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PART 1 OF 2

Compendium of Methods for the Determination of Air Pollutants in Indoor Air

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Method IP-5B

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

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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).

13. References

1. Palmes, E. D., Gunnison, A. F., DiMatto, J., and Tomcyzk, C., "Personal Sampler for Nitrogen Dioxide," *American Industrial Hygiene Association Journal*, 46:462-475, 1981

2. Ralph M. Riggin, *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, EPA - 600/4-83-027, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1983.

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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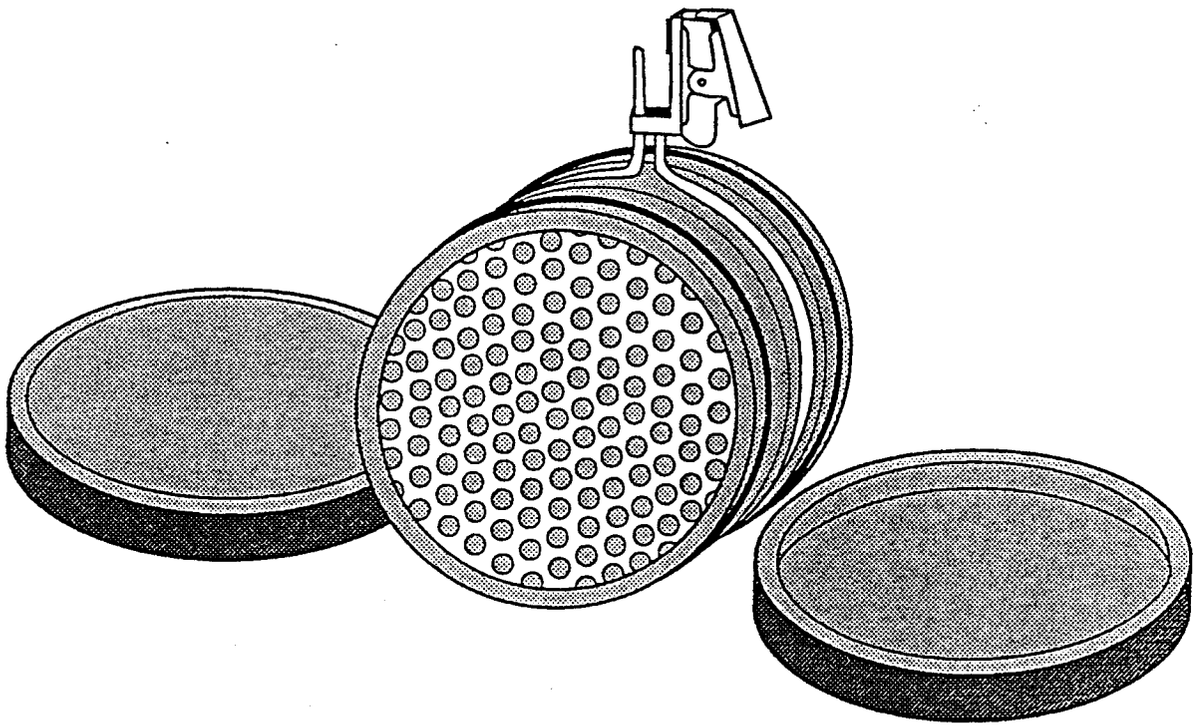

Figure 1. Commercially Available NO_2 Passive Sampling Device

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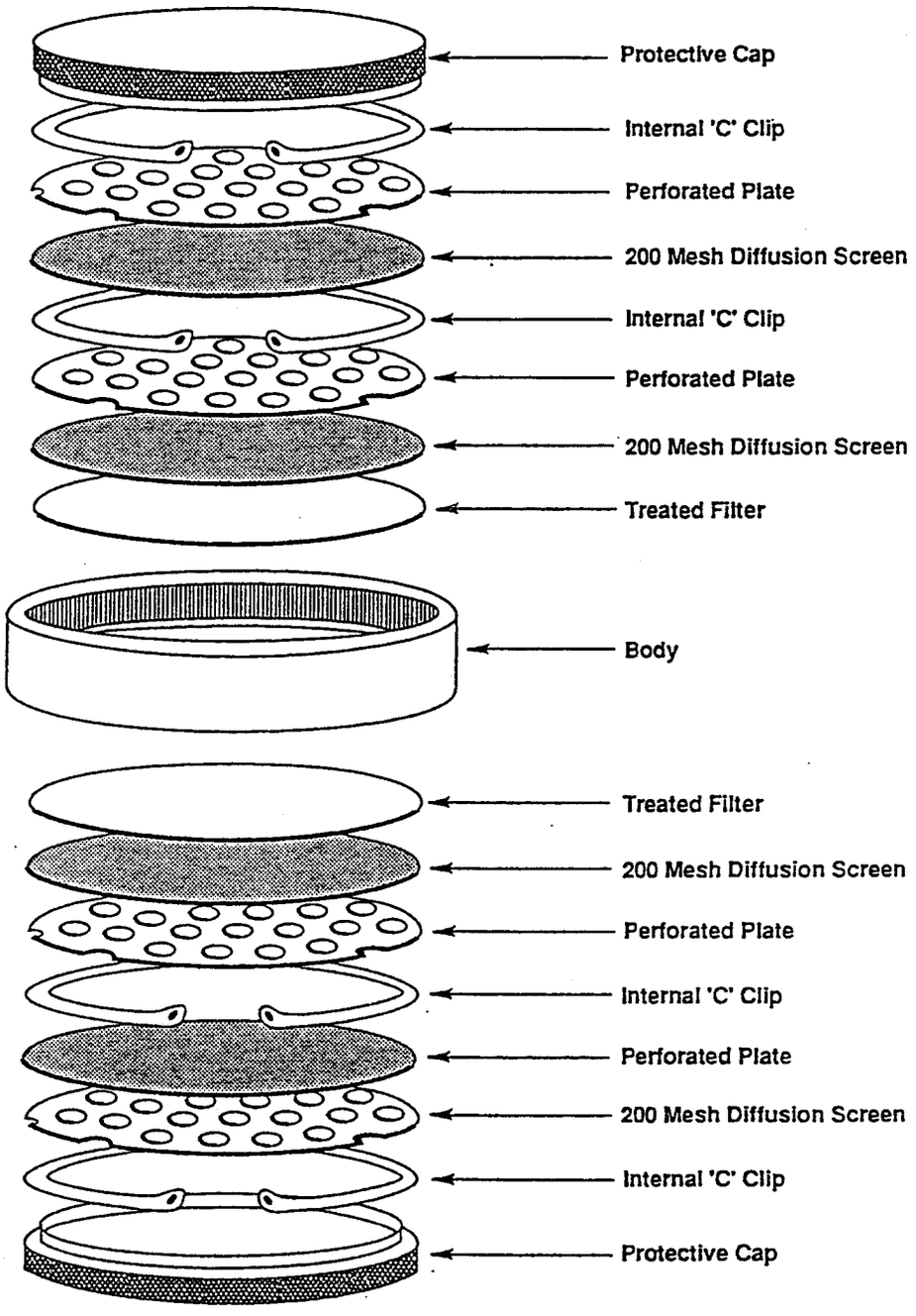

Figure 2. Exploded View of a Commercially Available Passive Sampling Device

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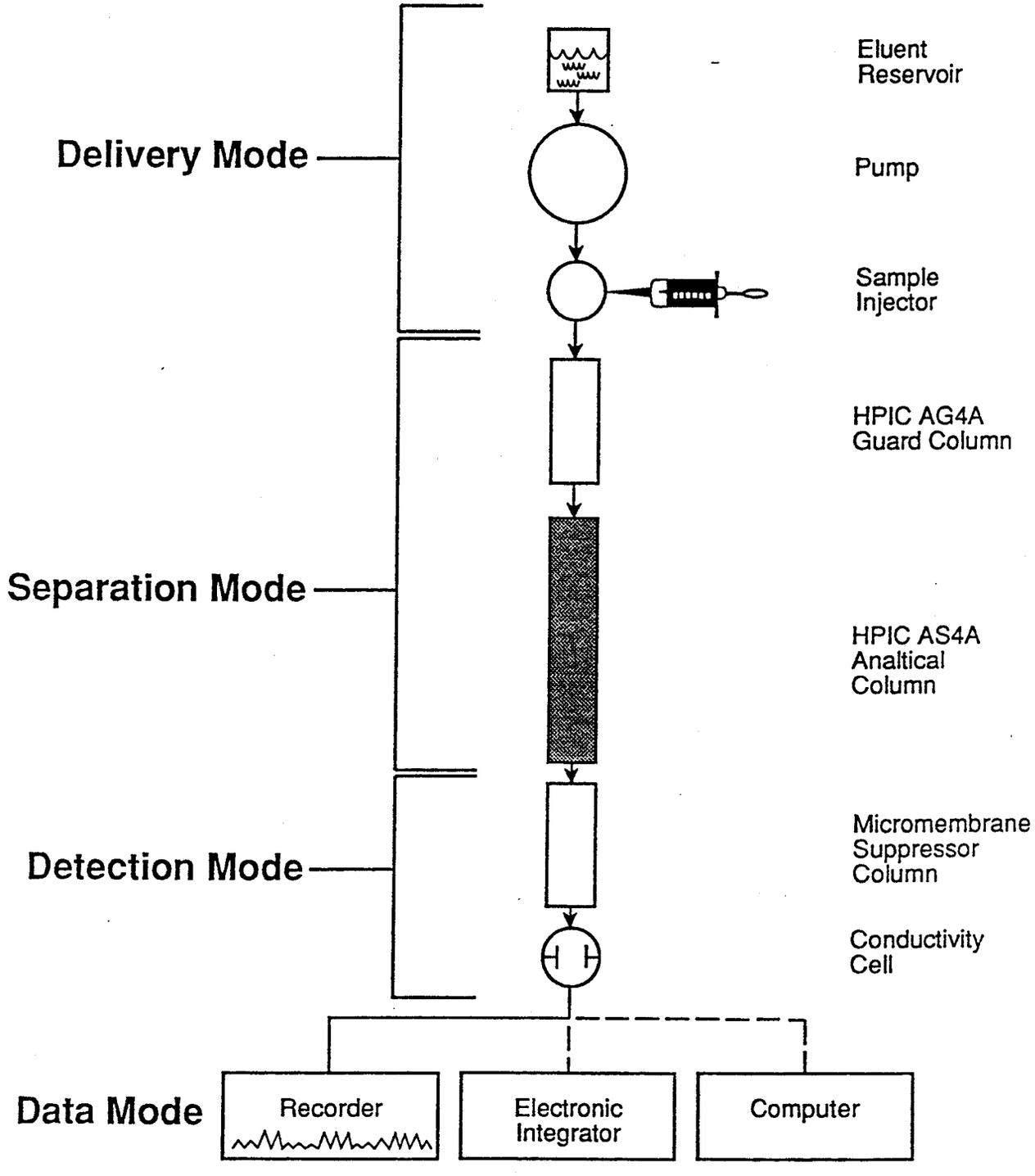

Figure 3. Major Components of a Commercially Available Ion Chromatograph

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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:

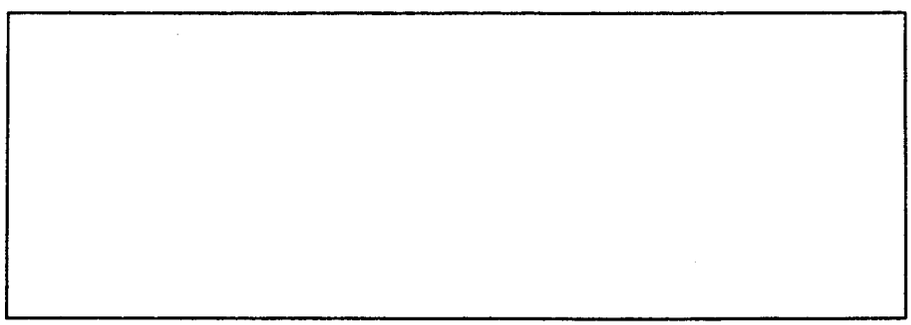

Figure 4. Field Test Data Sheet for PSD

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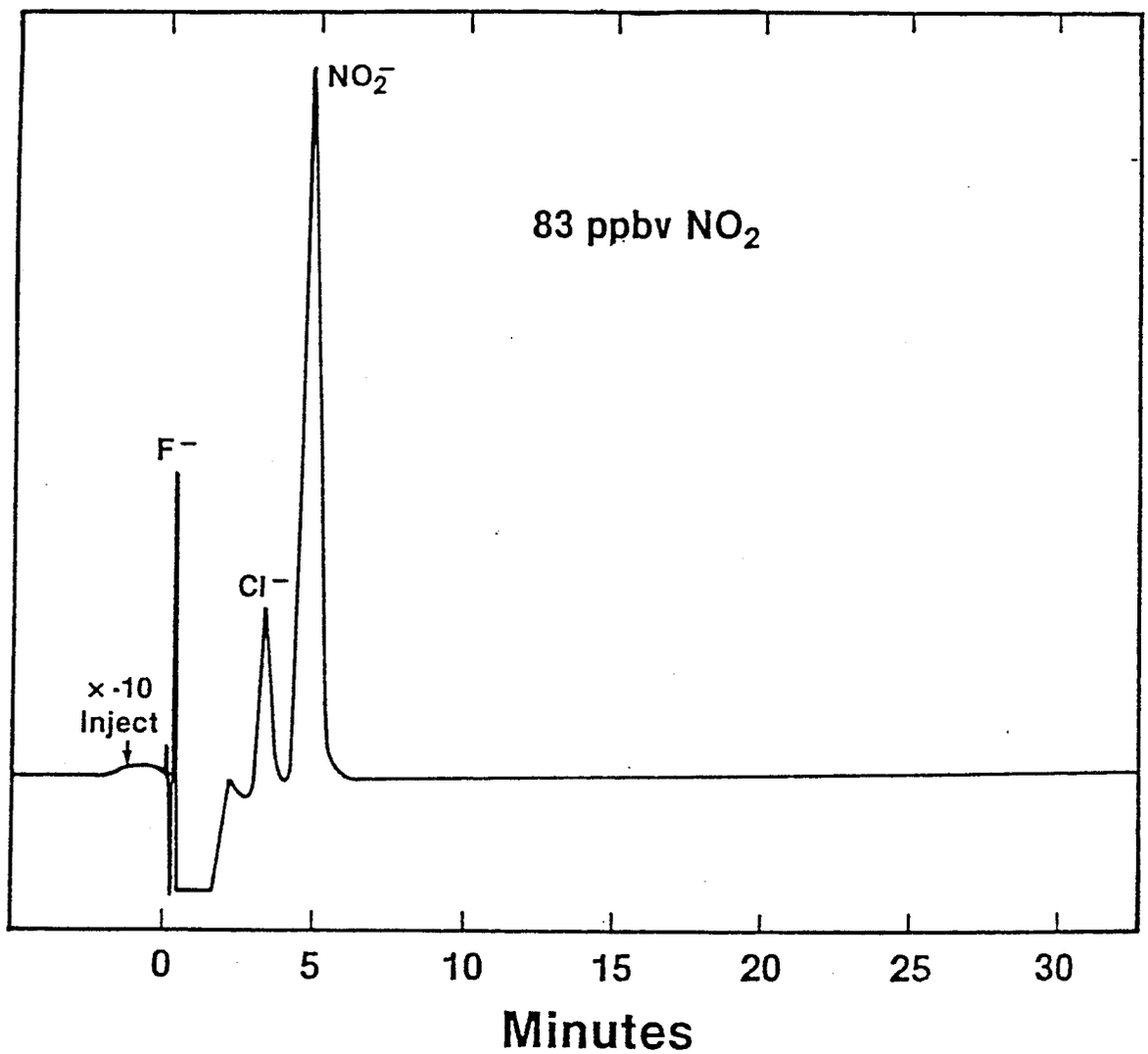

Figure 5. Typical Dionex Model 14 Chromatogram

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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

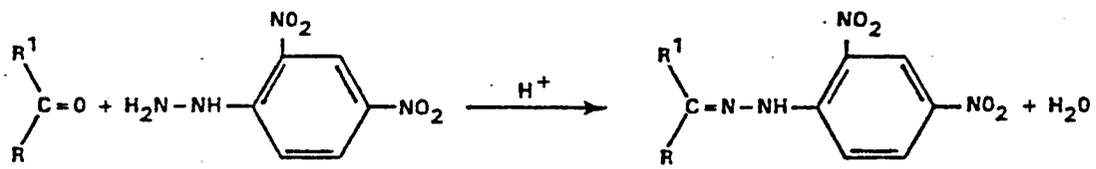
DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES IN INDOOR AIR USING A SOLID ADSORBENT CARTRIDGE

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

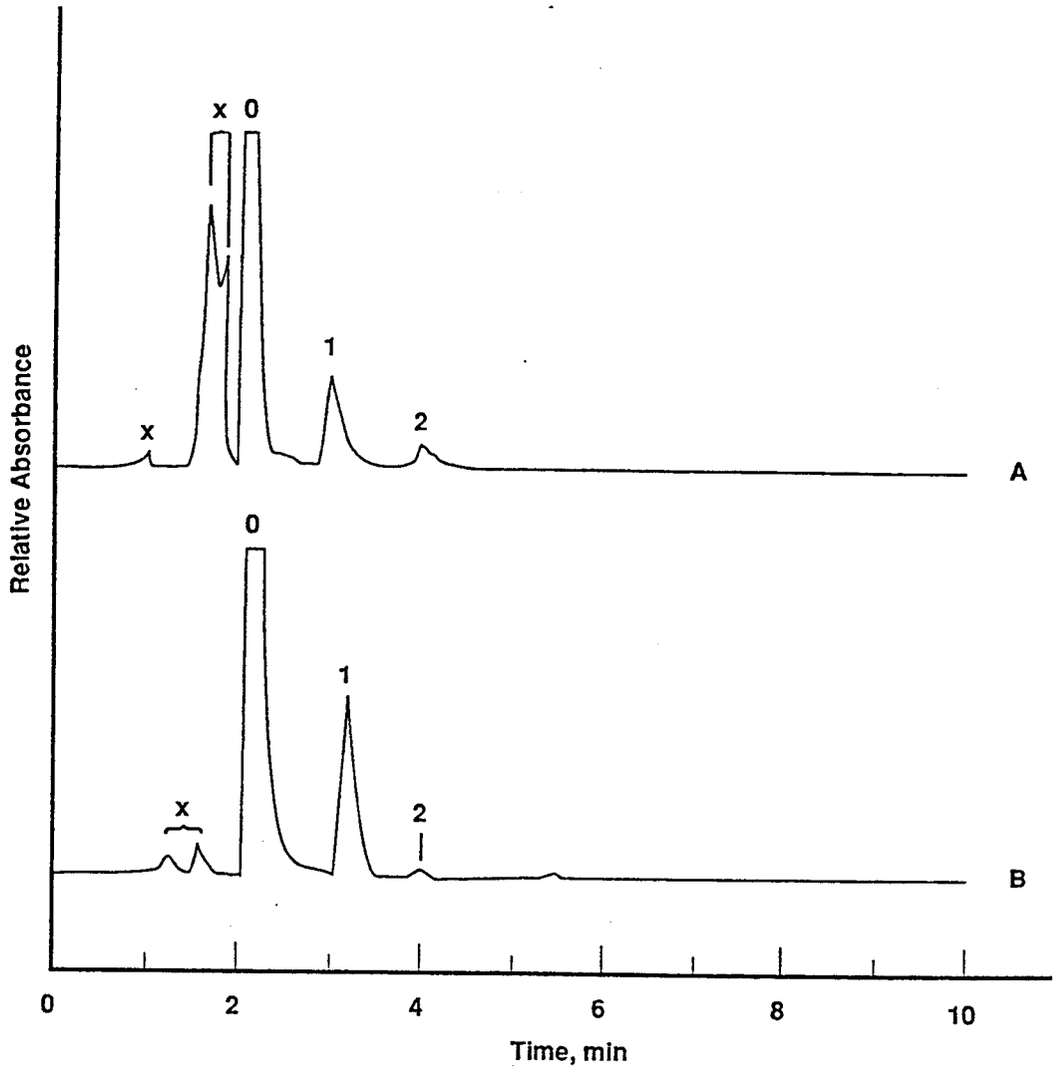
	Sample Volume, L										
Compound	10	20	30	40	50	100	200	300	400	500	1000
Formaldehyde	1.45	0.73	0.48	0.36	0.29	0.15	0.07	0.05	0.04	0.03	0.01
Acetaldehyde	1.36	0.68	0.45	0.34	0.27	0.14	0.07	0.05	0.03	0.03	0.01
Acrolein	1.29	0.65	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03	0.01
Acetone	1.28	0.64	0.43	0.32	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

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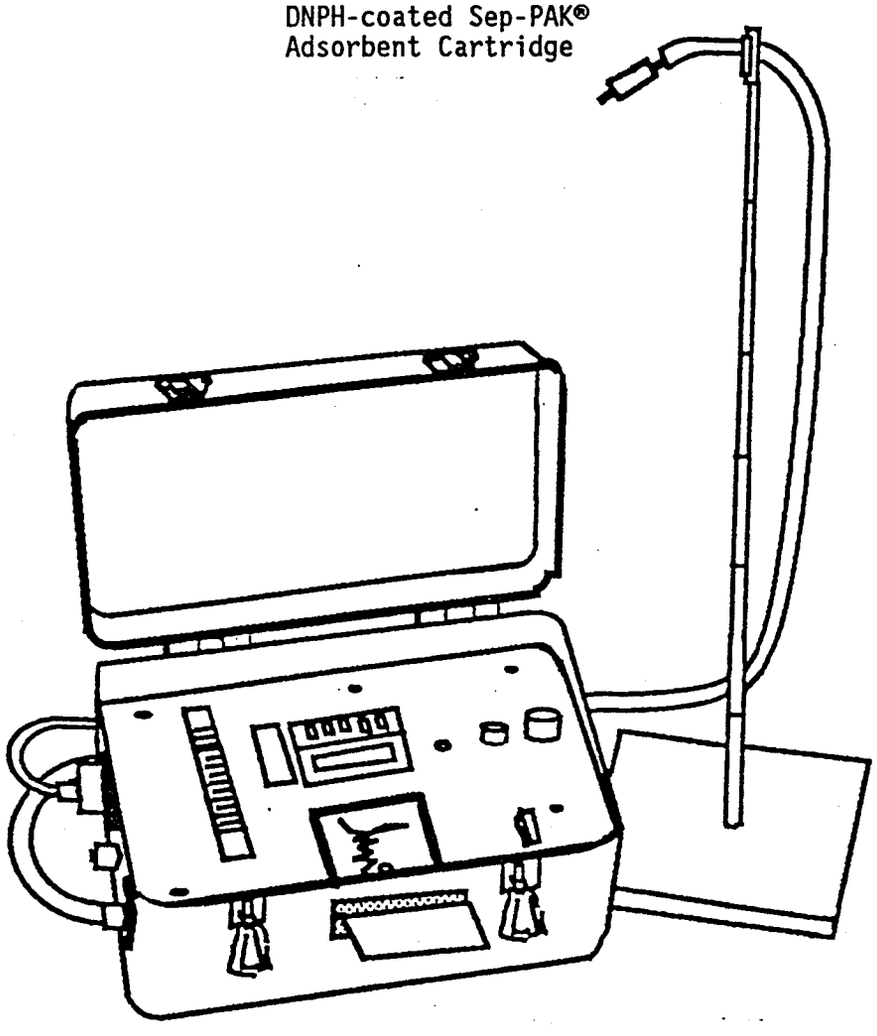

Figure 2. Portable Sampling System for Adsorbent Cartridges

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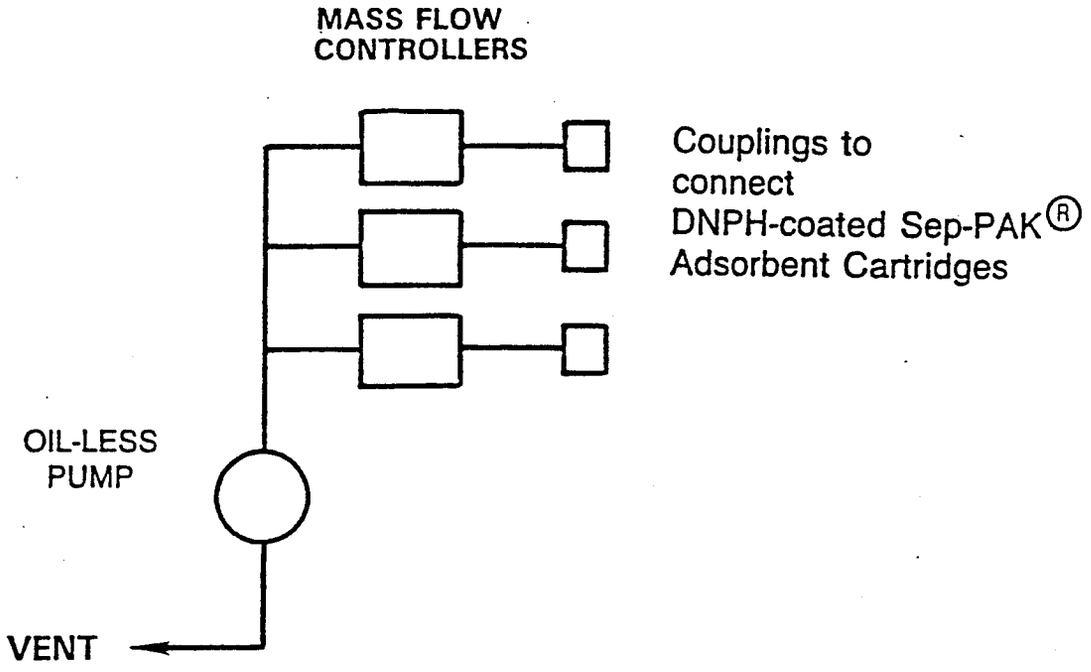
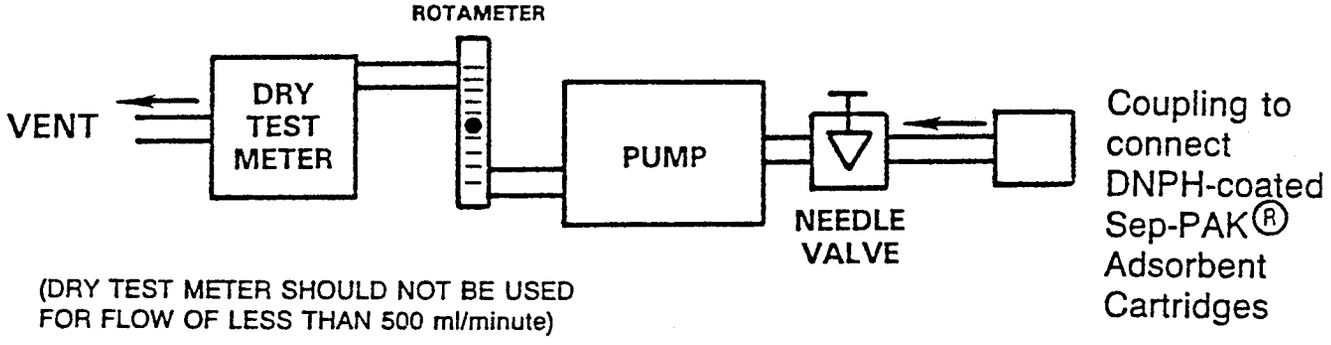


(a) MASS FLOW CONTROL



(b) NEEDLE VALVE/DRY TEST METER

Figure 3. Typical Sampling System Configurations

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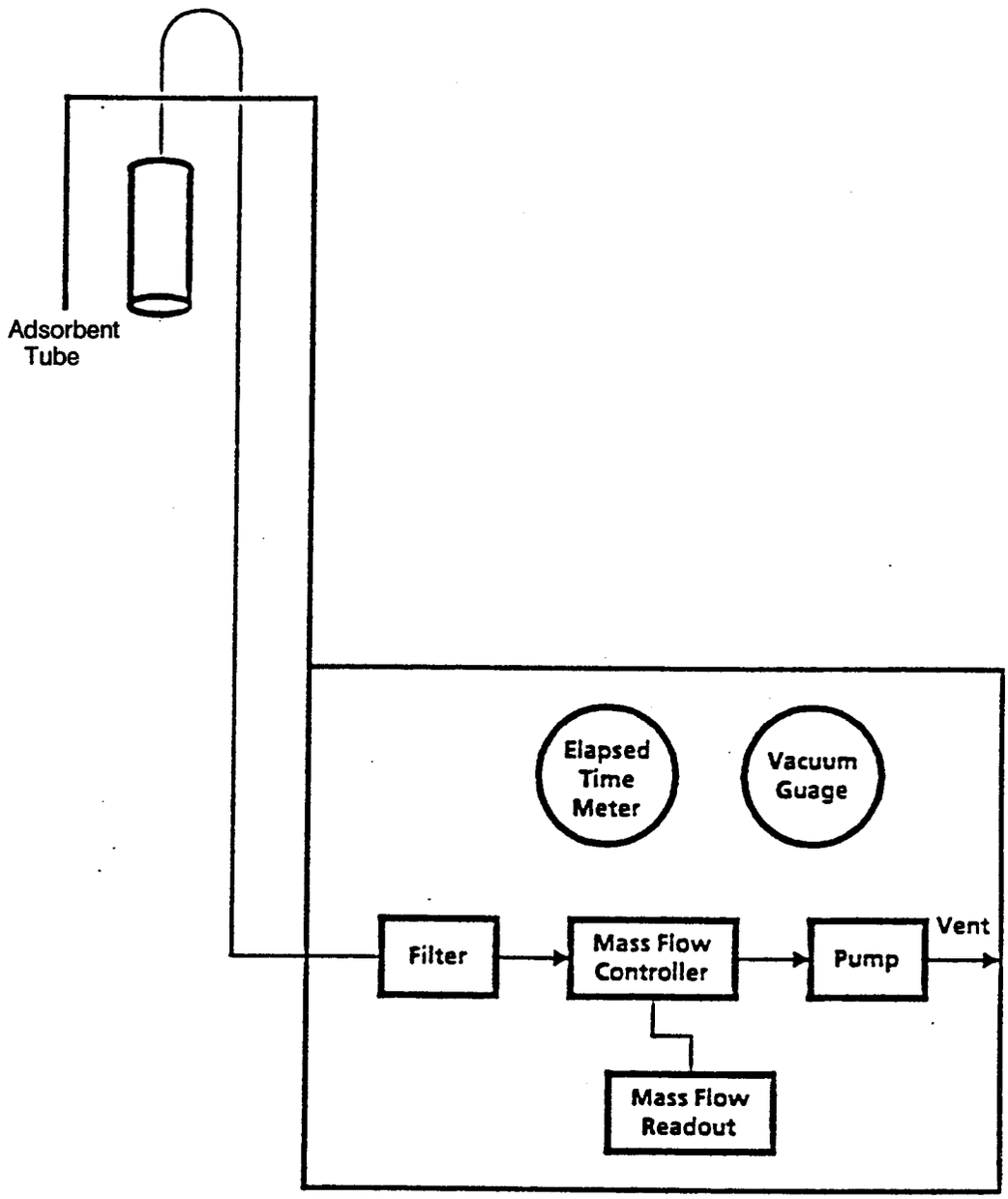

Figure 4. Diagram of Adsorbent Sampling Device for Airborne Aldehydes

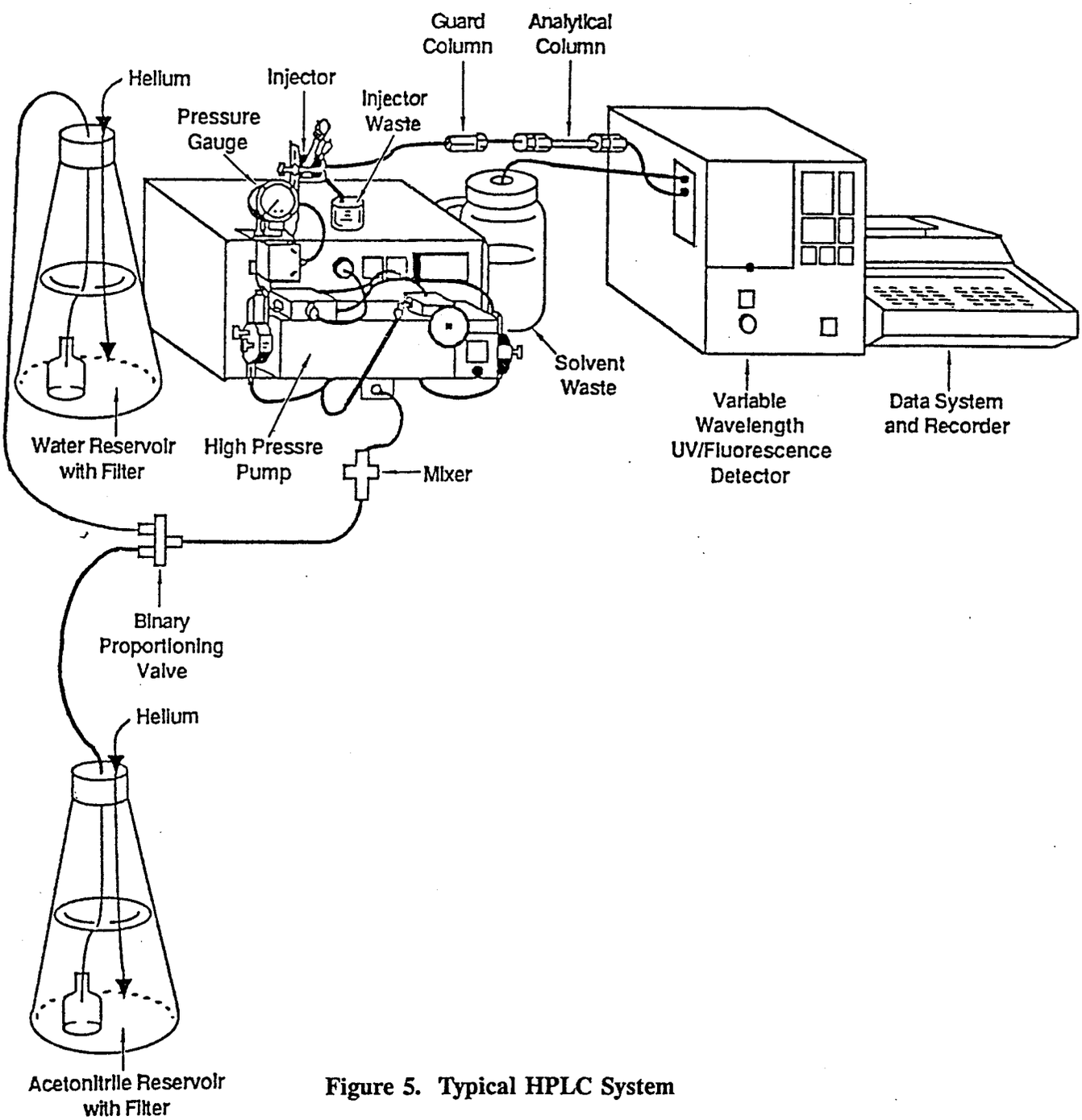

Figure 5. Typical HPLC System

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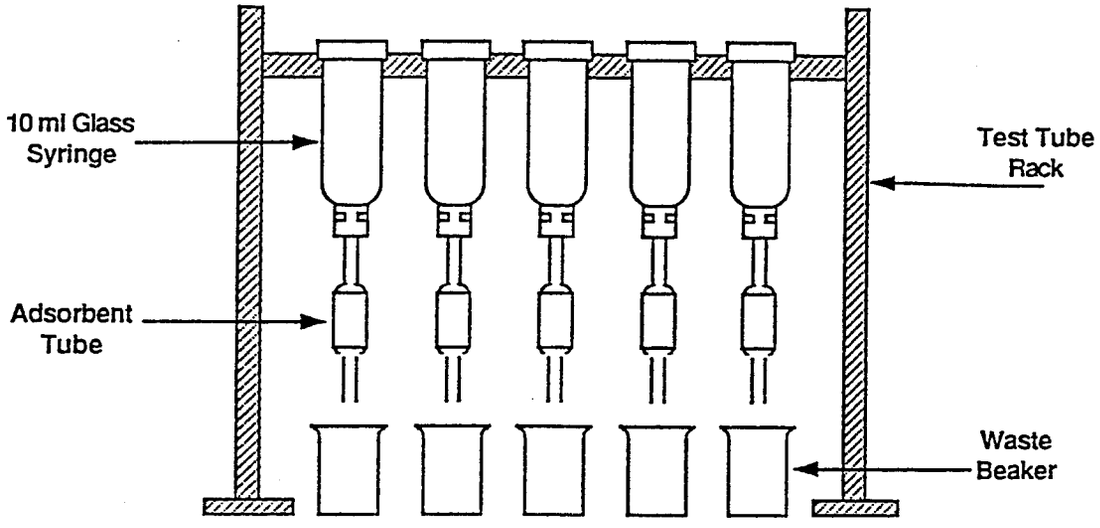
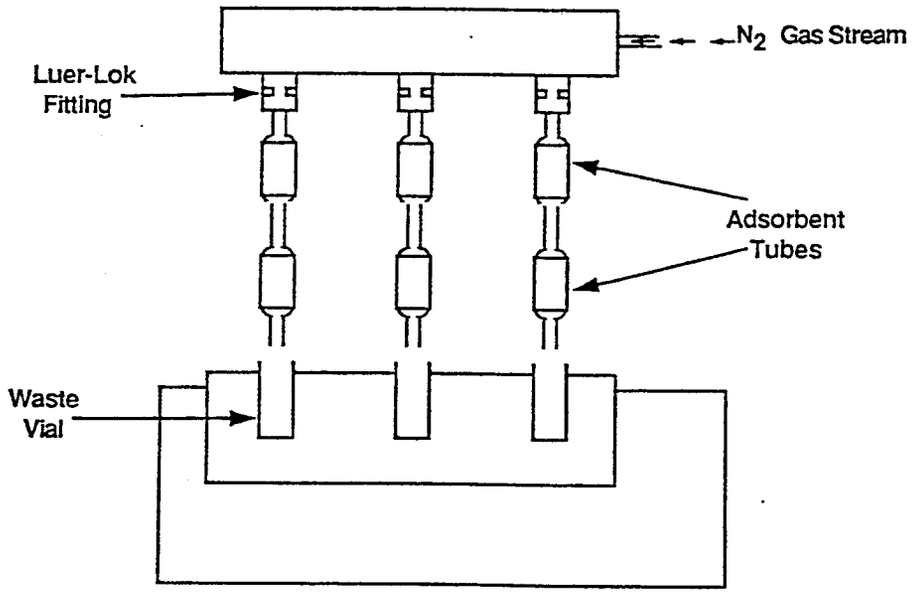


(a) RACK FOR COATING CARTRIDGES



(b) RACK FOR DRYING DNPH-COATED CARTRIDGES

Figure 6. Syringe Rack for Coating and Drying Sample Cartridges

509

496

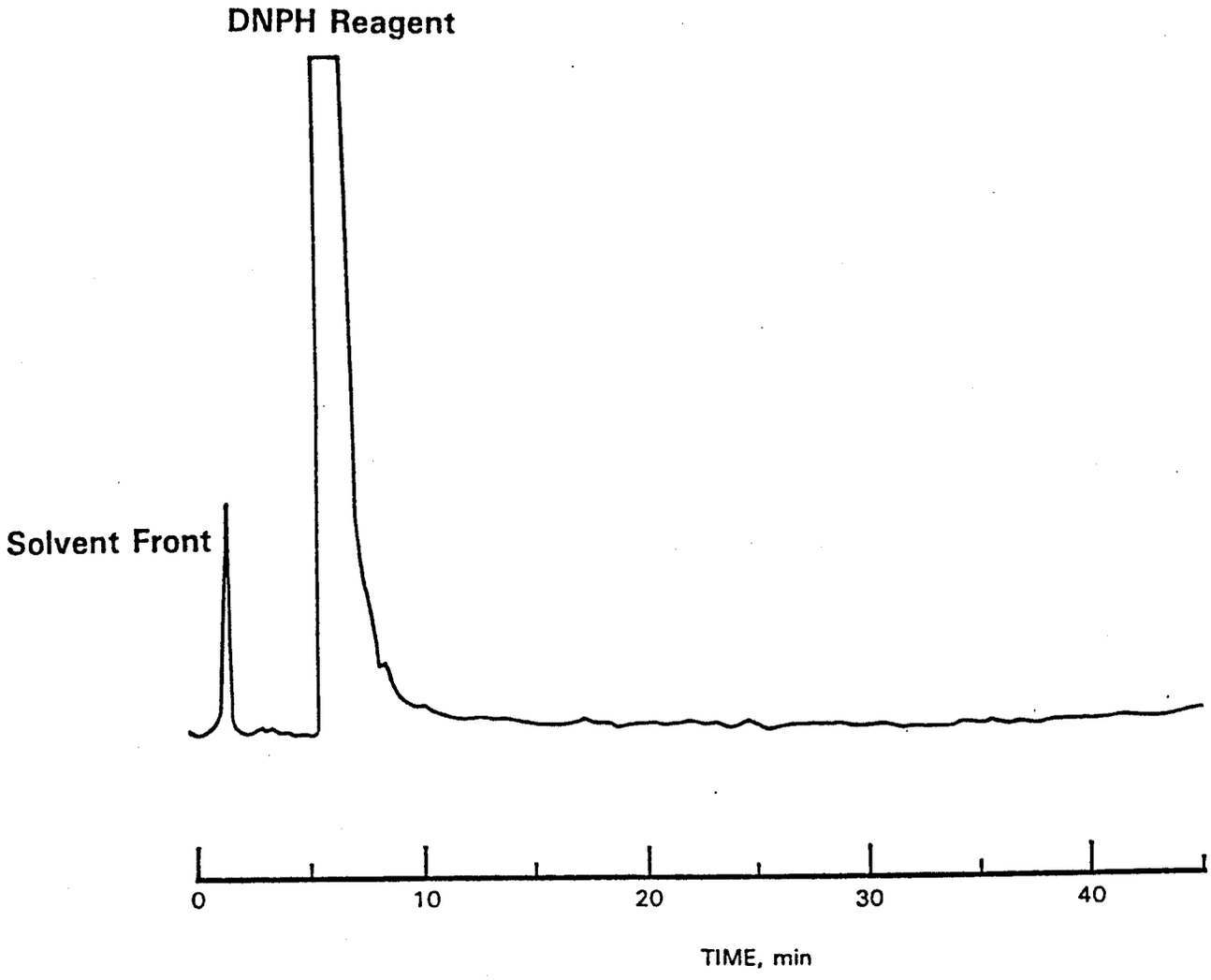


Figure 7. Impurity Level of DNPH after Recrystallization

516

497

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

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

Figure 8. Example Sampling Data Sheet

511

498

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

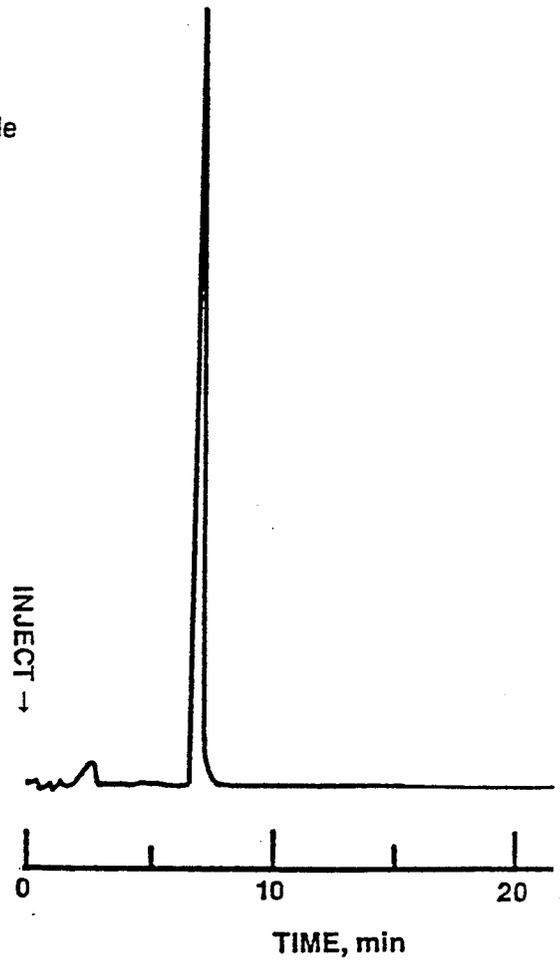
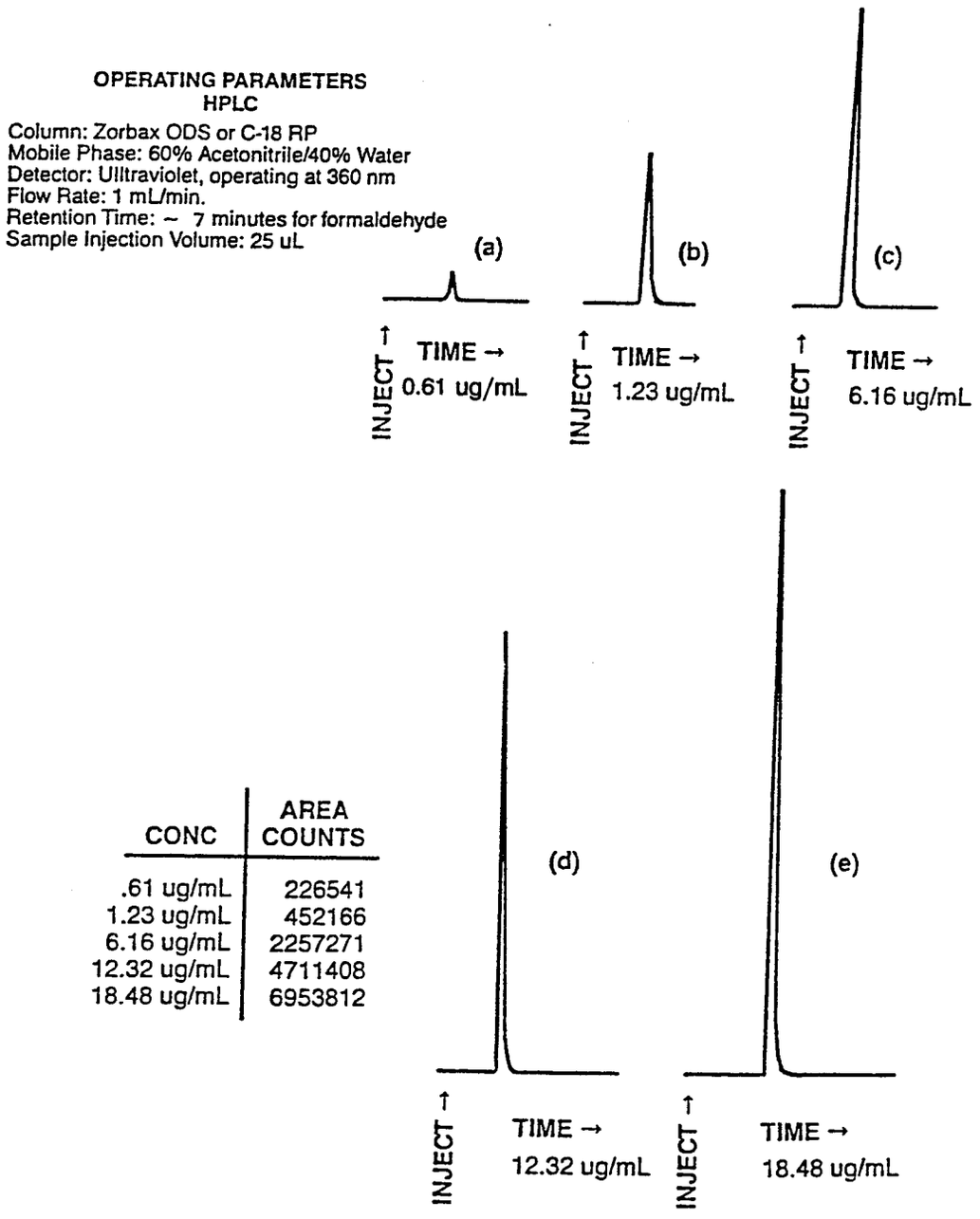


Figure 9. Chromatogram of DNPH-Formaldehyde Derivative



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

513

500

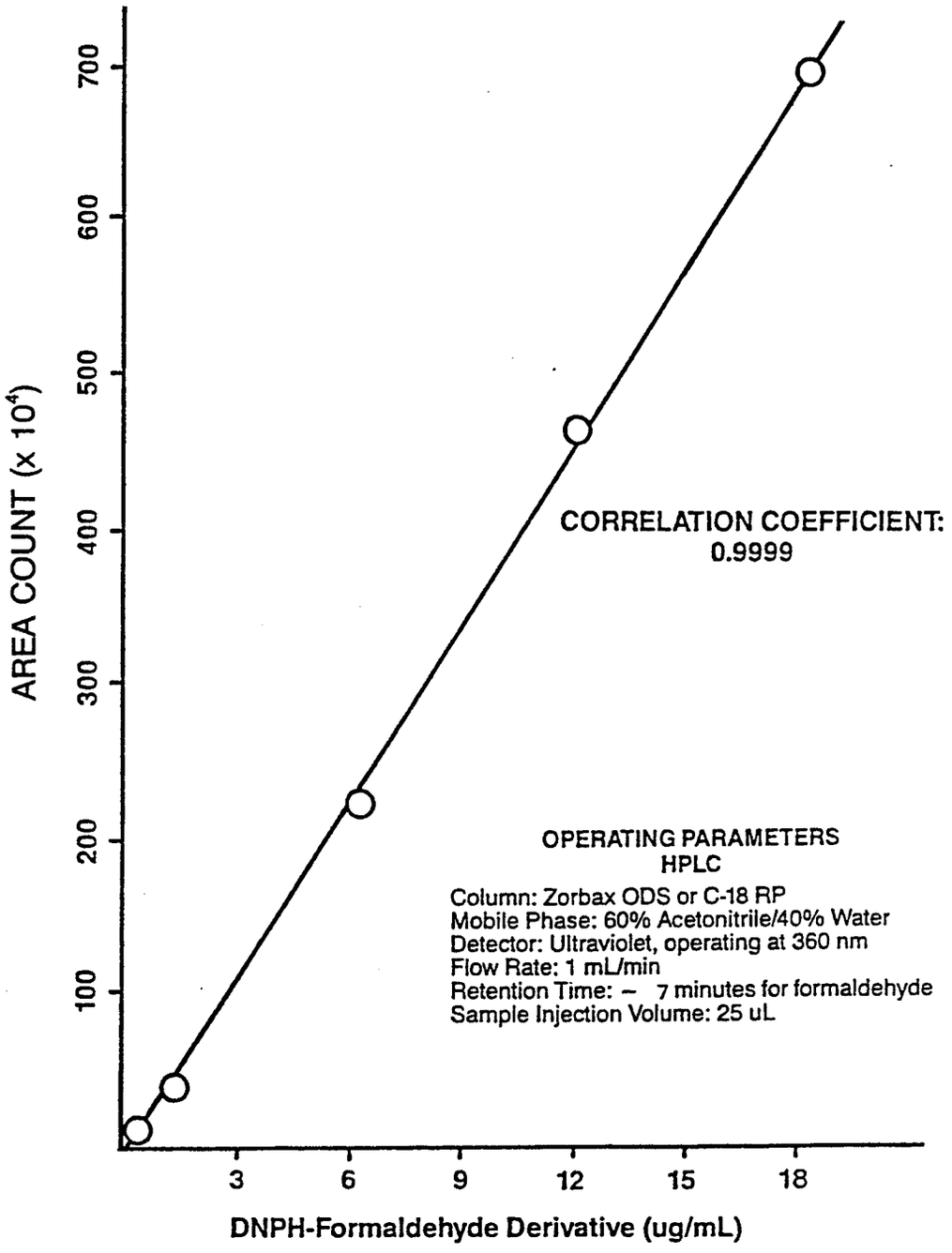
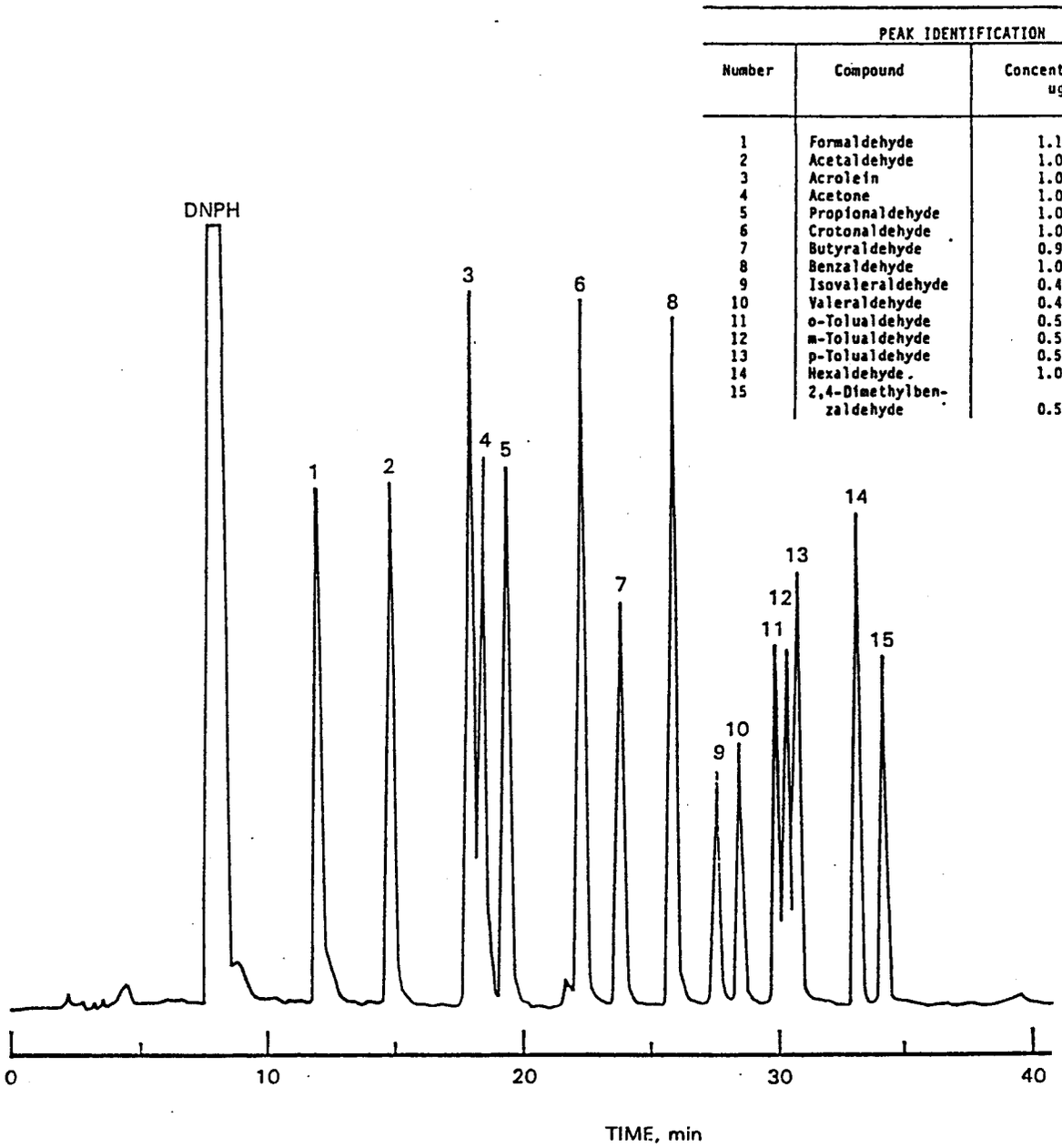


Figure 11. Typical Calibration Curve for Formaldehyde



PEAK IDENTIFICATION

Number	Compound	Concentration, ug/mL
1	Formaldehyde	1.140
2	Acetaldehyde	1.000
3	Acrolein	1.000
4	Acetone	1.000
5	Propionaldehyde	1.000
6	Crotonaldehyde	1.000
7	Butyraldehyde	0.905
8	Benzaldehyde	1.000
9	Isovaleraldehyde	0.450
10	Valeraldehyde	0.485
11	o-Tolualdehyde	0.515
12	m-Tolualdehyde	0.505
13	p-Tolualdehyde	0.510
14	Hexaldehyde	1.000
15	2,4-Dimethylbenzaldehyde	0.510

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

515

502

6. Method Limitations and Limits of Detection

6.1. The limitations on the test method are a minimum weight of 20 micro grams of particles on the filter, and a maximum loading of 600 micro grams/cm^2 and minimum of 20 micro grams/cm^2 on the filter.

6.2 The test method may be used at higher loadings if the flow rate can be maintained constant (± 5%) and degradation of the aerosol preclasifier performance is not adversely affected.

6.3 The MEM and PEM samplers' limit of detection (LOD) is a function of the weighing room environment and the precision of the microbalance used to perform mass measurements.

6.4 Using the recommended equipment specified in this procedure, a 12-hour LOD of 8 $\mu g/m^3$ can be achieved for the PEM, and 4 $\mu g/m^3$ for the MEM.

6.5 Overall precision is ± 2 $\mu g/m^3$ to ±25 $\mu g/m^3$ during dust loading studies (10 to 100 $\mu g/m^3$) at a flow rate of 4 L/min. for each sampler.

7. Apparatus Description

7.1 Microenvironmental Exposure Monitor (MEM) Description

7.1.1 As illustrated in Figure 2, the MEM is subdivided into four sections: 1) an inlet section, 2) a three-piece inertial impaction section, 3) the upstream section of the filter holder; and 4) the downstream section of the filter holder.

7.1.2 Inlet section - the inlet section has four large, circumferential slots for aerosol to enter the MEM. These horizontal inlet slots prevent very large particles, perhaps those greater than 100-μm aerodynamic diameter, from entering the MEM and placing an additional particle burden on the downstream impaction plate. The inlet section also acts as a cover, preventing large particles from entering the MEM by gravity settling. The inlet section should be shown to be unbiased with respect to the particle size distribution being sampled.

7.1.3 Impaction section - the impaction section consist of three separate parts: 1) a nozzle, 2) an impaction plate(s), and 3) a part designed for mounting the impaction plate. Two versions of the impactor assembly are available. With a one stage impactor plate assembly, aerodynamic particles of <10 μm are allowed to pass around the impactor plate and subsequently collected in the lower filter. With the two stage impactor assembly, as illustrated in Figure 2, those particles <2.5 μm are collected on the lower filter. A time share option provides the capability of using two heads with one pumping system. In this way, the total sampling time can be programmed to two samplers, enabling the collection of <2.5 μm and <10 μm particulate matter in the same general environment. These features could be used to sample in two locations or to collect carbon on quartz filters or acid aerosols through a unit equipped with an ammonia denuder.

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%

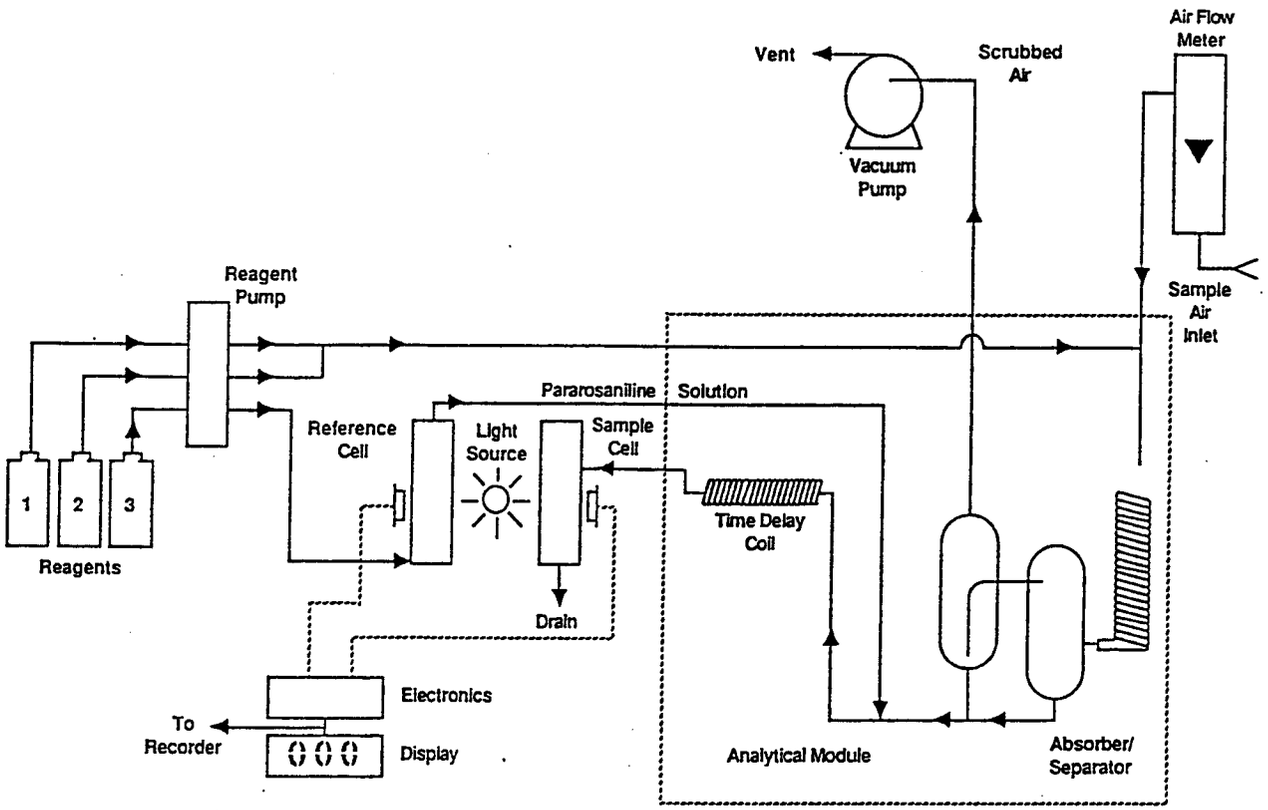

Figure 1. Flow Diagram of Formaldehyde Analyzer

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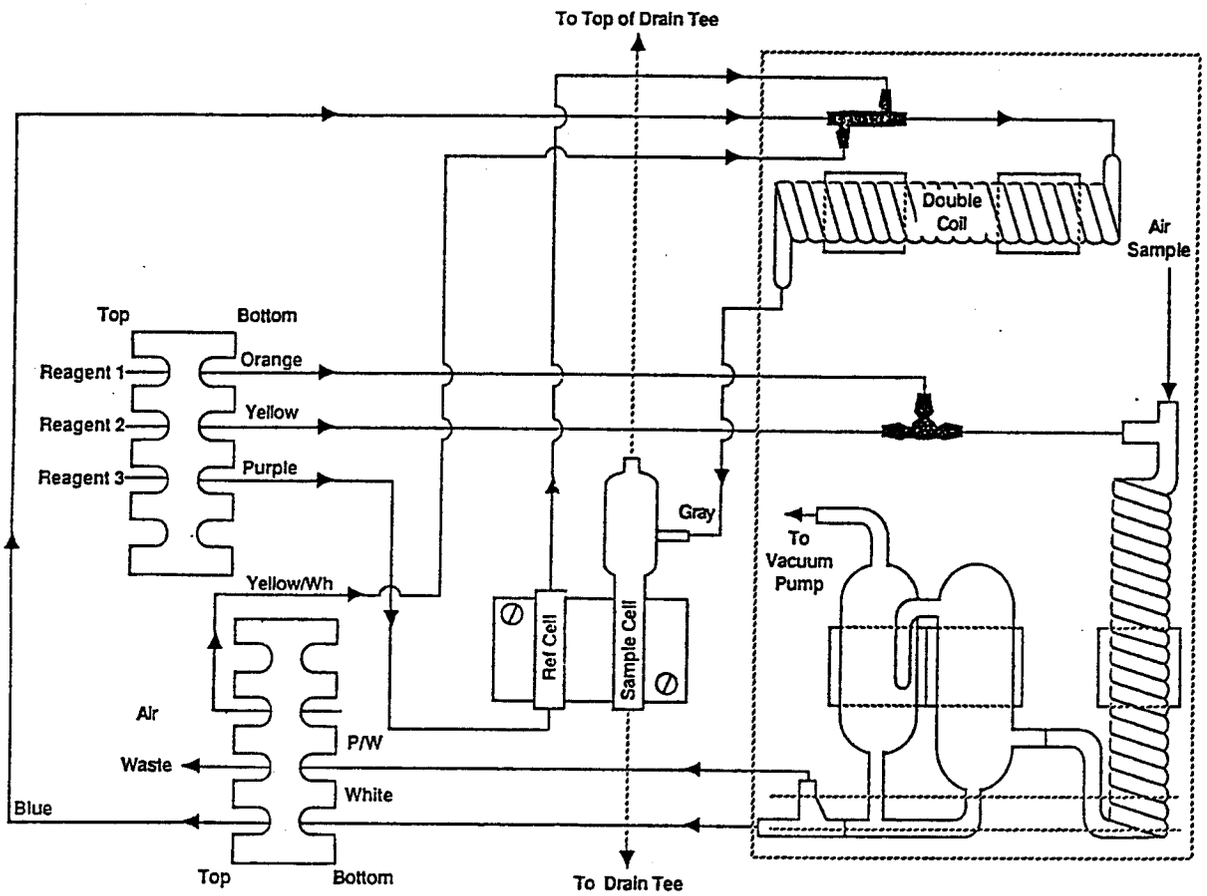

Figure 2. Flow Diagram of Reagents Through Analyzer

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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 Buchner 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.

14. References

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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

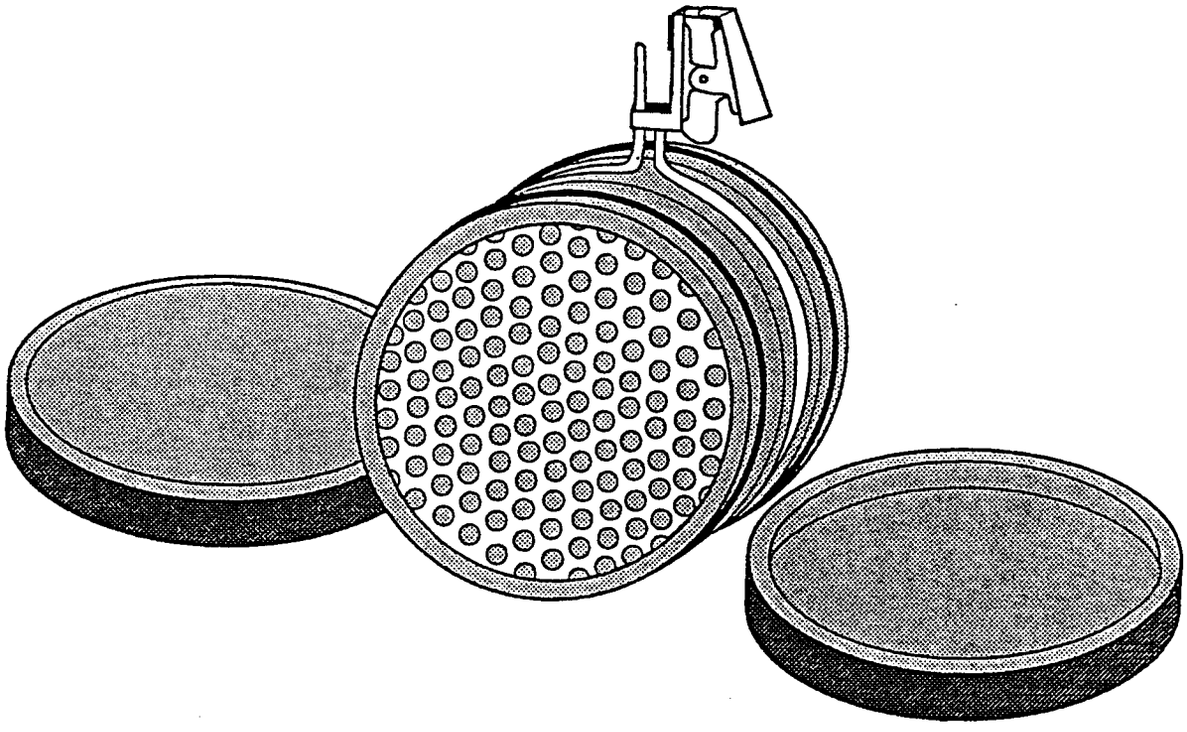

Figure 1. Passive Sampling Device (PSD) for Monitoring Formaldehyde

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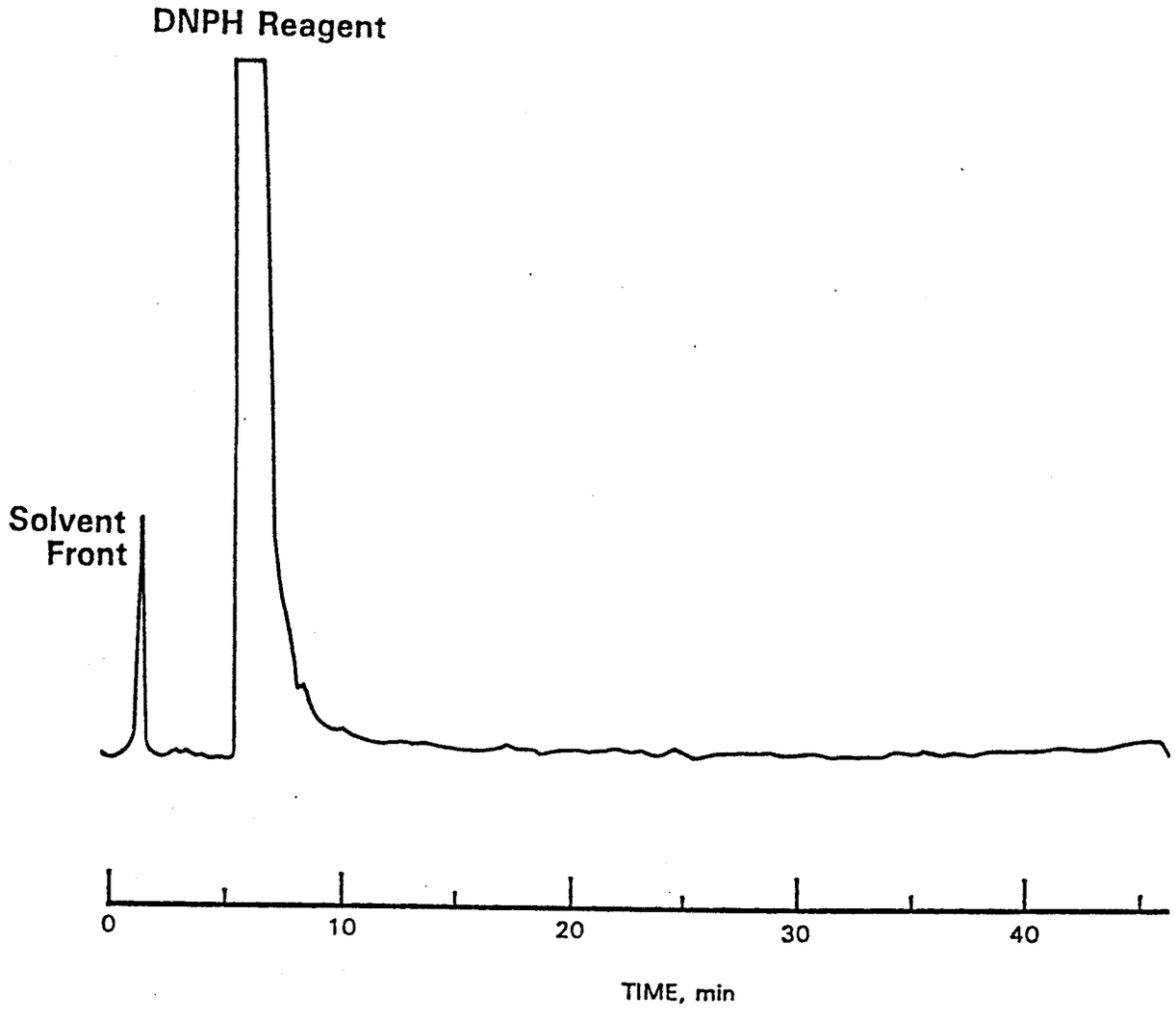

Figure 2. Impurity Level of DNPH After Recrystallization

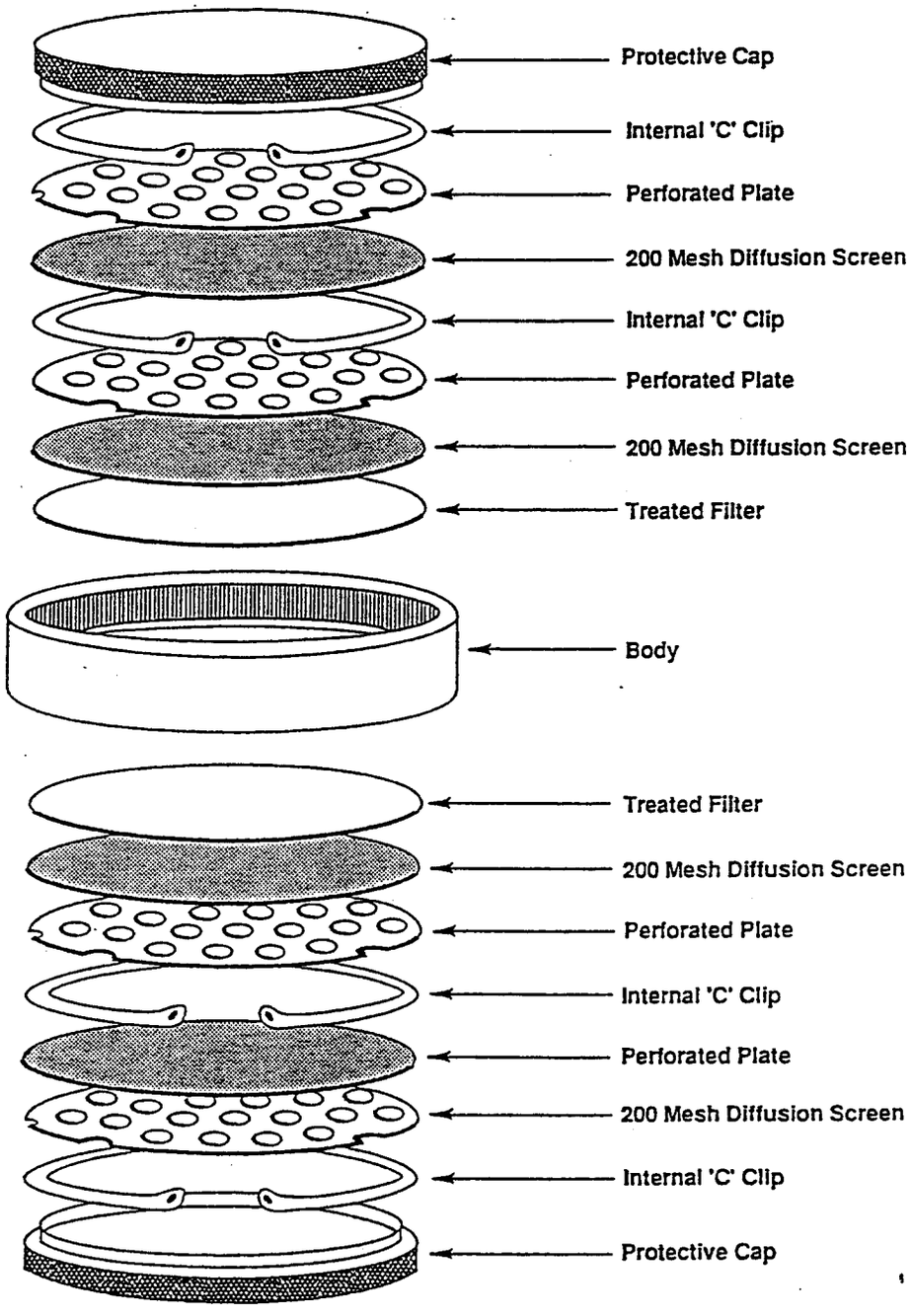

Figure 3. Exploded View of the Passive Sampling Device (PSD)

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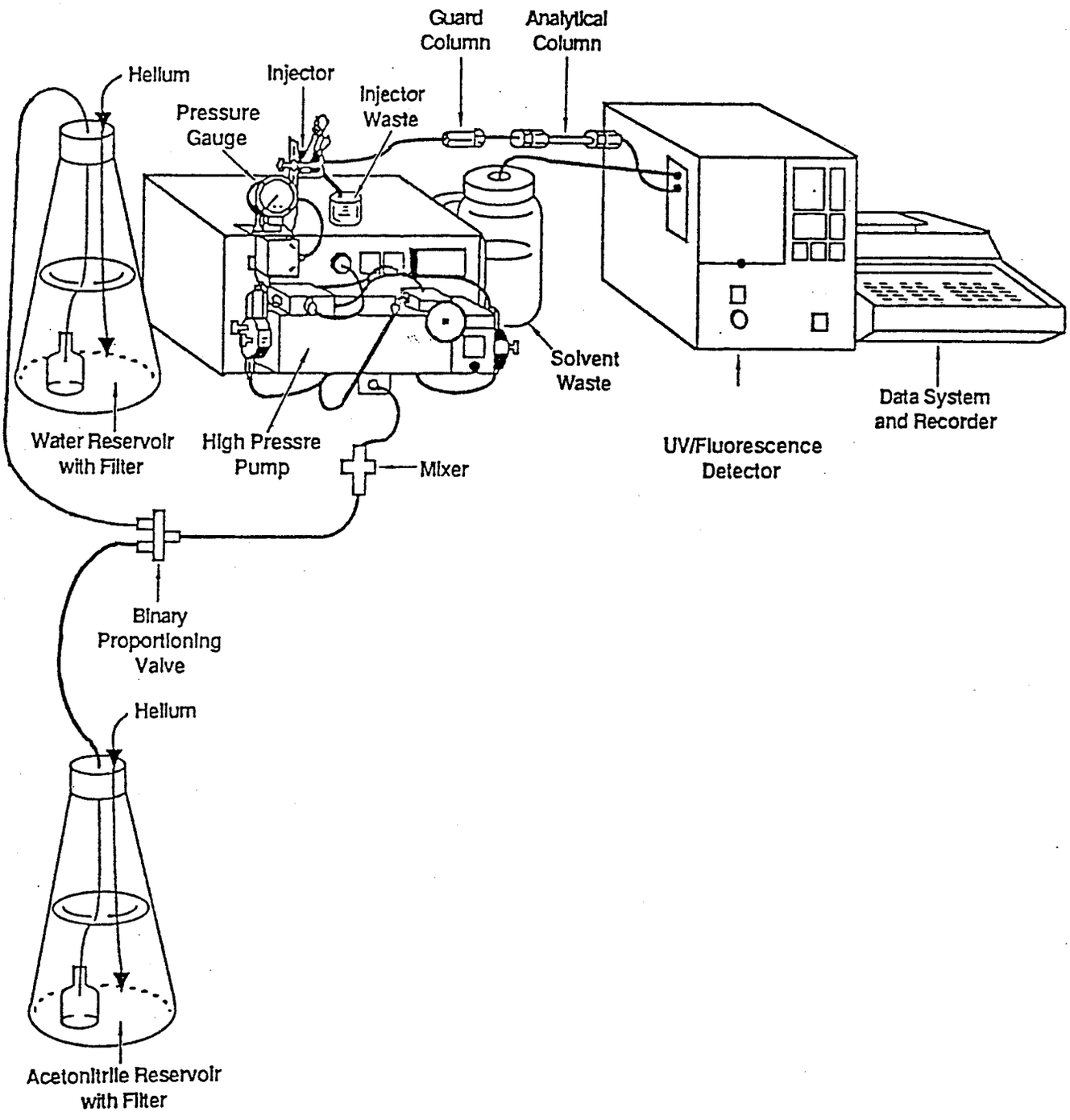

Figure 4. Typical Configuration Associated with a High Performance Liquid Chromatographic Analytical System

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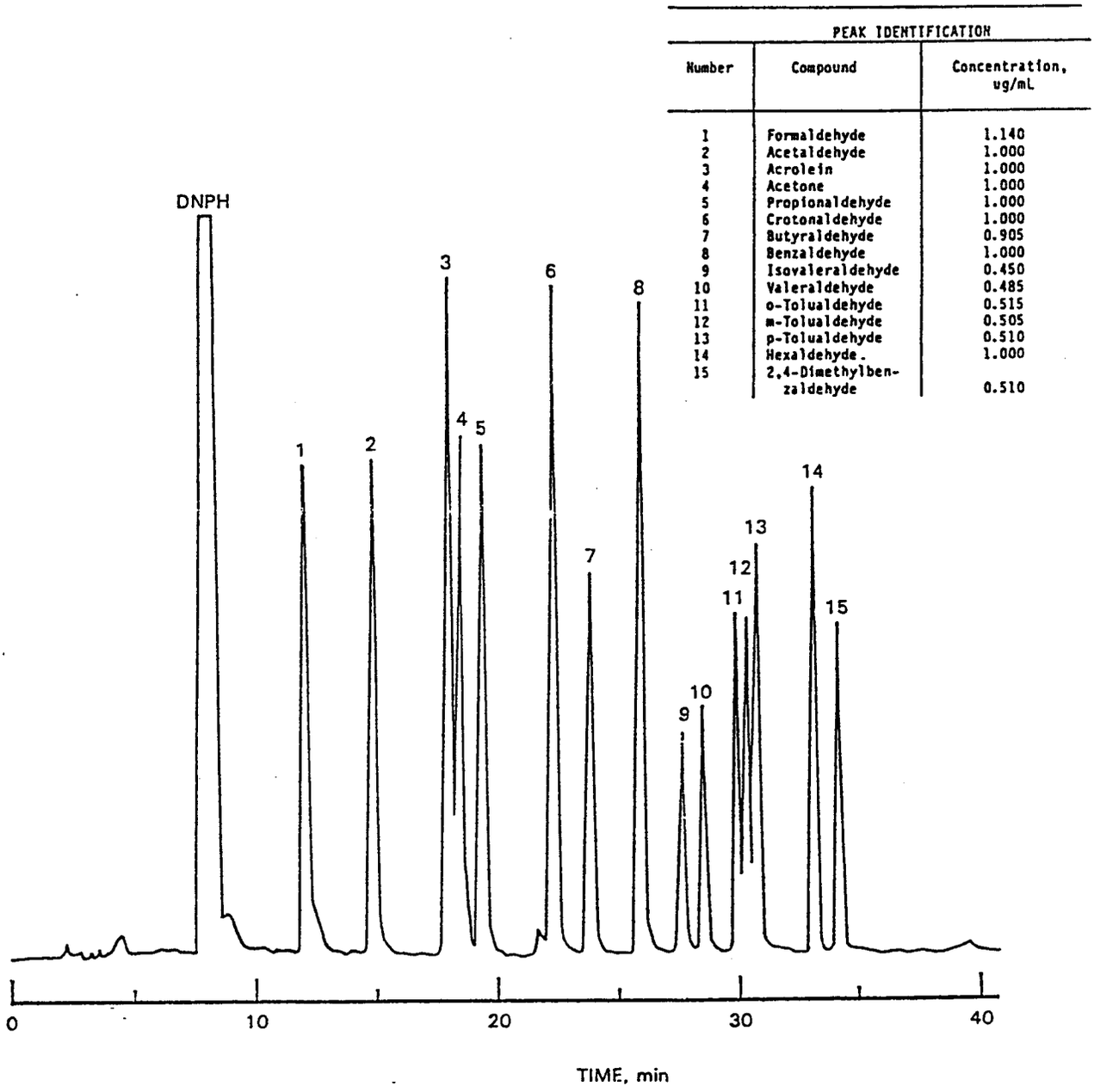

Figure 5. Chromatographic Separation of DNPH Derivatives of 15 Carbonyl Standards

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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 $\pm$ 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 ±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 $\pm$ 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 $\pm$ 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 ± 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

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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).

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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

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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.

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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

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7. Apparatus

Note: The following descriptions relate to Figure 2. Most of these parts are available commercially by University Research Glassware. However, it is important to note that these items can be made by any qualified vendor; therefore, it is not necessary that these specific items are obtained and utilized.

7.1 Sampling

7.1.1 Elutriator and acceleration jet assembly - Under normal sampling conditions, the elutriator or entry tube is made of either Teflon® coated glass or aluminum. When using glass, the accelerator jet assembly is fixed onto the elutriator and the internal surfaces of the entire assembly are coated with Teflon®. When aluminum is used, the accelerator jet assembly is removable. The jet is made of Teflon® or polyethylene and the jet support is made of aluminum. Again, all internal surfaces are coated with Teflon®. Both assemblies are available with 2, 3 and 4 mm inside diameter jets (nozzles) [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.2 Teflon® impactor support pin and impactor frit support tools - Made of either Teflon® or polyethylene and are used to aid in assembling, removing, coating and cleaning the impactor frit [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.3 Impactor frit and coupler assembly - The impactor frit is 10 mm x 3 mm and is available with a porosity range of 10-20 μm. The frits should be made of porous ceramic material or fritted stainless steel. Before use the impactor frit surface is coated with a Dow Corning 660 oil and toluene solution for use, and sits in a Teflon® seat support fixed within the coupler. The coupler is made of thermoplastic and has Teflon® clad sealing "0"-rings which are located on both sides of the seat support inside the coupler. The couplers are composed of two free moving female threads which house the support tools when assembling and removing the impactor frit, and couple the denuders when sampling. There are arrows printed on the metal band which holds the female threads together. These arrows should be pointing in the direction of air flow (see Figure 1) when the ADS is assembled.

Note: In situations when there are substantial high concentrations of coarse particles (>2.5 μm), it is recommended that a Teflon®-coated aluminum cyclone be used in place of the acceleration jet and impactor assembly, as illustrated in Figure 3. The cyclone is made of Teflon®-coated stainless steel. Figure 4 illustrates the location of the cyclone with respect to the denuder, heated enclosure and meter box assembly ready for sampling [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.4 Annular denuder - The denuder consists of two concentric glass tubes. The tubes create a 1 mm orifice which allows the air sample to pass through. The inner tube is inset 25 mm from one end of the outer tube; this end is called the flow straightener end. The other end of the inner tube is flush with the end of the outer tube. Both ends of the inner tube are sealed. In this configuration, the glass surfaces facing the orifice are etched to provide greater surface area for the coating. There are three types of denuders available. One is the older version which accommodates the impactor support pin assembly, and can

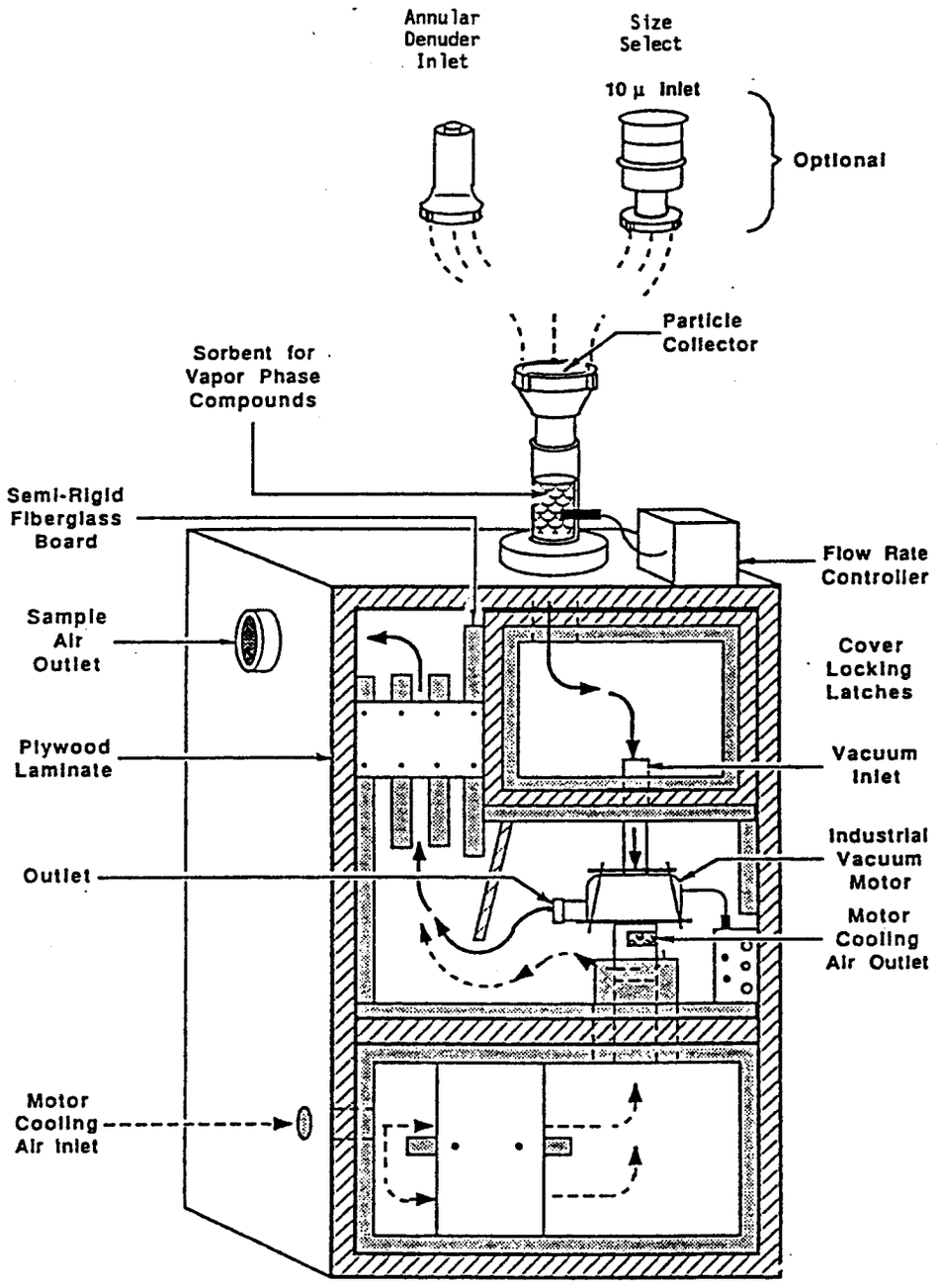

Figure 2. Acoustically Enclosed Medium Volume Sampler

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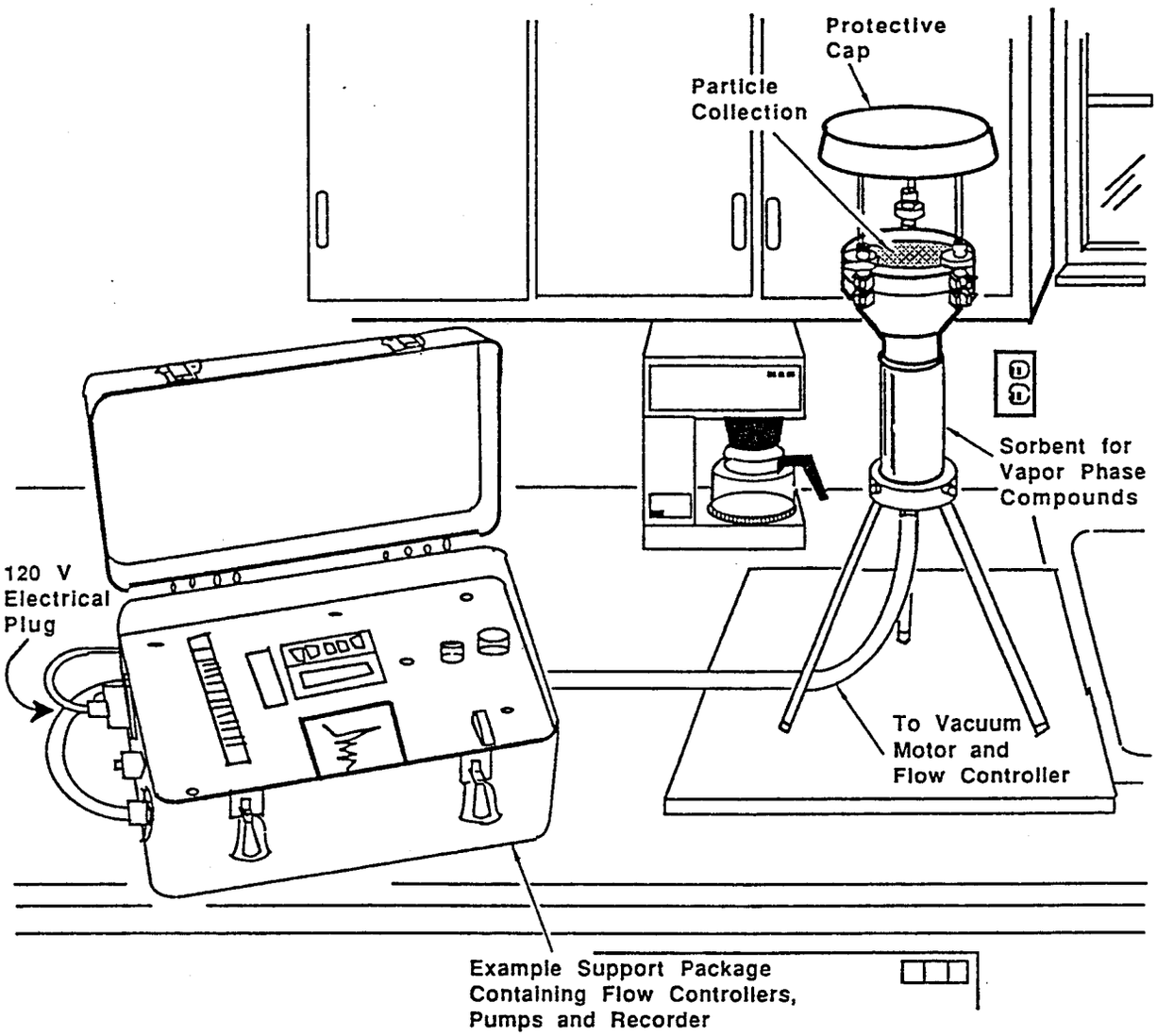

Figure 3. Tripod Sampler with Portable Meter Box Assembly

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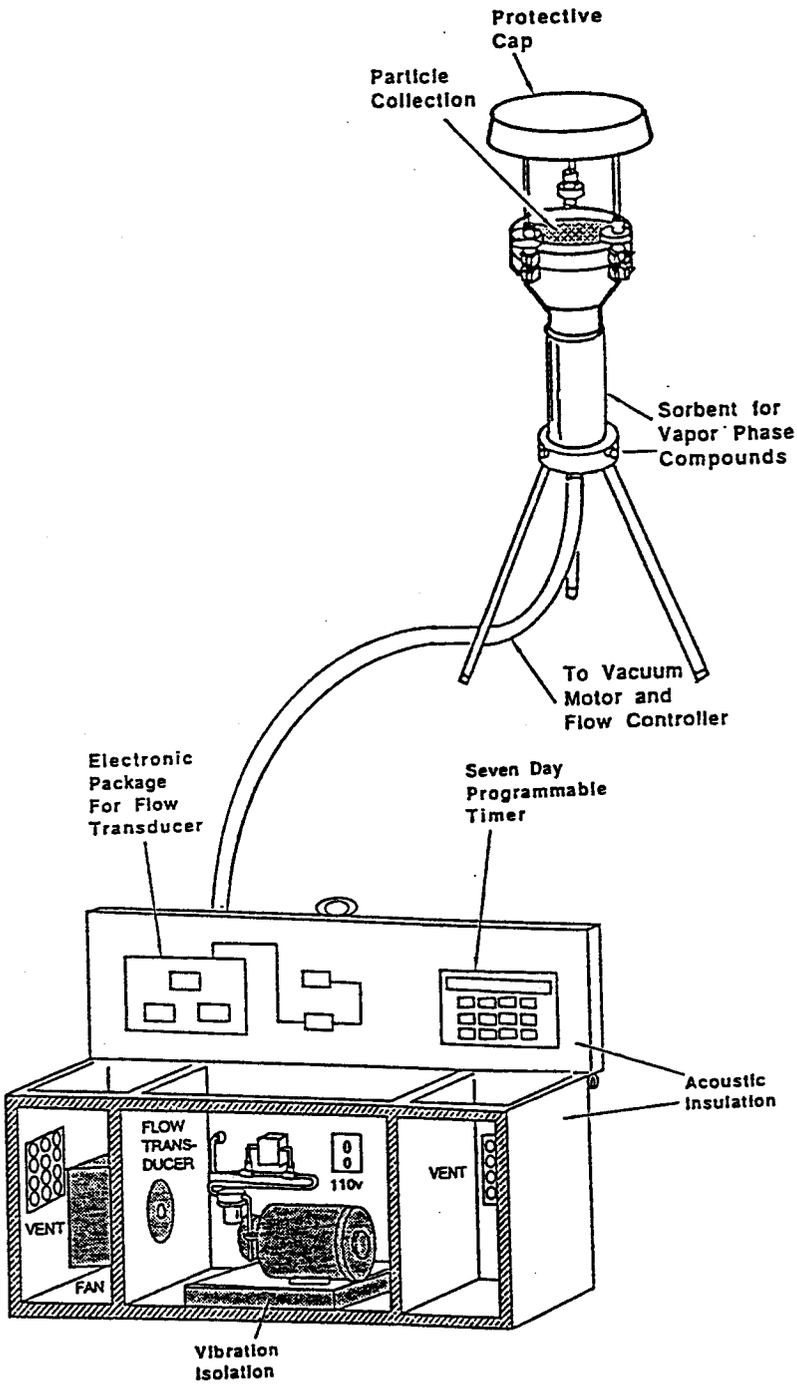

Figure 4. Battelle-Columbus Laboratory Medium Volume Air Sampler with Tripod Sampling Head

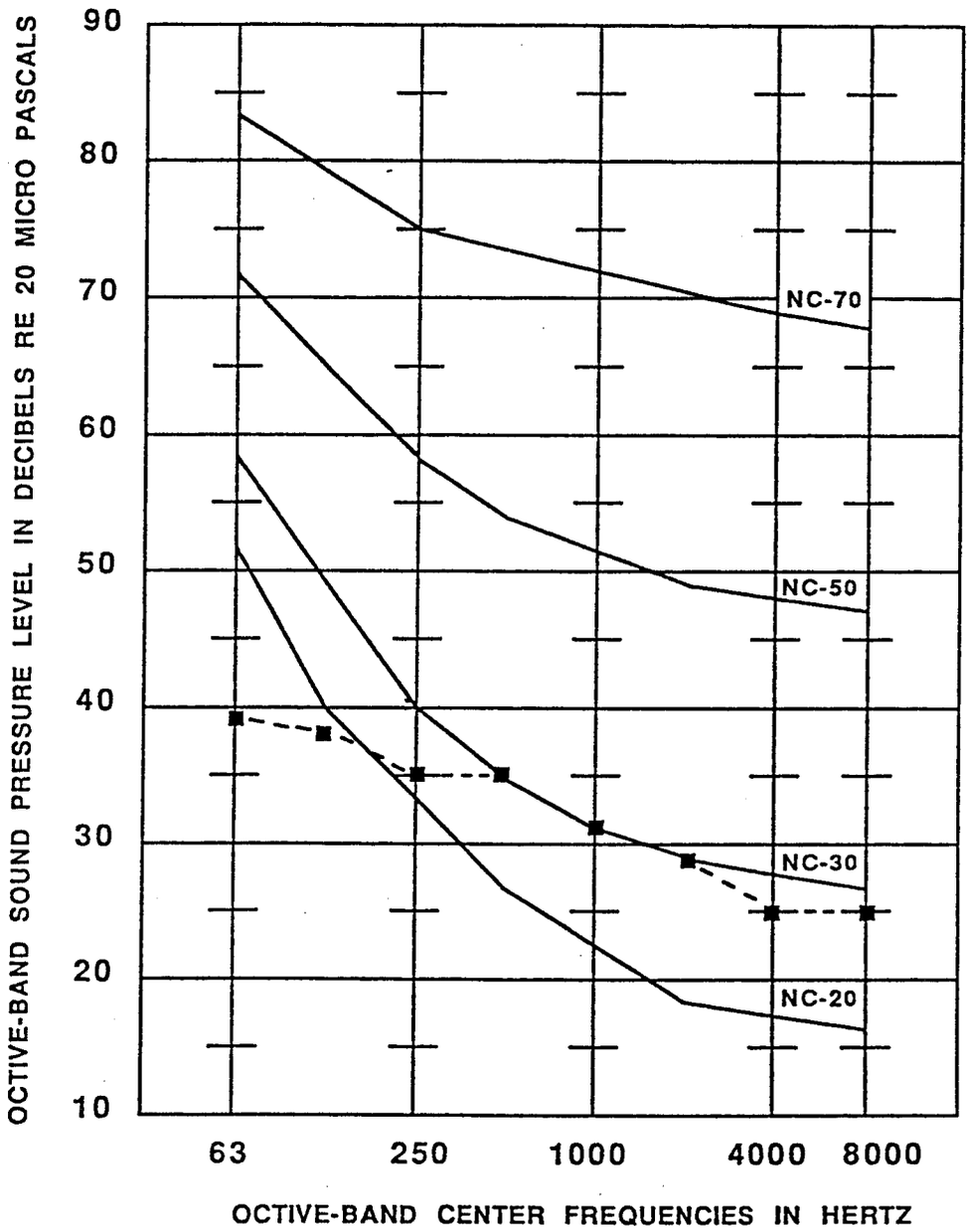

Figure 5. Noise Criterion for Indoor Air Sampler

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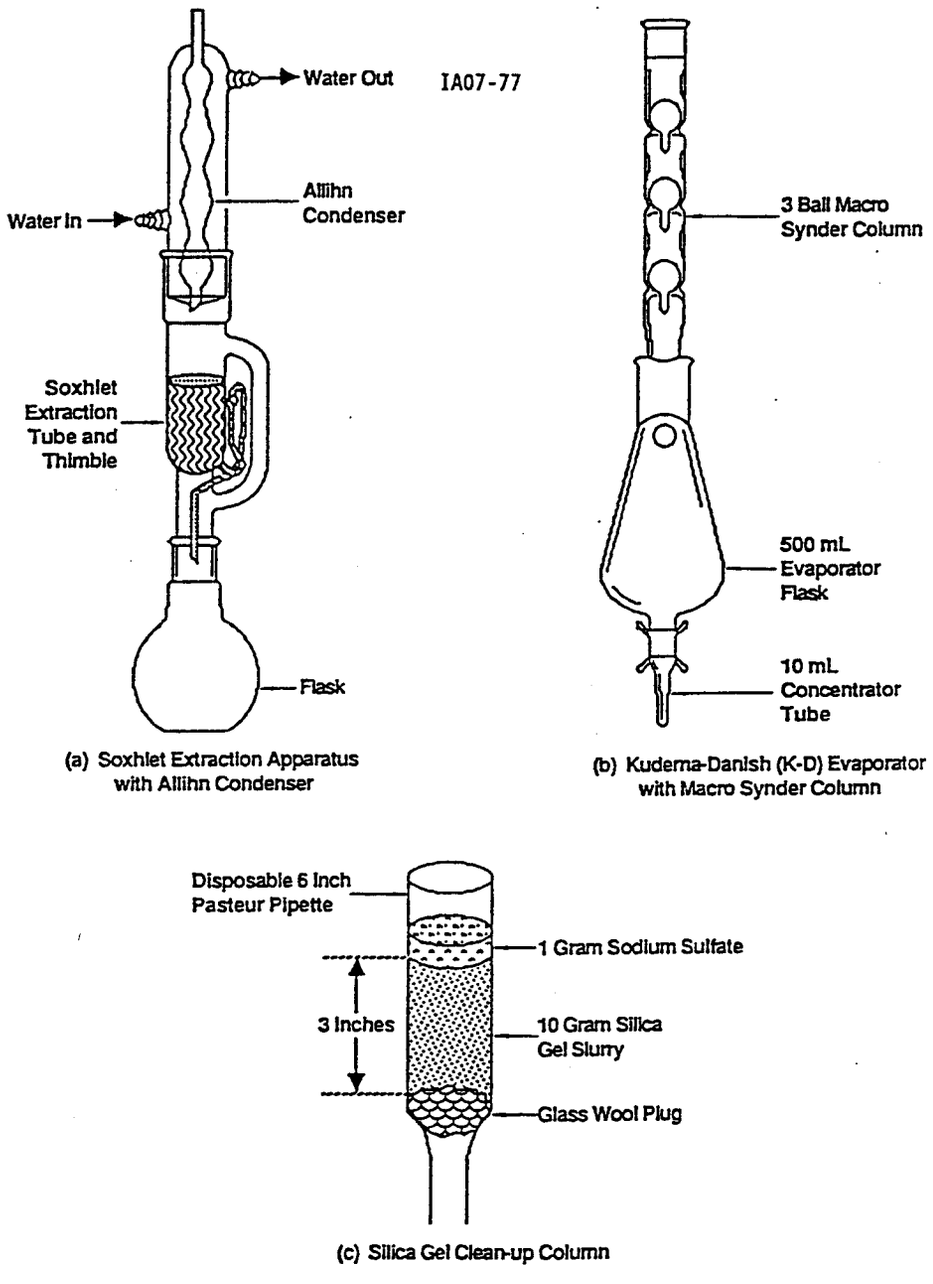

Figure 6. Apparatus Used in Sampling Analysis

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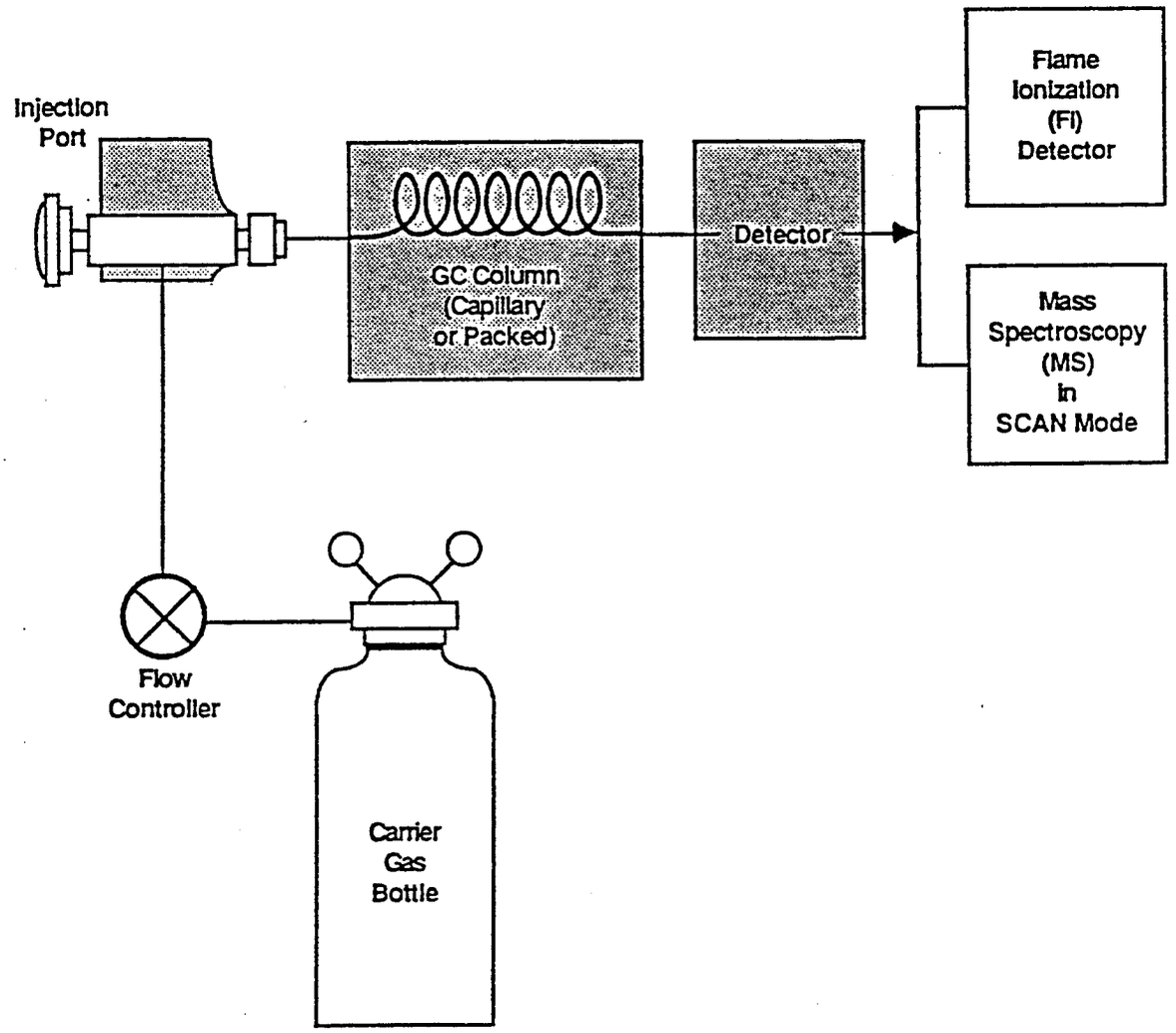

Figure 7. GC Separation with Subsequent Flame Ionization (FI) or Mass Spectroscopy (MS) Detection

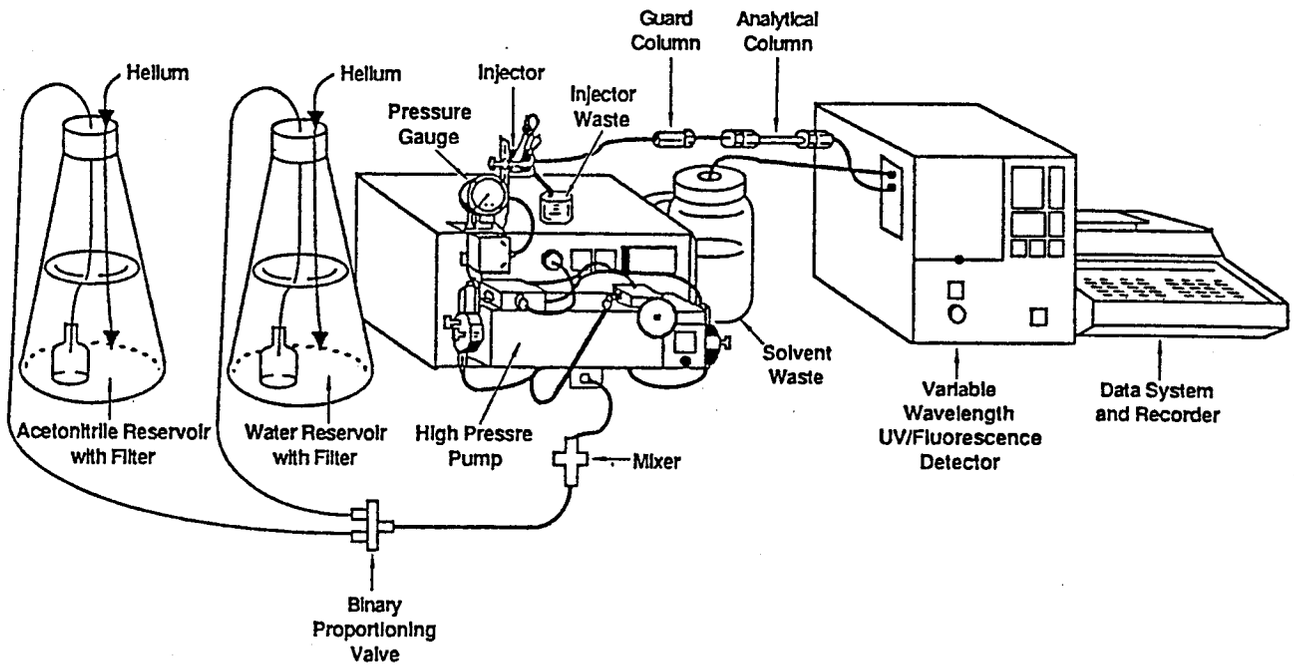

Figure 8. Important Components of an HPLC System

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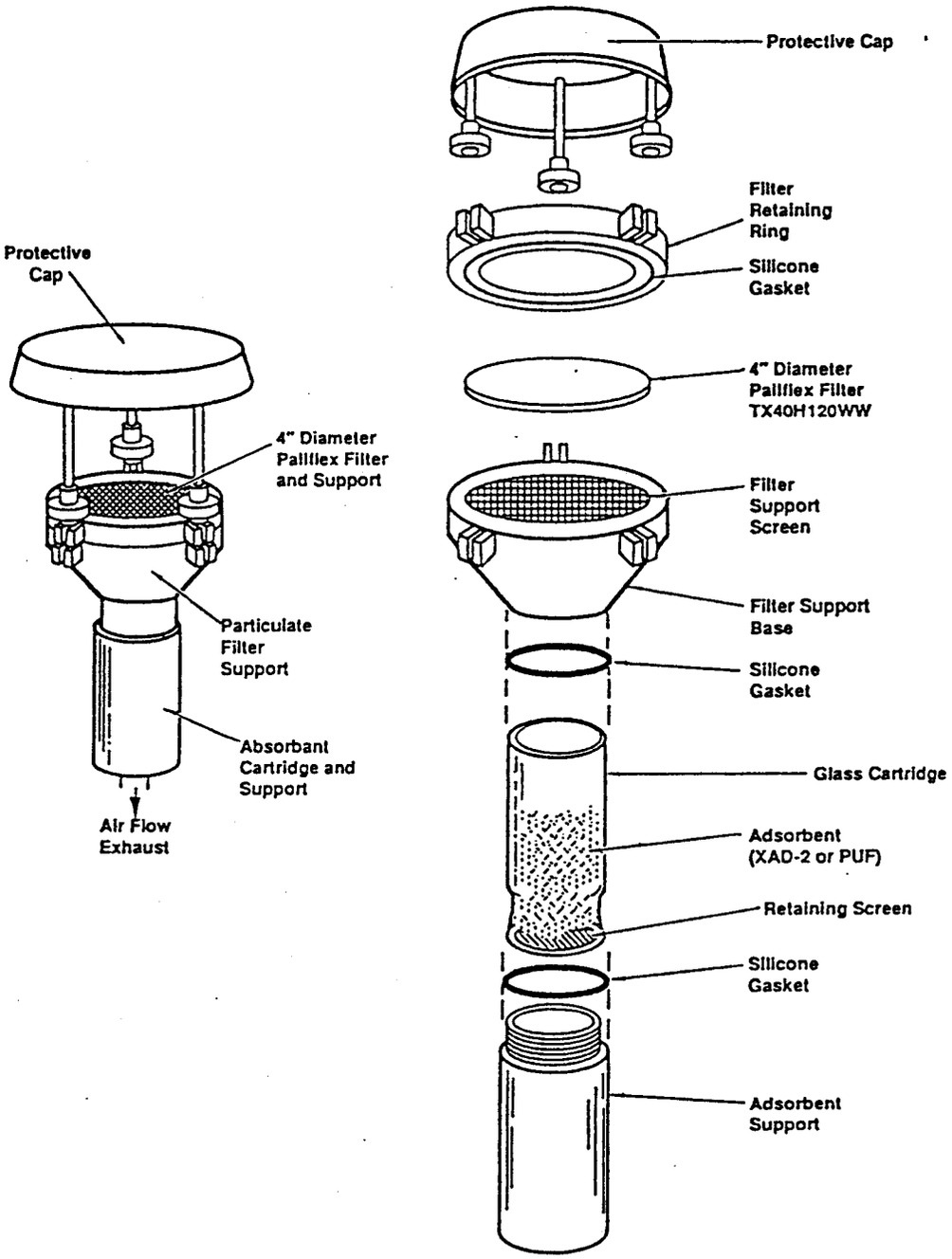

Figure 9. General Metal Works Sampling Head with Protective Cap

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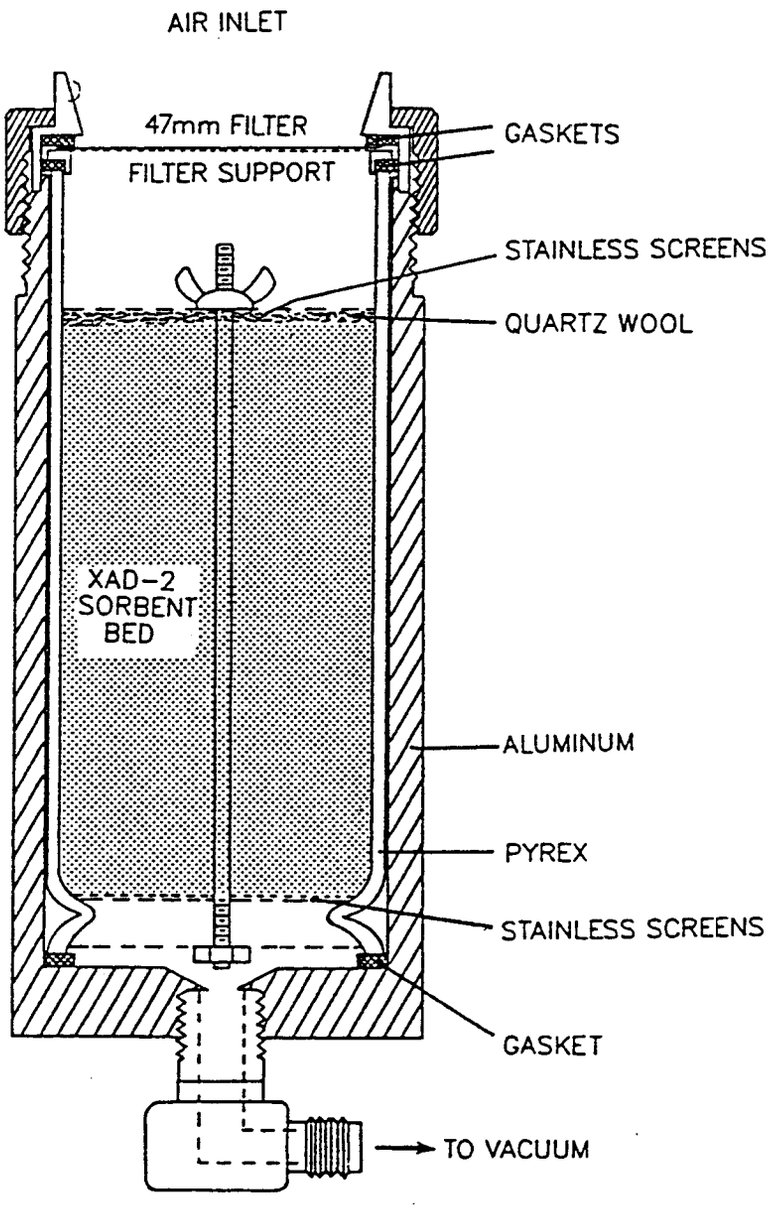

Figure 10. Alternative Design for Medium Volume Indoor Air Sampler with Open Face Filter Assembly

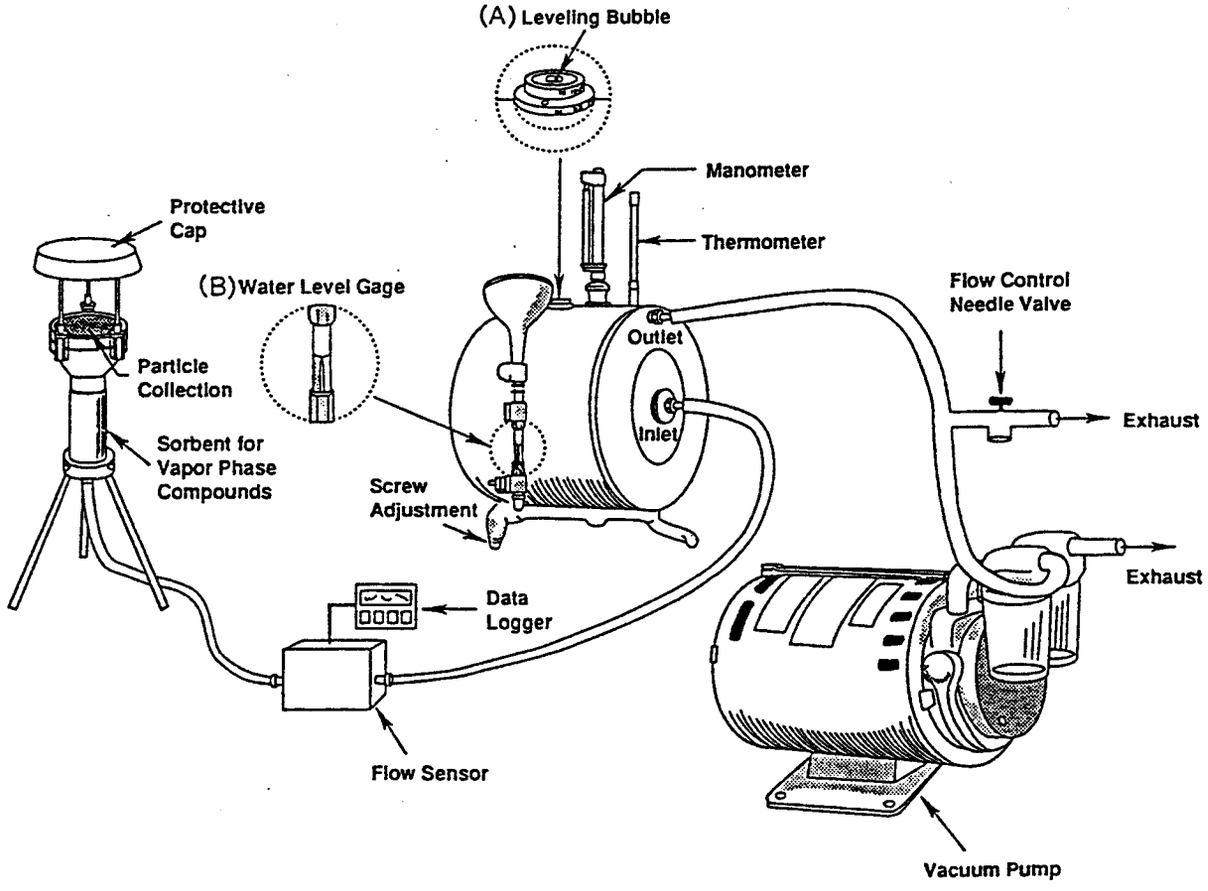

Figure 11. Calibration Assembly for Medium Volume Sampling System

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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
$\theta =$ 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

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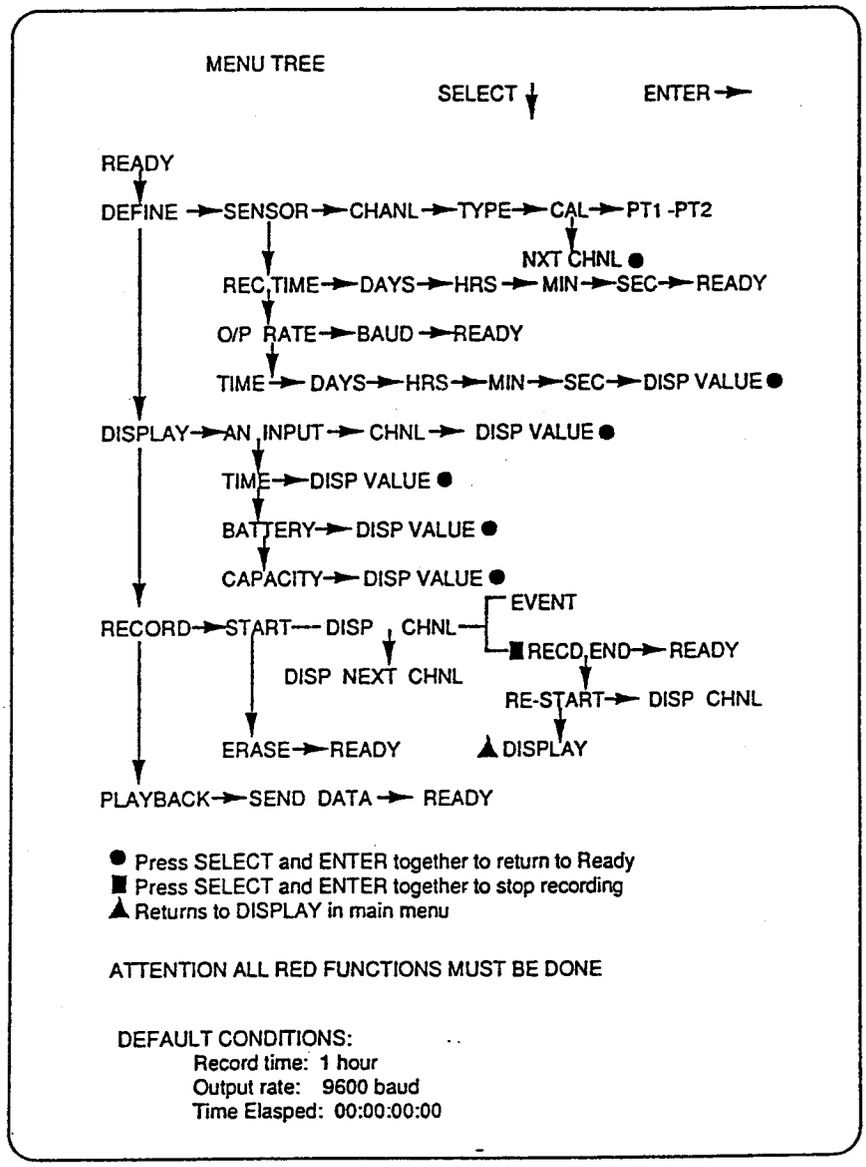

Figure 14. Data Logger Menu Tree

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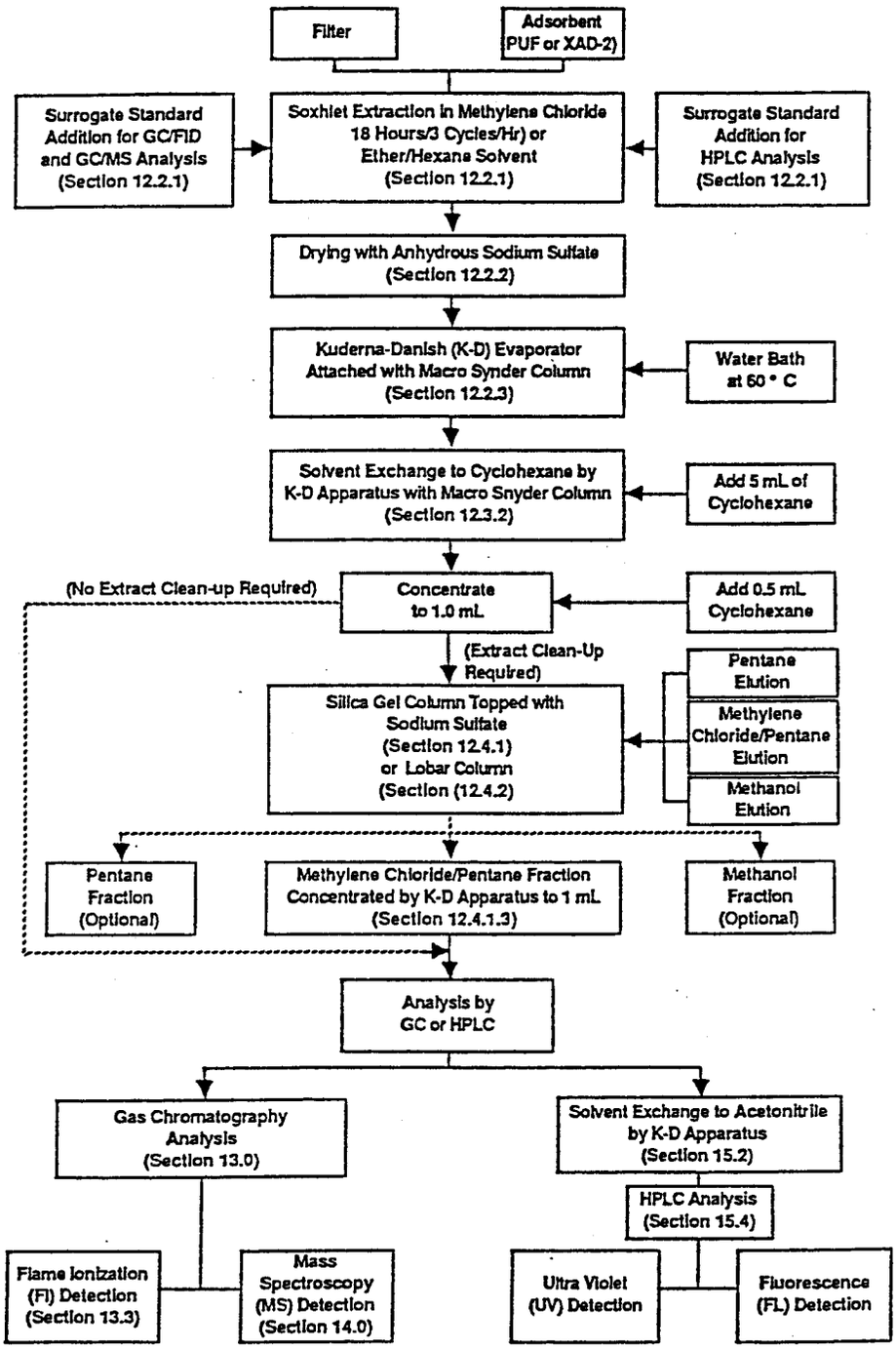

Figure 15. Sample Clean-Up, Concentration, Separation and Analysis Sequence

B34

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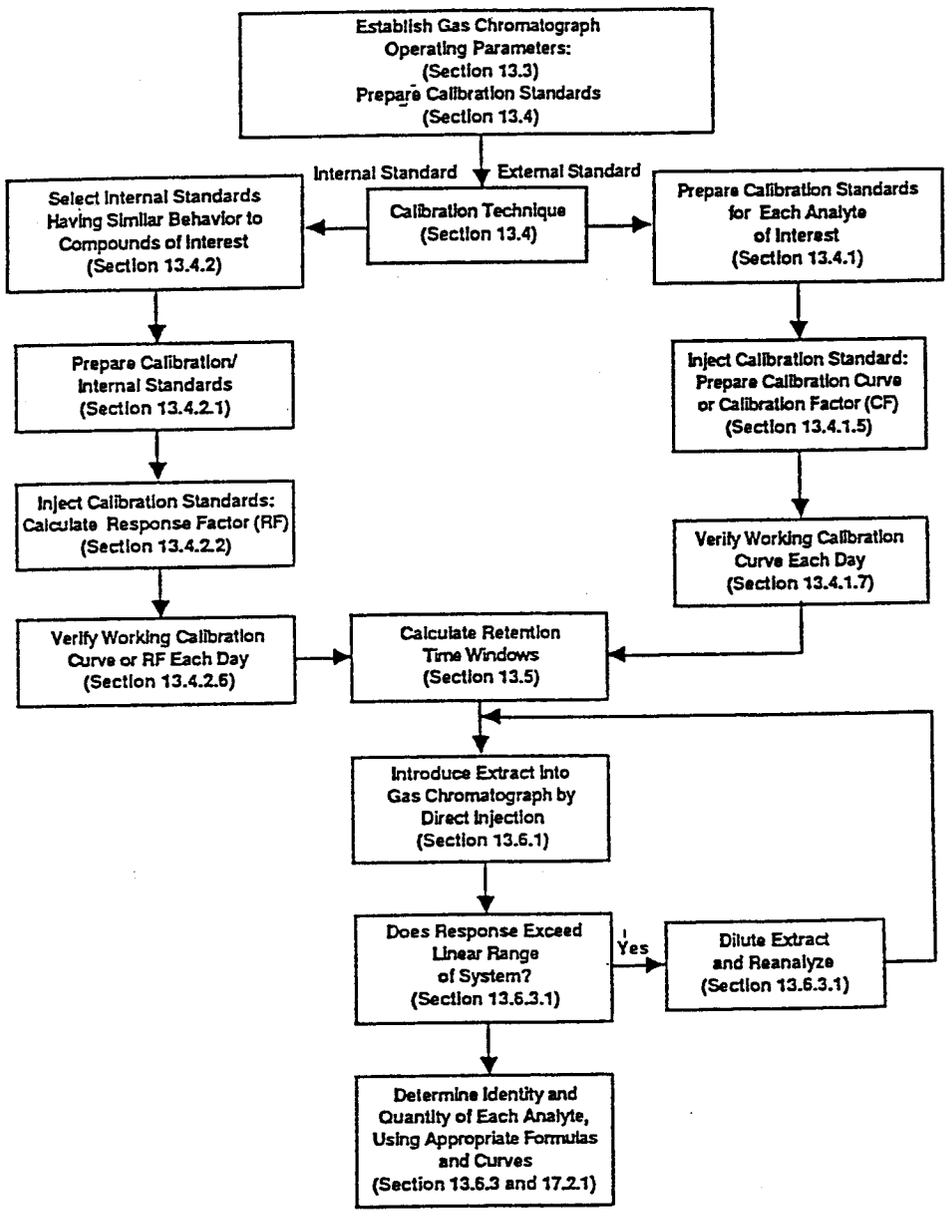

Figure 16. GC Calibration and Retention Time Window Determination

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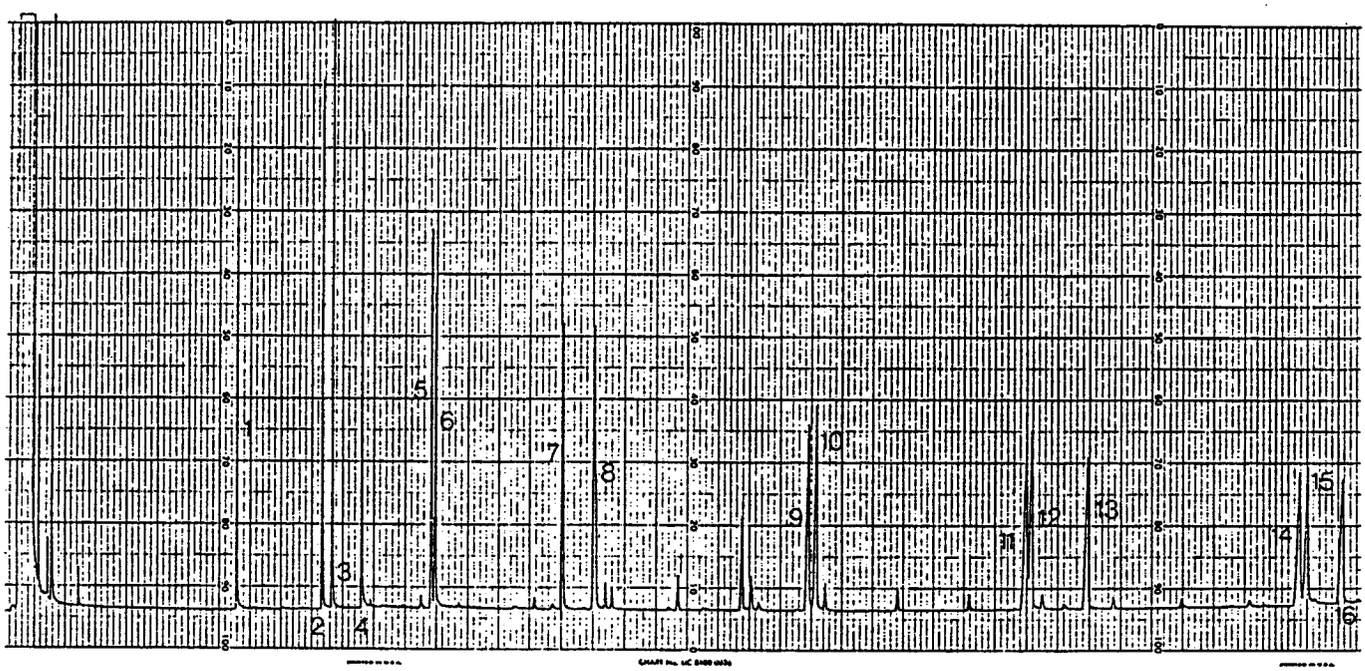

Injection: 1.0 µL on-column
Column: 30m x 0.25 mm DB-5 capillary with 0.25 µm film thickness
Program: 40°C (1 min), 15°C/min to 200°C, 3°C/min to 300°C
Detector: Flame ionization

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

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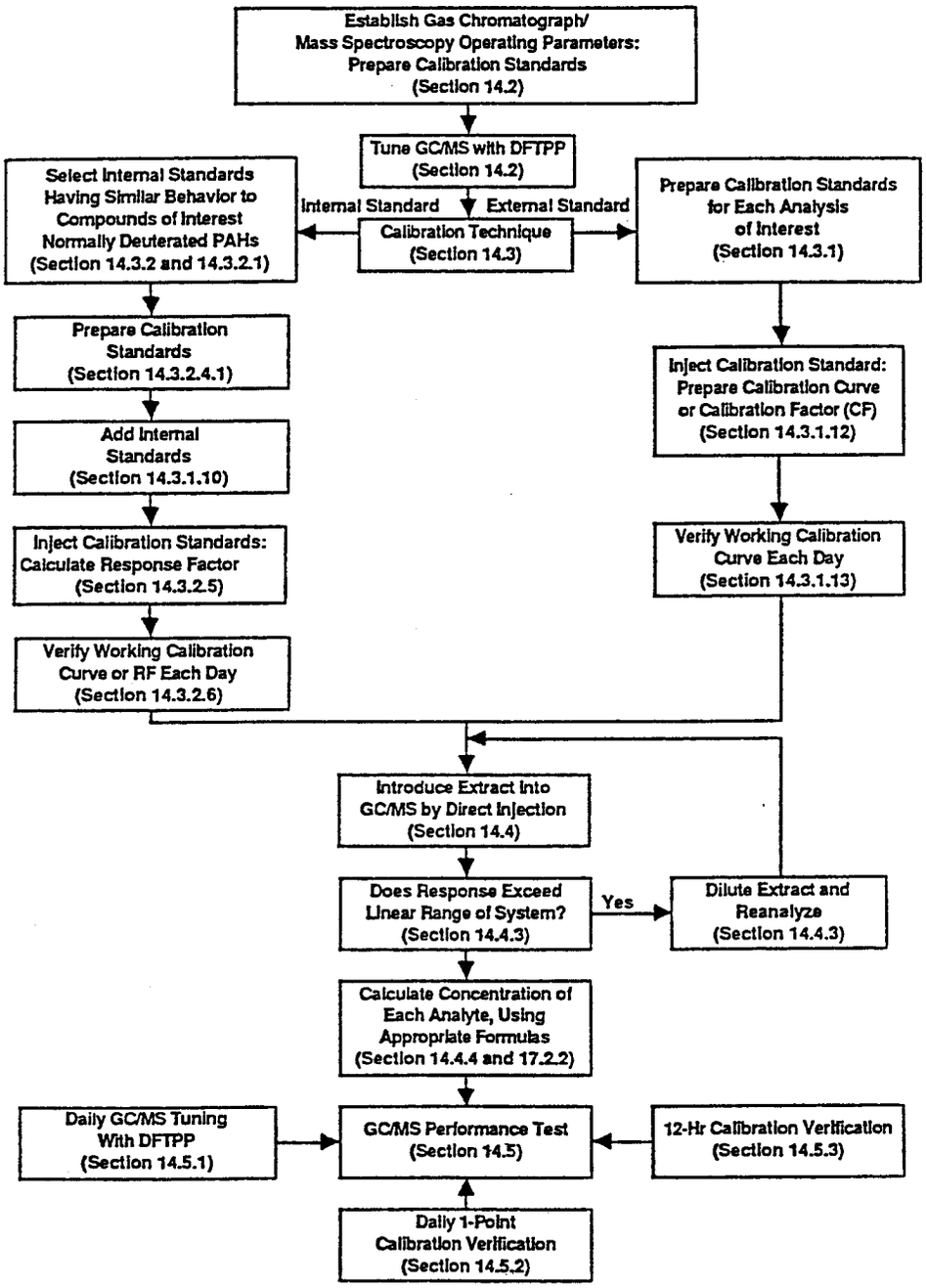

Figure 18. GC-MS Calibration and Analysis

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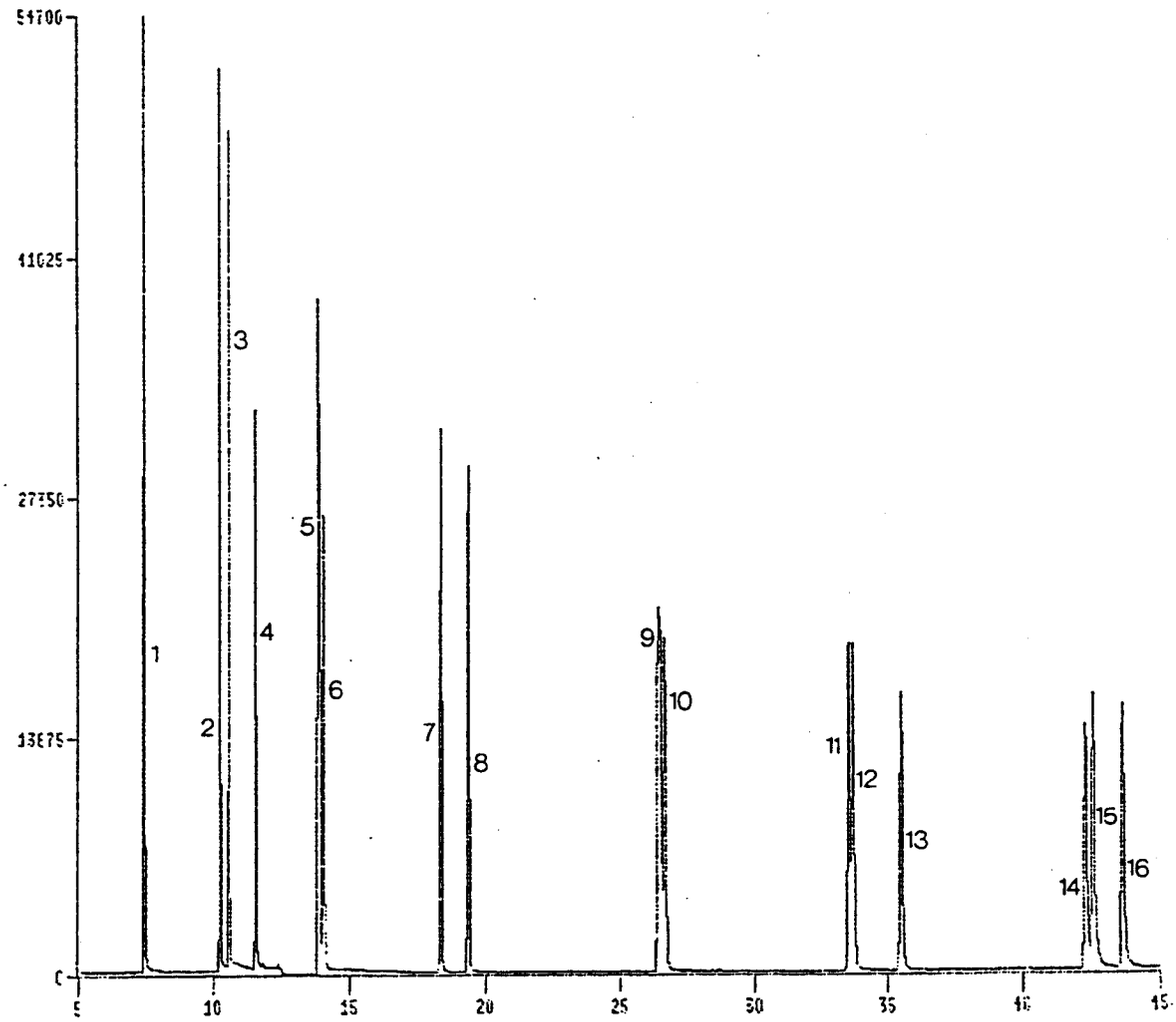

Injection: 1.0 µL on-column
Column: 30m x 0.25 mm DB-5 capillary with 0.25 µm film thickness
Program: 60°C (1 min), 15°C/min to 200°C, 3°C/min to 310°C
Detector: Mass selective detector

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

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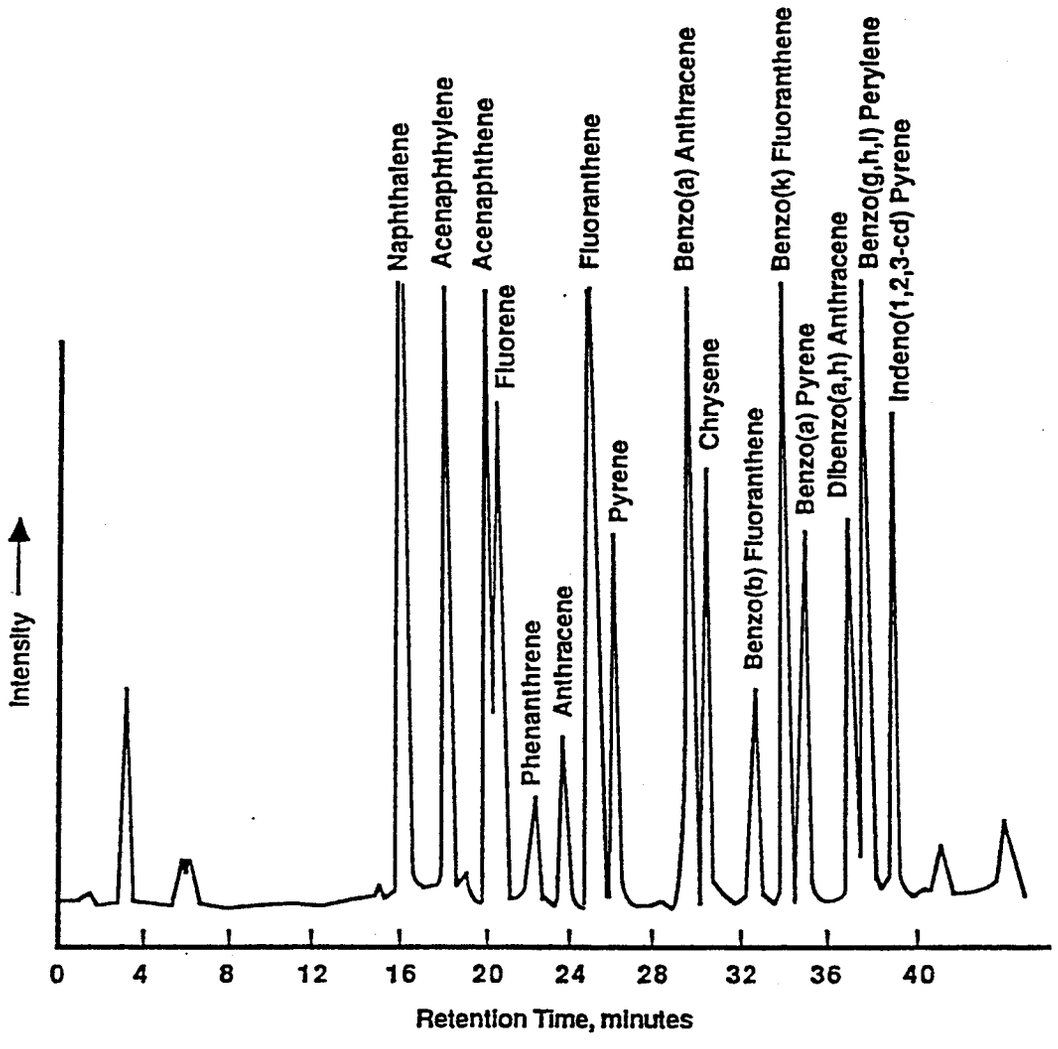

Figure 20. Typical Chromatogram of Selected PAHs Associated with HPLC Analysis Involving Ultraviolet Detection

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Chapter IP-8

DETERMINATION OF ORGANOCHLORINE PESTICIDES IN INDOOR AIR

1. Scope

This document describes a method for sampling and analysis of a variety of organochlorine pesticides in indoor air. The procedure is based on the adsorption of chemicals from indoor air on polyurethane foam (PUF) using a low volume sampler. The low volume PUF sampling procedure is applicable to multicomponent atmospheres containing organochlorine pesticide concentrations from 0.01 to 50 $\mu g/m^3$ over 4- to 24-hour sampling periods. The detection limit will depend on the nature of the analyte and the length of the sampling period. The analysis methodology described in this document is currently employed by laboratories using EPA Method 608. The sampling methodology has been formulated to meet the needs of pesticide sampling in indoor air. The sampling methodology involves a low volume (1 to 5 L/minute) sampler to collect vapors on a sorbent cartridge containing PUF. Airborne particles may also be collected, but the sampling efficiency is not known. Pesticides are extracted from the sorbent cartridge with 5% diethyl ether in hexane and determined by gas-liquid chromatography coupled with an electron capture detector (ECD). For some organochlorine pesticides, high performance liquid chromatography (HPLC) coupled with an ultraviolet (UV) detector or electrochemical detector may be preferable. This method describes the use of an electron capture detector.

2. Significance

2.1 Pesticide usage and environmental distribution are common to rural and urban areas of the United States. The application of pesticides can cause adverse health effects to humans by contaminating soil, water, air, plants, and animal life.

2.2 Many pesticides exhibit bioaccumulative, chronic health effects; therefore, monitoring the presence of these compounds in ambient air is of great importance.

2.3 Use of portable, low volume PUF sampling system allows the user flexibility in locating the apparatus. The user can place the apparatus in a stationary or mobile location. The portable sampling apparatus may be positioned in a vertical or horizontal stationary location (if necessary, accompanied with supporting structure). Mobile positioning of the system can be accomplished by attaching the apparatus to a person to test air in the individual's breathing zone. Moreover, the PUF cartridge used in this method provides for successful collection of most pesticides.

Method IP-8

DETERMINATION OF ORGANOCHLORINE PESTICIDES IN INDOOR AIR

Method IP-8

DETERMINATION OF ORGANOCHLORINE PESTICIDES IN INDOOR AIR

1. Scope

1.1 This document describes a method for sampling and analysis of a variety of organochlorine pesticides in indoor air. The procedure is based on the adsorption of chemicals from indoor air on polyurethane foam (PUF) using a low volume sampler.

1.2 The low volume PUF sampling procedure is applicable to multicomponent atmospheres containing organochlorine pesticide concentrations from 0.01 to 50 $\mu g/m^3$ over 4 to 24 hour sampling periods. The detection limit will depend on the nature of the analyte and the length of the sampling period.

1.3 Specific compounds for which the method has been employed are listed in Table 1. The analysis methodology described in this document is currently employed by laboratories using EPA Method 608. The sampling methodology has been formulated to meet the needs of pesticide sampling in indoor air.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis
D1605-60 Standard Recommended Practices for Sampling Atmospheres for Analysis of Gases and Vapors
D4861-88 Standard Practice for Sampling and Analysis of Pesticides and Polychlorinated Biphenyls in Indoor Atmospheres
E260 Recommended Practice for General Gas Chromatography Procedures
E355 Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

U.S. EPA Technical Assistance Documents (1)
Indoor/Ambient Air Studies (2-9)
Existing Procedures (10-11)

3. Summary of Method

3.1 A low volume (1 to 5 L/min) sampler is used to collect vapors on a sorbent cartridge containing PUF. Airborne particles may also be collected, but the sampling efficiency is not known.

3.2 Pesticides are extracted from the sorbent cartridge with 5% diethyl ether in hexane and determined by gas-liquid chromatography coupled with an electron capture detector (ECD). Note: For some organochlorine pesticides, high performance liquid chromatography (HPLC) coupled with an ultraviolet (UV) detector or electrochemical detector may be preferable. This method describes the use of an electron capture detector.

3.3 Interferences resulting from analytes having similar retention times during gas-liquid chromatography are resolved by improving the resolution or separation, such as by changing

the chromatographic column or operating parameters, or by fractionating the sample by column chromatography.

3.4 The sampling procedure is also applicable to other pesticides which may be determined by gas-liquid chromatography coupled with a nitrogen-phosphorus detector (NPD), flame photometric detector (FPD), Hall electrolytic conductivity detector (HECD), or a mass spectrometer (MS).

4. Significance

4.1 This procedure is intended to be used primarily for non-occupational exposure monitoring in domiciles, public access buildings and offices.

4.2 A broad spectrum of pesticides are commonly used in and around the house and for insect control in public and commercial buildings. Other semi-volatile organic chemicals, such as PCBs, are also often present in indoor air, particularly in large office buildings. This procedure will promote needed accuracy and precision in the determination of many airborne chemicals which may prove to present unacceptable long-term health risks or contribute to short-term episodes, such as "sick building syndrome."

4.3 Use of a portable, low volume PUF sampling system allows the user flexibility in locating the apparatus. The user can place the apparatus in a stationary or mobile location. The portable sampling apparatus may be positioned in a vertical or horizontal stationary location (if necessary, accompanied with supporting structure). Mobile positioning of the system can be accomplished by attaching the apparatus to a person to test air in the individual's breathing zone. Moreover, the PUF cartridge used in this method provides for successful collection of most pesticides. Figure 1(a) illustrates PUF sampling system in a fixed location and Figure 1(b) shows the sampling system attached to an individual.

5. Definitions

Definitions used in this document and in user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM D1356, D1605-60, and E355. All abbreviations and symbols are defined within this document at point of use. Additional definitions and abbreviations are provided in Appendices A-1 and B-2 of this Compendium.

5.1 Sampling efficiency (SE) - ability of the sampling medium to trap vapors of interest. %SE is the percentage of the analyte of interest collected and retained by the sampling medium when it is introduced as a vapor in air or nitrogen 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 efficiency (RE) - ability of sampling medium to retain a compound added (spiked) to it in liquid solution.

5.2.1 Static retention efficiency - ability of the sampling medium to retain the solution spike when the sampling cartridge is stored under clean, quiescent conditions for the duration of the test period.

5.2.2 Dynamic retention efficiency - ability of the sampling medium to retain the solution spike when air or nitrogen is drawn through the sampling cartridge under normal operating conditions for the duration of the test period. The dynamic RE is normally equal to or less than the SE.

5.3 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.

5.4 Relative retention time (RRT) - a ratio of RTs for two chemicals for the same chromatographic column and carrier gas flow rate, where the denominator represents a reference chemical.

6. Interferences

6.1 Any gas or liquid chromatographic separation of complex mixtures of organic chemicals is subject to serious interference problems due to coelution of two or more compounds. The use of capillary or narrow bore columns with superior resolution and/or two or more columns of different polarity will frequently eliminate these problems.

6.2 The electron capture detector responds to a wide variety of organic compounds. It is likely that such compounds will be encountered as interferences during GC-ECD analysis. The NPD, FPD, and HECD detectors are element specific, but are still subject to interferences. UV detectors for HPLC are nearly universal, and the electrochemical detector may also respond to a variety of chemicals. Mass spectrometric analyses will generally provide positive identification of specific compounds.

6.3 Certain organochlorine pesticides (e.g., chlordane) are complex mixtures of individual compounds that can make difficult accurate quantification of a particular formulation in a multiple component mixture. Polychlorinated biphenyls (PCBs) may interfere with the determination of pesticides.

6.4 Contamination of glassware and sampling apparatus with traces of pesticides can be a major source of error, particularly at lower analyte concentrations. Careful attention to cleaning and handling procedures is required during all steps of sampling and analysis to minimize this source of error.

6.5 The general approaches listed below should be followed to minimize interferences.

6.5.1 Polar compounds, including certain pesticides (e.g., organophosphorus and carbamate classes), can be removed by column chromatography on alumina. This sample clean-up will permit analysis of most organochlorine pesticides.

6.5.2 PCBs may be separated from other organochlorine pesticides by column chromatography on silicic acid.

6.5.3 Many pesticides can be fractionated into groups by column chromatography on Florisil (Floridin Corp.).

7. Apparatus

7.1 Sample Collection

7.1.1 Sampling pump - (DuPont Alpha-1 Air Sampler, E.I. DuPont de Nemours & Co., Inc., Wilmington, DE, 19898, or equivalent). The pump should be quiet and unobtrusive and provide a constant flow (< ±5%).

7.1.2 Sampling cartridge shown in Figure 2 - constructed from a 20 mm (i.d.) x 10 cm borosilicate glass tube drawn down to a 7 mm (o.d.) open connection for attachment to the pump via vinyl tubing. The cartridge can be fabricated inexpensively from glass by Kontes (P.O. Box 729, Vineland, NJ, 08360), or equivalent.

7.1.3 Sorbent, polyurethane foam (PUF) - cut into a cylinder, 22 mm in diameter and 7.6 cm long, fitted under slight compression inside the cartridge. The PUF should be of the polyether type, density of 0.022 g/cm^3. This type of foam is used for furniture upholstery, pillows, and mattresses; it may be obtained from Olympic Products Co. (Greensboro, NC), or equivalent source. The PUF cylinders (plugs) should be slightly larger in diameter than the internal diameter of the cartridge. They may be cut by one of the following means:

- High-speed cutting tool, such as a motorized cork borer. Distilled water should be used to lubricate the cutting tool.
- Hot wire cutter. Care should be exercised to prevent thermal degradation of the foam.
- Scissors, while plugs are compressed between the 22 mm circular templates.

Alternatively, pre-extracted PUF plugs and glass cartridges may be obtained commercially (Supelco, Inc., Supelco Park, Bellefonte, PA, 16823, No. 2-0557, or equivalent).

7.2 Sample Analysis

7.2.1 Gas chromatograph (GC) with an electron capture detector (ECD) and either an isothermally controlled or temperature programmed heating oven. The analytical system should be complete with all required accessories including syringes, analytical columns, gases, detector, and strip chart recorder. A data system is recommended for measuring peak heights. Consult EPA Method 608 for additional specifications.

7.2.2 Gas Chromatographic Columns

7.2.2.1 The following 4 or 2 mm (i.d.) x 183 cm borosilicate glass GC columns may be used packed with

- 1.5% SP-2250 (Supelco, Inc.)/1.95% SP-2401 (Supelco, Inc.) on 100/120 mesh Supelcoport (Supelco, Inc.)
- 4% SE-30 (General Electric, 50 Fordham Rd., Wilmington, MA, 01887, or equivalent)/6% OV-210 (Ohio Valley Specialty Chemical, 115 Industry Rd., Marietta, OH, 45750, or equivalent) on 100/200 mesh Gas Chrom Q (Alltec Assoc., Applied Science Labs, 2051 Waukegan Rd, Deerfield, IL, 60015, or equivalent)
- 3% OV-101 (Ohio Valley Specialty Chemical) on UltraBond (Ultra Scientific, 1 Main St., Hope, RI, 02831, or equivalent)
- 3% OV-1 (Ohio Valley Specialty Chemical) on 80/100 mesh Chromosorb WHP (Manville, Filtration, and Materials, P.O. Box 5108, Denver, CO, 80271, or equivalent)

7.2.2.2 Capillary GC columns, such as 0.25 mm (i.d.) x 30 m DB-5 (J&W Scientific, 3871 Security Park Dr., Rancho Cordova, CA, 95670, or equivalent) with 0.25 μm film thickness may be used.

7.2.2.3 HPLC columns, such as 4.6 mm x 25 cm Zorbax SIL (DuPont Co., Concord Plaza, Wilmington, DE, 19898, or equivalent) or μ-Bondapak C-18 (Millipore Corp., 80 Ashby Rd., Bedford, MA, 01730, or equivalent) can be used.

7.2.2.4 Other columns may also give acceptable results.

7.2.3. Microsyringes - 5 μL volume or other appropriate sizes.

8. Reagents and Materials

Note: For a detailed listing of various other items required for extract preparation, cleanup, and analysis, consult U.S. EPA Method 608 which is provided in Appendix A of Method TO-4 in the Compendium.

8.1 Round bottom flasks - 500 mL, best source.

8.2 Soxhlet extractors - 300 mL, with reflux condensers, best source.

8.3 Kuderna-Danish concentrator apparatus - 500 mL, with Snyder columns, best source.

8.4 Graduated concentrator tubes - 10 mL, Kontes, P.O. Box 729, Vineland, NJ, 08360, Cat. No. K-570050, size 1025, or equivalent.

8.5 Graduated concentrator tubes - 1 mL, Kontes, Vineland, NJ, Cat. No. K-570050, size 0124, or equivalent.

8.6 TFE fluorocarbon tape - 1/2 in, best source.

8.7 Filter tubes - size 40 mm (i.d.) x 80 mm, Corning Glass Works, Science Products, Houghton Park, AB-1, Corning, NY, 14831, Cat. No. 9480, or equivalent.

8.8 Serum vials - 1 mL and 5 mL, fitted with caps lined with TFE fluorocarbon, best source.

8.9 Pasteur pipettes - 9 in, best source.

8.10 Glass wool - fired at 500°C, best source.

8.11 Boiling chips - fired at 500°C, best source.

8.12 Forceps - stainless steel, 12 in, best source.

8.13 Gloves - latex or polyvinyl acetate, best source.

8.14 Steam bath, best source.

8.15 Heating mantle, - 500 mL, best source.

8.16 Analytical evaporator, nitrogen blow-down (N-Evap®, Organomation Assoc., P.O. Box 159, South Berlin, MA, 01549, or equivalent).

8.17 Acetone - pesticide quality, best source.

8.18 n-Hexane - pesticide quality, best source.

8.19 Diethyl ether preserved with 2% ethanol - Mallinckrodt, Inc., Science Products Division, P.O. Box 5840, St. Louis, MO, 63134, Cat. No. 0850, or equivalent.

8.20 Sodium sulfate - anhydrous, analytical grade, best source.

8.21 Alumina - activity grade IV, 100/200 mesh, best source.

8.22 Glass chromatographic column - 2 mm i.d. x 15 cm long, best source.

8.23 Soxhlet extraction system, including Soxhlet extractors (500 and 300 mL), variable voltage transformers, and cooling water source, best source.

8.24 Vacuum oven connected to water aspirator, best source.

8.25 Die - use to cut PUF adsorbent, best source.

8.26 Ice chest, best source.

8.27 Silicic acid - pesticide quality, best source.

8.28 Octachloronaphthalene (OCN) - research grade, Ultra Scientific, Inc., 1 Main St., Hope, RI, 02831, or equivalent.

9. Assembly and Calibration of Sampling System

9.1 Description of Sampling Apparatus

9.1.1 The entire sampling system is diagrammed in Figure 1. This apparatus was developed to operate at a rate of 1-5 L/minute and is used by U.S. EPA for low volume sampling of indoor air. The method writeup presents the use of this device.

9.1.2 The sampling module in Figure 2 consists of a glass sampling cartridge in which the PUF plug is retained.

9.2 Calibration of Sampling System

9.2.1 Air flow through the sampling system is calibrated by the assembly shown in Figure 3. The air sampler must be calibrated in the laboratory before and after each sample collection period, using the procedure described below.

9.2.2 For accurate calibration, attach the sampling cartridge in-line during calibration. Vinyl bubble tubing (Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA, 15219, Cat. No. 14-170-132, or equivalent) or other means (e.g., rubber stopper or glass joint) may be used to connect the large end of the cartridge to the calibration system. Refer to ASTM Standard Practice D3686, Annex A2 or Standard Practice D4185, Annex A1 for procedures to calibrate small volume air pumps.

10. Preparation of Sampling (PUF) Cartridges

10.1 The PUF adsorbent is white and yellows upon exposure to light. For initial cleanup and quality assurance purposes, the PUF plug is placed in a Soxhlet extractor and extracted with acetone for 14 to 24 hours at 4 to 6 cycles per hour. (If commercially pre-extracted PUF plugs are used, extraction with acetone is not required.) This procedure is followed by a 16 hour Soxhlet extraction with 5% diethyl ether in n-hexane. When cartridges are reused, 5% ether in n-hexane can be used as the cleanup solvent.

10.2 The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for 2 to 4 hours (until no solvent odor is detected). The clean PUF is placed in labeled glass sampling cartridges using gloves and forceps. The cartridges are wrapped with hexane-rinsed aluminum foil and placed in glass jars fitted with TFE fluorocarbon-lined caps. The foil wrapping may also be marked for identification using a blunt probe.

10.3 At least one assembled cartridge from each batch should be analyzed as a laboratory blank before any samples from that batch are considered acceptable for use. A blank level of <10 ng/plug for single component compounds is considered to be acceptable. For multiple component mixtures, the blank level should be <100 ng/plug.

11. Sample Collection

11.1 After the sampling system has been assembled and calibrated as per Section 9, it can be used to collect air samples as described below.

11.2 The prepared sample cartridges should be used within 30 days of loading and should be handled only with clean latex or polyvinyl acetate gloves.

11.3 The clean sample cartridge is carefully removed from the aluminum foil wrapping (the foil is returned to jars for later use) and attached to the pump with flexible tubing. The sampling assembly is positioned with the intake downward or in a horizontal position. The sampler is located in an unobstructed area at least 30 cm from any obstacle to air flow. The PUF cartridge intake is positioned 1 to 2 m above the floor level. Air temperature(s) and barometric pressure(s) are recorded periodically on the Sampling Data Form shown in Figure 4.

11.4 After the PUF cartridge is correctly inserted and positioned, the power switch is turned on and the sampling begins. The elapsed time meter is activated and the start time is recorded. The pumps are checked during the sampling process and any abnormal conditions discovered are recorded on the data sheet.

11.5 At the end of the desired sampling period, the power is turned off and the PUF cartridges are wrapped with the original aluminum foil and placed in sealed, labeled containers for transport back to the laboratory. At least one field blank is returned to the laboratory with each group of samples. A field blank is treated exactly like a sample except

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that no air is drawn through the cartridge. Samples are stored at -10°C or below until analyzed.

12. Sample Preparation, Cleanup, and Analysis

Note: Sample preparation should be performed under a properly ventilated hood.

12.1 Sample Preparation

12.1.1 All samples should be extracted within 1 week after collection.

12.1.2 All glassware is washed with a suitable detergent; rinsed with deionized water, acetone, and hexane; rinsed again with deionized water; and fired in an oven (500°C).

12.1.3 Sample extraction efficiency is determined by spiking the samples with a known solution. Octachloronaphthalene (OCN) is an appropriate standard to use for pesticide analysis using GC-ECD techniques. The spiking solution is prepared by dissolving 10 mg of OCN in 10 mL of 10% acetone in n-hexane, followed by serial dilution with n-hexane to achieve a final concentration of 1 µg/mL.

12.1.4 The extracting solution (5% ether/hexane) is prepared by mixing 1900 mL of freshly opened hexane and 100 mL of freshly opened ethyl ether (preserved with ethanol) to a flask.

12.1.5 All clean glassware, forceps, and other equipment to be used are placed on rinsed (5% ether/hexane) aluminum foil until use. The forceps are also rinsed with 5% ether/hexane. The condensing towers are rinsed with 5% ether/hexane and 300 mL are added to a 500 mL round bottom boiling flask (with no more than three boiling chips).

12.1.6 Using clean gloves, the PUF cartridges are removed from the sealed container and the PUF is placed into a 300 mL Soxhlet extractor using prerinsed forceps.

12.1.7 Before extraction begins, 100 µL of the OCN solution are added dropwise to the top of the PUF plug. Addition of the standard demonstrates extraction efficiency of the Soxhlet procedure.

Note: Incorporating a known concentration of the solution onto the sample provides a quality assurance check to determine recovery efficiency of the extraction and analytical processes.

12.1.8 The Soxhlet extractor is then connected to the 500 mL boiling flask and condenser. The glass joints of the assembly are wet with 5% ether/hexane to ensure a tight seal between the fittings. If necessary, the PUF plug can be adjusted using forceps to wedge it midway along the length of the siphon. The above procedure should be followed for all samples, with the inclusion of a blank control sample.

12.1.9 The water flow to the condenser towers of the Soxhlet extraction assembly is checked and the heating unit is turned on. As the samples boil, the Soxhlet extractors are inspected to ensure that they are filling and siphoning properly (4 to 6 cycles/hour). Samples should cycle for a minimum of 16 hours.

12.1.10 At the end of the extracting process, the heating units are turned off and the samples are cooled to room temperature.

12.1.11 The extracts are concentrated to a 5 mL solution using a Kuderna-Danish (K-D) apparatus. The K-D is set up and assembled with concentrator tubes. This assembly

is rinsed and one boiling chip is added to each concentrator tube. The lower end of the filter tube is packed with glass wool and filled with anhydrous sodium sulfate to a depth of 40 mm. The filter tube is placed in the neck of the K-D. The Soxhlet extractors and boiling flasks are carefully removed from the condenser towers and the remaining solvent is drained into each boiling flask. Sample extract is carefully poured through the filter tube into the K-D. Each boiling flask is rinsed three times by swirling hexane along the sides. Once the sample has drained, the filter tube is rinsed down with hexane. Each Synder column is attached to the K-D and rinsed to wet the joint for a tight seal. The complete K-D apparatus is placed on a steam bath and the sample is evaporated to approximately 5 mL. Do not let sample go to dryness. The sample is removed from the steam bath and allowed to cool. Each Synder column is rinsed with a minimum of hexane and sample is allowed to cool. Sample volume is adjusted to 10 mL in a concentrator tube, which is then closed with a glass stopper and sealed with TFE fluorocarbon tape. Alternately, the sample may be quantitatively transferred (with concentrator tube rinsing) to prescored vials and brought up to final volume. Concentrated extracts are stored at -10°C until analyzed. Analysis should occur no later than two weeks after sample extraction.

12.2 Sample Cleanup

12.2.1 If only organochlorine pesticides are sought, an alumina cleanup procedure is appropriate. Before cleanup, the sample extract is carefully reduced to 1 mL using a gentle stream of clean nitrogen.

12.2.2 A glass chromatographic column (2 mm i.d. x 15 cm long) is packed with alumina, activity grade IV, and rinsed with approximately 20 mL of n-hexane. The concentrated sample extract is placed on the column and eluted with 10 mL of n-hexane at a rate of 0.5 mL/minute. The eluate volume is adjusted to exactly 10 mL and analyzed as per Section 12.3.

12.2.3 If other pesticides are sought, alternate cleanup procedures may be required (e.g., Florisil). EPA Method 608 identifies appropriate cleanup procedures.

12.3 Sample Analysis

12.3.1 Organochlorine pesticides and many nonchlorinated pesticides are responsive to electron capture detection (Table 1). Most of these compounds can be determined at concentrations of 1 to 50 ng/mL by GC-ECD.

12.3.2 An appropriate GC column is selected for analysis of the extract. (For example, 4 mm i.d. x 183 cm glass, packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 mesh Supelcoport, 200°C isothermal, with 5% methane/95% argon carrier gas at 65 to 85 mL/min). A chromatogram showing a mixture containing single component pesticides determined by GC-ECD using a packed column is shown in Figure 5. Corresponding chromatographic characteristics are shown in Table 2.

12.3.3 A standard solution is prepared from reference materials of known purity. Standards of organochlorine pesticides may be obtained from the National Bureau of Standards and from the U.S. EPA.

12.3.4 Stock standard solutions (1.00 µg/µL) are prepared by dissolving approximately 10 milligrams of pure material in isooctane and diluting to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or an independent source.

12.3.5 The prepared stock standard solutions are transferred to Teflon-sealed screw-capped bottles and stored at -10°C for no longer than six months. The standard solutions should be inspected frequently for signs of degradation or evaporation (especially before preparing calibration standards from them).

Note: Quality control check standards used to determine accuracy of the calibration standards are available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

12.3.6 The standard solutions of the various compounds of interest are used to determine relative retention times (RRTs) to an internal standard such as p,p'-DDE, aldrin, or octachloronaphthalens (OCN).

12.3.7 Before analysis, the GC column is made sensitive to the pesticide samples by injecting a standard pesticide solution ten (10) times more concentrated than the stock standard solution. Detector linearity is then determined by injecting standard solutions of three different concentrations that bracket the required range of analyses.

12.3.8 The GC system is calibrated daily with a minimum of three injections of calibrated standards. Consult EPA Method 608, Section 7 for a detailed procedure to calibrate the gas chromatograph.

12.3.9 If refrigerated, the sample extract is removed from the cooling unit and allowed to warm to room temperature. The sample extract is injected into the GC for analysis in an aliquot of approximately 2-6 µL using the solvent flush technique (Ref. ASTM D3687, Section 8.1.4.3-8.1.4.5). The actual volume injected is recorded to the nearest 0.05 µL. After GC injection, the sample's response from the strip chart is analyzed by measuring peak heights or determining peak areas. Ideally, the peak heights should be 20 to 80% of full scale deflection. Using injections of 2 to 6 µL of each calibration standard, the peak height or area responses are tabulated against the mass injected (injections of 2, 4, and 6 µL are recommended). If the response (peak height or area) exceeds the linear range of detection, the extract is diluted and reanalyzed.

12.3.10 Pesticide mixtures are quantified by comparison of the total heights or areas of GC peaks with the corresponding peaks in the best-matching standard. If both PCBs and organochlorine pesticides are present in the same sample, column chromatographic separation on silicic acid is used before GC analysis, according to ASTM Standards, Vol. 14.01. If polar compounds that interfere with GC-ECD analysis are present, column chromatographic cleanup on alumina (activity grade IV) is used as per Section 12.2.2.

12.3.11 For confirmation, a second GC column is used such as 4% SE-30/6% OV-210 on 100/200 mesh Gas Chrom Q or 3% OV-1 on 80/100 mesh Chromosorb WHP. For improved resolution, a capillary column is used such as 0.25 mm (i.d.) x 30 m DB-5 with 0.25 µm film thickness.

12.3.12 A chromatogram of a mixture containing single component pesticides determined by GC-ECD using a capillary column is shown in Figure 6. A table of the corresponding chromatographic characteristics follows in Table 3.

12.3.13 Class separation and improved specificity can be achieved by column chromatographic separation on Florisil as per EPA Method 608. For improved specificity, a Hall electrolytic conductivity detector operated in the reductive mode may be substituted for the electron capture detector. Limits of detection will be reduced by at least an order of magnitude.

13. GC Calibration

Appropriate calibration procedures are identified in EPA Method 608, Section 7 (11).

13.1 Establish gas chromatographic operating parameters. The gas chromatographic system may be calibrated using the external standard technique (Section 13.2) or the internal standard technique (Section 13.3).

13.2 External Standard Calibration Procedure

13.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

13.2.2 Using injections of 2 to 5 µL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can 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 (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

13.2.3 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 ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

13.3 Internal Standard Calibration Procedure

13.2.1 To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

13.3.2 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a

volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the 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 detector.

13.3.3 Using injections of 2 to 5 µL of each calibration standard, tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using

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

where:
A_s = response for the parameter to be measured
A_{is} = response for the internal standard
C_{is} = concentration of the internal standard, µg/L
C_s = concentration of the parameter to be measured, µg/L

If the RF value over the working range is a constant (<10% 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.

13.3.4 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 ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

14. Calculations

14.1 The concentration of the analyte in the extract solution is taken from a standard curve where peak height or area is plotted linearly against concentration in nanograms per milliliter (ng/mL). If the detector response is known to be linear, a single point is used as a calculation constant.

14.2 From the standard curve, determine the ng of analyte standard equivalent to the peak height or area for a particular compound.

14.3 Determine if the field blank is contaminated. Blank levels should not exceed 10 ng/sample for organochlorine pesticides or 100 ng/sample for other pesticides. If the blank has been contaminated, the sampling series must be held suspect.

14.4 Quantity of the compound in the sample (A) is calculated using the following equation:

$$A = 1000 \bullet [(A_s \times V_e)/V_i]$$

where:
A = total amount of analyte in the sample, ng

A_s = calculated amount of material injected onto the chromatograph based on calibration curve for injected standards, ng
V_e = final volume of extract, mL
V_i = volume of extract injected, µL
1000 = factor for converting microliters to milliliters

14.5 The extraction efficiency (EE) is determined from the recovery of octachloronaphthalene (OCN) spike as follows:

$$EE(\%) = (S/S_a) \times 100$$

where:
S = amount of spike recovered, ng
S_a = amount of spike added to plug, ng

14.6 The total amount of nanograms found in the sample is corrected for extraction efficiency and laboratory blank as follows:

$$A_c = (A - A_o)/EE(\%)$$

where:
A_c = corrected amount of analyte in sample, ng
A_o = amount of analyte in blank, ng

14.7 The total volume of air sampled under ambient conditions is determined using the following equation:

$$V_a = [\sum_{i=1}^{n} (T_i \times F_i)]/1000$$

where:
V_a = total volume of air sampled, m^3
T_i = length of sampling segment between flow checks, min
F_i = average flow during sampling segment, L/min
1000 = factor for converting liters to cubic meters

14.8 The air volume is corrected to 25°C and 760 mm Hg (STP) as follows:

$$V_s = V_a \bullet [(P_b - P_w)/760 \text{ mm Hg}] \bullet [298/(237 + TA)]$$

where:
V_s = volume of air at standard conditions, m^3
V_a = total volume of air sampled, m^3
P_b = average ambient barometric pressure, mm Hg
P_w = vapor pressure of water at calibration temperature, mm Hg
T_A = average ambient temperature, °C

14.9 If the proper criteria for a sample have been met, concentration of the compound in a cubic meter of air is calculated as follows:

$$ng/m^3 = A_c/V_s \bullet 100/SE(\%)$$

where:
SE = sampling efficiency as determined by the procedure outlined in Section 15

If it is desired to convert the air concentration value to parts per trillion (wt/wt) in dry air at STP, the following conversion is used:

$$ppt = 0.844\ (ng/m^3)$$

The air concentration is converted to parts per trillion (v/v) in air at STP as follows:

$$pptv = 24.45\ (ng/m^3)/MW$$

where:
MW = molecular weight of the compound of interest

15. Sampling and Retention Efficiencies

15.1 Before using this procedure, the user should determine the sampling efficiency for the compound of interest. The sampling efficiencies shown in Tables 4 and 5 were determined for approximately 1 m^3 of air at about 25°C, sampled at 3.8 L/min. Sampling efficiencies for the pesticides shown in Table 6 are for 24 hours at 3.8 L/min and 25°C. Sampling efficiencies for carbonates, ureas, triazines, and pyrethrine are provided in Table 7. For compounds not listed, longer sampling times, different flow rates, or other air temperatures, the following procedure may be used to determine sampling efficiencies.

15.2 SE is determined by a modified impinger assembly attached to the sampler pump (see Figure 7). Clean PUF is placed in the pre-filter location and the inlet is attached to a nitrogen line. PUF plugs (22 mm x 7.6 cm) are placed in the primary and secondary traps and are attached to the pump.
Note: Nitrogen should be used instead of air to prevent oxidation of the compounds under test. The oxidation would not necessarily reflect what may be encountered during actual sampling and may give misleading sampling efficiencies.

15.3 A standard solution of the compound of interest is prepared in a volatile solvent (e.g., hexane, pentane, or benzene). A small, accurately measured volume (e.g., 1 mL) of the standard solution is placed into the modified midget impinger. The sampler pump is set at the rate to be used in sampling application and then activated. Nitrogen is drawn through the assembly for a period of time equal to or exceeding that intended for sampling application. After the desired sampling test period, the PUF plugs are removed and analyzed separately as per Section 12.3.

15.4 The impinger is rinsed with hexane or another suitable solvent and quantitatively transferred to a volumetric flask or concentrator tube for analysis.

15.5 The sampling efficiency (SE) is determined using the following equation:

$$\%\ SE = W_1/(W_o - W_r) \bullet 100$$

where:
W_1 = amount of compound extracted from the primary trap, ng
W_o = original amount of compound added to the impinger, ng
W_r = residue left in the impinger at the end of the test, ng

15.6 If material is found in the secondary trap, it is an indication that breakthrough has occurred. The addition of the amount found in the secondary trap, W_2, to W_1, will provide an indication of the overall sampling efficiency of a tandem-trap sampling system. The sum of W_1, W_2 (if any), and W_r must equal (approximately ± 10%) W_o or the test is invalid.

15.7 If the compound of interest is not sufficiently volatile to vaporize at room temperature, the impinger may be heated in a water bath or other suitable heater to a maximum of 50°C to aid volatilization. If the compound of interest cannot be vaporized at 50°C without thermal degradation, dynamic retention efficiency (RE_d) may be used to estimate sampling efficiency. Dynamic retention efficiency is determined in the manner described in 15.8. Table 6 lists those organochlorine pesticides for which dynamic retention efficiencies have been determined.

15.8 A pair of PUF plugs is spiked by slow, dropwise addition of the standard solution to one end of each plug. No more than 0.5 to 1 mL of solution should be used. Amounts added to each plug should be as nearly the same as possible. The plugs are allowed to dry for 2 hours in a clean, protected place (e.g., desiccator). One spiked plug is placed in the primary trap so that the spiked end is at the intake and one clean unspiked plug is placed in the secondary trap. The other spiked plug is wrapped in hexane-rinsed aluminum foil and stored in a clean place for the duration of the test (this is the static control plug, Section 15.9). Prefiltered nitrogen or ambient air is drawn through the assembly as per Section 15.3. Each PUF plug (spiked and static control) is analyzed separately as per Section 12.3.
Note: Impinger may be discarded.

15.9 Retention Efficiency (RE) is calculated as follows:

$$\% \text{ RE} = (W_1/W_0) \bullet 100$$

where:
W_1 = amount of compound recovered from primary plug, ng
W_o = amount of compound added to primary plug, ng

If a residue, W_2, is found on the secondary plug, breakthrough has occurred. The sum of $W_1 + W_2$ must equal W_o within 25% or the test is invalid. For most compounds tested by this procedure, % RE values are generally less than % SE values determined per Section 15.1. The purpose of the static RE determination is to establish any loss or gain of analyte unrelated to the flow of nitrogen or air through the PUF plug (see Table 8).

16. Method Variation

This section provides analytical procedures for a variety of pesticides other than organochlorine. Samples for the pesticides mentioned below are collected as described in Section 7.1.

16.1 Organophosphorus pesticides are responsive to flame photometric and nitrogen-phosphorus (alkali flame ionization) detection. Most of these compounds can be analyzed at concentrations of 50 to 500 ng/mL using either of these detectors. Procedures given in 12.3.2 through 12.3.9 and 12.3.11 through 12.3.3 apply, except for the selection of internal standards. Use parathion as an internal standard.

16.2 Carbamate and triazine pesticides are most commonly analyzed by HPLC because of poor thermal stability or high polarity. Detection limits will be in the 1 to 5 μg/mL range. Many carbamates and triazine pesticides may also be analyzed intact by GC on a 2 mm (i.d.) x 183 cm glass column of 3% OV-101 on Ultra-Bond and determined by HECD. Detection limits will be about 1 μg/mL.

16.3 Carbaryl®, atrazine®, propoxur®, bendiocarb® and captan® have been successfully analyzed by capillary column chromatography as discussed in Section 12.3.11.

16.4 Many urea pesticides, pyrethrins, phenols, and other polar pesticides may be analyzed by HPLC with fixed or variable wavelength UV detection. Either reversed-phase or normal phase chromatography may be used. Detection limits are 0.2 to 10 μg/mL of extract. An acceptable procedure follows: Select HPLC column (for example, Zorbax-SIL, 4.6 mm i.d. x 25 cm, or u-Bondapak C18, 3.9 mm x 30 cm, or equivalent). Select solvent system (for example, mixtures of methanol or acetonitrile with water or mixtures of heptane or hexane with isopropanol). Follow analytical procedures given in 12.3.2 through 12.3.9. If interferences are present, adjust the HPLC solvent system composition or use column chromatographic clean-up with silica gel, alumina or Florisil. An electrochemical detector may be used to improve sensitivity for some ureas, carbamates and phenolics. Much more care is required in using this detector, particularly in removing dissolved oxygen from the mobile phase and sample extracts. Chlorophenols have been successfully analyzed intact by GC on a 4 mm (i.d.) x 60 cm glass column packed with double support-bonded diethylene glycol succinate (DEGS).

16.5 Mass spectrometric analyses may be used for more unambiguous confirmation of pesticides. Essentially all pesticides may be determined by GC-MS or HPLC-MS.

16.5.1 Many of the pesticides shown in Table 1 have been successfully analyzed by GC-MS by the following procedure:

16.5.1.1 GC column carrier gas and flow rate as described in 12.3.2.

16.5.1.2 Temperature program, 40°C (2 min) to 295°C (10°C per min).

16.5.1.3 Splitless injection, 2 μL maximum volume (injection time 30 to 40 sec); injector temperature, 205°C.

16.5.1.4 Interface temperature, 240°C.

16.5.1.5 Mass spectrometer, quadrupole, electron ionization, multiple ion detection mode.

16.5.1.6 Internal standards, D_{10}-phenanthrene and D_{12}chrysene.

16.6 See ASTM Standard Practice D3687 for solvent-flush injection technique, determination of relative retention times, and other procedures pertinent to GC and HPLC analyses.

16.7 If concentrations are too low to detect by the analytical procedure of choice, the extract may be concentrated to 1 mL or 0.5 mL by carefully controlled evaporation under an inert atmosphere. The following procedure is appropriate:

16.7.1 Place K-D concentrator tube in a water bath and analytical evaporator (nitrogen blow-down) apparatus. The water bath temperature should be 25°C to 50°C.

16.7.2 Adjust nitrogen flow through hypodermic needle to provide a gentle stream.

16.7.3 Carefully lower hypodermic needle into the concentrator tube to a distance of about 1 cm above the liquid level.

16.7.4 Continue to adjust needle placement as liquid level decreases.

16.7.5 Reduce volume to slightly below desired level.

16.7.6 Adjust to final volume by carefully rinsing needle tip and concentrator tube well with solvent (usually n-hexane).

17. Performance Criteria and Quality Assurance

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

17.1 Standard Operating Procedures (SOPs)

17.1.1 Users should generate SOPs describing the following activities accomplished in their laboratory:

- assembly, calibration, and operation of the sampling system, with make and model of equipment used
- preparation, purification, storage, and handling of sampling cartridges
- assembly, calibration, and operation of the GC-ECD system, with make and model of equipment used
- all aspects of data recording and processing, including lists of computer hardware and software used

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

17.2 Process, Field, and Solvent Blanks

17.2.1 One PUF cartridge 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.

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

17.2.3 Before each sampling episode, one PUF plug from each batch of approximately twenty should be spiked with a known amount of the standard solution. The spiked plug will remain in a sealed container and will not be used during the sampling period. The spiked plug is extracted and analyzed with the other samples. This field spike acts as a quality assurance check to determine matrix spike recoveries and to indicate sample degradation.

17.2.4 During the analysis of each batch of samples, at least one solvent process blank (all steps conducted but no PUF cartridge included) should be carried through the procedure and analyzed.

17.2.5 Blank levels should not exceed 10 ng/sample for single components or 100 ng/sample for multiple component mixtures (e.g., for organochlorine pesticides).

17.3 Sampling Efficiency and Spike Recovery

17.3.1 Before using the method for sample analysis, each laboratory must determine its sampling efficiency for the component of interest as per Section 15.

17.3.2 The PUF in the sampler is replaced with a hexane-extracted PUF. The PUF is spiked with a microgram level of compounds of interest by dropwise addition of hexane solutions of the compounds. The solvent is allowed to evaporate.

17.3.3 The sampling system is activated and set at the desired sampling flow rate. The sample flow is monitored for 24 hours.

17.3.4 The PUF cartridge is then removed and analyzed as per Section 12.3.

17.3.5 A second sample, unspiked, is collected over the same time period to account for any background levels of components in the ambient air matrix.

17.3.6 In general, analytical recoveries and collection efficiencies of 75% are considered to be acceptable method performance.

17.3.7 Replicate (at least triplicate) determinations of collection efficiency should be made. Relative standard deviations for these replicate determinations of ±15% or less are considered acceptable performance.

17.3.8 Blind spiked samples should be included with sample sets periodically as a check on analytical performance.

17.4 Method Sensitivity

Several different parameters involved in both the sampling and analysis steps of this method collectively determine the sensitivity with which each compound is detected. As the volume of air sampled is increased, the sensitivity of detection increases proportionately within limits set by the retention efficiency for each specific component trapped on the polyurethane foam plug and the background interference associated with the analysis of each specific component at a given site sampled. The sensitivity of detection of samples recovered by extraction depends on the inherent response of the particular GC detector used in the determinative step and the extent to which the sample is concentrated for analysis. It is the responsibility of the analyst(s) performing the sampling and analysis steps to adjust parameters so that the required detection limits can be obtained.

17.5 Method Precision and Bias

17.5.1 Precision and bias in this type of analytical procedure are dependent upon the precision and bias of the analytical procedure for each compound of concern, and the precision and bias of the sampling process.

17.5.2 The reproducibility of this method has been determined to range from 5 to 30% (measured as the relative standard deviation) when replicate sampling cartridges are used (N>5). Sample recoveries for individual compounds generally fall within the range of 90 to 110%, but recoveries ranging from 65 to 125% are considered acceptable. PUF alone may give lower recoveries for more volatile compounds (e.g., those with saturation vapor pressures $>10^{-3}$ mm Hg). In those cases, another sorbent or a combination of PUF and Tenax GC should be employed.

17.6 Method Safety

This procedure may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the user's responsibility to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This should be part of the user's SOP manual.

18. References

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7. Johnson, D. E., Schattenberg, H. J., Brewer, J. H., Wheeler, H. G., and Hsu, J. P., "Evaluation of Sampling and Analytical Methods for Determination of Human Exposure to Selected Pesticides and PCBs by Inhalation, Ingestion and Dermal Contact," Southwest

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11. "Test Method 608, Organochlorine Pesticides and PCBs," in EPA-600/4-82-057, U. S. Environmental Protection Agency, Cincinnati, OH, July, 1982.

Table 1. Pesticides Determined by Gas Chromatography/Electron Capture Detector (GC-ECD)

Aldrin
BHC (α-and β-Hexachlorocyclohexanes)
Captan
Chlordane, technical
Chlorothalonil
Chlorpyrifos
2,4,-D esters
p,p,-DDT
p,p,-DDE
Dieldrin
Dichlorvos (DDVP)
Dicofol
2,4,5-Trichlorophenol
Folpet
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Lindane (γ-BHC)
Methoxychlor
Mexacarbate
Mirex
trans-Nonachlor
Oxychlordane
Pentachlorobenzene
Pentachlorophenol
Ronnel

Table 2. Chromatographic Characteristics of the Single Component Pesticide Mixture (5 µl) Determined by GC-ECD Using a Packed Column

Retention Time	Compound Name	Concentration in pg on Column	Area/ Height
2.77	gamma-BHC (Lindane)	500	8.2
3.37	Heptachlor	500	10.4
4.03	Aldrin	500	12.0
8.90	Dieldrin	500	24.7
14.63	p,p'-DDT	500	39.0
24.87	Dibutylchlorendate*	2500	61.4
26.82	Methoxychlor	2500	57.5

* Internal standard used for earlier pesticide detection.

Table 3. Chromatographic Characteristics of the Single Component Pesticide Mixture (2 μl) Determined by GC-ECD Using a Capillary Column

Retention Time	Compound Name	Concentration in pg on Column	Area/ Height
14.28	gamma-BHC (Lindane)	200	5.2
17.41	Heptachlor	200	5.3
18.96	Aldrin	200	5.4
23.63	Dieldrin	200	5.8
27.24	p,p'-DDT	200	5.6
29.92	Methoxychlor	1000	5.5
31.49	Dibutylchlorendate*	1000	5.4

* Internal standard used for earlier pesticide detection.

Table 4. Sampling Efficiencies for Some Organochlorine Pesticides

Compound	Quantity Introduced, µg	Air Volume, m^3	Sampling Efficiency, % mean	RSD	n
α-Hexachlorocyclohexane (α-BHC)	0.005	0.9	115	8	6
β-Hexachlorocyclohexane (Lindane)	0.05-1.0	0.9	91.5	8	5
Hexachlorobenzene**	0.5, 1.0	0.9	94.5	8	5
Chlordane, technical	0.2	0.9	84.0	11	8
p,p'-DDT	0.6, 1.2	0.9	97.5	21	12
p,p'-DDE	0.2, 0.4	0.9	102	11	12
Mirex	0.6, 1.2	0.9	85.9	22	7
Pentachlorobenzene**	1.0	0.9	94	12	5
Pentachlorophenol**	1.0	0.9	107	16	5
2,4,5-Trichlorophenol**	1.0	0.9	108	3	5
2,4-D Esters:					
isopropyl	0.5	3.6	92.0	5	12
butyl	0.5	3.6	82.0	10	11
isobutyl	0.5	3.6	79.0	20	12
isooctyl	0.5	3.6	>80*	--	--

* Not vaporized. Value based on %RE = 81.0 (RSD = 10%, n = 6).
** Semivolatile organochlorine pesticides.

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Table 5. Sampling Efficiencies for Organophosphorus Pesticides

Compound	Quantity Introduced,[b] µg	Sampling Efficiency, % mean	RSD	n
Dichlorvos (DDVP)	0.2	72.0	13	2
Ronnel	0.2	106		
Chlorpyrifos	0.2	108	9	12
Diazinon[a]	1.0	84.0	18	
Methyl parathion[a]	0.6	80.0	19	18
Ethyl parathion[a]	0.3	75.9	15	18
Malathion[a]	0.3	100[c]	--	--

[a] Analyzed by gas chromatography with nitrogen phosphorus detector or flame photometric detector.
[b] Air volume = 0.9 m^3.
[c] Decomposed in generator; value based on %RE = 101 (RDS = 7, n = 4).

Table 6. Extraction and 24-hour Sampling Efficiencies for Various Pesticides and Related Compounds

Compound	Extraction Efficiency, %*		Sampling Efficiency**, %, at:					
			10 ng/m^3		100 ng/m^3		1000 ng/m^3	
	mean	RSD	mean	RSD	mean	RSD	mean	RSD
Chlorpyrifos	83.3	11.5	83.7	18.0	92.7	15.1	83.7	18.0
Pentachloro-phenol	84.0	22.6	66.7	42.2	52.3	36.2	66.7	42.2
Chlordane	95.0	7.1	96.0	1.4	74.0	8.5	96.0	1.4
Lindane	96.0	6.9	91.7	11.6	93.0	2.6	91.7	11.6
DDVP	88.3	20.2	51.0	53.7	106.0	1.4	51.0	53.7
2,4-D methyl ester	--	--	75.3	6.8	58.0	23.6	75.3	6.8
Heptachlor	99.0	1.7	97.3	13.6	103.0	17.3	97.3	13.6
Aldrin	97.7	4.0	90.7	5.5	94.0	2.6	90.7	5.5
Dieldrin	95.0	7.0	82.7	7.6	85.0	11.5	82.7	7.6
Ronnel	80.3	19.5	74.7	12.1	60.7	15.5	74.7	12.2
Diazinon	72.0	21.8	63.7	18.9	41.3	26.6	63.7	19.9
trans-Nonachlor	97.7	4.0	96.7	4.2	101.7	15.3	96.7	4.2
Oxychlordane	100.0	0.0	95.3	9.5	94.3	1.2	95.3	9.5
α-BHC	98.0	3.5	86.7	13.7	97.0	18.2	86.7	13.7
Chlorothalonil	90.3	8.4	76.7	6.1	70.3	6.5	76.7	6.1
Heptachlor epoxide	100.0	0.0	95.3	5.5	97.7	14.2	95.3	5.5

* Mean values for one spike at 550 ng/plug and two spikes at 5500 ng/plug.
** Mean values for three determinations.

Table 7. Sampling Efficiencies for Carbamates, Ureas, Triazines, and Pyrethrins

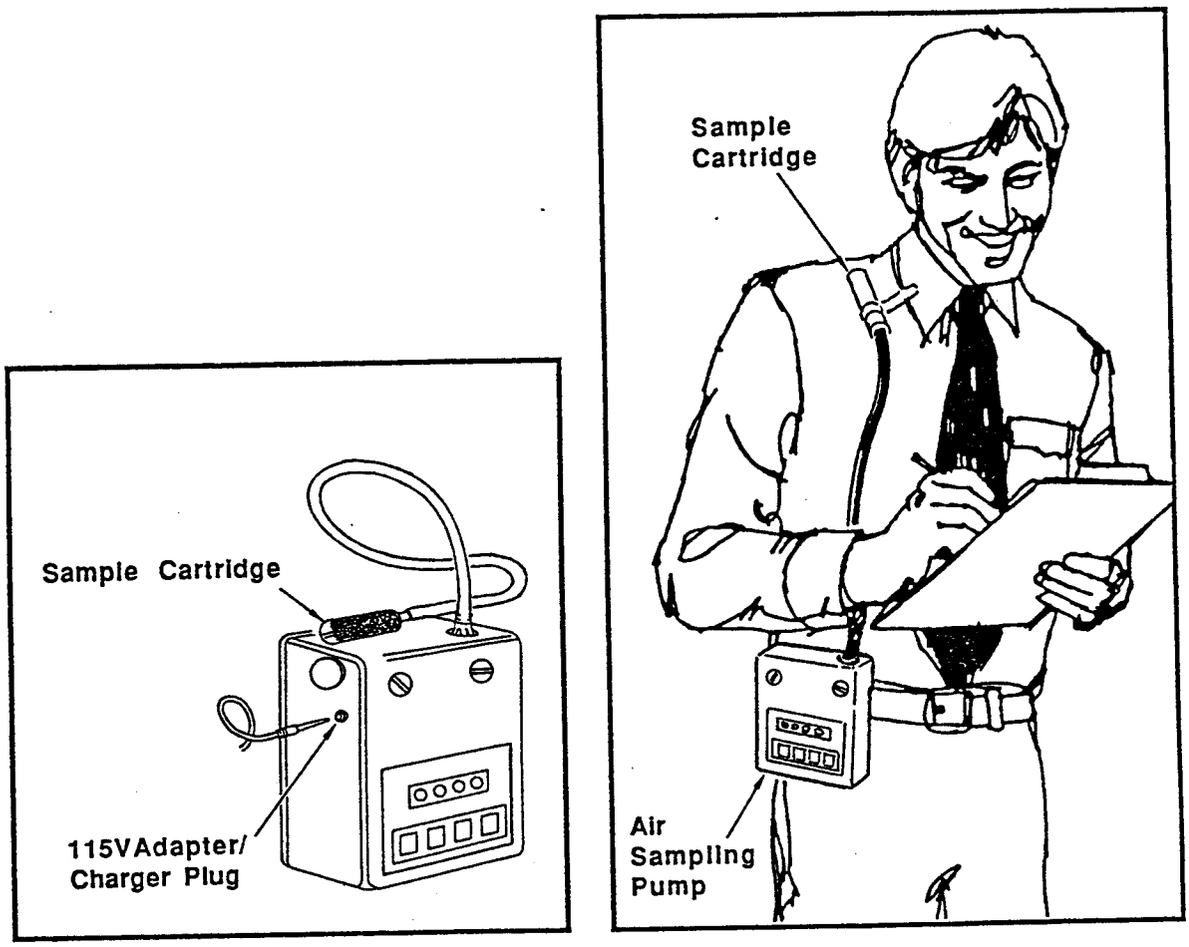
	Spike Level,[a]	Static Recovery,%			Retention Efficiency,%			Sampling Efficiency,%		
Compound	µg/plug	mean	RSD	n	mean	RSD	n	mean	RSD	n
Carbamates:										
Propoxur	5	61.4	10	6	77.6	37	6	96.7	11	6
Carbofuran	15	55.3	12	6	64.2	46	6	87.2	14	6
Bendicarb	50	57.3	11	6	69.8	43	6	62.1	14	6
Mexacarbate	10	62.8	19	6	62.7	41	6	89.8	14	6
Carbaryl	100	56.6	14	6	63.6	53	6	b	13	6
Ureas:										
Monuron	19	87.0		6	91.2	6	5	c		
Diuron	20	84.1	8	6	90.0	2	5	c		
Linuron	20	86.7	8	6	92.5	4	5	c		
Terbuthiuron	18	85.0	8	6	88.8	8	5	c		
Fluometuron	20	91.4	10	6	101	3	5	c		
Chlortoluron	20	86.2	11	6	92.0	7	5	c		
Triazines:										
Simazine	10	103	6	5	101	9	6	c		
Atrazine	10	104	7	5	98.9	7	6	c		
Propazine	10	105	11	5	99.9	14	6	c		
Pyrethrins:										
PyrethrinI	(9.7)[d]	90.5	10	6	95.6	22	5	c		
PyrethrinII	(6.1)[d]	88.6	11	6	69.9	29	5	c		
Allethrin	25	69.2	9	5	58.3	12	6	c		
d-trans-Allethrin	25	76.8	9	6	74.4	9	5	c		
Dicrotophos	25	72.0	22	6	71.7	8	5	c		
Resmethrin	25	76.5	14	6	66.7	14	6	c		
Fenvalerate	25	87.9	3	6	57.2	20	3	c		

[a]Air volume = 0.9 m^3.
[b]Decomposed in generator.
[c]Not vaporized.
[d]Estimated on the basis of 20 µg Pyrethrin with a composition of 48.4% and 30.3% by weight of Pyrethrins I and II, respectively.

Table 8. Extraction and 24-Hour Sampling Efficiencies for Various Pesticides and Related Compounds

Compound	Extraction Efficiency*, %		Retention Efficiency**, %, at:					
			10 ng/m^3		100 ng/m^3		1000 ng/m^3	
	mean	RSD	mean	RSD	mean	RSD	mean	RSD
Dicofol	57.0	8.5	38.0	25.9	65.0	8.7	69.0	--
Captan	73.0	12.7	56.0	--	45.5	64.3	84.3	16.3
Methoxlychlor	65.5	4.9	--	--	--	--	78.5	2.1
Folpet	86.7	11.7	--	--	78.0	--	93.0	--

* Mean values for one spike at 550 ng/plug and two spikes at 5500 ng/plug.
** Mean values for generally three determinations.



(a) Fixed Site Monitoring (b) Personal Monitoring

Figure 1. Sampling for Pesticides

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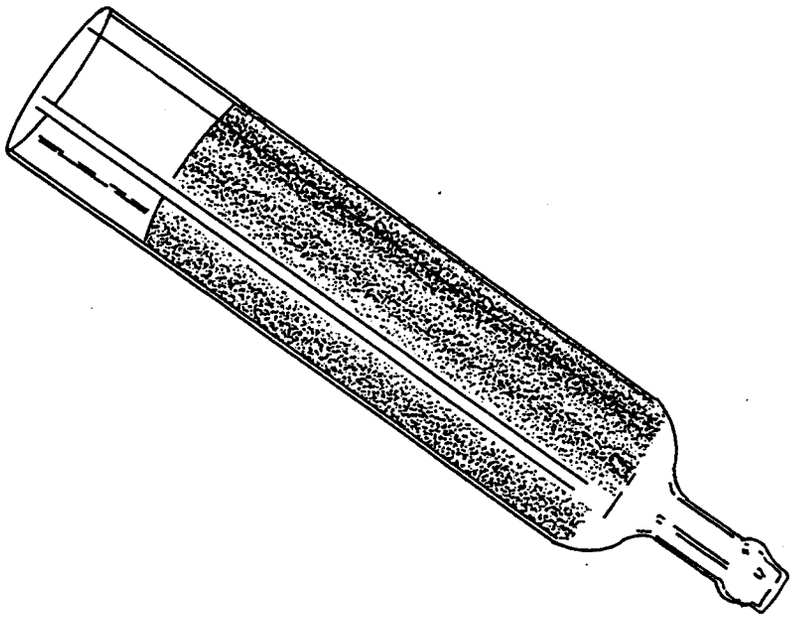

Figure 2. Polyurethane Foam (PUF) Sampling Cartridge

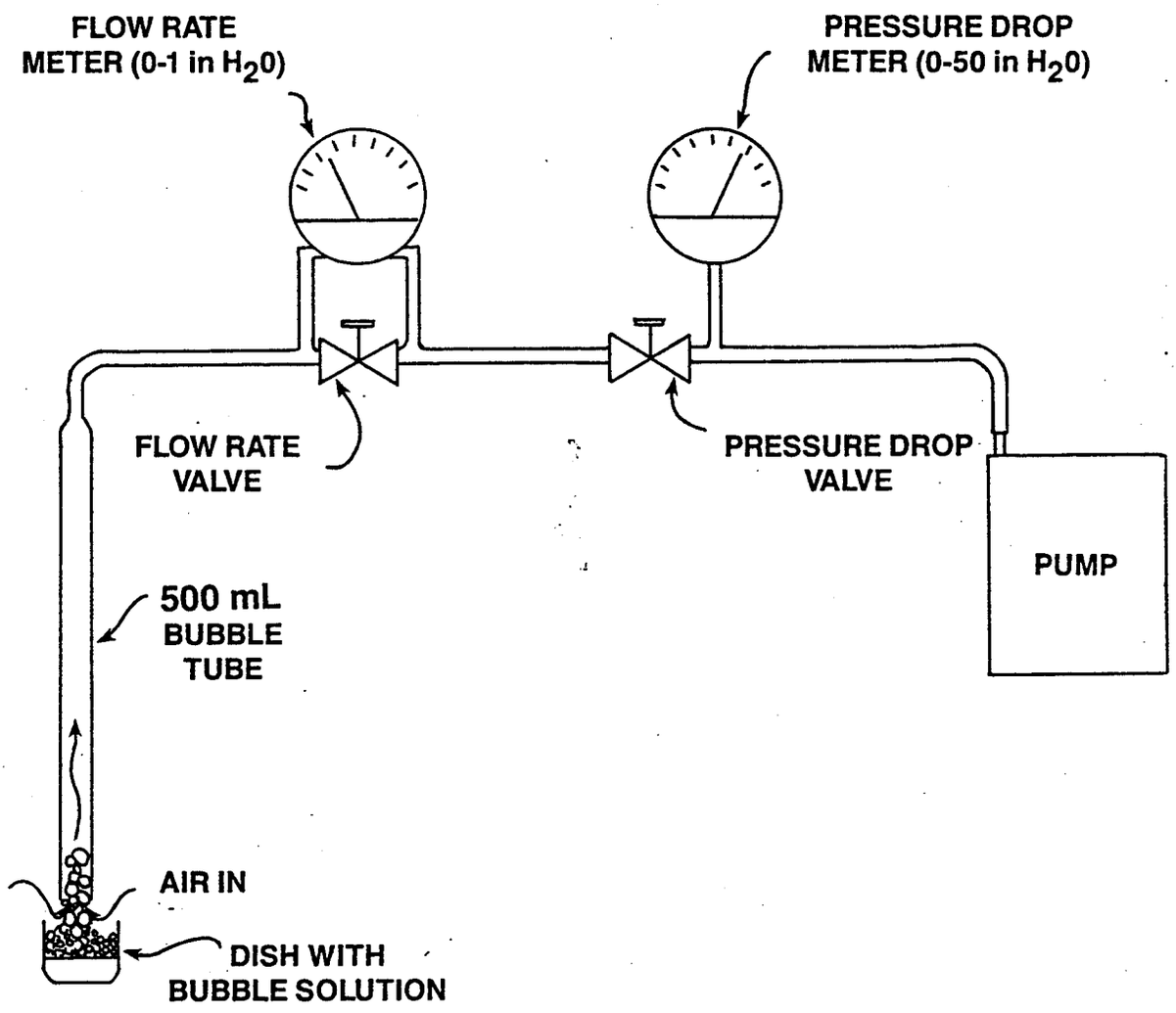

Figure 3. Calibration Assembly for Air Sampler Pump

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Site Date Performed by

Sampler S/N	Sampling Location I.D	Height Above Ground	PUF Cart. No.	Sampling Period Start	Sampling Period Stop	Sampling Time min.	Pump Timer hr. min.	Low flow Indication Yes	Low flow Indication No	Comments

Checked by_____

Date_____

Figure 4. Low Volume Pesticide Sampling Data Form

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OPERATING CONDITIONS

Column Type:	1.5% SP 2250/1.95% SP 2401, ¼" glass.
Temperature:	200°C isothermal.
Detector:	Electron Capture.
Carrier Gas:	5% Methane/95% Argon.
Flow Rate:	65 to 85 mL/min.

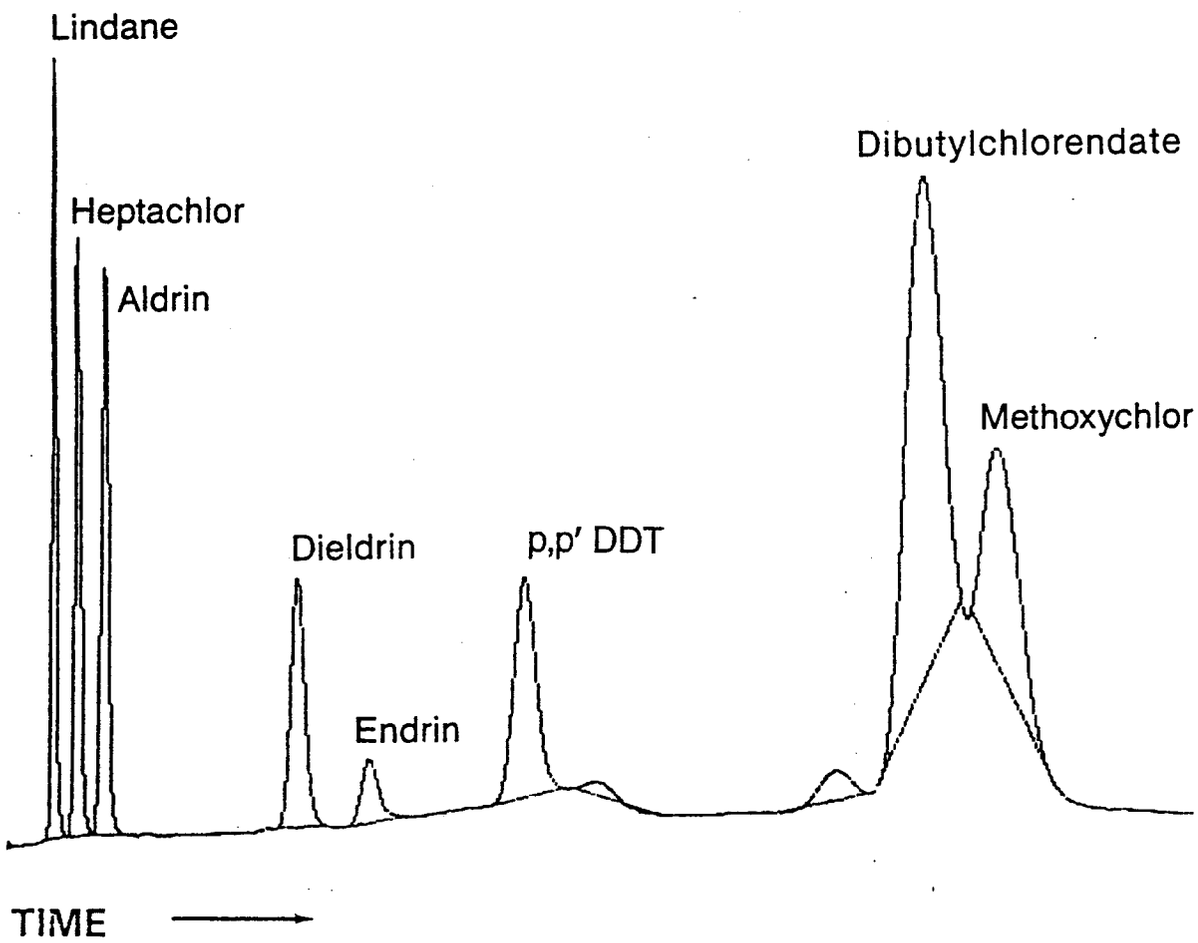

Figure 5. Chromatograph Showing a Mixture of Single Component Pesticides Determined by GC/ECD Using a Packed Column

OPERATING CONDITIONS

Column Type:	DB-5 0.32 capillary, 0.25 um film thickness
Column Temperature Program:	90°C (4 min)/16°C per min to 154°C/4°C per min to 270°C.
Detector:	Electron Capture
Carrier Gas:	Helium at 1 mL/min.
Make Up Gas:	5% Methane/95% Argon at 60 mL/min.

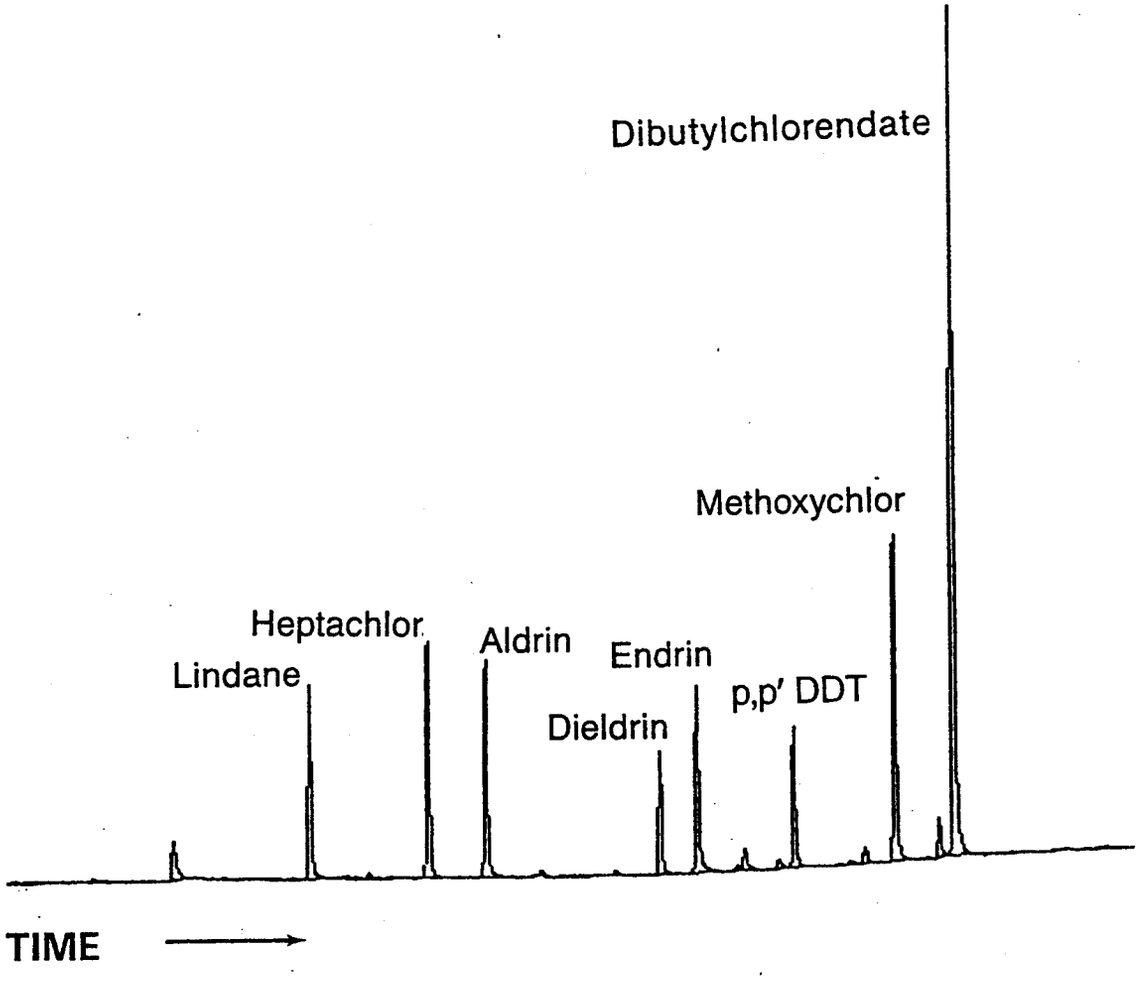

Figure 6. Chromatograph Showing a Mixture of Single Component Pesticides Determined by GC/ECD Using a Capillary Column

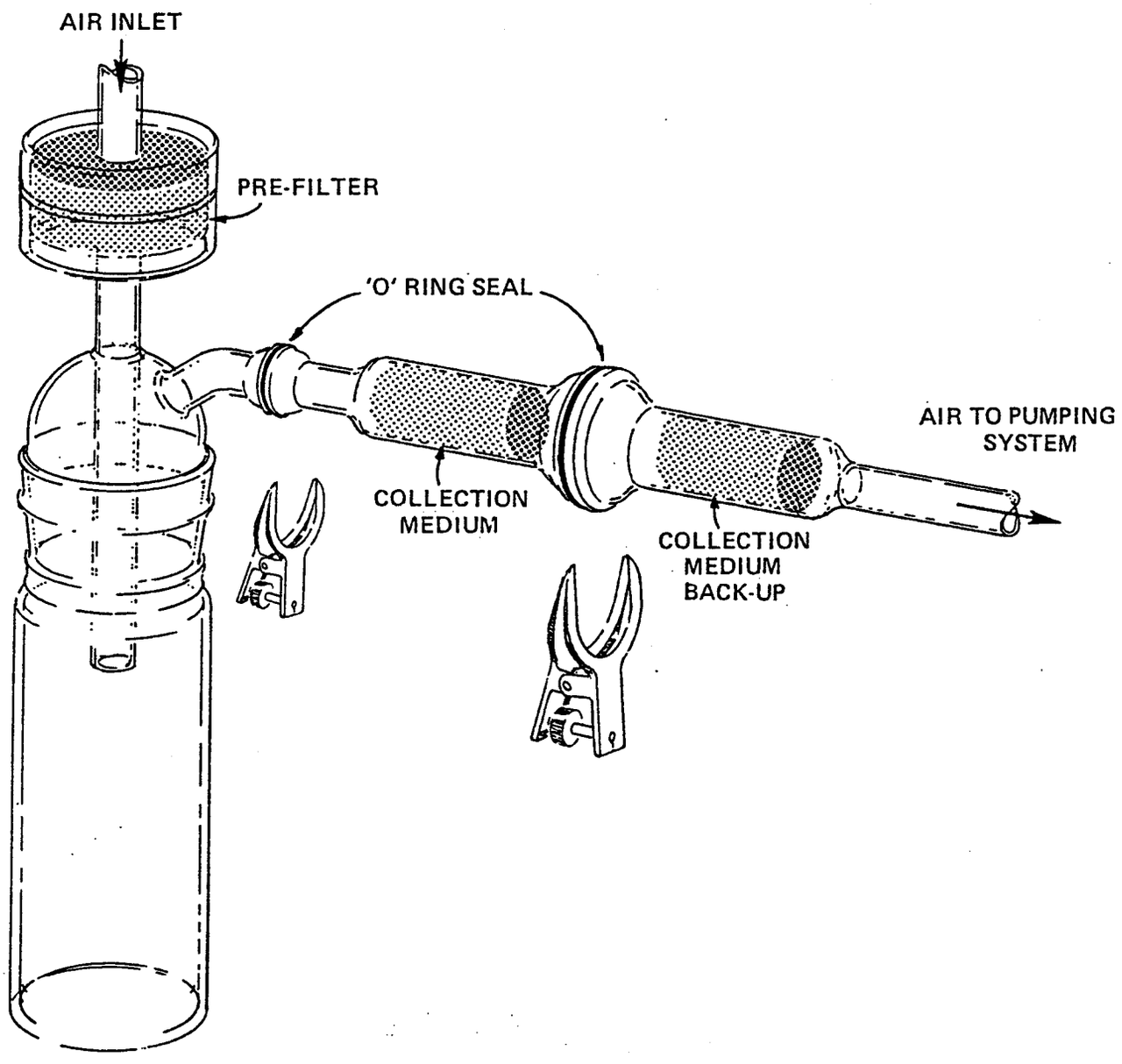

Figure 7. Apparatus for Determining Sampling Efficiencies

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Chapter IP-9

DETERMINATION OF REACTIVE ACIDIC AND BASIC GASES AND PARTICULATE MATTER IN INDOOR AIR (ANNULAR DENUDER TECHNIQUE)

1. Scope

This document describes a sampling and analytical protocol for the annular denuder system (ADS). This system was developed to measure reactive acidic and basic gases and particulate matter which are contained in indoor ambient air. The chemical species which can be measured by the ADS are gaseous SO_2, HNO_2, HNO_3 and NH_3 and particulate $SO_4^=$, NO_3^-, NH_4^+ and H^+. Other similar chemical species can be successfully collected by the system with just a few simple modifications (i.e., changing the denuder coating solutions, the denuder sequence and the liner or filter types and sequence). Once collected, the pollutant concentrations are quantified by ion chromatography (IC) analysis and/or Technicon colorimeter autoanalysis. The IC protocols for sample preparation, analysis and quantification are detailed within the ADS method. The Technicon autoanalyzer protocols are utilized to quantify ammonia (NH_3), nitrate (NO_3^-), and sulfate ($SO_4^=$) in ambient air samples.

2. Applicability

2.1 Recently, these and other acid gases and aerosols, and particulate matter have been of growing concern to indoor air quality groups. Much emphasis has been directed to understanding the many chemical forms in which these pollutants can exist and the conditions which cause chemical changes to occur. Industrial and commercial facilities, as well as hazardous waste storage and treatment facilities, contribute significantly to indoor air contamination through various source-specific emissions. Although several of the previously mentioned pollutants can be instrumentally measured to quantify their concentration in the ambient air, many of the established methods are not adequate (or sensitive enough) to measure these pollutants at the levels typically found in non-urban locations. As a result, monitoring and research efforts have been designed to assess what sources are responsible for targeted pollutant emissions, what health and ecological impacts are incurred, and what the maximum allowable ambient concentrations should be.

2.2 The ADS has been utilized in such research efforts. The system's configuration has made it a very appealing asset to monitoring crews. Its ability to collect the chemical species of interest with little or no interference from sampling artifacts has separated it from other air monitoring techniques. Each sampling network can assemble the treated denuders and filters in such a manner that specific pollutants, which can cause ambient concentrations to be falsely assessed, are withdrawn from the air stream before interfering chemical reactions can occur. Subsequently, it is very important to investigate all possible chemical reactions between the species of interest before setting up the ADS.

2.3 As with all monitoring methods, the ADS has its limitations. Operation below 20% relative humidity may result in less than quantitative collection of SO_2. Also, the annular denuders are fragile and require great care when handled. Studies are being conducted to

determine how well Teflon® coated aluminum denuders collect acid aerosols. Other studies include identifying interferents which can cause under- or over-estimations of pollutant concentrations to be made and accounting for interferant reactions in the calculations.

Method IP-9

DETERMINATION OF REACTIVE ACIDIC AND BASIC GASES AND PARTICULATE MATTER IN INDOOR AIR (ANNULAR DENUDER TECHNIQUE)

Method IP-9

DETERMINATION OF REACTIVE ACIDIC AND BASIC GASES AND PARTICULATE MATTER IN INDOOR AIR (ANNULAR DENUDER TECHNIQUE)

1. Scope

1.1 This document describes the protocol for the quantitative measurement of reactive acidic and basic gases and particulate matter which are contained in indoor atmospheres.

1.2 The chemical species which can be determined by this method are gaseous SO_2, HNO_2, HNO_3, and NH_3 and particulate $SO_4^=$, NO_3^-, NH_4^+, and H^+, as well as the mass of fine particulate matter ($d_{50} < 2.5\ \mu m$). Detection and quantitation limits are given in Table 1.

1.3 The methodology detailed in this document is a composite of methodologies developed by U.S. Environmental Protection Agency (USEPA), Harvard University and the CNR Laboratories. It is currently employed in a number of air pollution studies in Italy, U.S.A., Canada, Mexico, Germany, Austria, and Spain, and in such institutions as public health services, epidemiology and environmental research centers.

1.4 The equipment described herein is utilized to measure acidic and basic gases and particulate matter contained in both indoor and outdoor atmospheres. The outdoor method was originally developed for monitoring regional-scale acidic and basic gases and particulate matter in support of U.S. EPA field programs involving the Integrated Air Cancer Research Program and the Acid Deposition Network. Similarly, the methodology has been used to characterize the urban haze in Denver, Houston and Los Angeles.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis

2.2 Other Documents

Ambient Air Studies (1-9)
U.S. EPA Technical Assistance Document (10)

3. Summary of Method

3.1 Indoor air is drawn through an elutriator-accelerator jet assembly, an impactor frit and coupler assembly, and past glass denuder walls which have been etched and coated with chemicals that absorb the gaseous species of interest. The remaining air stream is then filtered through Teflon® and Nylasorb® membrane filters. Teflon® and nylon membrane filters are used to capture ammonium and nitrate aerosol and sulfate particulate matter. Nitric acid and sulfur dioxide will also be collected by the nylon filter but these measurements are treated as interference. Figure 1 illustrates the annular denuder system (ADS) assembled ready for testing. Figure 2 shows the field sampling box with the ADS and pump-timer (11).

3.2 After sampling, the annular denuders are extracted with 5 mL of deionized water. The extracted solutions are subsequently analyzed for ions corresponding to the collected gaseous species (see Figure 1). The filters are placed into filter bottles where five or ten mL of the IC eluent are pipetted into each filter bottle with the filters face downward and completely covered by the eluent. The filter bottle is capped and put in an ultrasonic bath for 30 minutes. The bottles are stored in a clean refrigerator at 5°C until analysis.

3.3 The analysis of anion and cation concentrations collected by the denuders and filter pack is typically performed by ion chromatographic and Technicon® colorimeter autoanalytic procedures. The H^+ concentration of extracts from the Teflon® filter downstream of the denuders is performed by use of pH measurements using commercially available pH meters calibrated with standards (11).

4. Significance

4.1 Reactive acidic (SO_2, HNO_2 and HNO_3) and basic (NH_3) gases and particles are found in the atmosphere as a result of emission from a variety of fossil fuel combustion sources including industrial and commercial facilities, hazardous waste storage and treatment facilities, etc. Measurements of these chemical species are currently being used in a broad range of environmental studies such as in 1) epidemiological programs to assess the impact of acid aerosols on respiratory impairment, 2) receptor modeling to determine the origin of particles that impact EPA's PM-10 air particulate standard, 3) assessment of the impact of particulate nitrate and sulfate on visibility, and 4) the quantification of the impact of acidic and basic air pollutants on issues related to acid rain.

4.2 The unique features of the annular denuder which separates it from other established monitoring methods are elimination of sampling artifacts due to interaction between the collected gases and particles, and the preservation of the samples for subsequent analysis which is accomplished by removing NH_3 in the gas stream by the citric acid coated denuder and reducing the probability of the particulate sulfate ($SO_4^=$) captured by the filter pack being neutralized to ammonium sulfate [$(NH_4)_2SO_4$]. If NH_3 is not extracted from the gas stream prior to filtration, correction of particulate sulfate and gaseous sulfur dioxide would be required for accurate measurements to be obtained.

5. Definitions

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

5.1 Particulate mass - a generic classification in which no distinction is made on the basis of origin, physical state, and range of particle size. (The term "particulate" is an adjective, but it is commonly used incorrectly as a noun.)

5.2 Primary particles (or primary aerosols) - dispersion aerosols formed from particles that are emitted directly into the air and that do not change form in the atmosphere. Examples include windblown dust and ocean salt spray.

5.3 Secondary particles (or secondary aerosols) - dispersion aerosols that form in the atmosphere as a result of chemical reactions, often involving gases. A typical example is sulfate ions produced by photochemical oxidation of SO_2.

5.4 Particle - any object having definite physical boundaries in all directions, without any limit with respect to size. In practice, the particle size range of interest is used to define "particle." In atmospheric sciences, "particle" usually means a solid or liquid subdivision of matter that has dimensions greater than molecular radii (~10 nm); there is also not a firm upper limit, but in practice it rarely exceeds 1 mm.

5.5 Aerosol - a disperse system with a gas-phase medium and a solid or liquid disperse phase. Often, however, individual workers modify the definition of "aerosol" by arbitrarily requiring limits on individual particle motion or surface-to-volume ratio. Aerosols are formed by 1) the suspension of particles due to grinding or atomization, or 2) condensation of supersaturated vapors.

5.6 Coarse and fine particles - these two fractions are usually defined in terms of the separation diameter of a sampler. Coarse particles are those with diameters greater than 2.5 μm but less than 10 μm and that are collected by the sampler; the fine particles are those with diameters less than 2.5 μm and that are collected by the sampler.
Note: Separation diameters other than 2.5 μm have been used.

5.7 Annular - of, rotating to, or forming a ring. In the annular denuder sampler, the annular refers to the cylinder to which coating is applied to the interior parallel planes to remove gaseous pollutants by diffusion chemistry.

5.8 Denuder - the denuder refers to the process gaseous pollutants from the gas stream.

6. Interferences

6.1 Operation below 20% relative humidity (RH) may result in less than quantitative collection of SO_2. Atmospheric water vapor in concentrations above 30% RH has been shown not to be an interferant for SO_2 collection.

6.2 Studies are being conducted to identify interferents and calculations are being developed to correct the measurements obtained by the annular denuder system for identifiable interferents. For example, the presence of ozone (O_3) is known to oxidize nitrous acid (HNO_2) to nitric acid (HNO_3); therefore, measurements of HNO_2 are often underestimates. Calculations have been developed to adjust for this oxidation process and provide more accurate estimations of HNO_2 concentrations in the atmosphere.

6.3 Other studies include the possible chemical reactions (organic and inorganic) which may occur with selected coating solutions which interfere with the accurate measurement of the chemical species of interest.

6.4 The efficiency of impactor collection decreases when the impactor surface is loaded. The average operational time before such loading occurs has not been determined.

7. Apparatus

Note: The following descriptions relate to Figure 2. Most of these parts are available commercially by University Research Glassware. However, it is important to note that these items can be made by any qualified vendor; therefore, it is not necessary that these specific items are obtained and utilized.

7.1 Sampling

7.1.1 Elutriator and acceleration jet assembly - Under normal sampling conditions, the elutriator or entry tube is made of either Teflon® coated glass or aluminum. When using glass, the accelerator jet assembly is fixed onto the elutriator and the internal surfaces of the entire assembly are coated with Teflon®. When aluminum is used, the accelerator jet assembly is removable. The jet is made of Teflon® or polyethylene and the jet support is made of aluminum. Again, all internal surfaces are coated with Teflon®. Both assemblies are available with 2, 3 and 4 mm inside diameter jets (nozzles) [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.2 Teflon® impactor support pin and impactor frit support tools - Made of either Teflon® or polyethylene and are used to aid in assembling, removing, coating and cleaning the impactor frit [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.3 Impactor frit and coupler assembly - The impactor frit is 10 mm x 3 mm and is available with a porosity range of 10-20 μm. The frits should be made of porous ceramic material or fritted stainless steel. Before use the impactor frit surface is coated with a Dow Corning 660 oil and toluene solution for use, and sits in a Teflon® seat support fixed within the coupler. The coupler is made of thermoplastic and has Teflon® clad sealing "0"-rings which are located on both sides of the seat support inside the coupler. The couplers are composed of two free moving female threads which house the support tools when assembling and removing the impactor frit, and couple the denuders when sampling. There are arrows printed on the metal band which holds the female threads together. These arrows should be pointing in the direction of air flow (see Figure 1) when the ADS is assembled.

Note: In situations when there are substantial high concentrations of coarse particles (>2.5 μm), it is recommended that a Teflon®-coated aluminum cyclone be used in place of the acceleration jet and impactor assembly, as illustrated in Figure 3. The cyclone is made of Teflon®-coated stainless steel. Figure 4 illustrates the location of the cyclone with respect to the denuder, heated enclosure and meter box assembly ready for sampling [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.4 Annular denuder - The denuder consists of two concentric glass tubes. The tubes create a 1 mm orifice which allows the air sample to pass through. The inner tube is inset 25 mm from one end of the outer tube; this end is called the flow straightener end. The other end of the inner tube is flush with the end of the outer tube. Both ends of the inner tube are sealed. In this configuration, the glass surfaces facing the orifice are etched to provide greater surface area for the coating. There are three types of denuders available. One is the older version which accommodates the impactor support pin assembly, and can

only be the first denuder in sequence. It is available in glass with the impactor support holder made of glass and the impactor support pin assembly made of Teflon®. The denuder is 265 mm long with size #30 threads for coupling. It is available with flow straighteners at both ends; however, most denuders in use today only have one flow straightener end. The second most recent denuder version, which can be used as any denuder in sequence, is available in glass with only one flow straightener end. It is 242 mm long and has size #30 threads. Finally, the third denuder design involves two inner concentric glass tubes (1 mm separation) positioned around a solid center glass rod as illustrated in Figure 5. Once again, the glass surfaces are etched to provide greater surface area for the coating. The inner glass tubes and coater rod are inset 25 mm from one end of the outer Teflon®-coated stainless steel tube to serve as the flow straightener end. All denuder types should be equipped with thermoplastic or polyethylene caps when purchased [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.5 Caps for annular denuder - Caps are made of either polyethylene or thermoplastic and are used in the coating and drying processes, for storage and for shipment. The thermo-plastic caps include a removable Teflon® seal plate when purchased. Repeated reuse of these types of caps have caused some contamination due to the improper cleaning of the cap and Teflon® seal plate, i.e., fluid tends to be trapped under the seal plate. The polyethylene caps are not equipped with seal plates. Observation has concluded that polyethylene caps tend to dry faster and seal better than the thermoplastic caps. Less sample contamination has been reported, also [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.6 Annular denuder couplers - The couplers should be made of thermoplastic and equipped with Teflon® "O"-rings which sandwich a silicone rubber ring on three sides. This provides elasticity for better sealing under extremely cold temperature conditions in which Teflon® does not give. There are two types of couplers available. In the older version, the couplers have removable seal rings. Problems with denuder breakage and leakage due to improper threading of the couplers with the denuders led to the development of a second type of coupler. The new couplers are equipped with permanent seal rings which provide more even threading and a better seal when coupled. Some couplers have built-in flow-straighteners. The couplers are used to couple the annular denuders together and for coupling the last denuder with the filter pack [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.7 Drying manifold assembly - The manifold is made of pyrex and is available to accommodate as many as 4 drying denuders. The denuders are attached to the manifold with back-to-back Bakalite bored caps. The bored caps are connected with a Teflon® connector ring. Air is pushed through an air dryer/ cleaner bottle made of 2 1/2 inch heavy wall pyrex which contains silica gel, calcium sulfate and activated charcoal (not available with assembly). The tubing which connects the dryer/cleaner bottle to the drying manifold should be secured at each cap with either Teflon® washers or Teflon® washers coupled with Teflon® hose barbs [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.8 Filter pack assembly - The filters are supported by stainless steel porous screens and are housed in a polyethylene filter ring housing. The Teflon® filter ring housing directly follows the Teflon® filter housing inlet component. The "nylon" filter ring housing follows the Teflon® filter ring housing and sits on a Teflon® "O"-ring which seals the filter ring housing components to the filter housing outlet component. (There can be up to 4-filters in series depending on the species of interest.) The filter housing outlet component is aluminum and accommodates a polyethylene screw sleeve which seals the filter pack assembly. The sleeve is available in different lengths to accommodate up to 4 filter ring housing units. A stainless steel "Quick-Release" plug screws into the aluminum outlet component for connecting the pump-timer to the filter pack assembly. It is equipped with an orange "dust cover" (male plug) upon purchase [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.9 Vacuum tubing - Low density polyethylene tubing, 3/8 inch diameter for distances of less than 50 ft., 1/2 inch diameter for distances greater than 50 ft. Since this tubing is used downstream from the sampler, similar sized tubing or pipe of any material may be substituted. The tubing must have sufficient strength to avoid collapsing under vacuum [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA, 15219, (412-787-6322)].

7.1.10 Tube fitting - Compression fittings (Swagelok®, Gyrolok® or equivalent) to connect vacuum tubing (above) to an NPT female connector or filter holder and connect vacuum tubing to fitting on differential flow controller. The fittings may be constructed of any material since they are downstream of the sampler [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA, 15219, (412-787-6322)].

7.1.11 Annular denuder system (ADS) sampling box - The housing box is made of a "high-impact" plastic and is insulated with polyurethane. It is 4 feet long by 6 inches wide and 6 inches deep. There are two heater units, a fan blower and an air outlet located in the lid of the housing. Also, located on the lid are the automatic and manual control switches and a 12-V power supply outlet for the heater and fan. The bottom of the box houses the ADS. The elutriator end of the ADS protrudes through one end of the box, while the denuders are supported in the box by chrome plated spring clips. If the Teflon®-coated aluminum cyclone is used to remove coarse particles, it is also housed in the heated sampling box, with the elutriator end protruding through the sampling box, as illustrated in Figure 4. There is a vacuum plug known as a "quick-release" coupler that is linked to the filter pack of the ADS. This connects the ADS to 1 1/4 in. Teflon® rubber "clad" shrink tubing which exhausts the air stream to the ambient air. The box is sledge hammer proof [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.12 Annular denuder field-to-lab case - The field-to-lab case is made of rigid plastic and insulated with polyurethane. It is made to be hand carried, not shipped, and is used to transport 4 total annular denuder systems each consisting of either 3 annular denuder sections or 2 annular denuder sections and 1 denuder-impactor assembly. The systems are packed already assembled and capped, and either ready for sampling or ready for sample analysis. The case has a carrying handle, a lock and 3 latches and is equipped with 2 keys

[University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.13 Annular denuder shipping case - The shipping case is made of formica, backed with plywood and insulated with polyurethane. The corners are reinforced with metal. It is made to withstand shipping by truck, UPS and Federal Express. Each case is stackable and lockable and has a carrying handle. Seven total annular denuder systems can be packed in the case, provided each system contains 4 denuders each. The systems can consist of either 3 denuders (242 mm long) and 1 denuder-impactor assembly (265 mm long) or 4 denuders (242 mm long). Each component of the system is packed in its own storage compartment. The personal sampler assemblies can also be placed and shipped in this case [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.14 Differential flow controller (pump) - This unit pumps air through the sampler at a fixed rate of between 5 and 20 standard L/min (typically 10 L/min) with a precision of ±5% over the range of 25 to 250 mm Hg vacuum [University Research Glassware, 118 E. Main St., Carrboro, NC, 27510, (919-942-2753)].

7.1.15 Dry gas meter (DGM) - The DGM should pull 10 L of gas per revolution [Nutech, Corp., 2806 Cheek Rd., Durham, NC, 27704, (919-682-0402)].

7.2 Analysis

7.2.1 Ion chromatograph - A chromatograph equipped with the appropriate anion and cation exchange resin filled separator and suppressor columns and conductivity detector for measuring acidic (SO_2, HNO_2 and HNO_3) and basic (NH_3) ions in solution (i.e. denuder and filter extracts) [Dionex Corp., 1228 Titan Way, Sunnyvale, CA, 94086, (408-737-0700)].

7.2.2 Technicon colorimeter autoanalyzer - Colorimetic analyzer able to detect specific ions of interest in aqueous extracts [Technicon Industrial Systems Corp., 511 Benedict Ave., Tarrytown, NY, 10591-5097, (800-431-1970)].

7.2.3 pH meter - A pH or pH/ion meter with an "integral" automatic temperature compensation and calibrated with (EPA, N.S.T.) standard buffers (pH 4 and 7). Including 2 and 4 mL analysis cups (Orion and other vendors).

7.2.4 Polyethylene bottles with polyethylene screw caps - 50 mL and 100 mL, used for storage of coating solutions, best source.

7.2.5 Erlenmeyer flasks - 250 mL and 2 L borosilicate glass or polyethylene flasks with calibration, best source.

7.2.6 Graduated cylinders - 10 mL and 100 mL borosilicate glass or polyethylene cylinders, best source.

7.2.7 Pipets - Class A 5 mL and 10 mL borosilicate glass pipettes or automatic pipettes. Calibrated "to deliver," best source.

7.2.8 Pipet bulb - Made of natural rubber. Recommended to meet OSHA requirements, best source.

7.2.9 Micropipettes - Recommended 50 µL, calibrated "to contain," borosilicate glass micropipette, best source.

7.2.10 Forceps - Recommended dressing forceps made of stainless steel or chrome-plated steel and without serrations. Used for handling filters (Millipore).

7.2.11 Stopwatch - Used for measuring flow rate of gas stream through DGM, best source.

7.2.12 Ultrasonic cleaner - Used for filter extractions and parts cleaning. Most are temperature controlled. It is recommended to control the temperature during extraction at 65°C [Cole-Palmer Instrument Co., 7425 N. Oak Park Ave., Chicago, IL, 60648, (800-323-4340)].

7.2.13 Clean air hood - Closed air hood with ammonia free air circulation. Used for Teflon® filter extraction for pH analysis, best source.

8. Reagents and Materials

8.1 Teflon® filters - Zefluor® (PTFE) membrane filters 47 mm diameter with a 2 μm pore size. Only one side is Teflon® coated; this side should face the air stream [Gelman Sciences, 600 S. Wagner Rd., Ann Arbor, MI, 48106, (800-521-1520)].

8.2 Nylasorb® filters - Membrane filters 47 mm diameter with a 1 μm pore size. These filters are specially prepared and batch analyzed for low $SO_4^=$, NO_2^-, and NO_3^- background levels. If other brands of nylon membrane filters are used, they should be batch analyzed to ensure low and replicable levels of $SO_4^=$, NO_2^-, and NO_3^- [Gelman Sciences, 600 S. Wagner Rd., Ann Arbor, MI, 48106, (800-521-1520)].

8.3 Denuder extract storage vials - 30 mL (1 oz) screw-cap polyethylene sampling vials (Nalgene or equivalent). Allow eight (8) per sample for each sampling period, best source.

8.4 Filter extract storage vials - 100 mL polyethylene vials (Nalgene or equivalent). Allow two (2) vials for each sampling period, best source.

8.5 IC analysis vials and caps - The vials are available in 5 mL and 0.5 mL and are made of polypropylene. The filter caps are made of plastic and contain a Teflon® filter through which the sample is extracted for analysis. Both the vials and filter caps should be disposable, best source.

8.6 Labels - Adhesive, for sample vials, best source.

8.7 Parafilm - Used for covering flasks and pH cups during pH analysis, best source.

8.8 Kimwipes® and Kay-dry towels - Used for cleaning sampling apparatus and analysis equipment, best source.

8.9 Stoppers - Cork or polyethylene, best source.

8.10 Sodium carbonate (Na_2CO_3) - ACS reagent grade, best source.

8.11 Sodium chloride (NaCl) - ACS reagent grade, best source.

8.12 Methanol (methyl alcohol - CH_3OH) - ACS reagent grade, best source.

8.13 Toluene - ACS reagent grade, best source.

8.14 Glycerol (glycerin - $CH_2OHCHOHCH_2OH$) - ACS reagent grade, best source.

8.15 Citric acid (monohydrate - $HOC(CH_2CO)OH)_2COOH : H_2O$) - ACS reagent grade, best source.

8.16 Hydrogen peroxide (H_2O_2) - ACS reagent grade, best source.

8.17 Ethanol (C_2H_5OH) - ACS reagent grade, best source.

8.18 Sulfuric acid (H_2SO_4) - ACS reagent grade, best source.

8.19 Potassium chloride (KCl) - ACS reagent grade, best source.

8.20 Perchloric acid ($HClO_4$) - ACS reagent grade (60-62°C.), best source.

8.21 Distilled deionized water (DDW) - ASTM Type I water.

8.22 pH buffers - Standard buffers 4.00 and 7.00 for internal calibration of pH meter, best source.

8.23 Silica gel - ACS reagent grade (indicating type), best source.

8.24 Sodium bromide (NaBr) - ACS reagent grade, best source.

8.25 Activated charcoal - ACS reagent grade, best source.

8.26 Balance - Electronic analytical with internal calibration weights and enclosed weighing chamber. Precision of 0.1 mg [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA, 15219, (412-787-6322)].

8.27 Gloves - Polyethylene disposable. Used for impactor frit assembly and filter pack assembly, best source.

8.28 Dow Corning high temperature vacuum oil - Dow Corning 660 oil used for impactor frit coating solution, best source.

8.29 Zero air - A supply of compressed clean air, free from particles, oil, NO, NO_2, SO_2, HNO_3, and HONO. The supply may be either from a commercial cylinder or generated on site, best source.

8.30 IC eluent solution - For extracting filters. This should be the same eluent as used for the ion chromatographic analysis of the filters. If the filter analysis is not to be performed by ion chromatography, then a slightly basic solution (e.g., 0.003 N NaOH or sodium carbonate/bicarbonate) should be used to extract the Nylasorb® filter, while the Teflon® filter should be extracted with DDW.

9. Preparation of Coating and Extraction Reagents

9.1 Impactor frit coating solution preparation - Weigh 1 g of silicone oil (Dow Corning high temperature 660 oil) and place in a 100 mL polyethylene storage bottle. Add 100 mL of toluene. Mix thoroughly, close container, and store at room temperature. (WARNING - FLAMMABLE LIQUID).

9.2 Impactor frit extraction solution preparation - Add 100 mL of IC eluent to a clean polyethylene storage container. Pipette 5 mL of methanol into container. Mix thoroughly. Store, covered at room temperature.

9.3 Annular Denuder Coating Solutions Preparation

Note: Different coatings may be used depending on the chemical species of interest.

9.3.1 NaCl coating solution - Clean a 100 mL polyethylene storage vial and let dry at room temperature. Weigh 0.1 g of reagent grade NaCl and add to vial. Add 90 mL of deionized water and 10 mL of methanol. Mix thoroughly; store, covered at room temperature.

9.3.2 Na_2CO_3 coating solution - Clean a 100 mL polyethylene storage vial and let dry at room temperature. Measure 50 mL of methanol (WARNING - TOXIC, FLAMMABLE LIQUID) with a graduated cylinder and pour into vial. Measure 50 mL of DDW with a graduated cylinder and add to vial. Weigh 1 g of glycerol and add to DDW. Weigh 1 g of a_2CO_3 and add to vial. Mix thoroughly, solution may fizz; wait for fizzing to stop before sealing vial. Store at room temperature.

9.3.3 Citric acid coating solution - Clean a 100 mL polyethylene storage vial and let dry at room temperature. Measure 50 mL of methanol (WARNING - TOXIC, FLAMMABLE LIQUID) with a graduated cylinder and pour into vial. Weigh 0.5 g of citric acid and add to vial. Mix thoroughly; store, covered at room temperature.

10. Elutriator and Acceleration Jet (Inlet) Assembly

Note: Figure 6A shows the all glass configuration.

10.1 The internal walls of the elutriator and jet assembly are coated with Teflon® to prevent losses of reactive species (SO_2, HNO_3, NH_3) during sampling. The elutriator prevents water and large particles from entering the inlet and thus extends the life of the impaction surface located immediately downstream of this assembly.

10.2 Figure 6B shows an aluminum version of this inlet. All inner surfaces of the aluminum unit are Teflon® coated. The main difference between the all glass and the aluminum inlet is the jet component of the aluminum inlet is replaceable as shown in Figure 3B. The jet component is made of either Teflon® or polyethylene and is available in various diameters as needed to accommodate selected sample flow rates. The jet may be replaced using the tool shown in Figure 6B. The jet diameter for a sample flow rate of 10 L/min is 3.33 mm. At this flow rate the inlet has a D_{50} cutpoint of 2.5 μm. If a different flow rate is to be used, the jet diameter must be changed to retain a D_{50} cutpoint to 2.5 μm. Figure 7A shows the relationship between jet diameter and flow rate to retain a D_{50} at 2.5 μm. Table 2 contains the jet diameters and Reynolds number to maintain a D_{50} of 2.5 μm cutpoint at different flow rates between 1 and 20 L/min.
Note: If the sampling area has substantial concentrations of coarse particles (>2.5 μm), the user may select to replace the acceleration jet and impactor assembly with the Teflon®-coated aluminum cyclone. The D_{50} cutpoint at a flow rate of 10 L/min is 2.5 μm, as illustrated in Figure 7B.

11. Impactor Frit Preparation and Installation

11.1 Impactor Frit Installation

11.1.1 Impactor-coupler - The impactor-coupler assembly shown in Figure 8 is comprised of two parts: the replaceable impactor frit and the coupler-impactor housing seat. The impactor surface is a porous ceramic or porous stainless steel frit, 10 mm x 3 mm. This frit is inserted into the coupler-impactor housing using the tools shown in Figure 9. It is imperative that the in-tool is completely screwed in behind the impactor seat before the frit is pressed into place. The impactor frit is pressed gently but firmly into the seat of the impactor housing with your clean gloved finger. The impactor should fit into the housing so that it does not protrude above the seat. The impactor frit has a slight bevel. The narrow surface should be inserted into the impactor seat.

11.1.2 Impactor-denuder - The impactor-denuder assembly shown in Figure 9 is comprised of three parts: the replaceable impactor frit, the impactor seat support pin and the annular denuder impactor-pin support. The impactor frit is the same as described in Section 11.1.1 and is inserted, as previously described, into the impactor seat support pin. The impactor support pin can either be hand-held while inserting the frit or it can be placed upright into the aluminum frit holder #3 (see Figure 10). Press the support pin into the denuder pin support. The pin is grooved and has a viton "O"-ring to keep the pin snug in the denuder support during cold weather use (Teflon® tends to shrink at low temperatures). The support pin is removed by using the removal tool shown in Figure 9.

11.2 Impactor Frit Preparation

With the impactor frit in the impactor seat of either the coupler (see Figure 8) or the Teflon® impactor seat support pin which fits into the first denuder (see Figure 9), pipette 50 μL of the toluene-660 oil coating solution onto the impactor frit surface and allow to dry at room temperature. Cap both sides of the coupler impactor or denuder-impactor until use.

12. Filter Pack Preparation and Assembly

Note: Any number of filters can be used depending on the target species of interest. The configuration referred to in this section does not collect NH_{4+}.

12.1 With clean gloves, disassemble the filter pack (see Figure 11) by unscrewing the large outer Teflon® collar (sleeve) from the aluminum filter housing outlet component.
Note: It is necessary to remove the polyethylene cap first. Lay the pieces out on clean Kimwipes®. Insert black viton "O"-rings (see Figure 11).

12.2 Lay a clean Teflon® filter ring housing, with its large opening face-up, on a clean Kimwipe®. Place a clean stainless steel screen in the filter ring housing.

12.3 Using clean filter forceps, place a Nylasorb® nylon filter on the screen. Insert a second filter ring housing on top of the nylon filter with its large opening face-up. This forms a "sandwich" with the nylon filter held between the two filter ring housings.

12.4 Place another clean screen on the second filter ring housing. Using clean filter forceps, place a Teflon® filter on the screen.
Note: If a Teflasorb® Teflon® filter is used, be sure to place the Teflon® coated side, not the webbed side, toward the air stream. If the webbed side is facing the air stream, $SO_4^=$ extraction from the filters may be inefficient.

12.5 Place the Teflon® filter housing inlet component (see Figure 11) on top of the Teflon® filter. This forms another "sandwich" with the Teflon® filter held between the second filter ring housing and the housing inlet component. The housing inlet component connects the filter pack assembly to the last annular denuder through a thermoplastic coupler. Be careful not to twist the filterpack components, or damage will occur to the filters.

12.6 Lay the aluminum filter housing outlet component, with its large opening face-up, on a clean Kimwipe®. Insert a black viton "O"-ring in the aluminum filter base.

12.7 Insert the filter ring sandwiches (prepared in Sections 12.1-12.5) with the filter housing inlet component extending upward, on the viton "O"-ring in the aluminum filter base. Place the large outer Teflon® sleeve over the filter sandwich and screw onto the aluminum filter base. DO NOT OVERTIGHTEN! AND DO NOT TWIST FILTER PACK COMPONENTS!

12.8 Install the "Quick-Release" plug into the filter outlet component. DO NOT OVERTIGHTEN!

12.9 Install the polyethylene cap onto the filter inlet component and the orange dust cover onto the Quick-Release plug until ready to attach denuders.

13. Annular Denuder System Preparation

All new annular denuder parts obtained from suppliers should be cleaned by placing them in a dilute soap solution in an ultrasonic cleaner for about 10 minutes. The parts should then be thoroughly rinsed in DDW and allowed to dry at room temperature.

13.1 Annular Denuder Coating Procedure

Note: If the first denuder holds the impactor, a blank Teflon® impactor support pin should be installed in the pin support holder before the coating procedure.

13.1.1 Cap the end of the denuder which has the inner tube flush to the outer tube and set denuder upright on the capped end. For the denuders with flow-straighteners at both ends, either end can be capped. Measure 10 mL of the appropriate coating solution into a graduated cylinder. Pipette the 10 mL into the flow-straightener end of the upright capped annular denuder.

13.1.2 Cap the open end of the denuder and holding horizontally, rotate the denuder to distribute the coating solution evenly (see Figure 12).

13.1.3 Remove cap from flow-straightener end of denuder and decant excess coating solution into a clean denuder extract storage bottle labeled "denuder blank." Bottle label should include denuder number, coating solution and date.

13.1.4 Repeat this procedure with each denuder; label the denuders and bottles appropriately.

13.2 Annular Denuder Drying Procedure

Note: As denuders dry, they change from translucent to a frosted appearance. Denuders are dry when they become uniformly frosted.

13.2.1 Drying train and manifold clean air flow should be adjusted to 2 to 3 L/min. Close toggle valve controlling clean air flow through manifold before attaching denuders.

13.2.2 Attach flow-straightener end to drying manifold port at the back-to-back bored caps (see Figure 13).

13.2.3 Open toggle valve and allow clean air to flow through the tube for several minutes.

13.2.4 Close toggle valve, and reverse ends of tubes attached to manifold.

13.2.5 When an even frosted appearance is achieved, remove tubes from manifold, cap both ends with clean caps and store until ready for use. Turn off air to drying manifold.

13.3 Annular Denuder System (ADS) Assembly

Note: Described herein is an annular denuder system consisting of 4 denuders in series. Any number of denuders can be used as per the operators discretion. It is recommended to assemble the denuders in such a way that the flow-straightener end always follows the flush end of the previous denuder, except, in the event that denuders with flow-straighteners at both ends are used. This type of assembly allows laminar flow conditions to be restored.

13.3.1 Lay the ADS pieces on a clean surface (i.e., Kimwipes®).

13.3.2 Remove the end caps from the first denuder. Denuder 1 is coated with NaCl and may or may not hold the impactor frit pin support. If the first denuder is equipped with the impactor frit pin-support, remove the blank impactor support pin. Gently insert the impactor support pin and coated frit assembly into the denuder-pin support. If the first denuder does not hold the impactor pin-support, attach the impactor frit seat equipped coupler assembly to the flow-straightener end of the first denuder.

Note: DO NOT TIGHTEN! Do not tighten during the following procedure until Section 13.4.12 is reached.

13.3.3 Attach a thermoplastic coupler to the opposite denuder end. Place a Teflon® clad "O"-ring inside the coupler, if needed.

13.3.4 Remove the end caps of the second denuder (Na_2CO_3 coated). Attach the end with the flow-straightener section to the first denuder-coupler assembly.

13.3.5 Attach a thermoplastic coupler to the opposite denuder end. Place a Teflon® clad "O"-ring inside the coupler, if needed.

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13.3.6 Remove the end caps of the third denuder (Na_2CO_3 coated). Attach the end with the flow-straightener section to the second denuder-coupler assembly.

13.3.7 Attach a thermoplastic coupler to the opposite denuder end. Place a Teflon® clad "O"-ring inside the coupler, if needed.

13.3.8 Remove the end caps from the fourth denuder (citric acid coated). Attach the end with the flow-straightener section to the third denuder-coupler assembly.

13.3.9 Attach a thermoplastic coupler to the opposite denuder end. Place a Teflon® clad "O"-ring inside the coupler, if needed.

13.3.10 Attach the filter pack inlet to the fourth denuder coupler assembly.

13.3.11 When using the first denuder equipped with the impactor frit-pin support, a thermoplastic coupler with a Teflon® clad "O"-ring is used to attach the inlet assembly. Attach but do not tighten!

13.3.12 Attach the elutriator-acceleration jet assembly to the first denuder-coupler assembly. Tighten very gently - DO NOT OVERTIGHTEN or breakage will result. (This applies when using either first denuder described).

13.3.13 Tighten the remaining couplers very gently - do not overtighten or breakage will result (see Figure 1).

13.3.14 Cap elutriator with orange dust cover until use.

Note: When collecting and measuring gaseous $HN0_2$, HNO_3, SO_2, and NH_3, and particulate NO_3^-, NH_4^+, and $SO_4^=$, it is essential to assemble the annular denuders as previously described. It is impossible to distinguish the difference between deposited HNO_2 and HNO_3 if the NaCl coated denuder does not precede the Na_2CO_3 coated denuder. It is impossible to quantify the amount of HNO_2 collected if there are not two Na_2CO_3 coated denuders in series. Also, NH_3 must be taken out of the gas stream prior to the air stream entering the filter pack. Otherwise, reaction of the unneutralized sulfate will result. If ammonia (NH_3) and/or H^+ measurements are not to be analyzed for, then the use of a citric acid coated denuder is not important. However, with the removal of NH_3, some nitrate collected on the Teflon® filter will tend to evaporate and be found on the nylon filter.

13.4 Laboratory Leak-Check of ADS

Note: CAUTION - Do not subject the system to sudden pressure changes or filters may tear.

13.4.1 Remove the orange dust cap from the impactor opening. Attach the "Quick-Release" to a pump module. Turn on the pump. Be certain that flow through the ADS occurs by checking the rotameter.

13.4.2 Briefly cap the elutriator with the orange dust cap. The flow as indicated on the rotameter should drop to zero if no leaks exist.

13.4.3 Disconnect the pump from the ADS at the "Quick-Release" plug. Cap the "Quick-Release" plug with an orange dust cover. Turn off the pump. REMEMBER - Never overtighten joints or breakage will result. If the joints can not be sealed with gentle tightening, then the Teflon® "O"-rings are worn or defective and must be replaced.

13.4.4 Place the assembled sampler in its field-to-lab carrying case for transport to the field (see Figure 14).
Note: It is recommended that the ADS joints be loosened slightly when extreme temperature changes are incurred during transportation. This will prevent unnecessary breakage or distortion of the ADS components. Remember to allow the system to adjust to the indoor air temperature before tightening the joints and checking for leaks.

14. Sampling

14.1 Start-up

14.1.1 Remove the ADS from its field-to-lab carrying case and load into the field sampling box. The ADS field sampling box is insulated with polyurethane which is configured to hold the ADS without allowing movement. Chromeplated spring clips hold the denuders in place. Automatic and manual control switches allow the sampling box to control the temperature of the ADS. The automatic switch should be used when the ADS is not in use and when the ADS is sampling for extended periods of time without constant supervision to prevent low temperature or sudden pressure change exposure of the ADS (these types of exposure can cause leaks to occur, condensation, or the filters to tear). When sampling, the ADS should be kept 1°C above the indoor temperature to prevent condensation. The sampling box has two connections with the pump timer: the plastic suction hose connected with "Quick-Release" couplers and the 12-V power cord with a "Quick-Disconnect" coupler. The power cord remains connected, and the suction hose is disconnected from the box each time the unit is opened. Inside the box, the hose is connected to the top of the filter pack with a "Quick-Release" coupler. During sampling the sample box is kept securely closed (see Figure 2).

14.1.2 Allow the pump to warm up for 20-30 minutes prior to testing so the pump will provide steady flow during testing.

14.1.3 To check the Heat/Cool cycles, flip one switch from "AUTO" to "MANUAL" and the other between "COOL" and "HEAT." Check to insure that the fan and heater (i.e., light bulb) work, respectively.

14.1.4 With the elutriator still capped, turn on the pump with the switch on the timer. The rotameter should indicate zero flow. If there is a flow, the assembly pieces need to be recoupled. Run leak check for 5-10 seconds, then turn off pump and remove elutriator cap. Record leak rate on Field Test Data Sheet (see Figure 15).

14.1.5 Attach DGM output to elutriator inlet. Turn on pump. Record start time on Field Test Data Sheet (see Figure 15). Using a stopwatch, record the time for 20.0 L to pass through the DGM. Record the DGM temperature and the absolute pressure of the DGM.

14.1.6 Calculate the flow rate as follows:

$$Q_{STD} = (V/T)(P_b/P_{STD})(T_{STD}/T_m)(F_c)$$

where:
Q_{STD} = flow rate corrected to standard conditions, O°C and 760 mm Hg, L/min
V = volume of gas pulled through denuder system, L

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T = time required to pull 20 L of gas through denuder system, minutes
P_b = barometric pressure, mm Hg
P_{STD} = standard barometric pressure, 760 mm Hg
T_{STD} = standard temperature, 273°C
T_m = temperature of dry gas meter, 273°C + T_m
F_c = dry gas meter correction factor, dimensionless

14.1.7 If the calculated flow rate is not between 5 and 16 L/min, typical 10 L/min, then readjust the flow rate and repeat Sections 14.1.4 and 14.1.5 until the rate is in the above range. Preliminary studies should be conducted to obtain an estimate of the concentrations of the species of interest.

14.1.8 Record the flow rate on Field Test Data Sheet.

14.1.9 Remove DGM connection tubing from elutriator inlet. Pump should remain running so that sampling continues. Higher flow rates may be used for shorter sampling periods. Concentration of the species of interest in indoor air and the configuration of the sampling equipment, determine the appropriate flow rates. Sampling at 10 L/min, requires a sampling time of 24 hours for the collection of pollutant concentrations between 0.02 and 0.83 $\mu g/m^3$.

14.2 Sample Shutdown

14.2.1 Attach DGM connection tubing elutriator inlet with pump still running. Measure flow rate as in Sections 14.1.5 and 14.1.6. Record flow time, temperature, and pressure on Field Test Data Sheet (See Figure 15).

14.2.2 Turn off pump. Record time and elapsed time meter reading on log sheet. Remove DGM connection tubing from elutriator inlet. Remove ADS from the sampling box, cap the ends, and place the ADS in field-to-lab carrying case for transport to lab. Be careful not to stress the ADS during the transfer or breakage will result. CAUTION - When the ADS is brought from a cold field sampling location to a warm laboratory, it is necessary to loosen the denuder couplings to prevent thermal expansion from breaking the denuders.

14.3 Corrective Action for Leak Test Failure

Note: These steps should be followed when failure occurs during testing at the laboratory before transport to the field and in the field before testing.

14.3.1 Sampler leaks - Note the problem on the Field Test Data Sheet. Check assembly of ADS components. Replace gaskets. Check for proper seating of denuder surfaces. Replace any defective parts.

14.3.2 Cracked or chipped denuders or elutriator assemblies - Note problem on Field Test Data Sheet. Discard defective pieces. Do not try to extract cracked pieces. WARNING - use caution when disassembling cracked glassware. Pieces may shatter and cause severe cuts. Wear protective clothing.

14.3.3 Contaminated blank solutions - Note problem on Field Test Data Sheet. Follow parts cleaning procedures closely. Examine the sampler preparation area for possible sources of contamination and remove source, if found. Check DDW being used in the

solution preparations and extractions: Fill a clean 25 mL polyethylene extraction bottle with the DDW used in solution preparation and extraction, send to lab for analysis. If contaminated, correct deionization system.

14.3.4 Flow rate disagreement - Note problem on Field Test Data Sheet. Check vacuum gauge on flow module. If a high vacuum exists then the sampler has become blocked. This may be due to dust or smoke particles clogging the filters or to obstructions in the system or tubing. Check flow module. Repair as needed.

14.3.5 Inadequate flow rate - Note problem on Field Test Data Sheet. Check rotameter on flow controller. If adequate flow is shown here, then a leak exists between the controller and the DGM. If no flow is shown on rotameter, then check vacuum gauge on controller. If no vacuum exists, then pump needs repair. If a high vacuum is shown, then an obstruction exists in the system. Check to see that the paper filter dividers were not accidentally installed with the filters in the filter pack. Check tubing for kinks.
Note: Typically the pressure drop across the filters should be approximately 1 inch Hg at 10 L/min flow rate at sea level. This pressure drop can vary from 1-10 L/min depending on elevation.

15. ADS Disassembly

15.1 Remove the ADS from the field-to-lab carrying case using both hands. To prevent stress, hold the ADS by its ends. CAUTION - Do not stress the ADS while removing it from the case.

15.2 Decouple the elutriator - jet assembly from the first denuder-impactor-coupler assembly.

15.3 When using the denuder-impactor, the frit-pin must be removed from the support in the denuder before removing the frit from the pin (see Figure 9). The frit is then extracted from the pin using pin tool #3 and the frit extraction tool (see Figure 10). When using the impactor-coupler assembly, the frit is removed from the coupler seat using pin tool #3 and the "out" frit removal tool (see Figure 16). Put frit in covered dish and set aside for chemical extraction.

15.4 Remove the denuders from the couplers and cover each end of the denuders with clean end caps until extraction.

15.5 Label a clean 100 mL polyethylene bottle with the sampler ID number and filter type (i.e., Teflon® or Nylasorb®, as appropriate) for each of the filters.

15.6 Disassemble the filter pack in a clean, ammonia-free air hood. Clean all hood surfaces and utensils with methanol. Wearing clean gloves and using clean filter forceps, remove the filters and place each in its storage (protective) bottle, with the exposed filter surface facing downward, until extraction.
Note: Be careful to place the filters in the properly labeled bottles.

16. Extraction Procedures

Special precaution: Samples should be analyzed as soon after collection as possible. It is imperative that the solutions and extraction procedures are prepared and performed on the day of pH analysis. Extraction must take place in a clean, ammonia-free, air hood. The extracts must be processed in the order in which they will be analyzed, so that each sample will have a similar time interval between extraction and analysis. Denuder extracts and filters should be stored in the refrigerator until just prior to analysis. Samples stored longer than 30 days tend to degrade due to bacteria growth and/or losses to the walls of the extraction vessel.

16.1 Impactor Frit Coating Extraction

16.1.1 Place the impactor (which was removed before denuder extraction) into a small extraction bottle.

16.1.2 Label the bottle appropriately. Pipet 10 mL of impactor extraction solution into the bottle. The solution must cover the surface of the impactor frit.

16.1.3 Close the extraction bottle and place in an ultrasonic bath for 30 minutes.

16.2 Denuder Extraction

Note: If the denuder was the first denuder, which is equipped with the impactor frit-pin support, insert a clean Teflon® impactor frit-pin, without frit in place. Then extract as described below. This procedure is to be followed for each denuder.

16.2.1 Cap one end of the denuder. Add 5 mL of DDW with a pipet. Cap other end.

16.2.2 Rotate the denuder to wet all surfaces thoroughly with the water. Remove the cap and pour the liquid into a clean 25 mL polyethylene extraction bottle.

16.2.3 Repeat this procedure with a second 5 mL of DDW extract (total extract volume is 10 mL which is placed into a single bottle).

16.2.4 Replace the extraction bottle cap and label the bottle with the sampler ID number, denuder number and type (as appropriate).

16.3 Filter Extraction

16.3.1 Teflon® Filter Extraction (for pH analysis followed by ion chromatography (IC) analysis)

Note: Teflon® is not wet by water; therefore, the filter will float on top of aqueous solutions. It is imperative that the solutions and extraction procedures are prepared and performed on the day of pH analysis. Extraction of the filters must take place in a clean, ammonia-free, air hood. The filters must be processed in the order in which they will be analyzed, so that each sample will have a similar time interval between extraction and analysis.

16.3.1.1 Allow the hood to be flushed with ammonia-free air for at least 5 minutes before filter extraction. All of the hood surfaces and extraction utensils must be cleaned with a Kimwipe® moistened with ethanol.

16.3.1.2 Pipet 3 mL of 0.0001 N perchloric acid ($HClO_4$) solution into the appropriately labeled extraction vial (4 mL).
Note: It is necessary to use $HClO_4$ because it inhibits CO_2 from dissolving into the solution and keeps the organic compounds in solution from dissociating. Both these activities, if allowed to take place, can cause the ionic strength of solution to change.

16.3.1.3 Place the Teflon® filter in the extraction vial. Cap tightly. Store at 5°C in the dark until ready for analysis.

16.3.1.4 When ready for analysis, the filter must be prepared (within the air hood) in the following manner: Using forceps and gloved hands, lift the filter from the extraction vial. Let the excess solution drain off into the vial. Holding the filter over the extraction vial, and using an automatic pipet, apply 100 ± 5 mL of ethanol to the filter. Add the ethanol slowly to ensure that all portions of the membrane are wet with ethanol. Immerse the filter in the aqueous solution once again. Tap the forceps against the inside of the vial to remove liquid. Tightly replace cap. Put in ultrasonic bath for 15 minutes total, rotating the rack 90° every 5 minutes.
Note: Perchloric acid is used in place of potassium chloride, initially, to prevent interference in the measurements of cations and anions by ion chromatography. Potassium chloride must be added to the portions of the sample extract which are used for pH analysis (the purpose of the salt, final concentration 0.04 M, is to increase the ionic strength and thus to reduce the time for equilibrium of the pH electrode used for measurement). Note also that it is necessary to use the same bottle (freshly opened) of ethanol for the extraction of the Teflon® filters that is used for the preparation of sulfuric acid standards.

16.3.1.5 When ready for pH analysis, the extracts are prepared in the order of pH measurement. Inside the air hood, remove the caps from 4 mL extraction vials. Wipe off any drops which may leak onto the outside of the cup.

16.3.1.6 Using gloved hands and a 1 mL automatic pipet, transfer 1 mL of the extract to each of two correspondingly labeled 2 mL cups.
Note: The first 2 mL cup for each extract has the same I.D.# as the 4 mL cup and the second 2 mL cup has the same I.D.# with a hyphen (-). This is the same system used with the working standards.

16.3.1.7 After transferring the extracts to the 2 mL cups, recap the 4 mL extract cup. Then store the 4 mL cups at 5°C in a refrigerator pending sulfate analysis by IC.

16.3.2 Nylon Filter Extraction

16.3.2.1 Pipet 10 mL of IC eluent into the appropriately labeled filter vial or bottle with caps.
Note: Be sure that the filter lies flat on the bottom of the bottle and that all of the filter is covered by the extraction solution.

16.3.2.2 Replace the bottle's cap and put in an ultrasonic bath for 30 minutes.

16.3.2.3 Store the bottles in a clean (i.e., pollutant free) refrigerator at 5°C in the dark until analysis.

17. Ion Chromatography Analysis

Note: The analytical procedure described here is not the only appropriate procedure available for quantifying the analytes of interest. It is not necessary that an automated system be utilized. This particular analytical procedure was chosen because it is presently being utilized by EPA. Modifications to this procedure may be required depending on the intended use of the data, however, any modifications made must be justified in order to obtain comparable data quality.

17.1 Standards Preparation

Special Precaution: Storage of these solutions should be no longer than one week. All of the working standard solutions are used to calibrate the IC and are made from reagent grade stock. The crystals are dried overnight in covered petri dishes at 110°C in a vacuum oven prior to preparing the standard solutions. Any yellowish discoloration of the dried crystals indicates decomposition and crystals should be discarded.

17.1.1 Sodium Sulfate Stock Solution

17.1.1.1 In a clean, calibrated, 1 L flask, add 500 mL of DDW.

17.1.1.2 On weighing paper, weigh out enough reagent (Na_2SO_4) to make the solution 2000 ppm concentration. The target weight is 0.7394 g. Record the gross weight. Note: It is best to weigh out slightly more than the target weight due to the adherence of the residual crystals to the weighing paper (the residual left on the paper is generally between 0.1 mg and 1 g).

17.1.1.3 Add the reagent crystals to the 500 mL of DDW. Reweigh weighing paper and subtract weight from the gross weight. The difference is the actual net weight.

17.1.1.4 Using a proportion, calculate the actual volume needed to make the solution 2000 ppm (see below).

$$\text{target wt/actual net wt} = 500 \text{ mL (target)/actual volume}$$

or

$$\text{actual volume} = (500 \text{ mL} * \text{actual net wt})/\text{target wt}$$

17.1.1.5 Using the appropriate calibrated pipet, add the amount of DDW needed to achieve the calculated actual volume. Mix well and cover with parafilm.

17.1.2 Sodium Nitrate Stock Solution

17.1.2.1 In a clean, calibrated, 1 L flask, add 500 mL of DDW.

17.1.2.2 On weighing paper, weigh out enough reagent ($NaNO_3$) to make the solution 2000 ppm concentration. The target weight is 0.6854 g. Record the gross weight.
Note: It is best to weigh out slightly more than the target weight due to the adherence of residual crystals to the weighing paper.

17.1.2.3 Follow Sections 17.1.1.3 through 17.1.1.5.

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17.1.3 Sodium Nitrite Stock Solution

17.1.3.1 In a clean, calibrated, 1 L flask, add 500 mL of DDW.

17.1.3.2 On weighing paper, weigh out enough reagent ($NaNO_2$) to make the solution 1000 ppm concentration. The target weight is 0.7499 g. Record the gross weight.
Note: It is best to weigh out slightly more than the target weight due to the adherence of residual crystals to the weighing paper.

17.1.3.3 Follow Sections 17.1.1.3 through 17.1.1.5.

17.1.4 Standard working solutions - The working solutions are made up as follows: Add 10 mL each of the three stock solutions (Na_2SO_4, $NaNO_3$, and $NaNO_2$) to a 200 mL volumetric flask and dilute to the mark with DDW. Subsequent dilutions are carried out using a 10 mL volumetric pipet and appropriate flasks. Standards of 20, 10, 5 and 1 ppm Na_2SO_4 and $NaNO_3$ (and one-half these concentrations of $NaNO_2$) are prepared. These are used to calibrate the IC.

17.2 Reagent Preparation

Note: Storage of these reagents should be no longer than one week.

17.2.1 Anion eluent - The anion eluent is a solution of 1.8 μm Na_2CO_3 and 1.7 μm $NaHCO_3$. A concentrated solution can be prepared and diluted as needed.
Note: See Anion Storage Solution

17.2.1.1 Concentrated Na_2CO_3 solution (0.36 M) - Weigh out 38.156 g of Na_2CO_3 (MW = 105.99). Dissolve into 1 L of DDW. Store in refrigerator until ready to dilute.

17.2.1.2 Concentrated $NaHCO_3$ solution (0.34 M) - Weigh out 28.564 g of $NaHCO_3$ (MW = 84.01). Dissolve into 1 L of DDW. Store in refrigerator until ready to dilute.

17.2.1.3 Dilution of stock solutions - Bring both solutions to room temperature. Accurately pipet 10 mL of each solution into a 2000 mL volumetric flask which has been partially filled with DDW. Bring to the mark with DDW (1:200 dilution).

17.2.2 Anion regenerant - The regenerant is a 0.025 N H_2SO_4 solution. VERY CAREFULLY dispense 2.8 mL of concentrated Ultrex sulfuric acid (36 N) into a graduated cylinder. Partially fill the regenerant reservoir with DDW (3 L). Slowly add the acid to the regenerant reservoir. Bring to the mark with DDW (4 L).
Note: Protective clothing and eye protection should be utilized.

17.2.3 Cation eluent - There are two cation eluents that are used for the analysis of monovalent and divalent cations. The strong cation eluent is: 48 μm HCl, 4 μm DAP.HCl, 4 μm Histidine.HCl (DAP = Diaminoproprionic acid). The weak eluent consists of 12 μm HCl, 0.25 μm DAP.HCl, 0.25 μm Histidine.HCl.

17.2.3.1 Strong cation eluent - Weigh 0.560 g DAP and 0.840 g histidine into a one liter volumetric flask. Add 48 mL of 1 M HCl (Ultrex) to the flask. Bring the eluent to the final volume by bringing to the mark with DDW. Mix thoroughly to dissolve.

17.2.3.2 Weak cation eluent - Place 63 mL of the strong cation eluent in a 1 L flask. Add 9 mL of 1 M HC1 to the flask. Bring the eluent to the final volume by bringing to the mark with DDW. Mix thoroughly to dissolve.

17.2.4 Cation regenerant - The cation regenerant consists of 100 μM Tetrabutyl-ammoniumhydroxide (TBAOH). Place the TBAOH container into a warm water bath to dissolve any crystals that may have formed. Measure 266.7 mL of the TBAOH (stock reagent is supplied as 1.5 M, 40% in water) into a graduated cylinder. Add the TBAOH to 4 L of DDW.

17.2.5 Anion storage solution - Since the anion columns contain carbonates from the eluent, protection must be taken against microorganisms that will live on this food source and clog up the columns. If the columns are not being used for long periods of time (>2 weeks), a storage solution of 0.1 M NaOH should be pumped into them.

17.3 Sample Preparation

17.3.1 Mark the auto sampler vials with the appropriate identification numbers. Place the vials in an (IC) autosampler tray.

17.3.2 Using clean, calibrated 0.5 mL pipets transfer the denuder and the remainder of the filter extracts from the extraction vials to a clean disposable 0.5 mL (IC) autosampler (polyethylene) vial. Fill the autosampler vial up to the line on the side.

Note: If refrigerated, the contents of the 4 mL extraction vial must be vortex-mixed prior to transfer to the autosampler vials.

17.3.3 Place black filter caps on top of the vials. Use the tool provided to push the caps into the vials until they are flush with the top. (see the IC manual for more detailed instructions).

17.3.4 Wipe away any excess fluid from the top of the vial to avoid contamination from other samples.

17.3.5 After all of the trays are filled, place them into the left side of the autosampler. The white dot on the tray indicates the first sample. Press the button labeled RUN/HOLD to the RUN position. The trays should move until the first sample is under the sampling head. The front panel should indicate a READY message. Press local/remove switch to remove.

17.4 Basic System Operations - Start-up and Shut-down

17.4.1 Start-up Procedure for Ion Chromatograph

17.4.1.1 Figure 17 illustrates the major components of the Dionex 2020i Ion Chromatography system. Turn helium and nitrogen tanks on by opening the valve on top of each tank (pressure in either tank should not be less than 500 psi. Replace if necessary). Open valves at the outlet end of both regulators. Pressure on the nitrogen regulator is adjusted to 100 psi. Pressure on the helium regulator is adjusted to 14 psi.

17.4.1.2 Check the level of eluents and regenerating solutions. Turn the chromatography (CMA) values for the anion channel switch ON. Verify that the pressure

reading on the face of the degassing unit is 7 psi. Adjust by turning dial next to pressure gauge. Turn the degas switch to HIGH.

17.4.1.3 Turn the eluent reservoir switches, corresponding to the eluents to be degassed, to the ON position. Let the eluents degas on HIGH for 3-5 minutes, then turn degas switch to LOW.

17.4.1.4 Select the appropriate program on the gradient pump module using the PROGRAM switch. (Programs are recalled from memory by first pressing the PROGRAM switch, then the single digit reference number corresponding to the appropriate program).

17.4.1.5 Priming the eluent lines.

Note: All of the eluent lines used during analysis must be primed to remove any air bubbles that may be present. The selected program identifies which lines are used.

- Open the gradient pump drawer. Turn the pump to the START position for 10 seconds, or until a CLICK is heard, then turn the pump OFF. This step opens the valve to the eluent line displayed on the front panel.
- Attach a 10 mL syringe to the priming block on the face of the gradient pump module. With the priming block valve closed, pull the syringe plunger out to the end of the syringe.
- Open the priming block valve. The syringe will quickly fill with eluent. Close the valve on the priming block when the syringe is almost full. Remove syringe from block and discard collected eluant.
- This priming procedure can be repeated if necessary. All of the eluent lines that are to be used during a day of analysis should be primed at this time.

17.4.1.6 Open the door of the Advanced Chromatography Module. On the back of the door, at the bottom, is the conductivity detector. There are four labeled lines (anion, cation, waste, and cell) located next to the cell. The plumbing must be configured according to the type of analysis to be performed. If anions are being analyzed, the ANION line must be attached to the CELL line, and the CATION line must be attached to the WASTE line. If cations are being analyzed, the CATION line must be attached to the CELL line, and the ANION line must be attached to the WASTE line. The line coming from the pump must be attached to the correct port on the advanced chromatography module. SYSTEM 1 on the left is for anions, SYSTEM 2 on the right is for cations.

Note: If switching from one system to the other, the pump and the lines coming from the pump must be purged of the original eluent. This is done by disconnecting the pump line from the chromatograph module, turning the pump on and running the new eluent into a waste beaker for 2-3 minutes.

17.4.1.7 Select the columns to be used (labeled pH or NO_2) by pressing the blue button located below the labels. To verify that the correct columns are being used, the switch should be pressed at least once, and then set to the appropriate position. This is done in case the indicator light is reflecting a "default" setting, regardless of the actual position of the switch.

17.4.1.8 Turn the power switch on the autosampler ON (switch is located on the back of the unit, on the right). The default settings will be displayed on the front panel. Attach

the SAMPLE OUT line from the autosampler to the advanced chromatography module. The connection should be made to the port marked SAMPLE of the appropriate system. Turn the pump to START.

17.4.1.9 Turn the conductivity cell ON. Switch is located on the gradient pump module. Turn the REGEN switch for the appropriate system ON. Verify that regenerant is flowing by inspecting the regenerant waste line which empties into the sink. Open the advanced chromatography module door and inspect for leaks at columns, fittings, etc. Shut pump off if leaks are found.

17.4.1.10 Turn stripchart recorder ON. Baseline should stabilize in less than 20 minutes. If baseline is not stable, see troubleshooting Section 17.5 for assistance.

17.4.2 Data acquisition start-up - The following is a description of the current data acquisition program used by the U.S. EPA. The program is available (U.S. EPA, Atmospheric Chemistry and Physics Division, Office of Research and Development, Research Triangle Park, NC) and is for IBM or IBM compatible computers. Other appropriately designed programs may be used to compile the data collected for any given sampling network. It is not necessary to use a computer programmed integrator for the computation of data, however, for large sampling networks, it is recommended.

17.4.2.1 Turn on the IBM XT computer. From the C:>prompt, type: cd/cchart, then type: cchart. This loads the Chromatochart software. Turn switch on relay box to ENABLE, indicator light could go on.

17.4.2.2 Press F2 to enter the methods development module. Select option number 1 - "select channel # and load method file." "Select channel # <0>" type 0 or press ENTER to select the default choice shown in the brackets (in this case 0). "Load method file named" type the name of the appropriate method, then press ENTER. A directory of all of the current methods in memory can be obtained by pressing the F2 function key.

17.4.2.3 Press F3 to enter the Data Acquisition module. At this point you will be asked to save the method file. If there has not been any changes to the methods file, it does not need to be saved. Select option #4 - "Collect Data." Press ENTER to deactivate the method queue. "Load Run Queue named," type the name of the run queue if one has been created. Type ENTER to deactivate the run queue.

17.4.2.4 "Total # runs for method <1>," type how many times the method is to be repeated (total number of samples). "Autoanalyze Data" type Y. "Autosave data to disc" type Y. "Data file name (xxxxx) change?", type data file name. "Press ENTER to begin methods." Press ENTER only after the samples have been loaded into the autosampler and the baseline has stabilized.

17.4.2.5 Figure 18 illustrates the chromatograms for each of the samples as output by the programmed Spectra-Physics integrator. The program used to generate these outputs can be found in the Appendix of this method. Note that actual output is by individual run as illustrated by Figure 19. Most information provided here is optional to the operator.

17.4.3 Calibration of IC - The instrument should be brought to normal conditions with a warm-up time of at least thirty minutes.

17.4.3.1 With the "Reading" light on, check to ensure the flow rate is 1.5 mLs/minute, the fluid pressure is 600 psi ± 100 psi and the conductivity is constant as measured by offset difference.

17.4.3.2 Fill the IC vials with the prepared standard solutions and (10, 5 and 1 ppm Na_2SO_4 and $NaNO_3$) and pure eluent. This will allow a four-point calibration curve to be made.

Note: For low-level applications, more standards and blanks may be necessary in order to obtain accurate reference curves.

17.4.3.3 Load the four vials into the sample vial holder, and place the holder in the automated sampler tray.

17.4.3.4 The tray is controlled by a Spectra-Physics SP4200 or SP4270 Computer Integrator. Use the integrators operation manual to begin calibrating. (A typical program in Basic for integrators which illustrates integrator capability is shown in the Appendix of this procedure). By using the RUN command the analysis and data treatment phases of the calibration are set in motion. Four calibration standards are run, the chromatograms and peak areas displayed for each run, and the run results for each anion are fitted to a quadratic curve by a least squares regression calculation. The three curves are plotted and the correlation coefficients are calculated. The values of the coefficients are normally greater than 0.999, where 1.000 indicates a perfect fit. Values of less than 0.99 indicate the calibration procedure should be repeated.

Note: Recalibration should be carried out whenever standard concentrations show consistently high or low results relative to the calibration curve is compared to the calibration curve from the old standards. Comparability of points should be within ± 0.1 ppm or ± 10%. For standard concentrations of greater than 1 ppm, comparability will normally be within 5% or better. Old standards are assumed correct since they are referenced to the entire historical series of previous standard solutions all of which are comparable.

17.4.4 System Shut-down

17.4.4.1 Shut off the pump. Turn the REGEN switch and the conductivity cell to the OFF position.

17.4.4.2 Switch the eluent degas switch to HIGH.

17.4.4.3 Turn the stripchart recorder OFF, cap the pen. Press the F10 function key on the computer. Select option 3, to exit to DOS. Shut off the printer and the computer.

17.4.4.4 Shut the eluent degas system and reservoir switches and the autosampler to the OFF position. Close the valves on both gas cylinders. Then close the regulator valves.

17.5 Basic Troubleshooting

Before proceeding with the troubleshooting guide, make sure that the reagents used were prepared correctly, and are not "old."

17.5.1 Unstable Baselines

17.5.1.1 Wavy baseline - The most common reason for a wavy baseline is an air bubble in the gradient pump. This is diagnosed by observing the pump head indicator lights on the gradient pump module front panel. If the baseline is pulsing in phases with pump pistons, it usually indicates a bubble. Other possibilities include a dirty or stuck check valve, piston seal or "O"-ring, as well as an air bubble in the conductivity cell.

17.5.1.2 Drifting baseline - Steadily increasing or decreasing baselines usually indicate that the suppressor column is not performing as it should. Parameters to change include the regenerant and eluent concentrations and flow rates. Check temperature routinely as changes in temperature can cause drifting. Balancing these should stabilize the baseline, if the suppressor is functioning correctly. The Dionex manual describes clean-up procedures if the suppressor is believed to be contaminated.

17.5.1.3 High baselines - As with drifting baselines, the parameters to change are eluent and regenerant concentrations and flow rates. A high baseline usually indicates that there is not enough baseline suppression, this can be controlled by increasing the regenerant flow rate.

17.5.1.4 Low baselines - Low baselines usually indicate that there is too much suppression. Oversupression can be controlled by decreasing the flow of the regenerant.

17.5.2 Backpressure - Variations in system backpressure are common and should not raise concern UNLESS the pressure change is greater than 200 psi.

17.5.2.1 High backpressure - The system is protected from pressure related damage through the high and low pressure alarm settings on the front panel of the gradient pump module. If the high pressure setting is correctly selected (200 psi above normal operating range), the pump will automatically shut-off if this value is exceeded. The reason for high backpressure is that there is some kind of blockage in the system. Possibilities include: loading against a closed valve; a plugged line; contaminated columns; etc. Diagnosis of the problem is done by removing one component of the system and observing how the pressure changes.

17.5.2.2 Low pressure - Low pressure readings usually indicate a leak somewhere in the system. Carefully check all fittings for leaks, tighten if necessary.

17.5.3 Flow

17.5.3.1 Regenerant lines - If there is no flow at the waste outlet end of the regenerant line, check the following:

- Make sure that the correct regenerant switch is turned on
- Verify that the reservoir is not empty
- Make sure the nitrogen tank is turned on
- Check that the regulator is correctly set

17.5.3.2 Eluent lines - If there is no flow at the outlet end of the eluent lines check the following:

- Check that the pump is on
- Check that the eluent lines are connected to the correct port

17.5.4 Software - refer to the ChromatoChart manual for detailed information on software problems.

18. Ammonia Analysis By Technicon Autoanalysis

Presented in Sections 18.1 and 18.2 are the recipes for the standards and reagents required for the analysis of the ammonium ion (NH_4^+ - or ammonia (NH_3)) by Technicon autoanalysis. The prelude of these Sections briefly describes the TRAACS 800 autoanalyzer and the sample flow through the TRAACS 800 for NH_4^+ analysis. The Technicon TRAACS 800 autoanalyzer is illustrated in Figure 20. This instrument is capable of quantifying, from a single sample, three different species, simultaneously. An aliquot of the sample is taken from an automated sampler by syringe. A splitter divides the aliquot into the appropriate volumes required for the particular analyses. Each of the volumes is then transferred to the appropriate analytical cartridge. Sample flow diagrams which illustrate $SO_4^=$, NO_3^- and NH_4^+ analysis can be shown separately and independently of one another. Hence, for a one-channel system, one can readily adapt the sample preparation and analysis protocols for each individual analysis. The data computation (by computer) and quality assurance protocols, however, can not be readily adapted to single-channel instruments. These protocols need to be specific to the individual analytical instrument. In brief, for NH_4^+ analysis, Figure 21 illustrates how the sample is carried through the Technicon autoanalyzer. The samples, along with all standards, are taken from the auto-advance sampler tray by the use of a proportioning pump and automated syringe. Air and EDTA are first added to the samples and are mixed in the first set of coils. After mixing, phenolate is added and mixed in the next set of coils. Nitroprusside is then added and mixed, followed by the addition and mixing of hypochlorite. At this stage, the sample should be a bright blue color. After the last mixing stage, the sample is sent through a heated bath, followed by another mixing stage. Finally the sample is sent through a colorimeter where the results are recorded on a digital printer and stored in a computer file for further manipulation.

18.1 Standards and Stock Solutions Preparation

Note: Before discarding the old solution, it should be checked against the fresh solution by comparing calibration curves on the working solutions prepared from them. Slopes and intercepts are calculated for each set of standards. The old slope and intercept are used to calculate concentration values from readings for the new standards. This determines if the old solution has deteriorated or if an error has been made in preparing the new solution.

18.1.1 Ammonium solution standard (1000 µg/mL) - Dry ammonium chloride in an oven for one hour at 50 to 60°C and desiccate over silica gel for one hour. Weigh 2.9470 g ammonium chloride and dissolve in 800 mL DDW. Dilute to one liter with DDW and mix thoroughly. This solution is stable for one year.

18.1.2 Intermediate ammonium standards - To make a 100 μg/mL ammonium standard, pipet 10 mL of ammonium stock standard into a 100 mL volumetric flask. Dilute to volume with DDW and mix thoroughly. Keep refrigerated. This solution remains stable for one month. To make a 10 μg/mL ammonium standard, pipet 1.0 mL of ammonium stock standard into a 100 mL volumetric flask. Dilute to volume with DDW and mix thoroughly. This solution remains stable for one week.

18.1.3 Working ammonium standards in DDW - Pipet aliquots of the 100 μg/mL ammonium intermediate standards with appropriate volumes of nitrate and sulfate intermediate standards into 100 mL volumetric flasks according to the table below. Dilute to volume with DDW. Prepare fresh daily.

Standard	Stock or Intermediate Standard (μg/mL)	Aliquot (mL)	Concentration (μg/mL)
A	1000	40.0	40.0
B	100	4.0	4.0
C	100	3.0	3.0
D	100	2.0	2.0
E	100	1.0	1.0
F	100	0.5	0.5
G	10	2.0	0.2
H	10	1.0	0.1

18.1.4 Sodium citrate stock solution - Dissolve 294.1 g of sodium citrate in 800 mL DDW. Dilute to 1 liter and mix thoroughly. Store at room temperature.

18.1.5 20% citric acid/5% glycerol stock solution - Dissolve 25 g citric acid in 80 mL DDW. Add 5 mL glycerol and dilute to 100 mL with DDW. Mix thoroughly and store at room temperature.

18.1.6 Sodium citrate/citric acid/glycerol working solution - Put 100 mL sodium citrate stock solution into a 1000 mL volumetric flask. Add 20 mL of the 10% citric acid/5% glycerol stock solution and dilute to volume with DDW. Mix thoroughly and store at room temperature.

Note: This solution will be used to make up ammonium working standards for citric acid/glycerol-impregnated filter extract analyses.

18.1.7 Working ammonium standards in sodium citrate/ citric acid/glycerol working solution - Pipet aliquots of the 100 μg/mL volumetric flasks according to the table in Section 18.1.1.3. Dilute to volume with sodium citrate/citric acid/glycerol working solution and mix thoroughly. Prepare fresh daily.

18.1.8 Potassium chloride stock solution - Dissolve 74.6 g potassium chloride in 800 mL DDW. Dilute to one liter with DDW and mix thoroughly. Store at room temperature.

18.1.9 Potassium chloride working solution - Put 100 mL of the potassium chloride stock solution into a 1000 mL volumetric flask. Dilute to volume with DDW.

18.1.10 Working ammonium standards in potassium chloride working solution - Pipet aliquots of the 100 µg/mL ammonium stock standard or intermediate standards into 100 mL volumetric flasks according to the table below. Dilute to volume with potassium chloride working solution and mix thoroughly. Prepare fresh daily.

Standard	Stock or Intermediate Standard (µg/mL)	Aliquot (mL)	Concentration (µg/mL)
A	1000	40.0	40.0
B	100	4.0	4.0
C	100	3.0	3.0
D	100	2.0	2.0
E	100	1.0	1.0
F	100	0.5	0.5
G	10	1.0	0.1
H	10	0.5	0.05

18.2 Reagent Preparation

Note: When reagents are prepared, label the container with the contents, concentration, date prepared, and the preparer's initials.

18.2.1 Alkaline phenol - To 800 mL DDW in a one liter volumetric flask, add 83.0 g loose crystallized phenol. Keeping the flask in anice bath or under tap water, slowly add 96.0 mL 50% sodium hydroxide solution. Shake the flask while adding the sodium hydroxide. Cool to room temperature, dilute to one liter with DDW and mix thoroughly. Store in an amber glass container. This solution remains stable for three months, if kept out of direct light.

18.2.2 Sodium hypochlorite solution - The amount of sodium hypochlorite solution varies from batch to batch of sodium hypochlorite (5% commercial grade). Therefore, for each new batch, a base and gain experiment must be run to adjust the amount of sodium hypochlorite required to obtain the existing base and gain values. In a 150 mL volumetric flask, dilute 86 mL of 5% sodium hypochlorite solution to 100 mL with DDW and mix thoroughly. Check base and gain values. Reduce or increase the amount of sodium hypochlorite to obtain the same base and gain values as the previous sodium hypochlorite batch. This solution remains stable for one day.

18.2.3 Sodium nitroprusside solution - Dissolve 1.1 g of sodium nitroprusside in about 600 mL of DDW, dilute to 1 liter with DDW and mix thoroughly. Store in an amber container, and keep in refrigerator. This solution remains stable for one month, if kept out of direct light.

18.2.4 Disodi&2um EDTA solution - Dissolve 1.0 mL of 50% w/w sodium hydroxide and 41.0 g of disodium EDTA mix thoroughly. Add 3.0 mL of Brij-35 and mix. Store in plastic container. This solution remains stable for six months.

19. pH Analysis

19.1 Standard and Reagent Preparation

19.1.1 Standard H_2SO_4 Solution

Note: Each of the standard H_2SO_4 stock solutions must be prepared fresh the day of pH analysis.

19.1.1.1 Label seven 25 mL polyethylene stoppered volumetric flasks. Also, label each flask with the volume of 1 N H_2SO_4 solution indicated in the following table:

Flask #	Volume of IN Stock (μL)	Standard Concentration (μN)
1	0	0
2	25	1
3	50	2
4	100	4
5	200	8
6	400	16
7	800	32

19.1.1.2 Use the 25 μL automatic pipet to add 1 N stock H_2SO_4 to flasks #1-3. Use the 100 μL pipet to add 1 N stock H_2SO_4 to flasks #4-7. Dilute all flasks to the 25 mL mark with absolute ethanol. Cap with stoppers or parafilm and mix well.

19.1.2 2 M Potassium Chloride (KCl) Solution

19.1.2.1 Weigh 149.2 ± 0.1 g of KCl. Add the KCl to a 2 L flask.

19.1.2.2 Add about 700 mL of DDW water to the flask. Swirl the solution until the KCl is completely dissolved.

19.1.2.3 Pour this mixture into a 1 L graduated cylinder. Rinse the flask with a small amount of water and transfer the rinse into the cylinder. Fill the cylinder to the 1 L mark.

19.1.2.4 Pour the solution from the cylinder into the 1 L polyethylene bottle. Cap and shake the bottle to mix well. Mark the bottle with date of preparation.

19.1.3 0.1 N Perchloric Acid ($HClO_4$) Solution

19.1.3.1 Fill a 1 L graduated cylinder about 1/2 full with DDW. Transfer 10 ± 0.1 mL of 60-62% $HC10_4$ into the 1 L cylinder with a 10 mL pipet.

19.1.3.2 Fill the cylinder to the 1 L mark. Pour the solution into the 1 L polyethylene bottle.

19.1.3.3 Cap and shake the bottle to mix well. Mark the date of preparation on the bottle.

19.1.4 0.01 N $HClO_4$ Solution

19.1.4.1 Fill a 1 L graduated cylinder about 1/2 full with DDW.

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19.1.4.2 Measure 100 mL of the 0.1 N $HClO_4$ solution with the 100 mL graduated cylinder. Add this to the 1 L cylinder.

19.1.4.3 Fill a 1 L cylinder with DDW to the 1 L mark. Pour the solution into the 1 L polyethylene bottle.

19.1.4.4 Cap and shake the bottle to mix well. Mark the date of preparation on the bottle.

19.1.5 Extraction Solution (ES)

Note: This solution has the same composition as the solution used to fill the sample vials for Teflon® filters. It must be prepared fresh on the day of pH analysis.

19.1.5.1 Measure 100 ± 10 mL of DDW into a 1 L graduated cylinder. Transfer to a 2 L erlenmeyer flask.

19.1.5.2 Using a 5 mL calibrated automatic pipet, add 10 ± 0.1 mL of 0.01 N perchloric acid ($HClO_4$), to flask of water.

19.1.5.3 Mix well and cover with parafilm until ready for use.

19.1.6 EA Solution

19.1.6.1 Measure 150 ± 2 mL of ES (prepared in 18.1.5) into a 250 mL graduated cylinder. Transfer to a 250 mL erlenmeyer flask.

19.1.6.2 Using a 5 mL graduated cylinder, add 5 ± 0.1 mL of ethanol (this must be from the same fresh bottle of ethanol that was used to prepare the standards in 18.1.1) to the flask.

19.1.6.3 Again using a 5 mL graduated cylinder, add 3 ± 0.1 mL of 2 M potassium chloride (KCl) solution to the flask.

19.1.6.4 Mix well and cover with parafilm until ready for use.

19.1.7 Working Standard Test Solutions

19.1.7.1 Place fourteen-4 mL polystyrene sample cups (as used with Technicon Auto-Analyzer II system) labeled 1, 1*, 2, 2*...7, 7* into racks. Using the calibrated dispensing pipet bottle, add 3 mL of ES solution to each 4 mL cup.

19.1.7.2 Using the displacement pipet, add 50 uL of absolute ethanol to each cup. Pour about 3 mL of standard (H_2SO_4 solution) #1 into a labeled 4 mL cup.

19.1.7.3 Immediately, pipet 50 uL of this standard into the 4 mL cups labeled 1 and 1* containing the ES solution and ethanol.

Note: This transfer must be done without delay to prevent the standard concentration from increasing significantly due to evaporation of the ethanol solvent.

19.1.7.4 Repeat the procedure for each of the other 6 standards. If there is a delay of more than 5 minutes between the preparation of these mixtures, and the next step, put caps on the 4 mL cups.

19.1.7.5 To prepare for analysis, each must be mixed, then two aliquots from each cup are transferred to 2 mL sample cups. Place cup #1 in a rack. In a second rack place two-2 mL cups labeled 1 and 1-. Use the 1 mL automatic pipet to mix the contents of 4 mL cup #1 by drawing 1 mL into the pipet tip and then dispensing it back into the 4 mL

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cup three times. Then use the same pipet to transfer 1 mL of the mixture to each of the two labeled 2 mL cups. Place caps on the two 2 mL cups. After transferring the two aliquots to 2 mL cups, rinse the automatic pipet tip in a flask of DDW. Repeat the transfer procedure for each of the other working standard pairs.

19.2 Calibration of pH Meter

The pH meter requires temperature calibration whenever a new electrode is used. Use the manufacture's procedure in the instrument manual. This calibration should be repeated every three months while not in use. The pH meter is left with the power cord plugged into the AC outlet, the mode control knob is left in the standby position, the electrode lead is partially disconnected by pressing the plastic ring on its outer edge, and the combination electrode is immersed in a 4 M KCl solution (a slit rubber stopper seals the bottle with the electrode in it). Keep a record of the temperature calibrations in a lab notebook.

19.3 Pre-Analysis Calibration

19.3.1 Use pH lab analysis log form 418 to record all date. While still in standby mode, reconnect the electrode lead at the back of the pH meter.

19.3.2 Fill three 4 mL cups with pH 7 buffer. Withdraw the electrode from the 4 M KCl bottle and wipe the tip gently with a Kimwipe® to remove the bulk of the solution. Rinse the electrode with one cup of pH 7 buffer. Do not test pH of the first cup.

19.3.3 Immerse the electrode in the second cup of the pH 7 buffer. Use a small bottle or other support to hold the cup up to the electrode while waiting for the meter reading to equilibrate.

19.3.4 Test the pH by turning to the pH mode of the meter. Allow the reading to stabilize for at least 30 seconds. Record the result on the log for "1st cup."

19.3.5 Turn to standby mode, and then test the last cup of pH 7 buffer. Record the results on the log for the "2nd cup." If the pH value for the 2nd cup is not 7.00 ± 0.01, adjust the "calib." knob to obtain a reading of 7.00. Note this adjustment on the log.

19.3.6 Fill three 4 mL cups with pH 4 buffer. With the meter in the standby mode, remove the cup containing pH 7 buffer, wipe the tip of the electrode gently with a Kimwipe®, and then rinse the electrode with the first cup of pH 4 buffer.

19.3.7 Test the next two cups of pH 4 buffer as above, recording the results on the log. If the pH value for the 2nd cup is not 4.00 ± 0.01, adjust the "slope" knob to get a reading of 4.00. If the value for the second cup was not 4.00 ± 0.03, the calibrations at pH 7 and at pH 4 must both be repeated.

19.4 pH Test 0.01 N $HClO_4$ Solution

Note: The 0.01 N $HClO_4$ solution is used to prepare the ES solution which, in turn, is used to prepare the EA solution. It is imperative that the pH value for the EA solution be 4.09 ± 0.04. If this pH value is not achieved, then the 0.01 N $HClO_4$ solution must be reprepared.

19.4.1 Calibrate the pH meter with pH 4 buffer.

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19.4.2 Rinse the pH electrode with DDW. Wipe the tip of the electrode with a Kimwipe®.

19.4.3 Fill three 4 mL cups with EA solution. Measure the pH of the test EA solution as with the buffer solutions this value must be 4.09 ± 0.04.

19.4.4 If the above pH value is not achieved, follow the steps 18.1.3 - 18.1.6 to reprepare the solutions. Test the pH of the new solutions. Repeat as necessary to obtain a pH of 4.09 ± 0.04.

19.4.5 Leave the electrode immersed in the "2nd cup" with the meter in the standby mode until ready to start analysis of the working standards.

19.5 Analysis of Working Standard

Note: Immediately following the EA analysis, start testing the working standards.

19.5.1 With the pH meter still in the standby mode, remove the last cup from the electrode, gently wipe the tip with a Kimwipe®, and then immerse the electrode into the working standard cup #1.

Note: Only two cups are available for each working standard (also for filter extracts). Thus, pH measurement is made for both of the two cups for each sample. Also, the electrode tip is not wiped between the 1st and 2nd cups of each sample.

19.5.2 After testing the pH of cup #1, test cup #1-. Record the results of both on the log sheet.

19.5.3 With the meter in the stand-by mode, remove the #1- sample cup, wipe the electrode with a Kimwipe® and test one 2 mL cup of EA solution, rinse with DDW.

19.5.4 Test a 2nd cup of EA solution; record the results for both cups on the logsheet. Discard the 1st cup of EA, but retain the 2nd cup to be used as the 1st cup for the next EA test.

19.5.5 Continue testing the remainder of the working standards, #1*, 1*-, ... 7, 7-, 7*, 7*-. Remember that the electrode tip is wiped both before and after each pair of test solutions, but not in between two cups of the same sample.

Note: If there is trouble in obtaining constant pH values, it may be necessary to use a magnetic stirrer to keep the contents to be measured uniform. If employed, ensure that the sample cups are insulated from any temperature increase of the stirring platform which may occur during extended use.

19.5.6 Use the mode control knob in the "temp." position to measure the temperature of the test solutions every 5-10 samples and record the results on the logsheet.

19.6 Analysis of Filter Extracts

Following measurement of the pH of the working standards, measure the pH of the filter extracts and record all results on the log. After all the filter extracts have been tested make an additional test with the EA solution. At the end make a final test of pH 4 buffer. With the mode control in the standby mode, shut down the pH meter by disconnecting the electrode lead at the back of the meter, leaving the meter power cord plugged into the AC line. Immerse the electrode tip in the bottle of 4 M KCl.

20. Atmospheric Species Concentration Calculations

The system described in the previous sections collects nitric acid (HNO_3), nitrous acid (HNO_2), sulfur dioxide (SO_2), ammonia (NH_3) particulate sulfate ($SO_4^=$), and particulate nitrate (NO_3^-). Figure 1 illustrates the collection of each of these species. Nitric acid and sulfur dioxide gases are collected on denuders one and two. Some SO_2 gas is collected on denuder three also. Nitrous acid gas is collected on denuders two and three. Ammonia gas is collected on denuder four. Particulate sulfate and nitrate are collected on the first (Teflon)® filter, while some of the particulate nitrate collected on the Teflon® filter can evaporate and be collected on the second (nylon) filter. Also collected on the Teflon® filter are fine particles which contain hydrogen ions (H^+), though probably not free H^+. Hydrogen ions are most likely present in the H_3O^+ form. The concentration of these H^+ ions indicates the atmospheres acid aerosol content. It is necessary to prepare the Teflon® filter extracts for pH analysis prior to IC analysis for the particulate sulfate contents. Special precautions must be taken to prevent contamination of the Teflon® filters by ammonia before either of the analyses.

20.1 Assumptions of the Annular Denuder System

There are a number of assumptions which are made about performance of the annular denuder system in order for validity of the calculations to be presented later in this section to hold true. As discussed in Section 6, there are significant interferences which need to be considered in order for accurate estimations of species concentrations to be made. The assumptions are as follows:

- The first denuder stage collects 100% of sampled HNO_3 as nitrate. (Since the diffusivity of HNO_3 is high, diffusion to the side walls is assumed to be very quick.)
- The second denuder stage collects 100% of sampled HNO_2 as nitrite, which can oxidize to nitrate.
- The first and second denuder stages together collect 100% of the SO_2 as sulfite, which can oxidize to sulfate.
  Note: Before analysis, it is recommended to add hydrogen peroxide (H_2O_2) to oxidize the sulfite (SO_3^-) to sulfate ($SO_4^=$) to simplify the calculations.
- The amounts of nitrite and nitrate collected on denuder 3 (d3) represent amounts of interfering gases such as NO_2 collected on denuder 2 (d2).
- The fourth denuder stage collects 100% of the sampled ammonia (NH_3) as ammonium ion (NH_4^+).
- The Teflon® filter (f1) is 100% efficient for particulate sulfate, nitrate and ammonia. Particle losses are less than 1% on each denuder. This assumption may or may not stand true depending on the concentrations of the components in the air sampled. Modifications may be needed to avoid low (or underestimates of) acidic measurements. For example, it may be necessary to add another filter stage to more accurately account for the particulate ammonia content of the air sampled. If ammonium nitrate (NH_4NO_3) was collected on the Teflon® filter, its probability of evaporation is high. Therefore, a citric acid-impregnated filter downstream would correct for the loss from the Teflon® filter. Also, interaction of ammonia and sulfuric acid neutralizes the filter

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and causes the acidic measurement to be biased. (Again diffusion rules the particle loss assumption; particles have lower diffusivities than gases).
- The nylon filter (f2) collects any nitrate that evaporates from the Teflon® filter (f1).

20.2 Calculations Using Results from IC Analysis

These assumptions lead directly to equations for computing atmospheric concentrations from denuder measurements.

20.2.1 Figure 22 illustrates the equation for nitric acid quantification. In this equation, $C_g(HNO_3)$ is the concentration of nitric acid gas expressed in $\mu g/m^3$. Subscript g denotes "gas." The computation depends on NO_3^- (d1), which is the measured amount nitrate in μg collected on denuder 1. The factor 1.016 represents the ratio of molecular weights of HNO_3 and NO_3^-. In the denominator, V is the sampled air volume expressed in m^3.

20.2.2 Figure 23 illustrates how the concentration of nitrous acid is deduced. The numerical factors 1.022 and 0.758 (both in μg) are used to convert the measured nitrite and nitrate to equivalent amounts of nitrous acid. Measured nitrate has to be included because some of the collected nitrite may oxidize to nitrate during sampling or during sample storage. Because a small portion of NO_2 may be collected on denuders 2 (d2) and 3 (d3), the nitrite and nitrate amounts measured on denuder 3 (d3) represent corrections for NO_2 and other interfering gases.

20.2.3 Figure 24 illustrates how sulfur dioxide concentrations are deduced. Because sulfur dioxide is collected on both stages d1 and d2, the results for both stages are added. To simplify the calculation, oxidize the collected sulfite to sulfate by adding H_2O_2 to the sample vial. Hence, the quantification of $SO_4^=$ gas directly estimates sulfur dioxide. A more complicated equation would result if the collected sulfite had not been fully oxided to sulfate. Sulfate measurements are expressed in mg. Sulfur dioxide concentrations are expressed in mg/m^3.

20.2.4 Figure 25 illustrates the equation for ammonia quantification. The numerical factor 0.944 is used to convert the measured ammonium ion to its equivalent amount of ammonia. Therefore the product of the factor and the NH_4^+ collected by d4 directly estimates the ammonia concentration ($C_g(NH_3)$).

20.2.5 Figure 26 illustrates how particulate sulfate concentration ($C_p(SO_4^=)$ is computed. The subscript p denotes "particle." This formula expresses the assumption that essentially all of the particulate sulfate is collected on the Teflon® filter (f1), and no evaporation occurs.

20.2.6 Figure 27 shows how particulate ammonium concentration is computed. This formula expresses the assumption that essentially all of the particulate ammonia is collected on the Teflon® filter (f1), and no evaporation occurs.

20.2.7 Figure 28 illustrates how the particulate nitrate concentration is computed. This equation is similar to the one for sulfate except that nitrate measured on the nylon filter (f2) must be included because nitrate collected on the Teflon® filter (f1) can evaporate. Note: It is important to note that four of the measurements are not used. For example, sulfate measured on the nylon filter represents a sulfate blank for nylon that is irrelevant to sulfate collected on Teflon®. Also, nitrite collected on the nylon filter represents the

possibility that some NO_2 is collected on the nylon filter, but that is not relevant to the way that nitrate is determined in the denuder system. The remaining unused data represent low concentrations and are also not relevant to deducing the concentrations of the atmospheric species considered here.

20.3 Estimates of Errors In Concentrations Deduced From Denuder Data

Note: The assumptions and formulas used to calculate the uncertainty of the measurements are illustrated in Section 20.3.3.

20.3.1 Figure 29 shows the formula used for the uncertainty in particulate sulfate. It includes errors in measuring sulfate and in deducing the air-volume sampled. It also includes a 3% error to account for the possibility of 1% particle loss in each of the three denuder stages. Error equations for the other species are shown in Section 20.3.3.

20.3.2 Assumptions on which error equations are based:

- X is the measurement error for species X.
- Measurement errors are random and uncorrelated among species.
- Possible particle-losses of 1% in each denuder introduces an overall uncertainty of + 3% for particulate sulfate and nitrate concentrations.
- Gases such as H_2S and CH_3HS can be collected on the denuder stages, and bias the results. Amounts collected on denuder stage 3 can be used to estimate the uncertainties that result from such bias. Thus, $SO_4^{=}(d3)$ is an estimate of the uncertainty in the amount of SO_2 collected on denuders 1 (d1) or 2 (d2).

20.3.3 Error equations:

For $SO_4^{=}$:

$$[\delta C_p(SO_4^{=})/C_p(SO_4^{=})]^2 = [\delta SO_4^{=}+(f1)/SO_4^{=}+(f1)]^2 + [0.03]^2 + [\delta V/V]^2$$

For NO_3^{-}:

$$[\delta C_p(NO_3^{-})/C_p(NO_3^{-})]^2 = [NO_3^{-}(f1) + NO_3^{-}(f2)] + [0.03]^2 + [\delta V/V]^2$$

For HNO_3 and HNO_2:

$$[\delta C_g(HNO_3)/C_g(HNO_3)]^2 = [\delta NO_2^{-}(d1)/NO_3^{-}(d1)]^2 + [\delta V/V]^2$$

$$[\delta C_g(HNO_2)/C_g(HNO_2)]^2 = [\delta A/(VC_g(HNO_2)]^2 + [\delta V/V]^2$$

where:

$$A^2 = (1.022)^2 [\delta NO_2^{-}(d2)^2 + NO_2^{-}(d3)^2] + (0.758)^2 [\delta NO_3^{-}(d2)^2 + NO_3^{-}(d3)^2]$$

20.4 Calculations Using Results from pH Analysis

Earlier determinations of pH have been based on the pH buffer concentrations, the activity of the solution, and the antilog of the measured pH value. More recent studies have steered away from the issue of activity by comparing the results of the standards, thus, alleviating errors introduced by basing the activities of ions retained on filters on those

retained in solution. The methodology developed from these more recent studies is described herein. The end results are reported in terms of mass of equivalent of ions. Appropriate values of accuracy and precision with respect to H^+ concentration for this method are 10% and 5%, respectively, for sample pH values in the 4.00 to 7.00 range.

20.4.1 Summary of method - There are two parts to this methodology, determination of the "nominal EQ," and determination of the "actual (EQ_N)." The nominal EQ is defined as the equivalent $\mu g\ H_2SO_4/m^3$ for a nominal 5.76 m^3 sample volume (24 hours at 4 LPM). The actual EQ_A is defined as the equivalent $\mu g\ H_2SO_4/m^3$ based on the actual sample air volume.

20.4.1.1 Determine the nominal EQ_N as follows:

20.4.1.1.1 To account for the difference between standards prepared with filters and standards prepared without filters, adjust the measured concentration values for the working standards (without filters) for each analysis day.

20.4.1.1.2 Calculate the standard curve, using a linear regression of the equivalent of $\mu g\ H_2SO_4/m^3$ (for 5.76 m^3 volume of sample) for each working standard vs the adjusted concentration values for the working standards.

20.4.1.1.3 Use the standard curve to determine EQ_N for each sample filter.

20.4.1.1.4 Calculate the actual air flow rate to determine the actual air sample volume. Divide the actual air sample volume into EQ_N to determine EQ_A.

20.4.1.2 Determine the actual EQ_A as follows:

20.4.1.2.1 The actual sample air volume, V, for each sample is calculated using data from the field log sheet. This data includes the initial and final elapsed time, the initial rotameter reading, and the rotameter I.D. No.

20.4.1.2.2 The calibration curve for the given rotameter reading is used to calculate the flow for the sample (LPM).

20.4.1.2.3 The nominal EQ_N is divided by the calculated flow to give the actual EQ_A.

20.4.2 Adjustment for filter vs. non-filter standards - This adjustment is necessary because experiments showed that the measured acid concentration from filters doped with H_2SO_4 stock standards yielded concentrations, as measured by the difference from EA solution, which were about 3% lower than the values found for working standards (prepared without filters from the same stock standards). The results gave the following relation (by linear regression):

$$C_f = -0.11 + 0.971\ (C_{nf}) \qquad (1)$$

where:

C_f = difference in units of 10^{-5} N, calculated using the pH of each filter standard and the pH of EA tested after that standard

C_{nf} = the same difference for non-filter standards (or the apparent net (strong acid concentration of H_2SO_4)

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For each working standard (non-filter), on a given analysis day, calculate the "apparent net concentration of H_2SO_4" as follows:

$$C_{nf} = 10^{-pHWS} - 10^{-pHEA} \quad (2)$$

where:
pHWS = measured pH for a working standard (or apparent strong acid concentration for H_2SO_4 - doped filter standards)
pHEA = measured pH for the EA solution (or apparent strong acid concentration for non-filter, non-H_2SO_4 doped standards)

After calculating the C_{nf} values for each working standard, use equation (1) above to calculate the adjusted values of Cf for each.

20.4.3 Determination of standard curve - For each working standard, the corresponding EQ_N value (the equivalent of μg H_2SO_4/m^3 [assuming a sample volume of 5.76 m^3]) is determined as follows:

$$EQ_N = m/5.76\ (10^6\ \mu g)/g \quad (3)$$

Note: 5.76 is the volume for a sample collected for 24 hours at 4 LPM, in m^3.
Note: It is the analyst's preference as to whether concentration or mass is calculated here and used to create the standard curve. If mass is used, a nominal sample air volume is not necessary. The value of m is determined as follows:

$$m = [1.000]\ [S/25]\ [5 \times 10^{-5}]\ [49] \quad (4)$$

where:
1.000 = concentration of the commercial standard H_2SO_4, in units of equivalents/L
S = volume of commercial standard H_2SO_4 used to prepare a given stock standard solution, mL
25 = volume of each stock standard solution, mL
5×10^{-5} (50 uL) = is the volume of each stock standard solution used to prepare its respective working standard, L
49 = equivalent weight of H_2SO_4, units of grams/equivalent

Note: When the value of S is 1 mL or greater for a final volume of 25 mL, the standard curve illustrates non-linearity. This is due to incomplete dissociation of bisulfate. An example table of the values of the nominal EQ_N for each working standard is shown in Table 3. For each analysis day, the standard curve should be determined by calculating the linear regression of EQ_N vs. C_f, with the result in the following equation:

$$EQ_N = \text{intercept} + [C_f]\ [\text{slope}] \quad (5)$$

20.4.4 Determination of nominal EQ_N for filter samples - The apparent net strong acid concentration of each sample filter extract, C_s, is calculated as with the working standards:

$$C_s = 10^{-pHS} - 10\text{-}pHEA \quad (6)$$

where:
pHS = measured pH of the sample filter extract (or apparent strong acid concentration for sample filters extracts)
pHEA = measured pH for the EA solution (or apparent strong acid concentration for non-filter, non-H_2SO_4 standards)

Note: The C_s values for the filter extracts are directly comparable to the C_f values for the working standards, since the C_f values have been adjusted for the difference in apparent acid concentration for tests made with filters and tests made without filters. Therefore, to determine the nominal EQ_N values for filter samples, use equation (5) transformed as follows:

$$EQ_N = \text{Intercept} + [C_s]\,[\text{Slope}] \quad (7)$$

20.4.5 Determination of actual EQ_A - The actual sample air value, V, for each sample is calculated using the data from the field log sheet. These data includes the initial and final elapsed times, the initial rotameter reading, and the rotameter I.D. No. Use the calibration curve for the given rotameter to calculate the flow for the sample, in LPM. Calculate the value of V as follows:

$$V = [F][T] \quad (8)$$

where:
F = flow from the calibration curve, LPM
T = net elapsed time, min

Since the nominal EQ_N values were determined assuming a flow of exactly 4 LPM and a net elapsed time of exactly 24 hours, the assumed volume was 5.76 m^3, therefore, calculate the value of the "actual EQ_A" by:

$$EQA = [EQ_N]/V \quad (9)$$

where:
EQ_A = units of $\mu g/m^3$

Nominal EQ_N as determined by Equations 3 and 4:

$$EQ_N = m/5.76\ (10^6\ \mu g/g)$$

where:
m = [1.000] [S/25] [5 x 10^{-5}] [49]
1.000 = concentration of commercial standard H_2SO_4, units of equivalents/L
S = volume of commercial standard H_2SO_4 used to prepare a given stock standard solution, mL
25 = volume of each stock standard solution, mL
5 x 10^{-5} (50 uL) = volume of each stock standard solution used to prepare its respective working standard, L
49 = equivalent weight of H_2SO_4, units of grams/equivalent

Working Standard #	S (mL)	M (g)	EQ_{N_3} ($\mu g/m^3$)
1	0.000	0	0.00
2	0.025	2.45	0.43
3	0.050	4.9	0.85
4	0.100	9.8	1.70
5	0.200	19.6	3.40
6	0.400	39.2	6.81
7	0.800	78.4	13.61
8	1.600	156.8	27.22

21. Variations of Annular Denuder System Usage

As mentioned in Section 3 and Section 4, the ADS as described previously, is used to measure reactive acidic (SO_2, HNO_2 and HNO_3) and basic (NH_3) gases and particles found in indoor air. The unique features of the ADS which separates it from established air monitoring methods are the ability of sampling artifacts to be eliminated from the collected gases and particles, and the preservation of the samples for subsequent analysis which is accomplished by removing NH_3 in the gas stream with a citric acid coated denuder, thus reducing the probability of the particulate acid sulfates ($SO_4^=$) captured on the Teflon® filter from being neutralized. The ADS configuration described in Section 13 clearly illustrates these unique features. The elutriator is designed to allow only particles with <2.5 μm diameter into the system. The impactor is designed to reduce the possibility of coarse particle infiltration even further. And finally, the sequence of the denuders reduces interference of possible chemical reactions which could cause under-or over-estimations of concentrations to be made. Although this configuration is recommended for measuring these gases and particulates, it may be in the interest of the user to measure only one or two of the chemical species. The following discussion will present possible variations of the ADS to accommodate such usages.

21.1 Today, the ADS is being used in intercomparison studies to assess NH_3 concentration differences indoors and outdoors. The assembly used here consists of an elutriator-impactor assembly, an annular denuder and a filter pack assembly. The elutriator-impactor assembly and the annular denuder are both smaller than those described earlier. The filter pack is available in the smaller size, but an adaptor is also available to assemble the smaller annular denuder to the larger filter pack assembly. This system is referred to as the personal sampler (see Figure 30). It is designed for sampling while attached to the shirt of a worker. The personal sampler can be used to measure other chemical species in indoor air by simply changing the reactive surface (coating) of the annular denuder and or by changing the types of filters used.

21.2 Another variation of ADS application is simultaneous use in parallel with a fine particle sampler. The fine particle sampler assembly is very similar to the annular denuder assembly. The main difference is that a flow-straightener tube replaces the annular denuder. The flow-straightener is a shorter version, 1-1/4 to 4 inches long, of the annular

denuder and serves to create even air flow across the filters for the collection of particulate matter. Figure 31 illustrates an exploded view of the fine particle sampler. Again the elutriator-impactor assembly and flow-straightener are available in smaller sizes with accommodating filter pack assemblies. In addition, the ADS carrying and shipping cases as well as the sampling box can be adjusted to accommodate the ADS and fine particle sampler. Figure 32 illustrates the assemblies as they would appear in the sampling box ready for sampling.

22. Method Safety

This procedure may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the user's responsibility to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This should be part of the user's SOP manual.

23. Performance Criteria and Quality Assurance (QA)

Required quality assurance measures and guidance concerning performance criteria that should be achieved within each laboratory are summarized and provided in the following section.

23.1 Standard Operating Procedures (SOPs)

23.1.1 SOPs should be generated by the users to describe and document 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 the sampler system; 3) purchase, certification, and transport of standard reference materials; and 4) all aspects of data recording and processing, including lists of computer hardware and software used.

23.1.2 Specific stepwise instructions should be provided in the SOPs and should be readily available to and understood by the personnel conducting the monitoring work.

23.2 Quality Assurance Program

The user should develop, implement, and maintain a quality assurance program to ensure that the sampling system is operating properly and collecting accurate data. Established calibration, operation, and maintenance procedures should be conducted on a regularly scheduled basis and should be part of the quality assurance program. Calibration procedures provided in Sections 17 and 19, operation procedures in Sections 14 and 17, and maintenance procedures in Section 17 of this method and the manufacturer's instruction manual should be followed and included in the QA program. Additional QA measures (e.g., trouble shooting) as well as further guidance in maintaining the sampling system are provided by the manufacturer. For detailed guidance in setting up a quality assurance program, the user is referred to the code of Federal Regulations (12) and the EPA Handbook on Quality Assurance (13).

24. References

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12. 40 CFR Part 58, Appendix A, B.

13. *Quality Assurance Handbook for Air Pollution Measurement Systems*, Volume II - Ambient Air Specific Methods, EPA 600/4-77-0272, May, 1972.

Table 1. Estimated Detection and Quantification Limits for the Annular Denuder System[1]

Detection Limits ($\mu g/m^3$)	Sampling Period		
	1 hour	1 day	1 week
a) gaseous species			
SO_2	3.1	0.13	0.02
HNO_3	2.0	0.08	0.01
HONO	0.5	0.02	0.01
NH_3	5.6	0.25	0.04
b) particulate			
$SO_4^=$	1.6	0.07	0.01
NO^{-3}	1.8	0.08	0.01

Quantification Limits ($\mu g/m^3$)	Sampling Period		
	1 hour	1 day	1 week
a) gaseous species			
SO_2	10.4	0.43	0.06
HNO_3	6.8	0.28	0.04
HONO	1.6	0.07	0.01
NH_3	20.0	0.83	0.12
b) particulate			
$SO_4^=$	5.3	0.22	0.03
NO_3^-	6.1	0.25	0.04

[1]Samples analyzed by ion chromatography. Detection limits are taken as three standards deviations above field blanks. Quantification limits are taken as ten standard deviations above field blanks. Both the detection and quantification limits were estimated assuming that the variance is independent of concentration.

Table 2. Accelerator Jet Diameters and Corresponding Reynolds Number (Re) for Selected Flow Rates to Obtain 2.5 μM Aerodynamic D_{50} Separation

Flow Rate L/min	Jet Diameter	Re
1.0	1.55	900
2.0	1.97	1400
5.0	2.65	2700
10.0	3.33	4200
12.0	3.55	4700
15.0	3.85	5500
16.7	4.00	6000
20.0	4.25	6600

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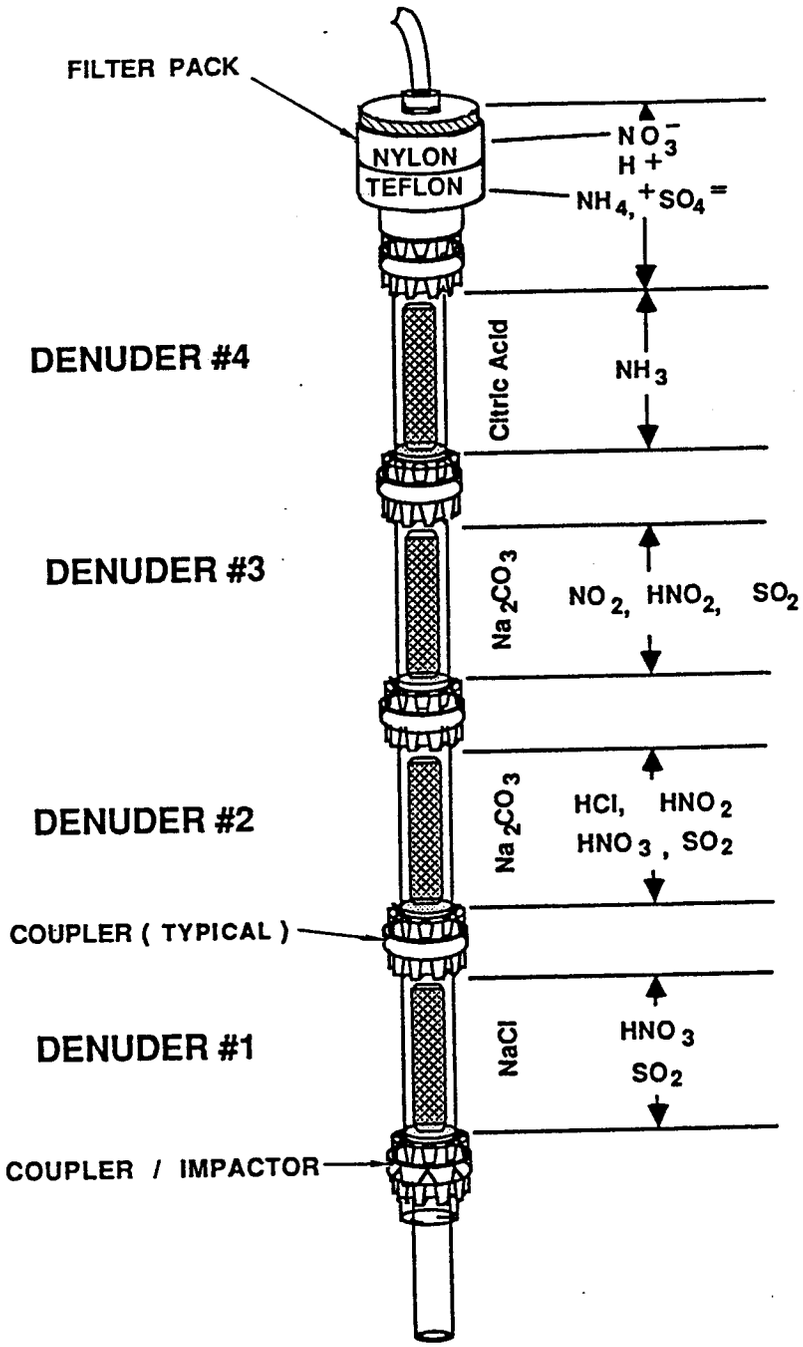

Figure 1. Schematic View of Annular Denuder Showing Species Collected

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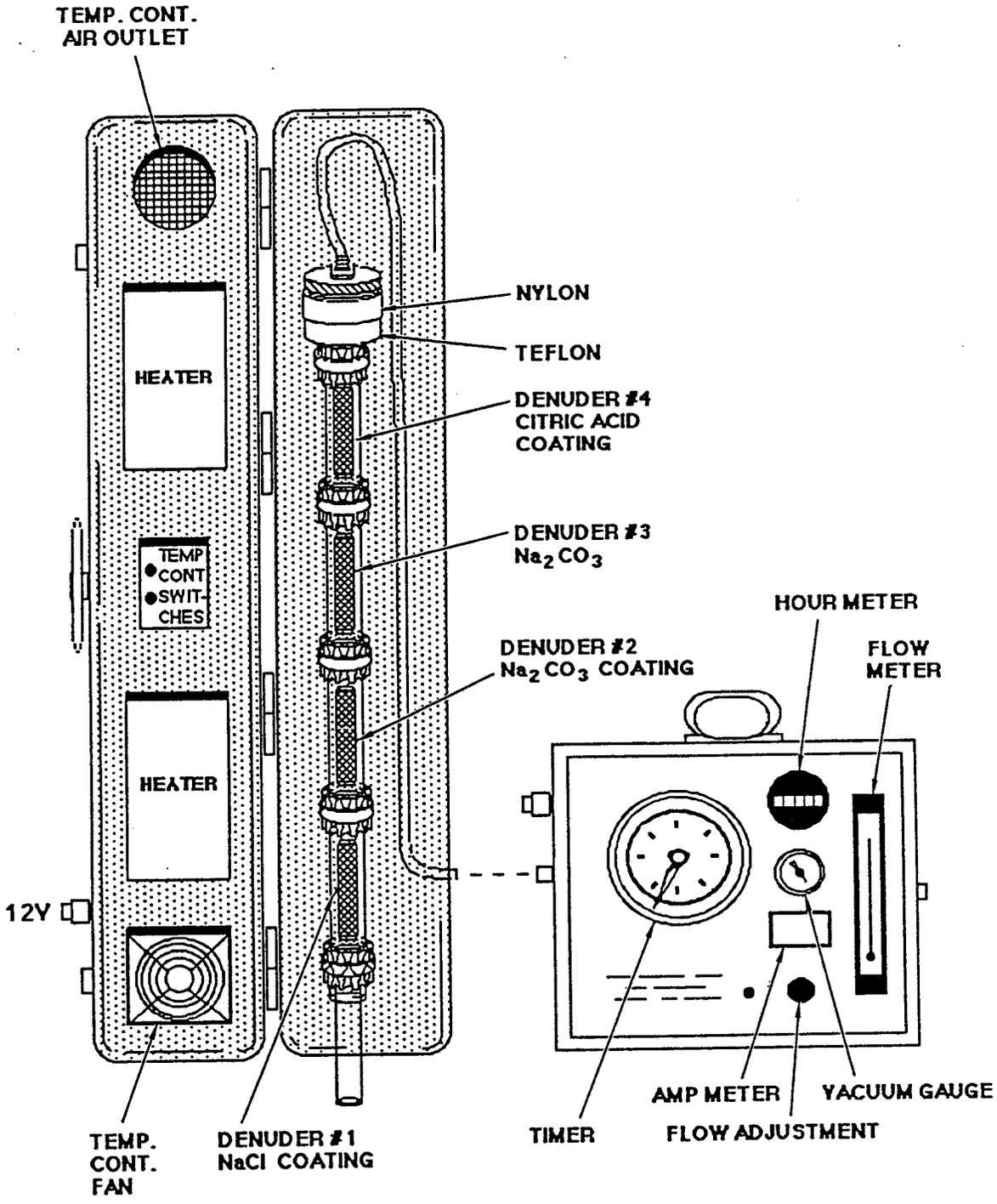

Figure 2. Annular Denuder System

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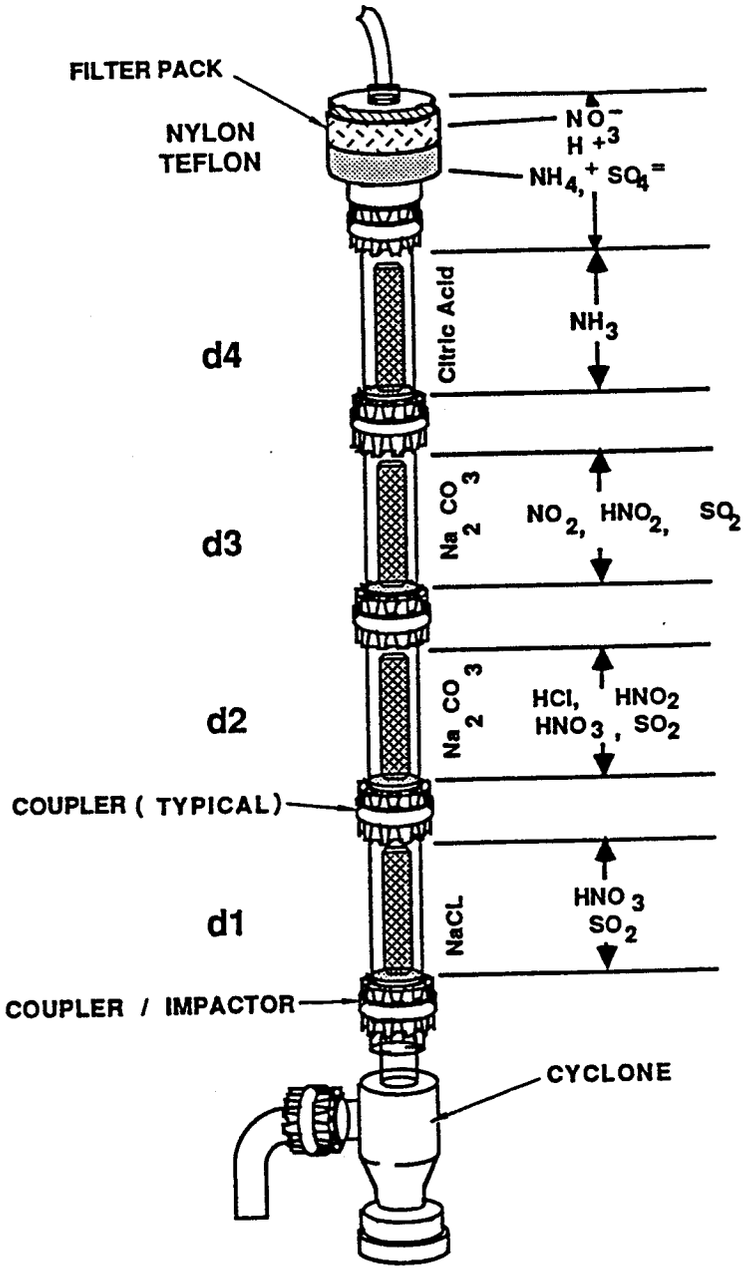

Figure 3. Schematic View of Annular Denuder with Cyclone Adaptor for Removal of Coarse Particles

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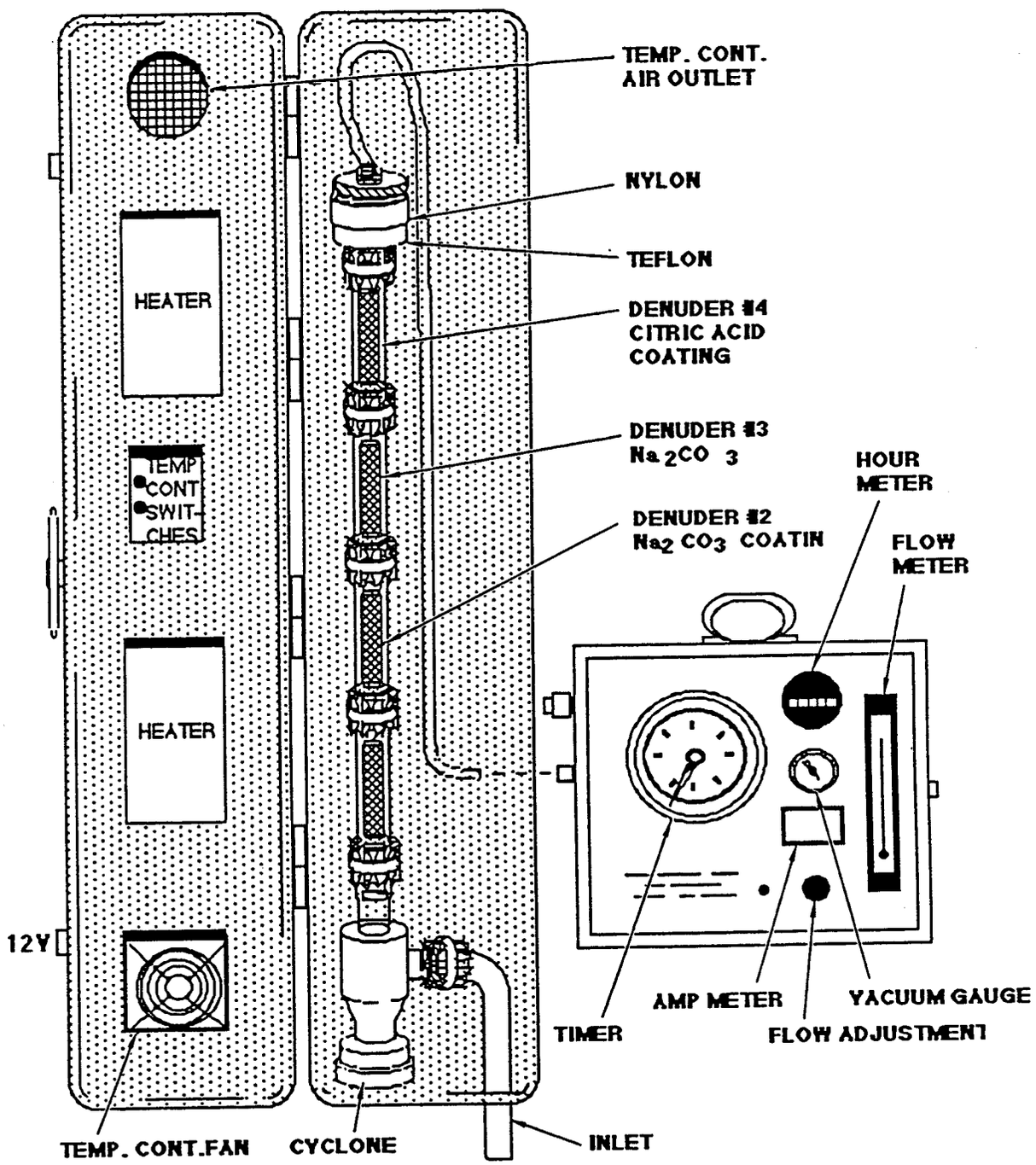

Figure 4. Annular Denuder System with Cyclone in Heated Sampling Case

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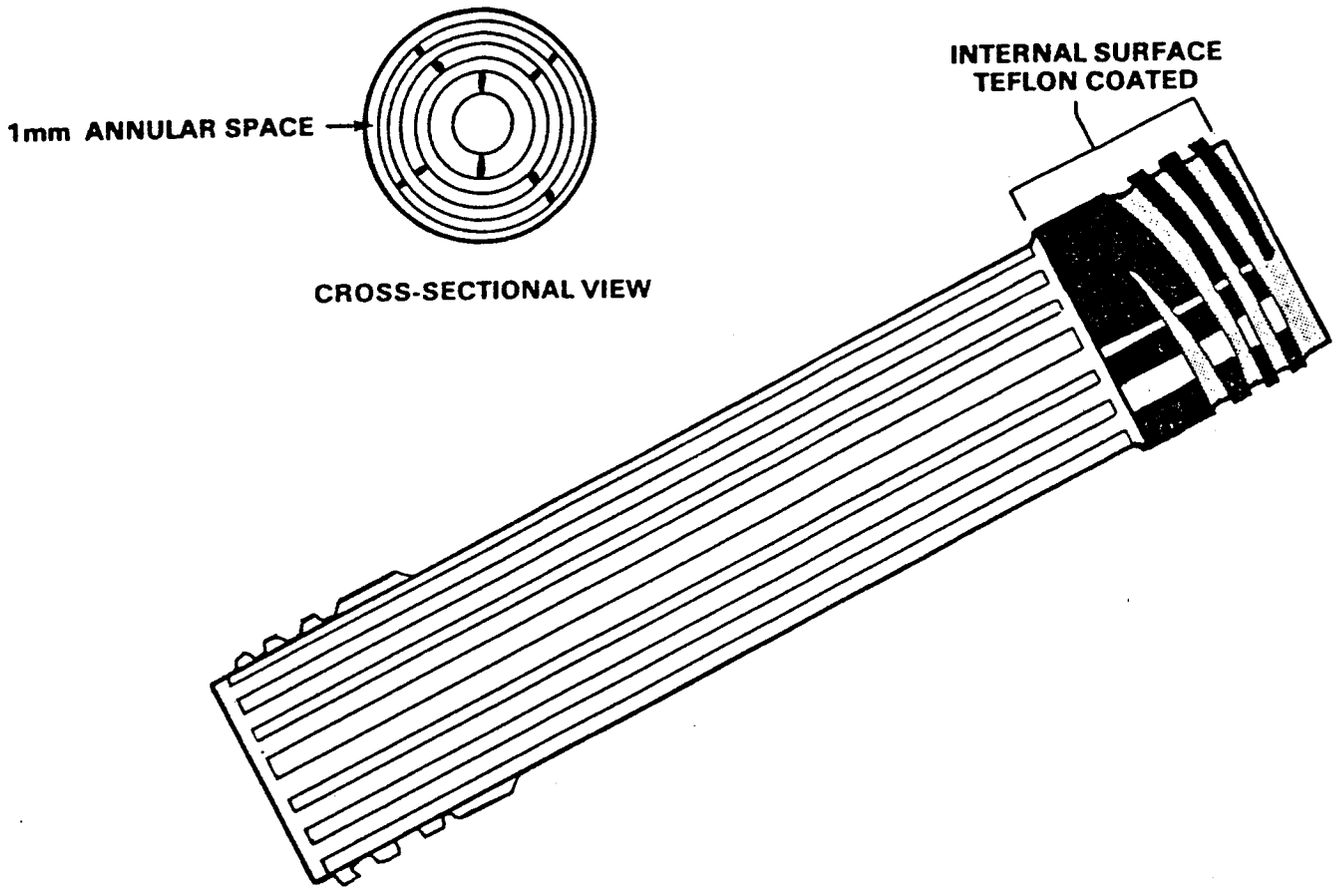

Figure 5. Internal Schematic of Annular Denuder

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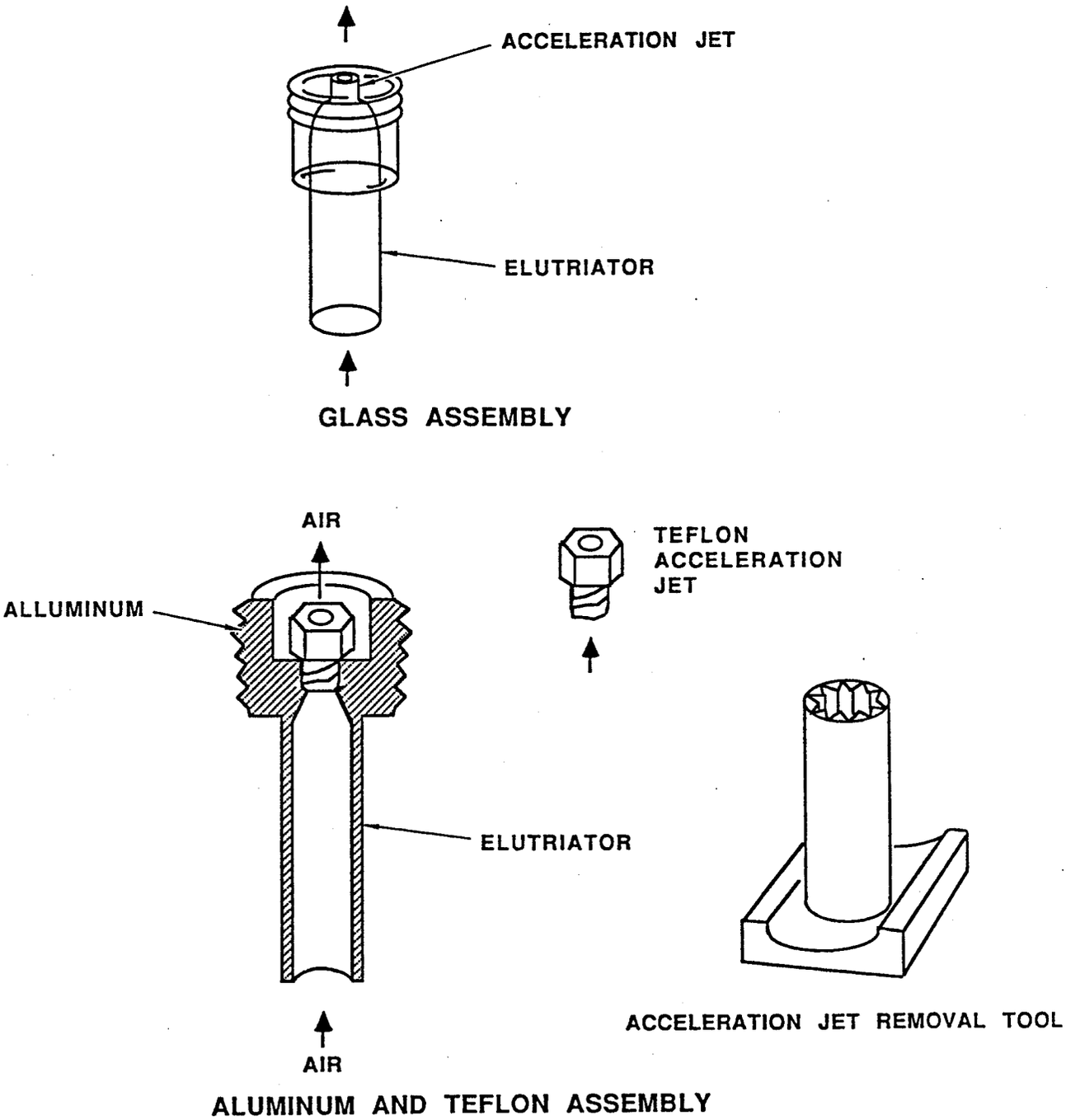

Figure 6. Available Elutriator and Acceleration Jet Assemblies

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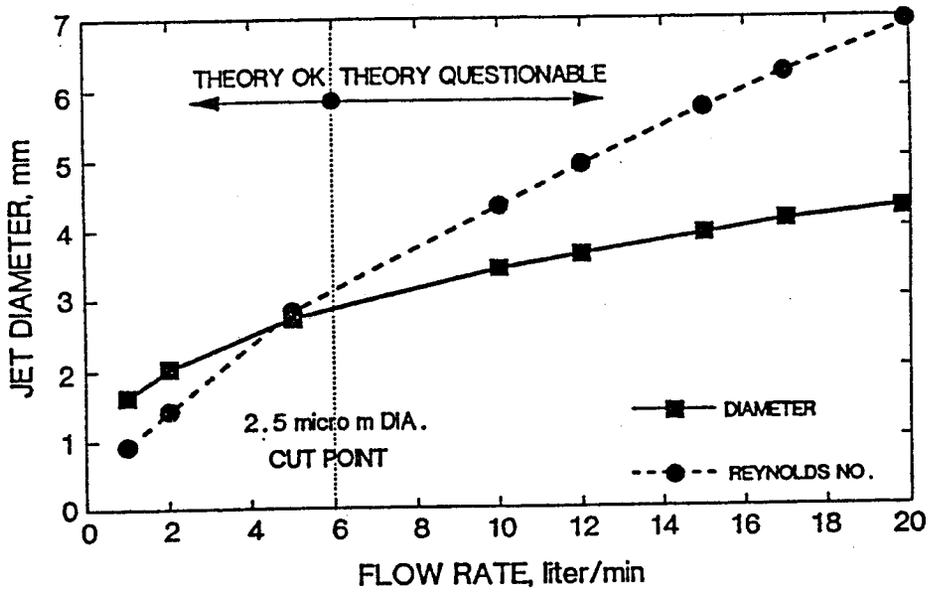

Figure 7A

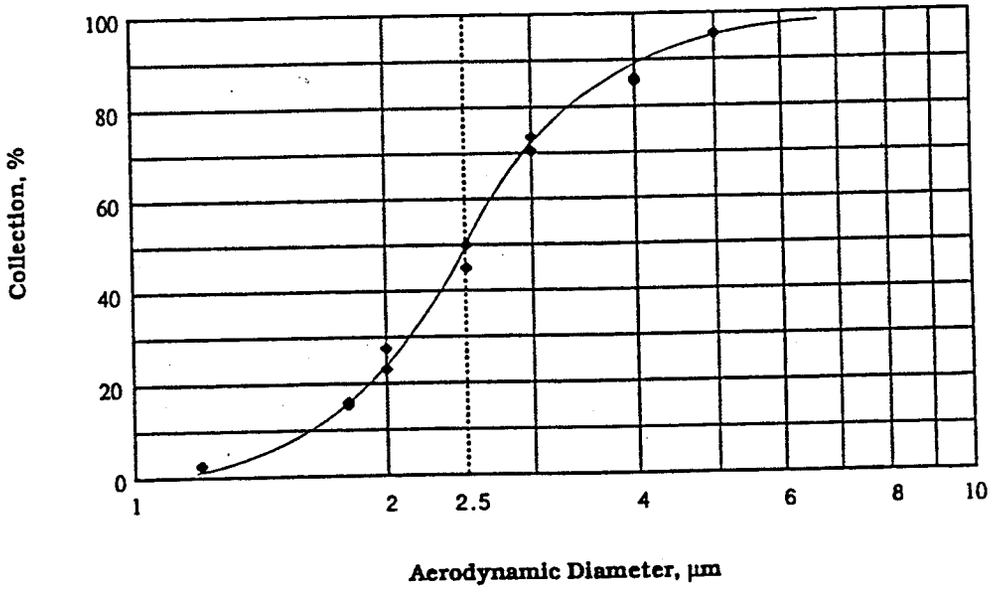

Figure 7B

Figure 7. D_{50} for Acceleration Jet (Figure 7A) and Teflon®-Coated Cyclone (Figure 7B)

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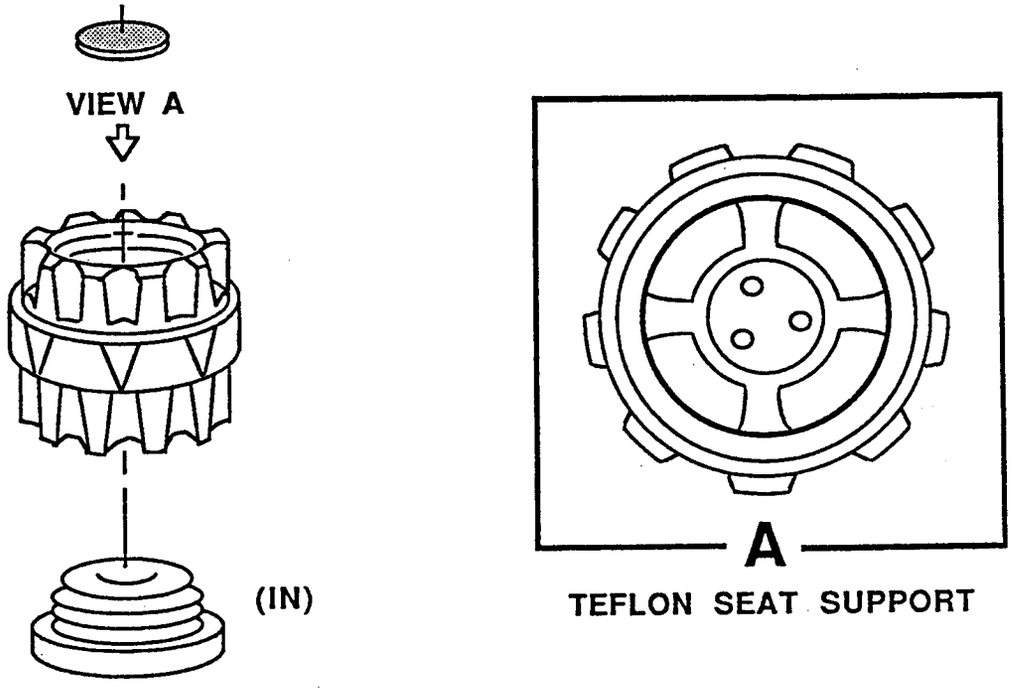

Figure 8. Side View Impactor/Coupler Assembly

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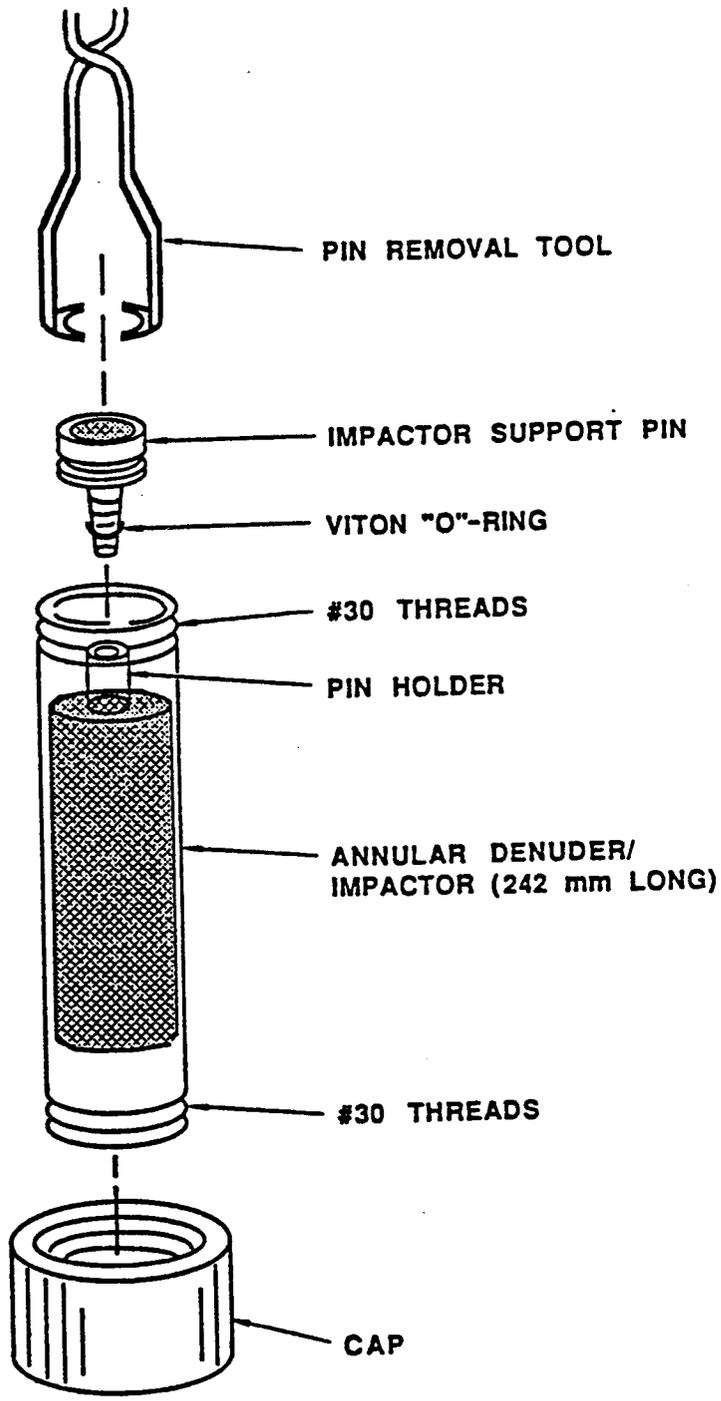

Figure 9. Glass Annular Denuder with Inset Impactor Assembly

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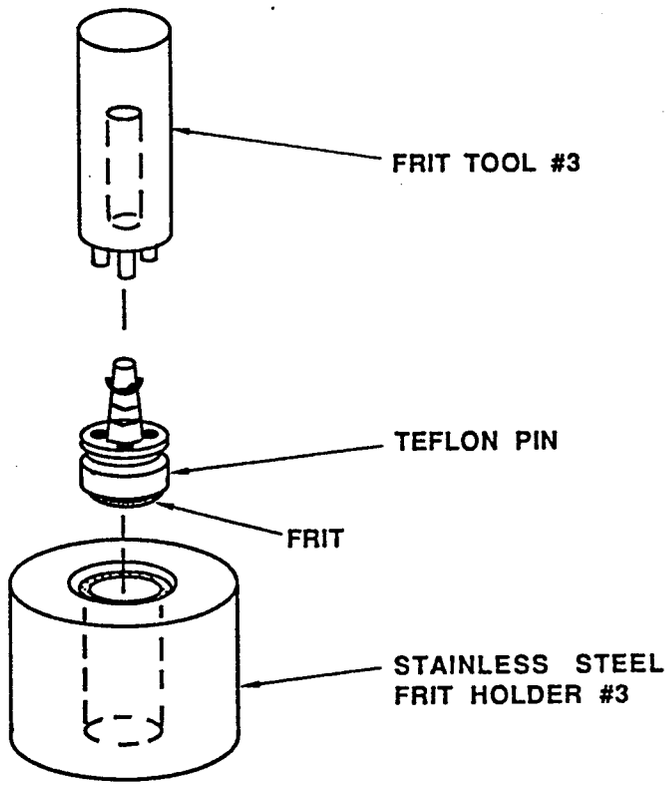

Figure 10. Frit Removal from Pin

134

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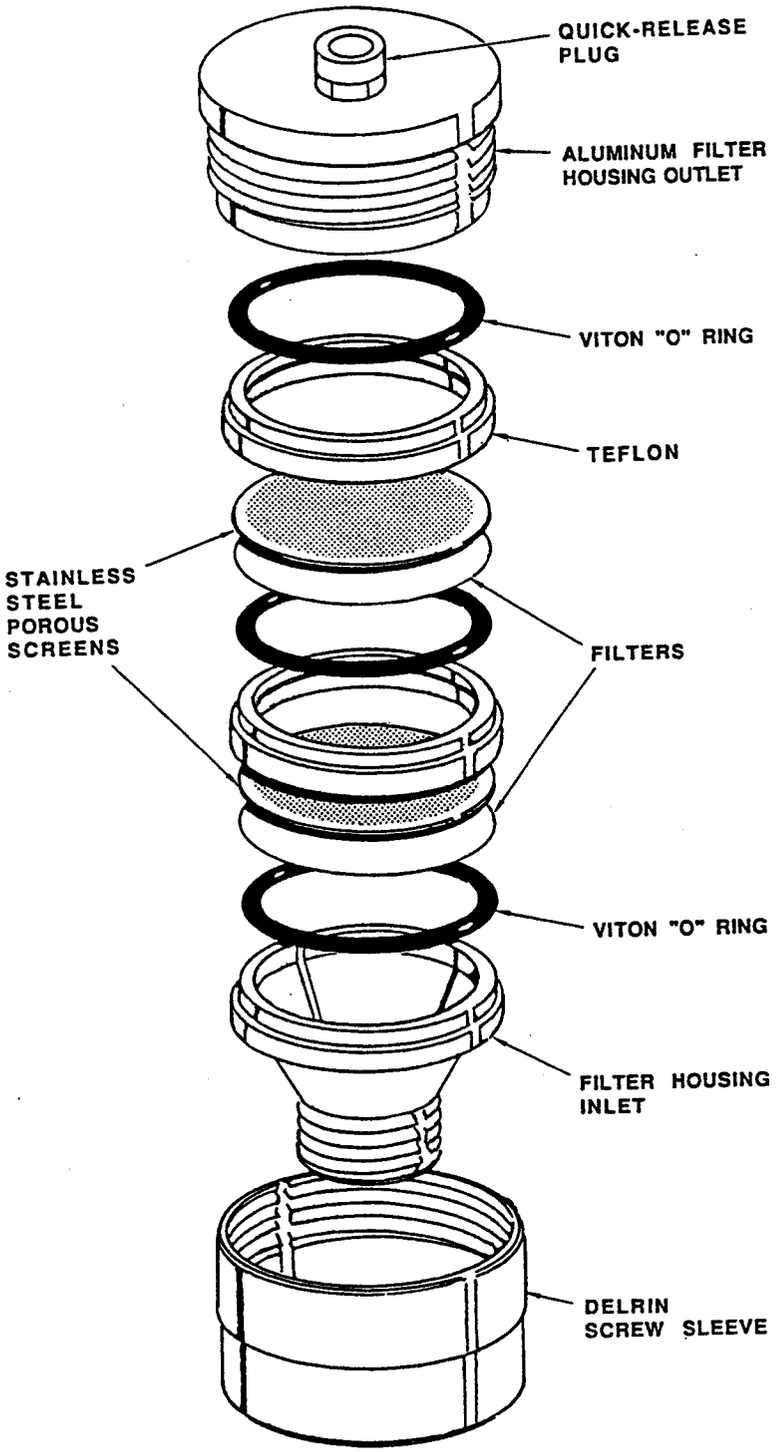

Figure 11. Filter Pack Assembly

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722

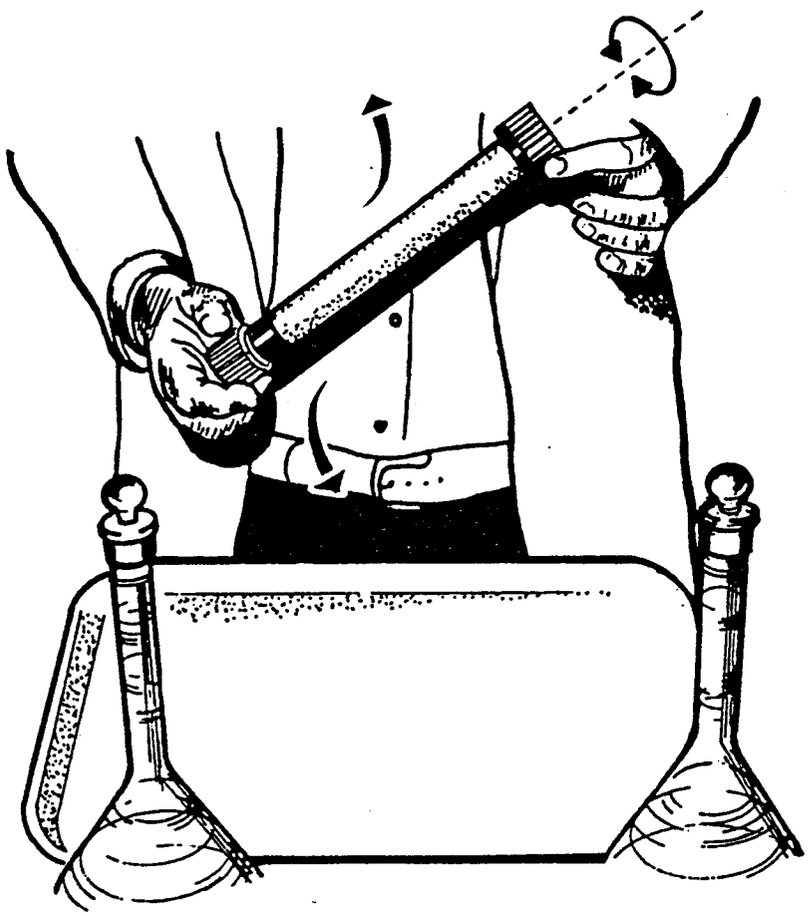

Figure 12. Annular Denuder Coating Procedure

136

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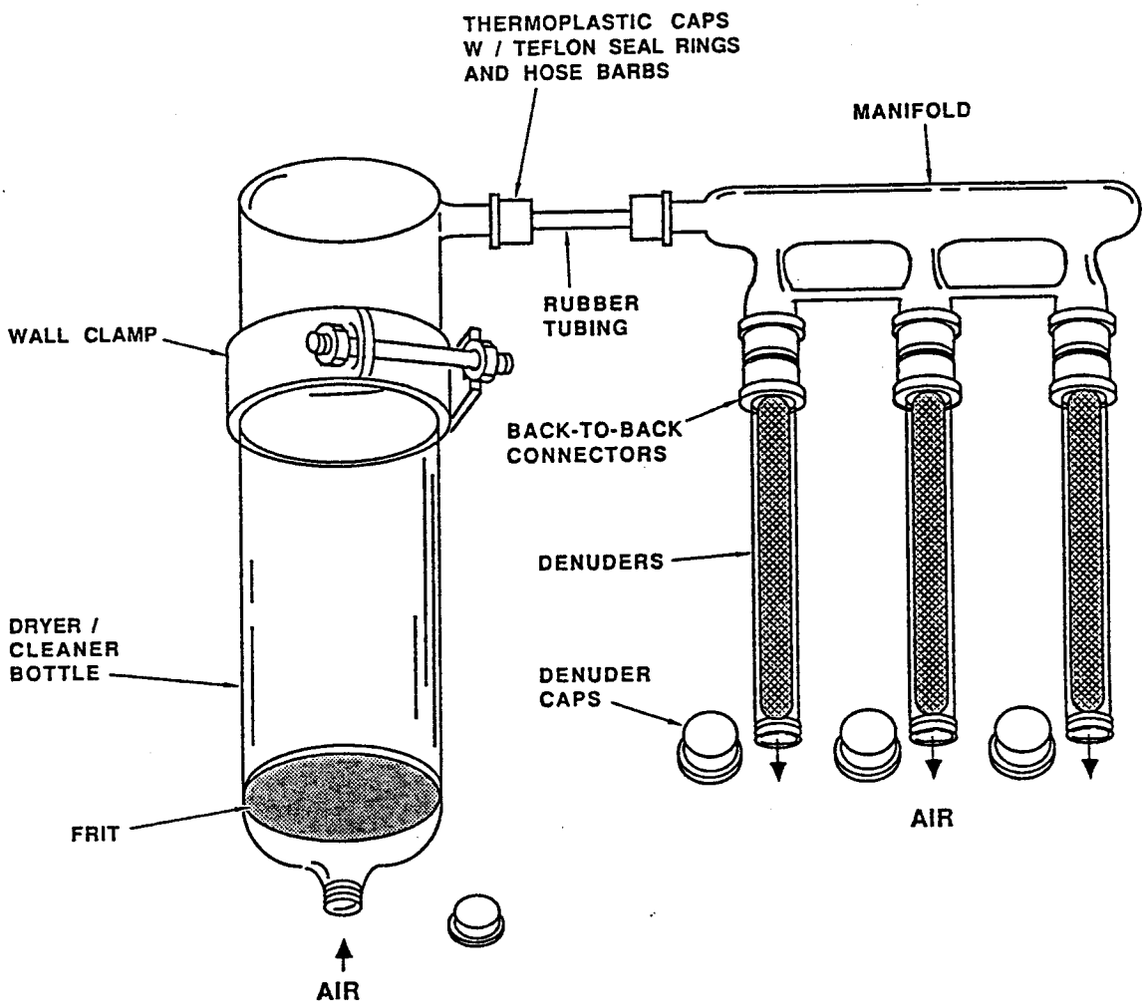

Figure 13. Drying Train and Manifold

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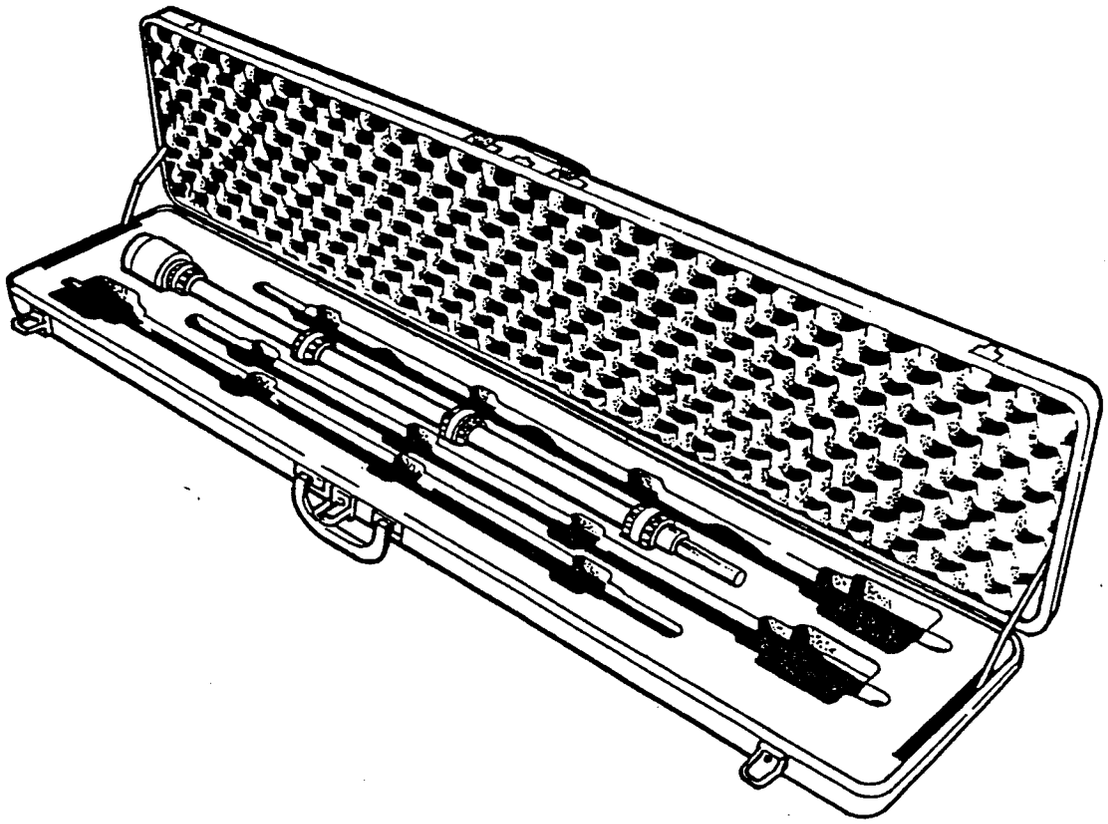

Figure 14. Annular Denuder in Field-to-Lab Case

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DENUDER LOG SHEET

Sample Period	Date	Time Start	Time Stop	Duration	Flow L/min	Denuder Sample #A	Denuder Sample #B	Denuder Sample #C	Nylon Filter Sample #	Teflon Filter Sample #	Comments

Figure 15. ADS Field Test Data Sheet

139

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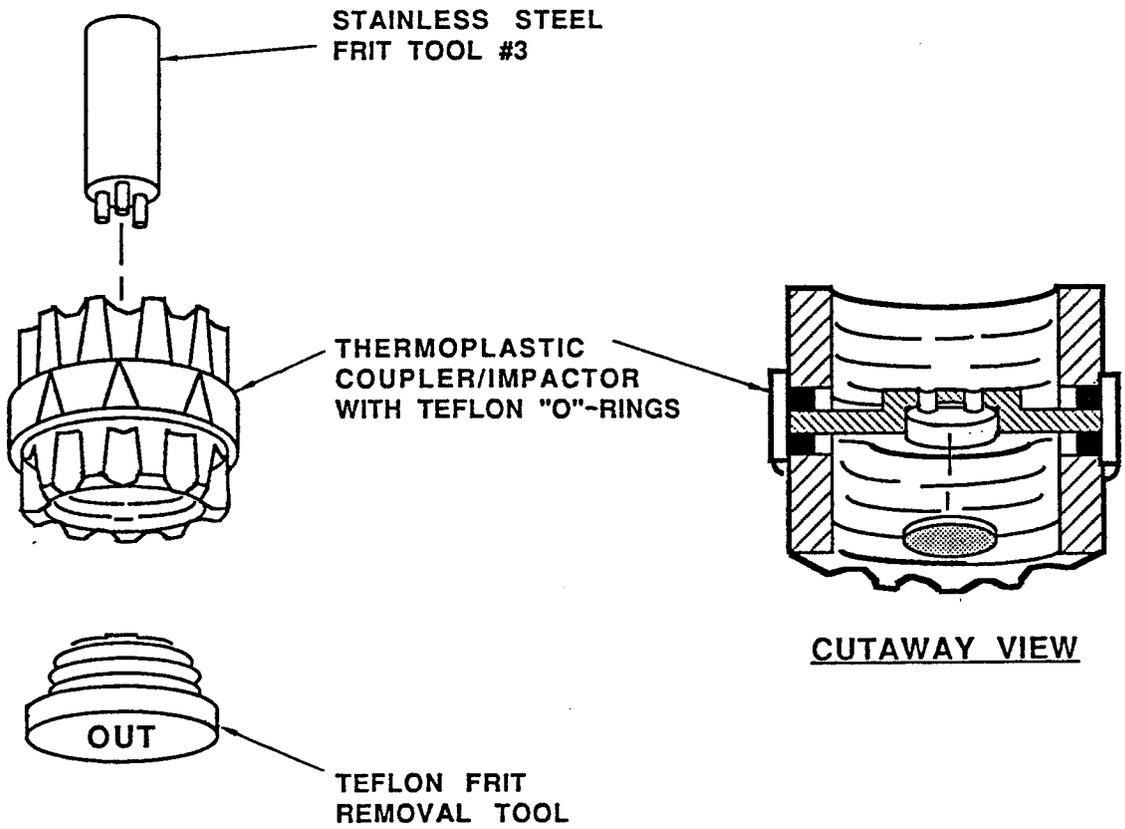

Figure 16. Side View Impactor/Coupler Assembly with Disc Removal Tools

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727

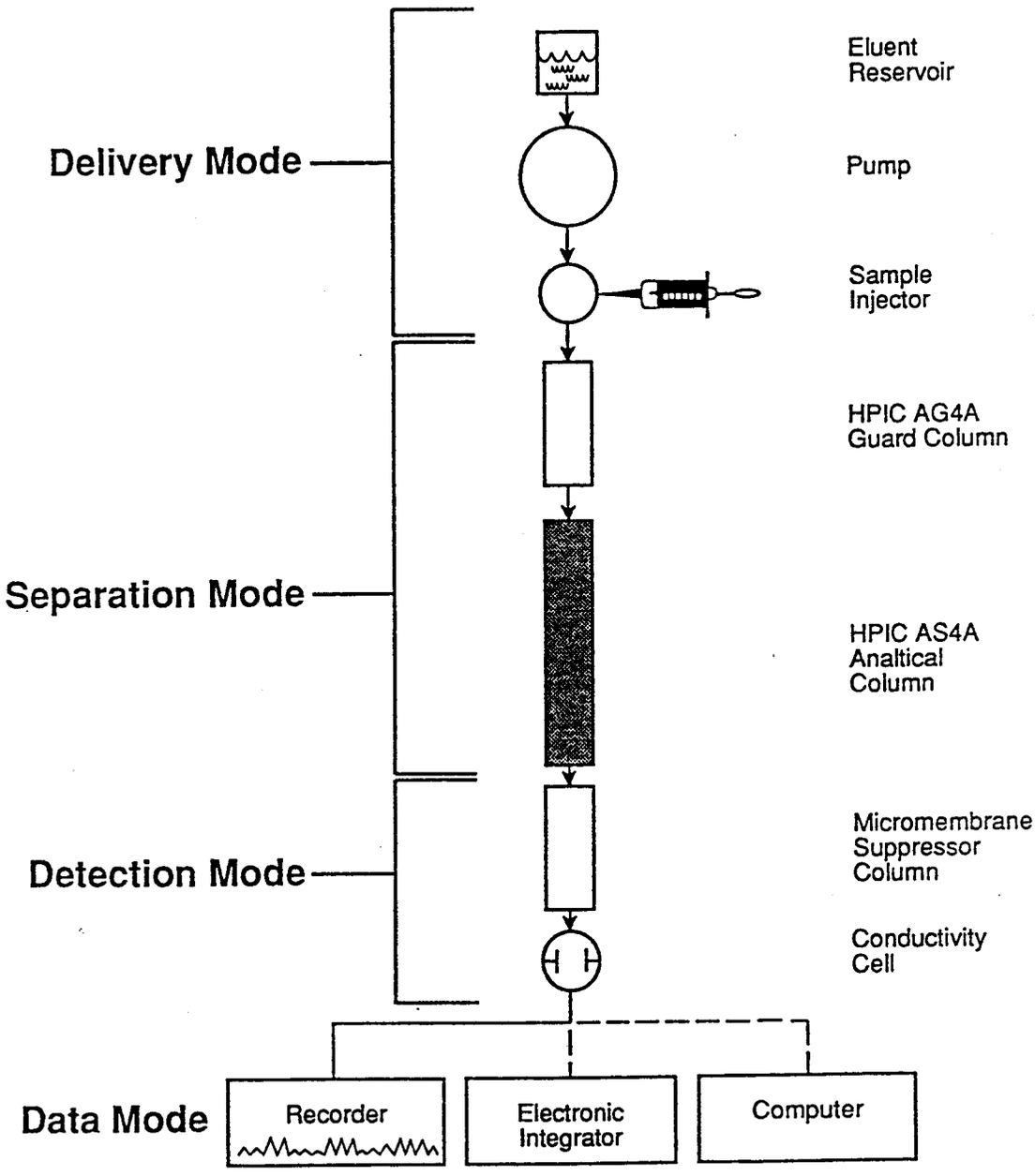

Figure 17. Major Components of a Commercially Available Ion Chromatographer

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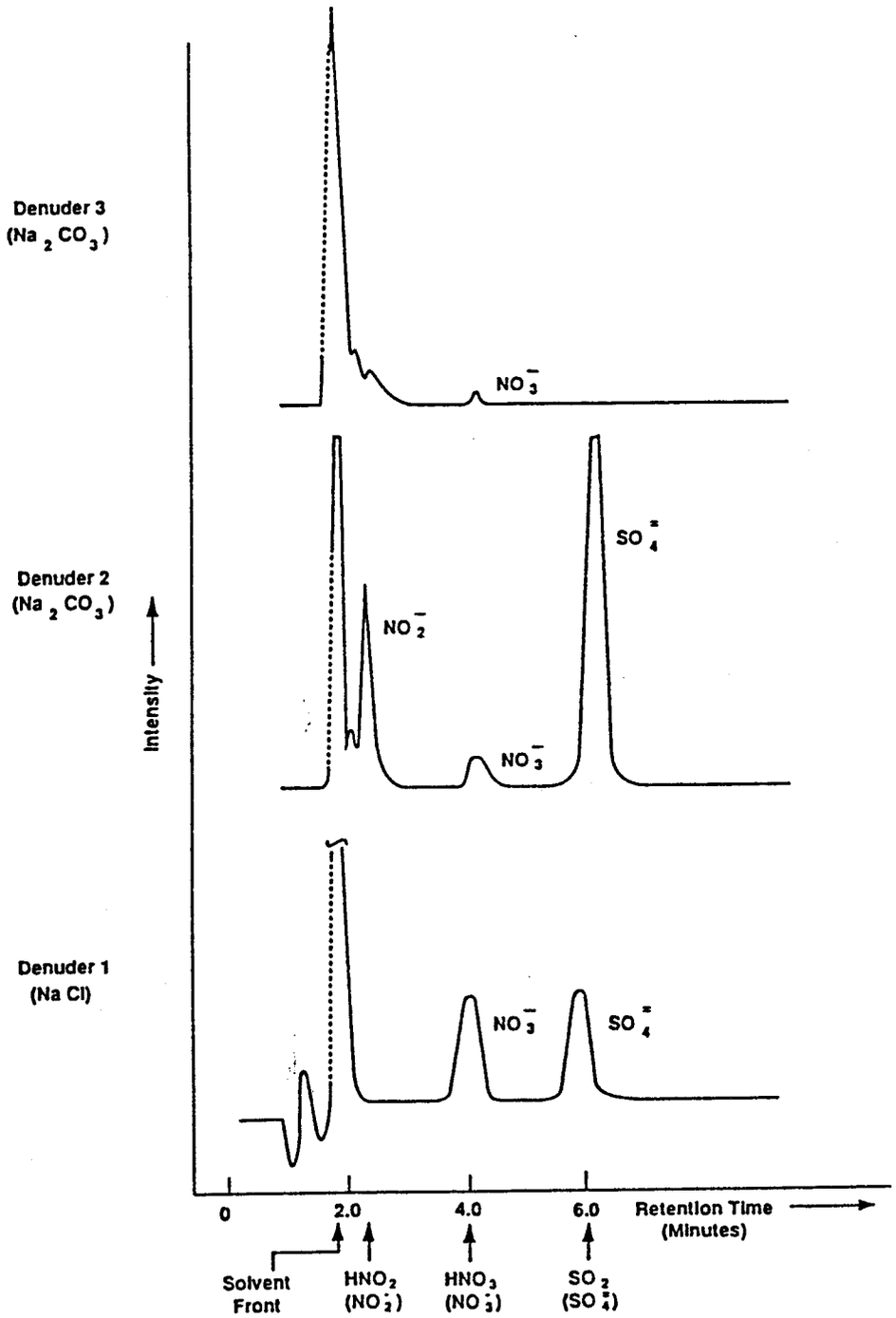

Figure 18. Chromatograms of Denuder/Filter Extract Performed by the Ion Chromatography

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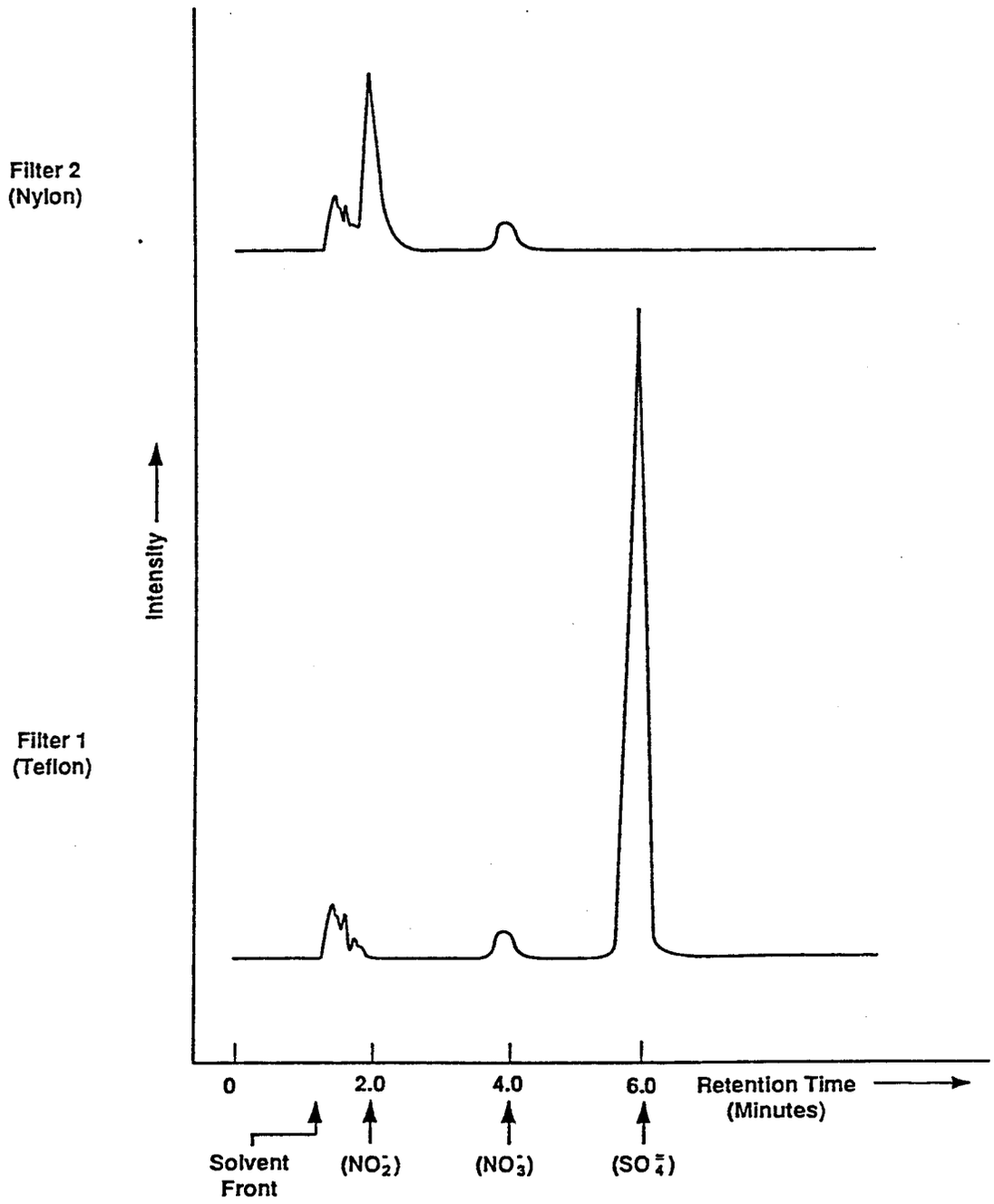

Figure 18 (Cont'd). Chromatograms of Denuder/Filter Extract Performed by the Ion Chromatography

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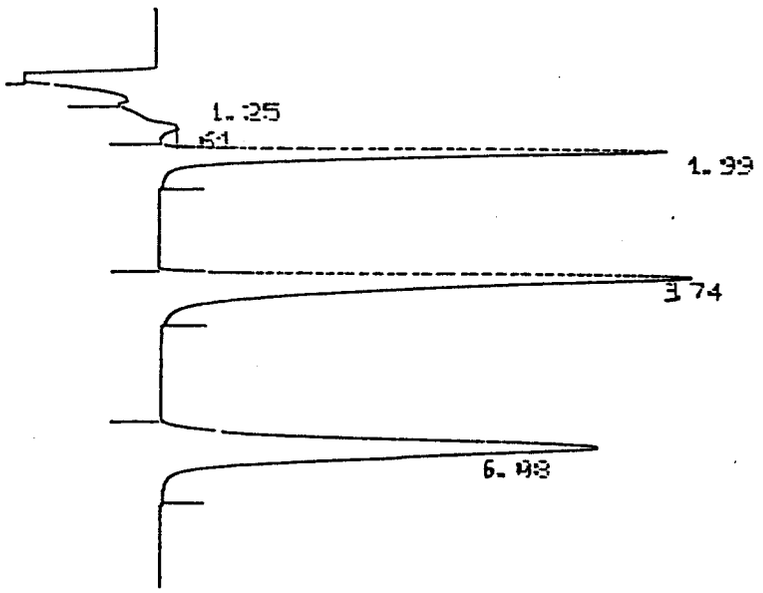
DATA. CHANNEL A

SAMPLES FROM 1. TO 12. REPLICATES= 1.
CHANNEL A INJECT 05:22:17



ANIONS 05:22:17 CH= "A" PS= 1

FILE 2. METHOD 5. RUN 1 INDEX 1

ANALYST= BELL

NAME	PPM	RT	AREA	BC	RF	RRT
NO2	2.463	1.99	3009801	033252050.75		0.327
NO3	4.329	3.74	11145516	012308038.104		0.615
SO4	3.83	6.08	11581441	013023874.934		1.
TOTALS	11.122		30736758			

PEAK HEIGHTS= 1 78** 2 38** 3 440** 4 437** 5 358**
RT SET 1.836 3.4834 5.3244

Figure 19. Chromatogram of a Standard with Nitrous Acid, Nitric Acid, and Sulfuric Acid

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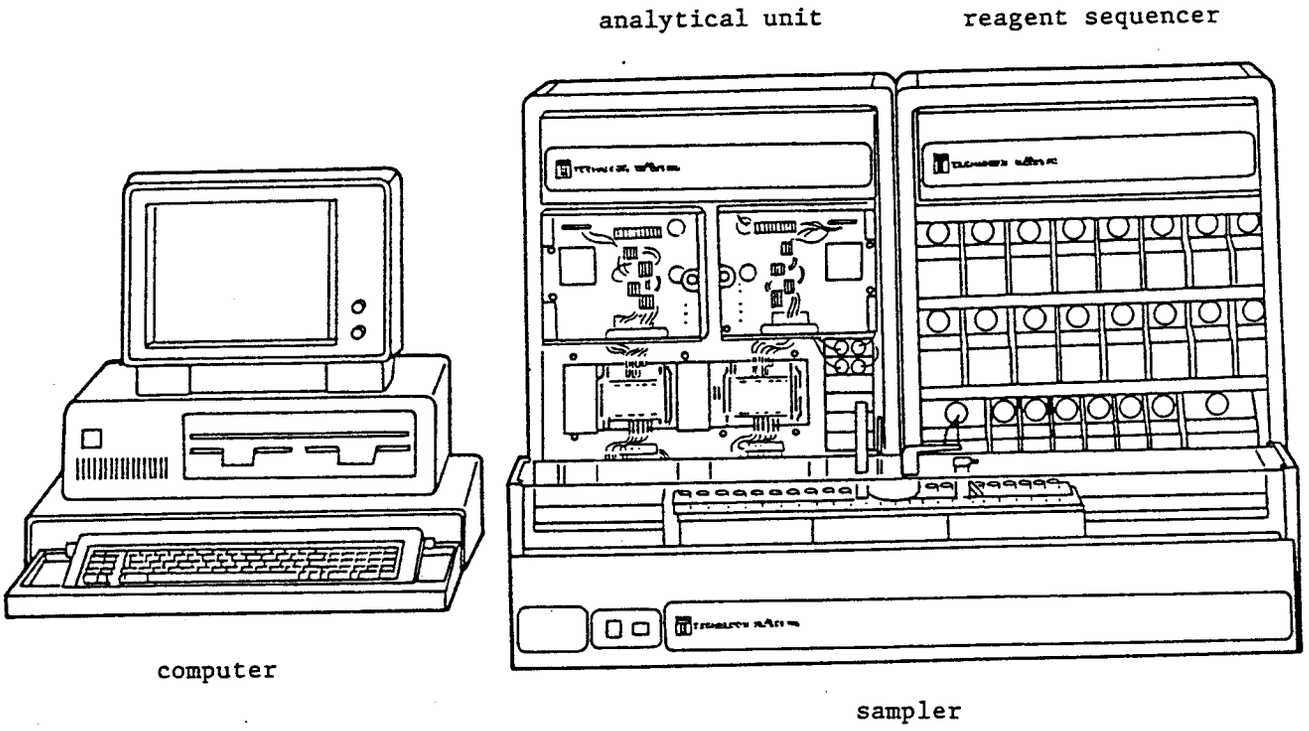

Figure 20. 4-Channel Traacs 800 System with Reagent Sequencer

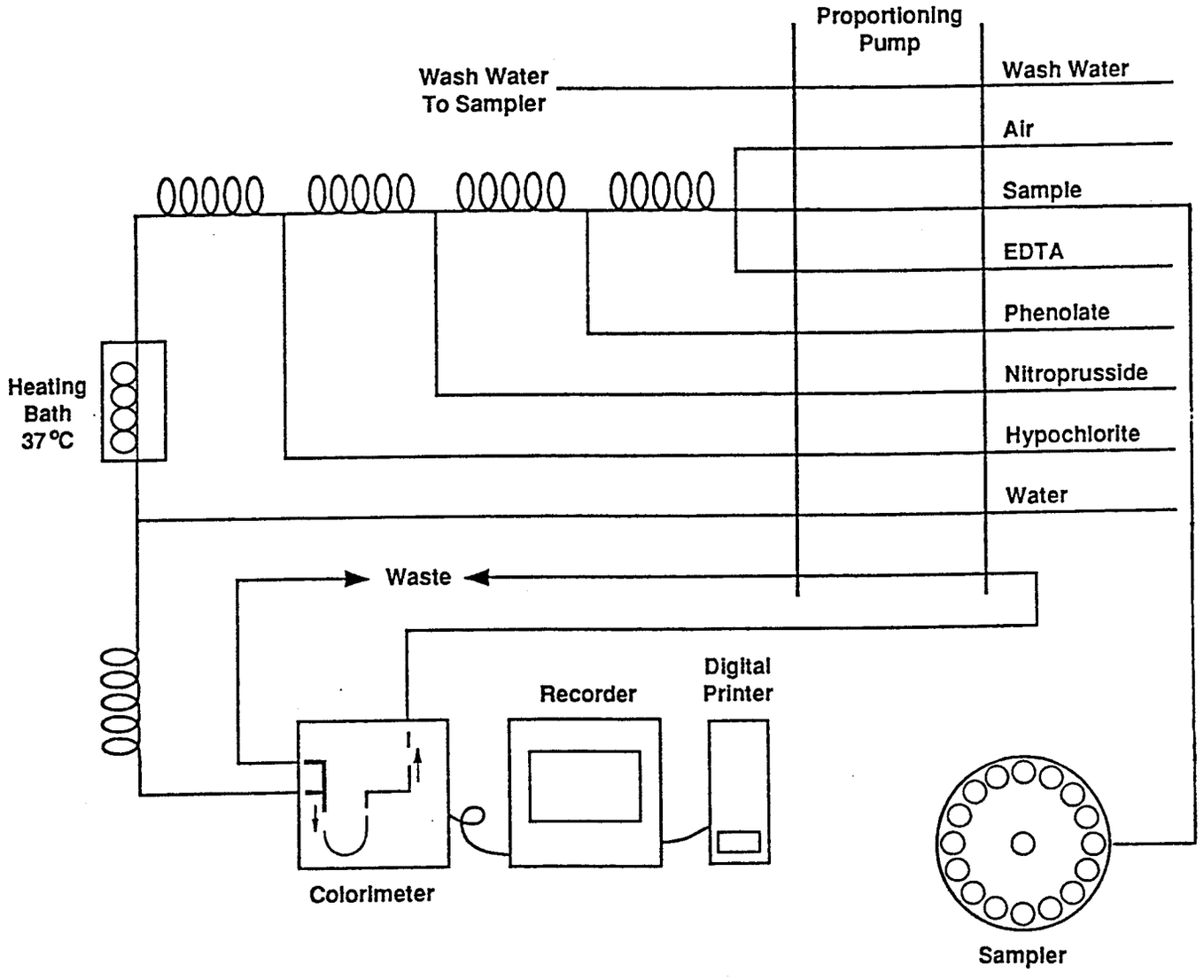

Figure 21. Technicon Autoanalyzer Flow Diagram for Ammonia Analysis

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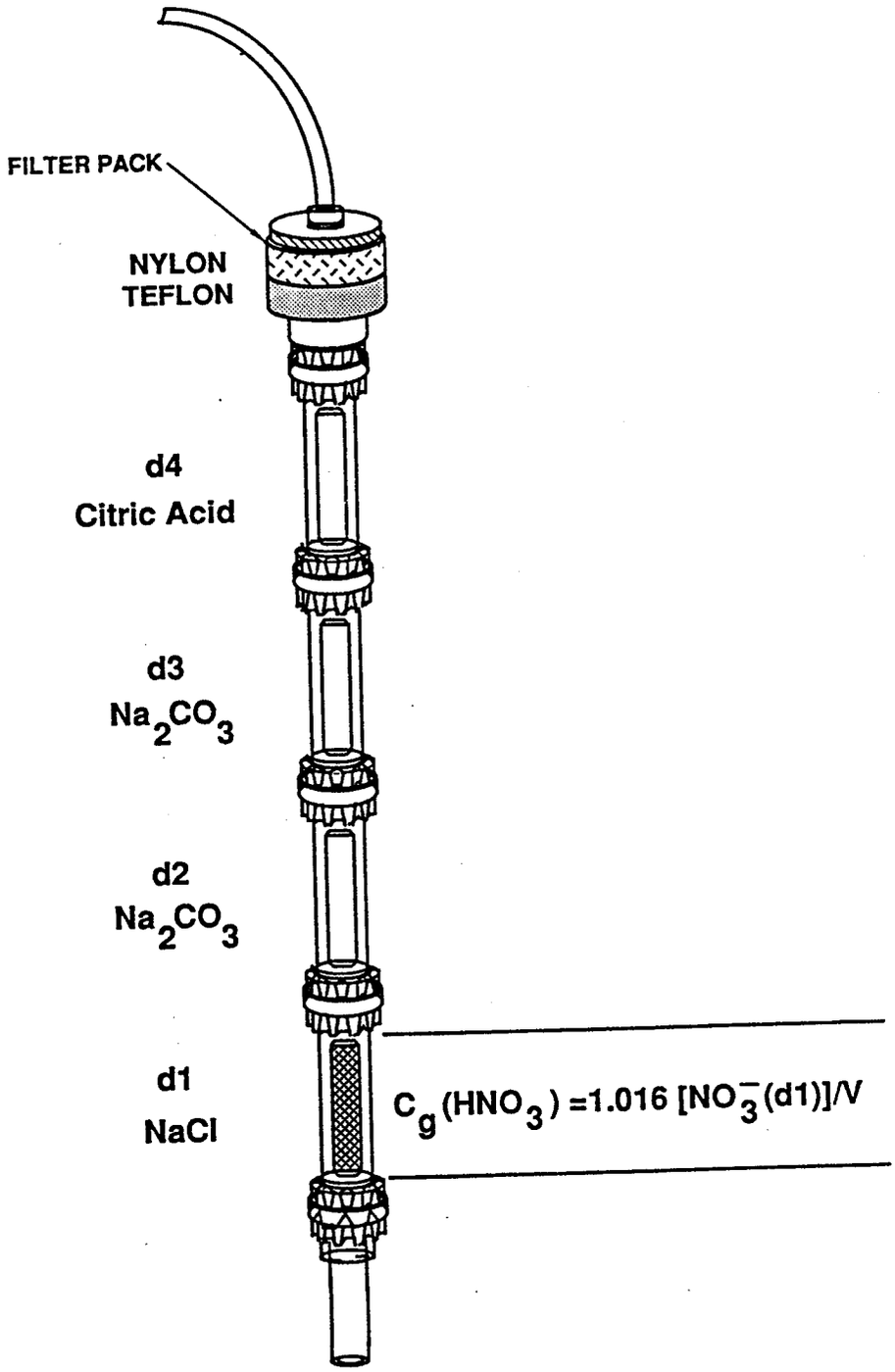

Figure 22. Nitric Acid Gas Measurement

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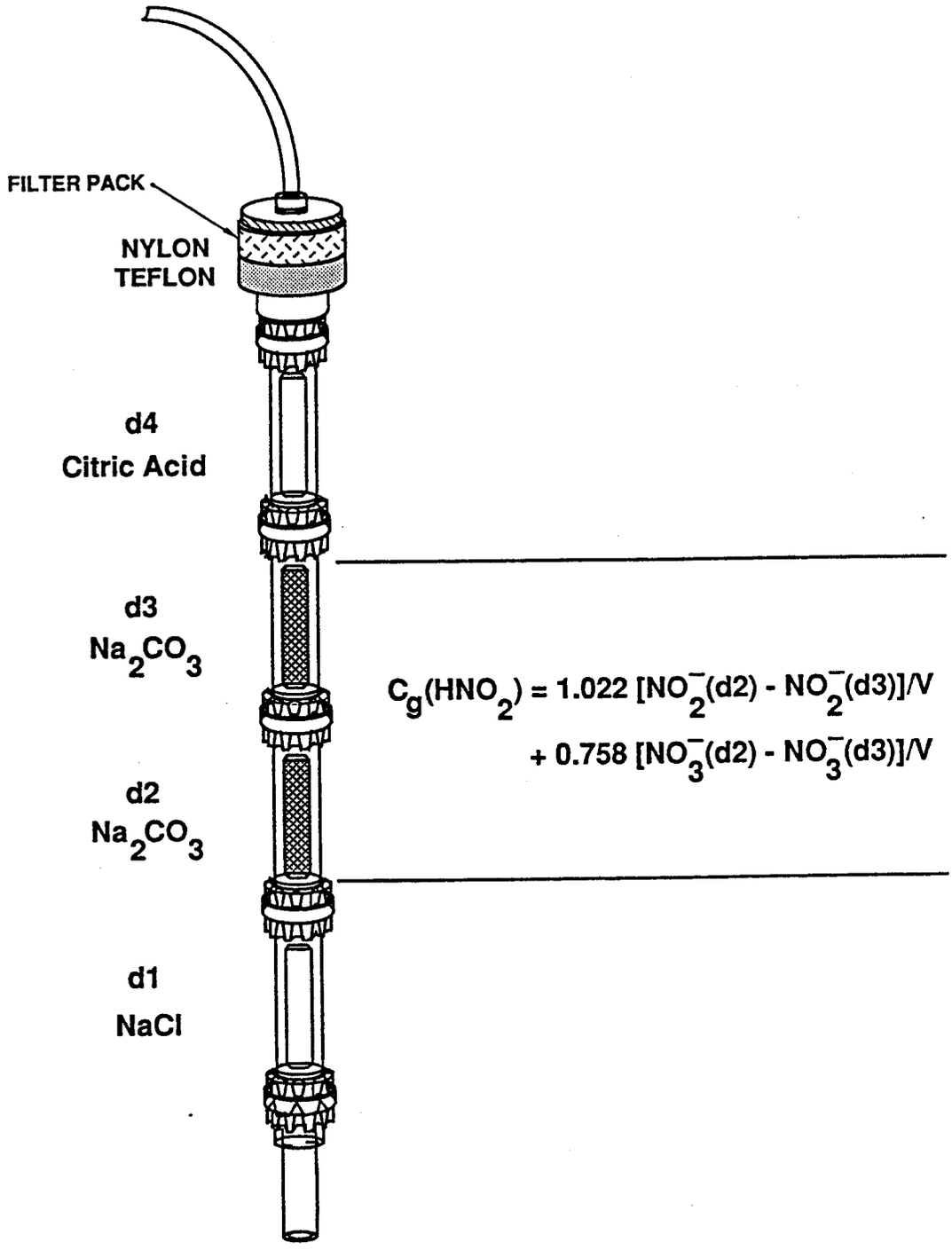

Figure 23. Nitrous Acid Gas Measurement

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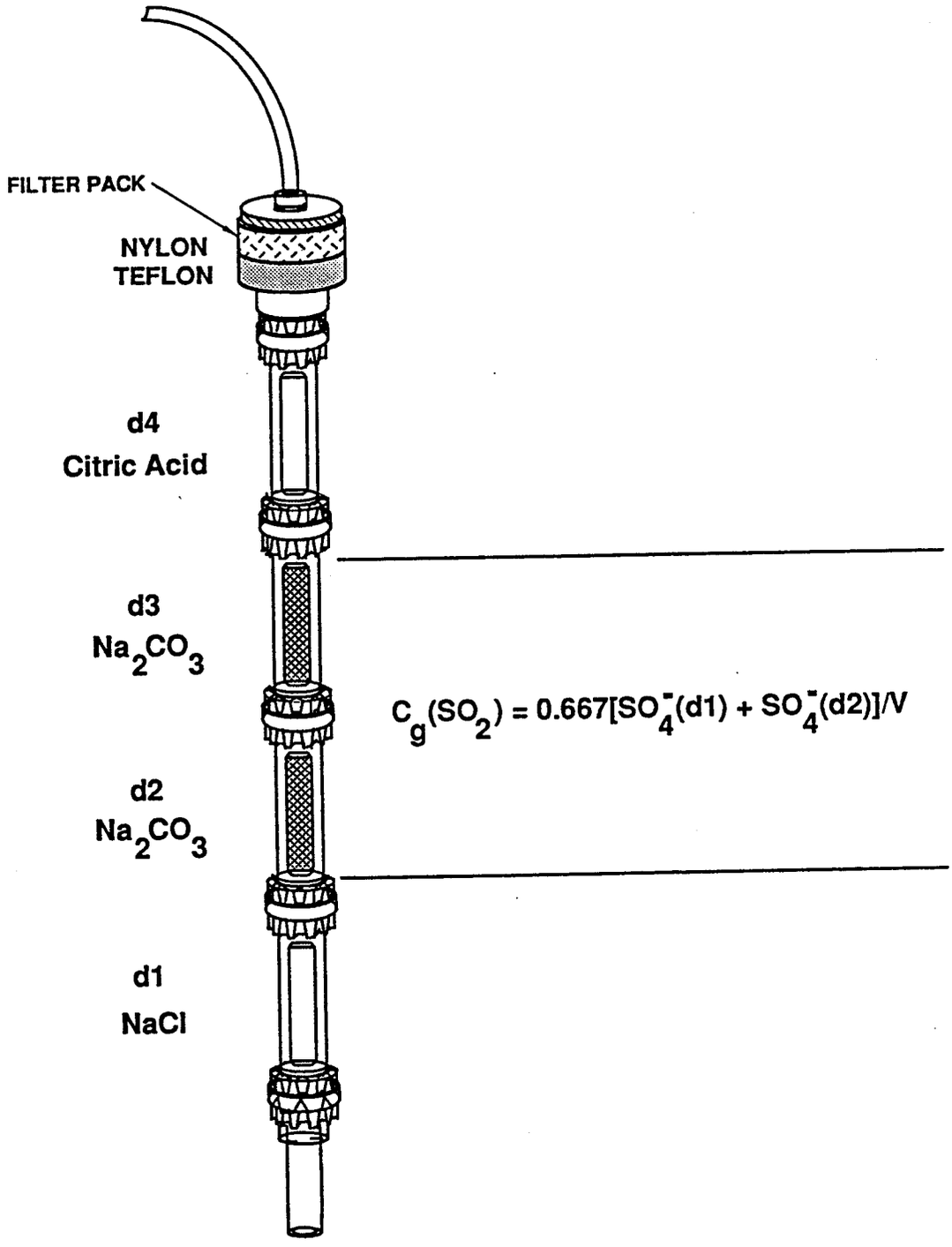

Figure 24. Sulfur Dioxide Gas Measurement

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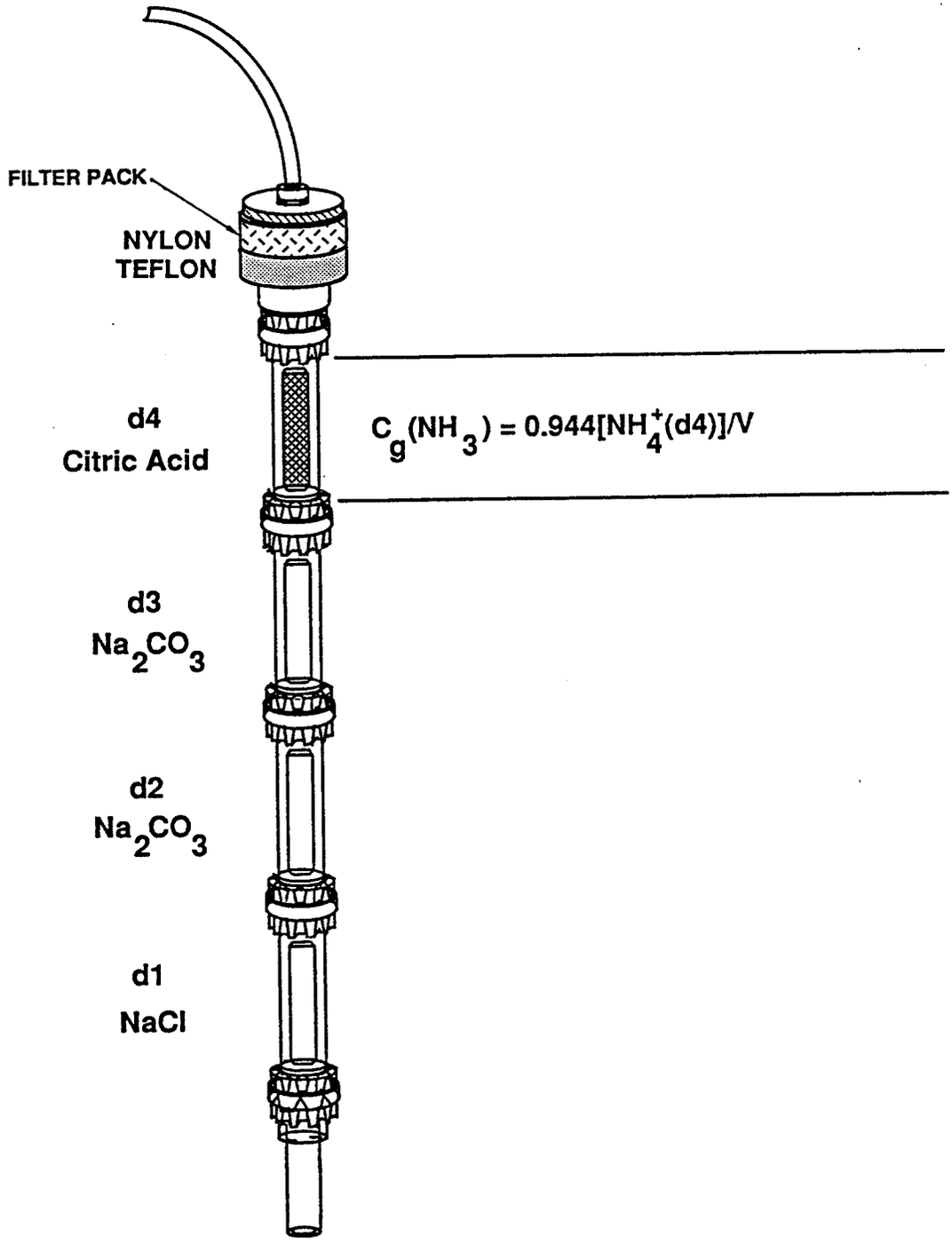

Figure 25. Ammonia Gas Measurement

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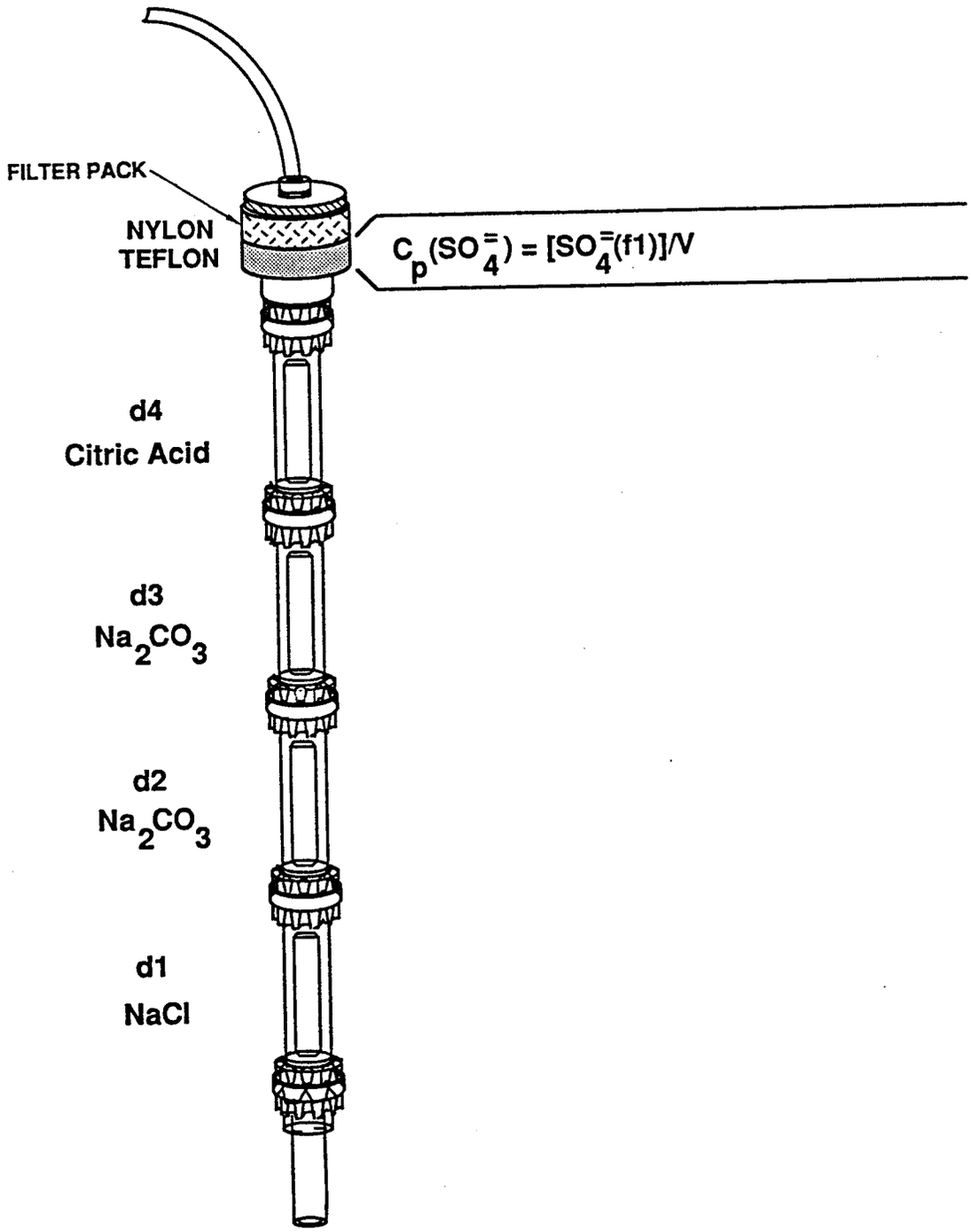

Figure 26. Particulate Sulfate Measurement

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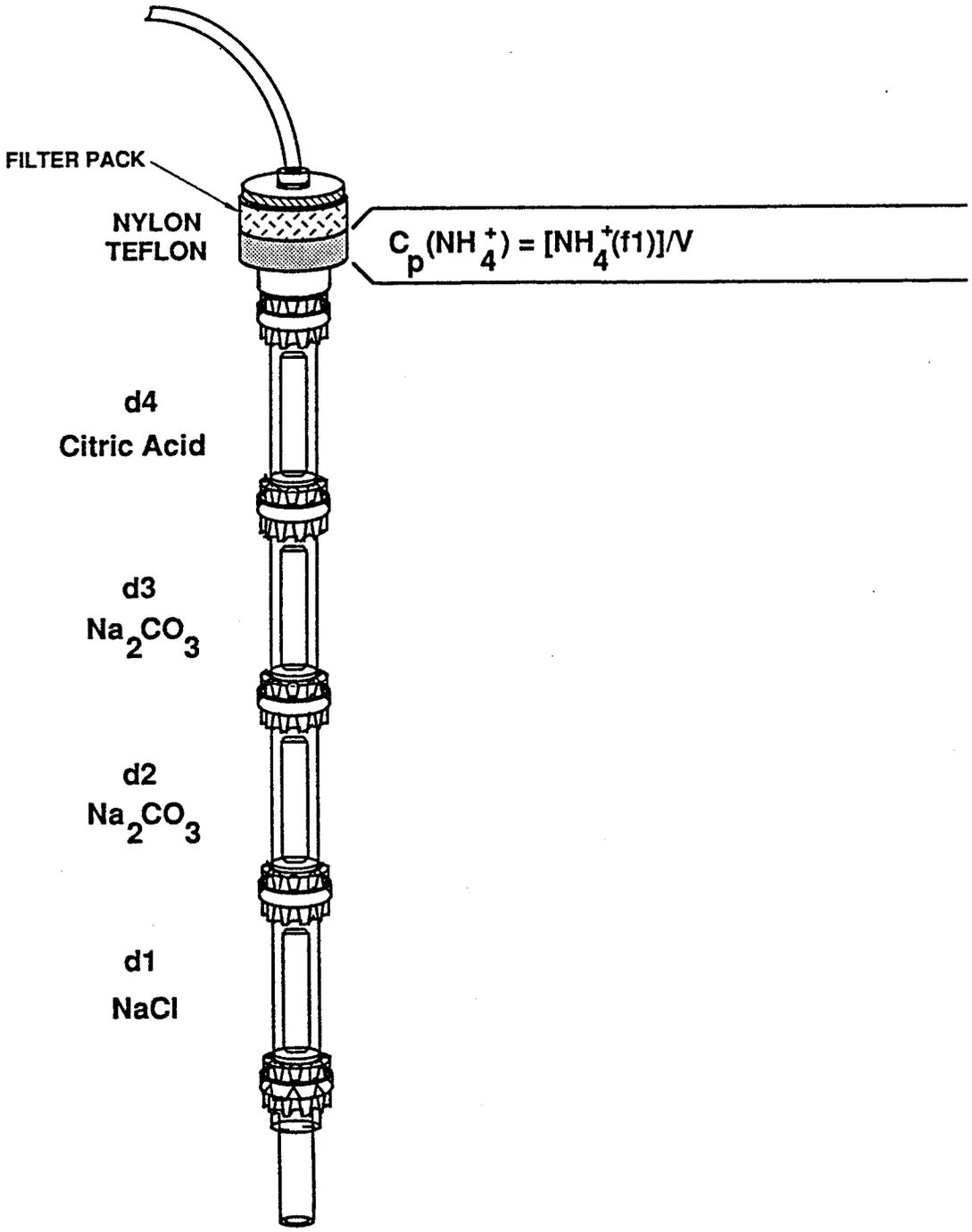

Figure 27. Particulate Ammonium Measurement

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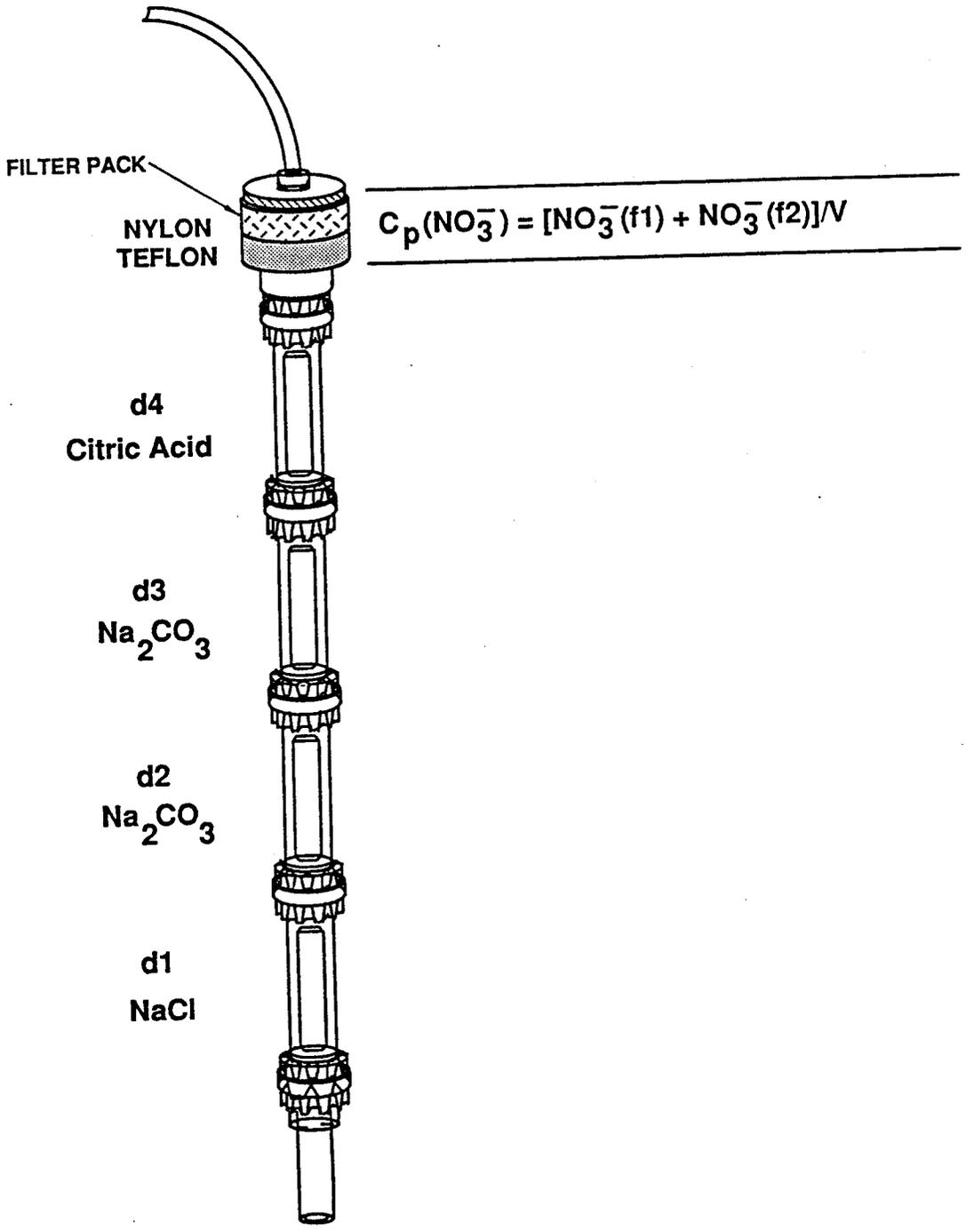

Figure 28. Particulate Nitrate Measurement

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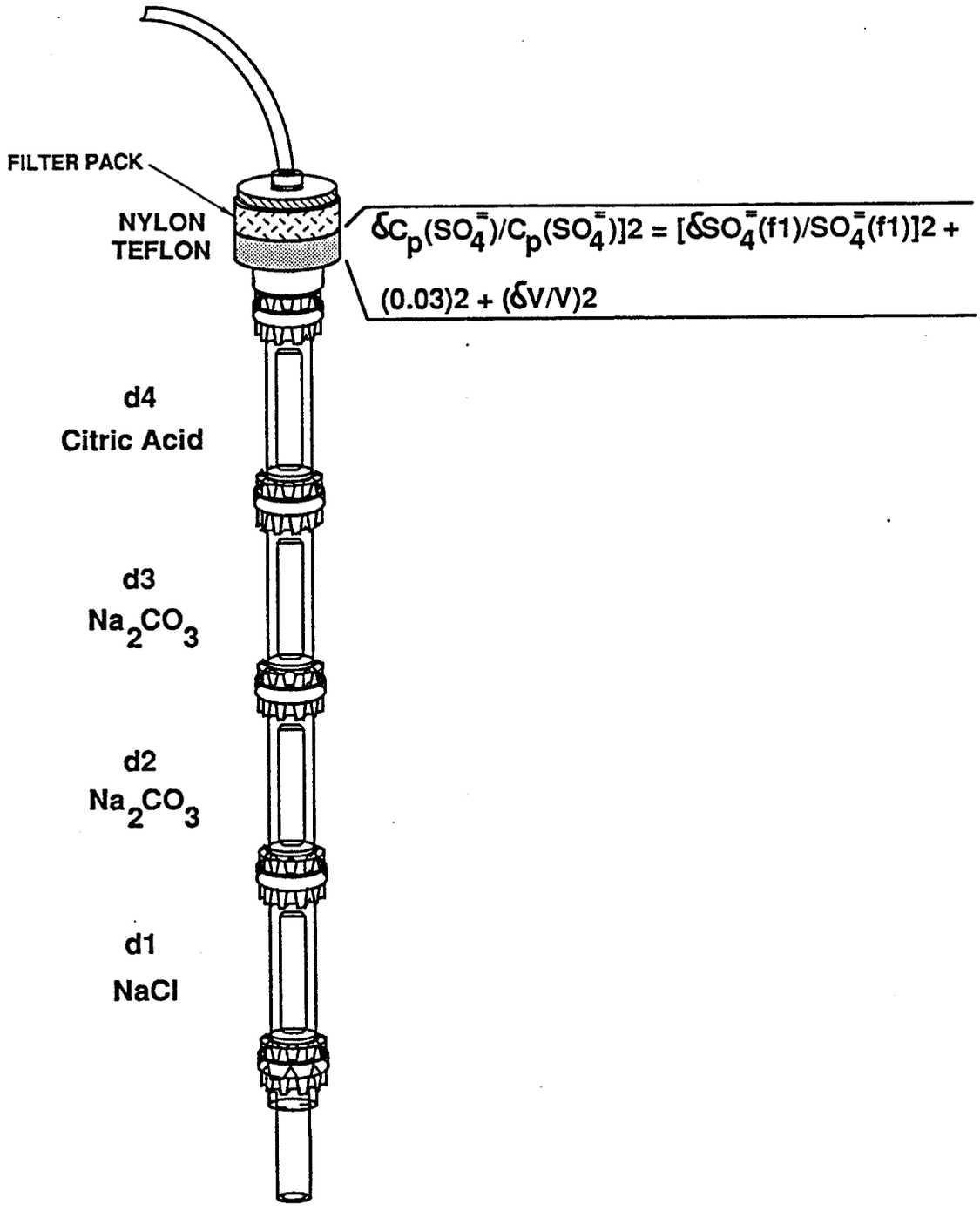

Figure 29. Particulate Sulfate Measurement and Uncertainties

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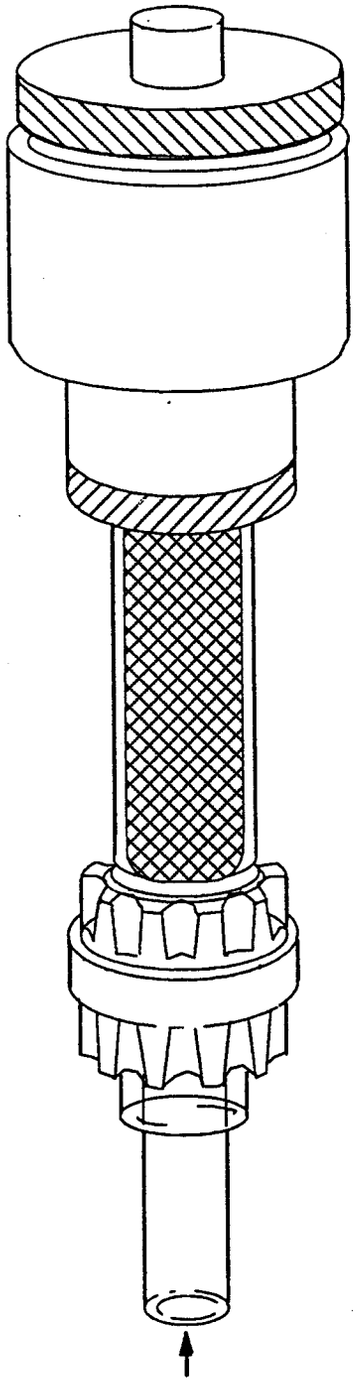

Figure 30. Annular Denuder Personal Sampler

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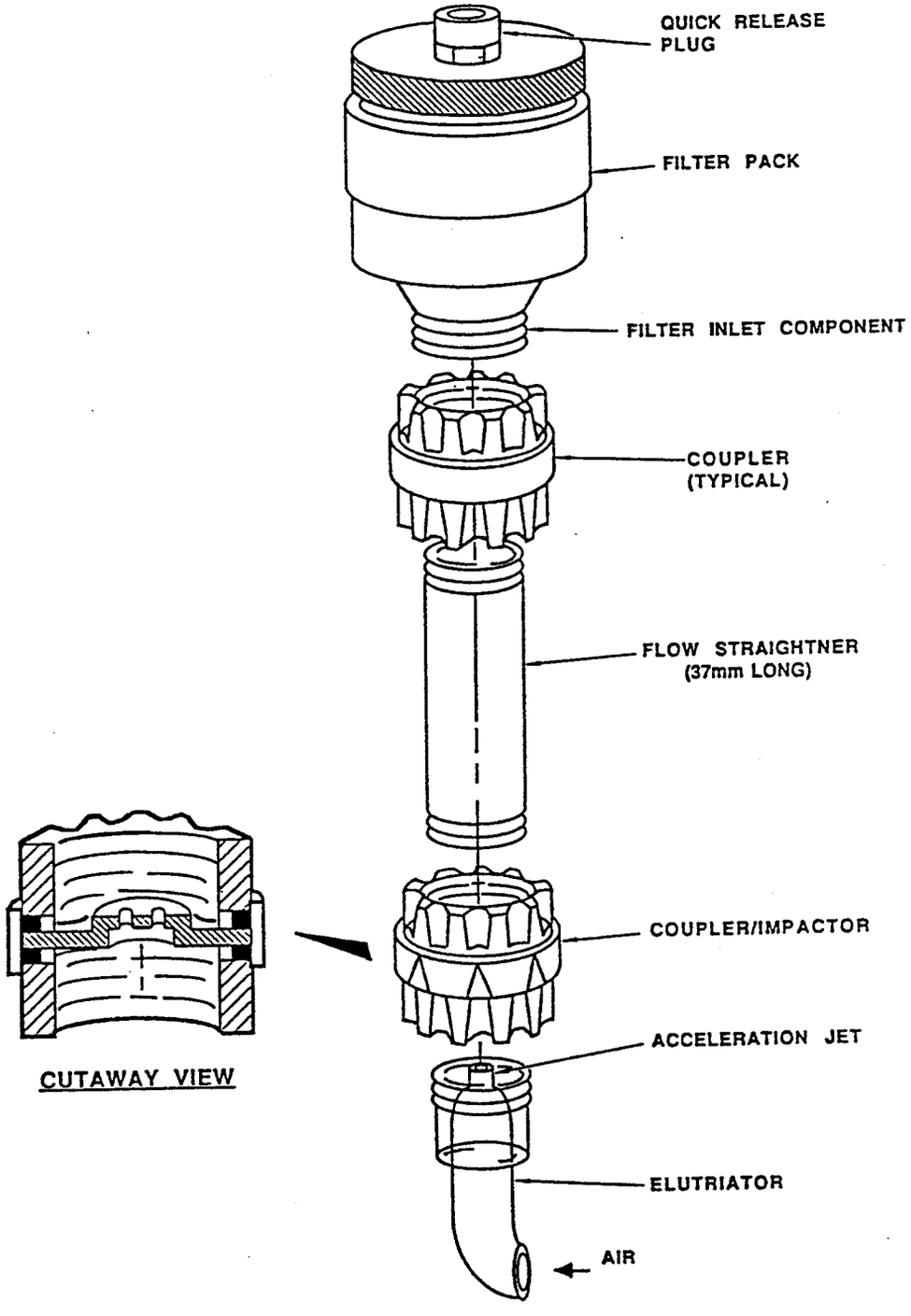

Figure 31. Fine Particle Sampler

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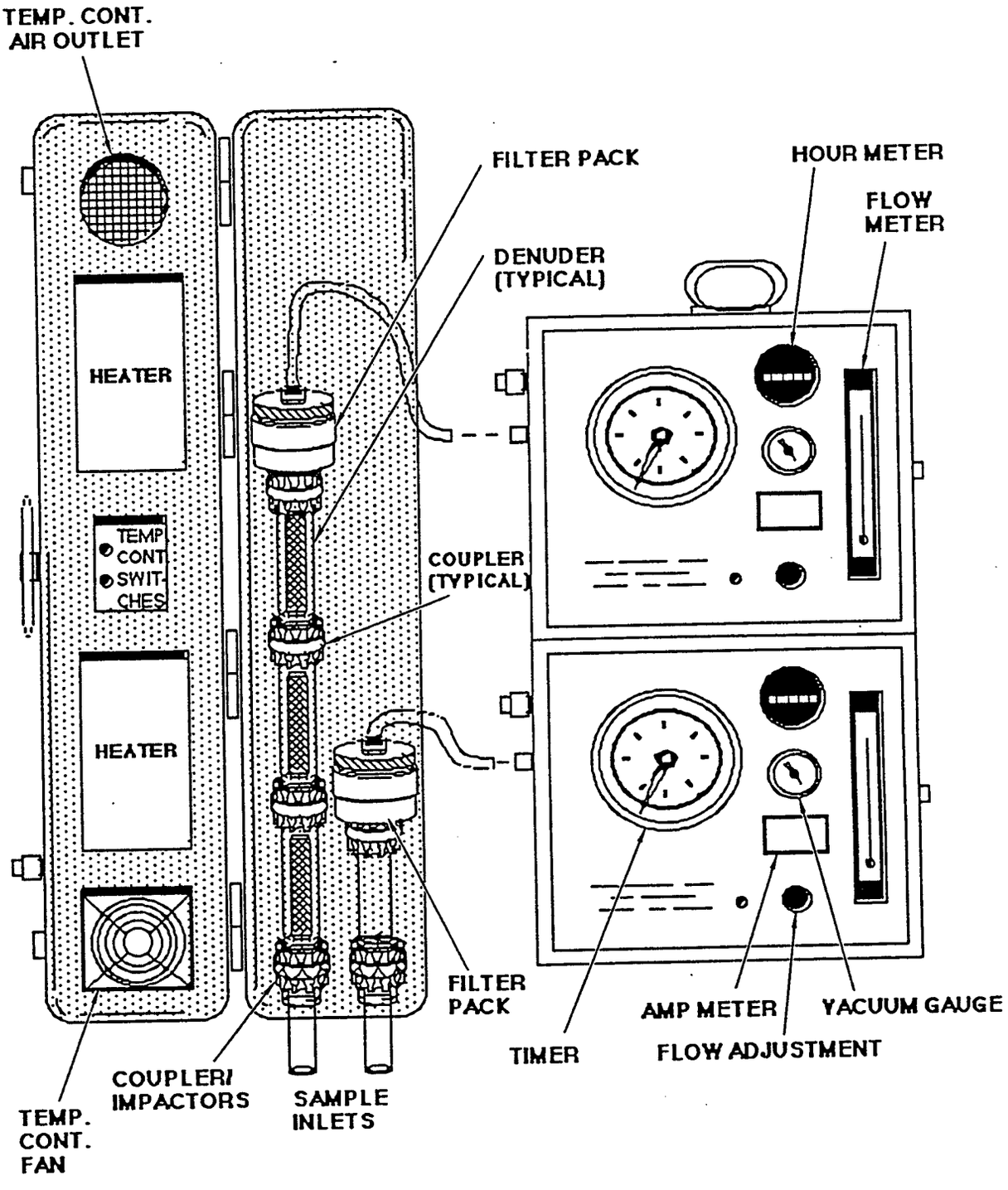

Figure 32. Annular Denuder System with Fine Particulate Sampler

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Spectra-Physics Integrator Program
for IC Analysis

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```
 2 !SKIP INJECT THEN RESTART: GO TO 99
 3 FI=2: F2=2: CA=1: !"COPY";: INPUT "V8=";: V9=1: V3=1: GO TO 25
 5 FI=5: !"USE FILE 5": GO TO 18000
 6 INPUT V4
 7 ON V4GO TO 24,65,3,5,30,255,220,229,205
24 F2=2: V3=0: CA=0
25 FI=F2: CS=1: IX=1: MC=0   : LC=1: RN=0: CW=.13: TFN"T5",1
26 T1=1.8: AC=1: AT=128 : PW=200: PT=5000: DP=3: MA=3260: MP=64
27 OF=-50: T1=.5: PW=6: PT=1000
29 !"CHECK PAPER AND CONDUCTIVITY      ";
30 GOTO 98
31 IF RC>-.01 THEN 33
32 RN=-1*RC: !"NEXT RUN IS";RN;: RN=RN-1: GO TO 30
33 IF RC=0 THEN 2074
34 IF RC=999 THEN INPUT "SCALE=";V9: GOTO 30
35 IF RC=99 THEN ABORT
36 IF RC=1 THEN RA=1: GOTO  42
40 INPUT "INJECTIONS PER STATISTICS=";RA
42 V1=RN+1
43 FI=0: !"CHECK SAMPLER FOR LOAD AND RUN";
45 PLOT OFF: PT=5000: CA=0: INJECT  : END
47 FI=F2: V2=RN+RC: !"SAMPLES FROM";V1"TO";V2"REPLICATES=";RA;
48 FI=F2: RT(4)=V8: RT(3)=V8*.87: RT(2)=V8*.62: RT(1)=V8*.34
49 CA=V3: PH=2: TT(8)=1.6+V8: TT(9)=2.9+V8: TT(10)=3.0+V8
50 PLOT A: INJECT  :  END
52 ! $10"PEAK HEIGHT(N)="PHS(1)/1000,PHS(2)/1000,PHS(3)/1000"
55 TD(RN)=AC(1):  TE(RN)=AC(2): TG(RN)=AC(3): TI(RN)=AC(4)
59 IF RA=1 THEN TD(RN)=-9.9
60 IF IX=1 THEN !;"RT SET",RT(1),RT(2),RT(3),RT(4) ELSE TD(RN)=-9.9
61 TA(RN)=LC(1): TZ(RN)=LC(2): TC(RN)=LC(3): TJ(RN)=LC(4)
62 IF RN=V2 THEN 190
64 GOTO 48
```


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```
   65 FI=2: RN=V2: PLOT OFF: INJECT  : END
   98 !"TOTAL NEW INJECTIONS=";
   99 INPUT RC;
  101 IF RC=-99 THEN 2: ELSE 31
  190 V5=V5+RN : !"LOOP=75UL;COL=AS4A; S/N09317;PAST CAL=";V5
  191 !"EL=.0018 nA2co3;.0017nAhco3=12.9US;10US=1v;fLOW=1.7ML/M=1200PSI
  192 IF V3=0 THEN 210
  193 !"X=ACTUAL   +=CALCULATED":  V5=0
  194 TFN "T5",0 : ABORT: END
  205 FI=F2: INPUT "SCALE=";V9
  210 !TAB 15"PARTS PER MILLION  (UG/ML)"
  212 !" RUN NUMBER ",$9.03,CN(1),CN(2),CN(3),CN(4)
  214 FOR K=V1 TO RN: !$9 K$9.3,TA(K)*V9,TZ(K)*V9,TC(K)*V9,TJ(K)*V9
  215 IF TD(K )=-9.9   OR RA=1 THEN 218
  216 !TAB 9 "AVERAGE"  $10.3;TD(K)*V9,TE(K)*V9 ,TG(K)*V9, TI(K)*V9
  218 A=A+(TA(K)*V9): B=B+(TZ(K)*V9): C=C+(TC(K)*V9): D=D+TJ(K)*V9
  219 NEXT K: !TAB 15"SUM"$9.3 ;A,B,C,D: END
  220 FI=9: GOTO 194
  229 FI=8: F2=8: CA=1: !"COPY";: INPUT "V8=";V8;: V9=1: V3=1: GOTO 25
  233 !Y;
  255 INPUT "CHANGE END  SAMPLE TO";V2: RC=V2-RN: GOTO 47
  356 !"PEAK HEIGHTS=";: A=SIZE"PS": IF A>10 THEN A=10
  358 FOR K=1 TO A : !$2 K $5 PSH(K)/1000"**";
  360 NEXT K: ! : END
  400 FOR I=1 TO 4 : ! KA(I),KB(I),KC(I),I: NEXT I: END
  410 FOR I=1 TO 4 : !I;: INPUT KA(I),KB(I),KC(I): NEXT I: END
 2050 STOP 64: END
 2074 GOTO 6
 8340 V="XF"GOSUB 8650NEXT !!GOTO 400
18635 !$8;T;: GOTO 18640
```


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Chapter IP-10

DETERMINATION OF RESPIRABLE PARTICULATE MATTER IN INDOOR AIR

1. Scope

Suspended particulate matter in air is generally considered to consist of all airborne solid and low vapor pressure liquid particles that are airborne. Suspended particulate matter in air presents a complex multiphase system consisting of a spectrum of aerodynamic particle sizes ranging from below 0.01 microns (μm) up to 100 μm and larger. Historically, measurement of particulate matter (PM) has concentrated on total suspended particulates (TSP), with no preference to size selection. Research on the health effects of TSP in ambient and indoor air has focused increasingly on those particles that can be inhaled into the respiratory system, i.e., particles of less than 10 μm aerodynamic diameter. It is now generally recognized that, except for toxic materials, it is this fraction (< 10 μm) of the total particulate loading that is of major significance in health effects.

2. Applicability

2.1 Recent studies involving particle transport and transformation suggest strongly that atmospheric total suspended particulate (TSP) matter commonly occurs in two modes. The fine or accumulation mode is attributed to growth of particles from the gas phase and subsequent agglomeration, while the coarse mode is made up of mechanically abraded or ground particles. Particles that have grown from the gas phase, either because of condensation, transformation or combustion, occur initially as very fine nuclei 0.05 μm in size. Those particles tend to grow rapidly to accumulation mode particles around 0.5 μm in size which are relatively stable in the air. Because of their initially gaseous origin, this range of particles sizes includes inorganic ions such as sulfate, nitrate, ammonia, combustion-form carbon, organic aerosols, metals (Pb), cigarette smoke by-products, and consumer spray-products.

2.2 Consequently, based upon the health effects of coarse and fine particulate matter, a method has been developed to determine both continuous and speciated coarse (< 10 μm) and fine (<2.5 μm) particulate matter in indoor air. A Microenvironmental Exposure Monitor (MEM) has been developed as a fixed site monitor. Similarly, Personal Exposure Monitors (PEMs) have been developed to estimate personal exposure to particles. Finally, a TEOM® continuous monitor is presented as a means of determining total mass on a real-time basis.

Method IP-10A

DETERMINATION OF RESPIRABLE PARTICULATE MATTER IN INDOOR AIR USING SIZE SPECIFIC IMPACTION

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Method IP-10A

DETERMINATION OF RESPIRABLE PARTICULATE MATTER IN INDOOR AIR USING SIZE SPECIFIC IMPACTION

1. Scope

1.1 Suspended particulate matter in air is generally considered to consist of all airborne solid and low vapor pressure liquid particles (1-3) that are airborne. Suspended particulate matter in air presents a complex multiphase system consisting of a spectrum of aerodynamic particle sizes ranging from below 0.01 microns (μm) up to 100 μm and larger. Historically, measurement of particulate matter (PM) has concentrated on total suspended particulates (TSP), with no preference to size selection (4). Research on the health effects (5-7) of TSP in ambient and indoor air has focused increasingly on those particles that can be inhaled into the respiratory system, i.e., particles of aerodynamic diameter less than 10 μm. It is now generally recognized that, except for toxic materials, it is this fraction (<10 μm) of the total particulate loading that is of major significance in health effects (8).

1.2 The two processes by which particles are formed are the grinding or atomization of matter (9-10), and the nucleation of supersaturated vapors, as illustrated in Figure 1. The particles formed in the first process are products of direct emissions into the air, whereas particles formed in the second process usually result from reaction of gases, then nucleation to form secondary particles. Particle growth in the atmosphere occurs through gas-particle interactions, and particle-particle infraction.

1.3 Recent studies (11-12) involving particle transport and transformation suggest strongly that atmospheric respirable particulate matter commonly occurs in two modes. The fine or accumulation mode is attributed to growth of particles from the gas phase and subsequent agglomeration, while the coarse mode is made up of mechanically abraded or ground particles. Particles that have grown from the gas phase, either because of condensation, transformation or combustion, occur initially as very fine nuclei 0.05 μm in size. Those particles tend to grow rapidly to accumulation mode particles around 0.5 μm in size which are relatively stable in the air. Because of their initially gaseous origin, this range of particles sizes includes inorganic ions such as sulfate, nitrate, ammonia, combustion-form carbon, organic aerosols, metals (Pb), cigarette smoke by-products, and consumer spray-products.

1.4 Coarse particles, on the other hand, are mainly produced by mechanical forces such as crushing and abrasion. Coarse particles therefore normally consist of finely divided minerals such as oxides of aluminum, silicon, iron, calcium and potassium. Coarse particles of soil or dust mostly result from entrainment by the motion of air or from other mechanical action within their area. Since the mass of these particles are normally >3 μm, their retention time in the air parcel is shorter than the fine particle fraction. Table 1 outlines the chemical constituents of the fine and coarse modes.

1.5 The composition and sources of coarse particles are not as thoroughly studied as those of fine particles. One reason is that course particles are more complex than fine particles

but similar to each other in chemical composition. It is possible, however, to recognize dozens of particle types, based on microscopical examination; these range from soil particles, limestone, flyash, oil soot to cooking oil droplets.

1.6 Outdoor concentrations of TSP, more specifically, are of major concern in estimating air pollution effects on visibility, ecological and material damage; however, people spend the majority of their time inside buildings or other enclosures.

1.7 Consequently, based upon the health effects of coarse and fine particulate matter, a method (14-17) has been developed to determine both coarse (>2.5μm to 10μm) and fine (<2.5μm) particulate matter in indoor air. A Microenvironmental Exposure Monitor (MEM) has been developed as a fixed site monitor. Similarly, Personal Exposure Monitors (PEMs) have been developed (18-20) to estimate personal exposure to particles. The PEMs can be connected to the participants lapel and are used in conjunction with personal pumps.

1.8 This method may involve hazardous materials, operations, and equipment. 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.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definitions of Terms Relating to Atmospheric Sampling and Analysis.
D1605 Sampling Atmospheres for Analysis of Gases and Vapors.
D1357 Planning the Sampling of the Ambient Atmosphere.

2.2 Other Documents

U.S. Environmental Protection Agency Technical Assistance Document (21)
Laboratory Studies for Monitoring Development and Evaluation (22-31)

3. Summary of Method

3.1 For monitoring indoor air, two distinct samplers have been illustrated in this procedure. The Microenvironmental Exposure Monitor (MEM) has been developed as a fixed site monitor, while the Personal Exposure Monitor (PEM) has been developed to estimate personal exposure to particles. In addition, the PEMs have been used in the Particle Total Exposure Assessment Methodology (Particle-TEAM) Program underway by the U.S. Environmental Protection Agency (32). One of the objectives of the Particle-TEAM is to establish the level of human exposure to particles and relate exposure to sources of aerosol matter through the application of the PEMs.

3.2 Both systems operate on the principal of impaction. A constant flow (4 Lpm) particulate laden gas stream enters the impactor assembly. The design of the impactor allows the particulate matters to be fractionated into the desired ranges of fine respirable

[<2.5 μm] or inhalable fraction [<10.0μm]). The flow rate through the sample coupled with the impactor design characteristics enables the particulate matter to be speciated. The 4 Lpm flow rate was chosen because it was technically achievable with both a battery powered flow controlled pumping system (ideal for the PEMs) and a line powered system (ideal for the MEMs). In a typical sampling program, the flow rate will allow a total sample volume of 5.5 m^3 per day, thus facilitating improved accuracy in gravimetric measurements for a typical indoor particulate loading air parcel.

3.3 A volume of air is accurately drawn for a measured period of time through the impactor assembly to a tared filter.

3.4 The total particulate matter loading is calculated from the weight gain of the filter and the total volume of air sampled.

4. Significance

4.1 When sampling particles for subsequent chemical/elemental analysis and possible association with human health effect, characterizing reliable size separation is important. Size fractionation of deposited particles occurs in the respiratory tract during inspiration. Further, physical and chemical processes result in bi- or tri-modal distribution of suspended particles in the atmosphere.

4.2 Because alkaline particles tend to be greater than 3 μm in diameter and acidic particles tend to be less than 1 μm, a sharp size separation in this range would be desired to prevent neutralization of acidic aerosols collected on a filter. Further, the distinct separation of particle mass by size permits source resolution by multivariate statistical analysis techniques using the elemental and chemical composition of the fine fraction particle mass.

4.3 For these reasons, it is imperative that a sampling protocol addressing the sampling and analysis of speciated particulate matter in indoor air be developed.

5. Definitions

Note: Definitions used in this document and any user prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Method D1356. All pertinent abbreviations and symbols are defined within this document at point of use. Additional definitions, abbreviations, and symbols are located in Appendices A-1 and B-2 of this compendium.

5.1 Particulate mass - a generic classification in which no distinction is made on the basis of origin, physical state, and range of particle size. (The term "particulate" is an adjective, but it is commonly used incorrectly as a noun.)

5.2 Dust - dispersion aerosols with solid particles formed by comminution or disintegration without regard to particle size. Typical examples include 1) natural minerals suspended

by the action of wind, and 2) solid particles suspended during industrial grinding, crushing, or blasting.

5.3 Smokes - dispersion aerosols containing both liquid and solid particles formed by condensation from supersaturated vapors. Generally, the particle size is in the range of 0.1 μm to 10 μm. A typical example is the formation of particles due to incomplete combustion of fuels.

5.4 Fumes - dispersion aerosols containing liquid or solid particles formed by condensation of vapors produced by chemical reaction of gases or sublimation. Generally, the particle size is in the range 0.01 μm to 1 μm. Distinction between the terms "smokes" and "fumes" is often difficult to apply.

5.5 Mists - suspension of liquid droplets formed by condensation of vapor or atomization; the droplet diameters exceed 10 μm and in general the particulate concentration is not high enough to obscure visibility.

5.6 Primary particles (or primary aerosols) - dispersion aerosols formed from particles that are emitted directly into the air and that do not change form in the atmosphere. Examples include windblown dust and ocean salt spray.

5.7 Secondary particles (or secondary aerosols) - dispersion aerosols that form in the atmosphere as a result of chemical reactions, often involving gases. A typical example is sulfate ions produced by photochemical oxidation of SO_2.

5.8 Particle - any object having definite physical boundaries in all directions, without any limit with respect to size. In practice, the particle size range of interest is used to define "particle". In atmospheric sciences, "particle" usually means a solid or liquid subdivision of matter that has dimensions greater than molecular radii (~10 nm); there is also not a firm upper limit, but in practice it rarely exceeds 1 mm.

5.9 Aerosol - a disperse system with a gas-phase medium and a solid or liquid disperse phase. Often, however, individual workers modify the definition of "aerosol" by arbitrarily requiring limits on individual particle motion or surface-to-volume ratio. Aerosols are formed by 1) the suspension of particles due to grinding or atomization, or 2) condensation of supersaturated vapors.

5.10 Total suspended particulate (TSP) mass - the particulate mass that is collected by the Sampler. (The system is classified in terms of the operational characteristics of the sampler).

5.11 Coarse and fine particles - these two fractions are usually defined in terms of the separation diameter of a sampler. Coarse particles are those with diameters of 2.5 μm to 10 μm and the fine particles are those with diameters less than 2.5 μm.
Note: Separation diameters other than 2.5 μm have been used.

6. Method Limitations and Limits of Detection

6.1. The limitations on the test method are a minimum weight of 20 micro grams of particles on the filter, and a maximum loading of 600 micro grams/cm^2 and minimum of 20 micro grams/cm^2 on the filter.

6.2 The test method may be used at higher loadings if the flow rate can be maintained constant (± 5%) and degradation of the aerosol preclasifier performance is not adversely affected.

6.3 The MEM and PEM samplers' limit of detection (LOD) is a function of the weighing room environment and the precision of the microbalance used to perform mass measurements.

6.4 Using the recommended equipment specified in this procedure, a 12-hour LOD of 8 $\mu g/m^3$ can be achieved for the PEM, and 4 $\mu g/m^3$ for the MEM.

6.5 Overall precision is ± 2 $\mu g/m^3$ to ±25 $\mu g/m^3$ during dust loading studies (10 to 100 $\mu g/m^3$) at a flow rate of 4 L/min. for each sampler.

7. Apparatus Description

7.1 Microenvironmental Exposure Monitor (MEM) Description

7.1.1 As illustrated in Figure 2, the MEM is subdivided into four sections: 1) an inlet section, 2) a three-piece inertial impaction section, 3) the upstream section of the filter holder; and 4) the downstream section of the filter holder.

7.1.2 Inlet section - the inlet section has four large, circumferential slots for aerosol to enter the MEM. These horizontal inlet slots prevent very large particles, perhaps those greater than 100-μm aerodynamic diameter, from entering the MEM and placing an additional particle burden on the downstream impaction plate. The inlet section also acts as a cover, preventing large particles from entering the MEM by gravity settling. The inlet section should be shown to be unbiased with respect to the particle size distribution being sampled.

7.1.3 Impaction section - the impaction section consist of three separate parts: 1) a nozzle, 2) an impaction plate(s), and 3) a part designed for mounting the impaction plate. Two versions of the impactor assembly are available. With a one stage impactor plate assembly, aerodynamic particles of <10 μm are allowed to pass around the impactor plate and subsequently collected in the lower filter. With the two stage impactor assembly, as illustrated in Figure 2, those particles <2.5 μm are collected on the lower filter. A time share option provides the capability of using two heads with one pumping system. In this way, the total sampling time can be programmed to two samplers, enabling the collection of <2.5 μm and <10 μm particulate matter in the same general environment. These features could be used to sample in two locations or to collect carbon on quartz filters or acid aerosols through a unit equipped with an ammonia denuder.

7.1.3.1 Nozzle - a single circular nozzle with a converging inlet and cylindrical throat to accelerate the aerosols through the nozzle to the filter. Two nozzle sizes are available: a nozzle with a throat diameter of approximately 8 mm, is used for removing particulate matter with an aerodynamic diameter greater than 10 μm; while smaller particles are collected on the downstream filter and saved for analysis. An approximate 3 mm diameter nozzle is used for collecting particulate matter with an aerodynamic diameter greater than 2.5 μm; while smaller particles are collected on the downstream filter and saved for analysis.

7.1.3.2 Impaction plate - a stainless-steel sintered disk is permanently mounted at the center of the impaction plate, flush with the impaction plate's surface. The pores of the sintered disk are filled with a light mineral oil in order to reduce bounce when the particles impact. The oil also wicks up through the particle deposit by capillary action so that a sticky surface continues to be available to incoming particles. The airstream containing the remaining smaller particles flows around the impaction plate through three large annular slots.

7.1.4 Upstream section of the filter holder - the upstream section of the sampler provides a flow-straightening zone directly downstream of the impactor plate so that uniform particle deposition on the filter is obtained.

7.1.5 Downstream section of the filter holder - in addition to acting as the downstream side of the filter holder, this section contains a plenum through which the filtered air exits via a side-mounted exit tube. It is also the MEM's base, which provides a surface on which the MEM can sit in the correct orientation.

7.1.6 Filter mounting and support - a 2-μm pore-size, PTFE (Teflon®), 41 mm filter disk with a polyolefin ring (Teflo #R2JO37 Gelman or equivalent) is mounted in a 2-inch x 2-inch standard Beckman-type frame and is used as the filtration medium. The downstream side of the filter is supported by a cellulose backing material (millipore AP-10 or equivalent). The two sections of the filter holder forming the filter assembly each have silicon rubber gaskets. Two draw latches hold the filter assembly together, compressing the two rubber gaskets, the cellulose backing material, and the polyolefin ring. This arrangement seals the filter assembly and prevents bypassing of the aerosol around the edge of the filter. The filter should be non-hygroscopic and should have a collection efficiency greater than 99% for the particle laden air stream of interest. The filter should be 37 mm in diameter.

Note: As an example, some glass fiber and most membrane filters with nominal pore size of 2 micrometers will nearly always fulfill this requirement. The equilibrated filter is preweighed by the user. The weight of the filter holder is not used in any determination of weight gain in this test method. The filter holder material must not contribute to any weight change of the filter.

7.1.7 Flow calibration section - to measure the volumetric flow through the MEM in the field, the inlet section is replaced with an adapter that connects via rubber tubing to a calibrated rotameter.

7.1.8 Pump - a sampling pump with a flow rate that can be determined accurately to ± 5%. Pulsation in the pump flow must be within ± 10% of the mean flow. The pump must maintain the flow constant to within ± 5% during the sampling period. The pump must be quiet enough so as to not cause undue disturbance in the area of use when being used indoors. The pumping unit has four components: a pump, a mass flow meter, a flow control circuit, and a timer. The system should be designed to provide constant flow by means of a voltage control system. The voltage control system should be designed to keep the flow at a constant 4 Lpm. The pump should be capable of maintaining up to a vacuum of 50 inches of water at the 4 Lpm flow rate. This is important since air flow to the impactor must not change as the filter loading increases. The mass flow meter should consist of a heated filament and an electrical circuit that measures the flow by determining how much heat is removed per second. If the flow is reduced (perhaps due to increased pressure drop across the impactor), the feedback circuit should apply a greater voltage to the pump to bring the flow back to the set point. A fan should be used to dissipate heat generated by the pump. The box cover should be closed and the fan running during use to maintain the accuracy of the control circuit.

7.2 Personal Exposure Monitor (PEM) Description

7.2.1 The PEM is illustrated in Figure 3 and consists of three sections: 1) an inlet-nozzle section, 2) an impactor plate, and 3) exit section.

7.2.2 Inlet and nozzle section - aerosol enters through six nozzles located on the inlet section's upstream surface, which is perpendicular to the direction of flow. Two inlet-nozzle sections are available: one has a throat diameter of approximately 1.8 mm for particulate matter cut size of <10 μm, and the other has a throat diameter of approximately 1.3 mm for particulate matter cut size of <2.5 μm.

7.2.3 Annular impactor plate - a stainless-steel sintered annulus is permanently mounted in the impaction plate, flush with the impaction plate's surface. The pores of the sintered annulus are filled with a light mineral oil in order to reduce bounce when the particles impact. The oil also wicks up through the particle deposit by capillary action so that a sticky surface continues to be available to incoming particles. The airstream containing the remaining smaller particles flows through the circular opening in the center of the impaction plate. The downstream circular edge of the impaction plate compresses the upstream face of the filter and backing material.

7.2.4 Exit section - the retaining lip of the exit section compresses the downstream face of the filter and backing material against the impactor plate edge, thereby preventing leakage and filter bypass. The exit section has an exit plenum and side-mounted exit tube, which connects by tubing to the pump.

7.2.5 Filter and support - a 2-μm nominal pore diameter, PTFE (Teflon®), 37 mm membrane filter disk with polyolefin ring (#R2JO37 Teflo, Gelman or equivalent) is used as the filtration medium. It is supported on its downstream face by cellulose backing material (Millipore AP-10 037 or equivalent).

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7.2.6 Flow calibration section - to measure the volumetric flow through the PEM in the field, an adapter, which connects via rubber tubing to a calibrated rotameter, is placed over the inlet nozzle section.

7.2.7 Pump - a 145 mm x 50 mm, tough, light, alloy case, which originally housed the Casella AFC 400 pump unit, which contains the muffled double acting diaphragm pump, integral motor, and pulse dampener from the Casella AFC 400; the remainder of the components were removed and replaced with sound-deadening material.

7.2.8 Electronics section - flow should be maintained constant within a tolerance of 5% by means of an electronic control circuit using current proportional feedback. When the pressure drop across the filter increases, this system should automatically sense the rising current demand by the motor and adjust its voltage to compensate. The electronics case should also house a digital electronic elapsed timer, the LED that indicates when the pump is running, and the electronics that automatically shut off the pump if the battery is weak.

7.2.9 Battery section - the battery pack should contain 3 or 4 lithium 9-volt batteries with snap-on connectors, allowing quick battery replacement.

7.3 Cahn Microbalance

7.3.1 The Cahn Model 30 balance is capable of weighing up to 3.5 g with an accuracy of ± 0.5 μg. It operates on the principle of balancing the sample with torque motor input. The electric current flowing in the torque motor produces an equal and opposite force on the balance beam when the beam is at the reference position, identified by a photocell detection system. The current is directly related to the sample weight through the calibration process.

7.3.2 The same analytical microbalance and weights must be used for weighing filters before and after sample collection.

7.4 Weighing Room Environment

The weighing room should be a temperature and relative humidity controlled environment. Temperature should be maintained within the range of 17° to 23°C. Relative humidity should be maintained between 38% and 42%. Weekly strip chart recordings of temperature and humidity should be maintained on a hygrothermograph. Temperatures should be read from a calibrated maximum-minimum thermometer and relative humidity should be calculated from a calibrated motor aspirated psychrometer. The weighing area should be cleaned with paper towels and deionized distilled water each day before weighing. Forceps should be cleaned once a week with detergent in a sonic bath and then rinsed in deionized distilled water. Approximately once a month, the balance chamber and pans should be cleaned with diluted ammonium hydroxide and each cleaning should be noted in the weighing room log. Filters, weights, and pans should be handled only with non-serrated tip forceps. The Cahn balance should be left on continuously because it requires six hours to warm up for stable operation. Polonium 210 alpha sources should be replaced at one year intervals from date of manufacture. The replace date should be engraved on the source by

the manufacturer, and noted in the weighing room log book. The filters should be conditioned in the weighing room for at least 24 hours before they are weighed. Each filter should be passed over a deionizing unit before weighing.

8. Apparatus Listing

8.1 Microenvironmental Exposure Monitor (MEM)

8.1.1 Sampler - William Turner, Air Diagnostics and Engineering, Inc., R.R. 1, Box 445, Naples, Maine.

8.1.2 Barometer, capable of measuring atmospheric pressure to ±0.13 kPa, best source.

8.1.3 Stopwatch, capable of measuring to ±0.1 s, best source.

8.1.4 Weighing room, with temperature and humidity control to allow weighing with a micro balance to ±5 micro grams.

8.1.5 Analytical micro balance, capable of weighing to ±5 μg.

Note: Particular care must be given to the proper zeroing of the balance.

8.1.6 Buret, capacity of 1 L, used as a soap bubble meter for calibration of the sampling unit. At flows greater than 5 L/min., a transfer standard must be employed which is traceable to a primary standard. Examples of transfer standard include wet test meter, dry gas meter, mass flow meter, rotameters, and linear flow meter.

8.1.7 Plane-parallel press, capable of giving a force of at least 1000N (may be required if plastic filter holders are used that must be pressed together after insertion of the filter).

8.1.8 Tapered tube flow meter, with precision ±2% or better within the range of the flow rate used. It shall be possible to connect the suction side of the flowmeter to the inlet of a leakproof container which contains the sampling head (in order to measure the flow rate before and after sampling).

8.1.9 Thermometer, dry bulb, 0 to 50°C with divisions every 0.1°C.

8.1.10 Manometer, 0 to 250 mm of water for measuring the pressure drop across the sampling head.

8.1.11 Flexible tube, the length of the tube is dependent on how the sampling unit is placed. A length of 1 to 10 m is suitable if the pump is separated from the sampling head.

8.1.12 Inlet adapter or leakproof container (holds partial vacuum of 4 psi for 5 min.) of suitable size to contain the sampling head.

8.1.13 Impactor base - ability to hold two types of Membrana Inc., Ghia., 2" x 2" PTFE filters holders.

8.1.14 Filters - 37 mm, 2.0 μm pore size, Membrana Inc., Ghia., filters.

8.1.15 Removable filter disks, i.e., 2.0 μm pore size PTFE disks with polyolefin rings and special flat spots mounted in 2" x 2" standard Beckman frames. (Ghia #R2PJO41 with special cut). These filters have historically been used in the Beckman type automatic dichotomous sampler by the U.S. EPA.

8.1.16 A one-week timer with 84 set points in 2-hour increments and battery backup.

8.1.17 Impactor classifier - 10 and 2.5 μm cut size.

8.2 Personal Exposure Monitor (PEM)

8.2.1 Sampler - Virgil Marple, MSP Corp., 1313-5th St. SE, Suite 206, Minneapolis, Minnesota 55414.

8.2.2 Filter - 2 μm nominal pore diameter, PTFE, 37 mm membrane filter disk with polyolefin ring (#R2JO37 Teflo, Gelman or Equivalent).

8.2.3 Filter support - cellulose backing material, Millipore AP-10 037 or equivalent.

8.2.4 Pump - Casella AFC 400 pump unit or DuPont P125-A constant flow pump.

8.2.5 Analytical micro balance - refer to Section 8.1.5.

8.2.6 Buret - refer to Section 8.1.6.

9. Filter Preparation

9.1 Overview

9.1.1 All filters are conditioned in the balance room for at least 24 hr. before initial or final weighing to reduce the humidity effects on the filter weights. The 37 mm filters should be stored in individual petri dishes after initial weighing.

9.1.2 A Cahn microbalance with electronic data transfer capability should be used to weigh the 37 mm filters used in the PEM and MEM samplers. A Cahn Model 31 balance should be connected to a Compaq portable computer through a serial port. Filter numbers are printed in bar code and assigned to filter containers. In operation, the filter number are scanned with a bar code reader and the filter placed on the balance pan. A key is then pressed on the computer keyboard to indicate that the filter is in position for weighing. The computer sends the balance a request to weigh. The balance responds with weight and stability code. The operator is signaled by a tone and a message on the computer screen when weighing is completed. The operator then removes the filter and places it back in its container. The process is repeated for each filter to be weighed. The initial weight, time, and data are written to the data file by the computer.

9.1.3 After the filter has been used, it is brought back for conditioning and final weighing. The weighing procedure is the same as for initial weighing. The computer will check the data file for the initial weight entry. The final weight will be matched with the initial weight for that filter number in the data file. The computer subtracts the initial weight from the final weight to determine the particulate catch, which is used to calculate the particulate concentration (in $\mu g/m^3$) at each sampler location. After weighing, the filters are carefully returned to the petri dishes for archiving or further analyses. Because the date and time are saved in the data file with each reading, a chronological history is therefore available for additional verification.

9.1.4 The filters must be pre-weighed before use in a temperature and humidity controlled weighing room. Since the objective of the sampling system is to determine mass particle loading of the indoor air, the filters do not need to be pre-treated.

9.1.5 Insure that the weighing room meets the specifications as outlined in Section 7.4.

9.2 Cahn Microbalance Operational Protocol

9.2.1 General - initiate a weighing session by typing operator name, balance room temperature, and relative humidity into the Compaq computer. Ensure that identical stirrups are attached to the "A" hang down loop and the "tare" hang down loop of the balance beam.

Note: The maximum weight that can be measured in this range is 250 mg. Teflon® 37 mm filters should weigh in the 80-100 mg range.

Note: An ionizing, static-eliminator unit should be in the bottom of the weighing chamber.

9.2.2 Balance zeroing - after checking that the two stirrups contain no sample and are clean, close the balance door and release the pan brake by pressing the "Brake" button. Press zero (0) and then ENTER on the computer. Wait for a computer tone, which indicates that weighing is completed.

9.2.3 Balance calibration - remove a 200 mg calibration weight from its container (using plastic tweezers) and place it on the sample stirrup ("A" loop). Close the balance door. Press "200" and then ENTER on the computer. Wait for the computer tone, which indicates that weighing is completed. Repeat the above procedure with a 90 mg calibration weight. Return the 90 mg calibration weight to its container.

9.3 Initial Filter Weighing

9.3.1 Put on a clean pair of lint-free gloves. Disposable latex gloves should not be used because of possible filter contamination with talcum powder inside the gloves.

9.3.2 Select a packet of pre-conditioned (minimum of 24 hours inside the weighing chamber), clean 37 mm Teflon® filters.

9.3.3 Select a series of pre-labeled petri dishes.

9.3.4 Using Teflon® tweezers, pick up the top filters and examine them over a black surface for holes or tears. Discard any filter with a hole or tear.

9.3.5 Pass each clean filter several times over the top of the static eliminator unit in the bottom of the weighing chamber.

9.3.6 Place the clean filter on the balance stirrup and close the door. Allow the weight display to stabilize.

9.3.7 Select a pre-numbered and labeled petri dish. Scan the label with the bar code recorder. Press the "w" key (for weigh) and then ENTER on the computer. Wait for the computer tone, which indicates weighing is completed.

9.3.8 Open the balance door. With tweezers, remove the filter from the balance pan and load it into the filter support.

9.3.9 Return the filter and its support to the corresponding petri dish, close, and secure with masking tape.

9.3.10 Place the tared filter, with petri dish, in a stack ready for field sampling.

9.3.11 Complete steps 9.3.4 through 9.3.10 for each filter to be initially weighed. After every tenth filter weighing, check the balance zero. The stable electronic readout should be 00.000 ± 00.004 mg. Check the balance calibration with 200 mg and 90 mg calibration

weights as illustrated above. The stable electronic display should read 90.000 ± 00.002 mg. If the balance zero and/or 200 mg or 90 mg standard weight calibration checks fall outside the limits described above, rezero/recalibrate the balance as outlined above, and reweigh the last ten filters. If the balance zero and 90 mg check are acceptable, continue to weigh the 37 mm Teflon® filters.

9.3.12 At the end of the weighing session, enter the balance scan, relative humidity, and temperature into the computer. Recheck the balance zero and 200 mg and 90 mg standard weights as outlined above.

9.3.13 Following the completion of a weighing session, a second individual as an auditor should select 10 percent of the filters (minimum of two) for reweighing. The second person should enter his or her name into the computer and complete the above steps for each filter to be reweighed. After all the selected filters have been reweighed, compare the initial weights recorded for each filter by both the auditor and the primary operator. If the difference between the two measurements exceeds 10 μg, the session is declared invalid, and the filters must be reweighed.

9.3.14 The first filter weighed in any batch is the batch blank and is stored in a petri dish in the weighing room. The batch blank is reweighed at the end of each batch and if it differs by more than 7 μg from the first weight, all the filters must be reweighed. If by more than 5 μg but less than 7μg, then all filters back to the last zero are reweighed.

9.4 Packaging Filters

9.4.1 After weighing, the filters are placed in the frames (with the flat edge of the filter matching the flat edge of the frames). A ring is then pushed in place on top of the filter. Care should be taken that the ring does not buckle and lies flat on top of the filter.

9.4.2 The filters are recorded in the field notebook with filter type, bar number, filter identification and initial weight.

10. Preparation of the MEM Impactor Assembly

Note: The following discussion relates to the MEM impactor assembly. All instructions are applicable to the PEM impactor assembly.

10.1 General

10.1.1 The preparation of an impactor takes place in three stages: 1) all impactor plates must be cleaned before use, 2) plates must be oiled, and 3) placed into the impactor underneath the nozzles.

10.1.2 The filter backings and the filters themselves are placed inside the base of the impactor. After assembly, the impactor is now ready for use.

10.2 Cleaning of Stainless Steel Impactor Plates

Note: The following protocols are designed for both laboratory and field cleaning situations.

10.2.1 Laboratory Environment

10.2.1.1 Remove impactor plates from impactor and place in beaker or plastic tube for cleaning. Mix laboratory detergent (Liquinox or equivalent) according to manufacturer's directions in hot (40-50°C) tap water just prior to washing. Make enough to immerse all plates to be cleaned.

10.2.1.2 Add enough detergent solution to cover all plates in the beaker or tub.

10.2.1.3 Soak for 10 minutes with intermittent gentle agitation. Remove them from the beaker.

Note: Rough handling will damage plate surface. Do not put them in an ultrasonic bath.

10.2.1.4 Check for any remaining visual deposit on the surface of the plates. If deposit remains, go back to Section 10.2.1.3 and repeat washing. If still not removed, deposit may need to be brushed off from each plate in the same detergent solution with a firm bristle brush.

10.2.1.5 Place clean but soapy plates into another beaker or tub. Rinse 2 or 3 times with hot tap water or until all trace of detergent is removed.

10.2.1.6 Rinse next with distilled-deionized water. Let sit for 6 minutes. Rinse a second time with distilled-deionized water.

10.2.1.7 Drain well. Place rinsed plates in a well-ventilated container (stainless steel or aluminum cage, or screen bottom plastic tub) and dry at 50-60°C MAXIMUM for 30 minutes or until dry.

Note: Do not exceed this temperature.

10.2.1.8 Store the cleaned, dry plates in a closed container. A zip lock bag is sufficient if handled gently.

10.2.2 Field Environment

10.2.2.1 Place the plates in a tub with two scoops of a powder detergent and cover the plates with hot water, making sure that the detergent is dissolved.

10.2.2.2 Let soak for 30 minutes, agitating frequently.

10.2.2.3 Rinse the plates thoroughly, drain, and place them in a clean tub and repeat Section 10.2.2.1 and Section 10.2.2.2.

10.2.2.4 After the second washing, rinse the plates again, drain, and place them in a clean tub to rinse.

10.2.2.5 Place the tub in a sink with the faucet running, let the water fill the tub and overflow into the sink for a few hours or until there is practically no more oil on the surface of the water. The plates should be agitated occasionally and the tub checked to see that its walls have not become oily or the oil may get onto the plates.

10.2.2.6 When the water appears to be cleared of oil, drain the plates and place them in a single layer, sintered disk side up, on a large cookie sheet.

10.2.2.7 Bake them in the oven at 200°F for about 3 hours, or until none of the plates appear damp.

10.2.2.8 Turn off the oven and leave the plates to cool in the oven.

10.2.2.9 When the plates cool, place them in a clean zip-lock bag marked "CLEAN".

10.2.2.10 There should be no dirt on the plates and no water in the cintered disk. If the cookie sheets are not large enough for the number of plates chosen, the excess wet plates can be left in a sealed zip-lock bag until the first batch is out of the oven.

10.3 Oiling of Impactor Plates

10.3.1 After drying, remove the plates from the zip-lock bag.

10.3.2 Place the plates on a clean, dry surface.

10.3.3 With the aid of an eye dropper, deposit light mineral oil on the surface of the impaction plate. Apply until excess is observed.

10.3.4 Using a pair of tweezers, tilt the plate to one side to allow excess mineral oil to drain from the plate. If after proper drying and application of the oil, the oil pools up on a plate, it is permissible to wipe off all the excess oil from the plate and still use the plate.

Note: The objective is to clean the plates of dirt and excess water to coat each plate with a uniform layer of oil.

10.3.5 Place the clean, oiled plates into the MEM sampler and secure.

11. Sampling

11.1 Placement of Filters in the MEM

11.1.1 Place the tared filter and filter support in the filter holder, close firmly with the two over-center draw latches.

Note: The filter holder consists of a base and a cover that presses the plastic filter slide between two gaskets.

11.1.2 The assembly should be suitably covered to avoid contamination prior to use.

Note: If other MEM assemblies are available, replace the unit as a whole without transferring filters under field conditions.

11.1.3 Clean and inspect the interior of the preclassifier (cover). If the inside surfaces are visibly scored, replace the classifier to insure that the design characteristics of the impactor are not altered.

11.1.4 Attach sampling pump unit to the MEM.

11.2 Initial Field Flow Check of Sampler

11.2.1 Run the sampler for approximately 10 minutes to stabilize the flow rate.

11.2.2 Detach the top of the impactor and replace it with a calibration adapter. Connect the adapter, using a small piece of tubing, to the calibrated rotameter. Start pump and record initial flow rate on the Field Data Sheet.

Note: Insure flow rate is acceptable to the monitoring protocol.

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11.2.3 Disconnect the rotameter. With the pump still running, close off the filter inlet. Flow should stop in 10 to 15 seconds or less if the system is leak free. If not, examine all connections and flexible tubing for leaks.

11.2.4 Check the meter box assembly for proper operation.

11.3 Placement of Sampler

11.3.1 The sampling head should be located in the area in which the particulate concentration is desired. During placement of the sampling head, care should be taken to prevent any extraneous debris from entering the head during sampling. Care should also be taken to avoid any restriction of the inlet. The sampler should be placed on a flat, stable surface at least 2 to 5 feet off the floor to prevent reentrainment of settled particles.

11.3.2 Initiate sampling by turning the pump on; allowing the pump to warm-up and set the flow rate according to the manufacture's instructions.

11.3.3 Record the flow rate and the start time on the Field Data Sheet which is provided in Figure 4.

Note: If the flow rate changes during sampling by more than ± 5%, record the change and the time of change (annotating the lapsed time). Reset the flow rate. If unable to reset the flow rate to the original setting, terminate sampling and note the reason for termination.

11.3.4 At the end of the sampling period, record the final flow rate and the stop time on the Field Data Sheet. Terminate sampling by turning the pump off.

11.3.5 If the sampler has an elapsed timer, record the elapsed time on the Field Data Sheet.

11.3.6 Calculate the sampling time (Final time - Initial time) to the nearest tenth of an hour.

Note: If the standard deviation of the run time is greater than 20% of the estimated run time, during the 24 hour sampling period, record the deviation on the Field Data Sheet.

11.4 Final Field Flow Check of Sampler

11.4.1 Check the final flow rate by attaching a calibrated rotameter to the outlet of the MEM unit.

11.4.2 Turn the unit on and record final flow rate on Field Data Sheet.

Note: The initial and final flow rates should be within ± 10%.

11.5 Changing Impactors

11.5.1 Change the sampled impactor by disconnecting the hose and reconnecting to the new, clean impactor.

11.5.2 Record impactor identification number, filter identification number, base number and filter batch number on the new Field Data Sheet.

11.5.3 Once again, connect a calibrated rotameter to the impactor and record initial flow rate on the Field Data Sheet.

11.5.4 If applicable, re-set programmable timer to desired setting.

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11.5.5 If you have a limited supply of impactors, you can change the filters and the impaction plates in the field. You should have a box in which to store and transport the filters. NEVER touch the filters during changing. If you touch a filter, the sample captured on it may be no longer valid.

11.5.6 The following procedures are recommended if one wishes to change filters in the field or in the laboratory.

11.5.6.1 Carefully swab the outer surface of the filter assembly with a lintless paper towel moistened with water before opening the filter holder to minimize sample contamination.

11.5.6.2 Open the filter holder and carefully remove the filter from the holder with the aid of filter tweezers. Handle the filters very gently by the edge to avoid loss of dust. Transfer the filter to a petri dish with cover or suitable holder. Do not turn the filter upside down. Record all pertinent information on the Field Data Sheet.

11.5.6.3 Return dishes to weighing room for 24 hour equilibration.

11.5.6.4 If the whole filter assembly is returned to the laboratory, it should be returned in a suitable container designed to prevent sample damage in transit.

11.5.6.5 For each set of 10 or less samples, submit a blank sample. The filters and filter holders to be used as blanks are handled in the same manner as the samples except that no air is drawn through them. Label these as blanks.

12. Filter Recovery and Final Weighing

12.1 24 hour Filter Equilibration Period

12.1.1 After sampling, filters are returned from the field as a complete batch. As the filters are unpacked, the date received and the condition of the filters are noted on the accompanying Field Data Sheet and laboratory logbook. The filter containers are then placed on a tray with the covers loosened.

12.1.2 The trays are placed in a protected area of the filter room and allowed to equilibrate for a minimum of 24 hours. Final weighing of a filter must be performed on the same balance as the original weighing. The balance is zeroed and calibrated as before, and date, relative humidity, temperature, blank mass, and tare mass are recorded on the sample weighing form.

12.2 Filter Inspection

12.2.1 Scan the bar code label on the petri dish of the first 37 mm Teflon® filter to be weighed.

12.2.2 Using Teflon® tweezers, carefully remove the filter from its container.

12.2.3 Inspect the filter for holes and tears. Enter any tear/hold or other comment in the computer or on the Filter Data Sheet.

12.3 Final Weighing

12.3.1 Place the filter on the balance stirrup and close the balance door.

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12.3.2 Press "w" and ENTER on the computer key board. Wait for the computer tone, which indicates that weighing is completed.

12.3.3 Open the balance door. Using tweezers, place the filter back into the corresponding petri dish, cover, and stack for archiving.

12.3.4 Complete Sections 12.3.1 through 12.3.3 for each filter during the final weighing process. After every tenth filter weighing, check the balance zero as in Section 9.2.2. The electronic readout should be 00.000 ± 00.004 mg. Check the balance calibration with a 200 mg and a 90 mg calibration weight as in Section 9.2.3.

12.4 Independent Audit of Weighted Filters

12.4.1 Following the completion of a weighing session, a second individual as an auditor should select 10 percent of the filters (minimum of two) for reweighing.

12.4.2 After all the selected filters have been reweighed, compare the final weights recorded for each filter by the auditor and the primary operator.

12.4.3 If the difference between the two measurements for any filter exceeds 10 μg, the session is declared invalid, and the filters must be reweighed.

12.4.4 If the difference in independent final weights is less than 10 μg, the auditor should enter his or her name into the computer, indicating valid weights. The 37 mm Teflon® filters should then be archived for future evaluation.

13. Calculation

13.1 Mass of Particles found on the sample filter:

$$M_S = (m_2 - m_1) - m_3$$

where:
M_S = mass found on the sample filter
m_1 = tare weight of the clean filter before sampling, μg
m_2 = the weight of the sample-containing filter, μg
m_3 = the mean value of the net mass change found on the blank filters, μg
Note: The blank filters must be subjected to the same equilibrium conditions.

13.2 The sampled volume is:

$$V_S = Q \times t/1000$$

where:
V_S = the volume of the air sampled, m^3
Q = the mean indicated flow rate of air sampled, L/min
t = the sampling time, min
1000 = conversion from L to m^3
Note: There are no temperature or pressure corrections for changes in sampled volume since it is critical that the flow rate required for the preclassifier be set at the time and location of sampling. Additional adjustments to the tared filter weight may be necessary

to improve the method's accuracy at very low filter weights. These can be developed by re-weighing the blank tared filter weight periodically.

13.3 The concentration of the particulate matter in the sampled air is expressed in micro grams/m^3.

$$C = K \times M_S/V_S$$

where:
C = mass concentration of particulate matter, $\mu g/m^3$
K = a dimensionless correction factor for the preclassifier (supplied by the manufacturer if not equal to 1.0)
M_s = mass found on the sample filter (see Section 13.1), μg
V_S = the volume of air sampled, (see Section 13.2), m^3

14. Sampling System Calibration

14.1 The primary calibration involve the MEM or PEM samplers with sampling head, a bubble tube and pressure drop meters.

14.2 Assemble the calibration system as illustrated in Figure 5.
Note: Since the flow rate given by a pump is dependent on the pressure drop across the sampling device (filter and inlet), the pump must be calibrated while operating with a representative sampling inlet and filter.

14.3 Calibration of the sampling unit should be performed at approximately the same temperature and pressure that the sample will be collected; otherwise, appropriate temperature and pressure connections must be applied to the volume flow rate.

14.4 Place the sampling head, with the same type of filter to be used to collect the sample, in the calibration test apparatus. Connect the sampling head to the outlet of the test apparatus.

14.5 Turn on the pump and moisten the inside of the bubble meter by drawing bubbles up the meter until the bubbles are able to travel the entire length of the buret without bursting.

14.6 Adjust the sampling unit to provide the desired flow rate.

14.7 Start a soap bubble up the buret and measure with a stopwatch the time it takes the bubble to pass through a graduation of 1.0 L.

14.8 Repeat Section 14.7 at least three times, calculate the flow rate by dividing the volume of air between the preselected marks of the buret by the time required for the soap bubble to traverse the distance and average the results. If the measure flow rate is outside the specification, readjust as in Section 14.6, and repeat Sections 14.7 and 14.8.

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14.9 Record the date of the calibration, the temperature, and barometric pressure at the time of the calibration on the Field Data Sheet and in the laboratory notebook.

15. Method Safety

This procedure may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the user's responsibility to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This should be part of the user's SOP manual.

16. Performance Criteria and Quality Assurance (QA)

16.1 Standard Operating Procedures (SOPs)

16.1.1 SOPs should be generated by the users to describe and document the following activities in their laboratory: assembly, calibration, leak check, and operation of hte specific sampling system and equipment used, preparation, storage, shipment, and handling of the sampler system, purchase, certification, and transport of standard reference materials and all aspects of data recording and processing, including lists of computer hardware and software used.

16.1.2 Specific stepwise instructions should be provided in the SOPs and should be readily available to and understood by the personnel conducting the monitoring.

16.2 Quality Assurance Program

The user should develop, implement, and maintain a quality assurance program to ensure that the sampling system is operating properly and collecting accurate data. Established calibration, operation, and maintenance procedures should be conducted on a regularly scheduled basis and should be part of the quality assurance program. Calibration procedures provided in Section 14, operation procedures in Sections 9-12, and maintenance procedures in Section 10 of this method and the manufacturer's instruction manual should by followed and included in the QA program. Additional QA measures (e.g., trouble shooting) as well as further guidance in maintaining the sampling system are provided by the manufacturer.

16.2.1 Sections 7.1 and 7.2 instruct the user to purchase instrumentation designed and calibrated to fractionate the particles in the gas stream.

16.2.2 Section 7.1.8 requires sampling pump to be accurate to ±5% and maintain flow to ±5% during the sampling period.

16.2.3 Section 7.4 requires the weighing room to be environmentally controlled: relative humidity maintained at 40 ±2 percent and temperature set at 20 ±3°C. In addition, a neutralizer is required to remove static charge on the filters.

16.2.4 Section 9.1.1 requires filters to be conditioned in the weighing room for at least 24 hrs. before initial and final weighing.

16.2.5 Section 9.2.2 requires the Cahn Microbalance to be zeroed and calibrated before and after a weighing session. The zero should be 00.000 ±00.004 mg, while the calibration should be within ±00.002 mg of standard.

16.2.6 Section 9.3.11 requires a check of zero after every tenth filter weighing.

16.2.7 Section 9.3.14 requires that the first filter weighed in any batch is the batch blank. The blank filter is reweighed at the end of each batch and if it differs by more than 00.007 mg from the first weight, all filters must be reweighed. If by more than 00.005 mg, then all filters back to the last zero are reweighed.

16.2.8 All filters must be recorded on the Field Data Sheet with filter type, bar number, filter identification and initial weight.

16.2.9 Section 11.2 requires an initial field flow check of the sampler.

16.2.10 Section 11.3.6 requires the run time to be within ±20% of estimated run time.

16.2.11 Section 11.4 requires a final field flow check of the sampler. The initial and final flow rates should be within ±10%.

16.2.12 Section 12.4 requires 10% of the filters (minimum of two) to be reweighed by a second, independent person. Differences between the two can not be any greater than 10 μg. If > 10 μg, session is declared invalid.

16.2.13 The Cahn Microbalancer must be audited once per month.

16.2.14 Section 14 requires the total sampling system be calibrated in the laboratory prior to field deployment.

16.2.15 The latest copy of the Quality Assurance Handbook for Air Pollution Measurement Systems (33) should be consulted to determine the level of acceptance of zero and span errors.

16.2.16 For detailed guidance in setting up a quailty assurance program, the user is referred to the code of Federal Regulations (8) and the EPA Handbook on Quality Assurance.

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Table 1. Chemical Constituents of the Coarse/Fine Mode Classification of Major Chemical Species Associated with Atmospheric Particles

Fine Fraction (<2.5 μm)	Coarse Fraction (2.5-10 μm)	Both Fine and Coarse Fractions	Variable
$SO_4^=$, C (soot), organic (condensed vapors), Pb, NH_4^+, As, Se, H^+	Fe, Ca, Ti, Mg, K, $PO_4^=$, Si, Al, organic (pollen, spores, plant parts)	NO_3^-, Cl^-	Zn, Cu, Ni, Mn, Sn, Cd, V, Sb

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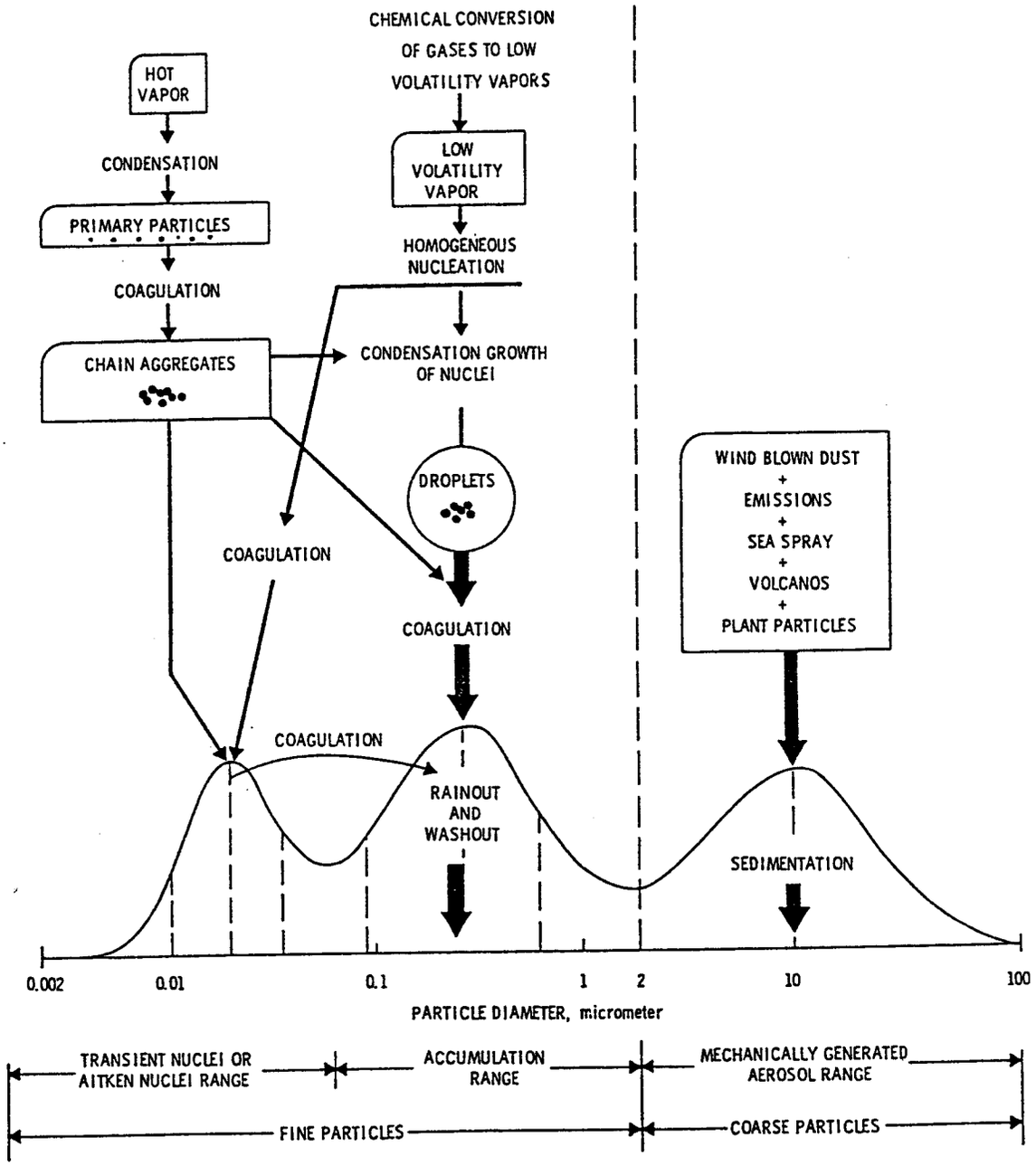

Figure 1. A Postulated Atmospheric Aerosol Formation Process

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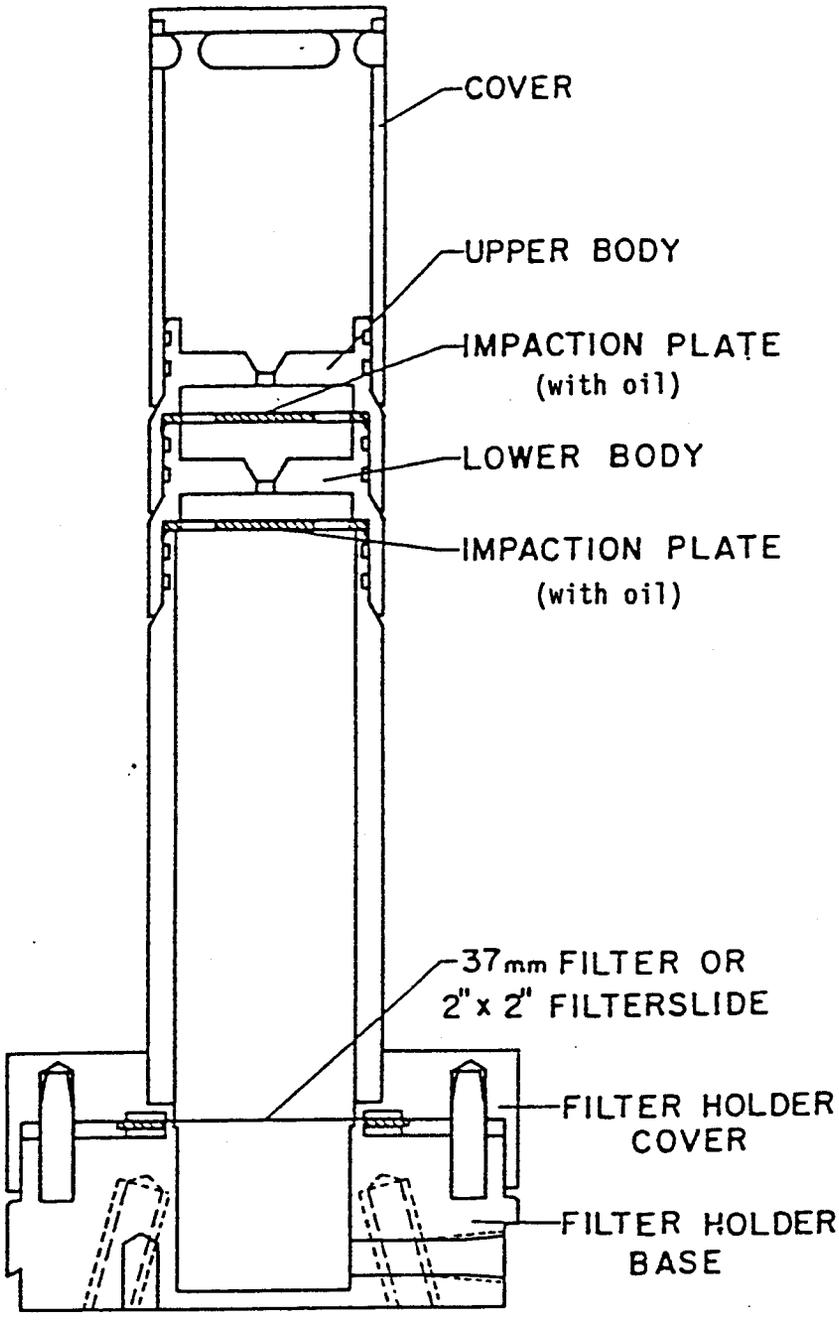

Figure 2. Schematic of Microenvironmental Exposure Monitor (MEMs)

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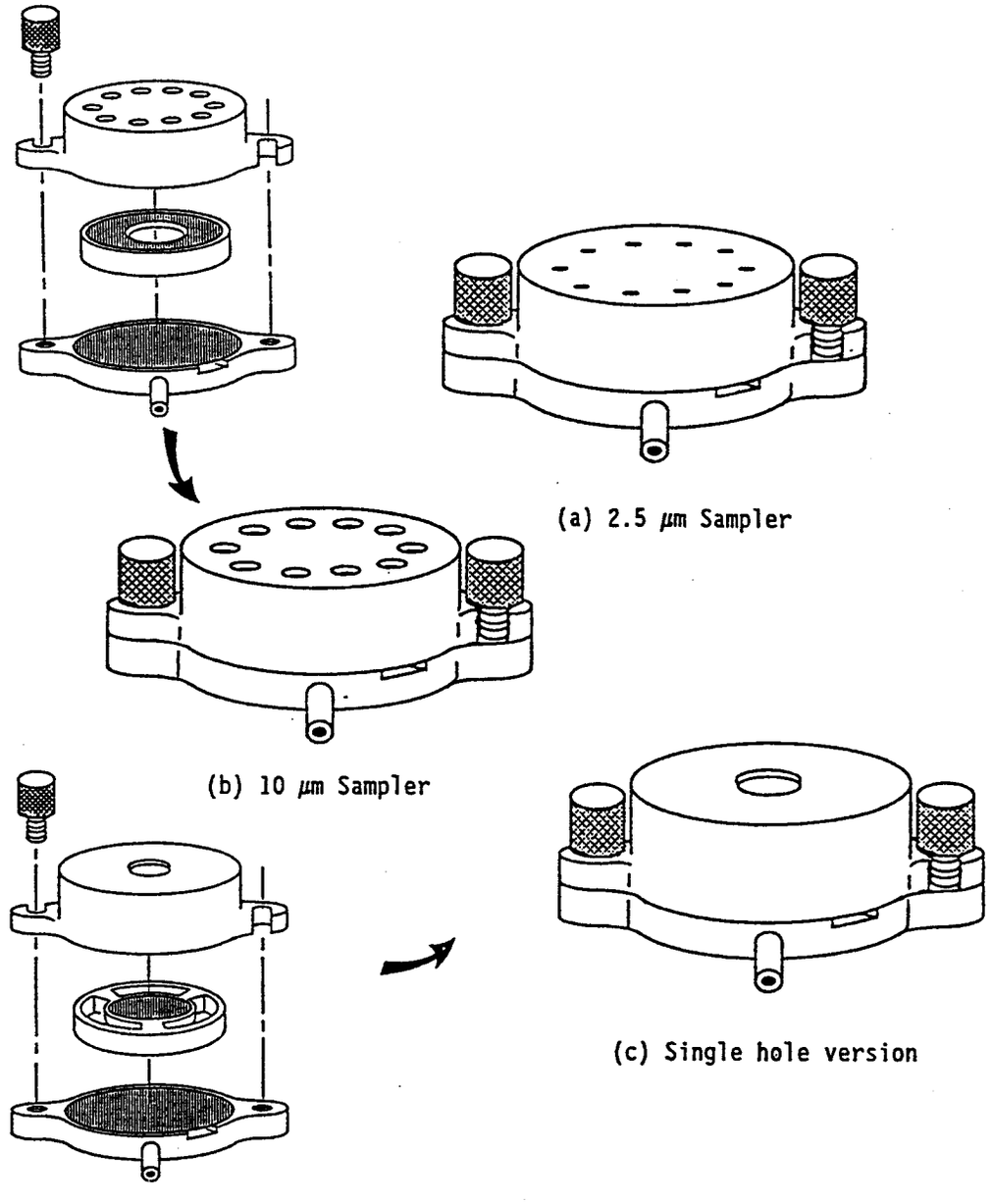

Figure 3. Schematic of Personal Exposure Monitor (PEMs)

[Examples illustrate exploded view of multiple orifices (a and b) and single orifice (c) approach. Each inlet consists of an impactor classifier, to remove particles larger than the predetermined cut size, and a filter to collect the remaining particles.]

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DETERMINATION OF RESPIRABLE PARTICULATE MATTER

GENERAL

Project: _____
Site: _____
Location: _____
_____
_____
Sample Code: _____

Date: _____
Location of Sampler: _____
_____
_____
Operator: _____
_____

EQUIPMENT

Pump

Pump Model: _____
Serial No.: _____
Lab Calibration Date: _____
Flow Rate Set Point: _____
Calibrated by: _____

Sampler

Sampler: Particle fraction
MEM _____ 2.5 μm _____
PEM _____ 10.0 μm _____
Both _____

SAMPLING DATA

	Start	Stop
Time:	_____	_____
Flow Rate:	_____	_____
Temperature:	_____	_____
Pressure:	_____	_____
Avg. Flow Rate:	_____	

Run Time: _____ (± 20% of estimate)

Total Sample Vol.: _____
Flow Maintained Rate: _____ (± 5%)

Time	Flow Rate(Q) mL/min	Ambient Temperature °C	Barometric Pressure mm Hg	Relative Humidity,%	Comments

Figure 4. Field Sampling Data Sheet

FILTER DATA

Filter I.D. No.: _____
Filter Bar No.: _____
Filter Case No.: _____
Filter Recorder in Laboratory Notebook: _____

WEIGHING ROOM

Atmosphere
Relative Humidity: _____ 40 ± 2%
Temperature: _____ 20 ± 3°C
Neutralizer: _____

Activity
Filters conditioned at least 24 hours: _____

Cahn Balance Zero: _____ ± 00.004 mg
After every 10th filter: _____

Cahn Balance Calibrated
- 200 mg _____ ± 00.002 mg
- 90 mg _____ ± 00.002 mg

Blank filter weight: _____

Reweigh at end: _____ ± 00.007 mg

10% of filters reweighed: _____
(no greater than 00.010 mg difference)

Cahn Balance last audited: _____ (once per month)

Figure 4 (cont'd.). Field Sampling Data Sheet

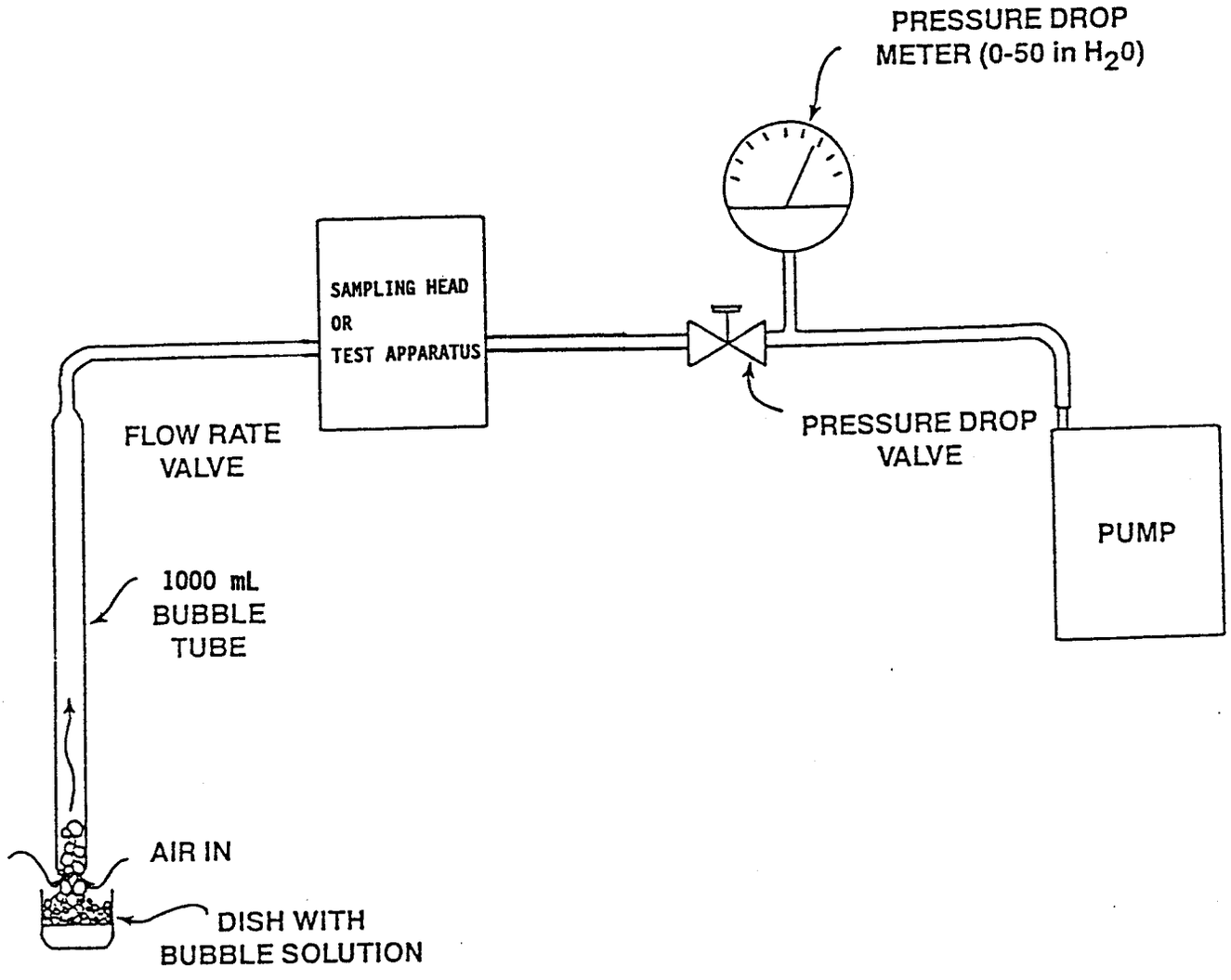

Figure 5. Calibration Assembly for Personal Sampling Pump

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Method IP-10B

DETERMINATION OF RESPIRABLE PARTICULATE MATTER IN INDOOR AIR USING A CONTINUOUS PARTICULATE MONITOR

Method IP-10B

DETERMINATION OF RESPIRABLE PARTICULATE MATTER IN INDOOR AIR USING A CONTINUOUS PARTICULATE MONITOR

1. Scope

1.1 This document describes the protocol for the Operation of a continuous particulate mass monitor which directly measures particulate mass at concentrations between 5 $\mu g/m^3$ and several g/m^3 on a real time basis.

1.2 The instrument calculates mass rate, mass concentration and total mass accumulation on exchangeable filter cartridges which are designed to allow for future chemical and physical analysis. In addition, the instrument provides hourly and daily averages.

1.3 The methodology detailed in this document is currently employed by such U.S. research organizations as the Argonne National Laboratory, R.J. Reynolds Tobacco Company and Philip Morris, Inc. for indoor and outdoor air quality studies, aerosol behavior studies, and cigarette smoke behavior studies.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis

2.2 Other Documents

Technical Manuals (1-2)
Laboratory and Field Studies (3-12)

3. Summary of Method

3.1 Particle-laden air is drawn in through a heated air inlet followed by an exchangeable filter cartridge, where the particulate mass collects. The inlet system may or may not be equipped with the optional sampling head which pre-separates particles at either a 2.5 or 10 μm diameter.

3.2 The filtered air then proceeds through the sensor unit which consists of a patented microbalance system and an automatic flow controller.

3.3 As the sample stream moves into the microbalance system (filter cartridge and oscillating hollow tube), it is heated to the temperature specified by the software.

3.4 The automatic flow controller pulls the sample stream through the monitor at flow rates between 0.5 and 5 Lpm. The hollow tube is attached to a platform at its wide end and is vibrated at its natural frequency.

3.5 As particulate mass gathers on the filter cartridge, the tubes's natural frequency of oscillation decreases. The electronic microbalance system continually monitors this frequency.

3.6 Based upon the direct relationship between mass and frequency, the instrument's microcomputer computes the total mass accumulation on the filter, as well as the mass rate and mass concentration, in real time.

3.7 The data processing unit contains software which allows the user to define the operating parameters of the instrumentation through menu-driven routines.

3.8 During sample collection the program plots total mass, mass rate and/or mass concentration on the computer screen in the form of scales. The program allows two y-axis scales to be displayed and up to 10 variables to be plotted simultaneously. In addition, the scales and variables used in plotting the data may be changed during collection without affecting stored data. Figure 1 illustrates the assembled TEOM sensor unit and data processing unit.

4. Significance

4.1 Suspended particulate matter in indoor air is generally considered to consist of all airborne solid and low vapor pressure liquid particles. Suspended particulate matter in indoor air presents a complex multiphase system consisting of a spectrum of aerodynamic particle sizes ranging from below 0.01 microns (μm) up to 100 μm and larger. Historically, measurement of particulate matter (PM) has concentrated on total suspended particulates (TSP), with no preference to size selection. Research on the health effects of TSP in ambient and indoor air has focused increasingly on those particles that can be inhaled into the respiratory system, i.e., particles of aerodynamic diameter less than 10 μm. It is now generally recognized that, except for toxic materials, it is this fraction (< 10 μm) of the total particulate loading that is of major significance in health effects.

4.2 Particles are formed by two processes: 1) the grinding or atomization of matter (13-14), and 2) the nucleation of supersaturated vapors. The particles formed in the first process are products of direct emissions into the air, whereas particles formed in the second process usually result from reaction of gases, then nucleation to form secondary particles. Particle growth in the atmosphere occurs through gas-particle interactions, and particle-particle (coagulation) interaction.

4.3 Recent studies (15-16) involving particle transport and transformation suggest strongly that atmospheric particles commonly occur in two distinct modes. The fine or accumulation mode is attributed to growth of particles from the gas phase and subsequent agglomeration, while the coarse mode is made up of mechanically abraded or ground particles. Particles that have grown from the gas phase, either because of condensation, transformation or combustion, occur initially as very fine nuclei 0.05 μm in size. These particles tend to grow rapidly to accumulation mode particles around 0.5 μm in size which are relatively stable in the air. Because of their initially gaseous origin, this range of particle sizes includes inorganic ions such as sulfate, nitrate, ammonia, combustion-form carbon, organic aerosols, metals (Pb), cigarette smoke by-products, and consumer spray-products.

4.4 Coarse particles, on the other hand, are mainly produced by mechanical forces such as crushing and abrasion. Coarse particles therefore normally consist of finely divided

minerals such as oxides of aluminum, silicon, iron, calcium, and potassium. Coarse particles of soil or dust result from entrainment, by the motion of air or from other mechanical action within their area. Since the mass of these particles is normally > 3 μm, their retention time in the air parcel is shorter than the fine particle fraction.

4.5 The composition and sources of coarse particles are not as thoroughly studied as those of fine particles. One reason is that coarse particles are more complex and similar in chemical composition. It is possible, however, to recognize dozens of particle types, based on microscopical examination; these range from soil particles, limestone, flyash, oil soot to cooking oil droplets.

4.6 Outdoor concentrations of TSP, more specifically, are of major concern in estimating air pollution effects on visibility, ecological and material damage. However, people spend the majority of their time inside buildings or other enclosures; they breath indoor air and therefore, indoor concentrations dominate average exposure. To the extent that indoor concentrations are different from the outdoors, population exposures are different from those estimated by outdoor monitors.

4.7 Consequently, based upon the health effects of coarse and fine particulate matter, a continuous particulate monitor has been developed to allow mass measurement of particulate concentration on a real-time basis.

4.8 The monitor utilizes the filter-based measurement system for providing real-time mass monitoring capability.

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.

6. Interferences

6.1 The instrument's primary operating mechanism is the microbalance system which relies upon changes in the frequency of an oscillating tapered element to determine changes in the particulate mass collected. Because of this characteristic, the instrument should be isolated from mechanical noise as much as practical. It should be located in the area to be measured so that external objects are not likely to contact or jar the instruments enclosure or the air sampling tube. Additionally, the instrument should be located in an environment with minimal temperature fluctuations. The units can operate effectively in environments with temperatures ranging between 7.2°C and 52°C.

6.2 Although the instrument may retrieve a sample from indoor or outdoor environments, it is important that the sample stream temperature is maintained within as narrow bounds as possible. Large abrupt temperature fluctuations (7-8°F/minute) of the sample stream may cause measurement accuracy to decrease due to the inlet systems inability to adjust the temperature of the sample to that specified by the software before travelling to the microbalance system. Sample temperature can range from ambient to 60°C.

Note: For aerosols such as cigarette smoke that may contain substantial fractions of dissolved semivolatiles, heating the aerosol may decrease the apparent mass and may introduce errors into subsequent chemical analyses. As a precaution the TEOM may be operated at low inlet temperatures (-30°C to 35°C).

7. Apparatus

The TEOM® Ambient Particulate Monitor is comprised of two main components (see Figure 1): the TEOM® Data Processing Unit and the TEOM® Sensor Unit. However, when purchased, these units are not fully assembled. Therefore, the following section describes the components contained in these two main units which are available separately as needed.

7.1 Enclosure cabinet - the enclosure cabinet (see Figure 2) houses a mass flow controller with an inline filter cartridge and silicone tubing, an electronic circuit chamber with the appropriate wiring for electricity and frequency signal output (inside left-covered by a plexiglass board).

7.1.1 Located on the outside right panel are the power, signals, microcomputer input/output and vacuum connections. The front of the metal door houses the ON/OFF switch and the pressure gauge which controls the mass flow controller. The inside of the door holds the silicone tubing which connects to the flow controller. The top wall of the enclosure cabinet contains a square hole (~3 in.) in the left side into which the sensor/preheater assembly fits.

7.1.2 The inside right side holds a toggle restraining clamp which secures the sensor/preheater unit when moving the unit small distances (R&P proprietary product).

7.2 Sensor/preheater assembly - the sensor/preheater assembly (see Figure 3) consists of the inlet and the microbalance.

7.2.1 The inlet consists of two concentric hollow (black) metal tubes. The outer tube is ~12" long and ~3" in diameter. The tip of the outer tube is configured to accommodate a 1/2" tubing for sampling or an additional sampling head, which separates particles by diameter allowing either ≤2.5 μm diameter or ≤10 μm diameter particles to enter the system. The base of the outer tube is welded to a rectangular metal mounting plate which is fixed to the top outside wall of the enclosure cabinet. The inner tube is connected to the outer tube at only one location to allow the microbalance to be suspended in the enclosure cabinet. The base of the inner tube is connected to the microbalance top outer wall. The connection accommodates an air temperature probe assembly which controls the temperature of the inner tube of the inlet.

7.2.2 The microbalance is a rectangular metal enclosure which houses a metal cylinder (the sensor head) the size of the inner inlet tube. The metal cylinder contains an oscillating tapered element, an electronic feedback system, and a filter cartridge. The tapered element is attached to a platform at its wide end (bottom) and has a small metal tip onto which the filter cartridge sits. The electronic feedback system consists of an amplifier board which maintains the elements oscillation and the electronics which allow frequency signals to be

transcribed to mass units. At the bottom of the microbalance, a silicone tube, which is connected to the mass flow controller, carries the air sample. Also attached to the bottom is the electrical cord. When purchased the whole unit is accompanied by a hardware manual which describes in detail the assembly and use procedures.

7.3 Filter cartridge - the filter cartridge (see Figure 4) is a half-inch diameter thin aluminum base (foil-like) assembly. The foil is crimped around the filter edges to contain it. Attached to the aluminum base is a water-resistant plastic cone which fits onto the metal tip of the oscillating element.

7.4 Filter exchange tool - the filter exchange tool (see Figure 4) is a four-inch long aluminum tube. The lower part of the tool has two perpendicular connections. The top connection is an aluminum disc which is slightly smaller than one-half inch in diameter. It is made to fit over the filter face when assembling and disassembling. The bottom connection is a "U-shaped" fork. The tines of the fork straddle the cone of the filter cartridge during assembling and disassembling.

7.5 Inline filter cartridge - standard filter cartridge, available from Fisher-Scientific.

7.6 Carbon-vane vacuum pump - oil-free pump with constant vacuum, available from Fisher-Scientific.

7.7 Microcomputer and keyboard - recommended IBM-compatible. The software should be able to plot real-time data on the screen and should give the user a number of options for saving data on disk, printing data, or transmitting information to other devices using analog or digital signals. The use of both hard disk and floppy disk systems should be available.
Note: The TEOM® is marketed and manufactured by Rupprecht and Patashnick Co., Inc., 8 Corporate Circle, Albany, NY, 12203. The following discussion addresses the receiving and setting-up of the monitor.

8. Assembly of Sensor Unit

The TEOM® Sensor Unit consists of two components: 1) the enclosure cabinet, and 2) the sensor/preheater assembly.

8.1 Remove both components from their shipping boxes. Set the enclosure cabinet upright in the designated location for the required sampling. Try to locate the enclosure cabinet at the source of the sample if possible (see Figure 2 for cabinet configuration).
Note: If the use of a sampling line cannot be avoided, keep its length to an absolute minimum and avoid sharp bends. Sampling line will cause some reduction in particulates reaching the microbalance. This, in turn, causing an underestimation of the sample content to be made.

8.2 Lay the sensor/preheater assembly flat on a table so that the shipping brace (the angle bracket painted red) faces upward. Remove the screws holding the shipping brace. When this bracket is removed, the air preheater tube flexes and allows the TEOM® Sensor Head

to drop until the air preheater tube touches the outer (3" ID) tube. Figure 3 illustrates the sensor/preheater assemblies.

8.3 Replace the cable and tubing support that connect the two side plates of the TEOM® Sensor Head using the 8-32 x 1/2" screws that were removed.

8.4 Make sure the TEOM® Sensor Head restraining clamp (the small orange handled toggle clamp) connected to the bottom right of the Sensor/preheater assembly is in its open (unclamped) position.

8.5 Carefully lift the sensor/preheater assembly. Hold it so that the air preheater tube is vertical and above the TEOM® Sensor Head. The long flange of the mounting plate should face left (i.e., the handle for opening the TEOM® microbalance should face toward you).

8.6 Carefully lower the sensor/preheater assembly through the square opening in the top of the enclosure cabinet (see Figure 3), making sure that the ribbon cable and vacuum tube precede the TEOM® Sensor Head through the opening. Line up the holes in the mounting flange with the threaded holes in the top of the enclosure, and secure with provided #10-32 x 3/8" screws.

8.7 Route the ribbon cable over the top of the power supply cover, which is behind the plexiglass printed circuit board cover, and plug its end (3-pronged) connector into the mating 25 pin connector (P12) at the printed circuit board cover.

8.8 Push the 1/4" vacuum tubing into the two support clips on the side of the large acrylic guard. Push the end of the hose over the free end of the inline filter which precedes the mass flow controller.
Note: Observe that the sensor unit contains an inline filter cartridge to protect the mass flow controller from being contaminated or blocked by particles contained in unfiltered air.

8.9 Check that the TEOM® Sensor Head is free to move in all directions--left, right, and forward and back. This is necessary to isolate the Head from any outside vibrations (i.e. it should be completely suspended within the enclosure cabinet). The only connection of the Sensor Head is in the heated air inlet where the inner tube is connected to the outer tube (see Figure 3).

9. Assembly of the Sensor Unit and the Data Processing Unit

9.1 Examine the front and side panels of the TEOM® Sensor Unit. Ensure that the power switch located on the front panel (door) is off. This switch should not be turned on until the TEOM® hardware is set up and Section 2 of the TEOM® Software Manual has been read (see Appendix).
Note: The black panel on the right side of the sensor unit contains all the external connections needed for power, signals, and vacuum pumps. Examine, also, the input/output connectors located on the side and back of the microcomputer.

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9.2 Attach the black coaxial cable between the BNC connector on the TEOM® Sensor Unit labelled "Freq Sig" and the BNC connector on the R&P Counter Board (see Figure 5).
Note: The BNC connector marked "Freq Sig" transmits the frequency output from the TEOM® Sensor Unit. The expansion card in the highest numbered slot (slot 4 in the Compac II personal computer) is the R&P Counter Board. This board contains a BNC connector for receiving the frequency signal from the TEOM® Sensor Unit. The nine-pin connector located on this board is not used in the TEOM® Series 1200 Ambient Particulate Monitor.

9.3 Attach the analog cable between the two 9-pin connectors on the TEOM® Sensor Unit and the 37-pin connector on the analog board in the microcomputer.
Note: The nine-pin connectors allow analog data to pass between the TEOM® Sensor Unit and the microcomputer. The expansion card in the next-to-highest numbered slot (slot 3 in the Compac II personal computer) is an analog input/output board with digital input/output capabilities.

9.4 Attach a 3/16" (inside diameter) hose from the barbed hose connector on the right side panel of the TEOM® Sensor Unit to the port of a suitable oil-free vacuum pump.
Note: The pump should be capable of maintaining approximately 20" Hg vacuum at a 4 Lpm flow rate. Pulsations from the vacuum line should be kept at a minimum. A small carbon vane pump of 1/10 hp or greater is suitable. Place the sample pump away from the TEOM® Sensor Unit to minimize the coupling of pump vibrations into the TEOM® Sensor Unit.

9.5 Attach the printer (optional) to the microcomputer with a parallel printer cable.
Note: The 15 pin "D" connector provides the user with analog input/output capabilities for user defined functions. Three channels of analog input and output are available for definition by the user. All analog signals are scaled from 0 to 5 VDC. For example, the user may choose up to three variables (such as mass concentration or total mass) to be output to a chart recorder or data acquisition system by entering the appropriate value in the Configuration Definition Routine (see Appendix or Section 6 of the TEOM® Software Manual). It is also possible to input three independent signals (for instance humidity and ambient temperature) into the TEOM® Sensor Unit. These inputs may be changed into engineering units, and plotted and/or saved on disk simultaneously with the TEOM® data.

9.6 Attach the power cords to the TEOM® Sensor Unit and microcomputer. Plug the power cords of the TEOM® Sensor Unit, microcomputer and optional printer into electric sockets with the appropriate voltage. Contact R&P, your distributor or representative if you have any questions about the voltage for which your instrument is configured. Do not apply power until instructed to do so in Section 11.1 or in Section 2 of the TEOM® Software Manual.

10. Exchanging the Filter Cartridge

Upon arrival of a new TEOM® series 1200 Ambient Particulate Monitor, the sensor/preheater unit will not be equipped with a filter cartridge. Therefore, it is necessary to follow the filter exchange procedures outlined below to prepare the instrument for operation. The new instrument comes with a box of 20 blank filter cartridges. Before proceeding with the exchange, some special precautions must be taken:

- Do not exchange filter cartridges when the TEOM® Series 1200 Ambient Particulate Monitor is taking data, i.e. when it is in the Collection Mode. Filter cartridges should be exchanged either when the instrument is in the Initialization Mode, or when both the TEOM® Sensor Unit and microcomputer are turned off.
- Do not handle new TEOM® filter cartridges with fingers. Use the filter tool provided with the instrument to exchange filters.
- Keep the sample pump running to facilitate filter exchange.

10.1 Loading the Filter Cartridge

10.1.1 Locate the TEOM® microbalance lever with the black ball in the down position (see Figure 3). Carefully rotate this lever upward. The TEOM® Sensor Head will swing forward into its filter changing position, exposing the filter cartridge.
Note: When the TEOM® Sensor Head is in this open position, the tapered element automatically stops vibrating to facilitate filter exchange.

10.1.2 Remove a clean filter cartridge from its shipping/storage box using the filter exchange tool. The tools upper metal disc should cover the filter's surface while the lower tines of the fork should straddle the hub of the filter base.

10.1.3 Hold the filter exchange tool in line with the tapered element and lightly insert the hub of the filter cartridge onto the tip of the tapered element. Ensure that the filter is seated properly. The tools metal disc should be centered over the filter before pressure is applied. Apply downward pressure to set it firmly in place. This will reduce the chances of distorting the crimped filter (see Figure 4).

10.1.4 Remove the filter exchange tool by retracting it sideways until it clears the filter. Do not disturb the filter.

10.1.5 Gently move the ball-ended lever to the down position to close the head. Allow the springs to pull it closed for the last centimeter so that the distinct sound of a metal-to-metal contact is heard.
Note: Do not let the TEOM® microbalance slam closed from the full open position.

10.1.6 Close and latch the door to the instrument enclosure cabinet. Keep the door open for as short a time as possible to minimize the temperature upset to the system.

10.1.7 Allow the unit to stabilize for one half-hour before taking data.

10.2 Removing the Filter Cartridge

Note: Filter lifetime depends upon the flow rate used, and the nature and concentration of the particulate sampled. The lower the flow, the longer the filter life. The filter lifetime is determined by the pressure drop across the filter, as shown by the vacuum gauge on the front panel of the TEOM® Sensor Unit. TEOM® filter cartridges must be exchanged when

the pressure drop reaches 15" Hg. This generally corresponds to a total mass accumulation of 5 to 10 mg. The automatic flow controller inside the TEOM® Sensor Unit cannot maintain the flow rate desired by the user when the pressure drop exceeds this level.

10.2.1 Using the filter exchange tool (see Figure 4), remove the filter cartridge from the sensor head. Carefully insert the lower fork of the tool under the filter cartridge so that the tines of the fork straddles the hub of the filter cartridge. The tool's upper metal disc should be centered over the filter's surface but not touching it. Gently lift the filter from the tip of the tapered element with a straight pull upwards.
Note: Never twist the filter cartridge to remove it or apply sideways force to the tapered element (see Figure 4).

10.2.2 Store the used filters or discard as necessary.

10.2.3 Remove a clean filter cartridge from its shipping/storage box using the exchange tool. Grasp the clean filter as instructed in Section 10.1.2. Do not touch the filter cartridge with your fingers - use only the exchange tool.

10.2.4 Follow the procedures detailed in Section 10.1.3 through Section 10.1.7 to insert the clean filter cartridge onto the sensor head and restore the instrument back to the operation mode.

11. Instrument Operation

Before the instrument start-up procedures are implemented, follow the instructions detailed below or those through Section 2.5 of the TEOM® Software Manual.

11.1 Preparation of Computer

11.1.1 Hard disk systems - make sure that diskette drive A does not contain a diskette. Remove any diskette that resides in diskette drive A.

11.1.2 Floppy disk systems - insert the TEOM® Program Diskette in diskette drive A. Insert the TEOM® Data Diskette or any formatted diskette with free storage capacity in diskette drive B.

11.1.3 When TP3 is not automatically executed, then it can be executed through MS-DOS.

11.1.3.1 For hard disk systems choose the proper disk drive: C: <Enter>; select the appropriate subdirectory: CD \TP3 <Enter>; start program execution: TP3/Instrument Name <Enter> - where InstrumentName is the model number of the TEOM® monitor, such as 1200. For example, type TP3 /1200 to start executing TP3 for the TEOM® Ambient Particulate Monitor.

11.1.3.2 For floppy disk systems choose the proper diskette drive: A: <Enter>; start program execution: TP3/Instrument Name <Enter> - where InstrumentName is the model number of the TEOM® monitor, such as 1200. For example, type TP3 /1200 to start executing TP3 for the TEOM® Ambient particulate Monitor.
Note: If an improper instrument name is entered, the instrument informs the user with a special screen. In this case, the program halts execution and waits for the user to press any

key before re-entering MS-DOS. If this condition is encountered, refer to Section 11.1.3.1 and/or 11.1.3.2 for instructions to re-start the program.

11.1.4 Once TP3 has begun execution, it displays a message for several seconds indicating that it is loading additional files. The system screen is then displayed. This screen gives information on the vendor. The next screen displays a copyright notice to the user.

11.1.5 After this input, the computer shows the main display screen [see Figure 6(a)]. The precise layout of this screen can vary from one type of TEOM® instrumentation to another. The main display screen is displayed by the computer during nearly every phase of instrument operation. All real-time data plotted and displayed by the instrument appear on this screen. Figure 6(b) illustrates the components of the main display screen.
Note: Do not turn on power to the TEOM® Sensor Unit unless the preceding steps have been taken and the TP3 software is running on the computer. Operating the instrument while not under computer control may lead to overheating and damage.

11.2 Instrument Start-up

11.2.1 Turn on the TEOM® Sensor Unit at the power switch located in the lower right-hand corner of the unit's front face.

11.2.2 Turn on the sample pump. Allow 2 hours (24 hours for highest accuracy) for the TEOM® monitor to warm up to its user-defined temperature set points and achieve its flow rate before beginning data collection. Pre-filtered (Ballston Filter 9933-05-CQ) air should be drawn through the instrumentation during the initial warm-up period. These filters are the same diameter as the inlet of the outer metal tube and are very similar to the inlet filter which precedes the mass flow controller. Each pre-filter fits directly onto the silicone "sampling" tubing which covers the outer metal inlet. Other filters which are similarly made can be used as long as they are demonstrated equivalent.
Note: The baseline performance of the TEOM® monitor in terms of mass concentration is shown in Figure 7. These data were taken after the device had operated continuously for a long period of time, with pre-filtered air drawn through the system and under stable ambient and sample stream temperatures. The data file shown in this figure is 1200BASE.PRN, which is provided as part of the instrument's software.

11.2.3 Turn on the optional printer.

11.2.4 When a baseline is achieved similar to that of Figure 7, remove the pre-filter from the heated air inlet-silicone tubing assembly while the vacuum is still being applied. This initiates sampling.

11.3 Instrument Shut-Down and Shipping

11.3.1 Turn off the TEOM® Sensor Unit at the power switch located in the lower right-hand corner of the unit's front face.

11.3.2 Turn off the sample pump and the optional printer.

11.3.3 When sampling at another location nearby, the sensor/ preheater assembly must be secured before moving the Sensor Unit. Close the sensor head restraining clamp located at the lower right side of the microbalance unit and inside right side of enclosure cabinet.

This secures the sensor head to the side of the enclosure cabinet to prevent damage during transport.
Note: Do not transport the assembled sensor unit large distances or by commercial carrier in the assembled condition.

11.3.4 Transport the assembled sensor unit by hand or cart to the new sampling location. Open the restraining clamp when the instrument is set up at its new location.

11.3.5 When transporting by commercial carrier, the sensor/preheater assembly must be removed from the instrument enclosure cabinet. The reverse of the assembly instructions should be followed to disassemble the sensor unit components (see Section 8). Each component should be packed separately in the original containers using suitable packing materials such as foam or bubble wrap.

12. Instrument Variable Settings

12.1 Setting Sampling Parameters

The software provided with the TEOM® Series 1200 Ambient Particulate Monitor contains three pre-defined configurations:

- plots mass concentration on the computer monitor during data collection
- plots mass concentration and 24-hour averaged mass concentration on the computer monitor during data collection
- plots mass concentration and total mass on the computer monitor during data collection

All of these configurations store the date, time, mass concentration and total mass on disk when data files are created by the program.
Note: Configurations U to Z are reserved for the TEOM® demonstration software. Do not create configurations with these names. These configurations may be changed and new configurations may be added by the user in the Configuration Definition Routine (Section 6 of the TEOM® Software Manual). Slots 13 to 18 of the Configuration Definition Routine allow the user to change the values for operating temperatures and flow rate (See Appendix or Section 6 of the TEOM® Software Manual). Since these settings are unique for each type of TEOM® instrumentation, they are defined below specifically for the TEOM® Series 1200 Particulate Mass Monitor:

Configuration Line	Description	Permissible Range
13	Sample Flow Rate	-5.0 to 0, 0.5 to 5.0 L/min
14	TEOM® Housing Temp	0, 25 to 60°C
15	Air Tube Temperature	0, 25 to 60°C
16	TEOM® Cap Temperature	0, 25 to 60°C
17	Enclosure Temperature	0, 25 to 50°C
18	Not Defined	

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The values of these settings are recorded in data files sorted on disk, and are also included in the numeric printouts of data files enabled by the F9 key.

12.1.1 Sample flow rate (slot 13) - the sample flow rate is the rate (Lpm) at which the particulate-laden sample is drawn through the TEOM® monitor. A negative value causes the flow controller to open its valve fully, allowing for external control of the flow rate. In this case the instrument computes mass concentration based upon the absolute value of the negative number entered. A value of 0 closes the valve of the flow controller, stopping the sample flow through the system. A positive value between 0.5 and 5.0 L/min automatically sets the flow controller to the entered flow rate.

12.1.2 Housing temperature (slot 14) - the value of this slot determines the temperature at which the TEOM® housing in the Sensor Unit is to be maintained. A value of 0 specifies that the temperature of the TEOM® housing is not to be controlled. A value between 25 and 60°C automatically causes the instrument to control the TEOM® housing temperature at the indicated temperature.

12.1.3 Air tube temperature (slot 15) - the value of this slot determines the temperature at which the sample air flow is maintained, as measured by a probe in the air stream. A value of 0 specifies that the temperature of the air tube is not to be controlled. A value between 25 and 60°C automatically causes the instrument to control the temperature of the air at the indicated temperature.

12.1.4 Cap temperature (slot 16) - the value of this slot determines the temperature at which the cap of the TEOM® microbalance is maintained. A value of 0 specifies that the temperature of the cap is not to be controlled. A value between 25 and 60° C automatically causes the instrument to control the temperature of the cap at the indicated temperature. This value is normally set to be the same as the TEOM® housing temperature (Slot 14)

12.1.5 Enclosure temperature (slot 17) - the value of this slot determines the temperature at which the interior of the enclosure is maintained. It should normally be set to 45° C. A value of 0 specifies that the temperature of the enclosure is not to be controlled. A value between 25 and 50° C automatically causes the instrument to control the temperature of the enclosure at the indicated temperature.

12.2 Instrument Frequency Clipping

Because the TEOM® Series 1200 Particulate Mass Monitor is ordinarily used to measure relatively long term changes in particulate concentrations, the instrument's clipping capability is normally turned on.

12.2.1 The instrument's clipping routine is used to lessen the effects of outlying frequency values (isolated "bad" data points) on mass calculations that can be caused by mechanical or electrical disturbances. When the clipping capability is turned on, a "window" is formed around the average frequency value (adjusted for slope).

12.2.2 If the next raw frequency value lies within the window, the frequency value is not affected and the span of the window is decreased by the decimal percentage prescribed by "inclip" (see below).

12.2.3 If the next raw frequency value lies outside the window, the frequency value is given the maximum or minimum value of the window, depending upon whether the raw frequency point was high or low. In addition, the span of the window is increased by the decimal percentage prescribed by "outclip" (see below). "Inclip" and "outclip" are assigned the following values in the TEOM® Series 1200 Particulate Mass Monitor:

Inclip 0.02
Outclip 0.02

13. Confirmation of Instrument Calibration

Note: The procedure below enables the user to confirm the calibration of the TEOM® microbalance set by the manufacturer. There is no need for frequent calibration checks, as the mass detection characteristics of the TEOM® system's tapered element do not change over time. Following is a description of the method used at the Automotive Emissions Laboratory of the New York State Department of Environmental Conservation for checking the calibration of the TEOM® monitor. The procedure allows the user to check the accuracy of the instrument's calibration constant, K_o, calculated by the manufacturer. It involves a comparison of the mass indicated on a gravimetric balance with that indicated by the TEOM® monitor for a given calibration mass. The calibration mass is a circular disk of Pallflex filter material 3 mm (1/8") in diameter. The instrument used to punch out circular Pallflex disks is a vacuum tweezer assembly which is also used to transport the Pallflex discs.

13.1 Punch circular discs out of Pallflex filter paper (type T60A20) using the disc punching instrument. A calibration dot 3 mm in diameter weighs approximately 100 mg.

13.2 Determine the mass of the calibration dot on a gravimetric laboratory balance that has microgram sensitivity.

13.3 Establish a baseline for total mass on the microcomputer screen with the sample flow rate set, for example, at 3 Lpm.

13.4 Drop the calibration dot onto the center of the TEOM® filter cartridge. This is done by decreasing the suction of the vacuum tweezer. Close the TEOM® microbalance to restart the vibration of the TEOM® monitor.
Note: Do not touch the TEOM® filter cartridge with the vacuum tweezer. As is the case with TEOM® filter cartridges, the calibration dot must never be touched by hand.

13.5 The TEOM® monitor will indicate the change in total mass that results from the calibration dot being placed on the filter cartridge.

13.6 Remove the calibration dot from the TEOM® filter cartridge using the vacuum tweezer. Do not touch the TEOM® filter cartridge with the vacuum tweezer. Make sure that the total mass reading returns to its original base line (to within a fraction of a microgram).

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13.7 Compare the masses determined gravimetrically and by the TEOM® system, and calculate a revised calibration constant, K_o, if necessary:

K_o (revised) = K_o (original) x Mass (gravimetric)/Mass (TEOM® Monitor)

13.8 If desired, revise the calibration constant, K_o, stored in the TEOM® monitor.

14. Main Display Screen

Note: This section describes the commands that manipulate the information shown on the main Display Screen. An understanding of this Section is important for the effective use of the TEOM® monitor. Figure 8 identifies the components of the main display screen.

14.1 Top Line of the Main Display Screen

14.1.1 Current configuration - each configuration has a single-letter name ranging from A to Z. When the computer is turned on, configuration A is automatically loaded into memory (see Figure 8). If a listing of the current configurations is desired or if a different configuration is to be loaded, consult Appendix for the correct procedures.

14.1.2 Operating mode - the operating mode indicates the current operating status of the TEOM® monitor. The instrument runs in the following modes.

14.1.2.1 The instrument is in the Initialization (INIT) Mode when it is first turned on, and after the main display screen has been cleared and the Initialization Mode chosen by pressing F3.

14.1.2.2 The instrument collects, plots and displays mass rate, mass concentration and total mass data when in the Collection Mode. Press F1 when in the Initialization Mode to enter the Collection Mode.

14.1.2.3 The instrument enters the Stop Mode after data collection has been stopped with the F2 key. The image on the main Display Screen may be printed while in the Stop Mode by pressing F9.

14.1.2.4 In the Replot Mode the user may replay data files stored on disk. Enter this mode by pressing F7 either in the Stop Mode (to replot the newest data file) or in the Initialization Mode (to replot any data file stored on disk).

14.1.2.5 The F9 key is used in the Stop and Replot Modes to print the image on the main display screen. When the F9 key is pressed while in the INIT Mode, the user may choose to print the numeric contents of any data file stored on disk.

Note: Because of the time required to print a screen image or the contents of a data file, the heating circuits in the TEOM® Sensor Unit are turned off during printing. The user may have to allow for temperatures to stabilize again before resuming data collection.

14.1.3 Data file name - all data file names have a .PRN extension even though this is not shown on the main display screen. This built-in program feature ensures file compatibility with all versions of Lotus 1-2-3® spreadsheet software. A listing of data files currently stored on disk may be obtained by entering ALT+D (hold down the ALT key and press D) when in the INIT Mode.

14.1.4 Current time - this part of the screen displays the current time of day. If this clock time is incorrect, exit from TP3 into MS-DOS by pressing F10. Then type TIME followed by <Enter>. The computer then displays the current time and gives the user a chance to enter a new time. Re-enter TP3 from MS-DOS by entering the commands shown in Section 11.1.

14.1.5 Current date - this part of the screen displays the current date. If this date setting is incorrect, exit from TP3 into MS-DOS by pressing F10. Then type DATE followed by <Enter>. The computer then displays the current date and gives the user a chance to enter a new date. Re-enter TP3 from MS-DOS by entering the commands shown in Section 11.1.

14.2 Bottom Line of the Main Display Screen

14.2.1 Y1-axis label - the Y1-axis Label displays the name of the variable whose scale is shown on the left-hand Y-axis. The abbreviations used to designate variables are listed in Table 1.

14.2.2 Error code - this field indicates whether a hardware malfunction has been detected by the instrument. An error code 0 represents no malfunction. The instrument detects the following types of error conditions:

Error Code	Description
0	No error condition
1	Error condition on R&P Counter Board
2	Error condition on analog input board
4	Error condition on analog output board
8	Error condition on digital input board
16	Error condition on digital output board
32	Unsupported programming feature used
64	Tapered element not oscillating or improper cable attachment

In the case of multiple simultaneous errors, the error code consists of the sum of the current error conditions. For example, the error code 65 indicates that an error condition has been detected on the R&P Counter board (code 1) and that the computer is not receiving a frequency signal from the TEOM® microbalance (code 64). Pressing F3 resets the error code to 0.

14.2.3 Status code - the status code conveys information about the calculation of data and the amount of disk space available for saving data. This field is blank under most operating conditions. A status code display most commonly occurs just after F1 has been pressed in the INIT Mode to begin data collection (codes M and R). In this case, the status display gives the user feedback that data collection has begun and indicates when the computer has calculated the first valid data point. Because total mass, mass rate and mass concentration calculations are based upon averaged raw data, a certain time elapses between the start of data collection and the calculation of the first valid data point. Total mass data are plotted and displayed as 0 until a sufficient number of raw frequency data

points have been collected for calculation. Likewise, mass rate and mass concentration data are plotted and displayed as 0 until the appropriate number of total mass data points have been processed.

Status Code	Description
M	Total mass, mass rate and mass concentration are plotted and displayed as 0--data not yet valid.
R	Total mass values are valid. Mass rate and mass concentration are not yet valid, and are plotted and displayed as 0.
D	The data disk has reached its maximum capacity. The current data file has been closed in an orderly fashion but data are no longer being stored on disk.
blank	Normal condition. If the instrument is in the Collection Mode, total mass, mass rate and mass concentration data are valid.

14.2.4 Y-axis selection - the arrow in this field indicates which Y-axis is the current Y-axis, i.e., which axis is influenced by commands that change the display of Y-axes. If the arrow points to the left, the Y1-axis (left) is the current Y-axis and is affected by Y-axis commands. Conversely, if the arrow points to the right, the Y2-axis (right) is the current Y-axis and responds to Y-axis commands. Press F5 to change the current Y-axis. This command toggles between the Y1-axis and Y2-axis. The following Y-axis commands act only upon the current Y-axis.

Command	Results
Shift+Fn	Display the selected Y-axis scale
Up Arrow, Down Arrow	Shift Y-axis up/down by one division
PG UP, PG DN	Shift Y-axis up/down by one page
2, 5, 0	Expand Y-axis scale by factors 2, 5, 10
ALT+2, ALT+5, ALT+0	Contract Y-axis scale by factors of 2, 5, 10
Home	Reposition Y-axis scale to center next Y-point

14.2.5 User input field - the user input field displays prompts and accepts inputs from the user. A number of function key commands, such as F1, F3, F4, F6, and F10 require input from the user. When a prompt appears in the User Input Field, the instrument awaits the user's input before continuing its operation. All user inputs must be followed by <Enter> in order to be accepted by the computer. Prompts which include the message "(Y or N)" require that a Y or N be entered by the user followed by <Enter>. The F6 command allows the user to change the variables shown in the Main Numeric Display and Short Numeric Display at any time. After F6 is pressed the computer displays the message

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"Command:". In response, enter the location at which the variable is to be displayed (explained below), followed by <Enter>. The computer then prompts the user with the message "Entry:". Then type the Program Register Code for the desired variable (see Table 1), followed by <Enter>. The location of the desired variable is determined by the following codes:

Code	Description
0	Short Numeric Display
1-42	Main Numeric Display. The Main Numeric Display may contain up to 14 lines of information, with three variables displayed per line. The locations are numbered from bottom to top in the following manner:

Code	Description		
Top Line	•	•	•
	•	•	•
	10	11	12
	7	8	9
	4	5	6
Bottom Line	1	2	3

Note: Certain models of TEOM® instrumentation do not have a Main Numeric Display. For example, the following key sequence causes raw frequency data to be displayed in the Short Numeric Display:

F6 0 <Enter> 86 <Enter>

14.2.6 Short numeric displays - this field displays the current value of a variable selected by the user. Variables may be displayed at this location in two ways:

- follow the procedure described above in Section 14.2.5, or
- If the variable to be shown in the short numeric display is represented by a function key, enter CTRL + Fn (hold down CTRL and press the desired function key). For example, enter CTRL + F5 to show real-time mass rate values in the short numeric display.

14.2.7 Y2-axis label - the Y2-axis Label displays the name of the variable whose scale is shown on the right-hand Y-axis. The abbreviations used to designate variables are listed in Table 1.

14.3 X-Axis and Y-Axis Scales

Figure 8 identifies the location of the X-axis and Y-axis scales of the main display screen.

14.3.1 X-axis scale - the X-axis scale always displays time. By making the appropriate selection in the configuration definition routine (see Appendix), time can be displayed as either the elapsed time of data collection or time-of-day. The format may be either hh:mm:ss (hours:minutes:seconds) or dd:hh:mm (days:hours:minutes). The span of the

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X-axis scale may be changed in the Initialization, Collection and Replot Modes in the following manner:

Command	Result
Left Arrow, Right Arrow	Decrease/increase span by a factor of 2.
CTRL + Left Arrow, CTRL + Right Arrow	Decrease/increase span by increments determined by the program.

These commands may be entered in any order and as often as desired. When they are used in the Collection or Replot Modes, the graphical display area is cleared.

14.3.2 Y-axis scales - the main display screen can display as many as two Y-axis scales at the same time. The Y1-axis is located to the left and the Y2-axis to the right of the bottom line of the main display screen (Section 14.2.4). A number of commands may be used to change the current Y-axis scale (see 14.2.4). These commands all function in the Initialization, Collection and Replot Modes.

14.3.2.1 For examples, follow these steps to display the scale for mass concentration on the Y2-axis: 1) press F5, if necessary, to point the Y-axis selector toward the Y2-axis, and 2) enter SHIFT + F6 to display the mass concentration scale. This command is a toggle switch. Executing it again turns off the current Y-axis scale.

14.3.2.2 The Up Arrow, Down Arrow, PG UP and PG DN commands allow the user to reposition variables vertically by shifting the scale of the current Y-axis either up or down. These keystrokes may be pressed in any order and repeated as often as desired.

14.3.2.3 The 2, 5, 0, ALT +2, ALT +5 and ALT + 0 commands change the scaling of the current Y-axis by factors of 2, 5, and 10. They may be executed in any order, and as often as desired.

14.3.2.4 The Home command is useful when a plotted variable such as total mass is about to go off the screen. Pressing Home in this case repositions the current Y-axis scale so that the next data point is plotted in the middle of the screen.

14.4 Variables Selected for Plotting

The variables currently selected for plotting in the Collection and Replot Modes are shown directly above the graphical display area (see Figure 8). These settings may be turned on and off any time the main display screen appears on the monitor. Variables may be added to or deleted from the list of plotted variables by entering an appropriate ALT +Fn command. For example, press ALT + F6 to add or subtract mass concentration from the list of plotted variables.

14.5 Main Numeric Display

This field displays the current values of selected variables. Its format varies from one model of TEOM® instrumentation to another. The main numeric display may be scrolled

up and down using the CTRL + UP and CTRL + DN commands. The variables shown here may be changed by the user according to instructions in Section 14.2.5.

14.6 Automatic Execution Setting

The operation of the TEOM® monitor may be directed from a remote location using the digital input capability of the computer. When the automatic execution setting is on, the TEOM® monitor executes the steps of the instrument cycle according to the values of digital inputs 0 and 1. The instrument's automatic collection capability may be turned on and off only in the Initialization Mode. Enter ALT + A to toggle this remote operation ability on and off (see Figure 9). The value of digital inputs 0 and 1 cause the instrument to execute the following steps of the instrument cycle when the automatic execution capability is turned on:

Digital Input 0	Digital Input 1	Description
0	0	The instrument awaits a digital input
1	0	Corresponds to F1: Begin data collection, enter Collection Mode
0	1	Corresponds to F2: Stop data collection, enter Stop Mode
1	1	Corresponds to F3 (when in Stop Mode): Clear screen, enter INIT Mode or Corresponds to F2 and F3 (when in Collection Mode): Stop data collection and clear screen, enter INIT Mode.

Generally, a digital input of 0 corresponds to ground, while an input of 1 refers to 5 VDC. Allow up to 5 seconds for the instrument to respond to the above digital input commands. These settings and the locations of the inputs can vary from one type of TEOM® monitor to another. Refer to the TEOM® Hardware Manual, or consult with R&P or your distributor, to determine the location and proper handling of these digital inputs.

15. Method Safety

This procedure may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the user's responsibility to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This should be part of the user's SOP manual.

16. Performance Criteria and Quality Assurance (QA)

Required quality assurance measures and guidance concerning performance criteria that should be activated within each laboratory are summarized and provided in the following section.

16.1 Standard Operating Procedures (SOPs)

16.1.1 SOPs should be generated by the users to describe and document the following activities in their laboratory:

- assembly, calibration, leak check, and operation of the specific sampling system and equipment used;
- preparation, storage, shipment, and handling of the sampler system;
- purchase, certification, and transport of standard reference materials; and
- all aspects of data recording and processing, including lists of computer hardware and software used.

16.1.2 Specific stepwise instructions should be provided in the SOPs and should be readily available to and understood by the personnel conducting the monitoring work.

16.2 Quality Assurance Program

The user should develop, implement, and maintain a quality assurance program to ensure that the sampling system is operating properly and collecting accurate data. Establish calibration, operation, and maintenance procedures should be conducted on a regularly scheduled basis and should be part of the quality assurance program. Calibration verification procedures provided in Section 13, operation procedures in Section 11,, and the manufacturer's instruction manual should be followed and included in the QA program. Additional QA measures (e.g., trouble shooting) as well as further guidance in maintaining the sampling system are provided by the manufacturer. For detailed guidance in setting up a quality assurance program, the user is referred to the code of Federal Regulations (18) and the EPA Handbook on Quality Assurance (19).

17. References

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18. 40 CFR, Part 58, Appendix A, B.

19. *Quality Assurance Handbook for Air Pollution Measurement Systems*, Volume II - Ambient Air Specific Methods, EPA 600/4-77-0272, May 1977.

Table 1. Program Register Codes

Code	Title	Description	Comments
Mass Rate			
80	MR00	Mass Rate (g/sec)	Use for disk storage
83	MR	Mass Rate (g/sec or selectable)	Use for plotting and printing
Mass Concentration			
81	MC00	Mass Conc (mg/m^3)	Use for disk storage
84	MC	Mass Conc (mg/m^3 or selectable)	Use for plotting and printing
Total Mass			
82	TM00	Total Mass (g)	Use for disk storage
85	TM	Total Mass (g or selectable)	Use for plotting and printing
TE Frequency			
86	FR00	Raw Frequency (Hz)	Use for disk storage
87	FR01	Clipped Frequency (Hz)	
88	FR	Average Frequency (Hz)	
89	SD	Std Dev of Frequency (10 sec)	Indicates stability of instrument
Clipping			
97	CLIP	Clipping Indicator	0 = Inactive; 1= Active
98	CLWI	Size of Clipping Window (Hz)	
Time and Date			
90	XTIM	Current Experimental Time (sec)	Automatically saved on disk
91	REPS	Calculation Repetitions	Number of program loops
92	CTIM	Clock Time	Format: 0.HHMMSS (hours, min, sec)
93	CDAT	Clock Date	Format: 0.MMDDYY (month, day, year)
Diagnostics			
95	ERR#	Current Error Code	
Automatic Instrument Operation			
148	D100	Digital Input 0	With instrument in Automatic Setting, these inputs control operation
149	D101	Digital Input 1	

TP3 refers to variables (such as mass concentration) by numbers called Program Register Codes. These Program Register Codes are common to all TEOM® instrumentation. Certain TEOM® monitors make use of additional codes. Consult Appendix A of the TEOM® Hardware Manual for a complete listing of codes applicable to your particular TEOM® instrument model.

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Table 2. Description of Stored Data Files

Line(s)	Description
1	The time and date at which the data collection cycle was begun, expressed in the following format: 1 + mmddyyhhmm (1 + month, day, year, hour, minute).
2	The unique calibration constant for the TEOM® monitor. It is used during replotting to calculate total mass, mass rate and mass concentration from raw frequency data stored on disk. This calibration does not change during the lifetime of the instrument.
3	The rate at which the computer gathers raw frequency data from the TEOM® Sensor Unit. Typical instrument settings are one data point every 1.68 and every 0.21 seconds.
4	The rate at which data are saved to disk in seconds.
5	The length of time over which raw frequency data are averaged to compute total mass values.
6	The length of time over which total mass values are averaged to compute mass rate and mass concentration.
7-12	Instrument settings such as the sample flow rate and temperatures. The definition of these settings can vary from one type of TEOM® instrument to another.
13-20	The Program Register Codes (see Table 1) and names of the variables stored in columns 1-8 of the data file.

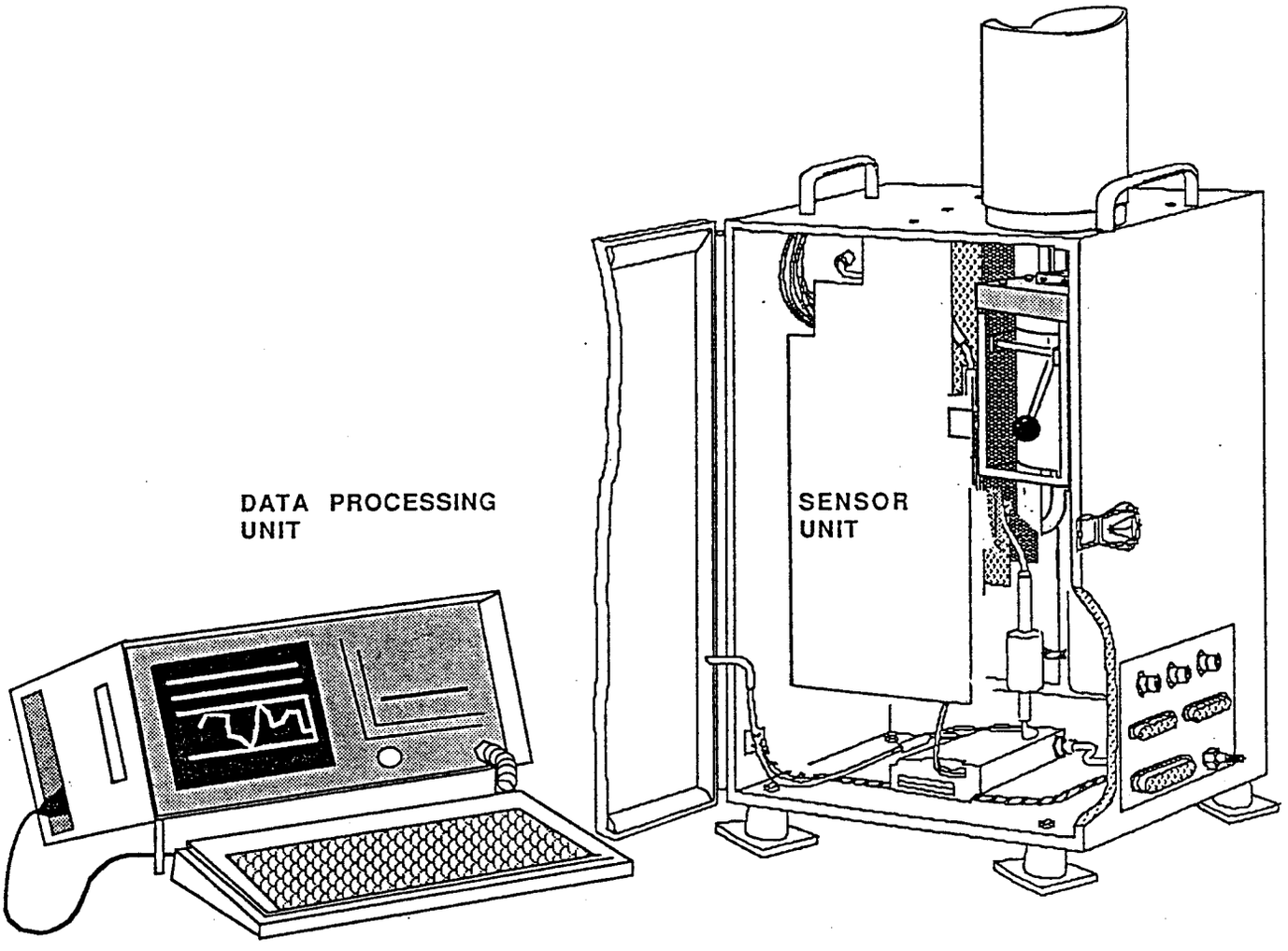

Figure 1. Assembled TOEM® Continuous Particulate Monitor

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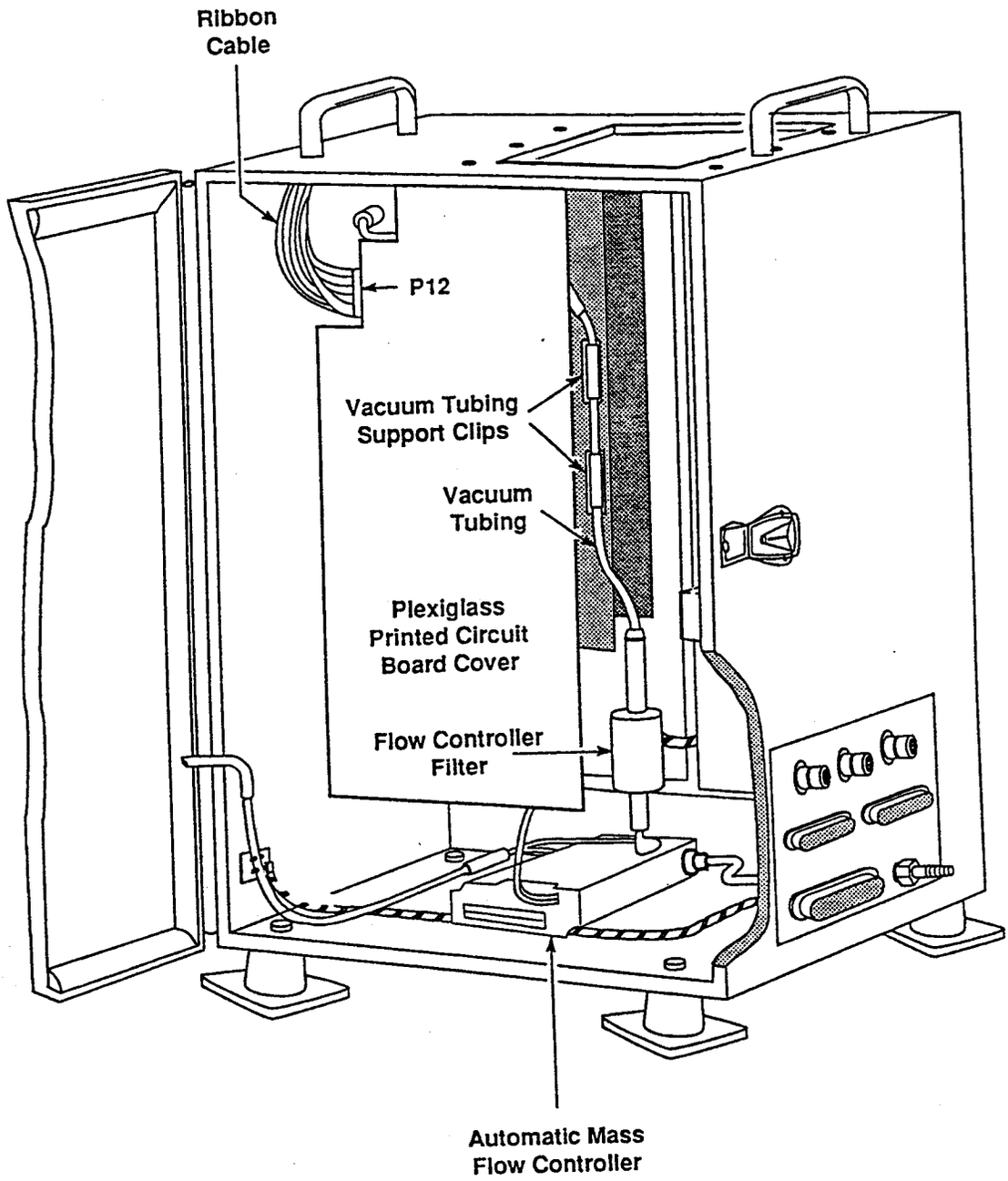

Figure 2. Enclosure Cabinet

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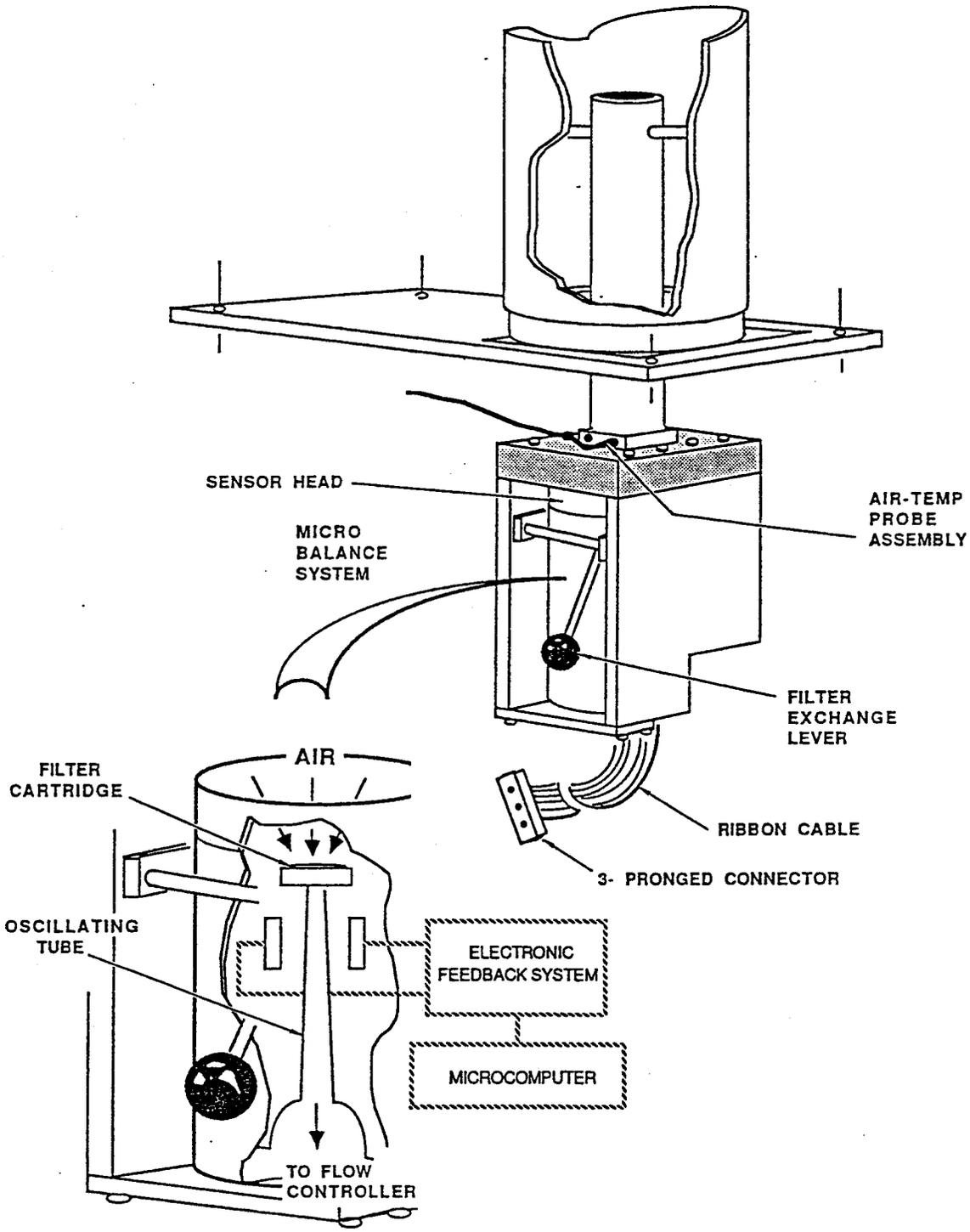

Figure 3. Sensor/Preheater Assembly

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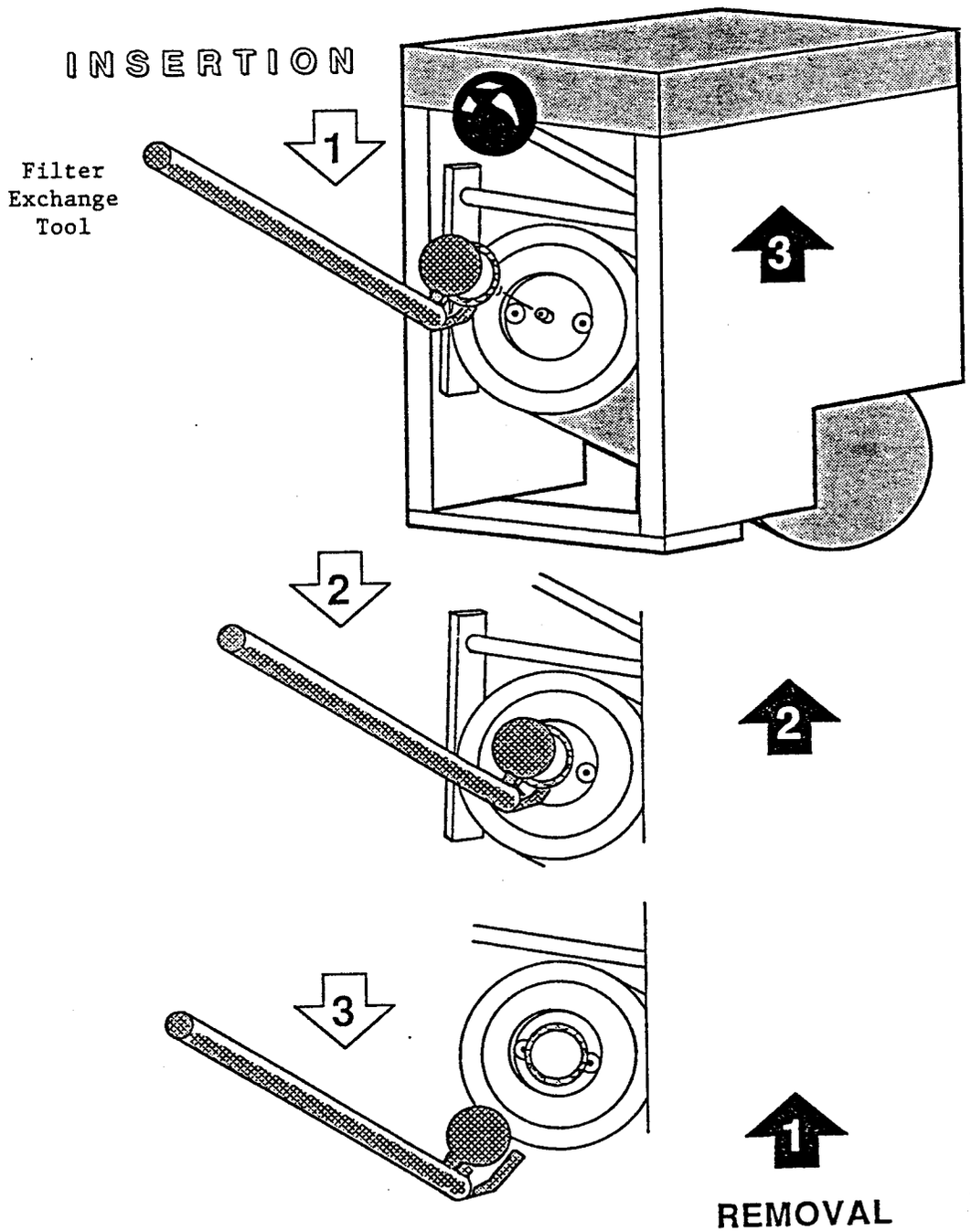

Figure 4. Loading/Removing Filter Cartridge Assembly

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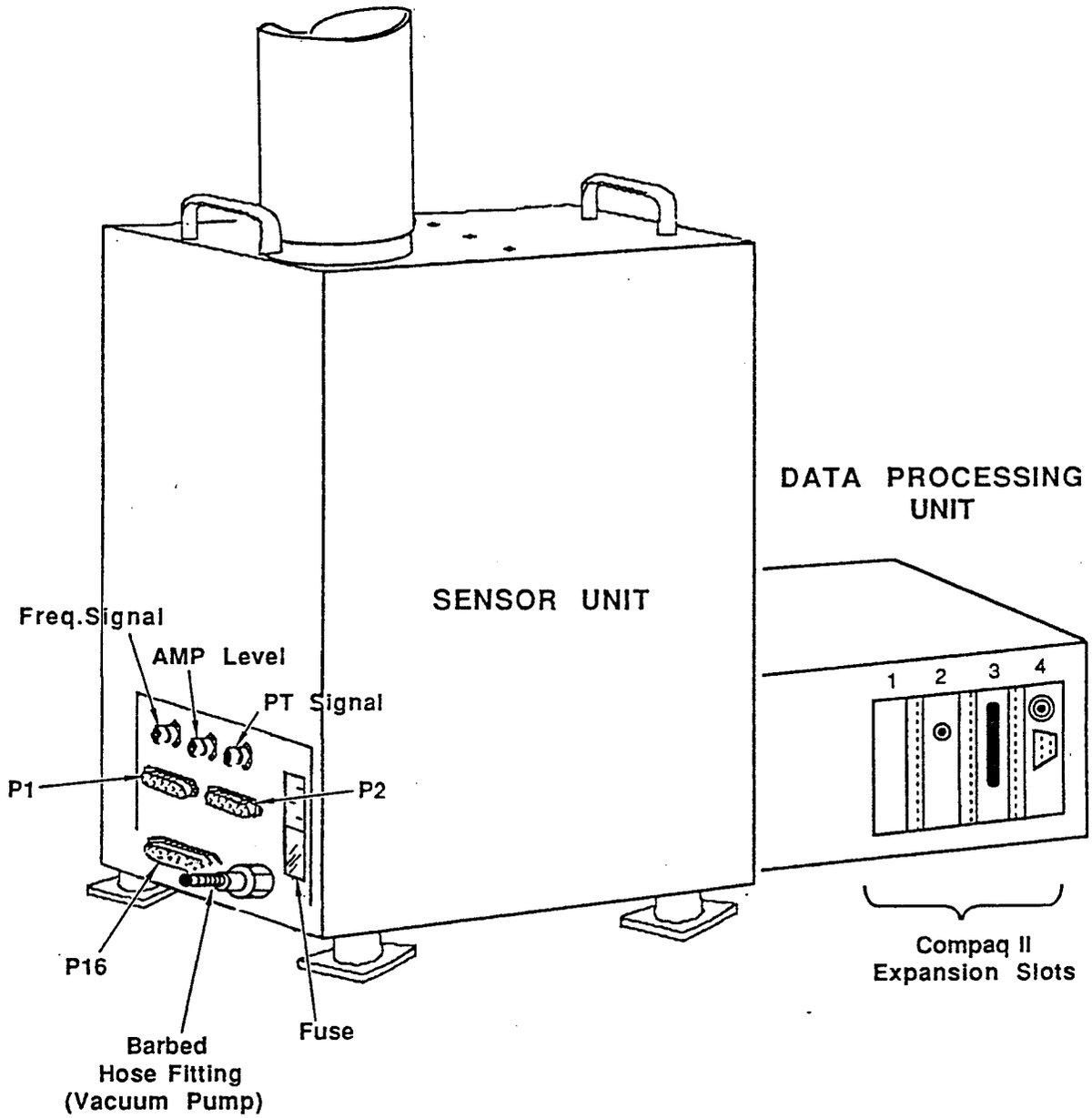

Figure 5. Electrical Connections Associated with the TEOM® Sensor Unit and Data Processing Unit

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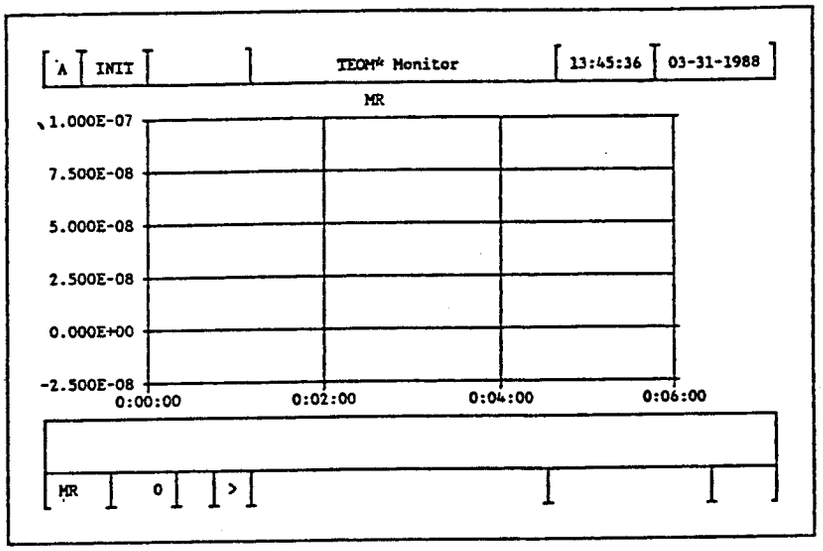
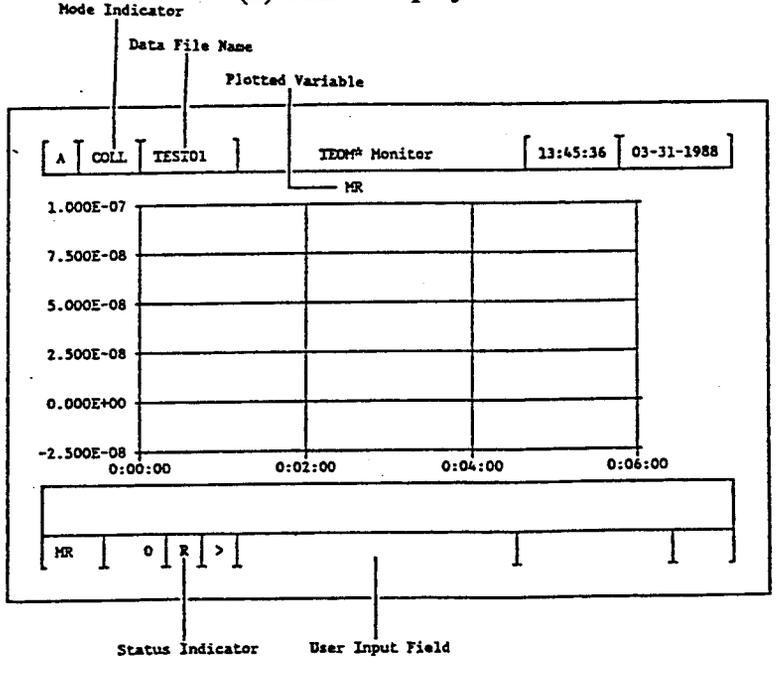


(a) Main Display Screen



(b) Components of the Main Display Screen

Figure 6. TEOM® Display Screen

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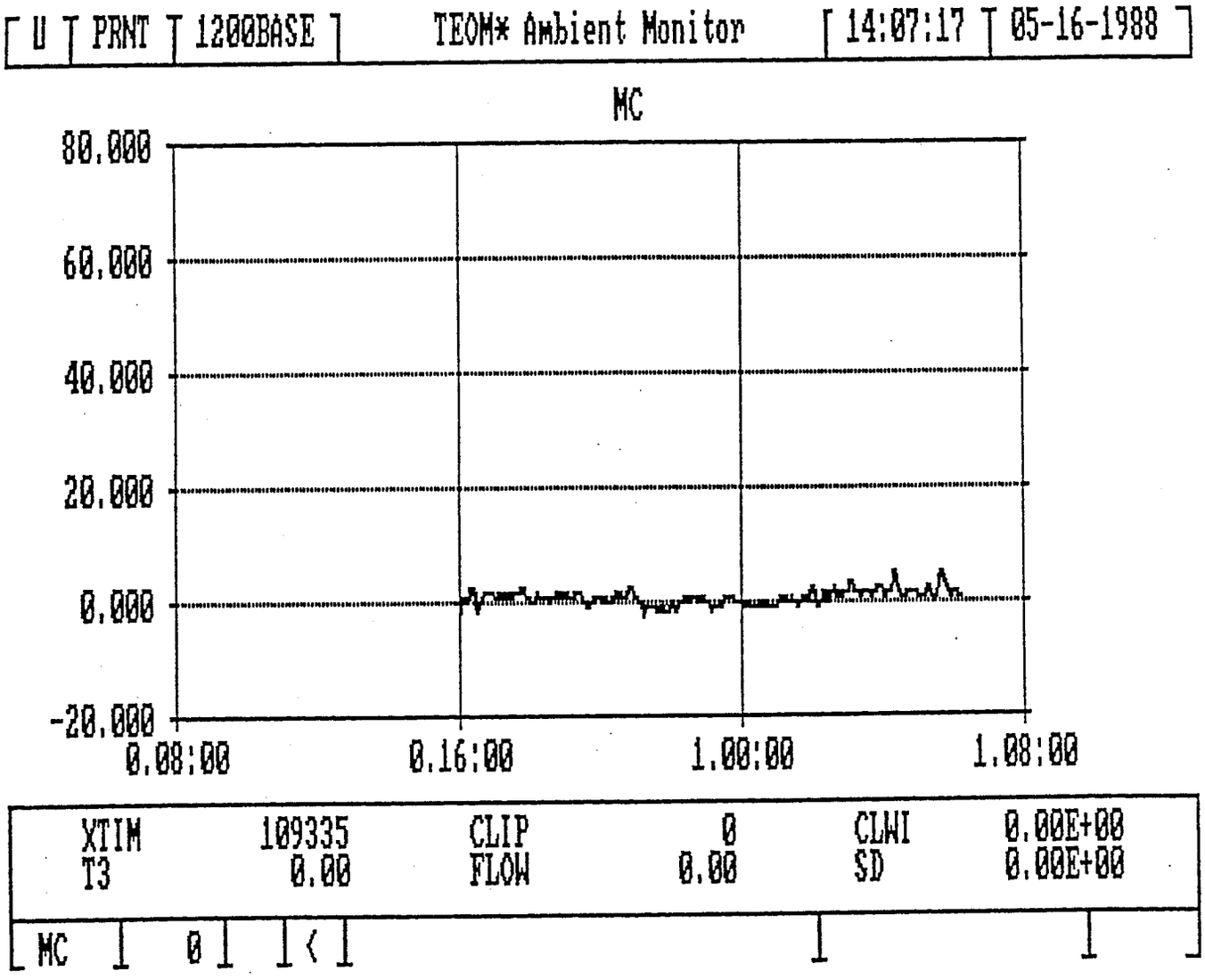

Figure 7. Baseline Performance of the TEOM® Monitor

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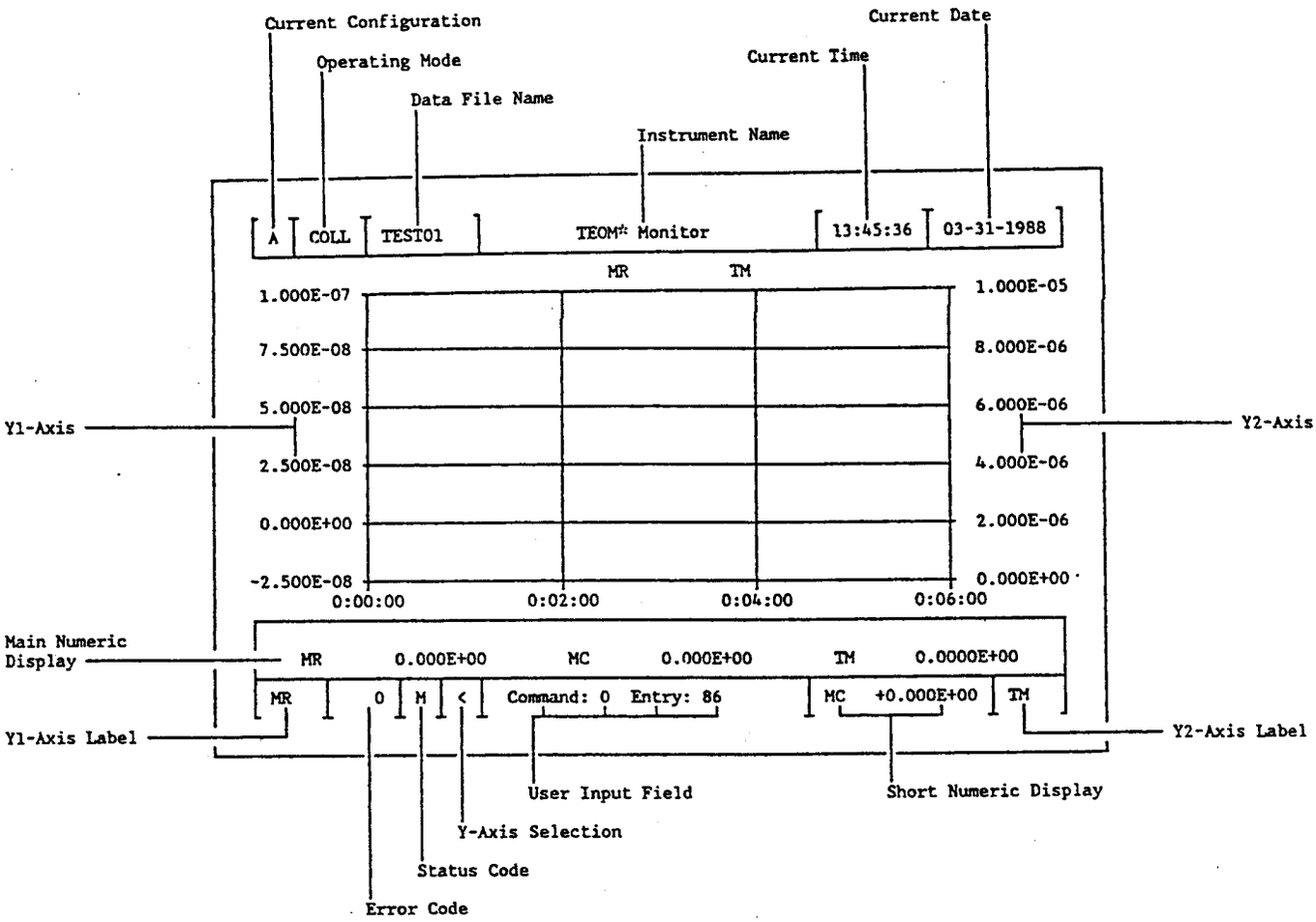

Figure 8. Components of the Main Display Screen of the TEOM® Particulate Monitor

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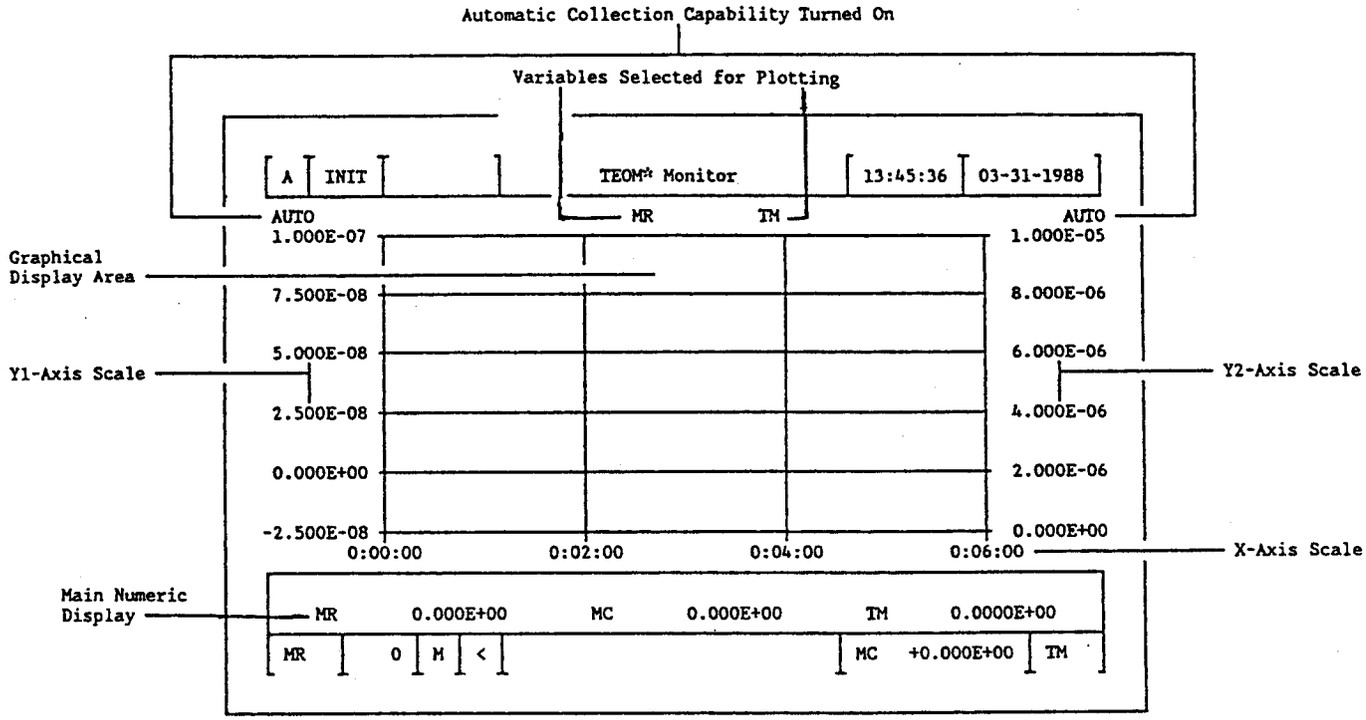

Figure 8. Components of the Main Display Screen of the TEOM® Particulate Monitor (cont'd)

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TP3 Programming

1. Description of the Instrument Cycle

This Section describes the steps involved in executing the instrument cycle of the TEOM® monitor. The instrument cycle is composed of the following modes:

Initialization Mode (INIT)	The instrument is in the INIT Mode when it is switched on, and after the main display screen has been cleared.
Collection Mode (COLL)	During the COLL Mode the TEOM® monitor collects mass rate, mass concentration and total mass data. The instrument plots and displays the information on the screen and saves data on disk.
Stop Mode (STOP)	The instrument enters the STOP Mode after the user has instructed the computer to stop data collection. In this mode, the user can print an image of the main display screen for future reference. After the screen is cleared in the STOP Mode, the monitor returns to the INIT Mode.

The function key commands used to switch the instrument from one operating mode to another are shown below:

F1	INIT Mode ------->	COLL Mode
F2	COLL Mode ------->	STOP Mode
F3	STOP Mode ------->	INIT Mode

Note: There is a Quick Reference Card which is supplied with the TEOM® monitor when purchased which provides a convenient summary of commands.

1.1 Executing the Instrument Cycle

Execution of these commands can only be done if the computer is equipped with the appropriate expansion boards.

1.1.1 Data collection (enter COLL Mode) - press F1 to start data collection. Entry into the COLL Mode is indicated by the mode indicator on the top line of the main display screen [see Figure 6(b)]. In this mode, the instrument collects, plots and displays mass rate, mass concentration and total mass data.
Note: If the instrument is configured to save data on disk, it requests a data file name in the User Input Field after F1 is pressed. In this case, enter one of these options followed by <Enter>.

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- A data file name up to 8 characters long composed only of letters and numbers
- The number 0. In this case the computer automatically assigns a data file name according to the present date and time in the format:

mmddhhmm.PRN

where:
mm is the current month
dd is the current day
hh is the current hour
mm is the current minute

1.1.1.1 If the instrument is successful in creating the data file, the file name appears on the top line beside the COLL cell, of the main display screen [see Figure 6(b)]. All data files written by TP3 are given the extension .PRN for direct use with Lotus 1-2-3® spreadsheet software.

1.1.1.2 The Status Code on the bottom of the screen shows that data collection has begun. The status code M indicates that data collection has begun, but that the first total mass data point has not yet been calculated. A status code R means that total mass data are being computed, but that valid mass rate and mass concentration data have not yet been generated. the delays in computation are due to the averaging times selected for total mass, mass rate and mass concentration in the current configuration.

1.1.1.3 A blank status code indicates that valid data are being calculated for total mass, mass rate and mass concentration. If the status code D appears, the data disk has run out of capacity and data are no longer being saved. The program always closes data files in an orderly manner so that they are available for later evaluation

1.1.1.4 The variables plotted on the main display screen are indicated by the variable names shown just above the graphical display window of the main display screen. The definitions of the variable names may be found in Table 1.

1.1.2 Stop data collection (enter STOP Mode) - press F2 to stop data collection. Entry into the STOP Mode is indicated by the Mode indicator on the top line of the main display screen [see Figure 6(b) - STOP should replace COLL]. In this mode, the user may print an image on the main display screen by pressing F9. The user also has the option of returning to the INIT Mode or entering the Replot Mode.

1.1.3 Printing or restarting (enter INIT Mode) - press F3 to clear the screen and enter the INIT Mode. If data were stored on disk during the COLL Mode, the instrument asks the user in the User Input Field if he wants to enter the INIT Mode. Enter Y followed by <Enter> in response to this prompt to enter the INIT Mode. Entry into the INIT Mode is indicated by the Mode Indicator on the top line of the main display screen. From the INIT Mode, the user is able to execute commands to print data files, replot data, start another instrument cycle, or exit from the program. Refer to this Appendix, Section 1.1 to begin another instrument cycle.

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1.2 Exiting the Program

The instrument must be in the INIT Mode to stop program execution and enter MS-DOS. Press F10 to exit from TP3 and enter MS-DOS. The instrument then asks in the user Input Field whether you want to exit from the program. Enter a Y followed by <Enter> to leave the program.
Note: Make sure that power has been turned off at the TEOM® Sensor Unit when the unit is not being controlled by the TP3 software.

2. Using Stored Data

2.1 Storage Format

All data files created by TP3 have the following attributes:

- The file name may be up to 8 characters long (letters and numbers), and is followed by the extension .PRN.
- Data files are stored in ASCII format, making them compatible with a wide range of commercially-available spreadsheet and word processing software. The files can also be read by programming languages such as BASIC, C and Pascal.
- The first 20 lines of each data file convey descriptive information about the instrument's hardware and software settings.
- The remaining part of the data file is made up of two or more columns containing real-time values for the variables stored on disk. The first column always contains the experimental time in seconds.

Table 2 lists the information contained in the 20 lines of the data files. the data file named BASELINE.PRN is provided in the C:/TEOMDATA subdirectory (hard disk systems) or on the TEOM® Data Diskette (floppy disk systems). The subdirectory C:\TP3 (or the provided floppy) also contains a LOTUS 1-2-3® template spreadsheet name AUTO3.WKS to aid in data analysis. The customer must own a copy of LOTUS 1-2-3® software to use the provided template file.

2.2 Replotting Stored Data in TP3

2.2.1 Data files may be replotted within the TP3 software by entering the Replot Mode. Data points may be replotted only if they have been saved on diskette or hard disk. The setting that causes the computer to store data on disk is part of the instrument's configuration. This parameter may be changed by entering the Configuration Definition Routine from either the INIT or Replot Mode.

2.2.2 The Replot Mode can be entered from either the STOP Mode or the INIT Mode. Press F7 when in the STOP Mode if the data file currently in the computer's memory is to be replotted. The TEOM® monitor enters the Replot Mode after this command is executed. Press F7 when in the INIT Mode to load a data file for replotting into the computer's memory. Then enter the name of the data file to be replotted (without the extension .PRN). The system then enters the Replot Mode. The same plotting, displaying and scaling commands are available in the Replot Mode as in the INIT and Collection

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Modes. However, the F1, F2, and F2 command sequence used to guide the instrument cycle for data collection have different functions in the Replot Mode.

2.2.2.1 The F1 command starts or re-starts the replotting of data. This command has no effect, however, if the replotting pointer has reached the end of the data file.
Note: Only those variables saved on disk may be replotted. All other variables are given a value of 0. The list of variables stored on disk during data collection is determined in the Configuration Definition Routine.

2.2.2.2 The F2 command stops the replotting of data. After replotting has stopped, the F9 command may be executed to print an image on the main display screen.
Note: Replotting may be resumed after F2 is entered by pressing F1 again.

2.2.2.3 The F3 command clears the screen and repositions the replotting pointer to the beginning of the data file. It also gives the user the option to re-enter the INIT Mode. Enter N to remain in the Replot Mode, or Y to re-enter the INIT Mode. Additional data files may be replotted by re-entering the INIT Mode and then executing the F7 command.

3. Configuration Definition Routine (CDR)

By entering the Configuration Definition Routine the user may define up to 26 different configurations. Each configuration has a single-letter name ranging from A to Z. When the computer is turned on, configuration A is automatically loaded into memory. To obtain a listing of the currently-defined configurations, enter ALT + C (hold down the ALT key and press C) when in the INIT Mode. The resulting display shows the full name of the files that store the operating parameters. These file names are made up of the instrument name, for example 1100 for the TEOM® Particulate Mass Monitor, and the configuration name ranging from A to Z. Press any key to return to the main display screen. Press F4 to load a different configuration into memory when in the INIT Mode or Replot Mode. AFter F4 has been pressed, the computer displays "Input New Config Name:" in the User Input Field. In response, enter the single-letter name of a different currently-defined configuration followed by <Enter>. The new configuration is then loaded into the computer's memory, and the settings of the new configuration are reflected on the main display screen. The name of the current configuration is changed in accordance with the user input.

3.1 Executing the CDR

The CDR can be executed when either in the INIT Mode or the Replot Mode. Press F8 when in the Initialization Mode. Press F8 when in the Replot Mode. This keystroke will only function if the replotting pointer is at the beginning of the data file, i.e., if you have just entered the Replot Mode or if you have just cleared the screen in the Replot Mode by pressing F3. The computer then lists the currently-defined configuration files in the TEOM® system. These file names are made up of the instrument model number, followed by single-letter configuration names. Press any key to continue.

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3.2 Displaying the Configuration Screens (F1-F4)

The CDR allows the user to change the values of up to 80 program parameters displayed on four different screens. Screen 1 appears on the monitor when the routine is first executed. The number of the current screen is shown in the bottom right-hand corner of the display. The name of the current configuration appears in the lower left-hand corner of the screen. Keys F1 through F4 display screens 1 through 4. These commands may be entered in any order and as often as desired. Each screen contains 20 lines (slots) of information. Each of these Slots contains a description of a parameter, as well as the current value of the parameter.

3.3 Changing a Parameter's Value

Follow the steps below to change the value of a parameter, for example slot 0 (X-axis span): To change the value of parameter "X-axis span", slot 0 must appear on the computer monitor. If this is not the case, press F1 to choose screen 1. Press F6 to obtain the computer prompt "Slot:". Enter the number of the slot to be changed followed by <Enter>. In this case, type 0 followed by <Enter>. The computer responds by displaying ":". Type the new parameter value followed by <Enter>. To change the span of the X-axis to 3 minutes, enter 3 followed by <Enter>.

3.4 Saving the Present Configuration

Press F7 to save the current configuration on disk. (This keystroke saves changes made to the present configuration.)

3.5 Creating or Switching to Another Configuration

Press F8 to create or switch to another configuration. The computer displays the prompt "Enter File Name:". To create a new configuration, enter the single-letter name of a configuration that does not presently exist, followed by <Enter>. The new configuration initially takes the parameter values of the configuration presently loaded in the computer, or to load another configuration into the computer's memory, enter the single-letter name of an existing configuration, followed by <Enter>.
Note: The F8 command does not save changes made to the current configuration before loading a new configuration or loading a different existing one. Press F7 to save changes made to the current configuration before executing the F8 command.

3.6 Printing Configuration Information

Turn the printer on. Make sure that it is "on line", and that its print head is at the top of a new page. Press F9 to print the contents of the current configuration. When the F9 key is pressed in the INIT Mode, the user may choose to print the numeric contents of any data file stored on disk. The instrument is in the Print Mode during all of these printing operations.

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Note: Because of the time required to print a screen image or the contents of a data file, the heating circuits in the TEOM® Sensor Unit are turned off during printing. The user may have to allow for temperatures to stabilize again before resuming data collection.

3.7 Exiting the CDR

Press F10 to exit to the main display screen and save the current configuration.

COMPENDIUM APPENDICES

Appendix A	Abbreviations and Symbols
Appendix B	Definitions of Terms
Appendix C-1	Procedure for Placement of Stationary Active Samplers in Indoor Environment
Appendix C-2	Procedure for Placement of Stationary Passive Samplers in Indoor Environment

ACGIH	American Conference of Governmental Industrial Hygienists
AIHA	American Industrial Hygiene Association
ASHRAE	American Society of Heating, Refrigeration and Air Conditioning Engineers
ASTM	American Society for Testing Materials
B(a)P	benzo-a-pyrene
°C	degrees Celsius
cm	centimeter
cm^2	square centimeters
CO	carbon monoxide
COC	chain of custody
EPA	U.S. Environmental Protection Agency
°F	degrees Fahrenheit
ft	foot
ft^2	square feet
g	gram
HPLC	high performance liquid chromatography
in	inch
in^2	square inches
L	liter
L/min	liters per minute
m	meter
min	minute
mg	milligram
mm	millimeter
m^3	cubic meter
µm	micrometer
n	nano (10^{-9})
NBS	National Bureau of Standards
ng	nanogram
NIOSH	National Institute for Occupational Safety and Health
nm	nanometer
NO	nitric oxide
NO_2	nitrogen dioxide
NO_x	nitrogen oxides
PAH	polynuclear aromatic hydrocarbons
ppm	parts per million
ppm-hrs	parts per million-hours
QA	quality assurance
QC	quality control
RH	relative humidity

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Accuracy	The difference between the measured value and the true value that has been established by an accepted reference method procedure. In most cases, a value is quoted by the manufacturer and no description is given to indicate how this value was obtained.
Active device	An instrument that employs a power source with a pump to pull the air across a sensing element or collector.
Air monitoring module	An assembly of air monitoring devices that are collected into one package to facilitate handling as a unit.
Analyzer	An analytical sampling device that determines the value of a pollutant concentration almost instantaneously.
Blank	A sample of the pollutant collection medium that is not exposed to air sampling but that is analyzed as part of the quality assurance program.
Calibration	The method for determining the instrument response to known-concentration gases (dynamic calibration) or artificial stimuli (static calibration).
Collection efficiency	The fraction of the incoming pollutant or parameter that is measured by the instrument.
Collector	A sampling device that collects a pollutant for subsequent laboratory analysis of pollutant concentration.
Fall time	The time interval between the initial response and a 90 percent response (unless otherwise specified) after a step decrease in the inlet concentration. This measurement is usually, but not necessarily, the same as the rise time.
Interferences	Any substance or species that causes a deviation of instrument output from the value that would result from the presence of only the pollutant of concern.
Lag time	The time interval from a step change in the input concentration at the instrument inlet to the first corresponding change in the instrument output.

Linearity	Expresses the degree to which a plot of instrument response versus known pollutant concentration falls on a straight line. A quantitative measure of linearity may be obtained by performing a regression analysis on several calibration points.
Long-term integrated	Techniques that produce an accumulated sample over an extended time period, such as a week.
Lower detectable limit	The smallest quantity of concentration of sample that causes a response equal to twice (sometimes 3 or 4 times) the noise level. (Not to be confused with sensitivity, which is response per unit of concentration.)
Microenvironment	A general location such as residence, office, car, bus, church, or supermarket that individuals move through during a 24-hour period of activity.
Monitor	The instrument or device used to measure air quality of meteorological parameters. Monitor also refers to the act of using the instrument or device.
Multi-parameter capability	Ability to measure other pollutants or parameters.
Passive	A sampling or analytical device that relies on diffusion to bring a pollutant in contact with a collector or an analyzer.
Personal monitors	Instruments for measuring pollutant concentration that can be worn conveniently on a person.
Portable monitors	Instruments that can be readily transported from one sampling location to another for personal or area sampling.
Protocol	Detailed scientific directions for performing a program.
Quality assurance	A system of activities that provides assurance that the quality control system is performing adequately.
Quality control	The activities performed that provide a quality product.

Range	The lower and upper detectable limits. (The lower limit is usually reported as 9.0 ppm. This is somewhat misleading and it would be better, however, to report it as the true lower detectable limit.)
Repeatability	The degree of variation between repeated measurements of the same concentration.
Reproducibility	The degree of variation obtained when the same measurement is made with similar instruments and many operators. In most cases, a value is quoted by the manufacturer and no description is given to indicate how this value was obtained.
Response time	The time interval from a step change in the input concentration at the instrument inlet to a reading of 90 percent (unless otherwise specified) of the ultimate recorded output. This measurement is the same as the sum of lag time and rise time.
Retention time	The time interval from a step decrease in the input concentration at the instrument inlet to the first corresponding change in the instrument output.
Rise time	The time interval between the initial response and a 90 percent response (unless otherwise specified) after a step increase in the inlet concentration.
Sampling	The process of withdrawing or isolating a representative portion of an ambient atmosphere, with or without the simultaneous isolation of selected components for subsequent analysis.
Short-term integrated	Techniques for sampling frequencies that are generally on the order of hours to 1 day. Resulting data are capable of describing some aspects of short-term peaks.
Span drift	The change with time in instrument output over a stated time period of unadjusted continuous operation when the input concentration is a stated value other than zero. (Expressed as percent of full scale.)
Stationary monitor	An instrument that cannot be readily transported. This may be because of size, weight, the need to operate in a laboratory environment, fragility, or high maintenance requirements.

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Warm-up time	The elapsed time necessary after startup for the instrument to meet stated performance specifications when the instrument has been shut down for at least 24 hours.
Zero air	Air which has been treated to ensure purity and lack of contaminants, that may be used to establish a zero reference point for an air quality analyzer.
Zero drift	The change with time in instrument output over a stated time period of unadjusted continuous operation when the input concentration is zero. (Expressed as percent of full scale.)

PROCEDURE FOR PLACEMENT OF STATIONARY ACTIVE SAMPLERS IN INDOOR ENVIRONMENTS

1. Scope

There are no standard practices available for selecting sampling areas for indoor environments. This procedure is intended to provide general guidelines in siting and locating stationary active samplers indoors. The purpose of this document is to ensure consistency of sampling site selection in indoor atmospheres.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definition of Terms Relating to Atmospheric Sampling and Analysis

2.2 Other Documents

2.2.1 Wadden, R. A., and Scheff, P. A., *Indoor Air Pollution Characterization, Prediction, and Control*, ISBN: 0-471-8763-9, Wiley Interscience Publishing Co., New York, NY, 1983.

2.2.2 Nagada, et al., *Guidelines for Monitoring Indoor Air Quality*, Hemisphere Publishing Corp., New York, NY, 1987.

3. Summary of Method

3.1 Indoor air is collected by a stationary sampling system. The sampled air is either analyzed directly or stored in an appropriate container for later analysis.

3.2 Guidelines are given for determining sampling site location.

4. Procedure

4.1 The sampling inlet/probe of the stationary sampler should be located in an area that best represents peak pollutant concentrations experienced by the individuals occupying the area. The sampling locations may be in a general area such as a basement or warehouse. However, for more specific monitoring, samplers can be placed in a kitchen, living room, or office. A particular site within the area is selected to depict the air quality of the entire area.

4.2 Site selection in an occupied (i.e., lived in) area is primarily dependent upon occupancy patterns of the inhabitants as well as structural characteristics of the dwelling (i.e., age and building materials, type of appliances and furniture, and use of appliances). Additionally, emission source locations, available air volume to dilute source emissions, air circulation and exchange rate are important considerations when determining sampler location. In summary, the sampling area should be representative of the air quality in the indoor environment of concern, contents of the area, and occupant practices.

4.3 Once indoor sampling areas have been identified, inlet/probe locations may be determined. When selecting inlet/probe locations, the following areas should be avoided:

- areas of direct sunlight
- areas with noticeable drafts
- areas directly influenced by return or supply ducts
- areas that are directly impacted from outdoor sources
- exterior corners and walls
- probe heights below 1 m or above 2 m unless vertical gradients are being measured

4.4 Sampler instrumentation is also an important factor in selecting probe location. Samplers should be situated to minimize interference with indoor air. For unoccupied areas, major consideration should be given to sample flow rates (i.e., to avoid sampling system cleaning the air or contributing local exhaust) and heat sources. For occupied areas, especially residences, available space is an important issue.

4.5 New analyzers are compact for placement indoors and are configured to operate from battery power or to operate from household electric supply without interfering with normal occupancy. These systems generally require repackaging for use in the field. For systems with multiple analyzers and sophisticated data recording devices, a container is useful for transport and security. Before placing such an instrument indoors, the following questions should be answered:

- How many people will be needed to transport the monitoring package?
- What is the size of the smallest doorway through which the system is to be carried, including vehicles used to transport the package from place to place?
- Can a toddler pull or push it over?
- Will the size of the package interfere with normal use of the area by its occupants?
- Will the sampling system emit noise or odors that may be considered offensive to occupants?

4.6 If the system is to be operated from wall current, electric power is important for two reasons. The first is heat generated during operation of transformers, pumps, etc. If packaging confines natural ventilation around the instruments, the casing should provide for compensatory air movement with small fans or other devices. If sampling inlets are very close to the cabinetry, sampling results may be biased. The second aspect of electric power is the system amperage and grounding requirements. If monitoring is to take place in occupied structures, available circuits will be at a premium. A blown fuse or tripped breaker leads to lost data and guilt-ridden, if not infuriated, occupants. There are many structures that still have two-prong outlets; a "cheater plug" does not necessarily ensure a grounded connection. Inexpensive test devices are available to verify ground connections.

PROCEDURE FOR PLACEMENT OF STATIONARY PASSIVE SAMPLERS IN INDOOR ENVIRONMENTS

1. Scope

This document covers the placement and use of passive sampling monitors in the indoor atmosphere. The purpose of this document is to help ensure consistency of sampling within a variety of indoor environments and to facilitate comparison of monitoring data. This procedure may involve hazardous materials, operations, and equipment. This procedure does not purport to assess all of the safety problems associated with its use. It is the responsibility of whoever uses this procedure to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definitions of Terms Relating to Atmospheric Sampling and Analysis Practice for Planning the Sampling of Indoor Air

3. Summary of Practice

3.1 Sample air is collected by adsorption onto a sorbent media or reacted with an appropriate chemical in order to subsequently undergo analysis for determination of concentration. The sampled air is circulated to the adsorption media or reaction chemical through diffusion.

3.2 Instructions are given for the handling and placement of passive monitors within an indoor environment.

4. Terminology

For definitions and terms used in this practice refer to D1356.

5. Significance and Use

5.1 Since 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 area of the passive monitor.

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

5.3 Placement and recovery of the monitors can be performed by unskilled personnel with suitable instruction (even an occupant).

6. General Principles

6.1 Passive monitors rely on normal convection of air currents within an indoor environment for circulation of a representative sample atmosphere to the vicinity of the monitor. Subsequent collection of the sample component is performed through diffusion. Sampling adequacy is directly influenced by the ability of the monitor to be exposed to the representative sample atmosphere.

6.2 Variability of the results will decrease with consistency in sampling protocol as well as with increased sample component concentration.

7. Procedure

7.1 Predeployment Considerations

7.1.1 The occupants, if any, in the indoor environment to be sampled should not alter normal activities within the measurement period.

7.1.2 Deployment during remodeling or redecorating is not recommended. Changes in major furnishings such as stoves, HVAC systems, etc., should be avoided.

7.1.3 Deployment when seasonal alterations in insulation or building tightness are occurring or will occur during the measurement period should be avoided. (When long-term measurements on the order of months are being taken, this consideration is minimal.)

7.2 Measurement Conditions

7.2.1 Doors should be operated (opening/closing) in a manner consistent with normal occupancy. Windows should be kept closed when possible. Over an extended sampling period, the effect of a few days of open windows should be minimal on results.

7.2.2 The ventilation system should be operated in a manner consistent with normal occupancy.

7.2.3 The method of heating should not be altered during the sampling period. The normal occupancy heating method should be maintained.

7.2.4 The use of humidifiers/dehumidifiers is not recommended.

7.2.5 Normal occupancy activities should continue.

7.2.6 No effort should be made to additionally tighten the indoor environment or to provide additional ventilation.

7.2.7 The placement of the monitor should not prevent normal occupancy activity from occurring.

7.3 Deployment

The monitor should be deployed as soon as possible after receipt and within the limitations of the indicated storage life. A blank exposure should be retained for completeness utilizing an unexposed monitor of the same manufactured lot.

7.4 Placement

7.4.1 Indoor Atmosphere Considerations

7.4.1.1 The monitor should be situated in a location such that the monitor is exposed to representative sample air at normal conditions.

7.4.1.2 Humidity - Locations near sinks, tubs, showers, stoves, washers, driers, or humidifiers/dehumidifiers should be avoided.

7.4.1.3 Temperature - Locations near furnaces, vents, sinks, tubs, showers, electric lights, or electrically operated devices which may produce heat should be avoided.

7.4.1.4 Meteorologic - Locations of direct sunlight and seasonal or short-term meteorologic variations should be avoided (e.g., drafty windows or doors).

7.4.1.5 Airflow - Location in direct airflow such as near furnace vents, appliance fan vents, computer cooling fans, and HVAC intake/exhaust should be avoided. Areas where a known draft or pressure differential between areas of a building should also be avoided.

7.4.2 Spacial Considerations

7.4.2.1 The monitor should be placed in an open and unobstructed area where normal air convection will be encountered. The monitor should be placed at least 20 cm (8 in) below the ceiling, 50 cm (20 in) above the floor and 15 cm (6 in) from a wall. Outside walls should not be used if possible. Suspending monitors from the ceiling may be suitable.

7.4.2.2 The monitor should be placed in a position where disturbance will not occur during the measurement period.

7.4.3 Occupant Considerations

7.4.3.1 The monitor should be placed out of the reach of small children and pets.

7.4.3.2 The placement of the monitor, if not deployed by the occupant, should be agreeable and approved by the occupant.

7.5 Sampling

7.5.1 The sampling period begins when the lid or container of the monitor is removed at which time the time and date should be transcribed into a log book. A means of either resealing the monitor in the container or replacing the lid should be assured prior to the end of the sampling period.

7.5.2 Since damage could occur during shipping and handling of the monitor, inspect the monitor and package carefully.

7.5.3 The monitor should have a permanently attached identification code or serial number which should be transcribed into a log book. The log book should include information describing the location of the monitor and pertinent information regarding the building such as construction type, heating system, insulation, occupancy number and patterns, and major appliance location. Include a diagram of the sampling location and building depicting the information listed in this subsection. If the occupant deploys the

monitor, sufficient instructions should be included regarding proper location and sampling conditions. A form should be included for easy collection of information necessary for log book entries.

7.5.4 If the monitor is deployed for other than a screening measurement, the monitor should be placed by a reliable professional familiar with the monitor used. For specific measurements, a deviation from the guidelines in Sections 7.2.1 through 7.4.2.2 is permissible.

7.6 Passive Monitor Recovery

7.6.1 The sampling period is terminated when the monitor is removed and sealed from the sample environment.

7.6.2 Record the time and date for measurement termination. Any damage or variance in the monitor since deployment should be noted in the log book.

7.6.3 Adequate information should be entered in the log book to permit interpretation of results and comparison to similar measurements. Any variation in the sampling location or building structure should be noted.

7.6.4 The monitor should be analyzed as soon as possible.

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