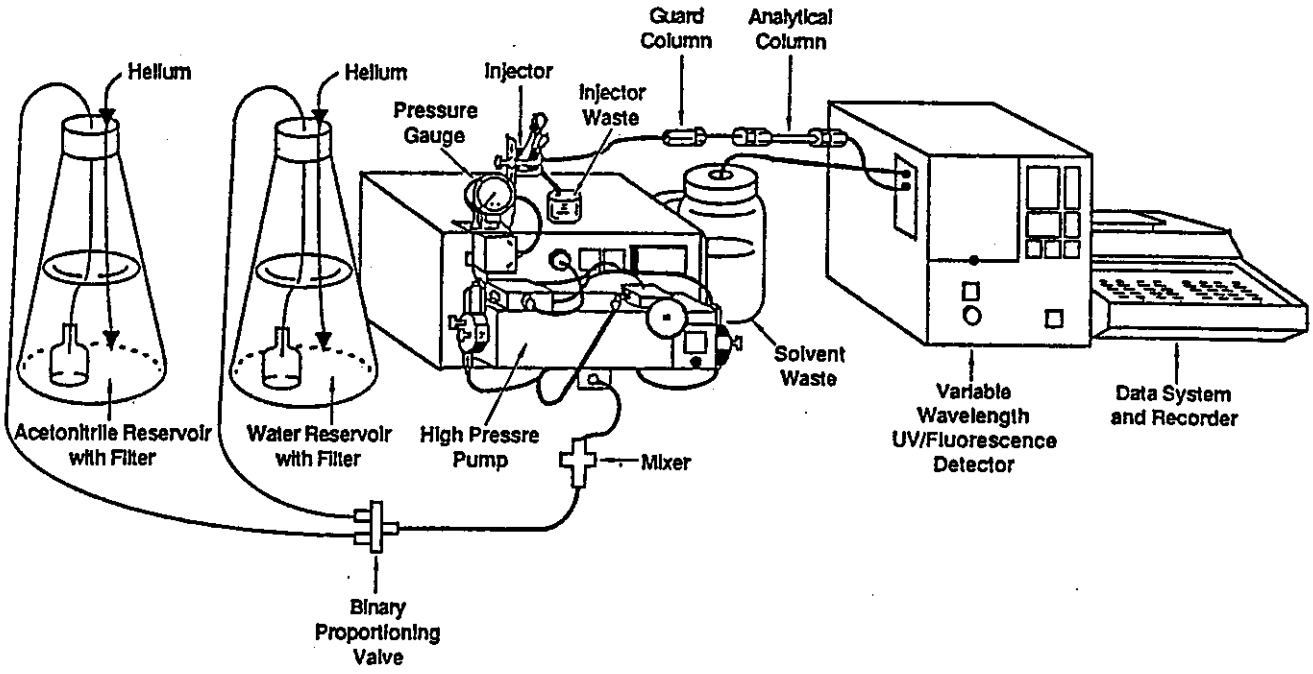

Figure 8. Important Components of an HPLC System

627

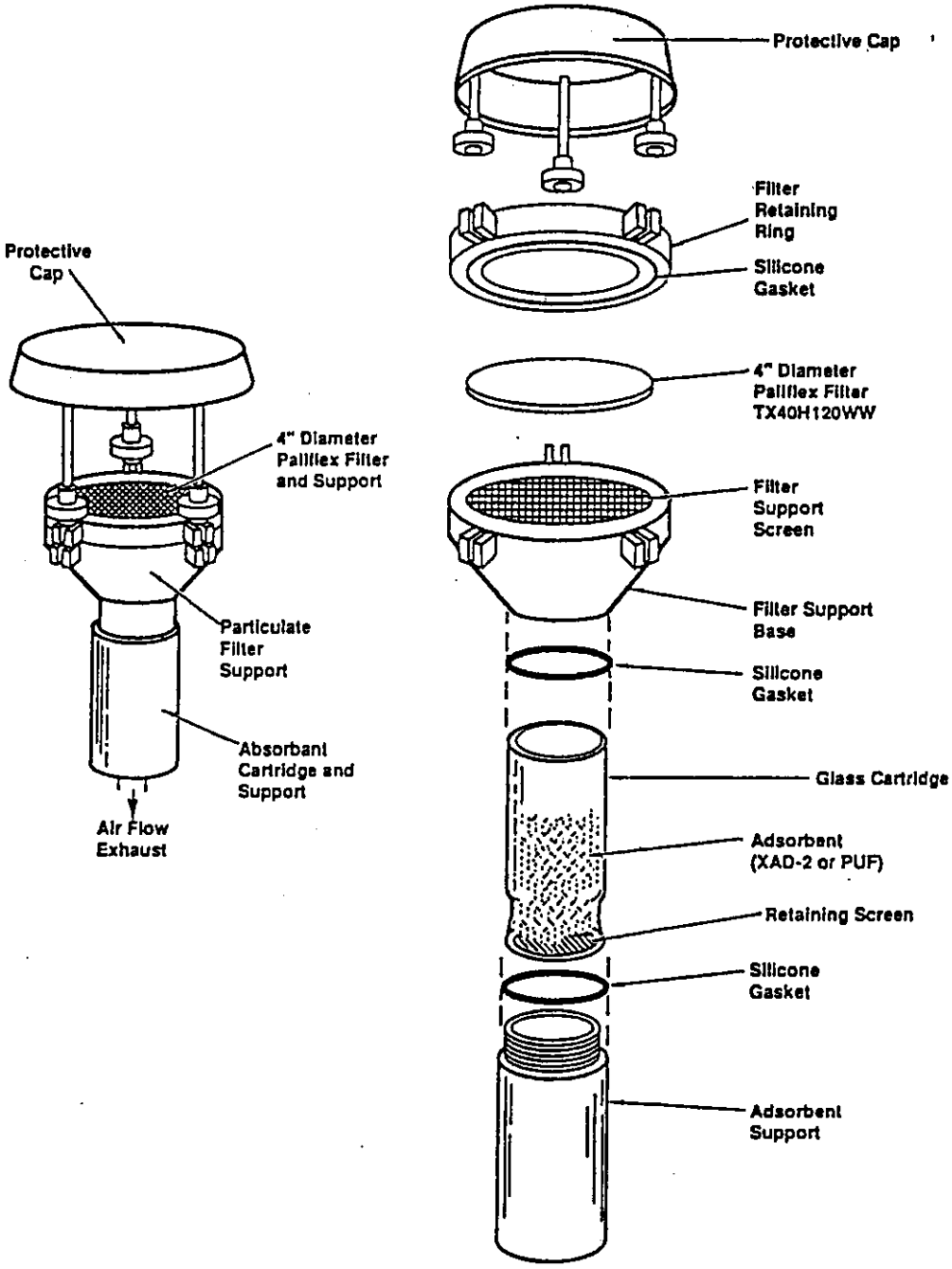

Figure 9. General Metal Works Sampling Head with Protective Cap

628

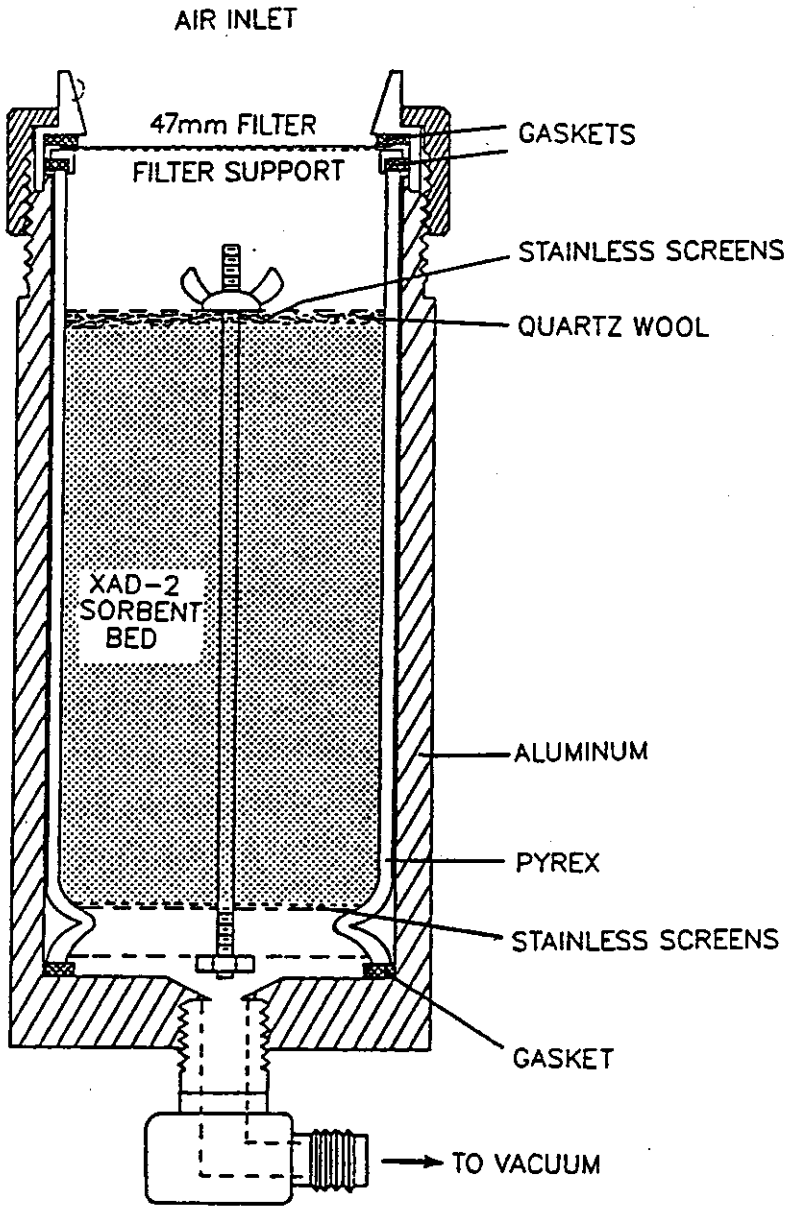

Figure 10. Alternative Design for Medium Volume Indoor Air Sampler with Open Face Filter Assembly

629

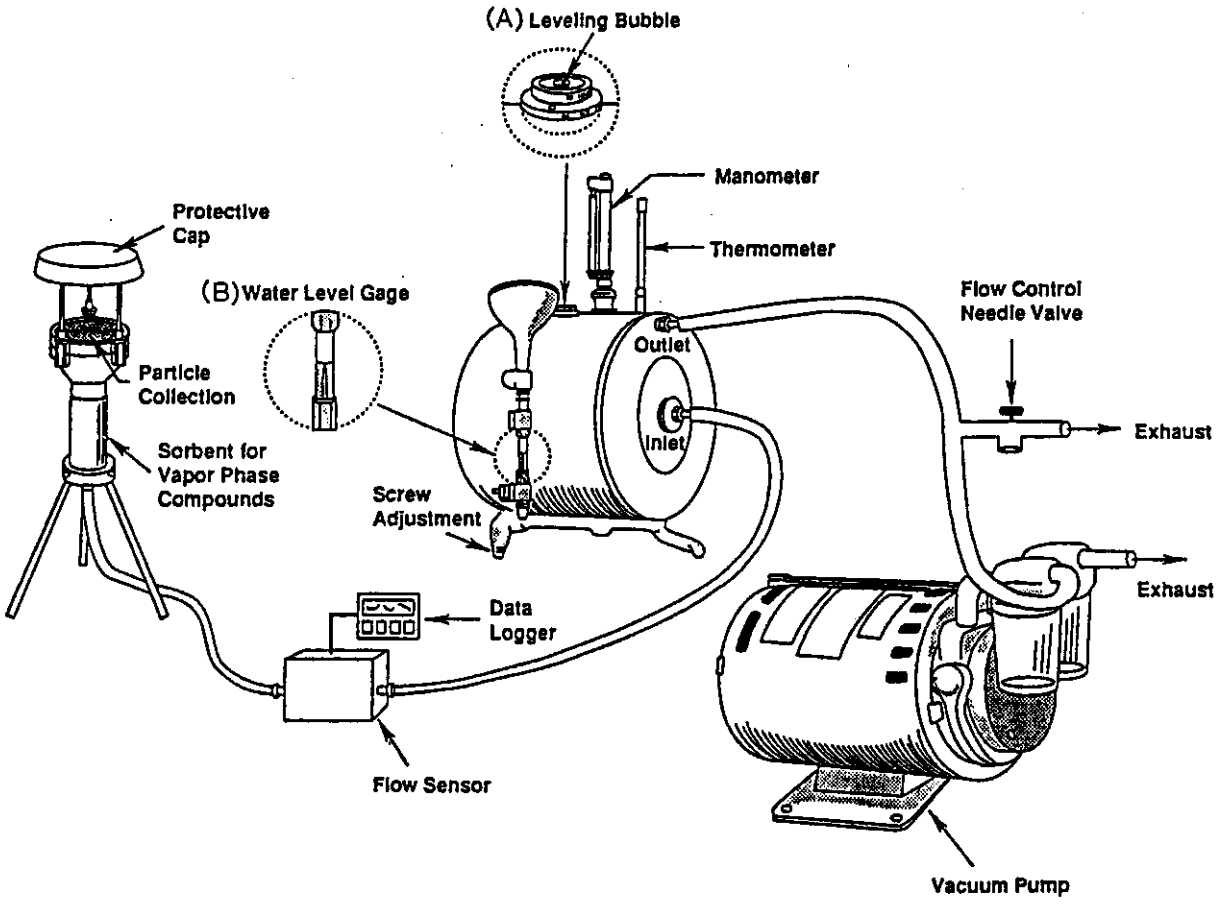

Figure 11. Calibration Assembly for Medium Volume Sampling System

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Flow Sensor Calibration Data Sheet

Name _____

Date _____

Wet test meter fluid temperature (T_m) _____°C _____°K
Mass flow meter # _____
Mass flow meter range setting _____
Barometric pressure (P_b) _____mm Hg WTM C.F. _____
Transducer # _____ WTM # _____
Water vapor pressure (p_v) _____ mm Hg

Flow Transducer		Wet Test Meter						Flow Rate	
% Full Scale	Volts	V_m	V_a	Δp	T_m	V_s	θ	V_s	Q_s
80									
60									
40									
20									
10									

$V_a = V_m \times C.F.$, L
$P_m = P_b$ (mm Hg) - Δp (mm Hg), mm Hg
$T_m = °V + 273.16$, °K
$V_s = (V_a)(P_m - p_v/P_s)(T_s/T_m)$, L
p_v = vapor pressure of wet test meter water, mm Hg
θ = time, minutes
Q_s = standard volumetric flow rate, L/min

Figure 12. Flow Sensor Calibration Data Sheet

Sampler Site _____

Sampler Location _____

Date _____

	Before	After
Barometric Pressure		
Ambient Temperature		

Site _____ Date _____ Performed By _____

Sampler S/N	Sampling Location I.D.	Height Above Ground	Identification No.		Sampling Period		Totaling Sampling Time, min.	Pump Timer Hr. Min.	Sampler Flow				
			Filter	XAD-2 or PUF	Start	Stop				V_s	Q_s		Within ± 10%

Checked By _____

Date _____

Figure 13. Field Test Data Sheet

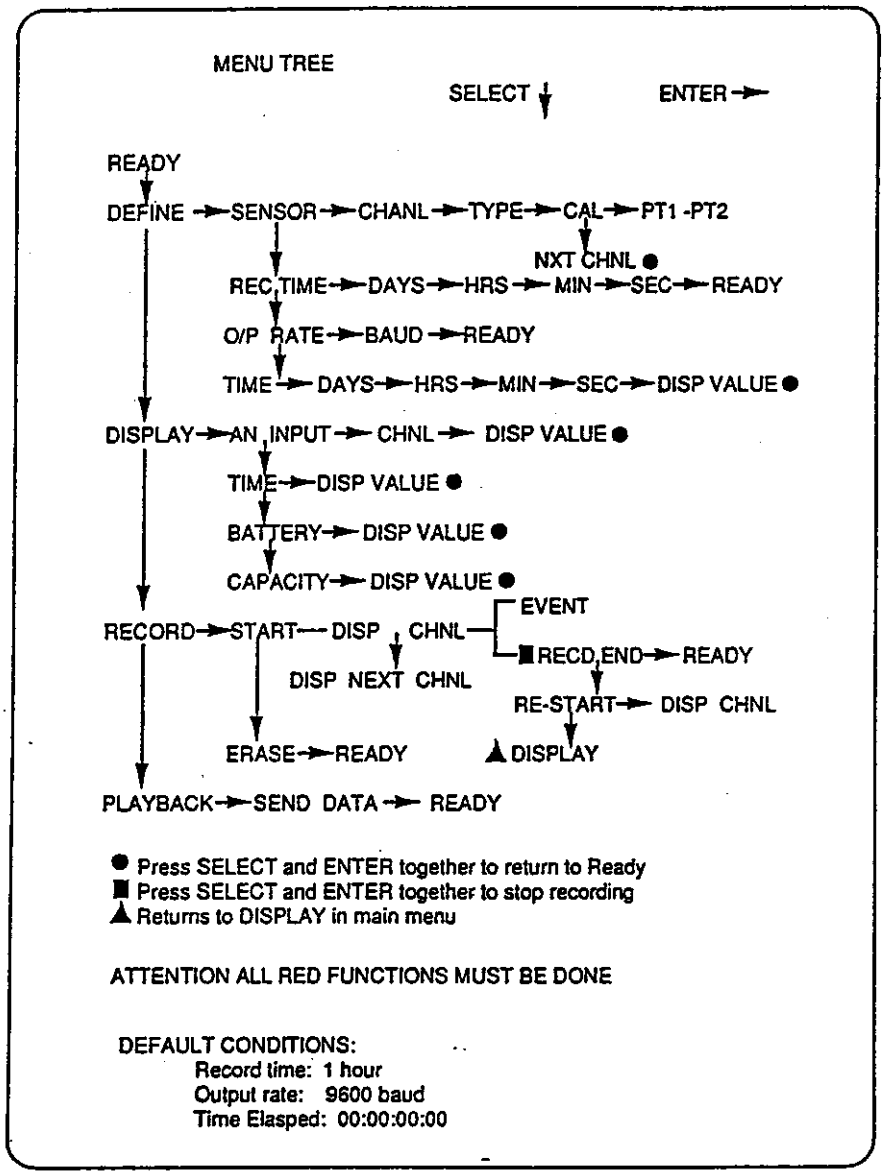


Figure 14. Data Logger Menu Tree

633

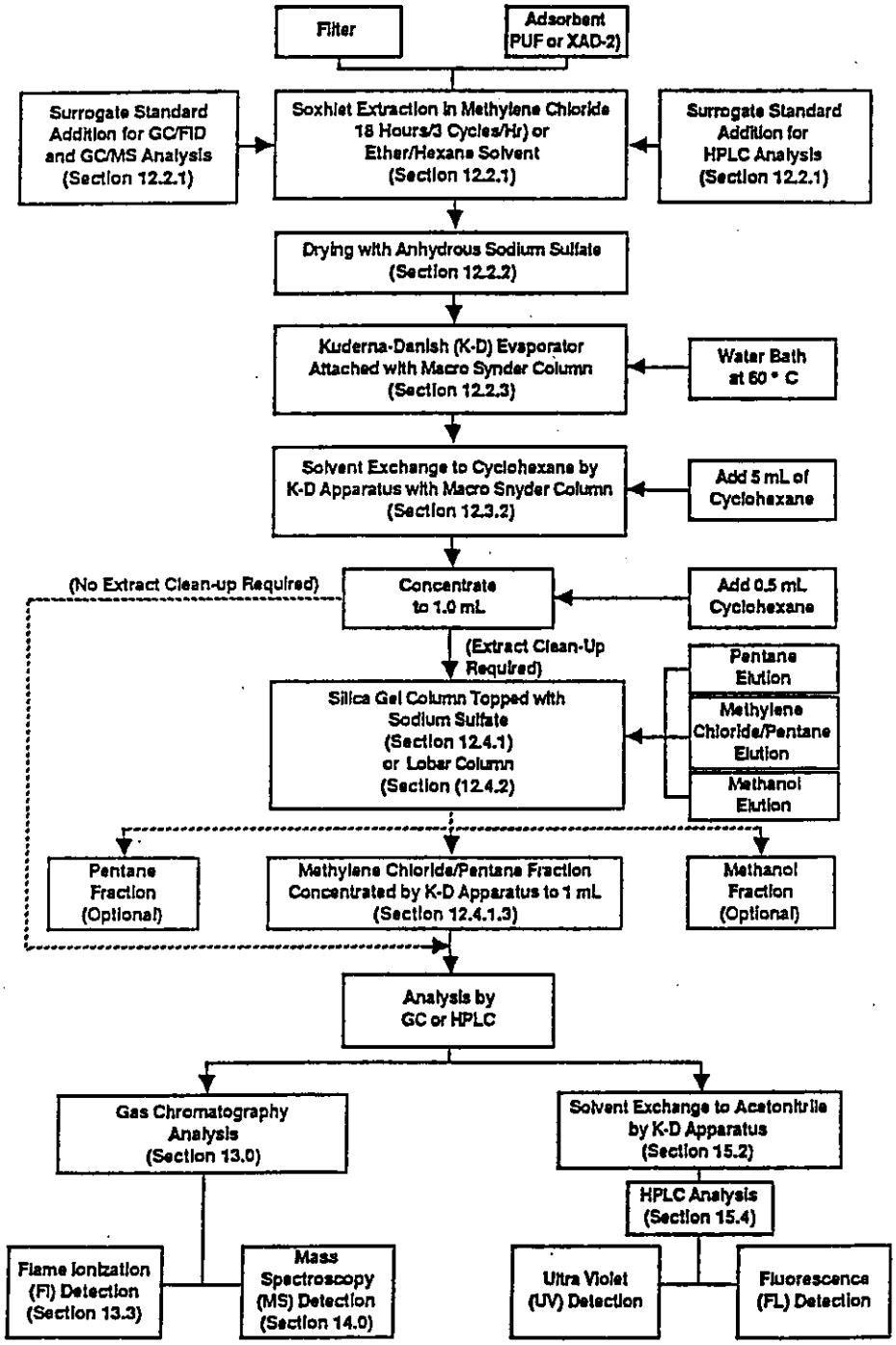


Figure 15. Sample Clean-Up, Concentration, Separation and Analysis Sequence

834

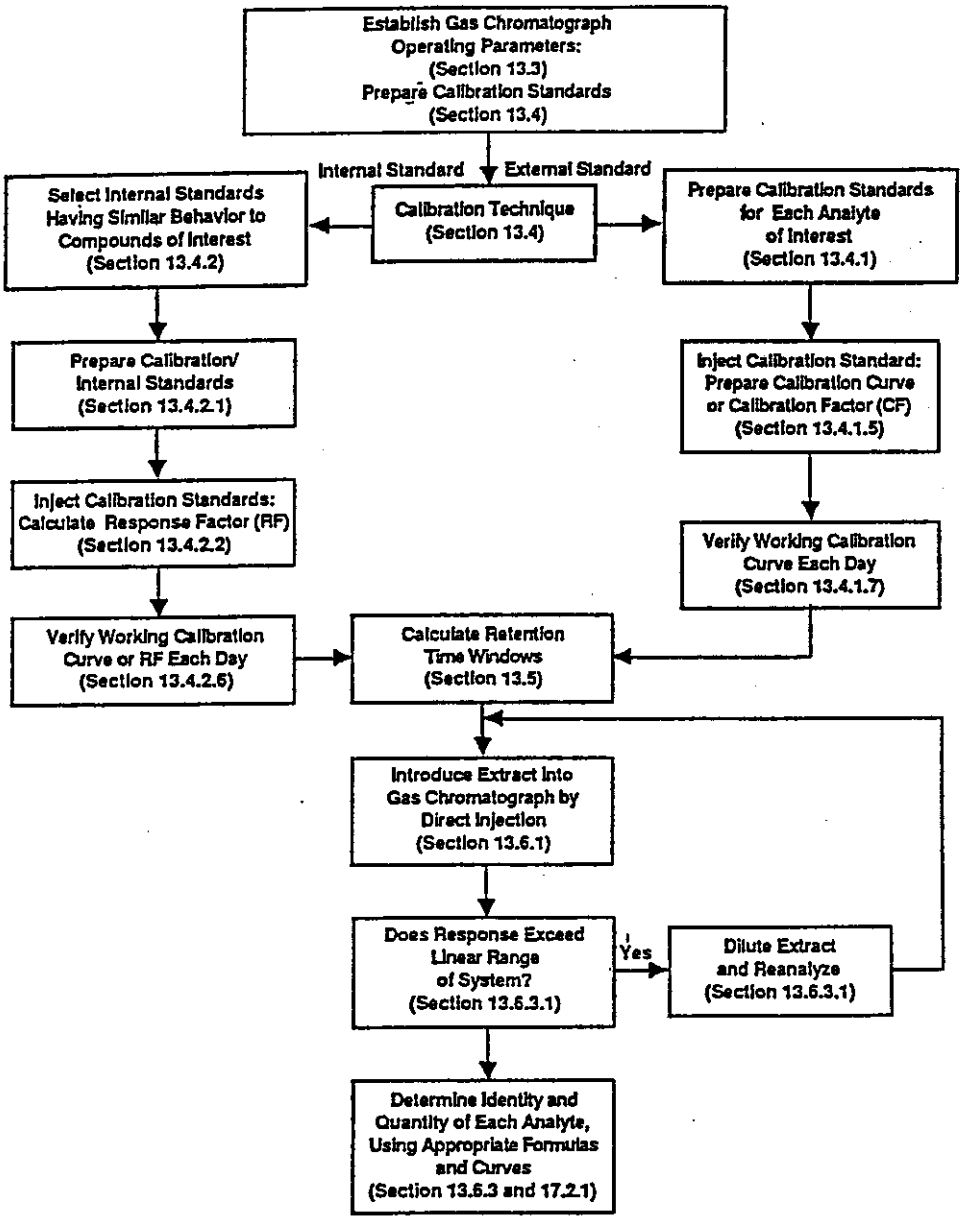
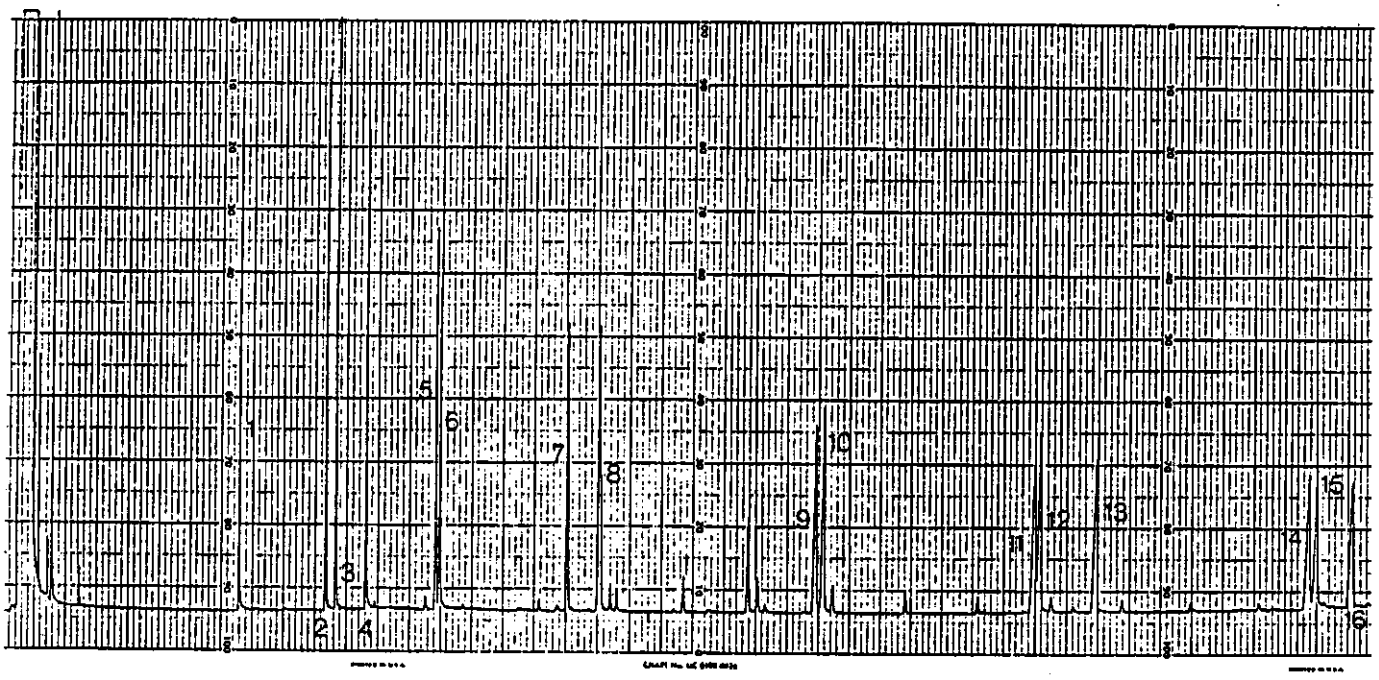


Figure 16. GC Calibration and Retention Time Window Determination

685



Injection: 1.0 µL on-column
Column: 30m x 0.25 mm DB-5 capillary with 0.25 µm film thickness
Program: 40°C (1 min), 15°C/min to 200°C, 3°C/min to 300°C
Detector: Flame ionization

1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo(a)anthracene
10. Chrysene
11. Benzo(b)fluoranthene
12. Benzo(k)fluoranthane
13. Benzo(a)pyrene
14. Indeno(1,2,3-cd)pyrene
15. Dibenzo(a,h)anthracene
16. Benzo(ghi)perylene

Figure 17. Typical Chromatogram of Selected PAHs by GC Equipped with FI Detector

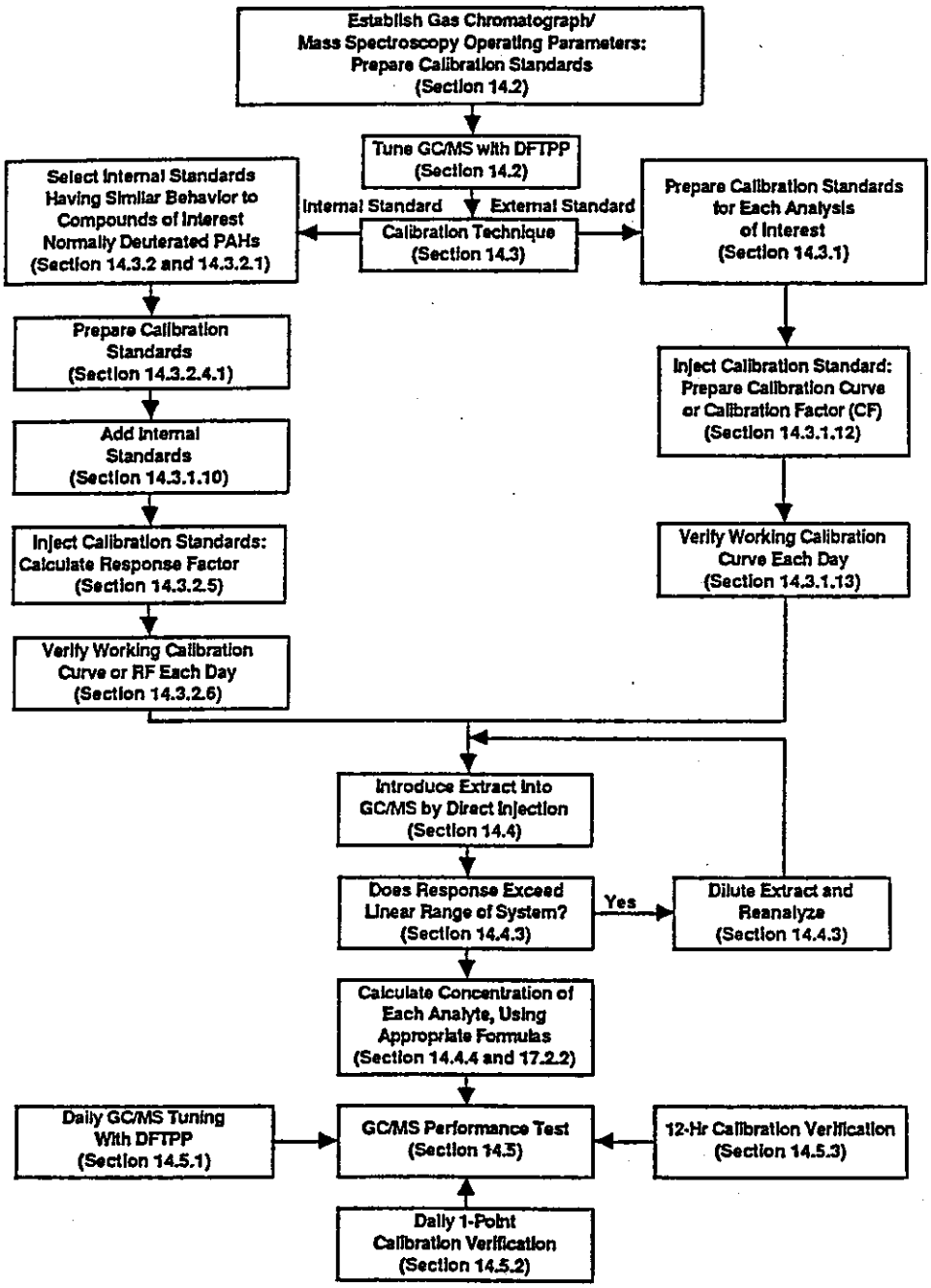
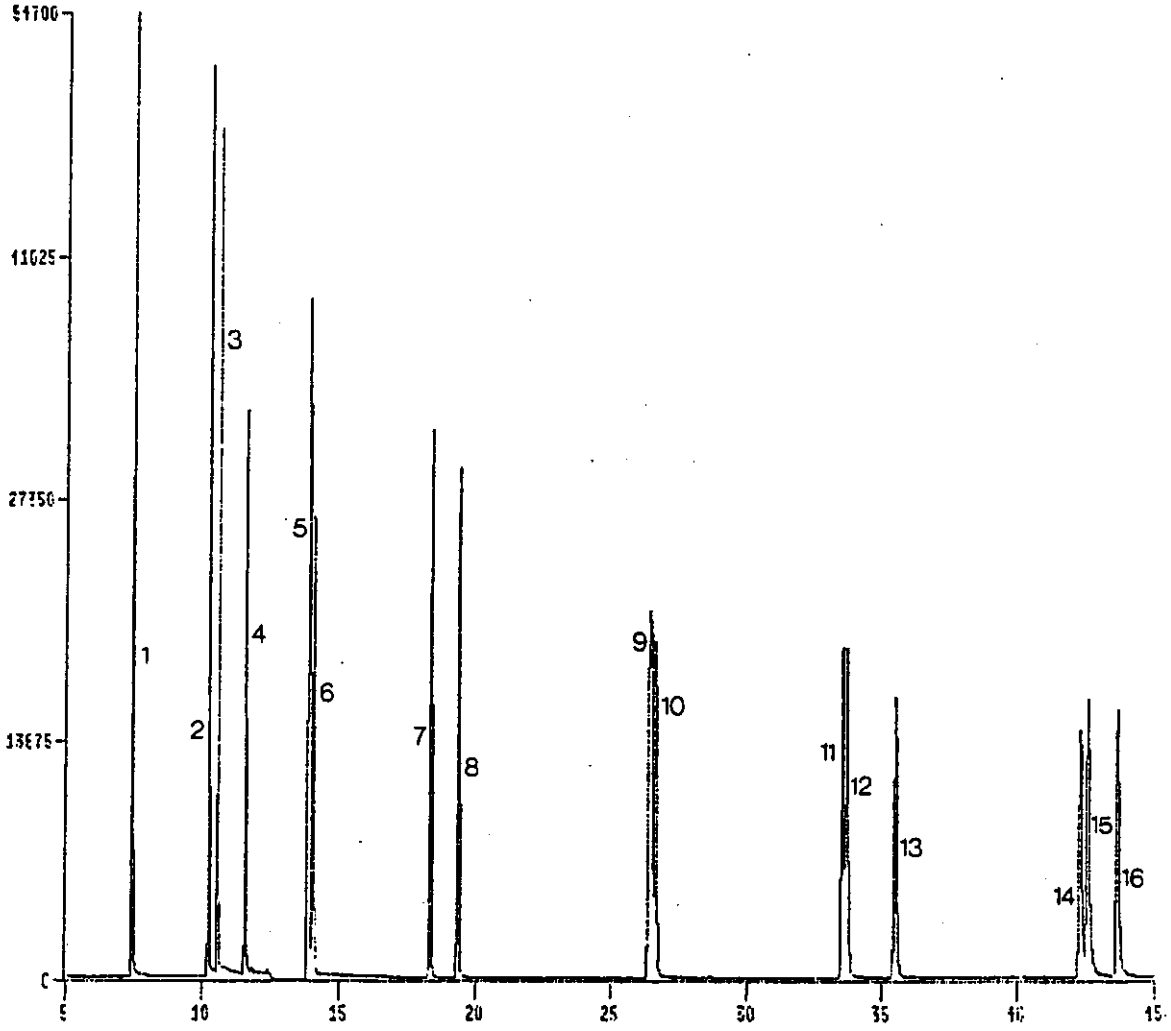


Figure 18. GC-MS Calibration and Analysis

637



Injection: 1.0 µL on-column
Column: 30m x 0.25 mm DB-5 capillary with 0.25 µm film thickness
Program: 60°C (1 min), 15°C/min to 200°C, 3°C/min to 310°C
Detector: Mass selective detector

1. Naphthalene + d_8-naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene + d_{10} phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo(a)anthracene + d_{12} chrysene
10. Chrysene
11. Benzo(b)fluoranthene
12. Benzo(k)fluoranthene
13. Benzo(a)pyrene
14. Indeno(1,2,3-cd)pyrene
15. Dibenzo(ah)anthracene
16. Benzo(ghi)perylene

Figure 19. Typical Chromatogram of Selected PAHs by GC-MS

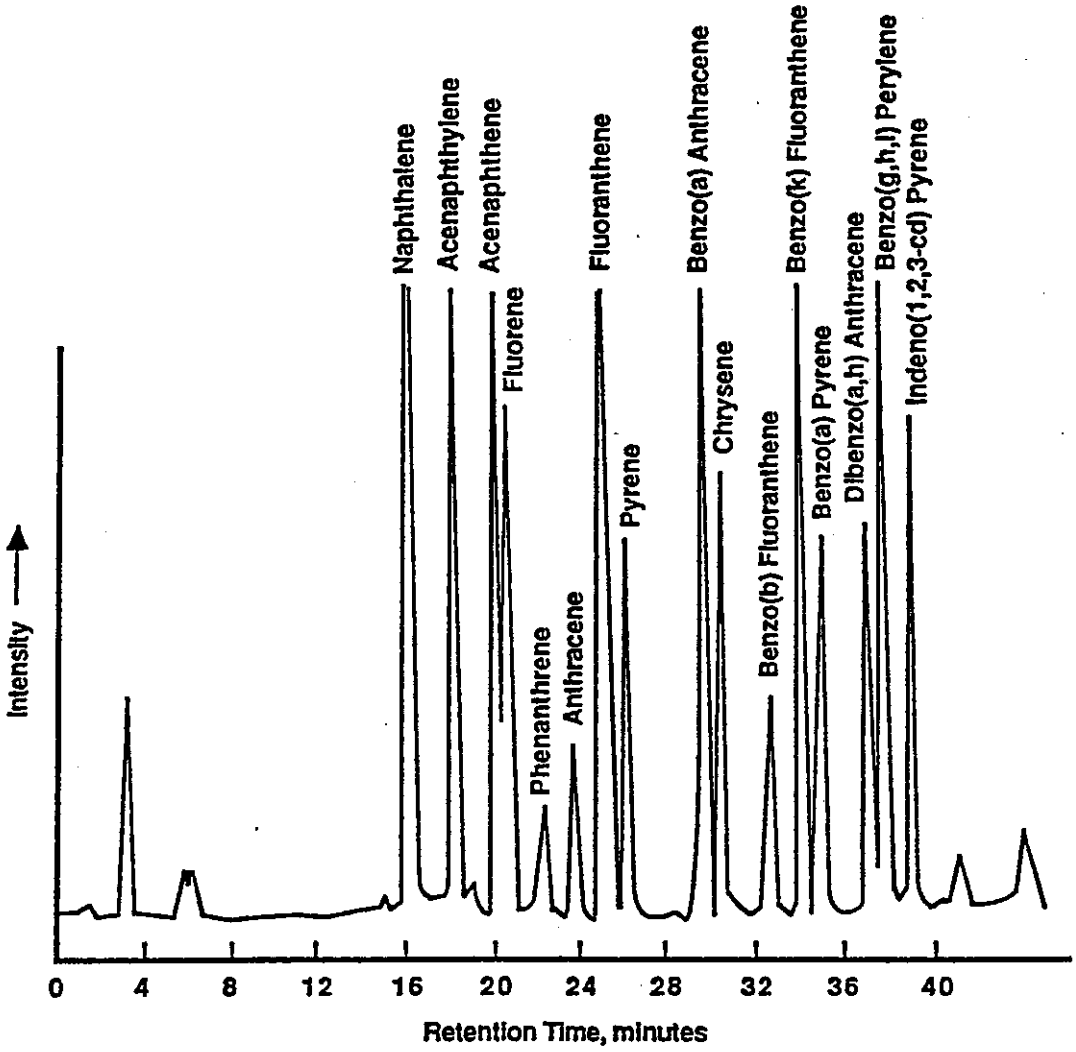


Figure 20. Typical Chromatogram of Selected PAHs Associated with HPLC Analysis Involving Ultraviolet Detection

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