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

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and
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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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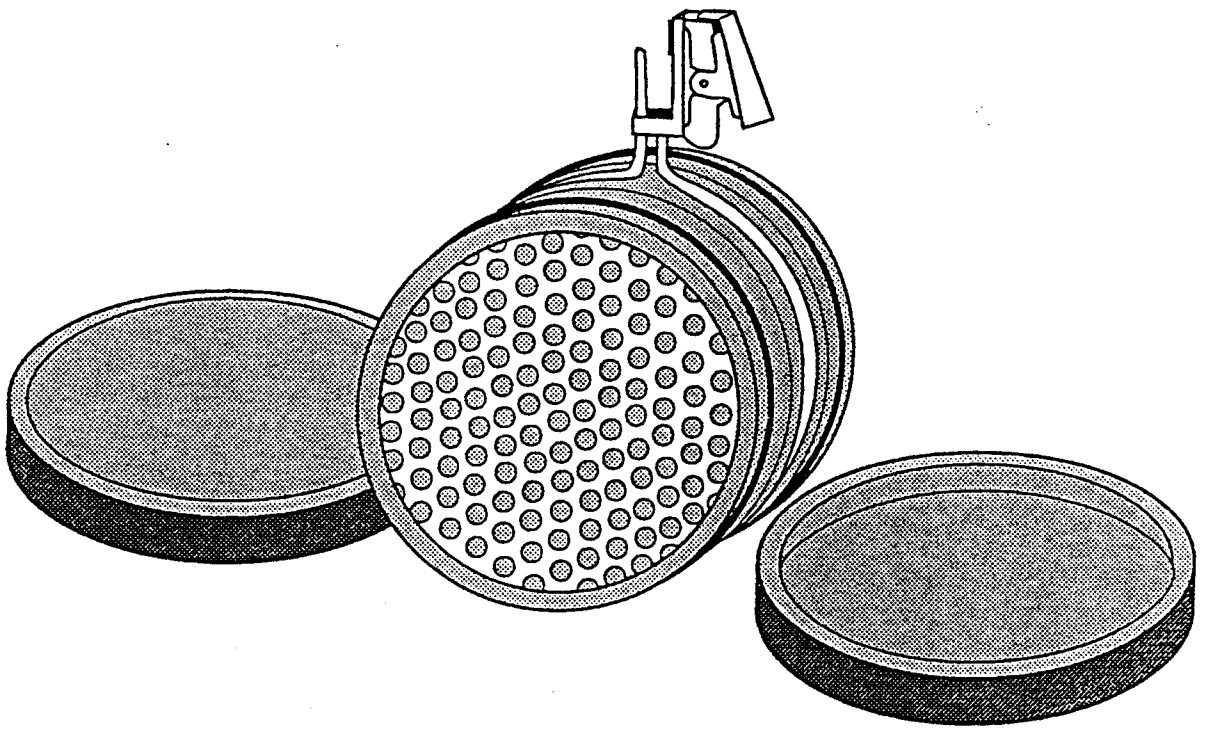

Figure 1. Commercially Available NO_2 Passive Sampling Device

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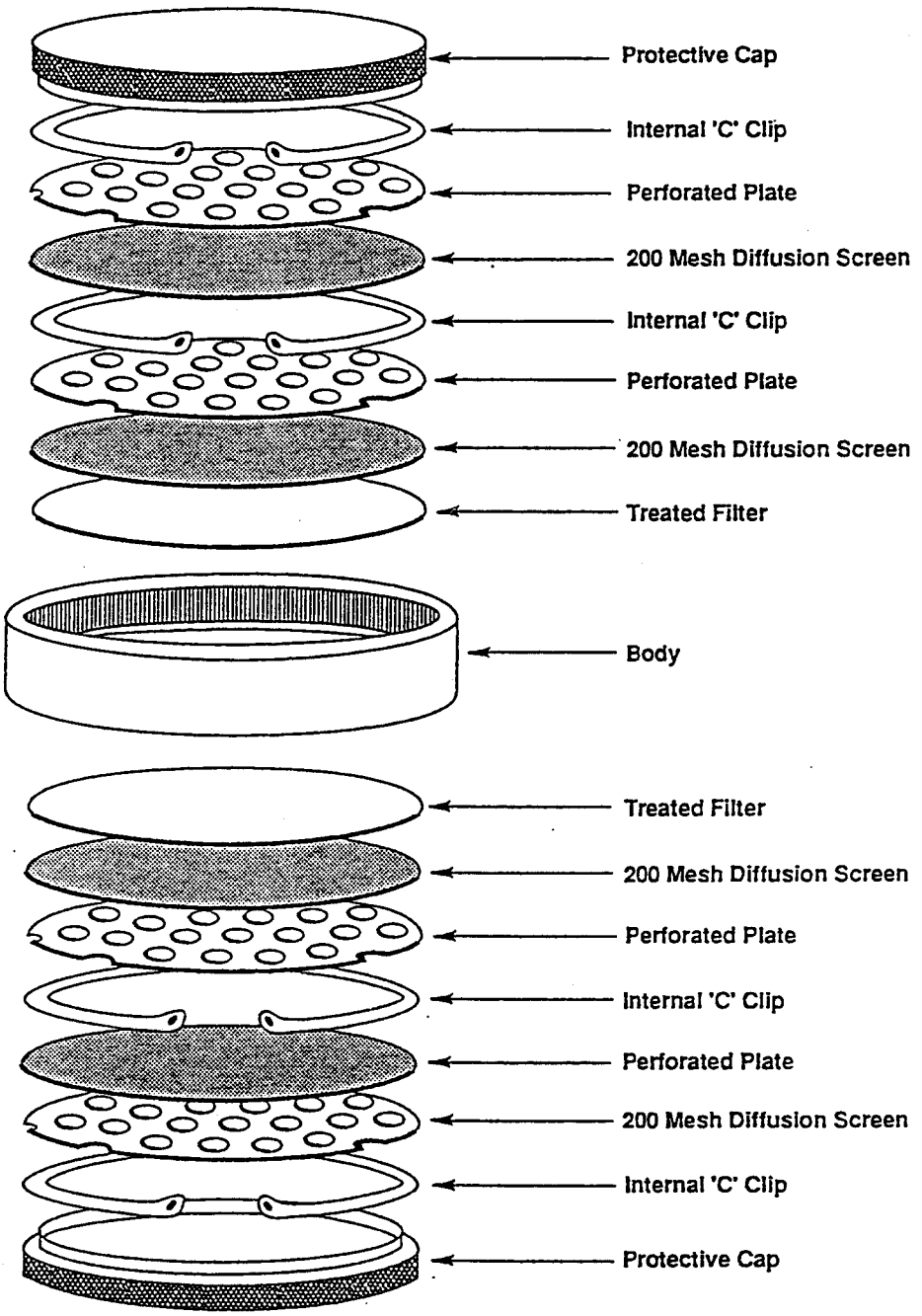

Figure 2. Exploded View of a Commercially Available Passive Sampling Device

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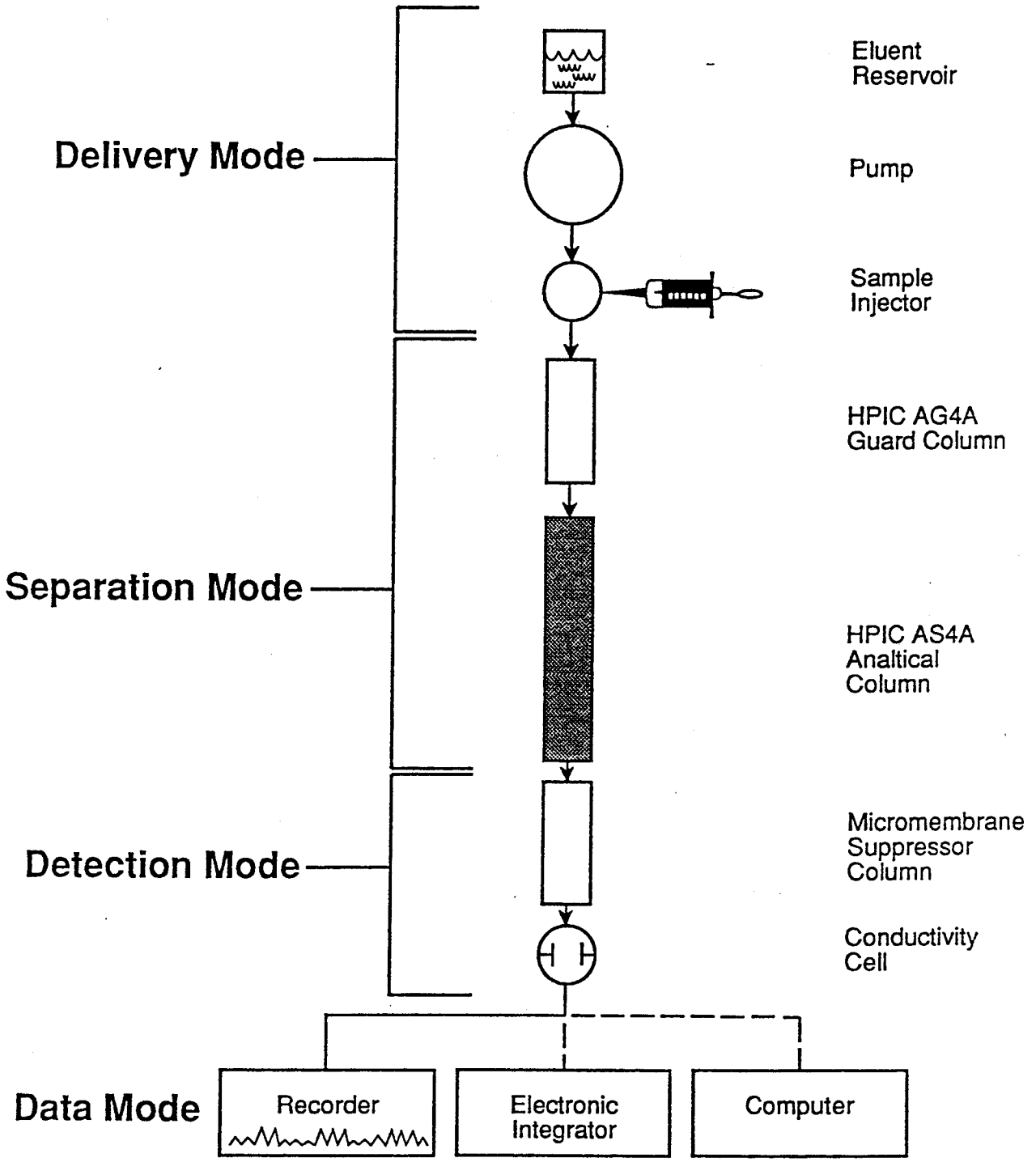

Figure 3. Major Components of a Commercially Available Ion Chromatograph

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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:

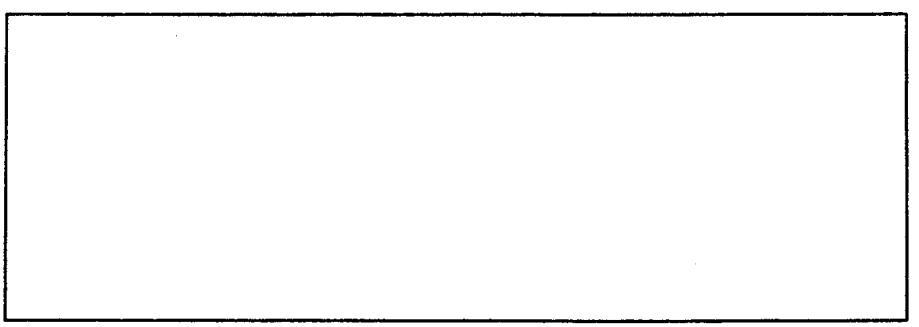

Figure 4. Field Test Data Sheet for PSD

477

464

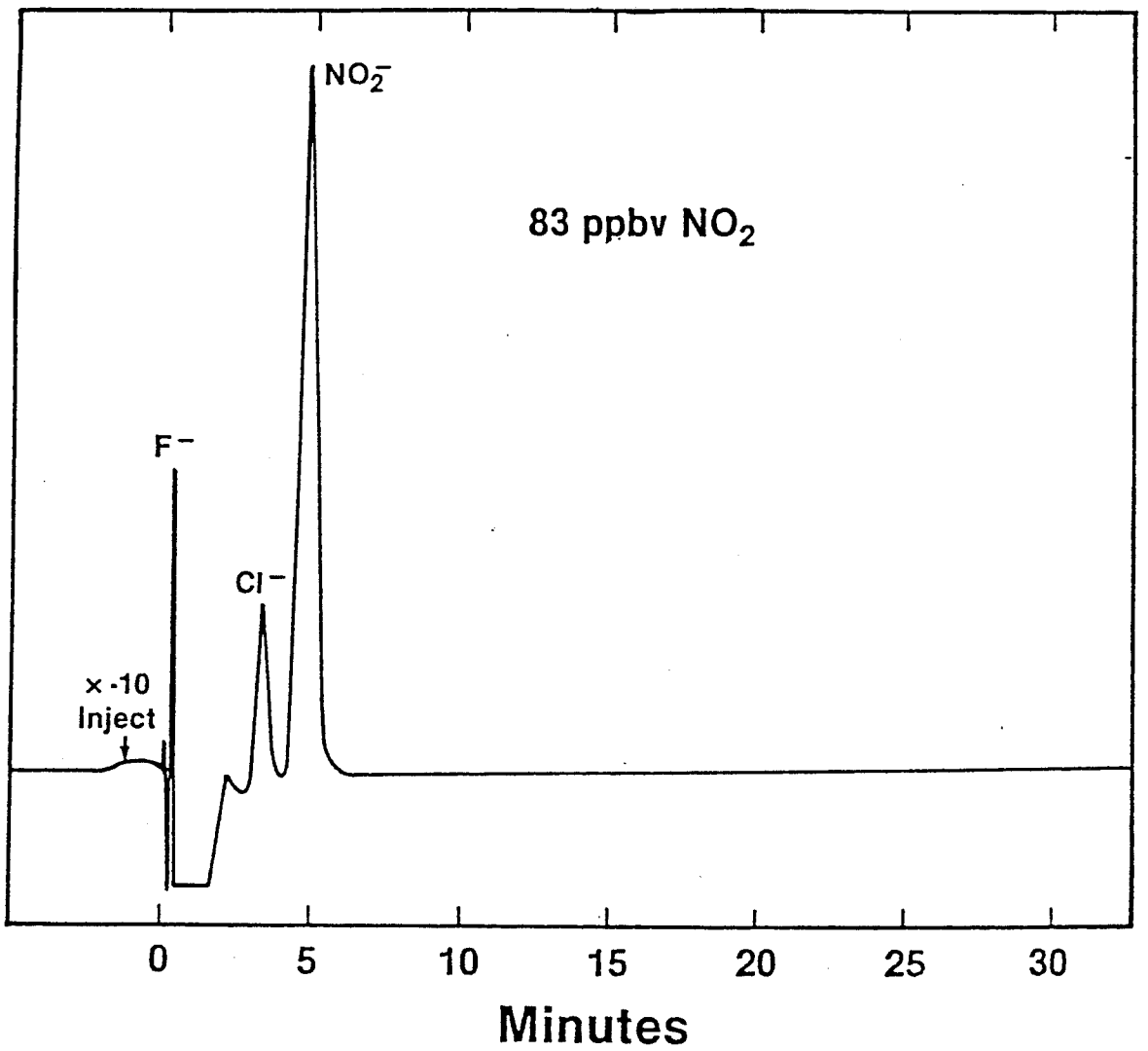

Figure 5. Typical Dionex Model 14 Chromatogram

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405

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

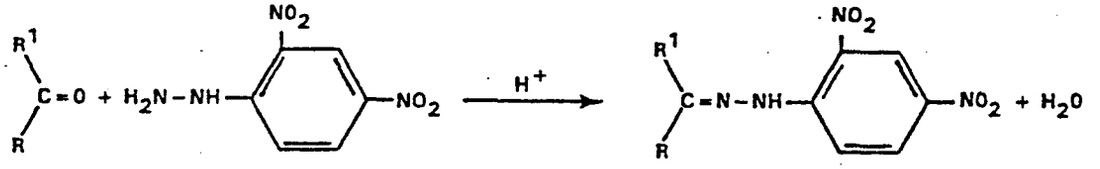
DETERMINATION OF FORMALDEHYDE AND OTHER ALDEHYDES IN INDOOR AIR USING A SOLID ADSORBENT CARTRIDGE

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):



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.

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

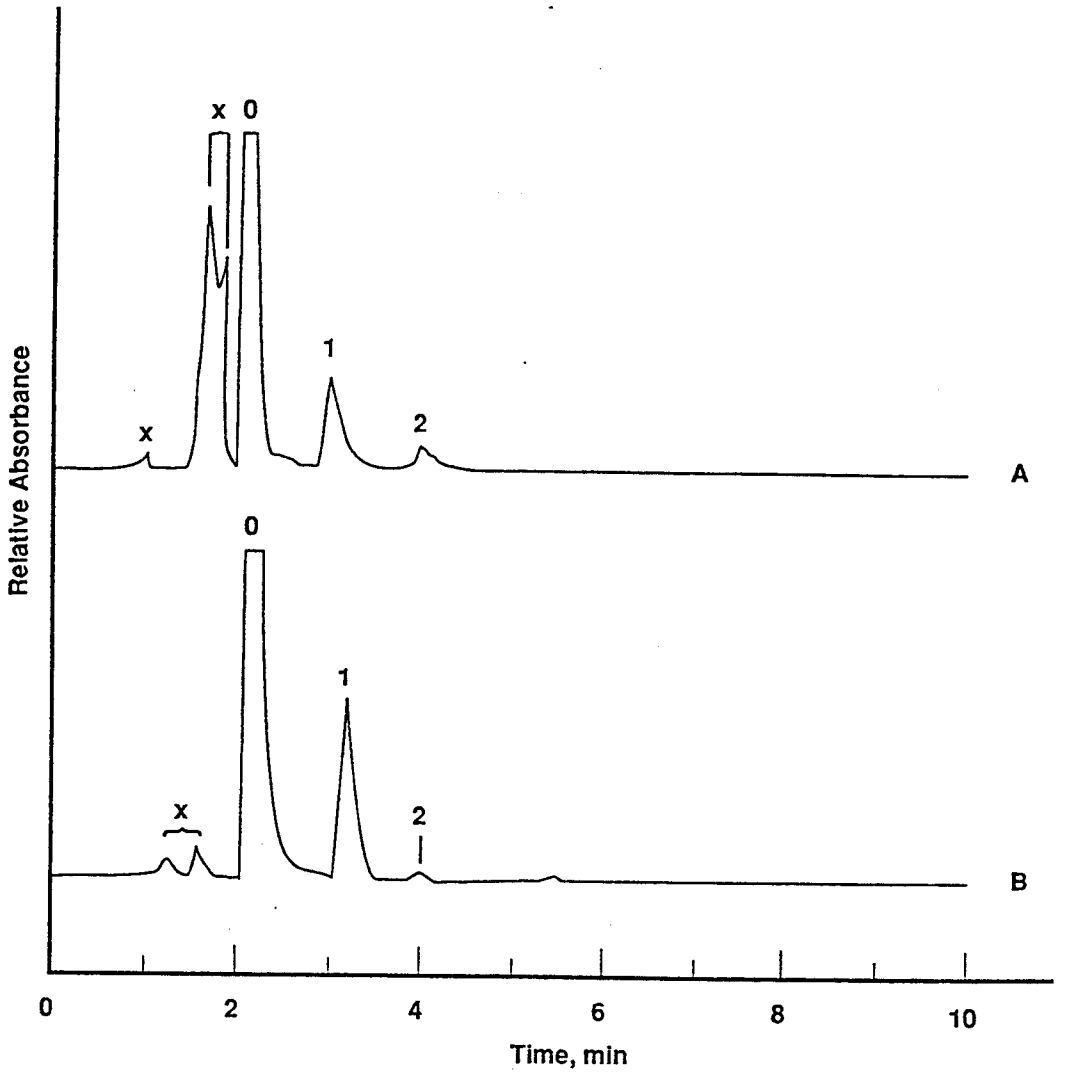
	Sample Volume, L										
Compound	10	20	30	40	50	100	200	300	400	500	1000
Formaldehyde	1.45	0.73	0.48	0.36	0.29	0.15	0.07	0.05	0.04	0.03	0.01
Acetaldehyde	1.36	0.68	0.45	0.34	0.27	0.14	0.07	0.05	0.03	0.03	0.01
Acrolein	1.29	0.65	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03	0.01
Acetone	1.28	0.64	0.43	0.32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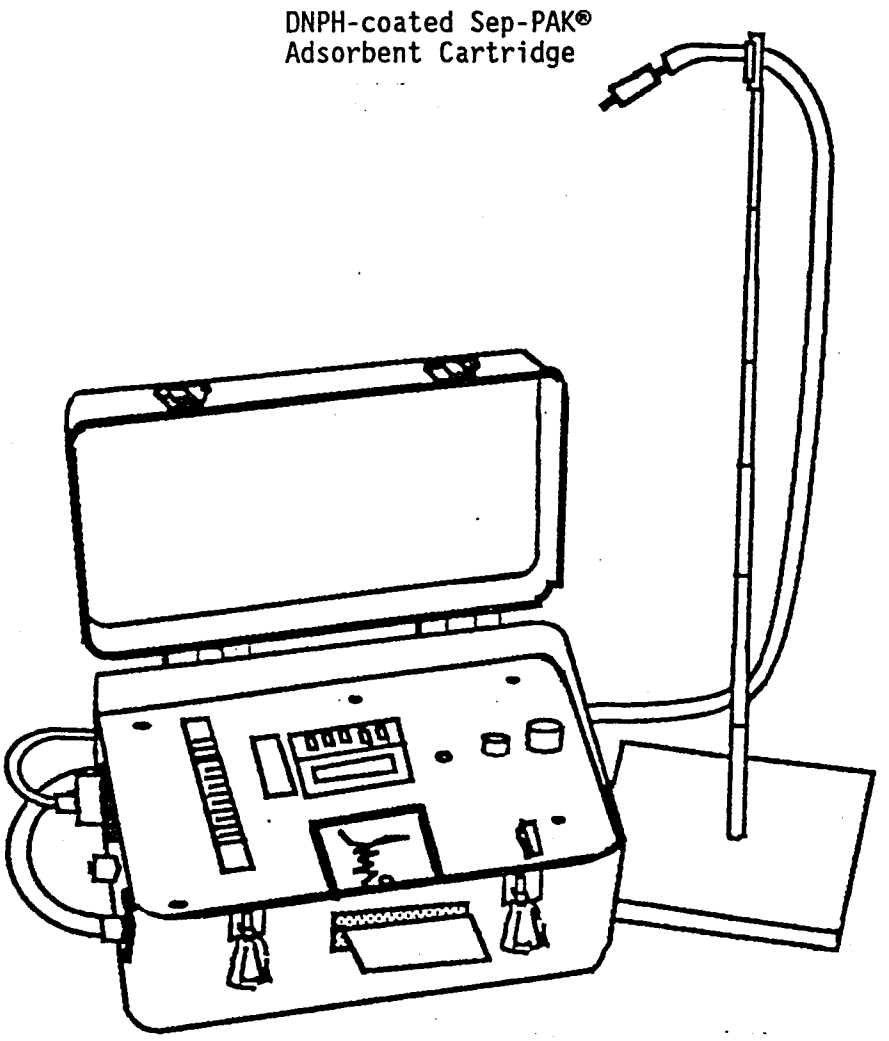

Figure 2. Portable Sampling System for Adsorbent Cartridges

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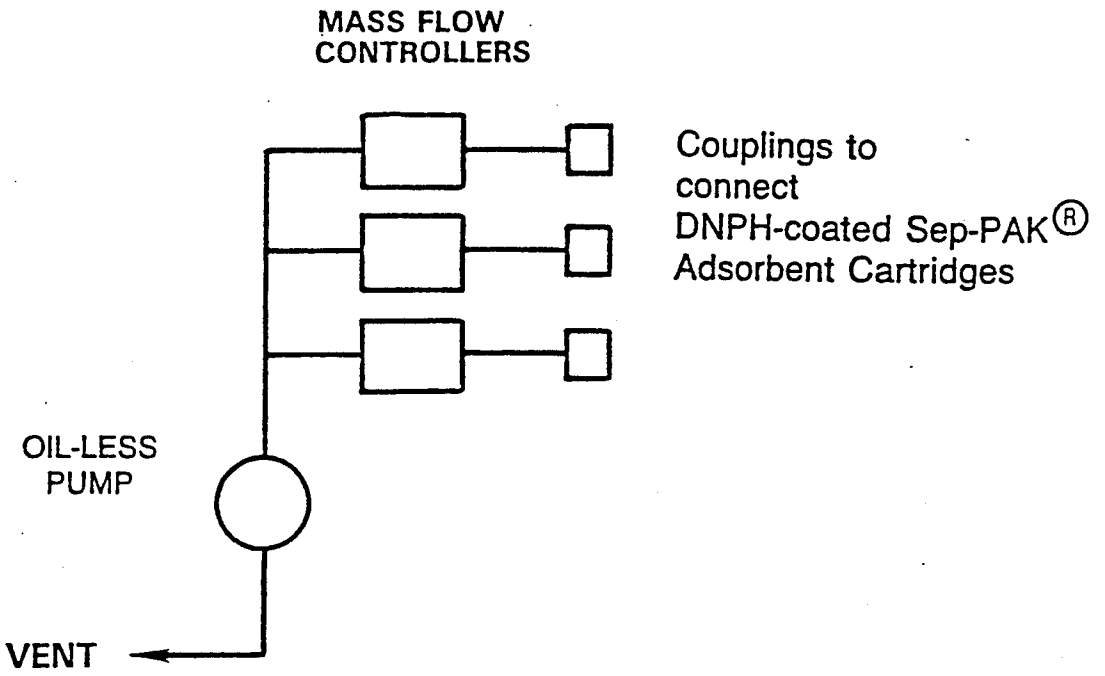
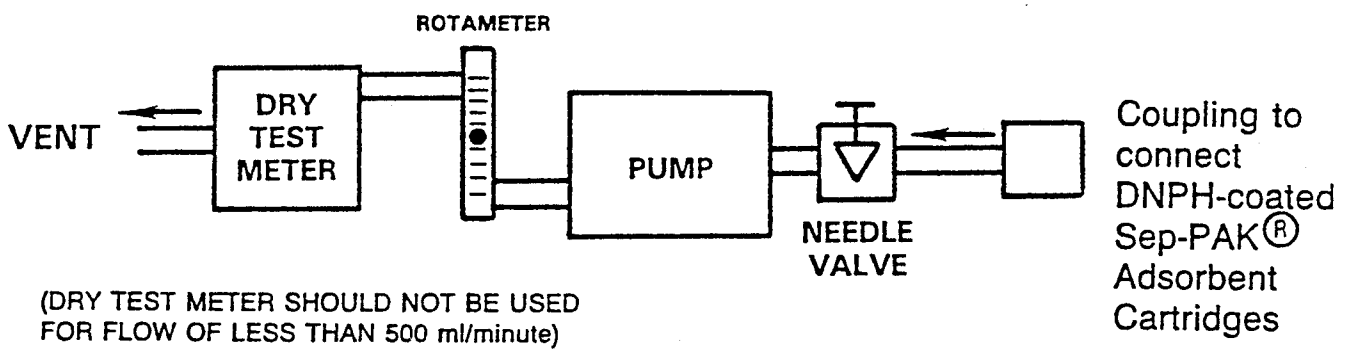


(a) MASS FLOW CONTROL



(b) NEEDLE VALVE/DRY TEST METER

Figure 3. Typical Sampling System Configurations

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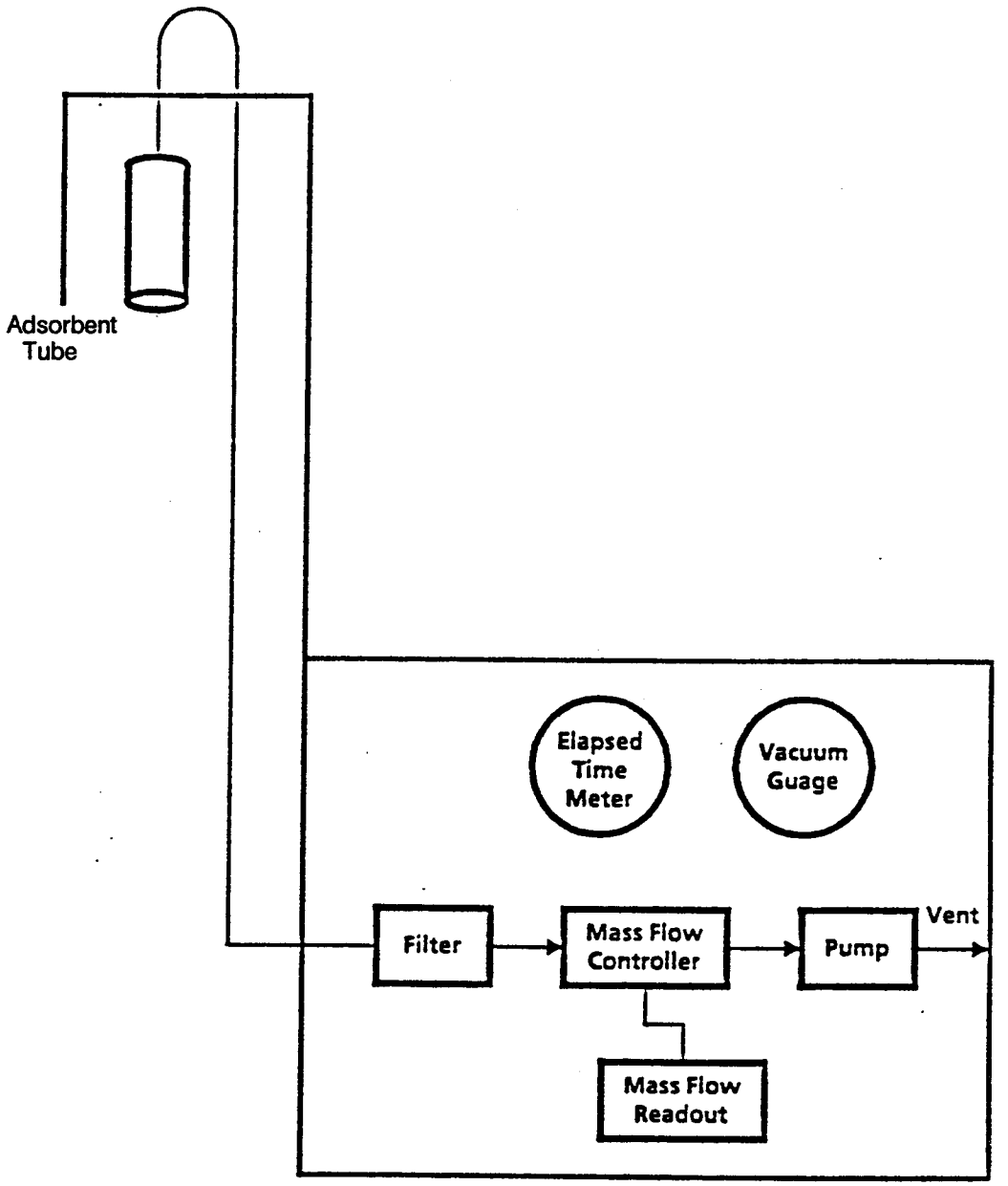

Figure 4. Diagram of Adsorbent Sampling Device for Airborne Aldehydes

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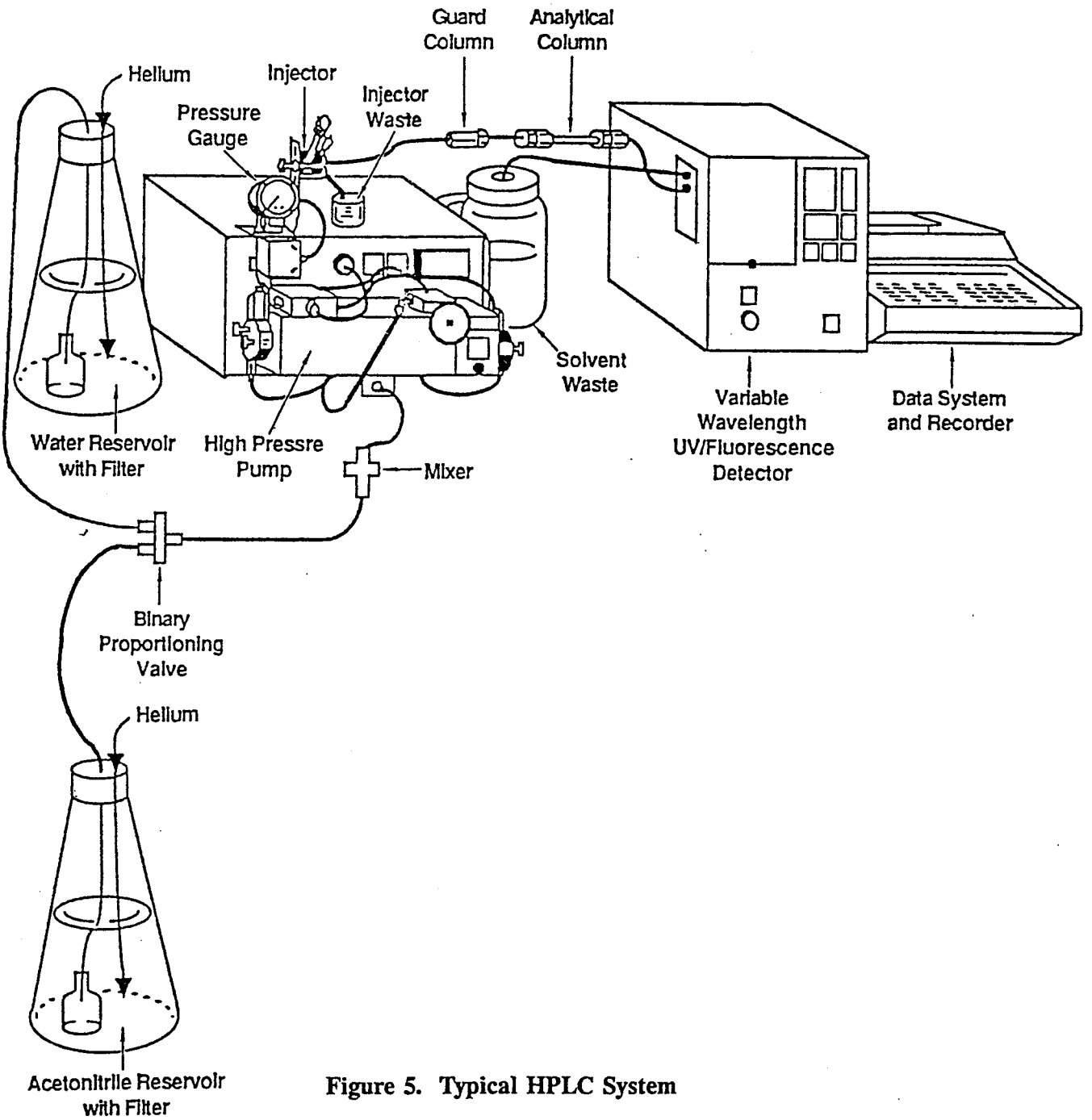

Figure 5. Typical HPLC System

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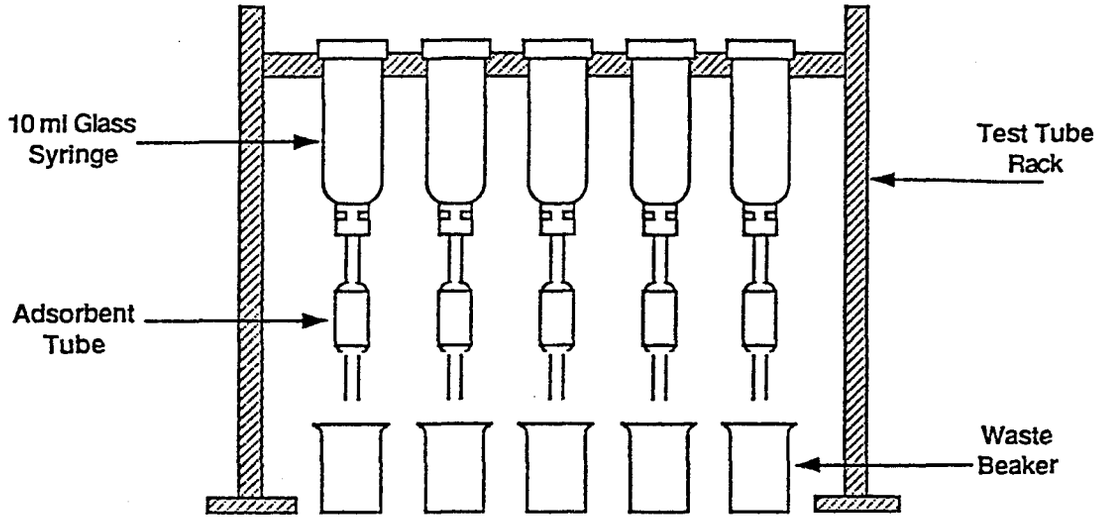
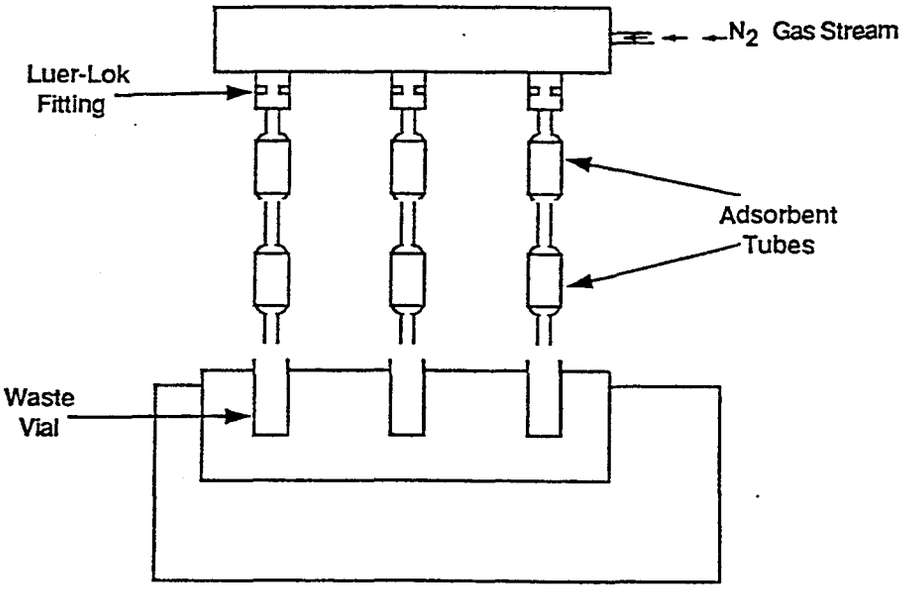


(a) RACK FOR COATING CARTRIDGES



(b) RACK FOR DRYING DNPH-COATED CARTRIDGES

Figure 6. Syringe Rack for Coating and Drying Sample Cartridges

509

496

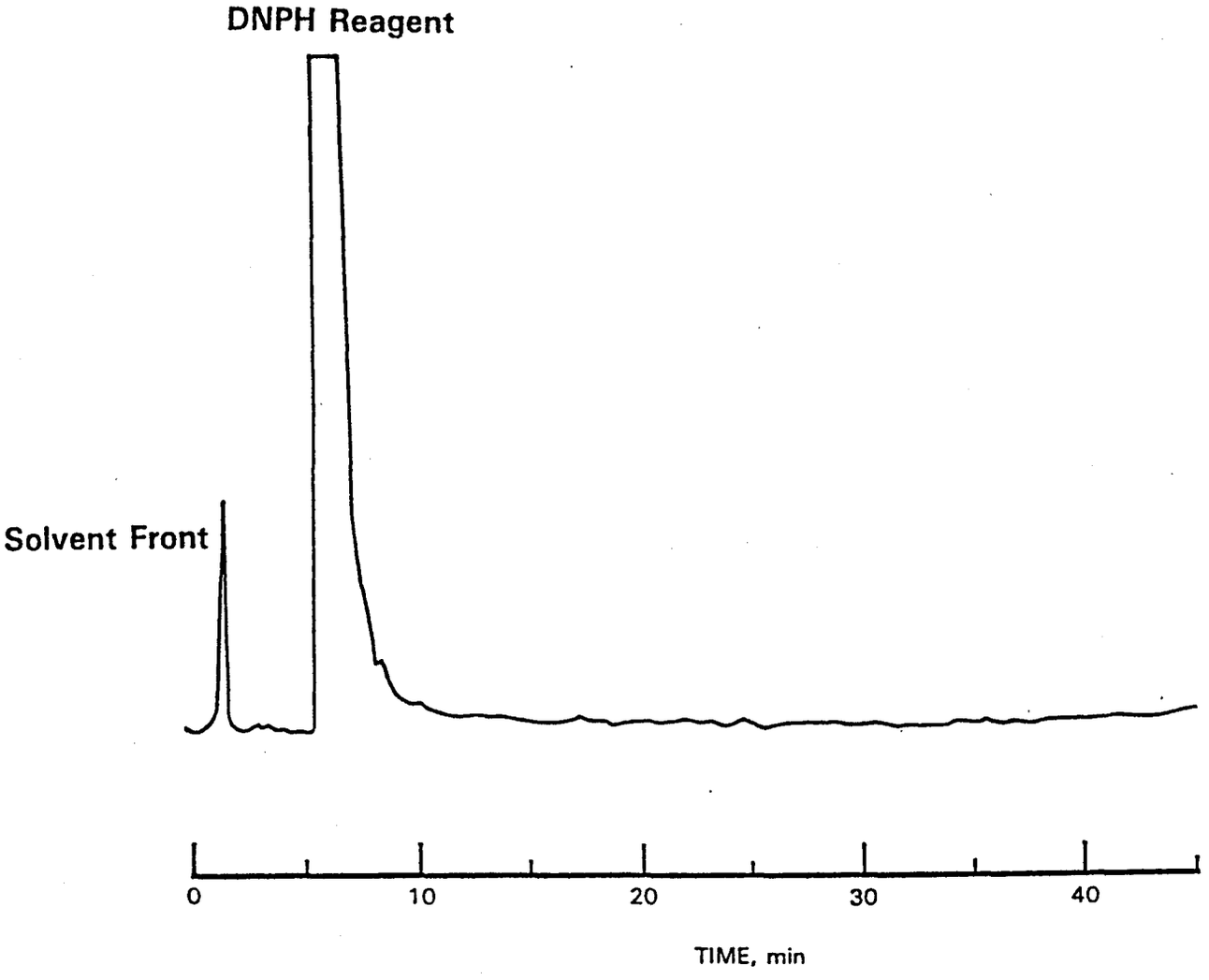


Figure 7. Impurity Level of DNPH after Recrystallization

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

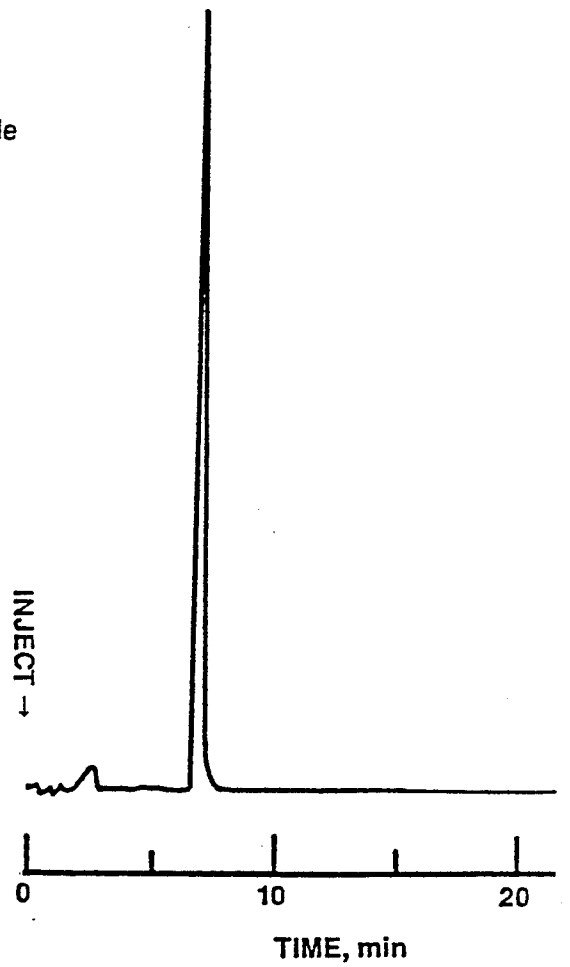
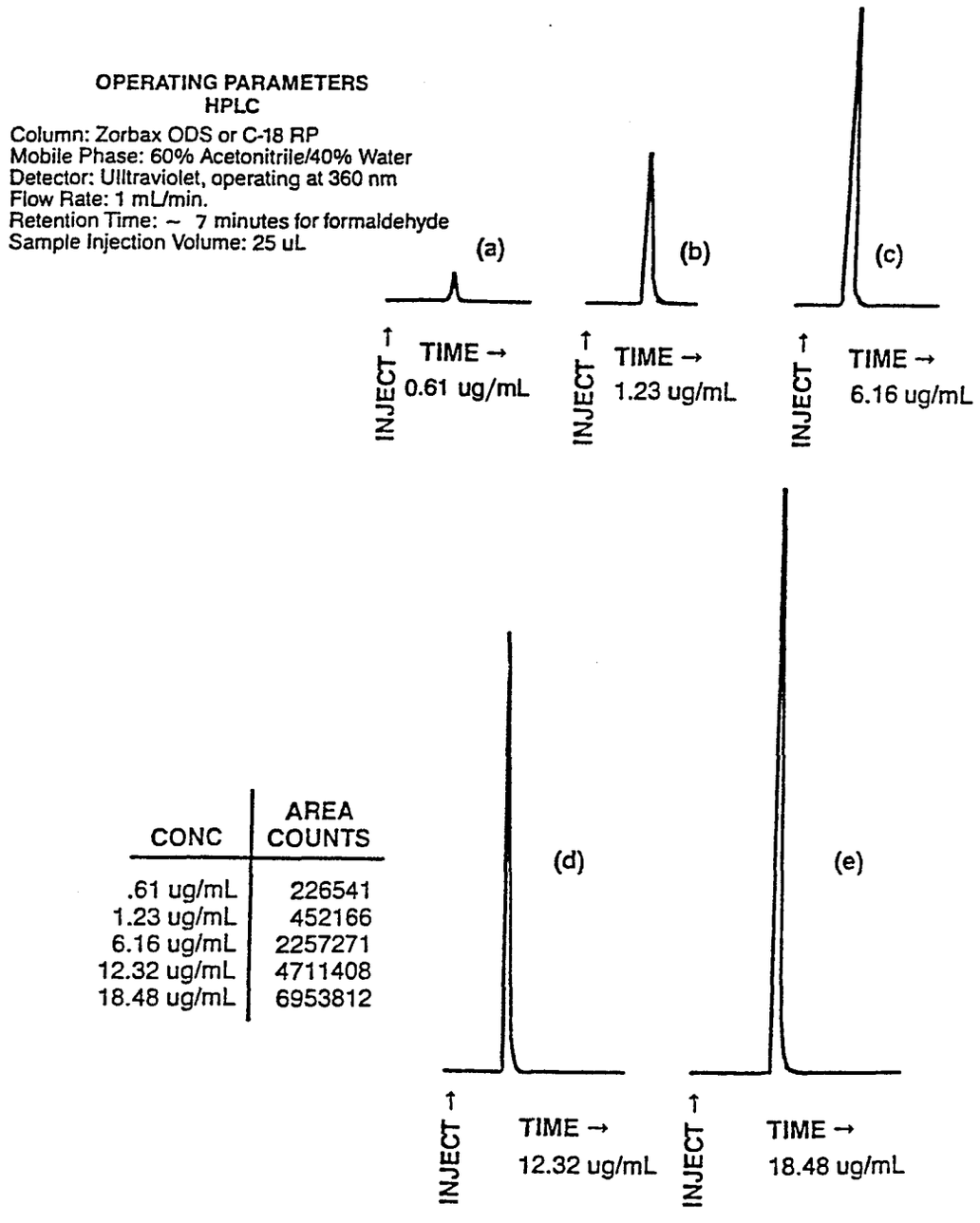


Figure 9. Chromatogram of DNPH-Formaldehyde Derivative



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

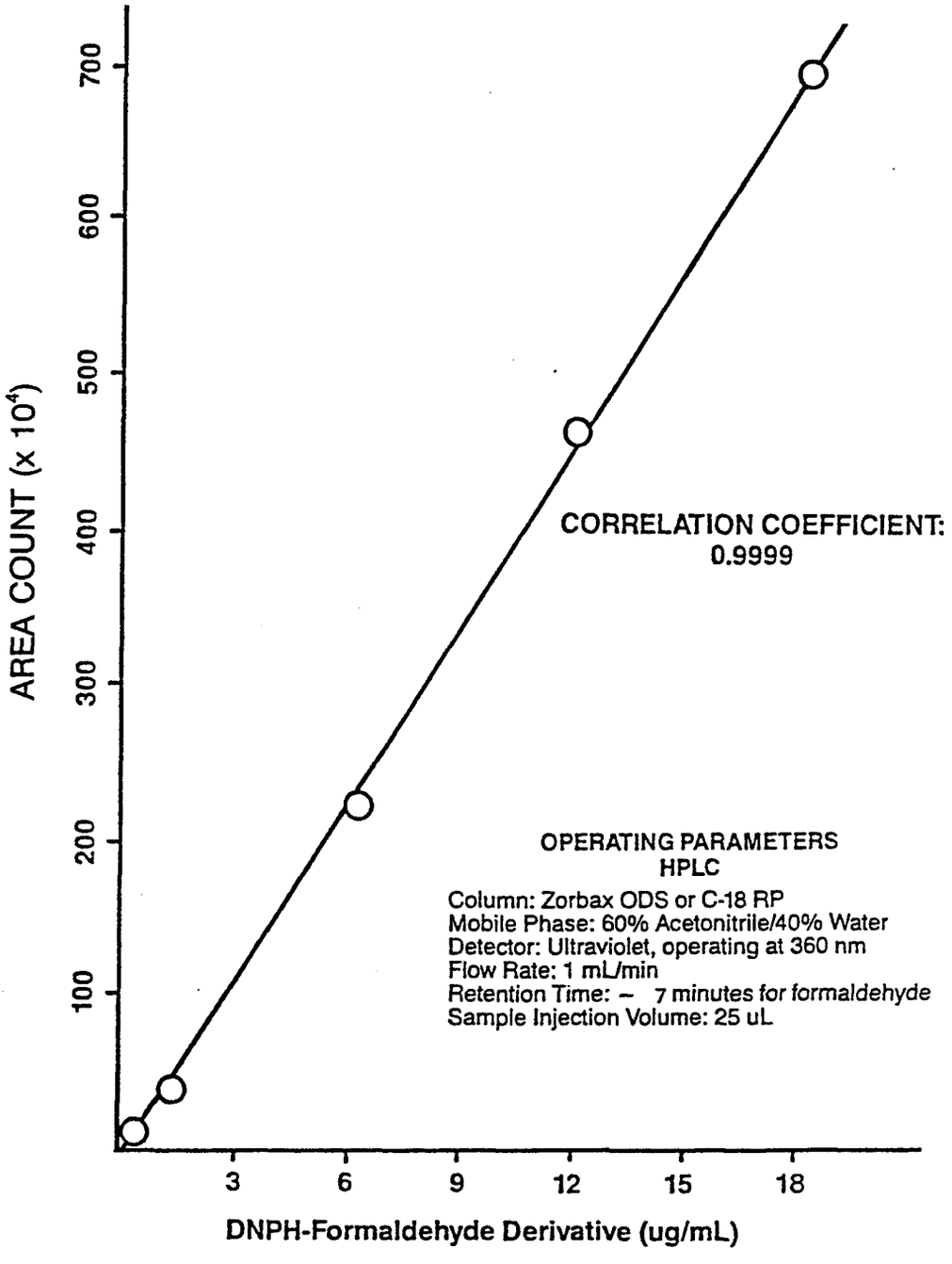
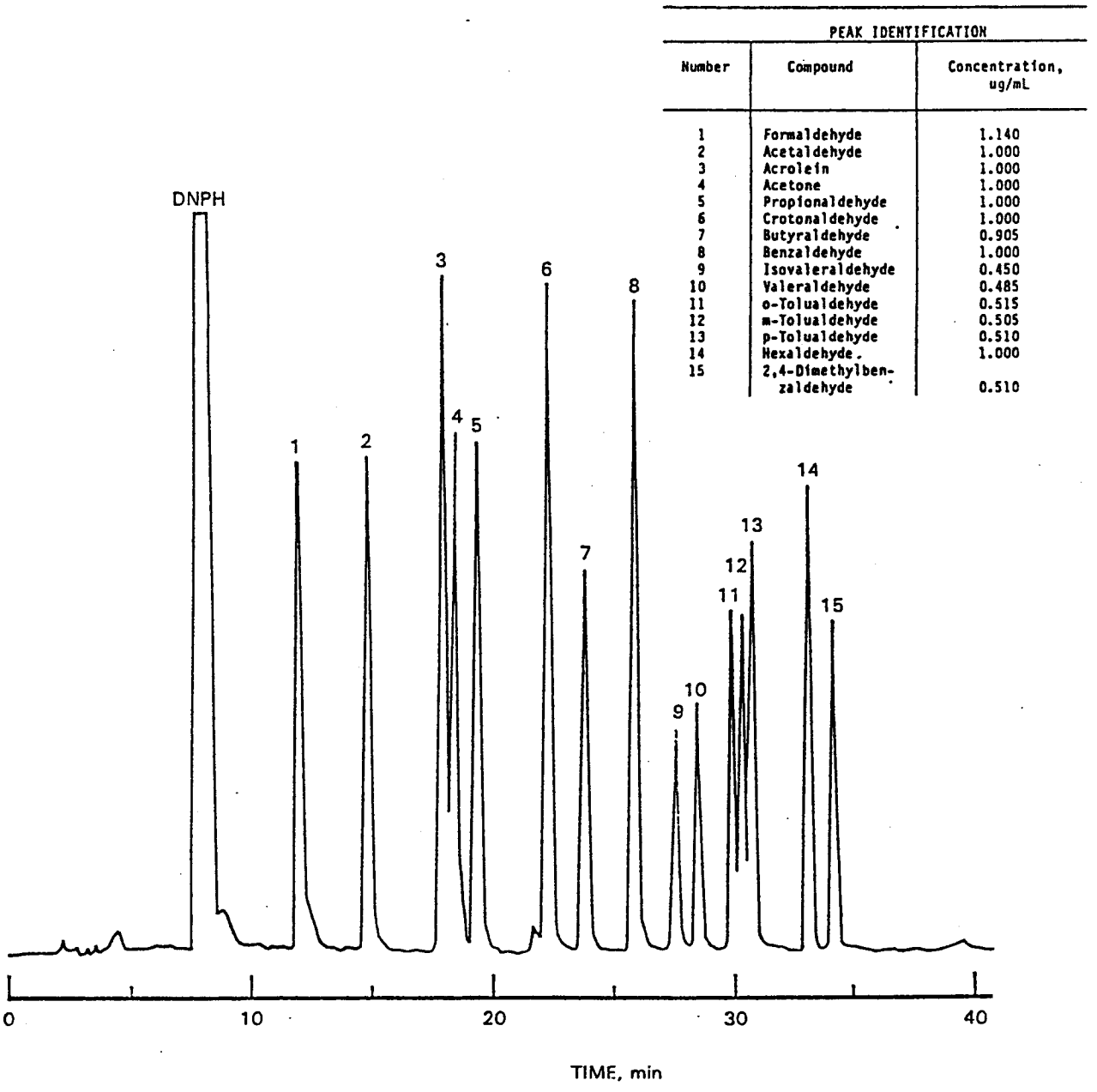


Figure 11. Typical Calibration Curve for Formaldehyde



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

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%

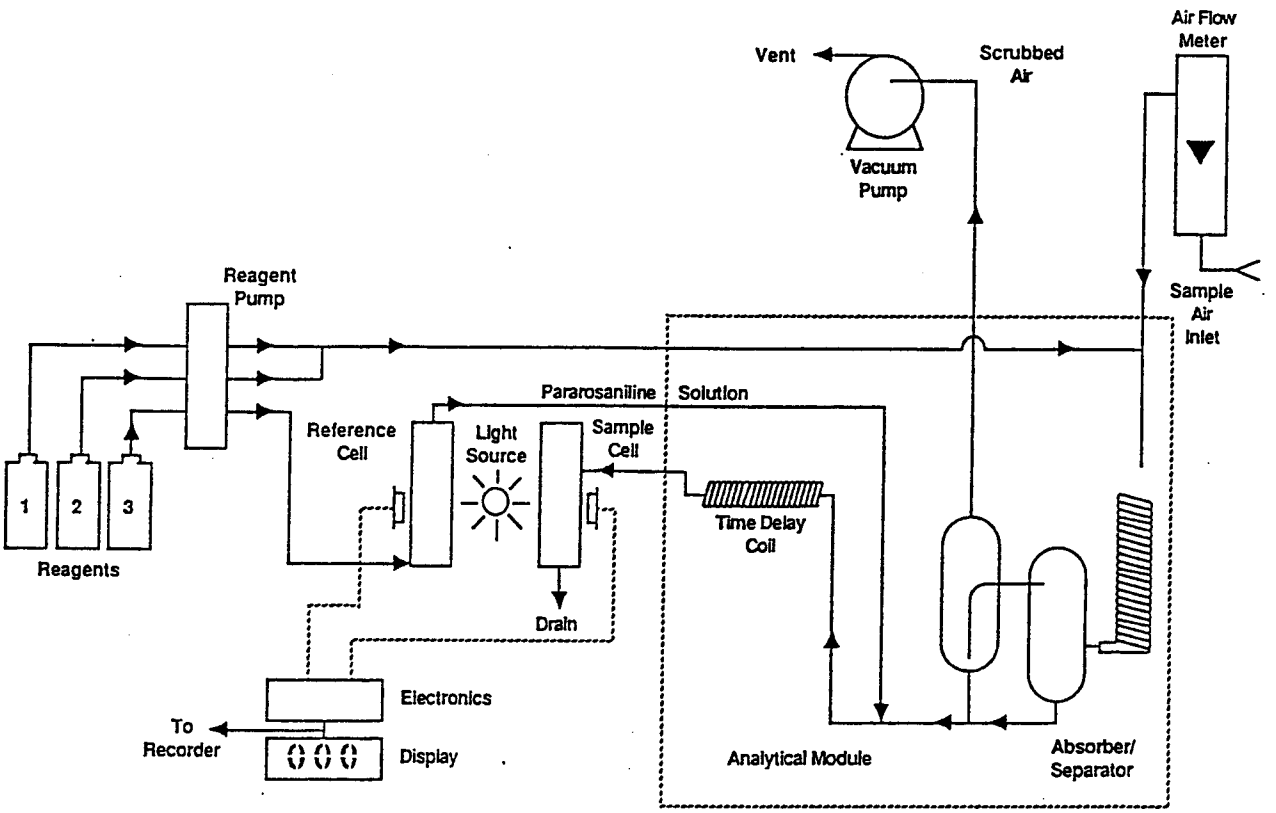

Figure 1. Flow Diagram of Formaldehyde Analyzer

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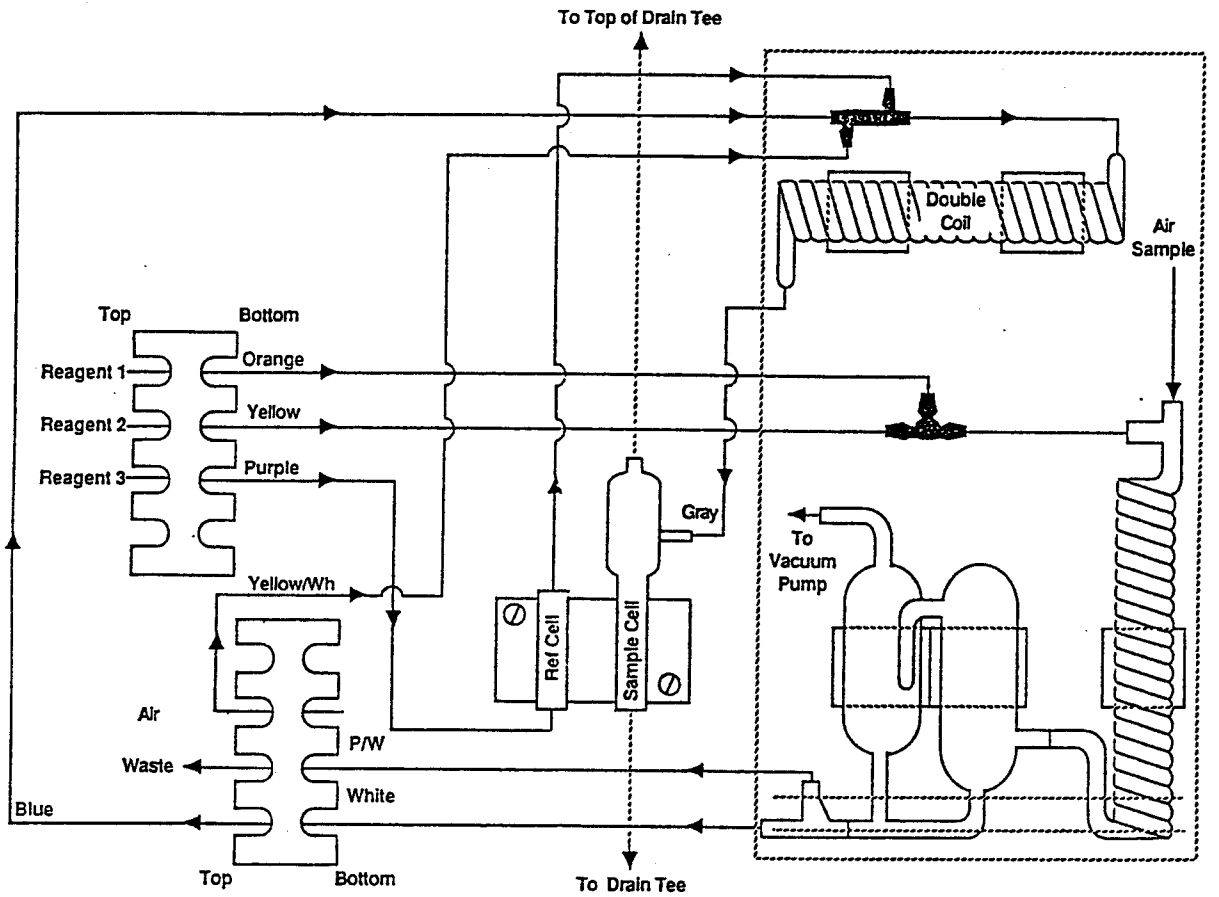

Figure 2. Flow Diagram of Reagents Through Analyzer

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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

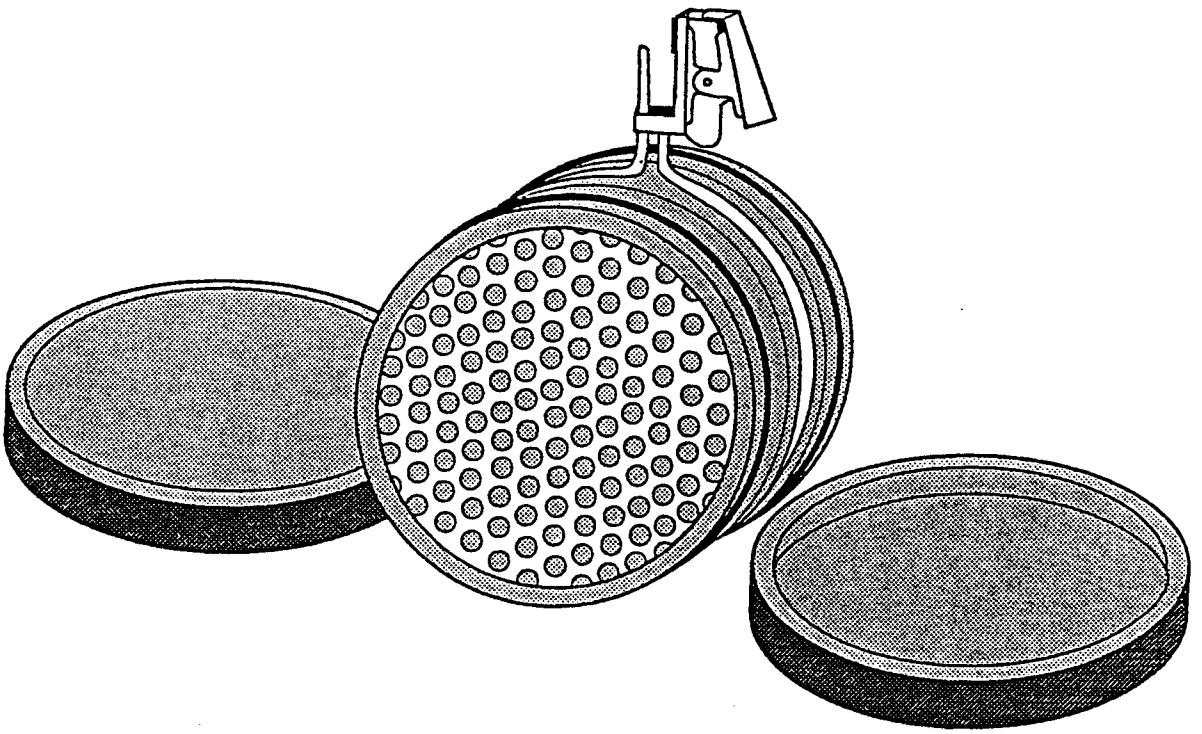

Figure 1. Passive Sampling Device (PSD) for Monitoring Formaldehyde

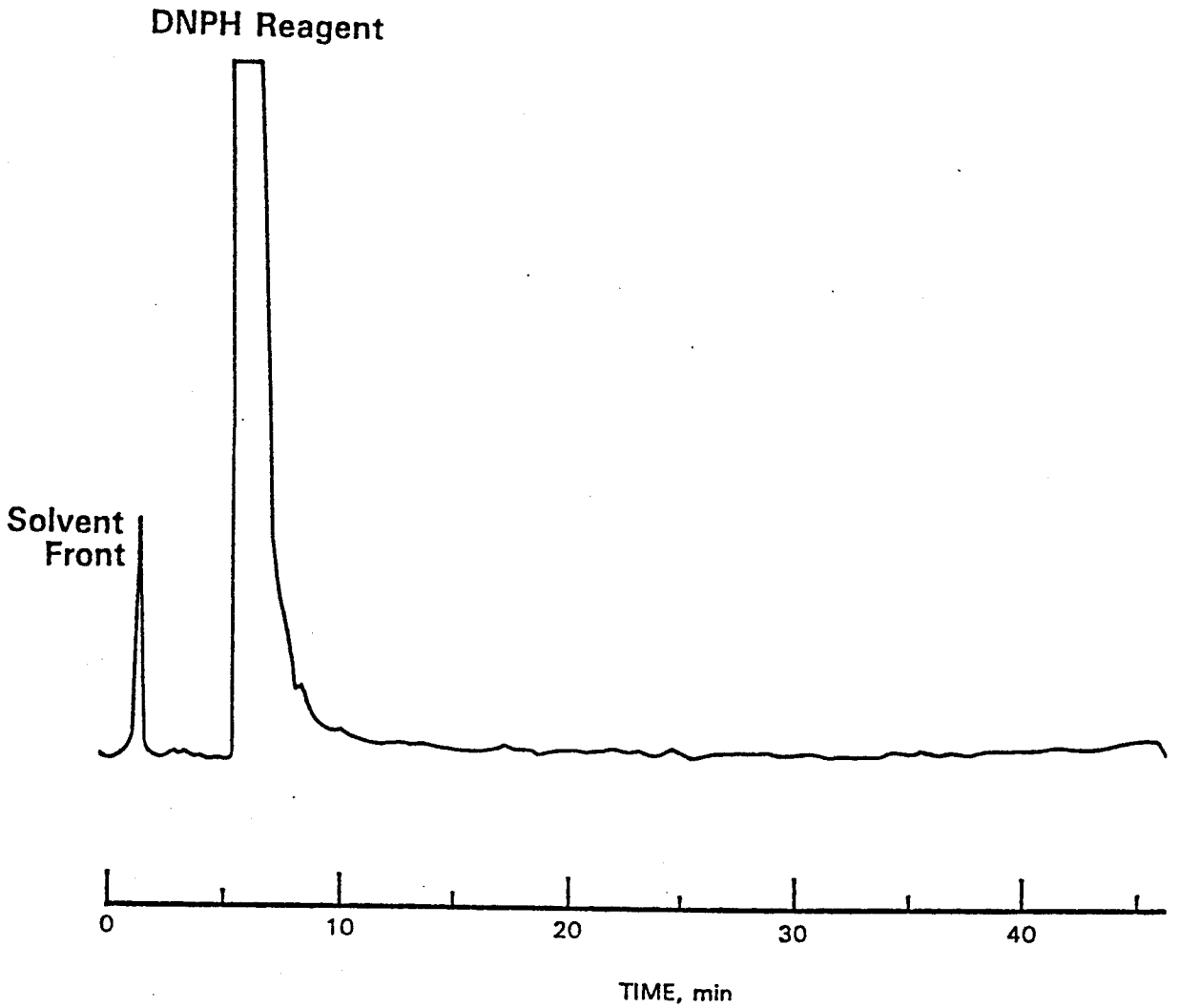

Figure 2. Impurity Level of DNPH After Recrystallization

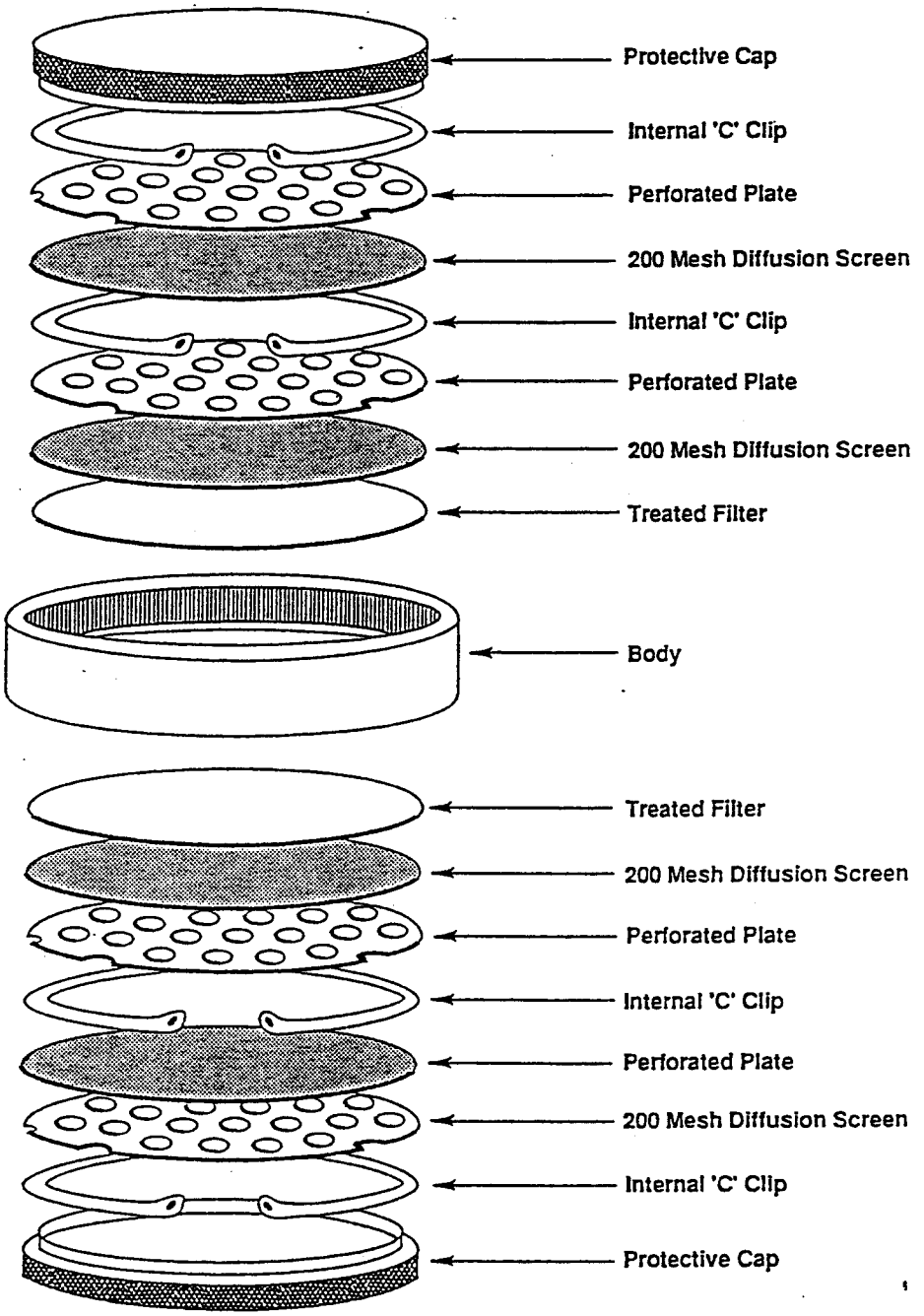

Figure 3. Exploded View of the Passive Sampling Device (PSD)

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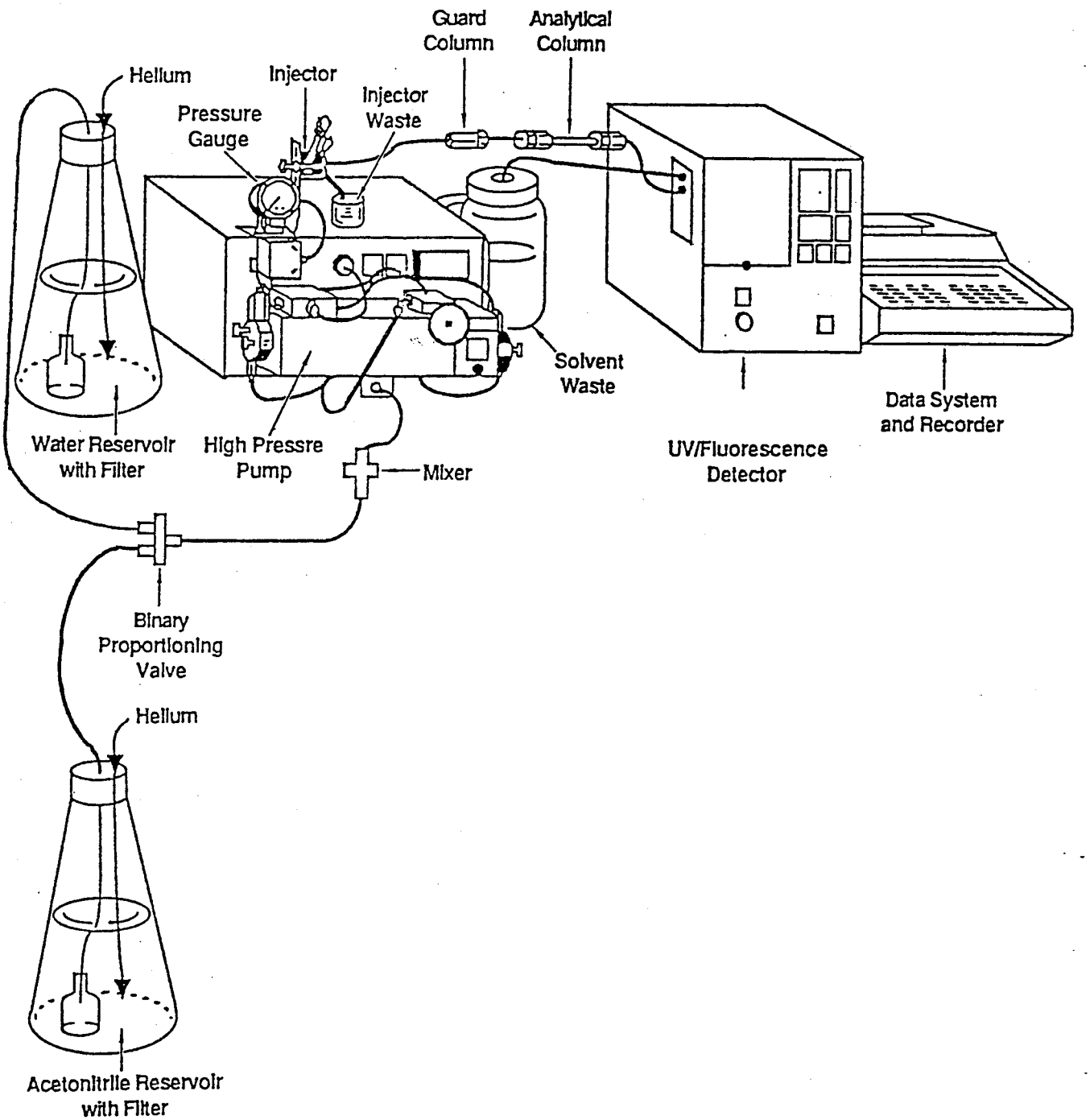

Figure 4. Typical Configuration Associated with a High Performance Liquid Chromatographic Analytical System

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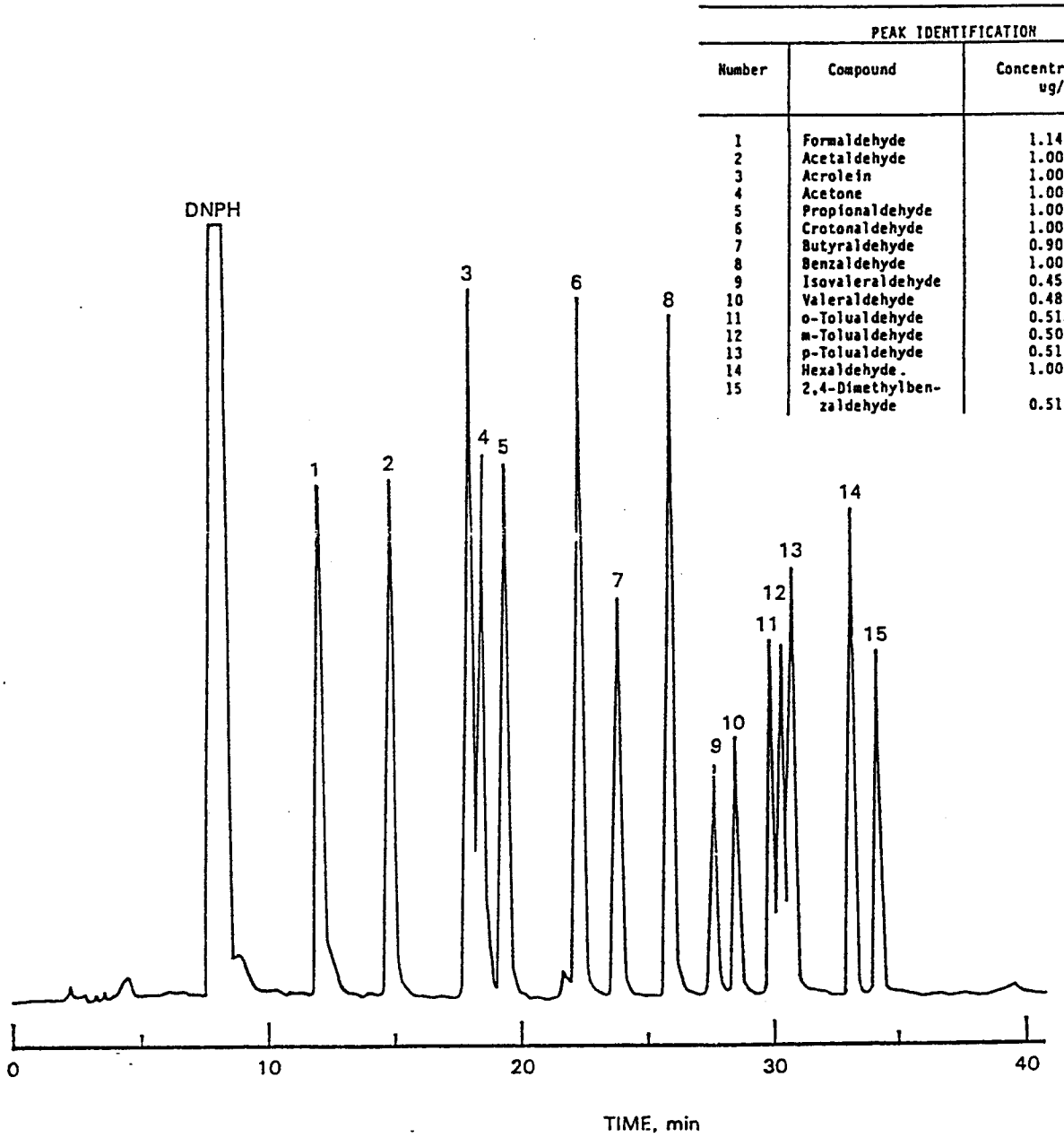

PEAK IDENTIFICATION

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 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.

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Method IP-7

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

Method IP-7

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

1. Scope

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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 perylene-d_{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	$C_{20}H_{1}2$	252.32	217	480	207-08-9
Chrysene	$C_{18}H_{1}2$	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).

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

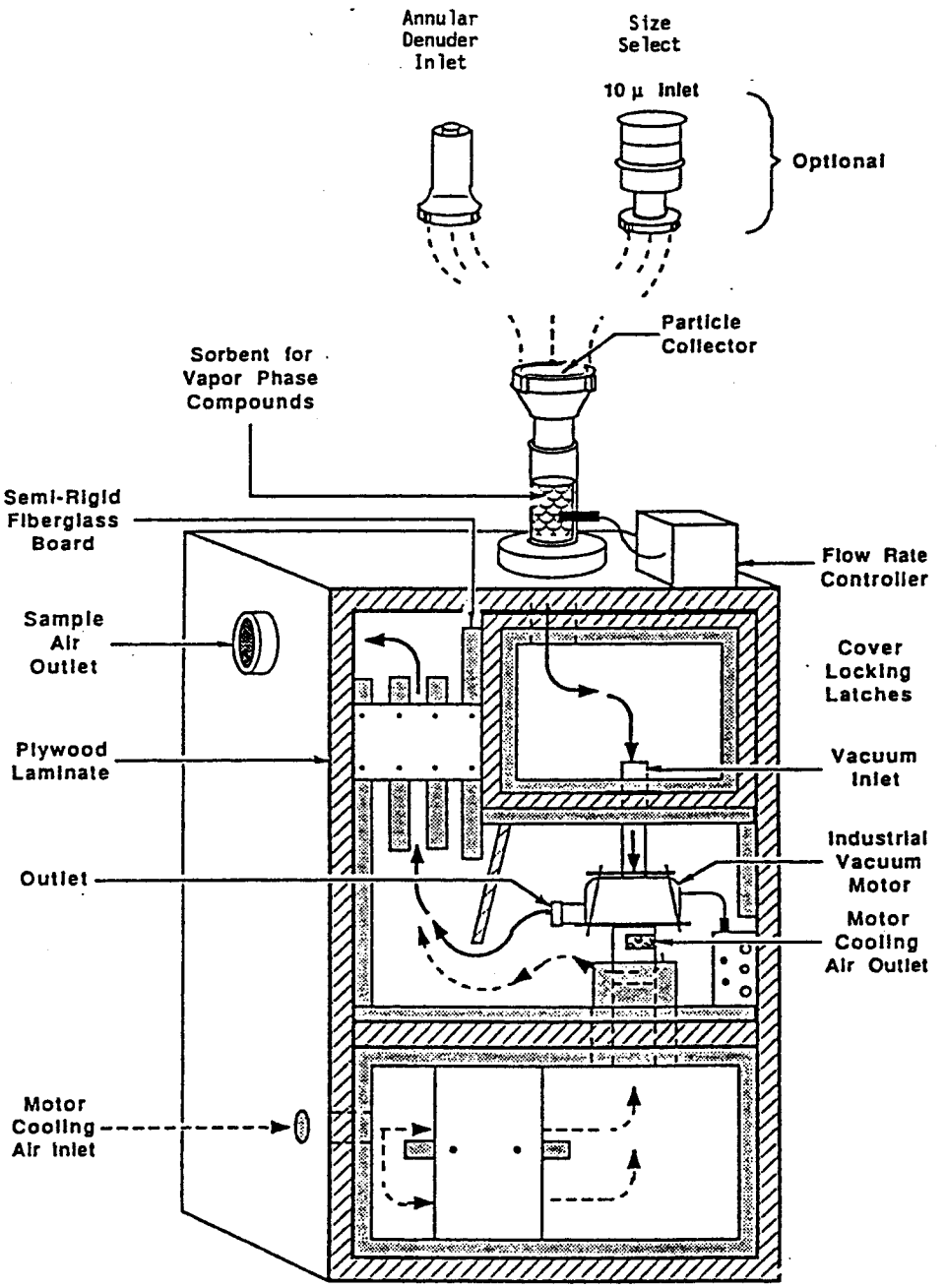

Figure 2. Acoustically Enclosed Medium Volume Sampler

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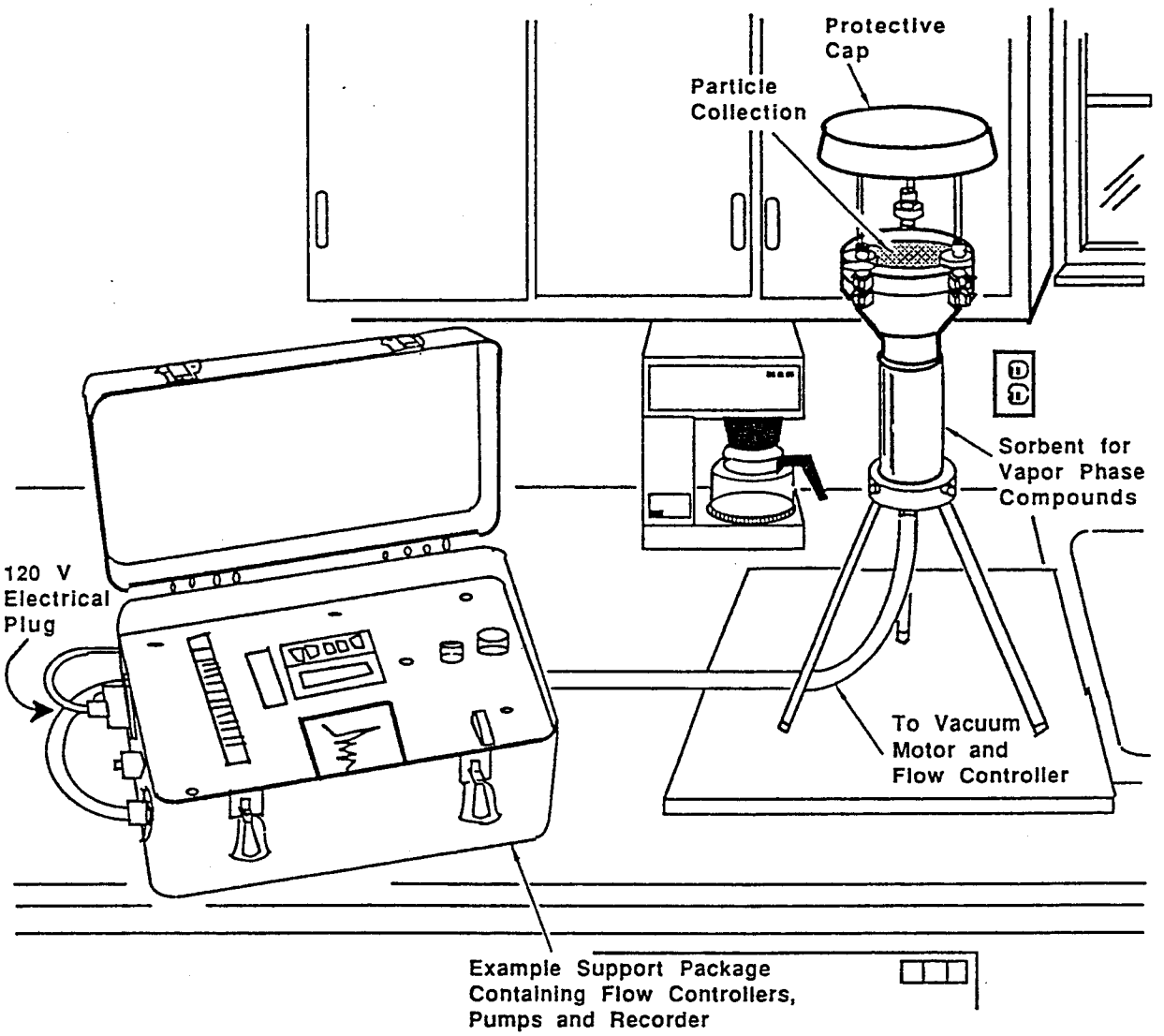

Figure 3. Tripod Sampler with Portable Meter Box Assembly

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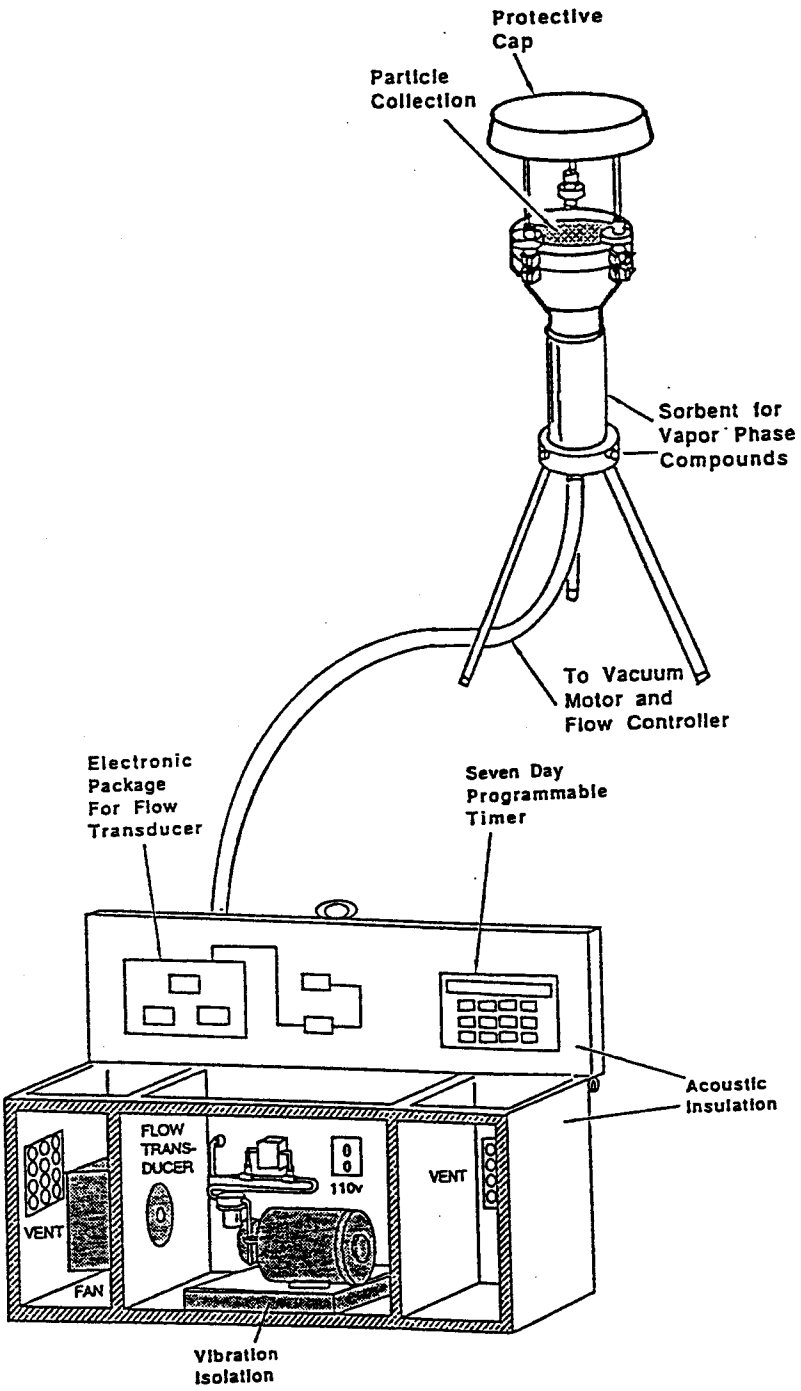

Figure 4. Battelle-Columbus Laboratory Medium Volume Air Sampler with Tripod Sampling Head

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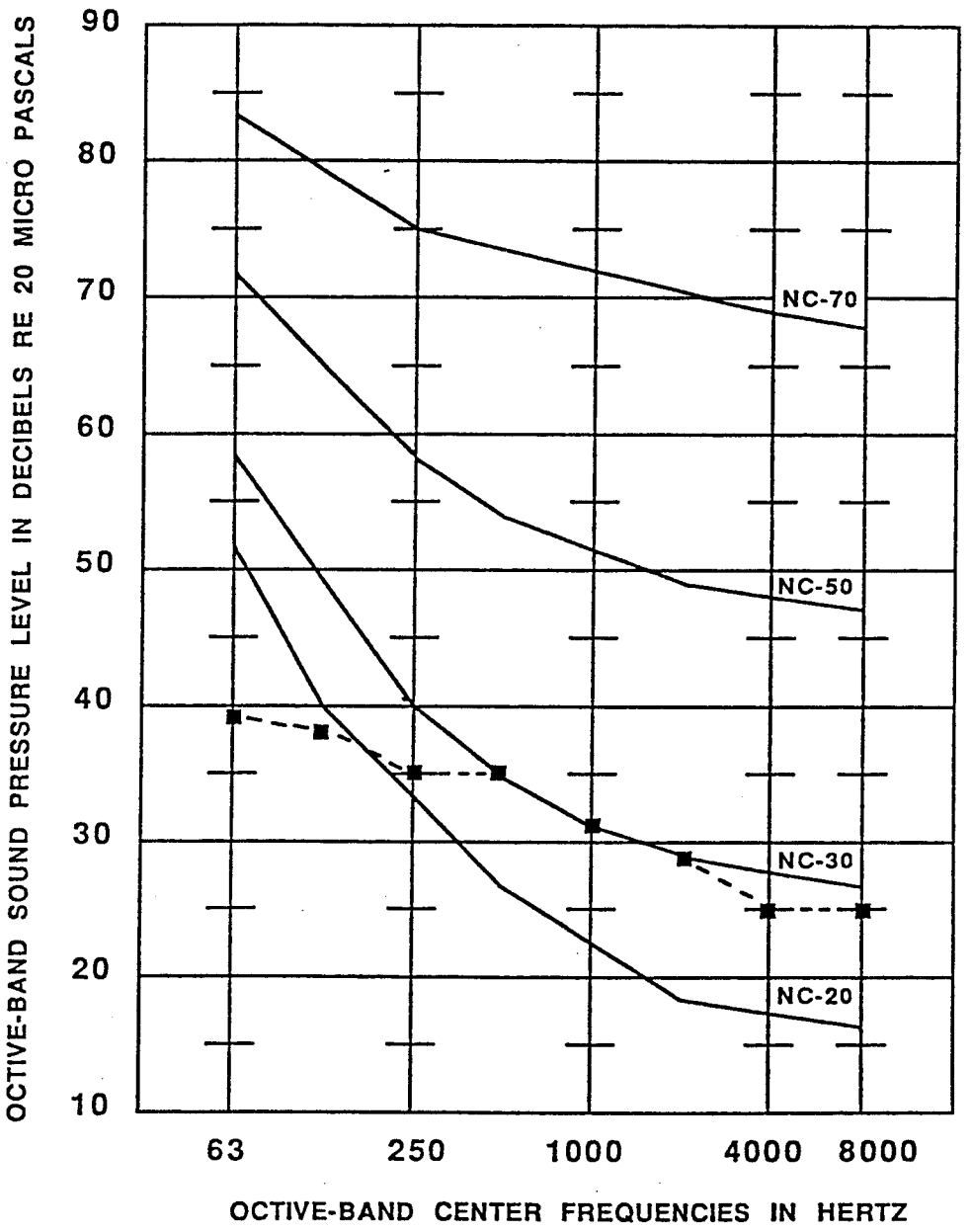

Figure 5. Noise Criterion for Indoor Air Sampler

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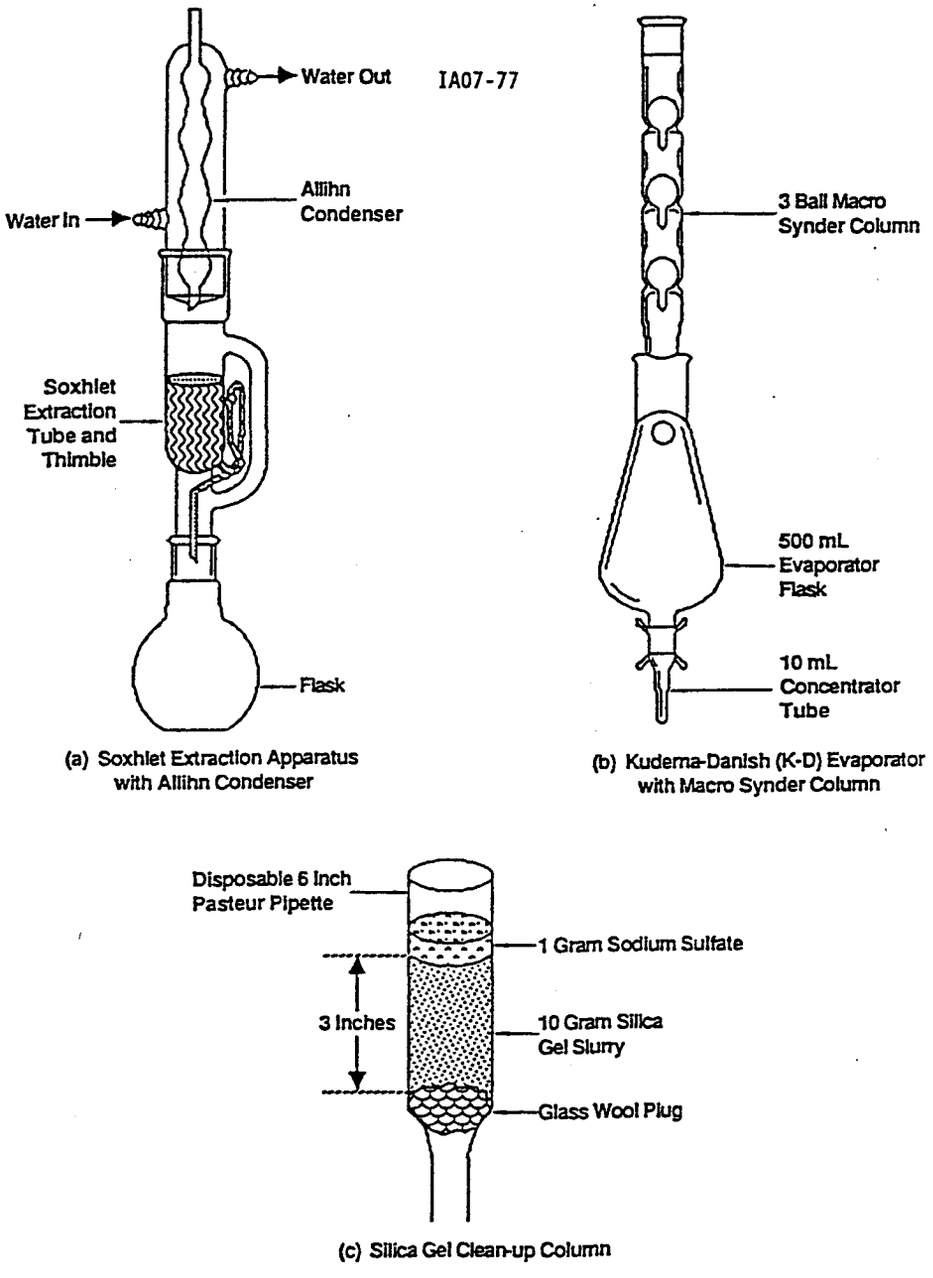

Figure 6. Apparatus Used in Sampling Analysis

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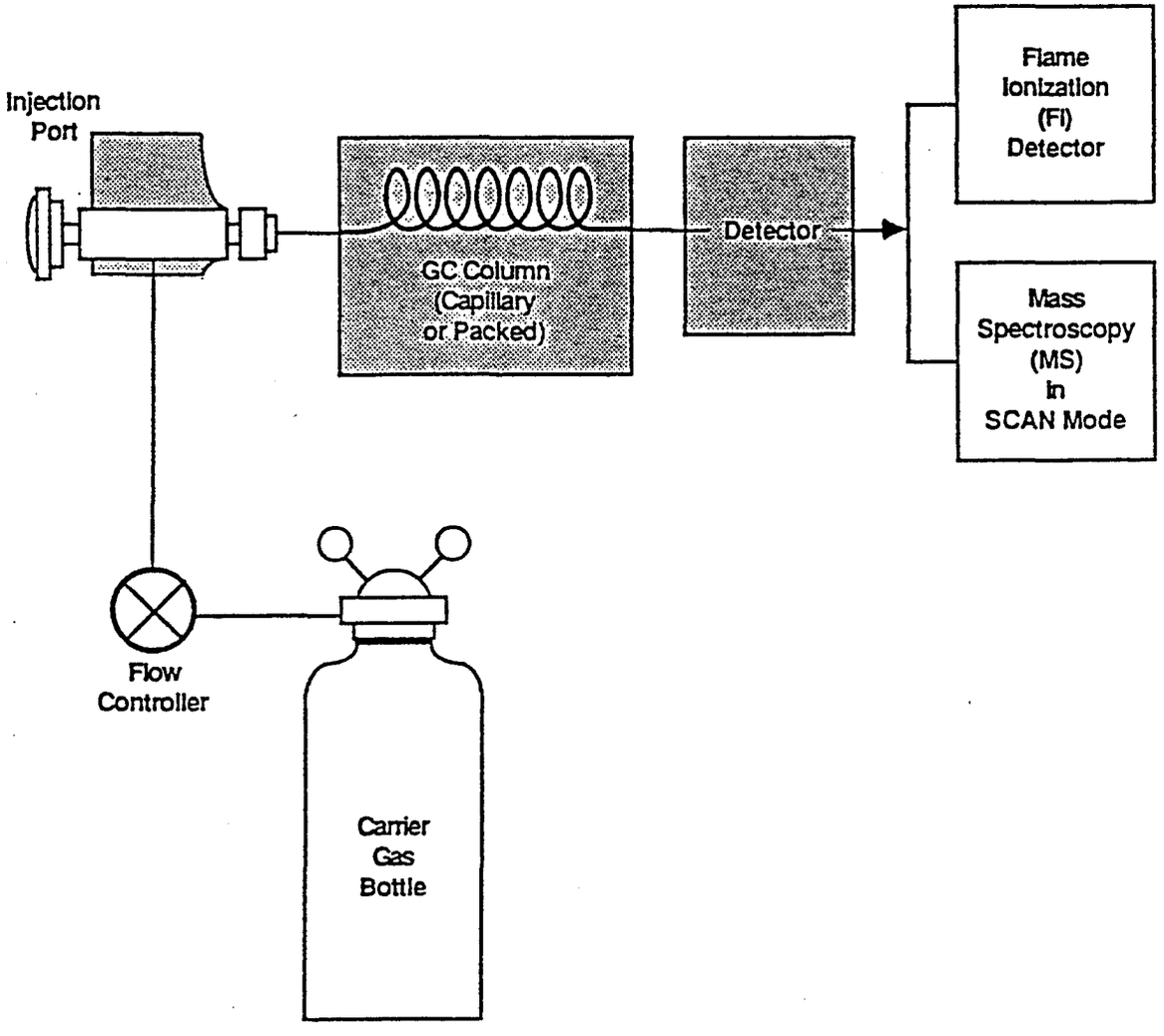

Figure 7. GC Separation with Subsequent Flame Ionization (FI) or Mass Spectroscopy (MS) Detection

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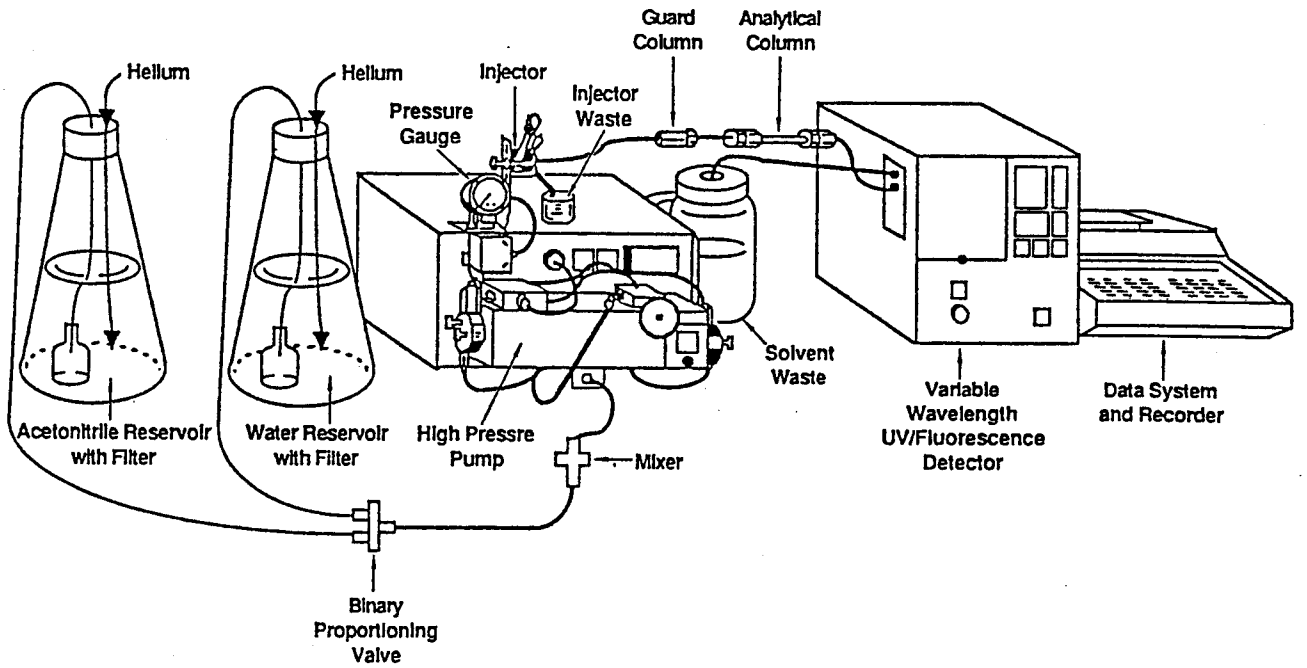

Figure 8. Important Components of an HPLC System

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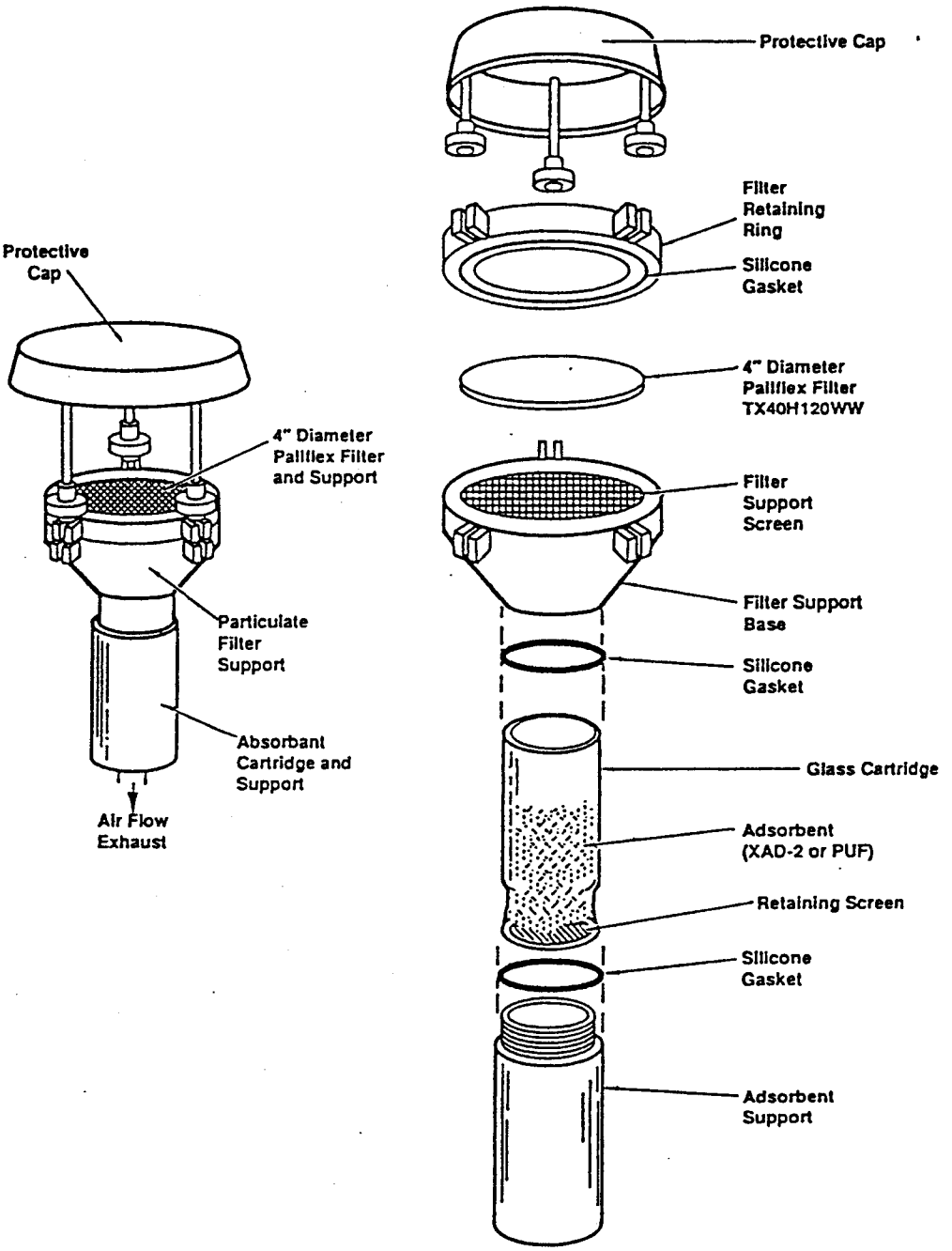

Figure 9. General Metal Works Sampling Head with Protective Cap

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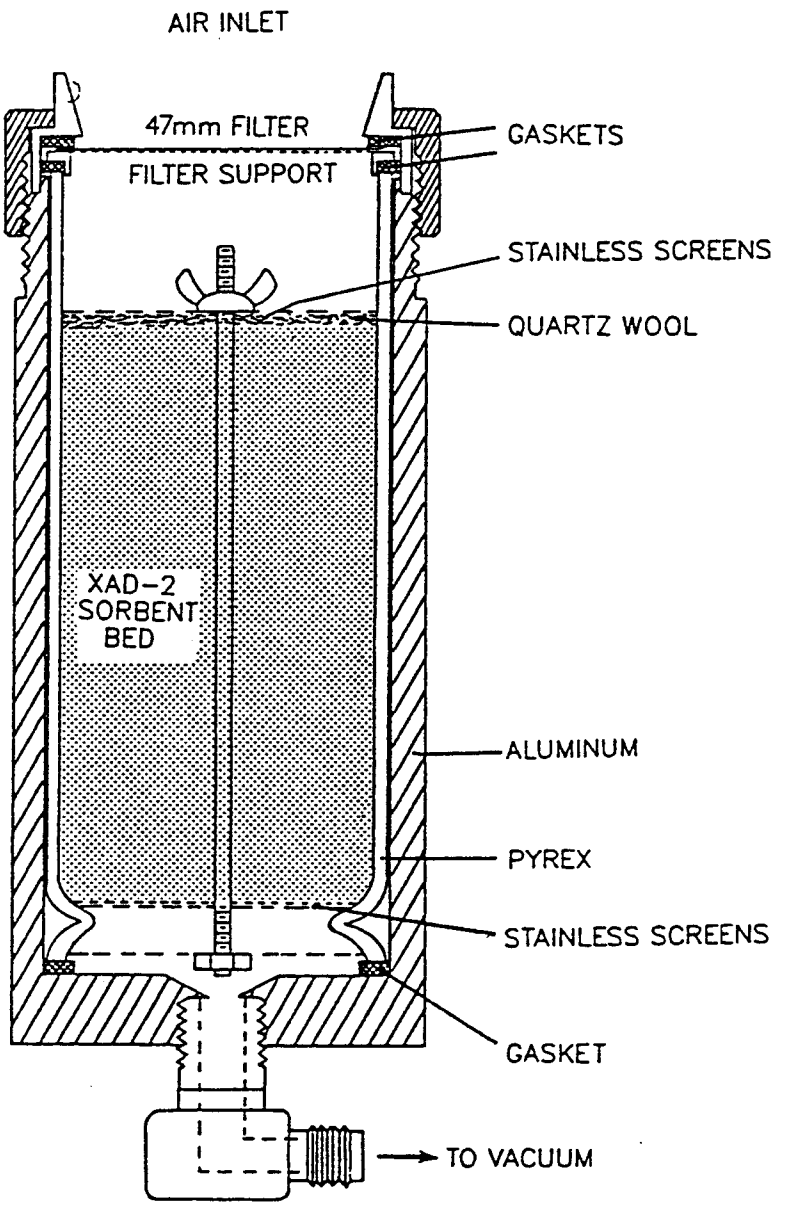

Figure 10. Alternative Design for Medium Volume Indoor Air Sampler with Open Face Filter Assembly

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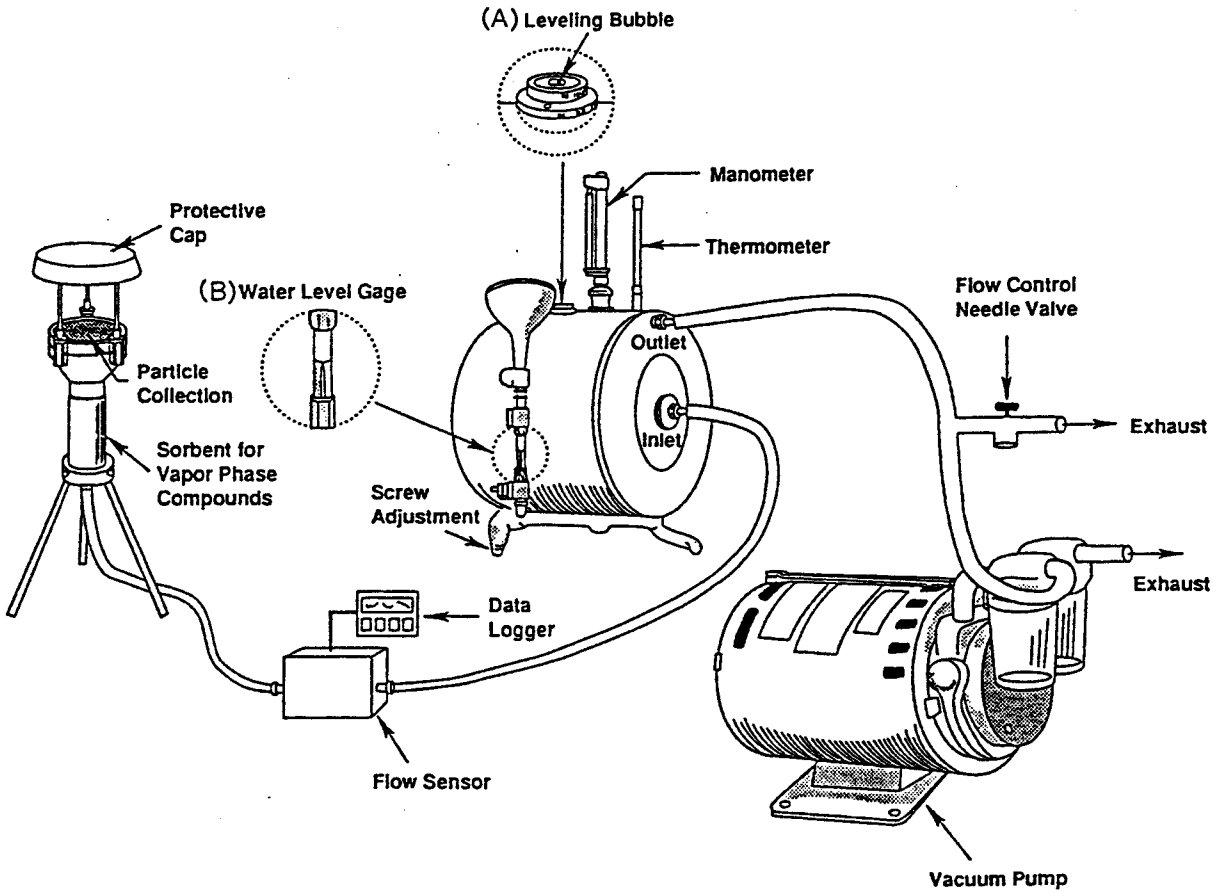

Figure 11. Calibration Assembly for Medium Volume Sampling System

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Flow Sensor Calibration Data Sheet

Name _____

Date _____

Wet test meter fluid temperature (T_m) _____°C _____°K
Mass flow meter # _____
Mass flow meter range setting _____
Barometric pressure (P_b) _____mm Hg WTM C.F. _____
Transducer # _____ WTM # _____
Water vapor pressure (p_v) _____ mm Hg

Flow Transducer		Wet Test Meter						Flow Rate	
% Full Scale	Volts	V_m	V_a	Δp	T_m	V_s	θ	V_s	Q_s
80									
60									
40									
20									
10									

$V_a = V_m \times C.F.$, L
$P_m = P_b$ (mm Hg) - Δp (mm Hg), mm Hg
T_m = °V + 273.16, °K
$V_s = (V_a)(P_m - p_v/P_s)(T_s/T_m)$, L
p_v = vapor pressure of wet test meter water, mm Hg
θ = time, minutes
Q_s = standard volumetric flow rate, L/min

Figure 12. Flow Sensor Calibration Data Sheet

Sampler Site _____

Sampler Location _____

Date _____

	Before	After
Barometric Pressure		
Ambient Temperature		

Site _____ Date _____ Performed By _____

Sampler S/N	Sampling Location I.D.	Height Above Ground	Identification No.		Sampling Period		Totaling Sampling Time, min.	Pump Timer Hr. Min.	Sampler Flow				
			Filter	XAD-2 or PUF	Start	Stop				V_s	Q_s		Within ± 10%

Checked By _____

Date _____

Figure 13. Field Test Data Sheet

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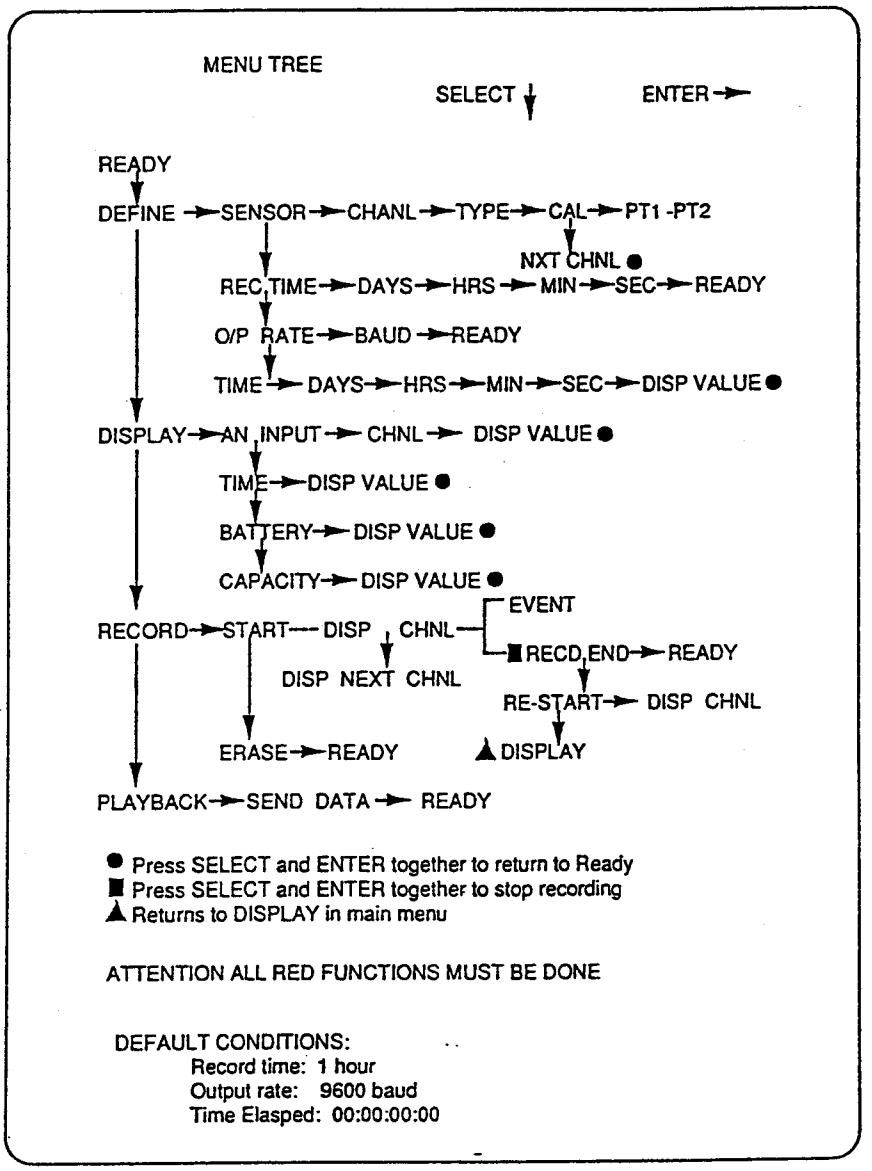

Figure 14. Data Logger Menu Tree

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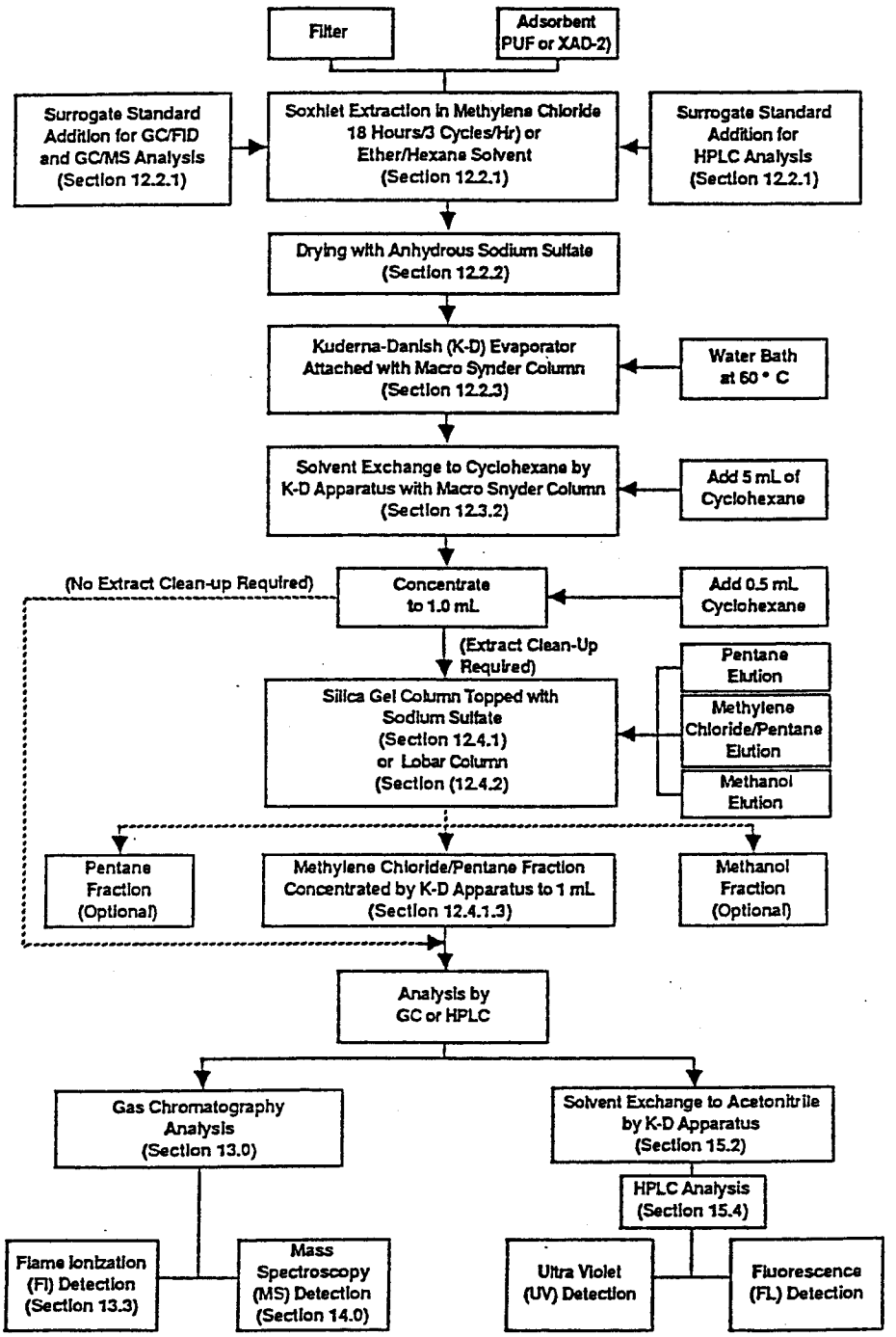

Figure 15. Sample Clean-Up, Concentration, Separation and Analysis Sequence

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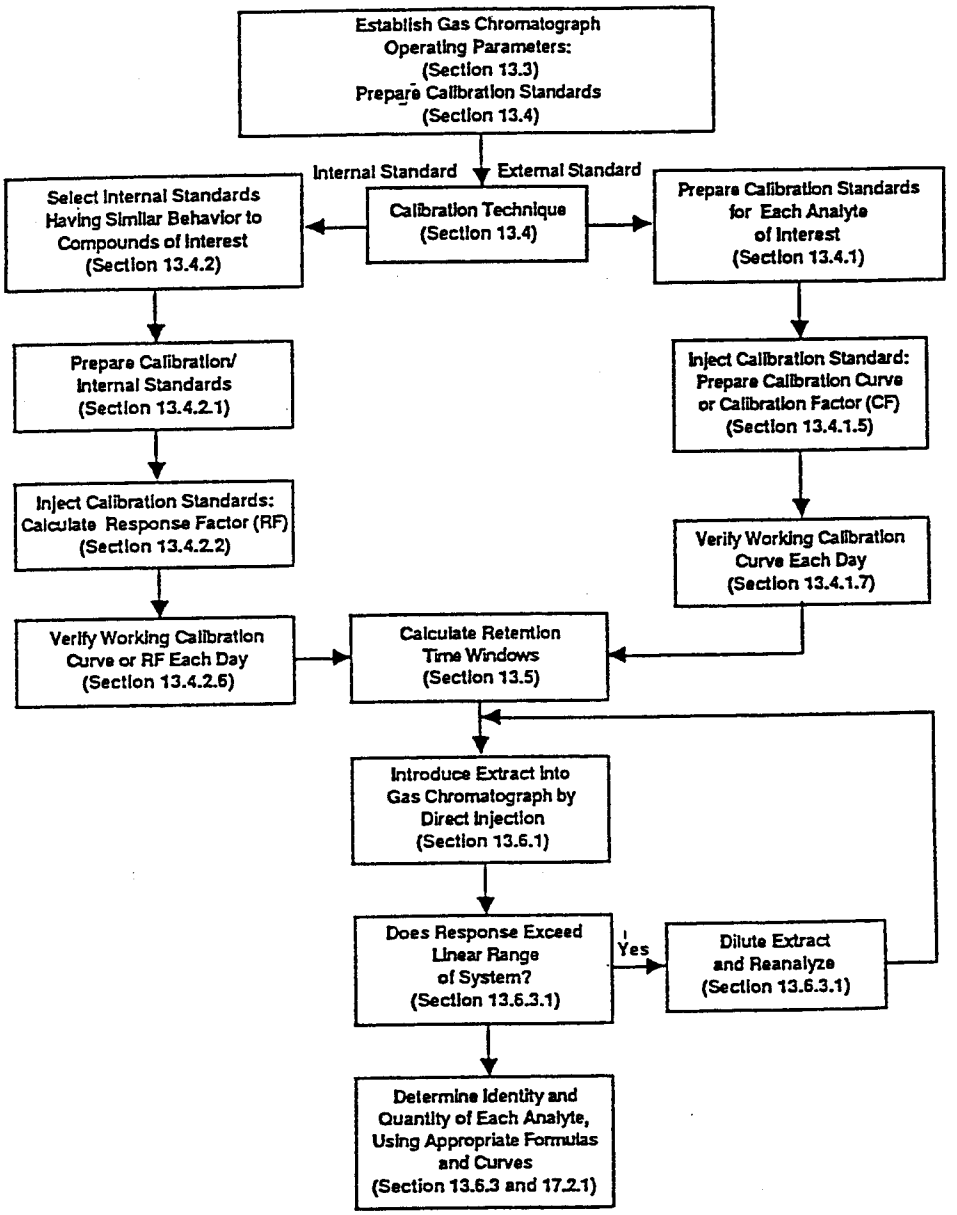

Figure 16. GC Calibration and Retention Time Window Determination

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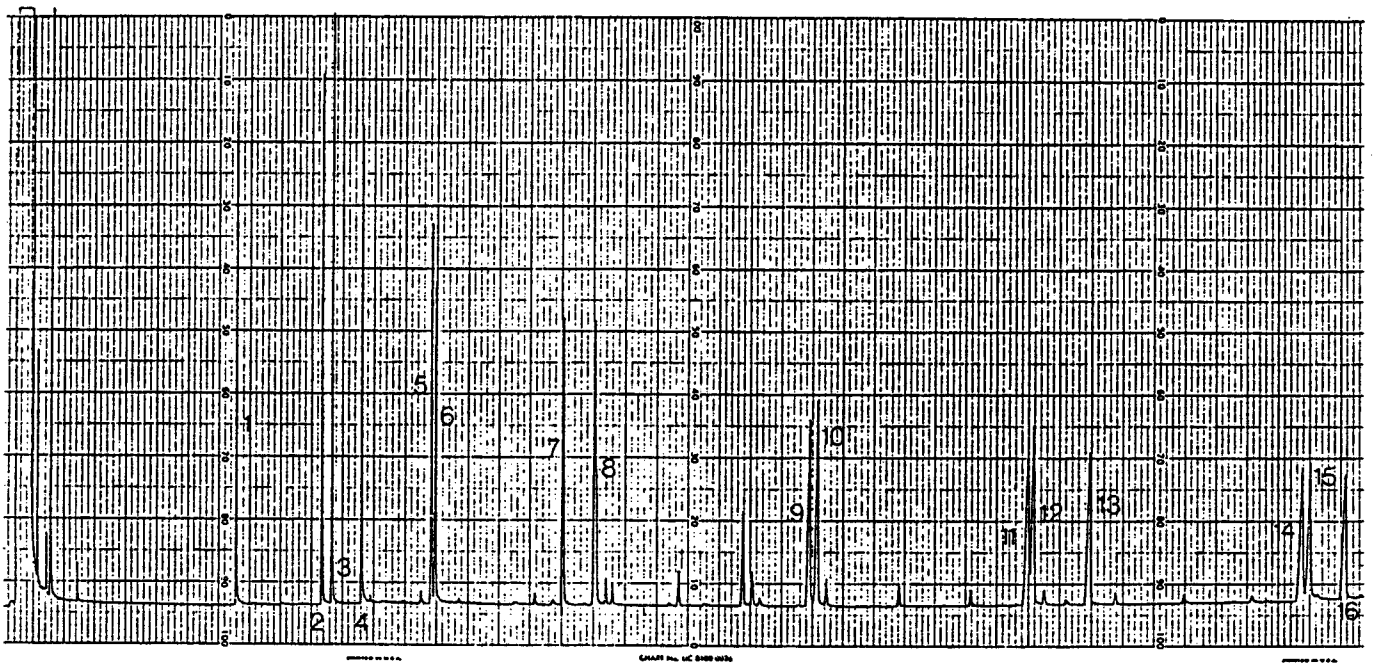

Injection: 1.0 µL on-column
Column: 30m x 0.25 mm DB-5 capillary with 0.25 µm film thickness
Program: 40°C (1 min), 15°C/min to 200°C, 3°C/min to 300°C
Detector: Flame ionization

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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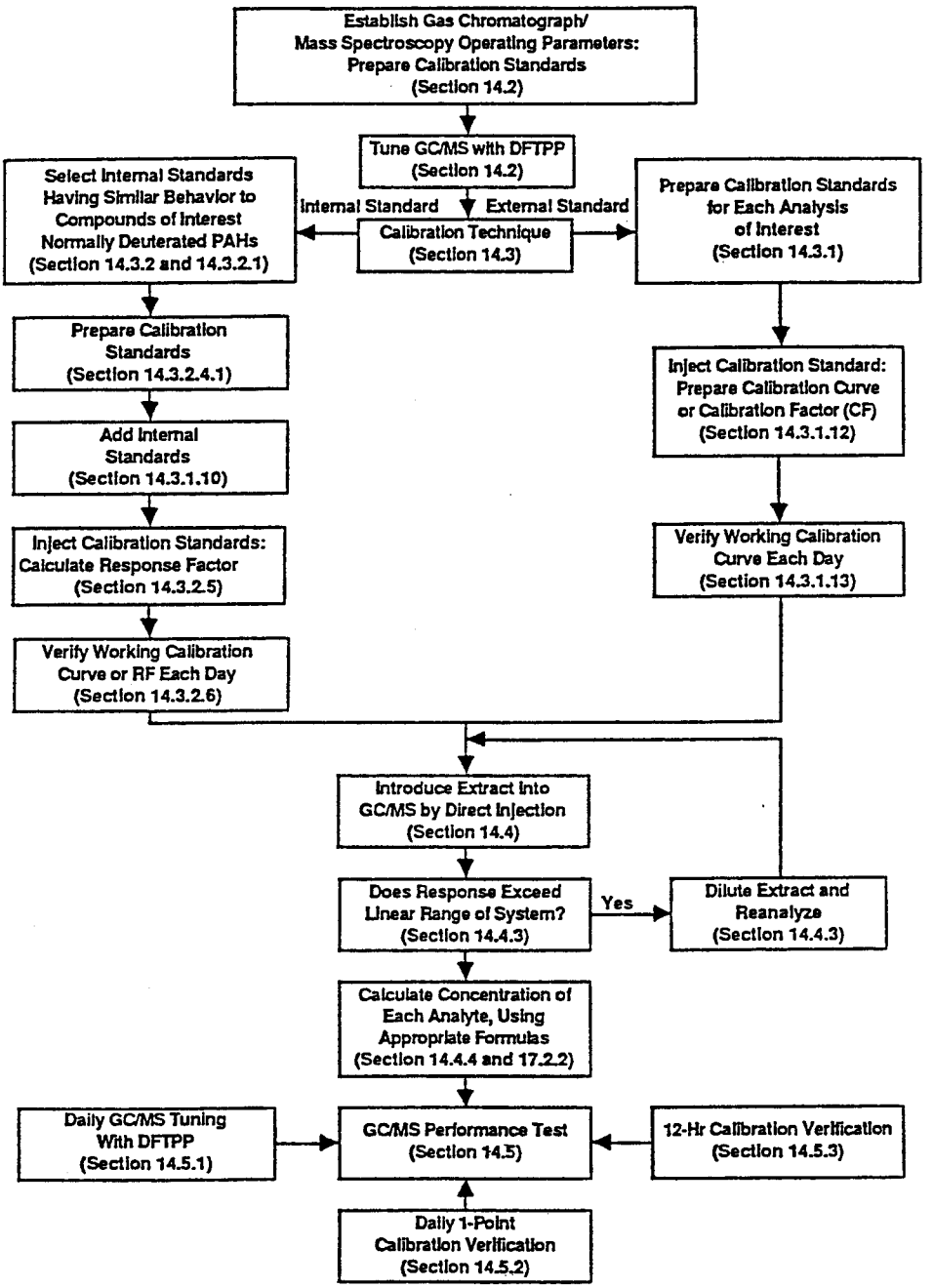

Figure 18. GC-MS Calibration and Analysis

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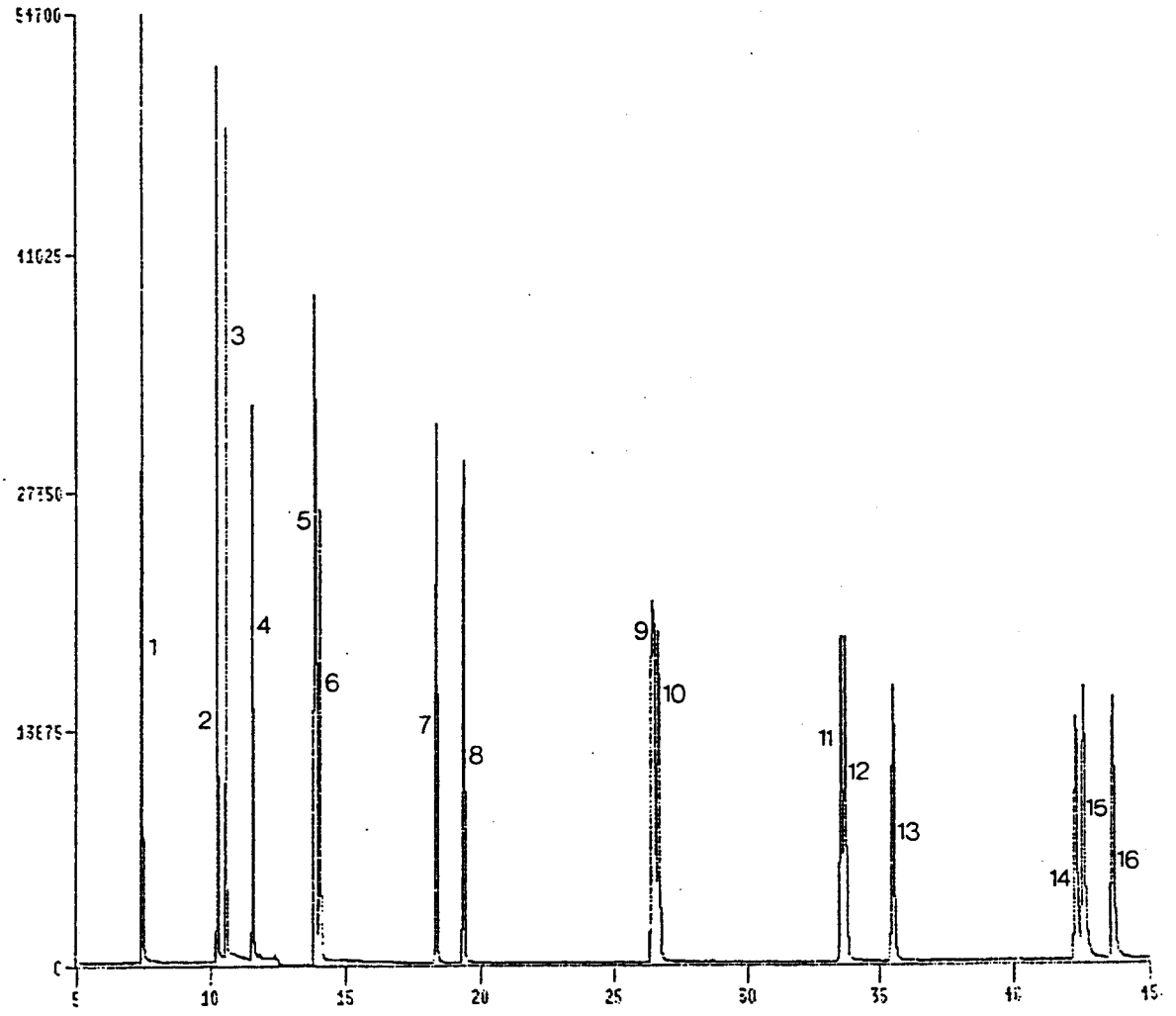

Injection: 1.0 µL on-column
Column: 30m x 0.25 mm DB-5 capillary with 0.25 µm film thickness
Program: 60°C (1 min), 15°C/min to 200°C, 3°C/min to 310°C
Detector: Mass selective detector

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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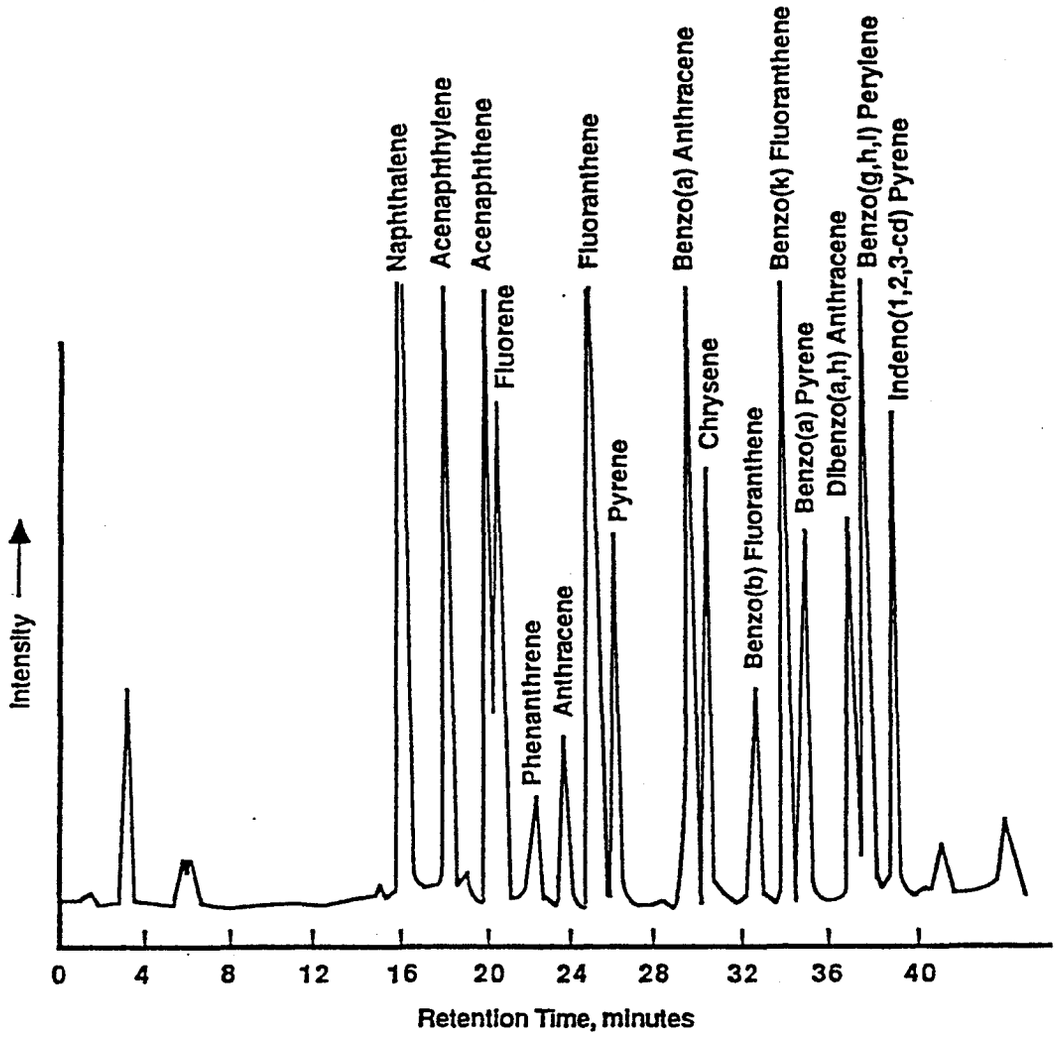

Figure 20. Typical Chromatogram of Selected PAHs Associated with HPLC Analysis Involving Ultraviolet Detection

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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

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:

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

655

642

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:

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

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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2. Lewis, R., and MacLeod, K., "Portable Sampler for Pesticides and Semivolatile Industrial Organic Chemicals in Air," *Analytical Chemistry*, 54:310-315, 1982.

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6. Hall, R., and Harris, D., "Direct Gas Chromatographic Determination of Carbamate Pesticides Using Carbowax-20M Modified Supports and the Electrolytic Conductivity Detector," *Journal of Chromatography*, 169:245-259, 1979.

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

Research Institute, San Antonio, Texas. Final Report under U.S. Environmental Protection Agency, Contract No. 68-02-3745.

8. Edgerton, T., and Moseman, R., "Gas Chromatography of Underivatized Chlorinated Phenols on Support Bonded Polyester Column Packings," *Journal of Chromatographic Science*, 18:25-29, 1980.

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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, %* mean	RSD	Sampling Efficiency**, %, at: 10 ng/m³ mean	RSD	100 ng/m³ mean	RSD	1000 ng/m³ 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

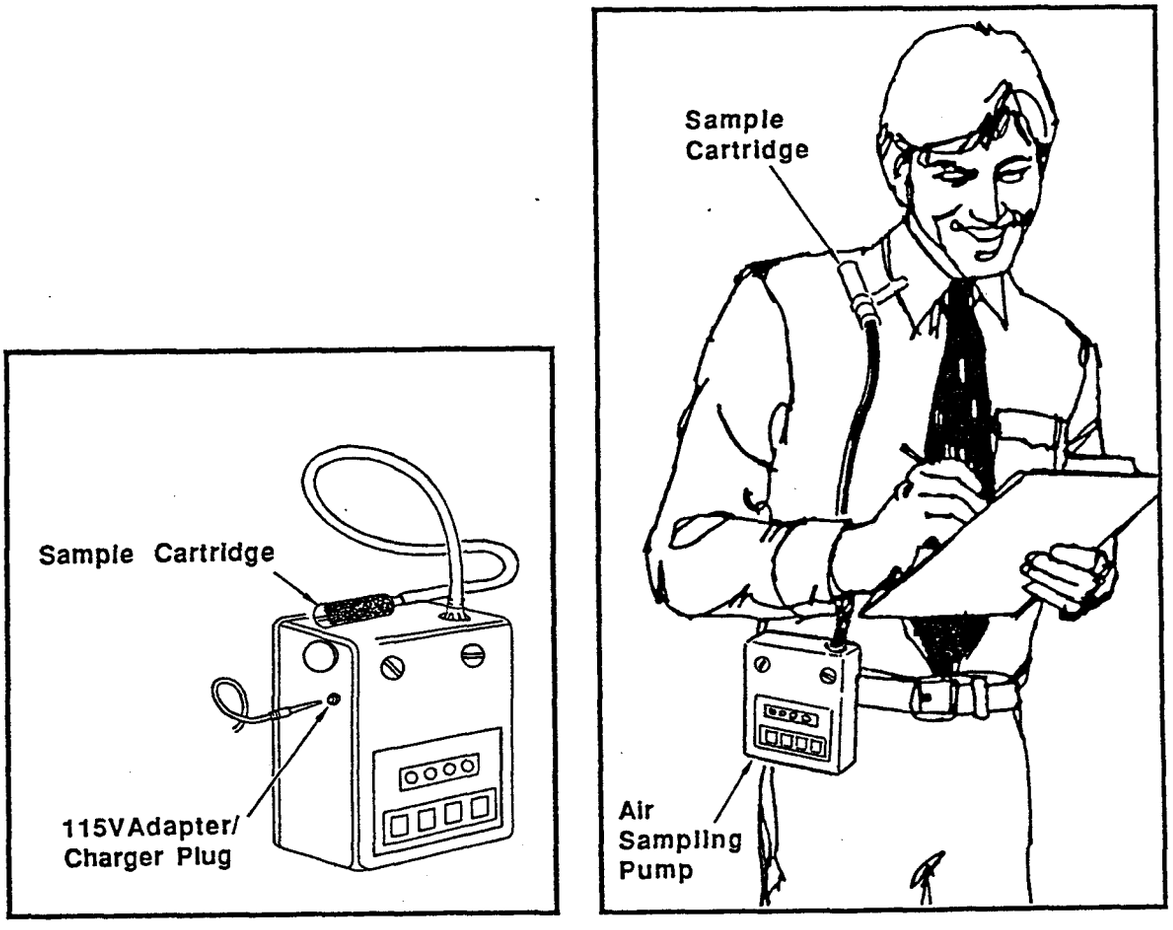
	Spike Level,[a]	Static Recovery,%			Retention Efficiency,%			Sampling Efficiency,%		
Compound	µg/plug	mean	RSD	n	mean	RSD	n	mean	RSD	n
Carbamates:										
Propoxur	5	61.4	10	6	77.6	37	6	96.7	11	6
Carbofuran	15	55.3	12	6	64.2	46	6	87.2	14	6
Bendicarb	50	57.3	11	6	69.8	43	6	62.1	14	6
Mexacarbate	10	62.8	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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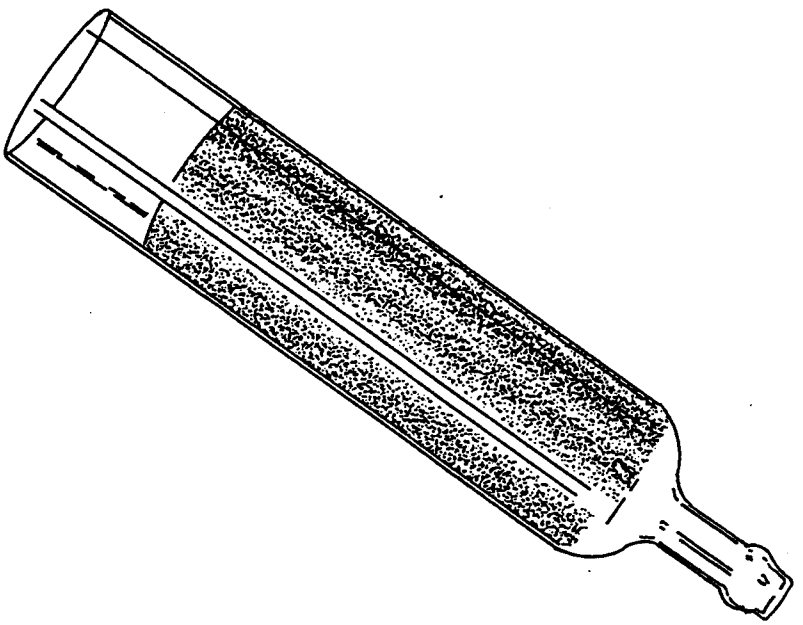

Figure 2. Polyurethane Foam (PUF) Sampling Cartridge

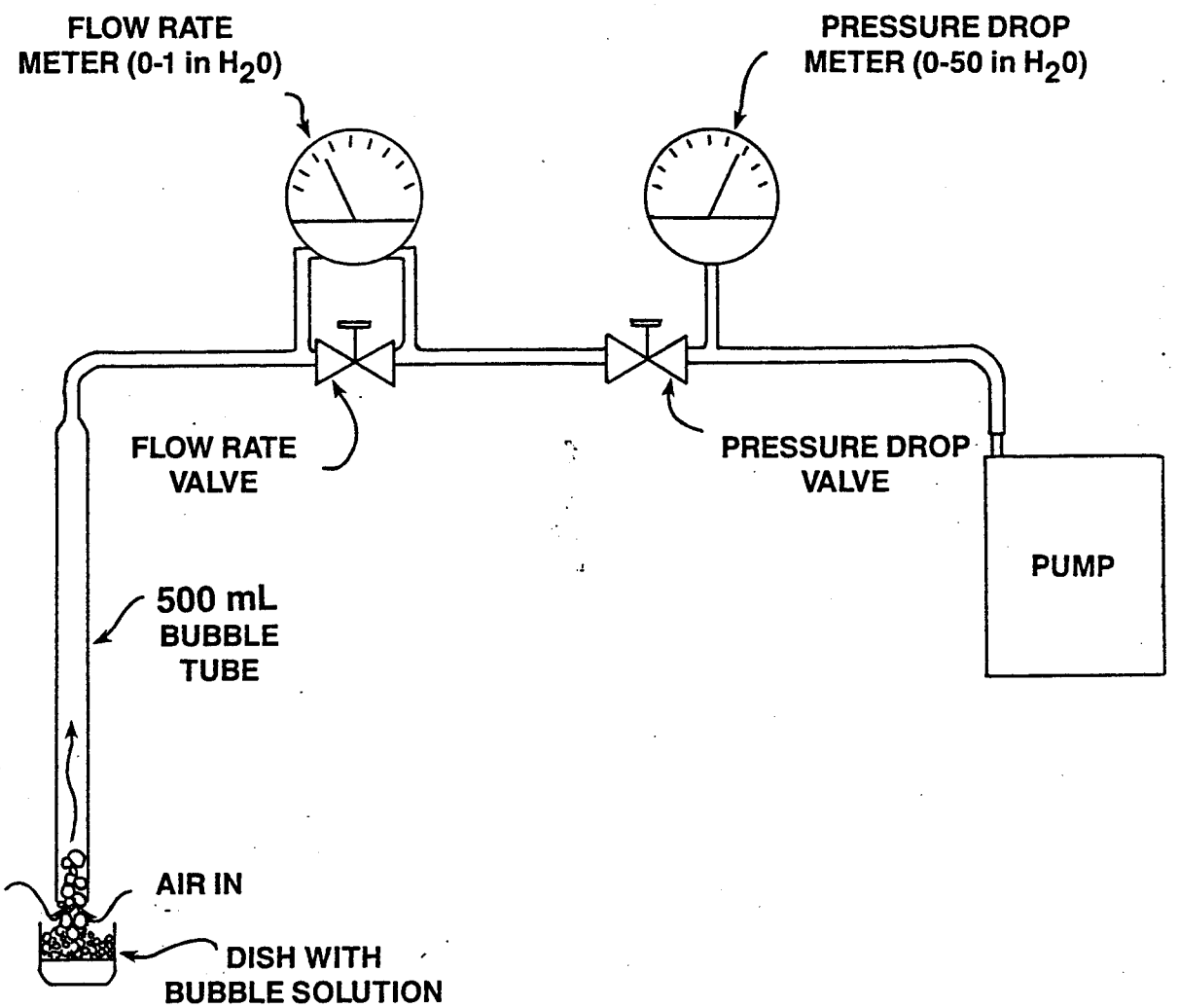

Figure 3. Calibration Assembly for Air Sampler Pump

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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

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.

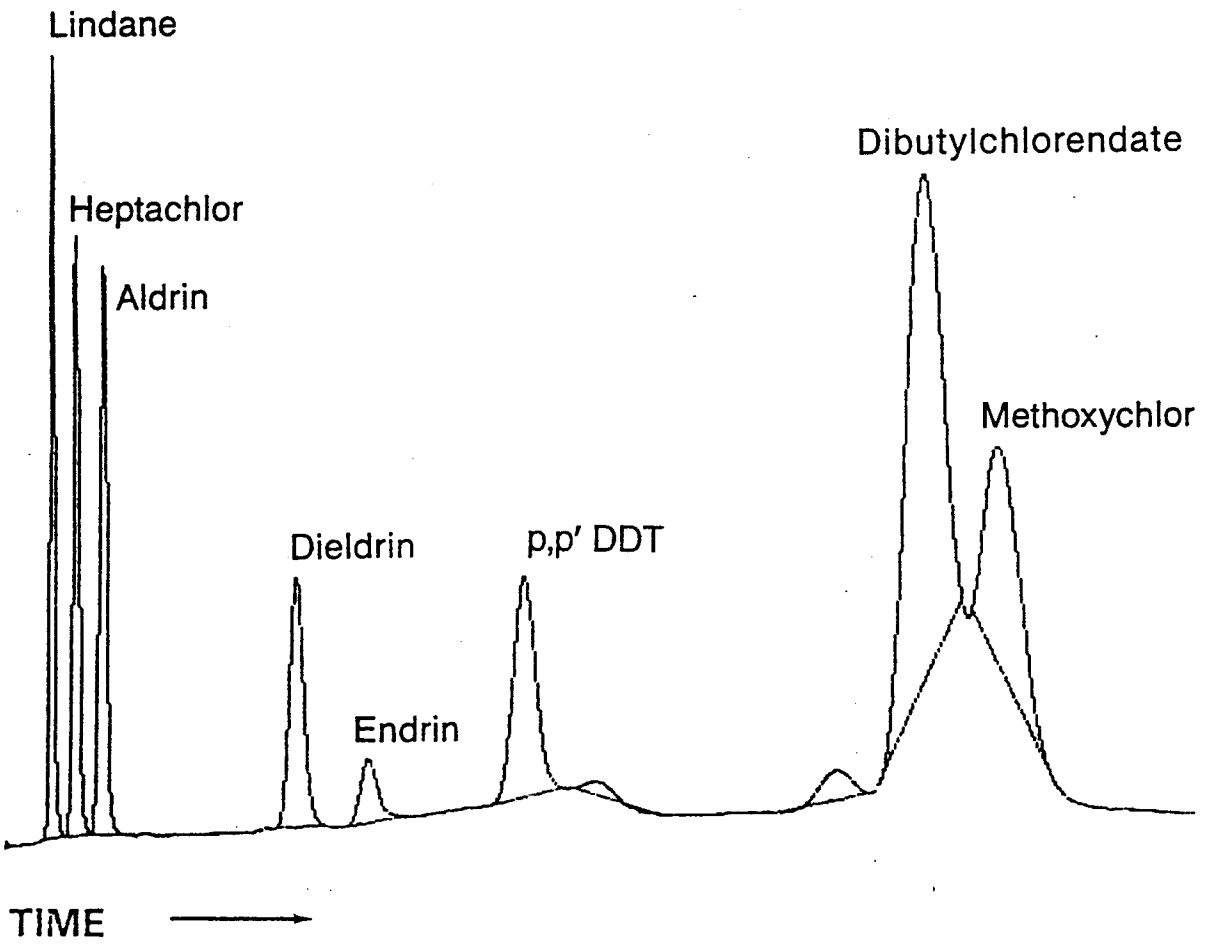

Figure 5. Chromatograph Showing a Mixture of Single Component Pesticides Determined by GC/ECD Using a Packed Column

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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.

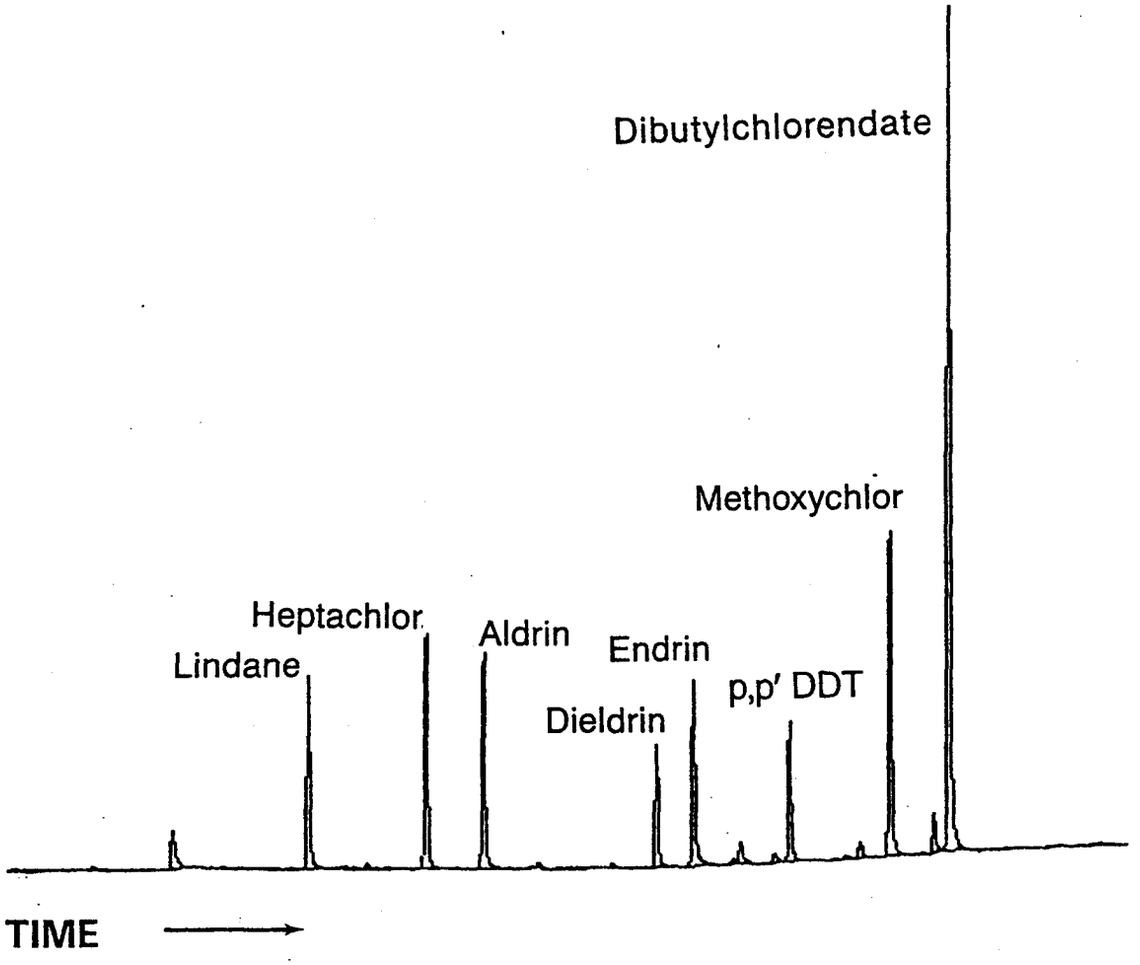

Figure 6. Chromatograph Showing a Mixture of Single Component Pesticides Determined by GC/ECD Using a Capillary Column

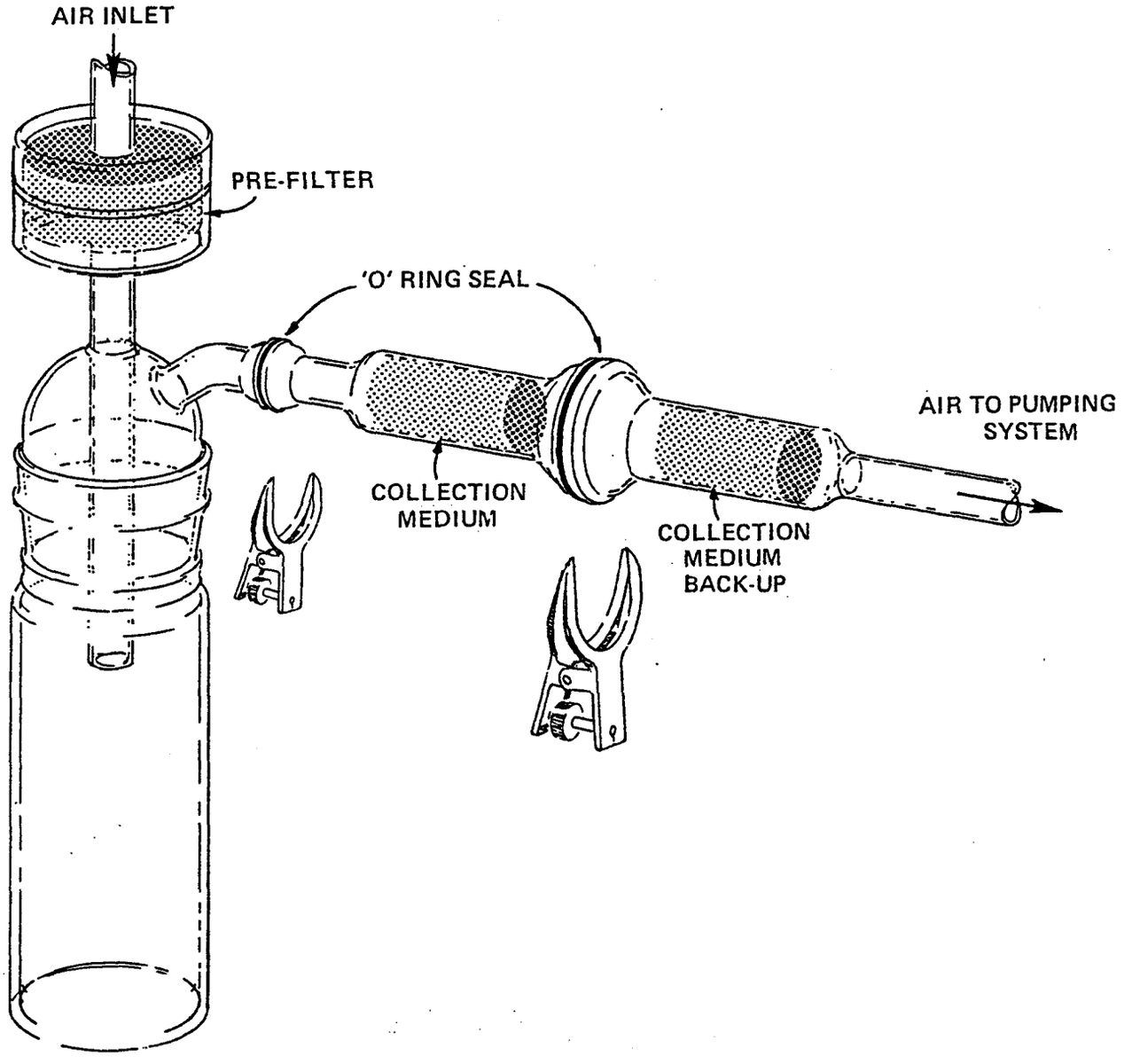

Figure 7. Apparatus for Determining Sampling Efficiencies

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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 μm). 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.

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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

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.

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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.

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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.

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

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.

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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.

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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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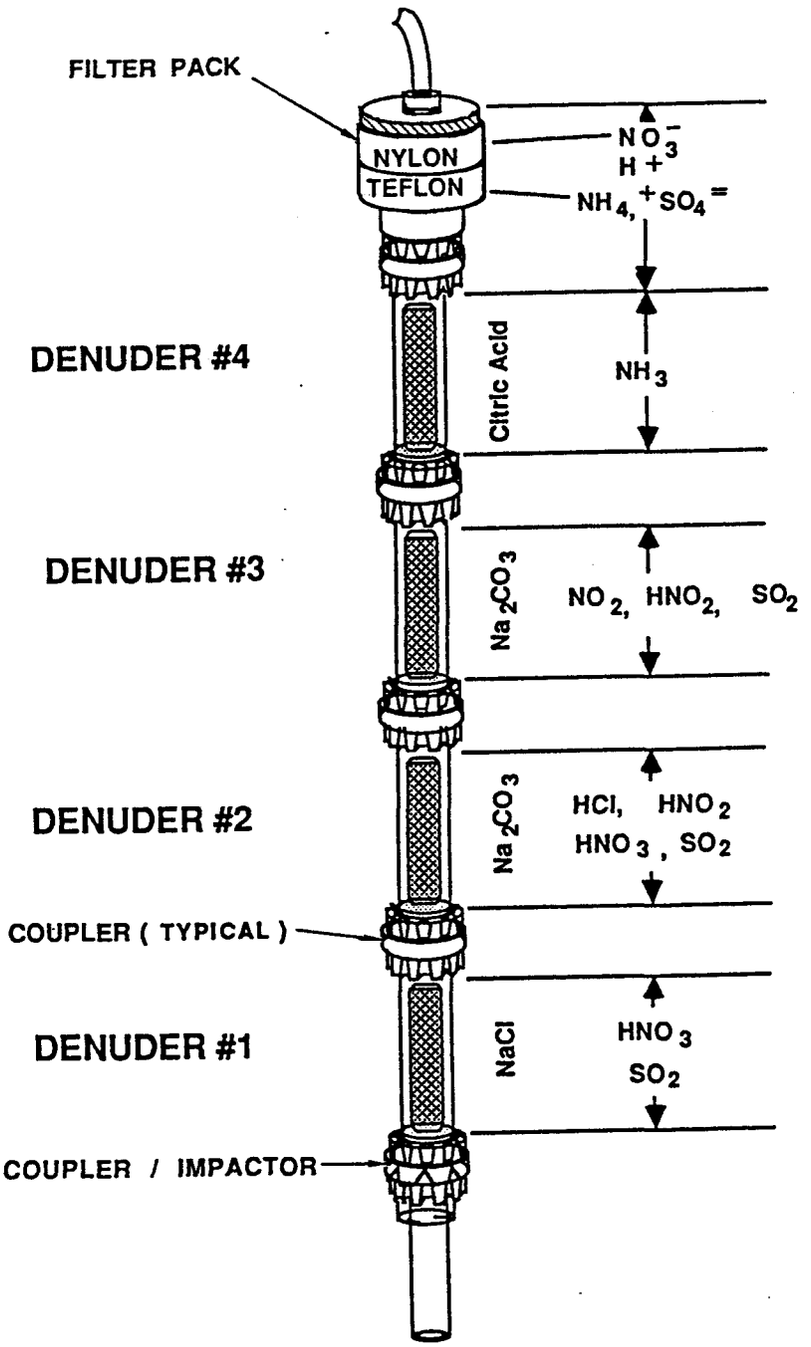

Figure 1. Schematic View of Annular Denuder Showing Species Collected

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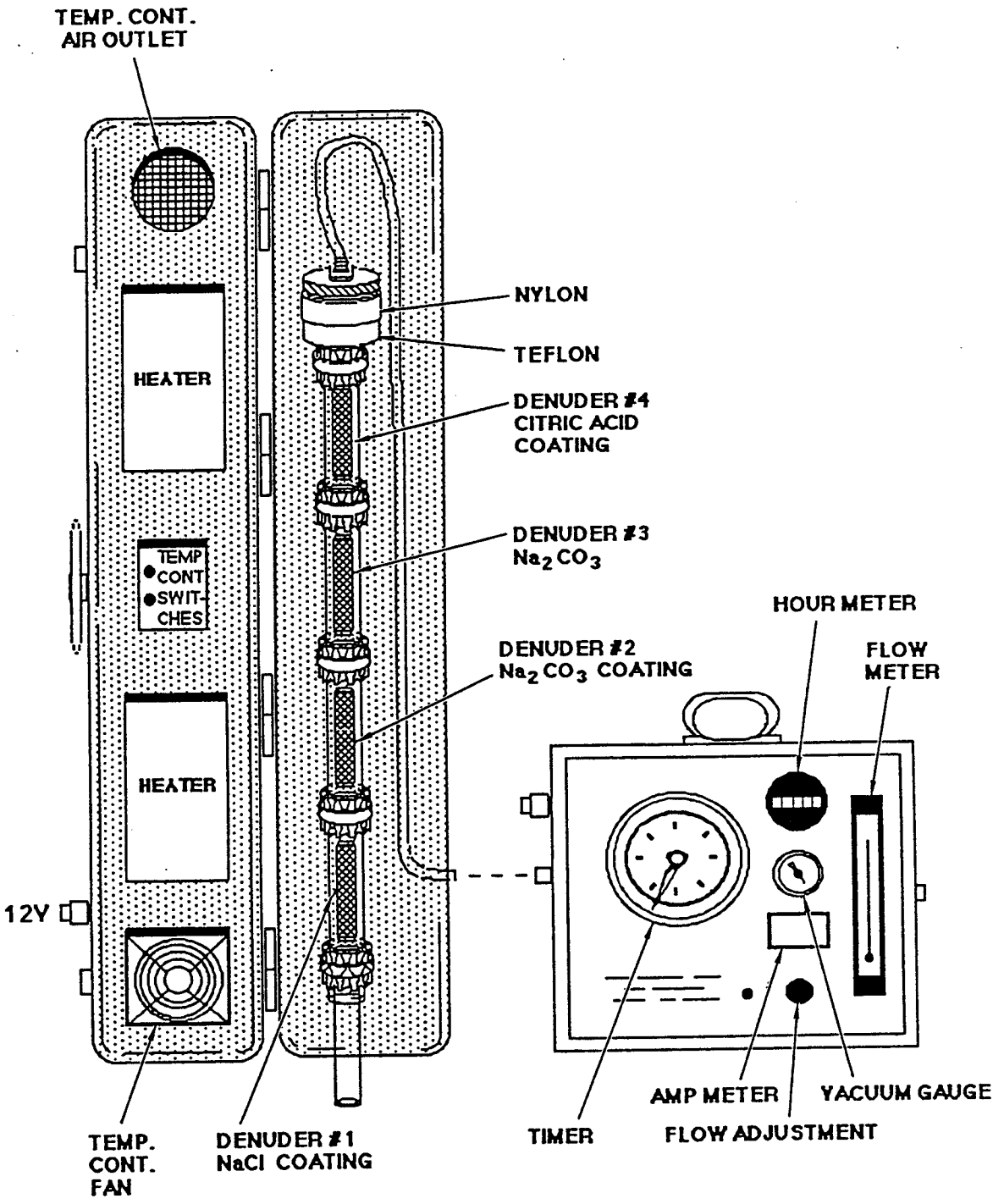

Figure 2. Annular Denuder System

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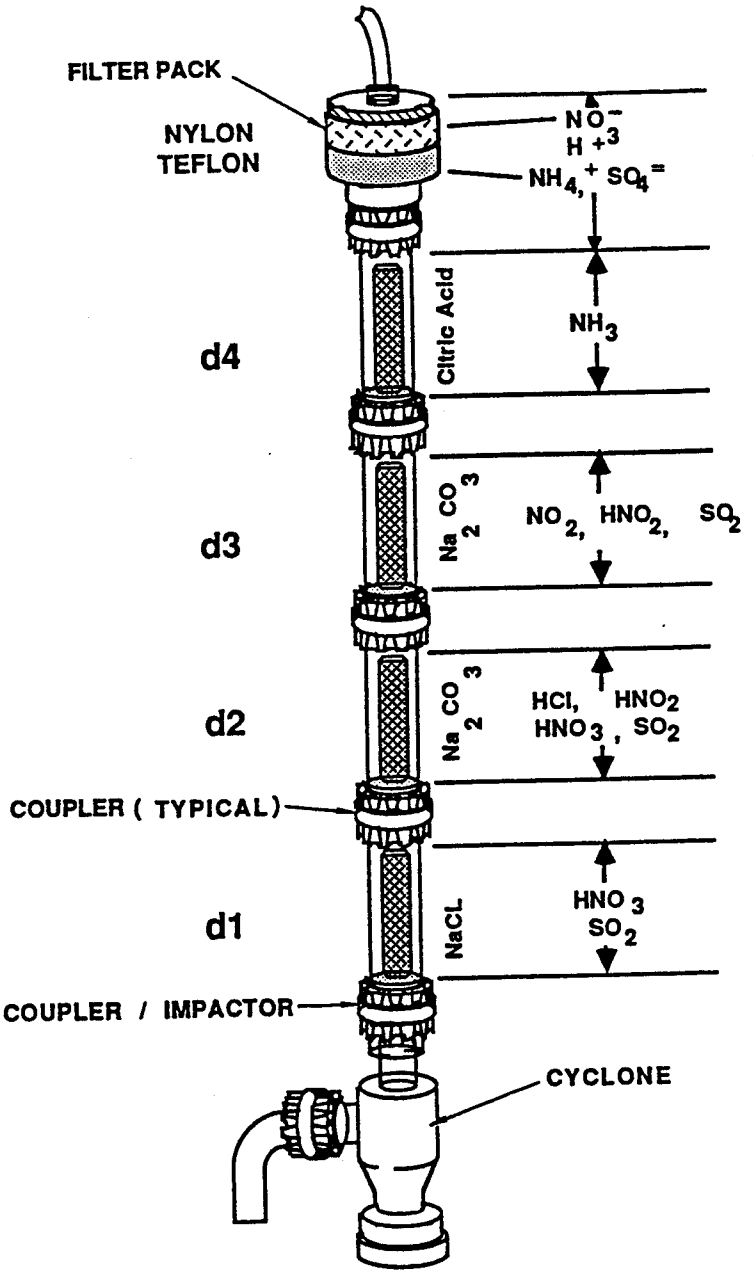

Figure 3. Schematic View of Annular Denuder with Cyclone Adaptor for Removal of Coarse Particles

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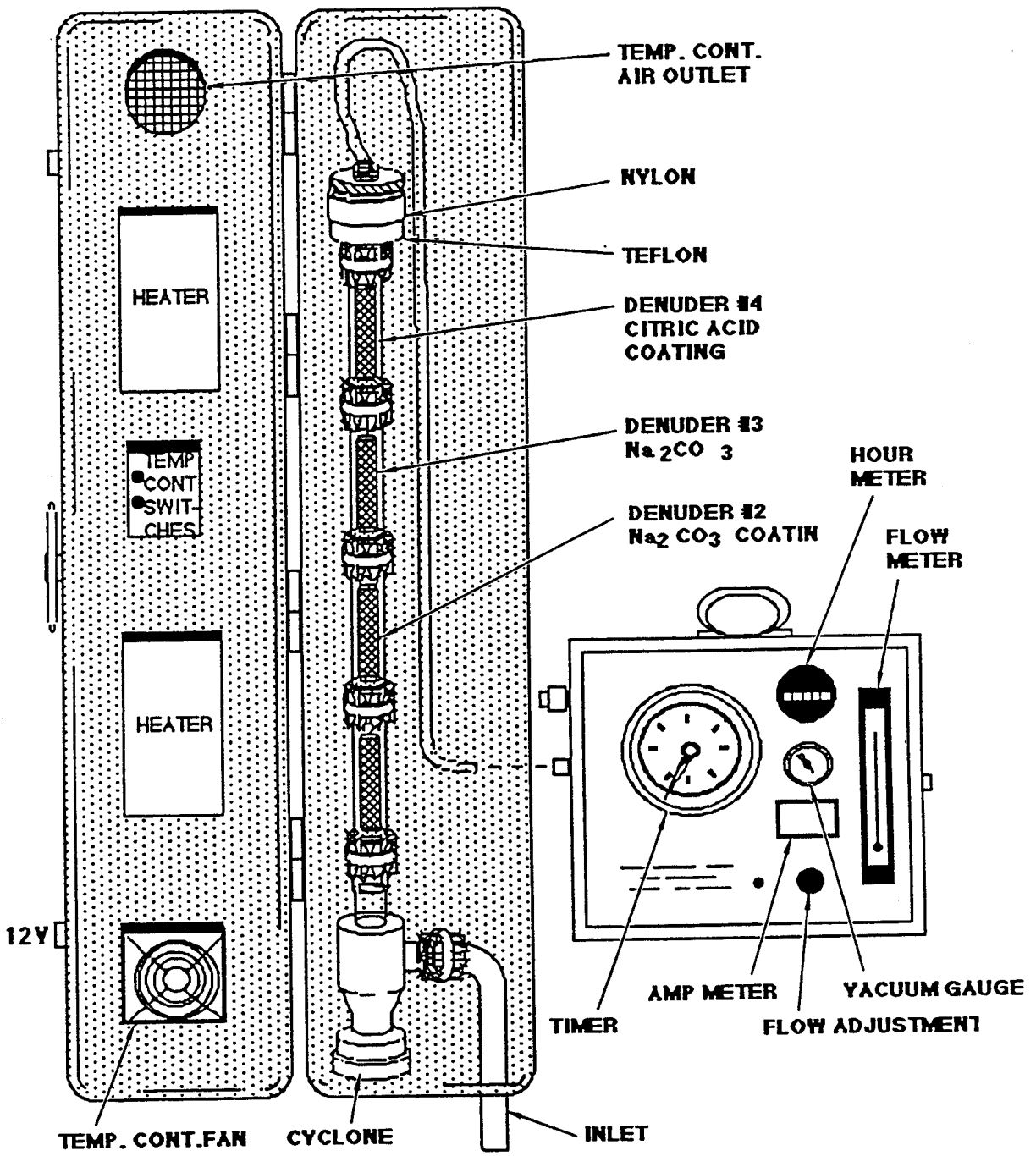

Figure 4. Annular Denuder System with Cyclone in Heated Sampling Case

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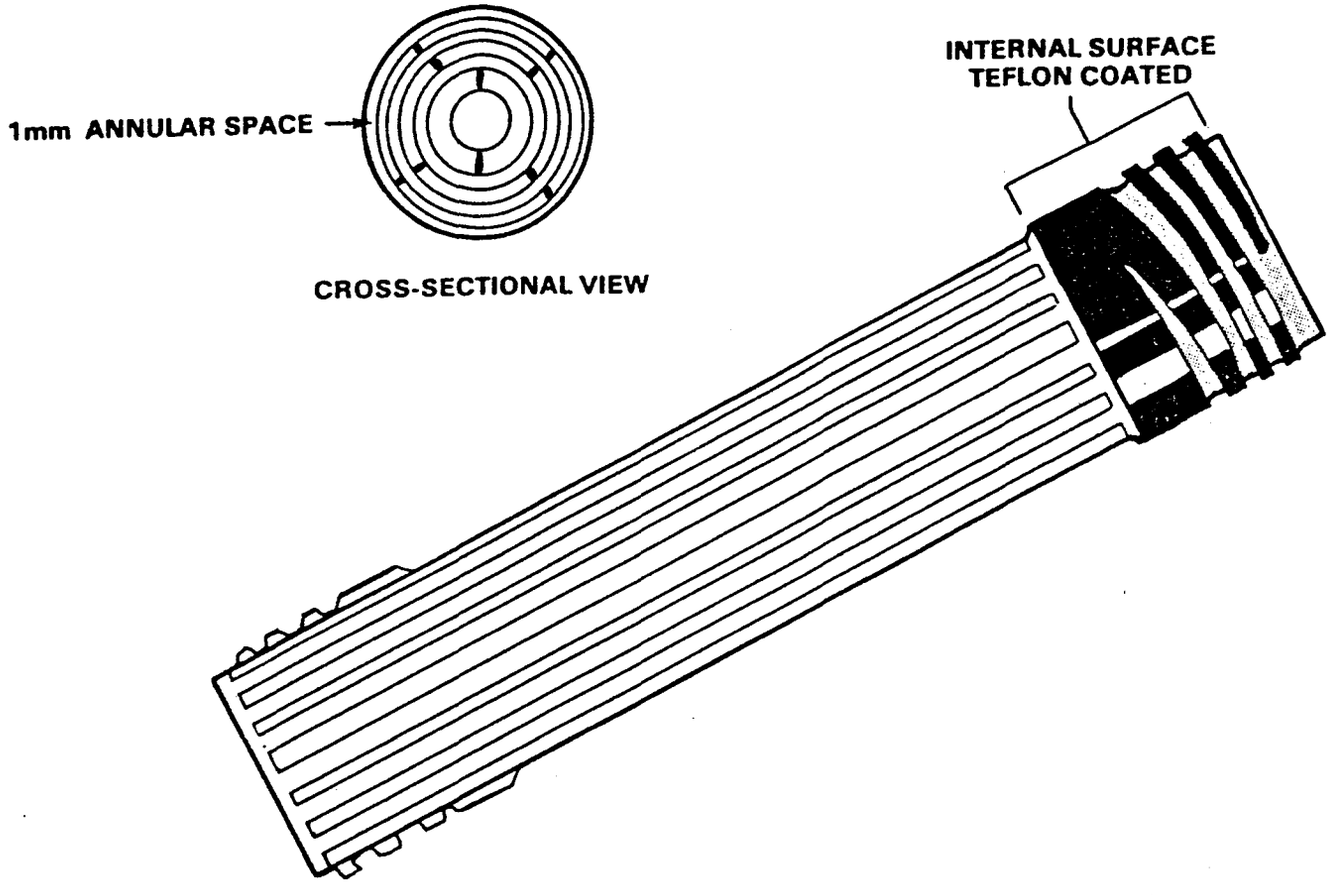

Figure 5. Internal Schematic of Annular Denuder

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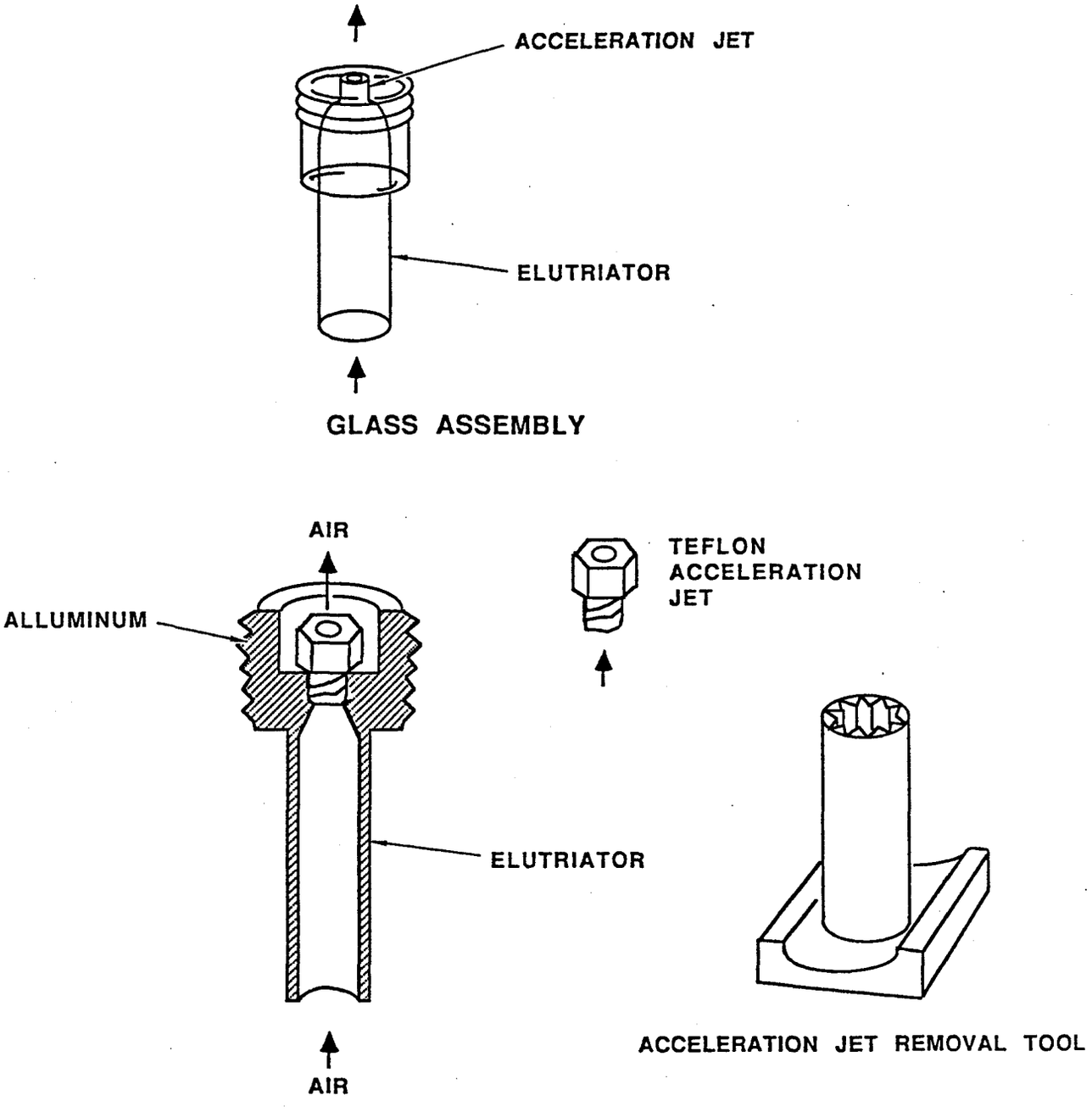

Figure 6. Available Elutriator and Acceleration Jet Assemblies

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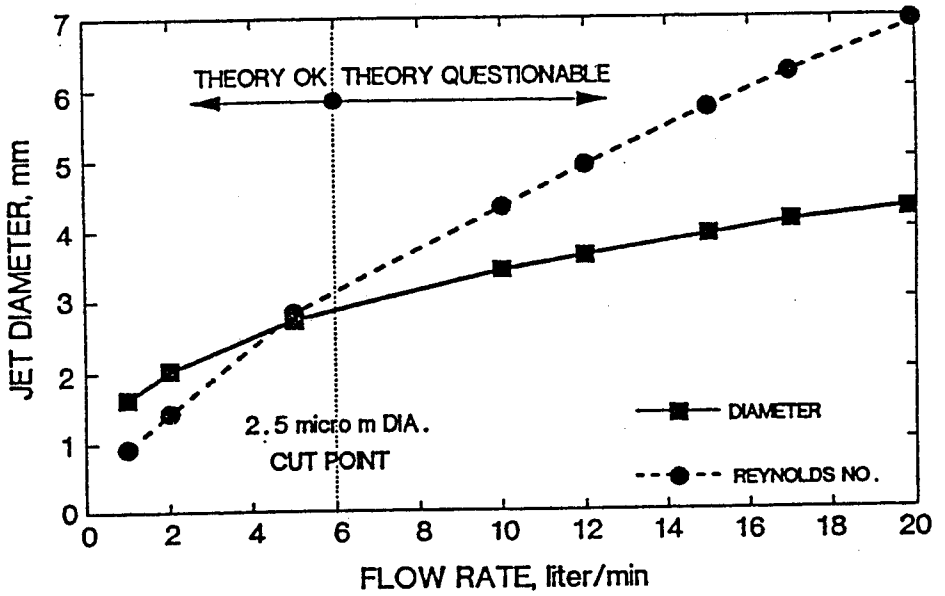

Figure 7A

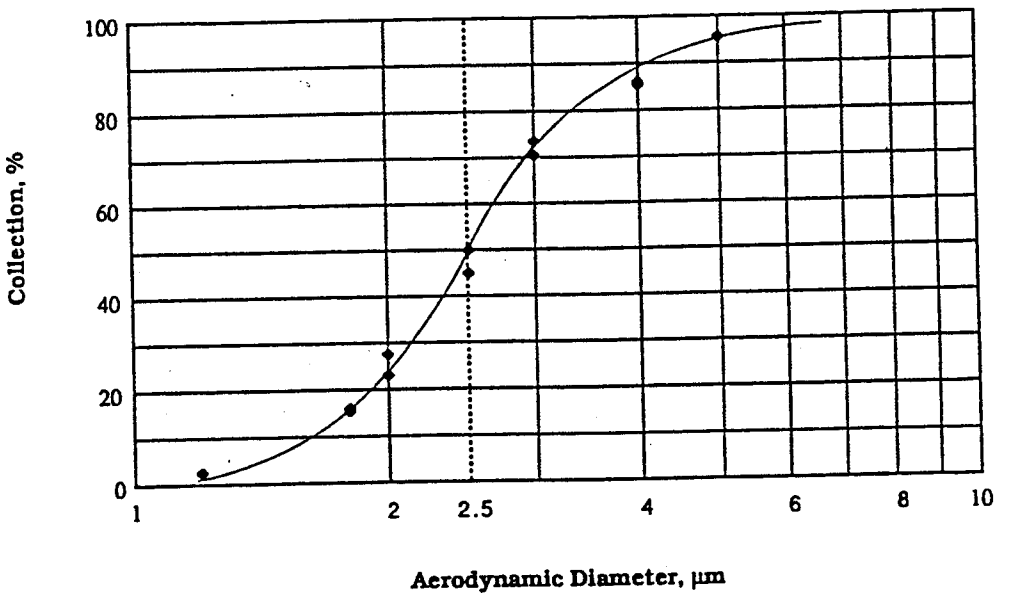

Figure 7B

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

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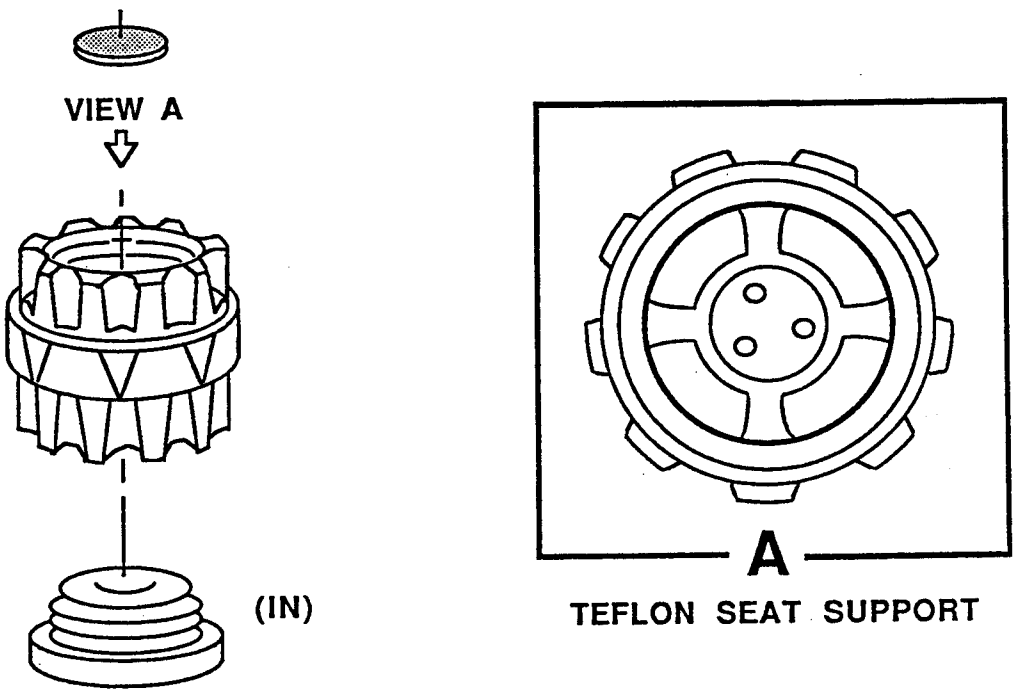

Figure 8. Side View Impactor/Coupler Assembly

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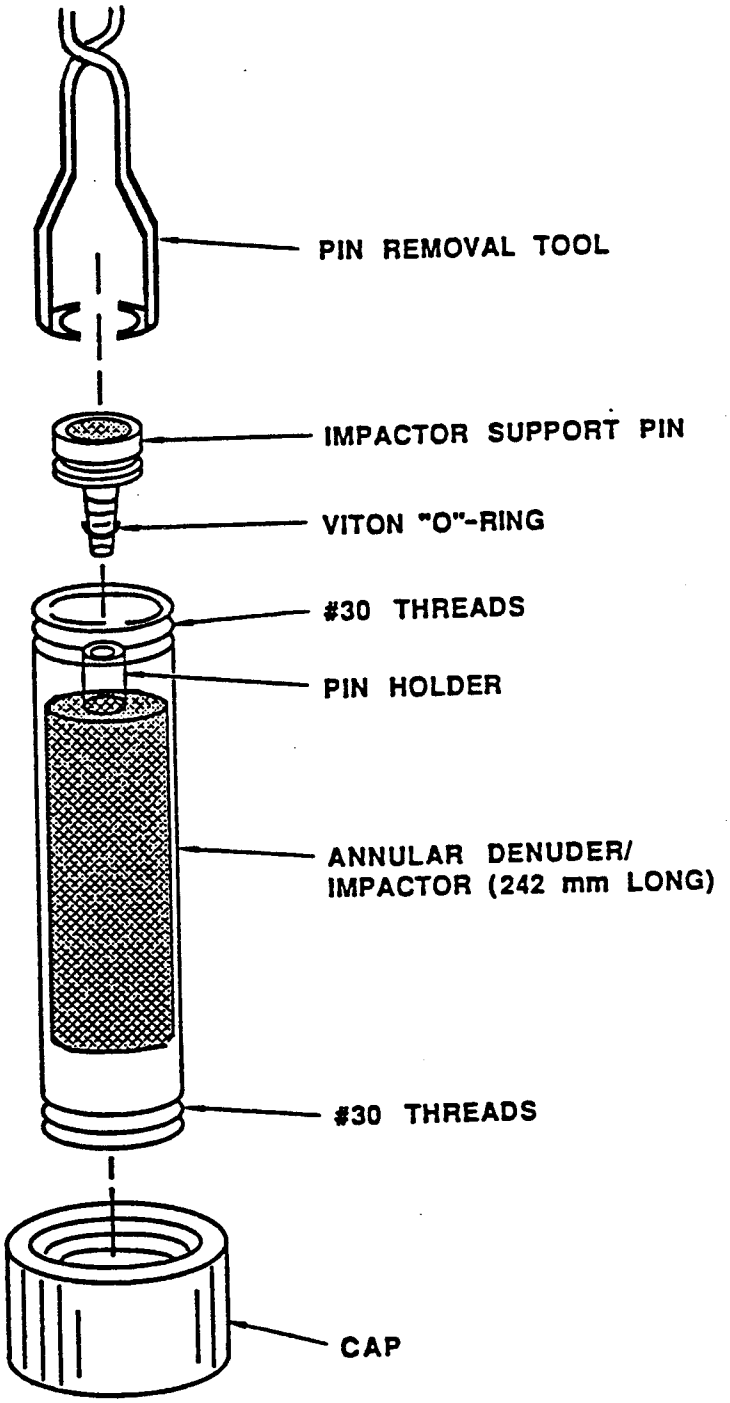

Figure 9. Glass Annular Denuder with Inset Impactor Assembly

720

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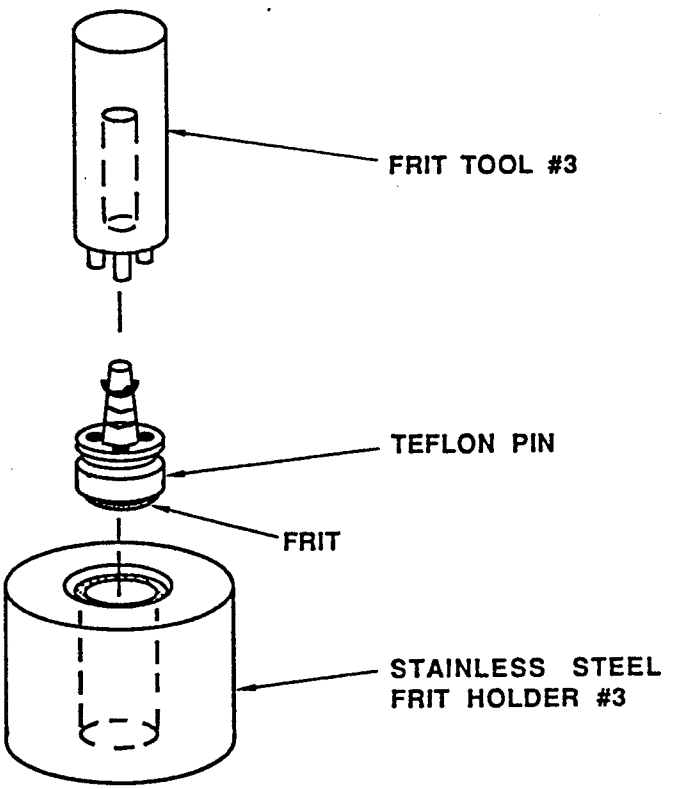

Figure 10. Frit Removal from Pin

134

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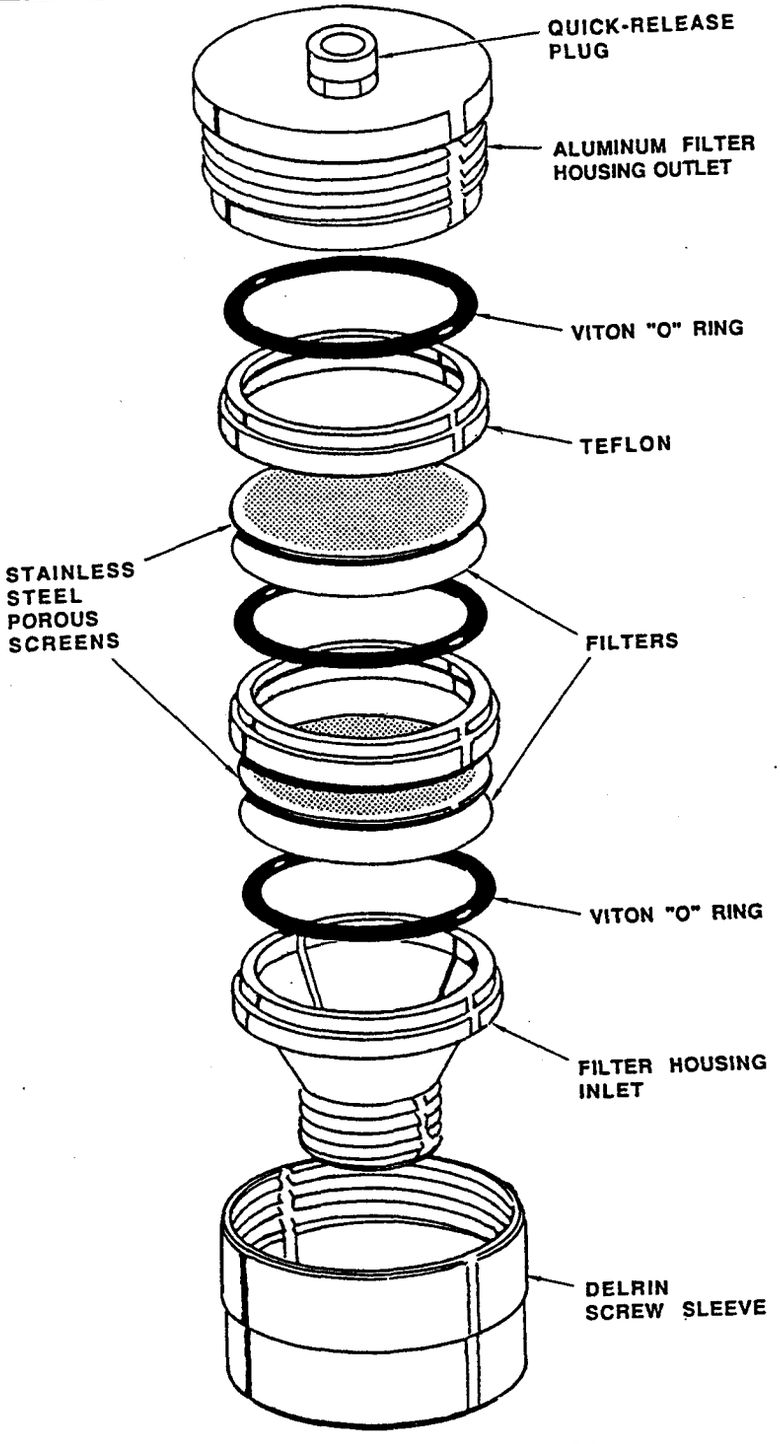

Figure 11. Filter Pack Assembly

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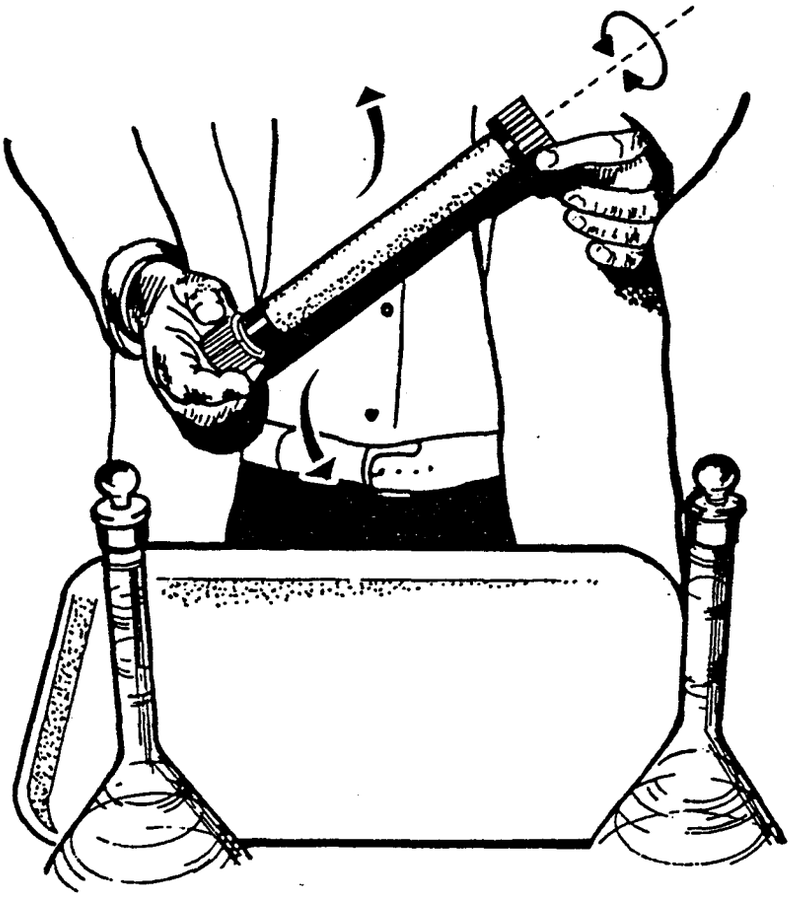

Figure 12. Annular Denuder Coating Procedure

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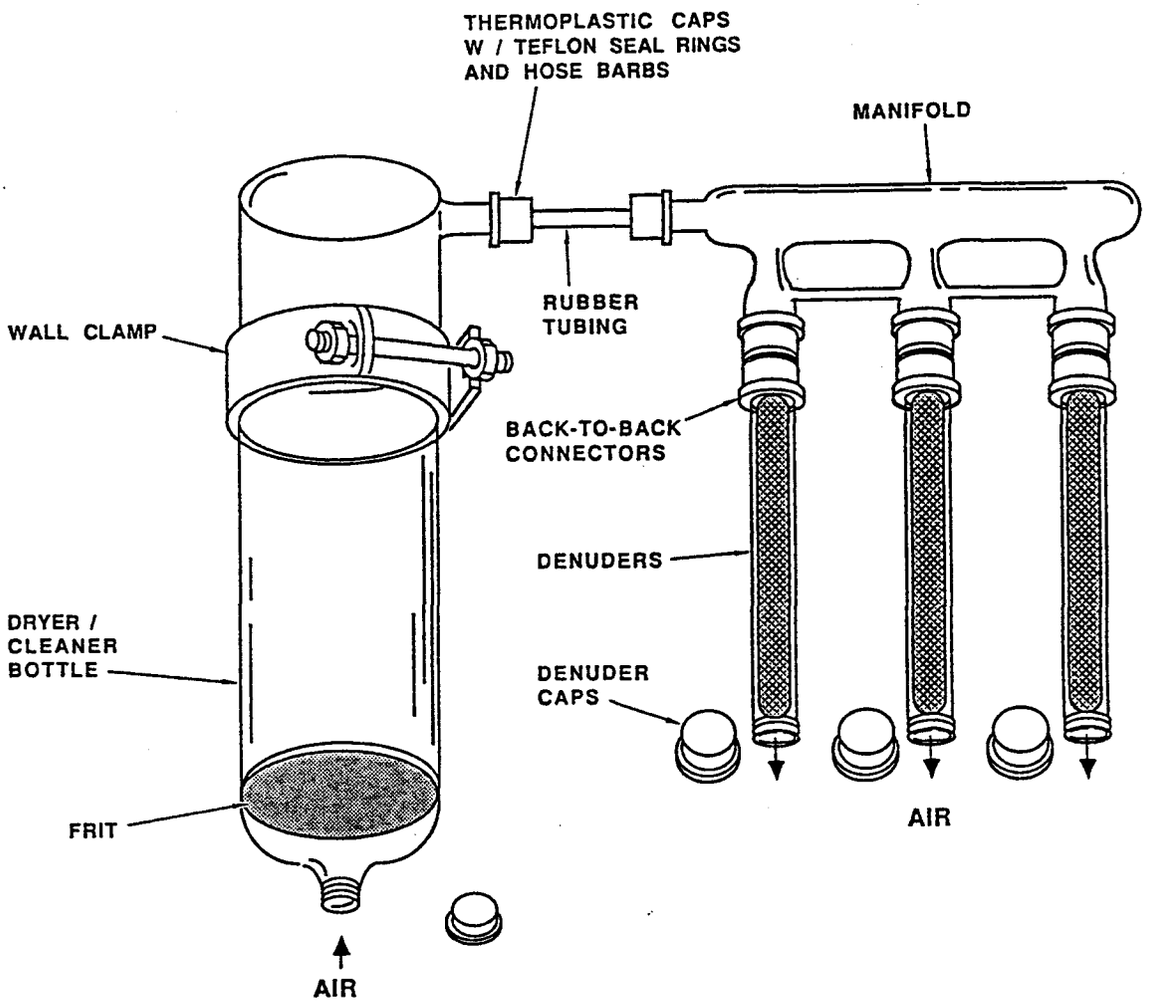

Figure 13. Drying Train and Manifold

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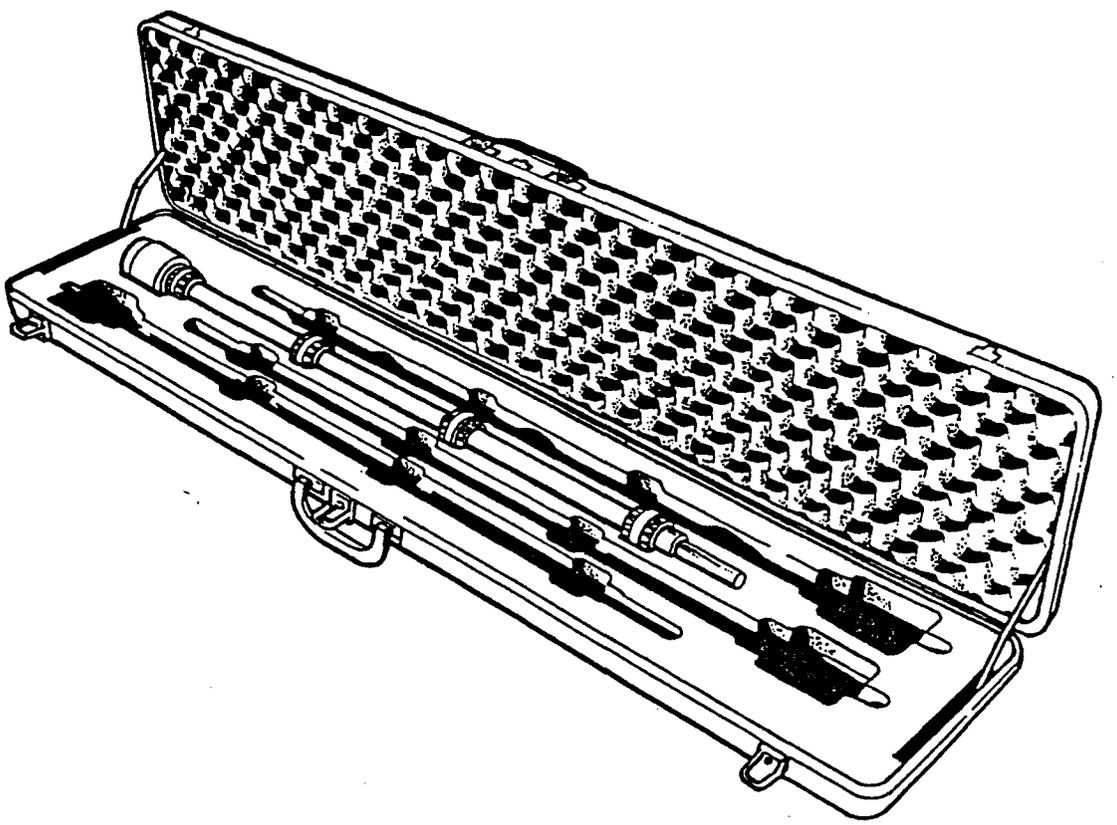

Figure 14. Annular Denuder in Field-to-Lab Case

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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

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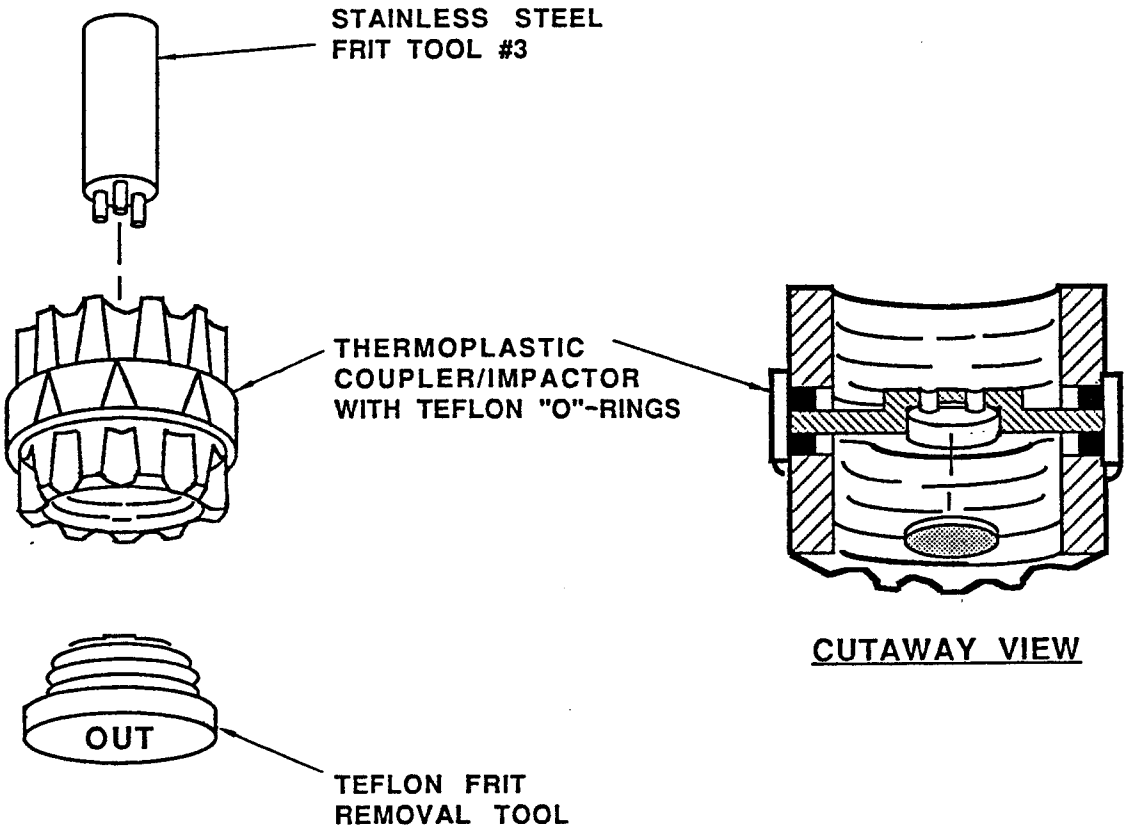

Figure 16. Side View Impactor/Coupler Assembly with Disc Removal Tools

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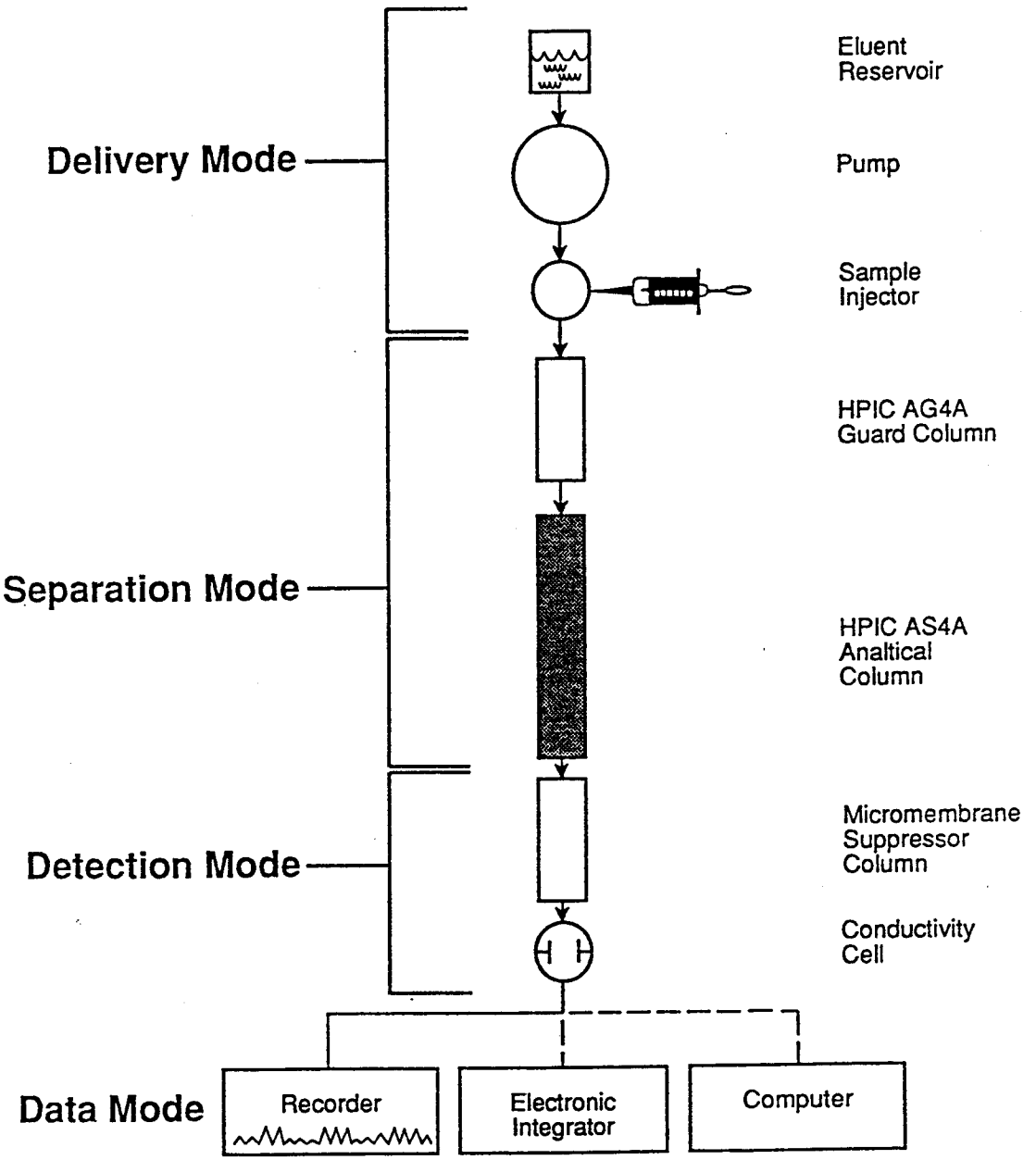

Figure 17. Major Components of a Commercially Available Ion Chromatographer

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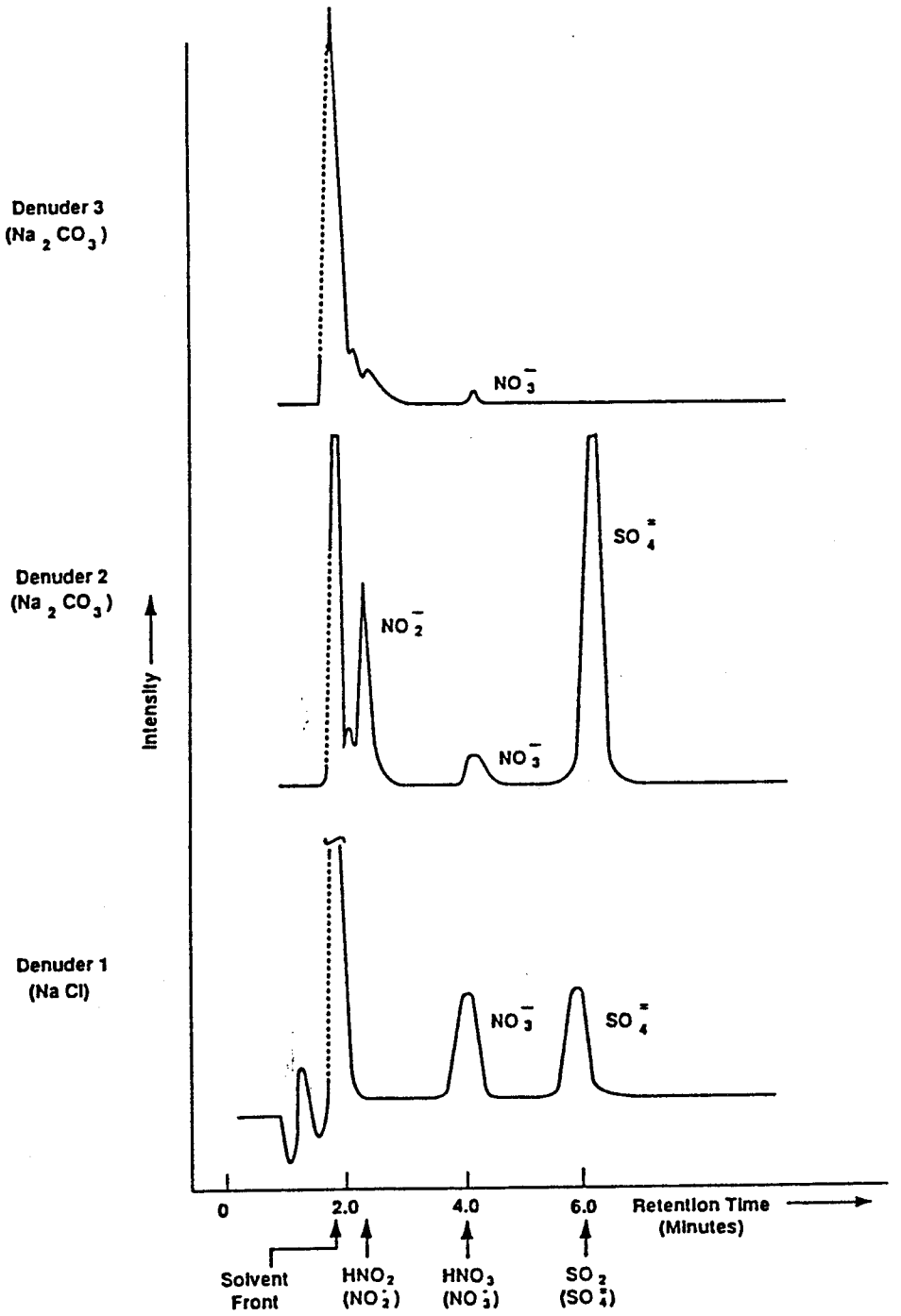

Figure 18. Chromatograms of Denuder/Filter Extract Performed by the Ion Chromatography

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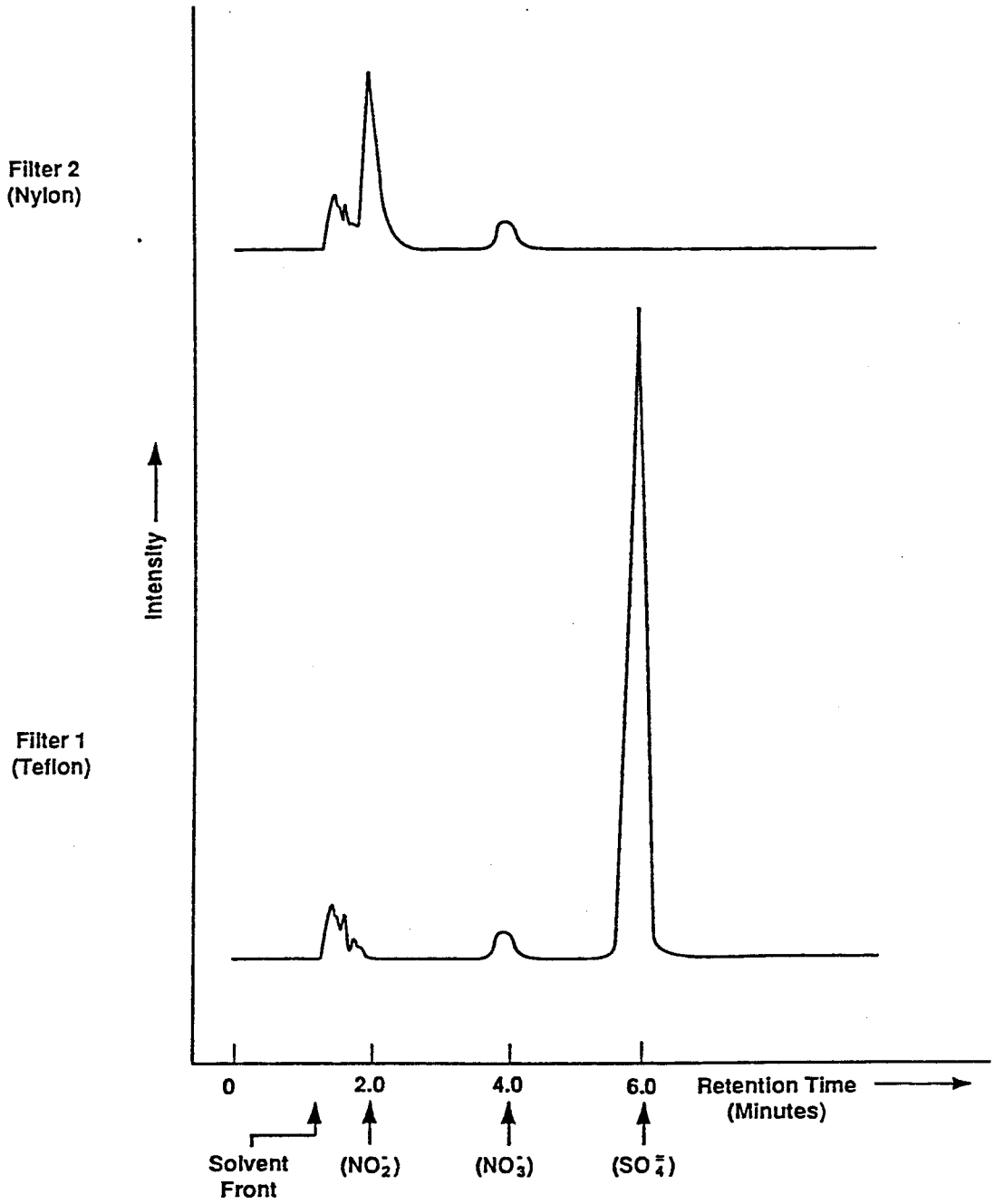

Figure 18 (Cont'd). Chromatograms of Denuder/Filter Extract Performed by the Ion Chromatography

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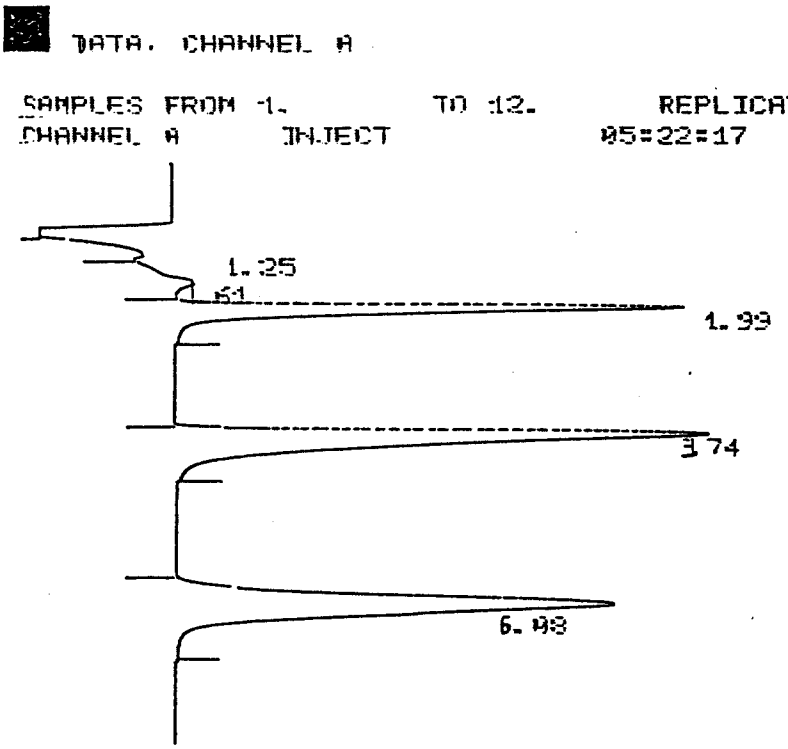
730



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	3009301	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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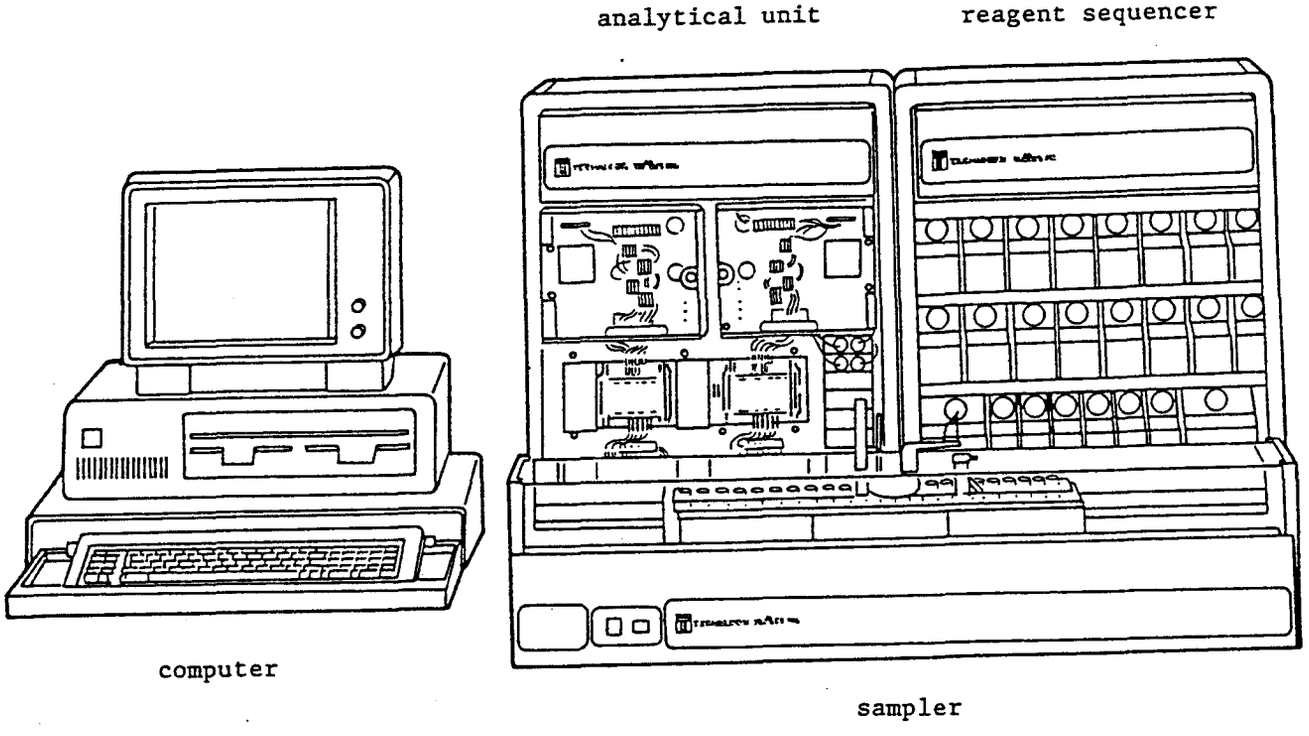

Figure 20. 4-Channel Traacs 800 System with Reagent Sequencer

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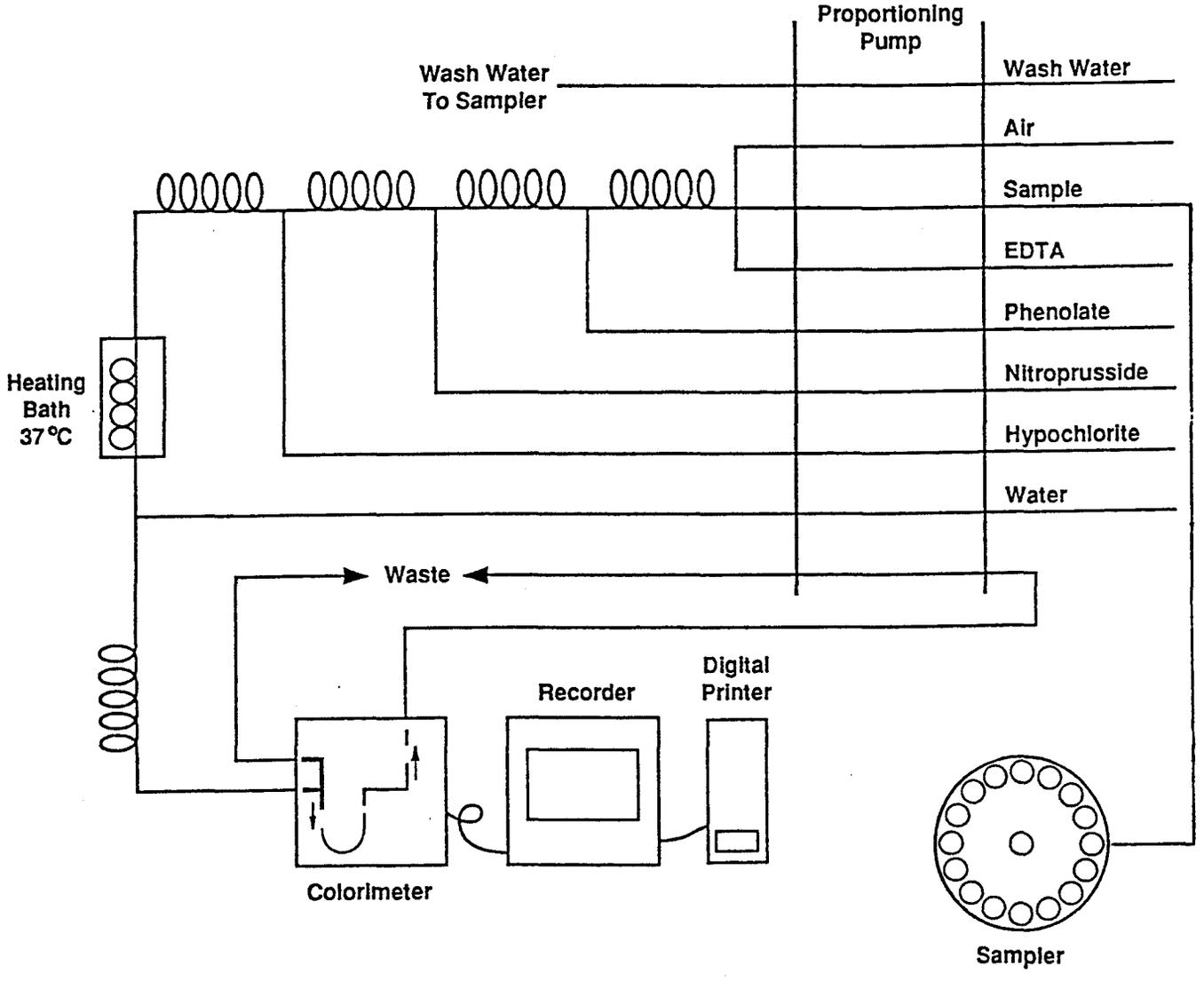

Figure 21. Technicon Autoanalyzer Flow Diagram for Ammonia Analysis

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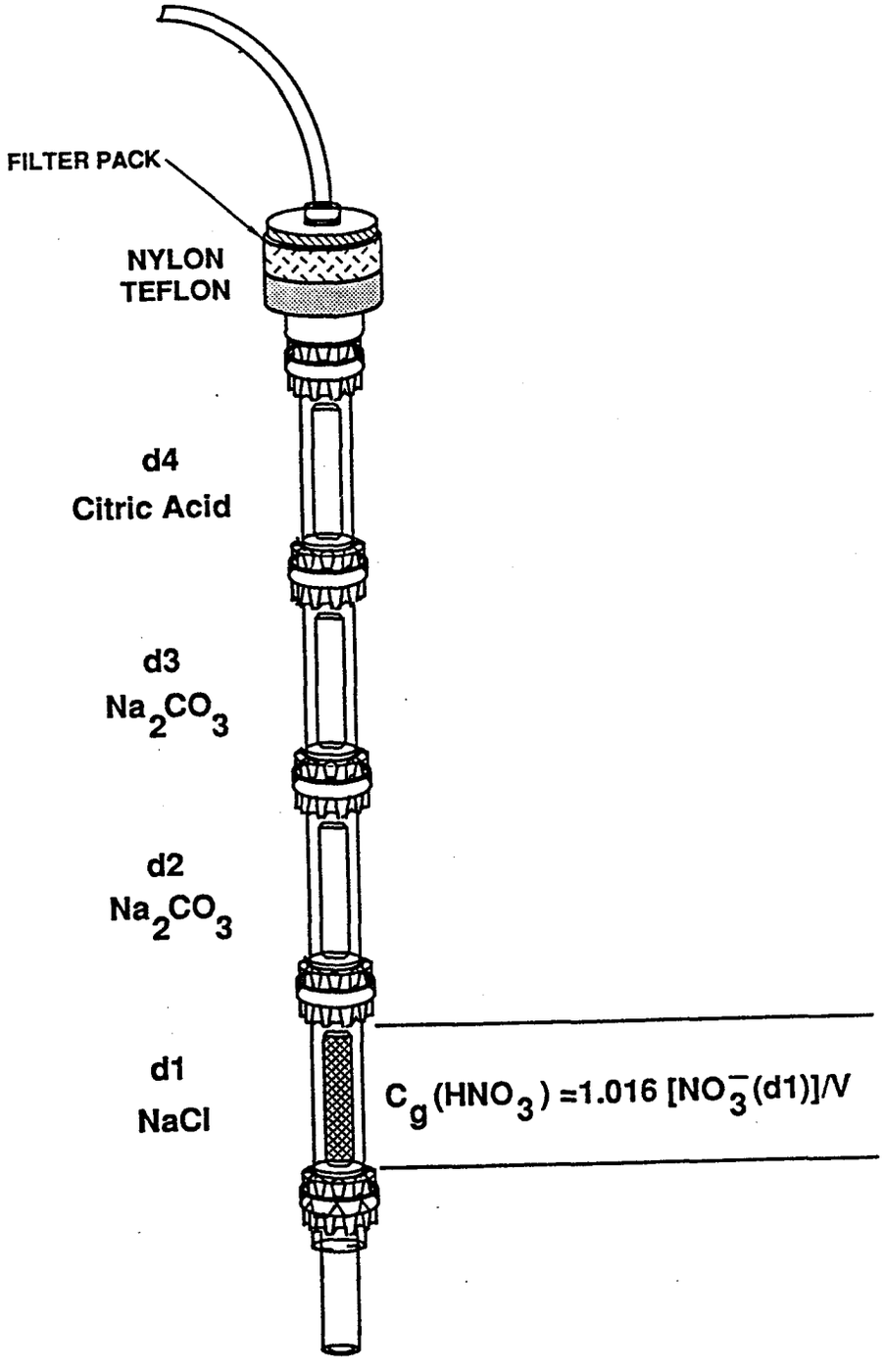

Figure 22. Nitric Acid Gas Measurement

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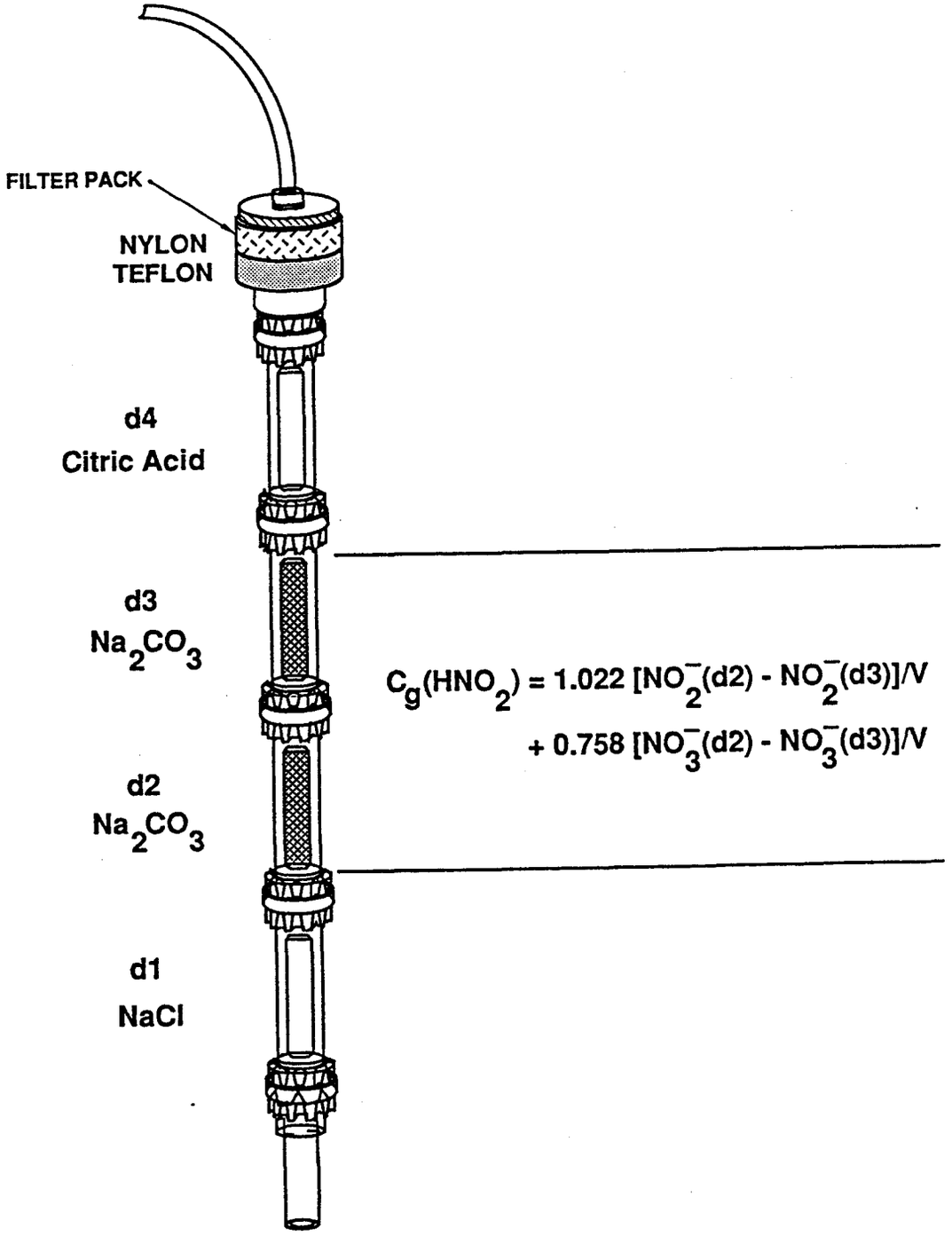

Figure 23. Nitrous Acid Gas Measurement

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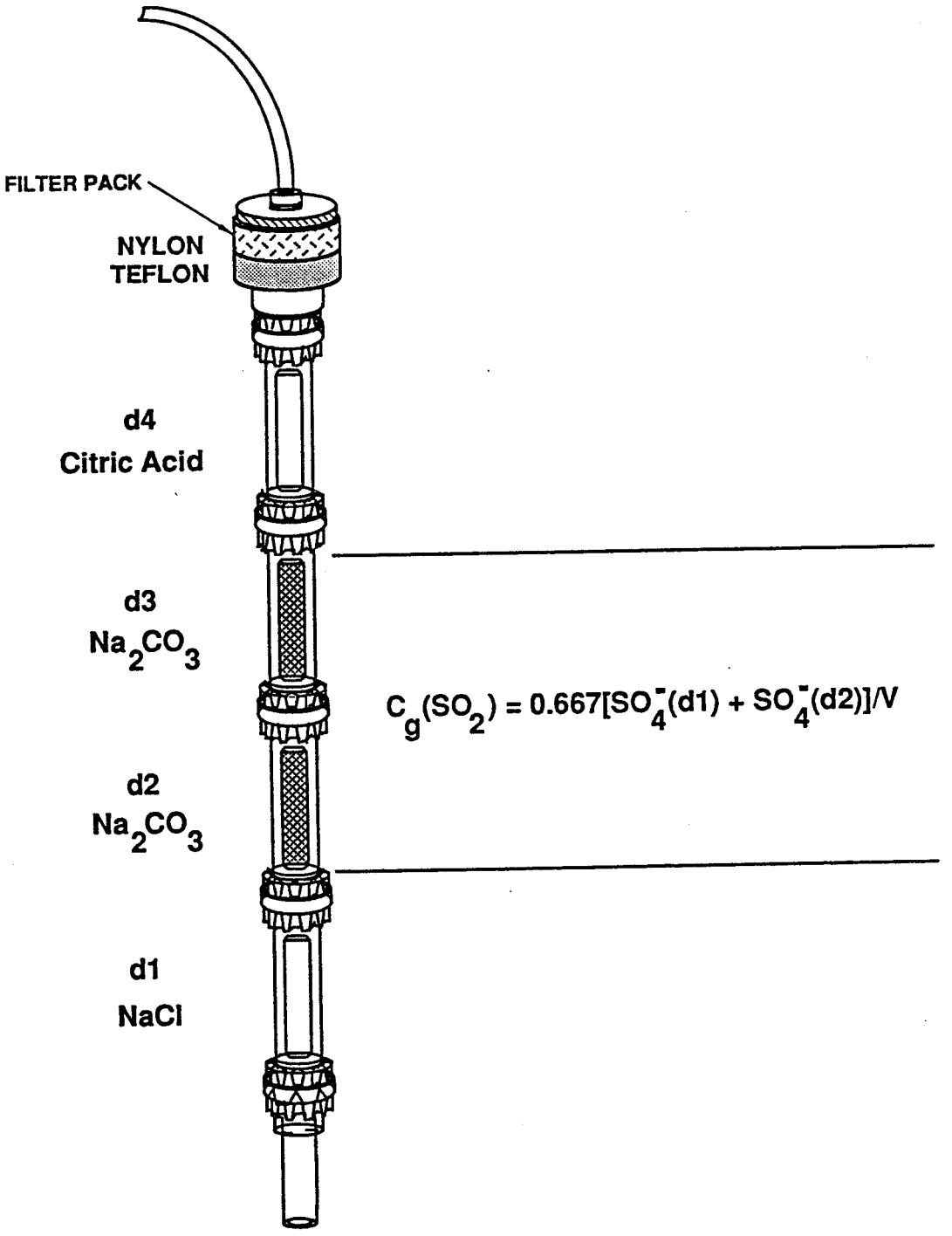

Figure 24. Sulfur Dioxide Gas Measurement

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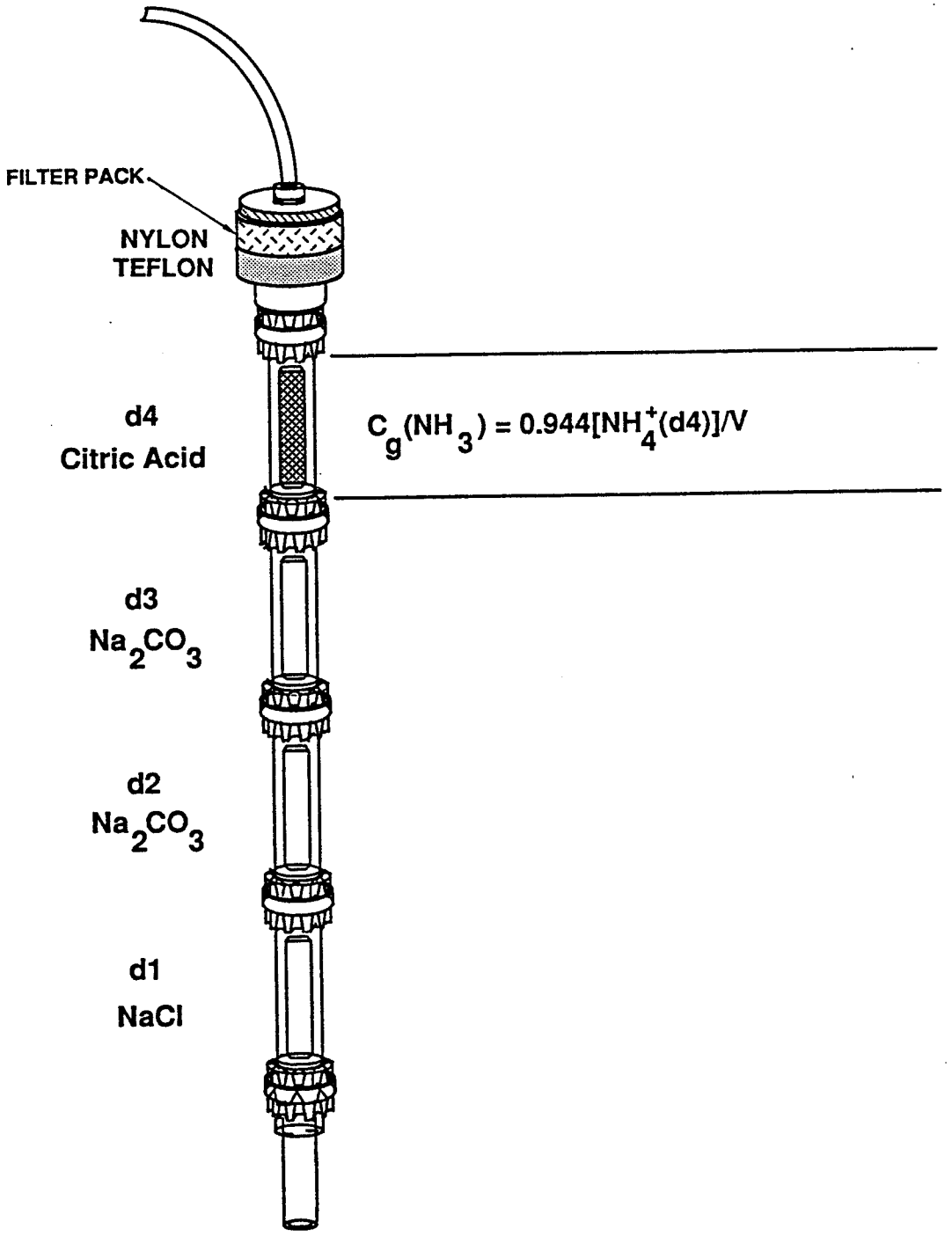

Figure 25. Ammonia Gas Measurement

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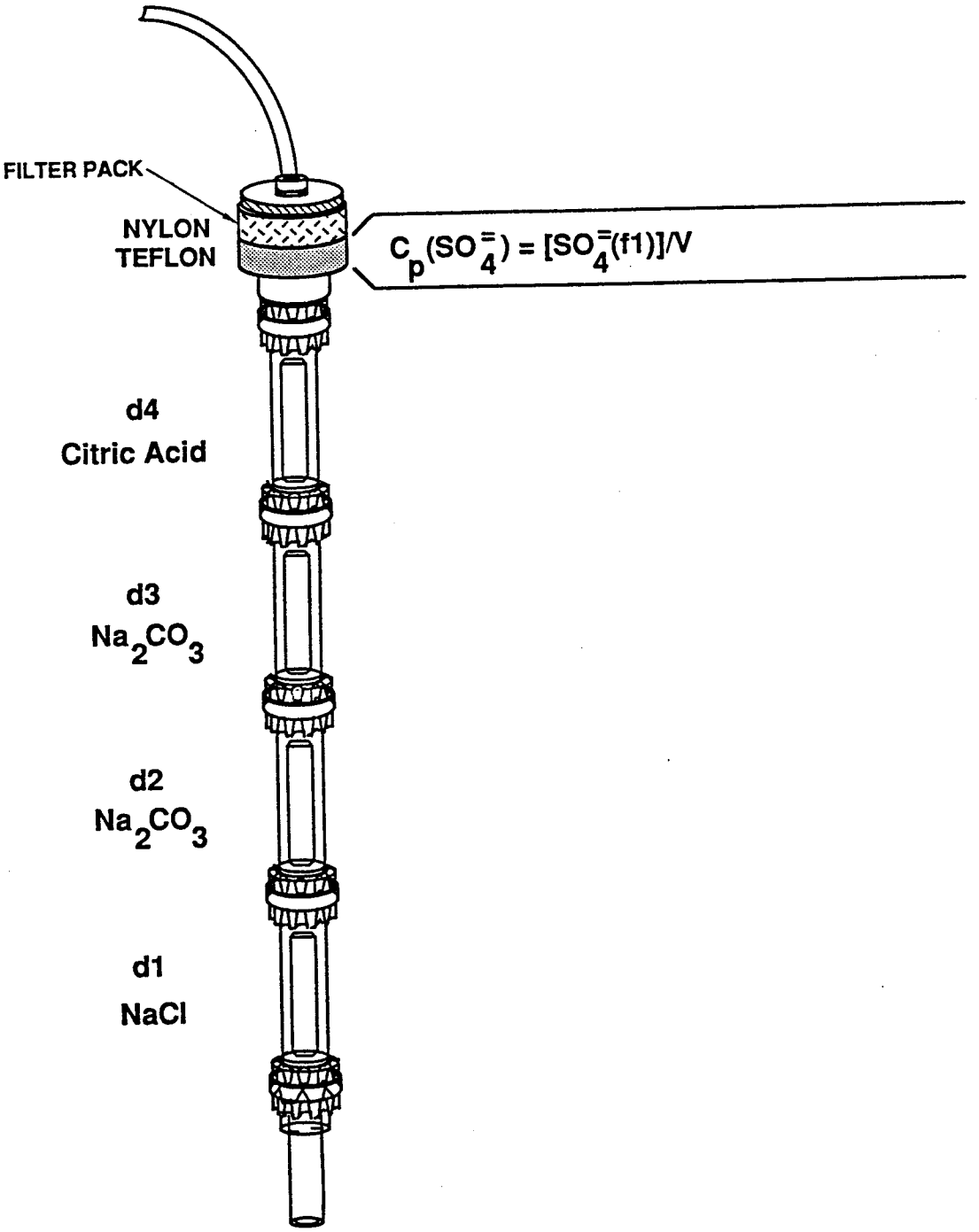

Figure 26. Particulate Sulfate Measurement

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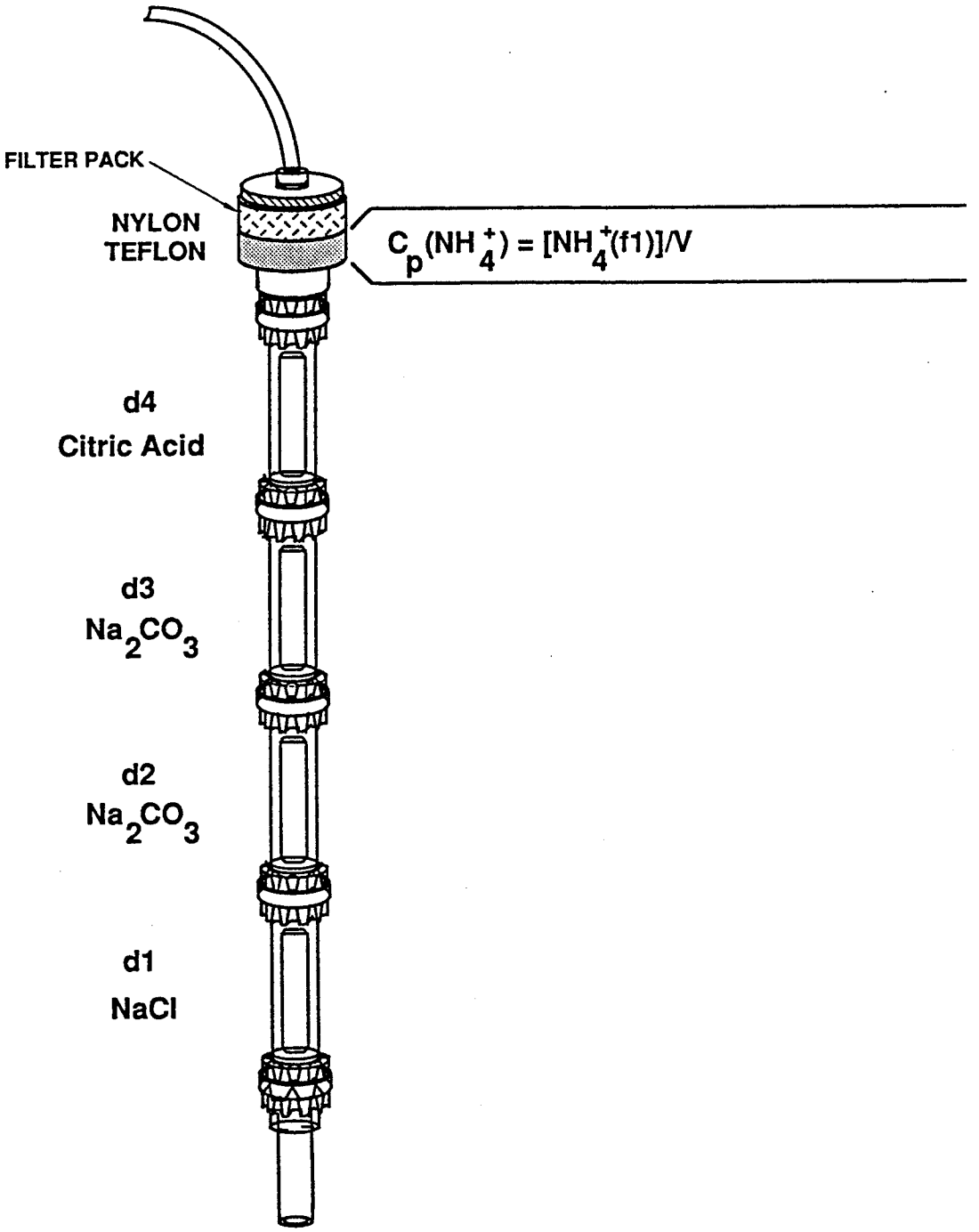

Figure 27. Particulate Ammonium Measurement

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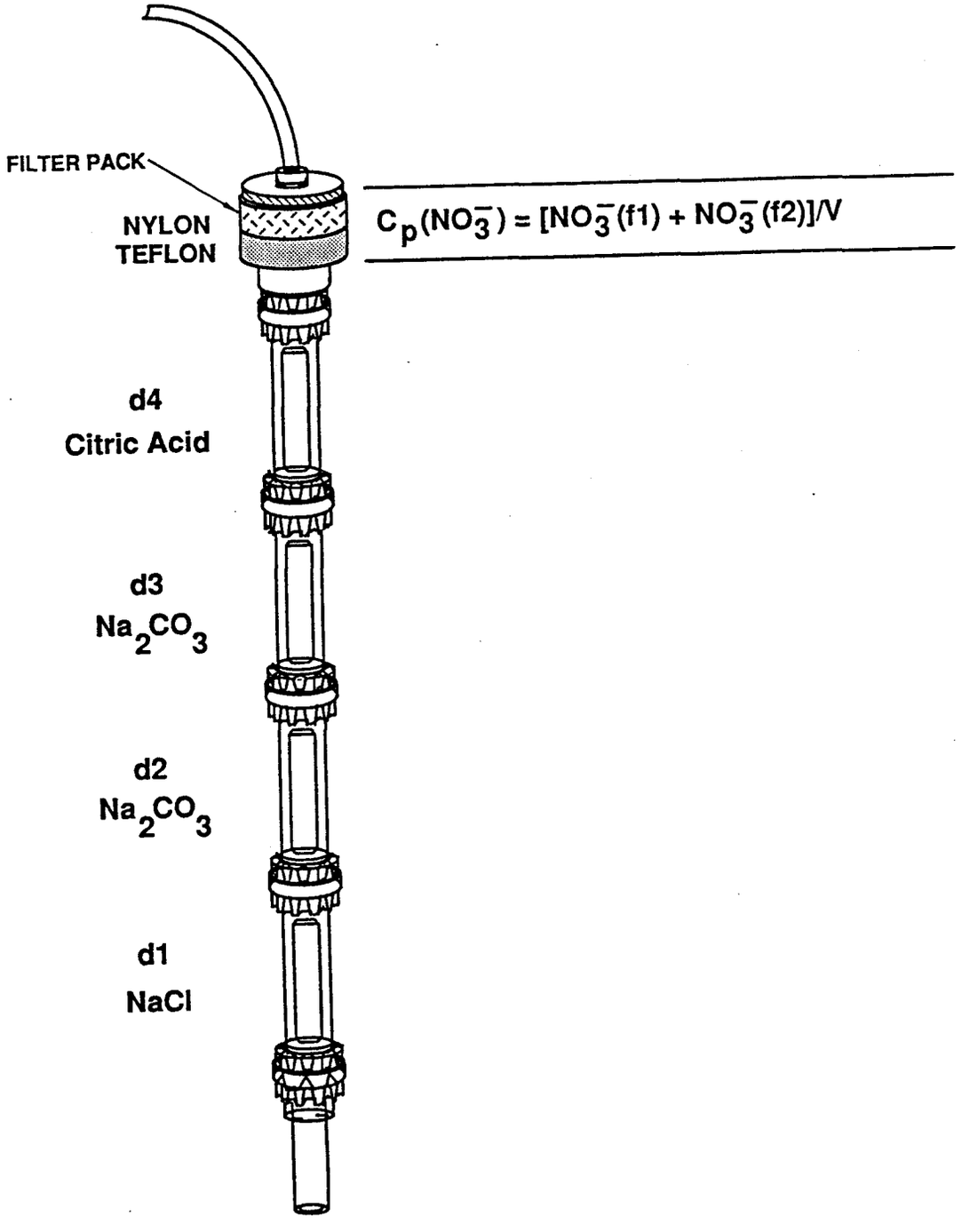

Figure 28. Particulate Nitrate Measurement

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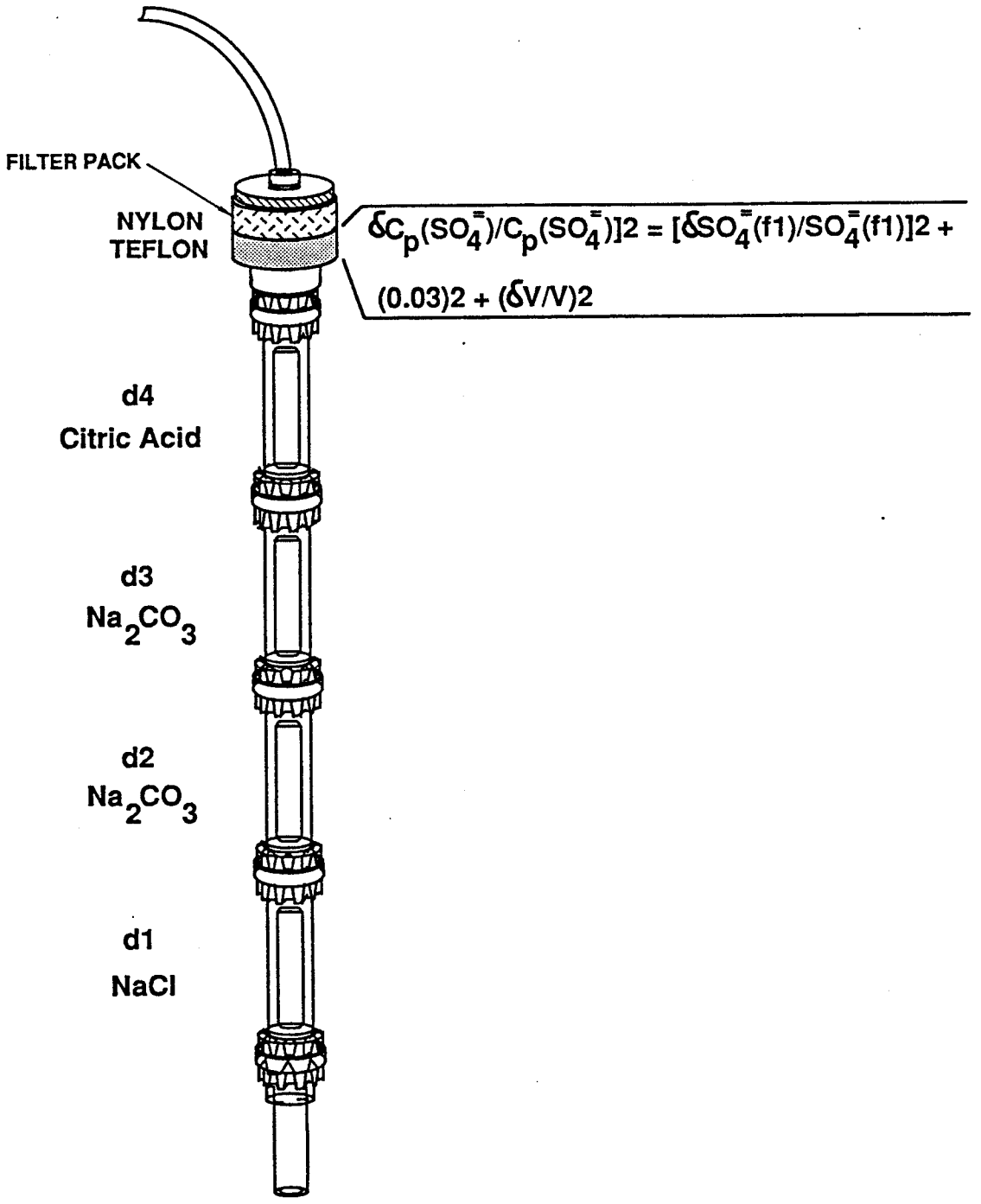

Figure 29. Particulate Sulfate Measurement and Uncertainties

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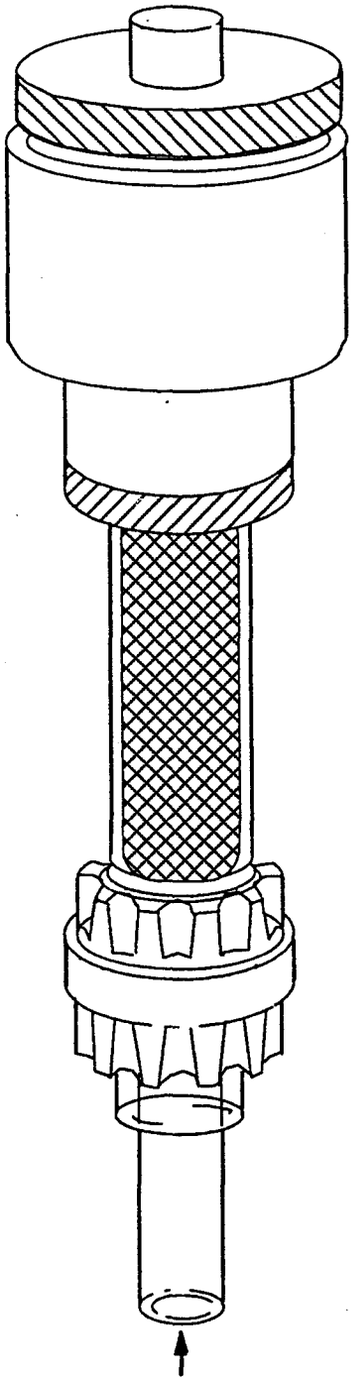

Figure 30. Annular Denuder Personal Sampler

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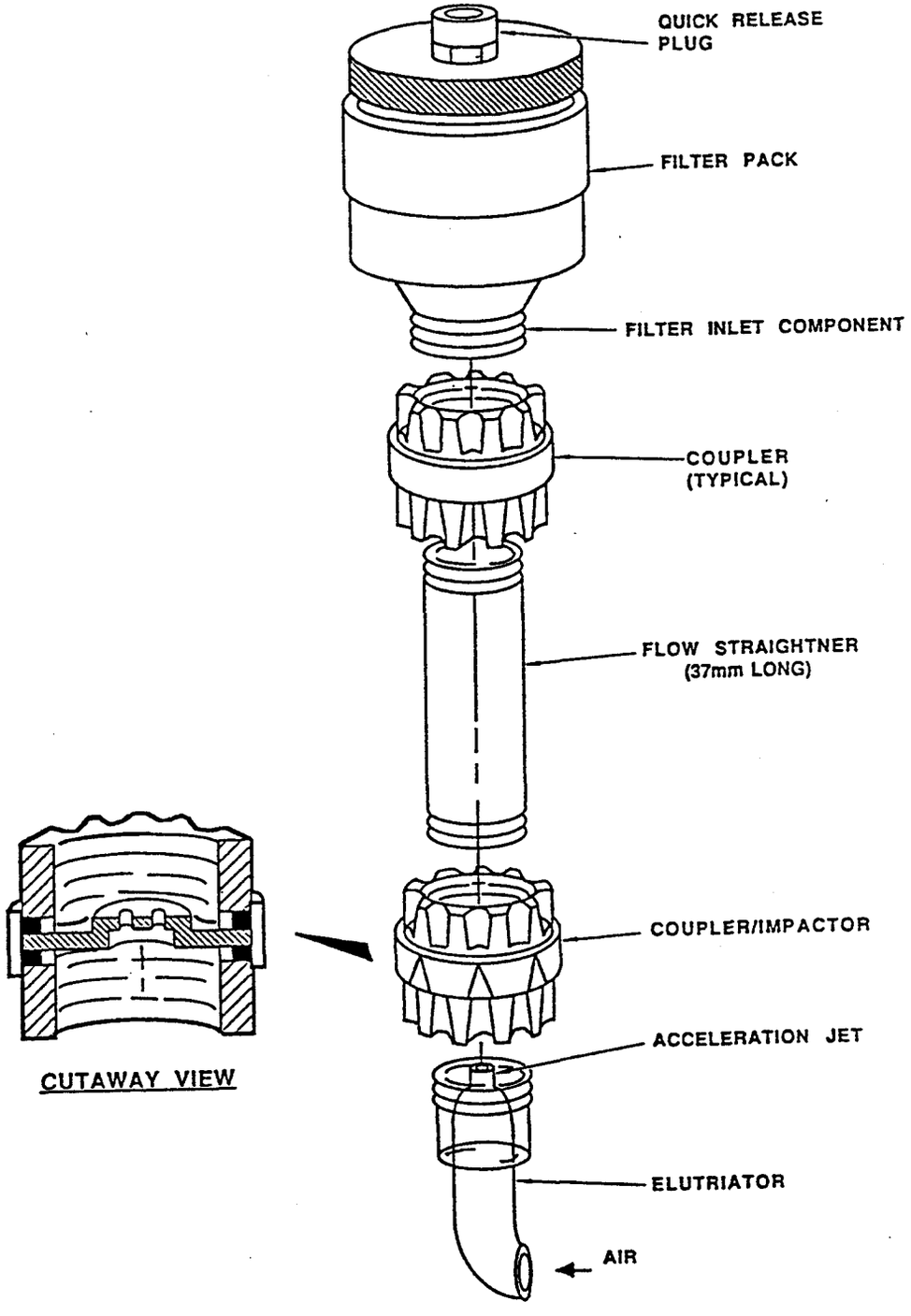

Figure 31. Fine Particle Sampler

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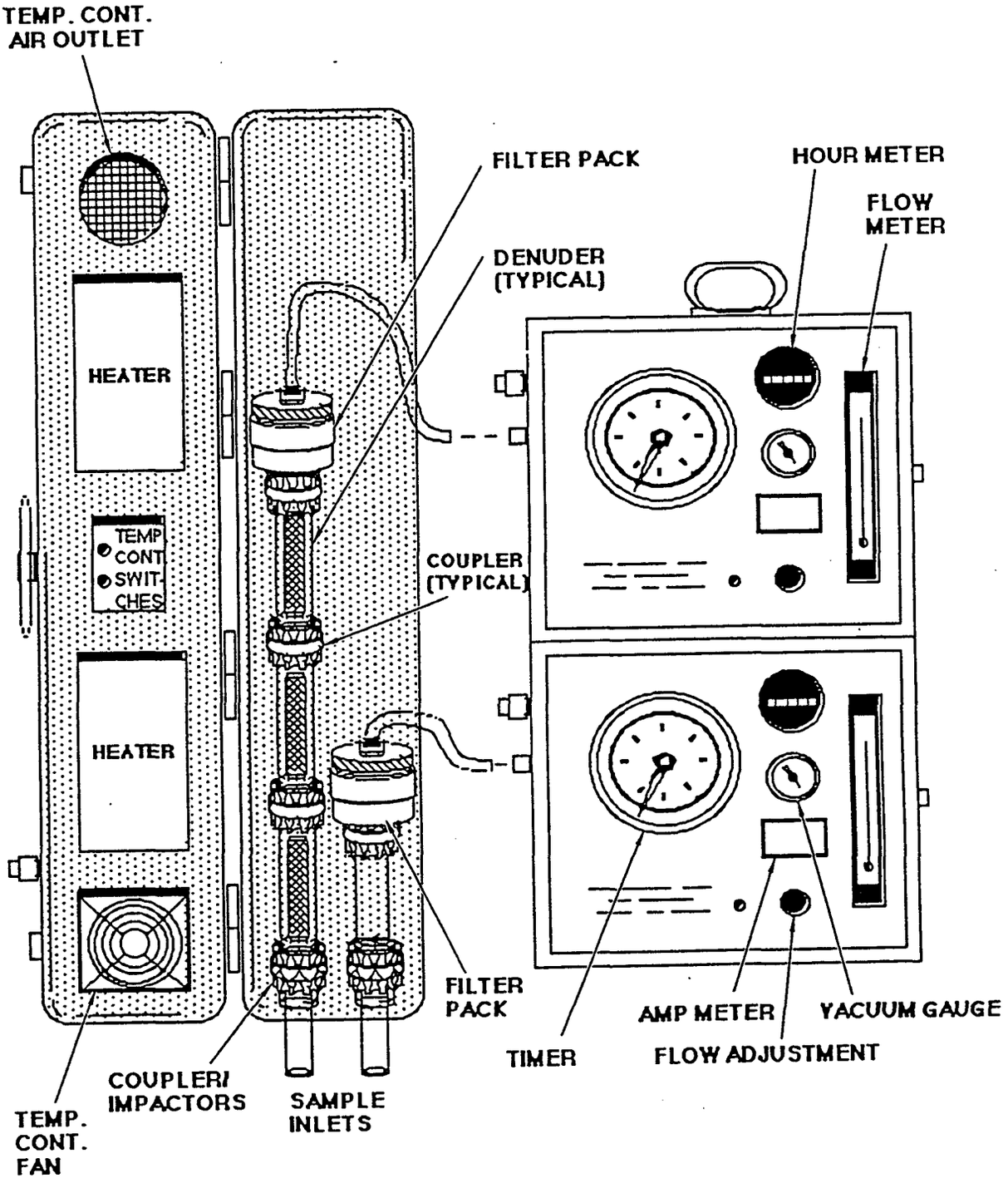

Figure 32. Annular Denuder System with Fine Particulate Sampler

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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

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

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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.

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.

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.

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

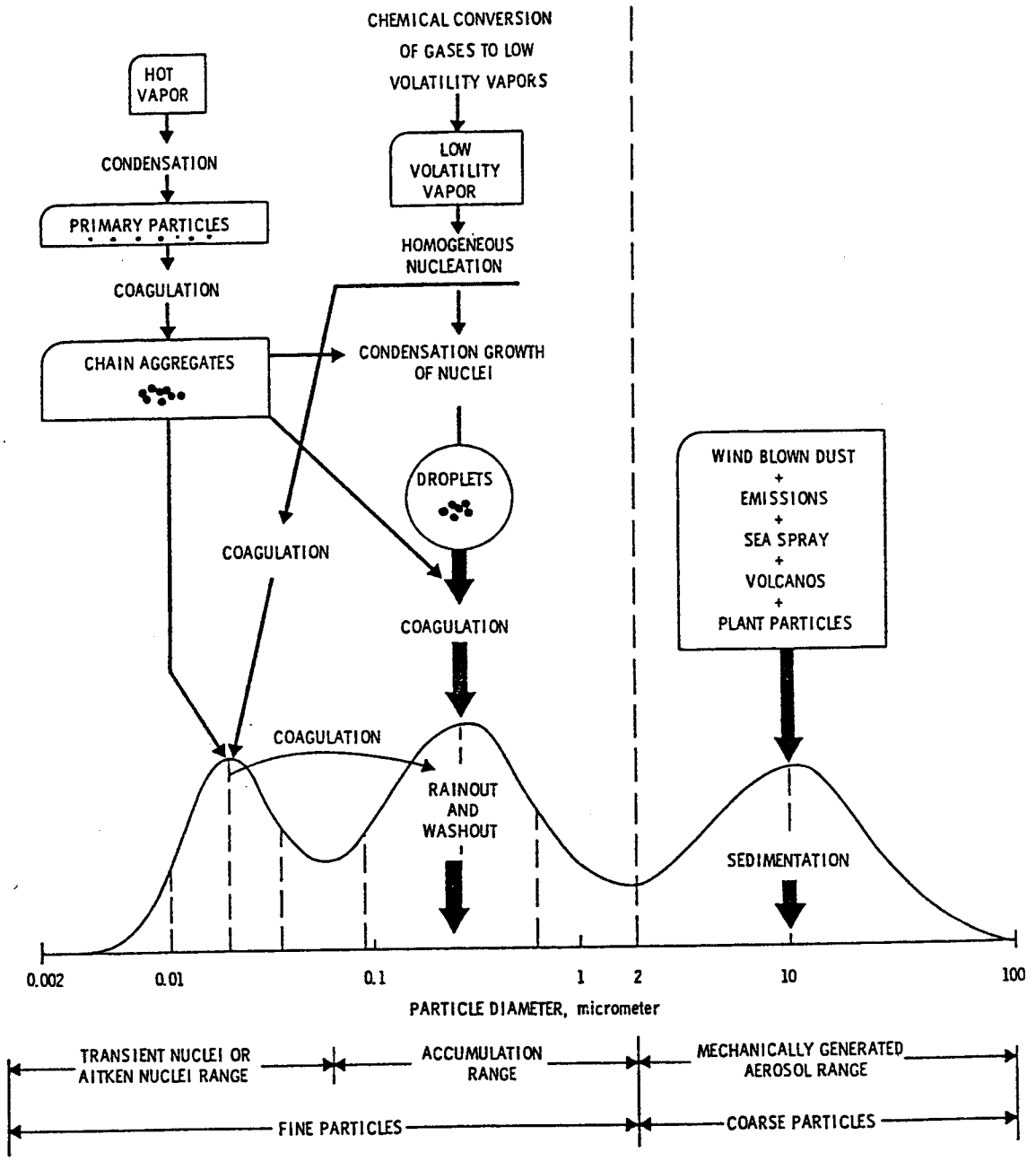

Figure 1. A Postulated Atmospheric Aerosol Formation Process

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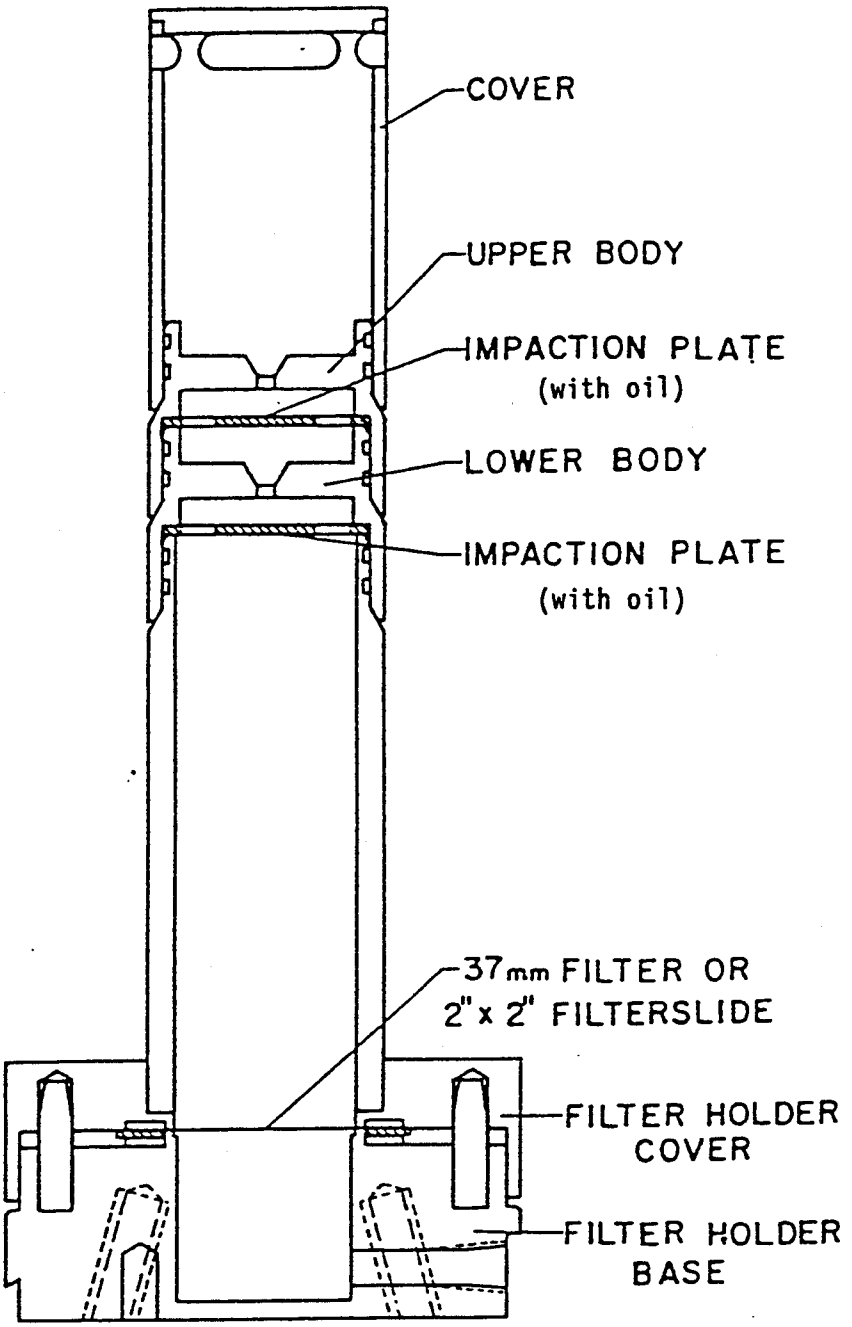

Figure 2. Schematic of Microenvironmental Exposure Monitor (MEMs)

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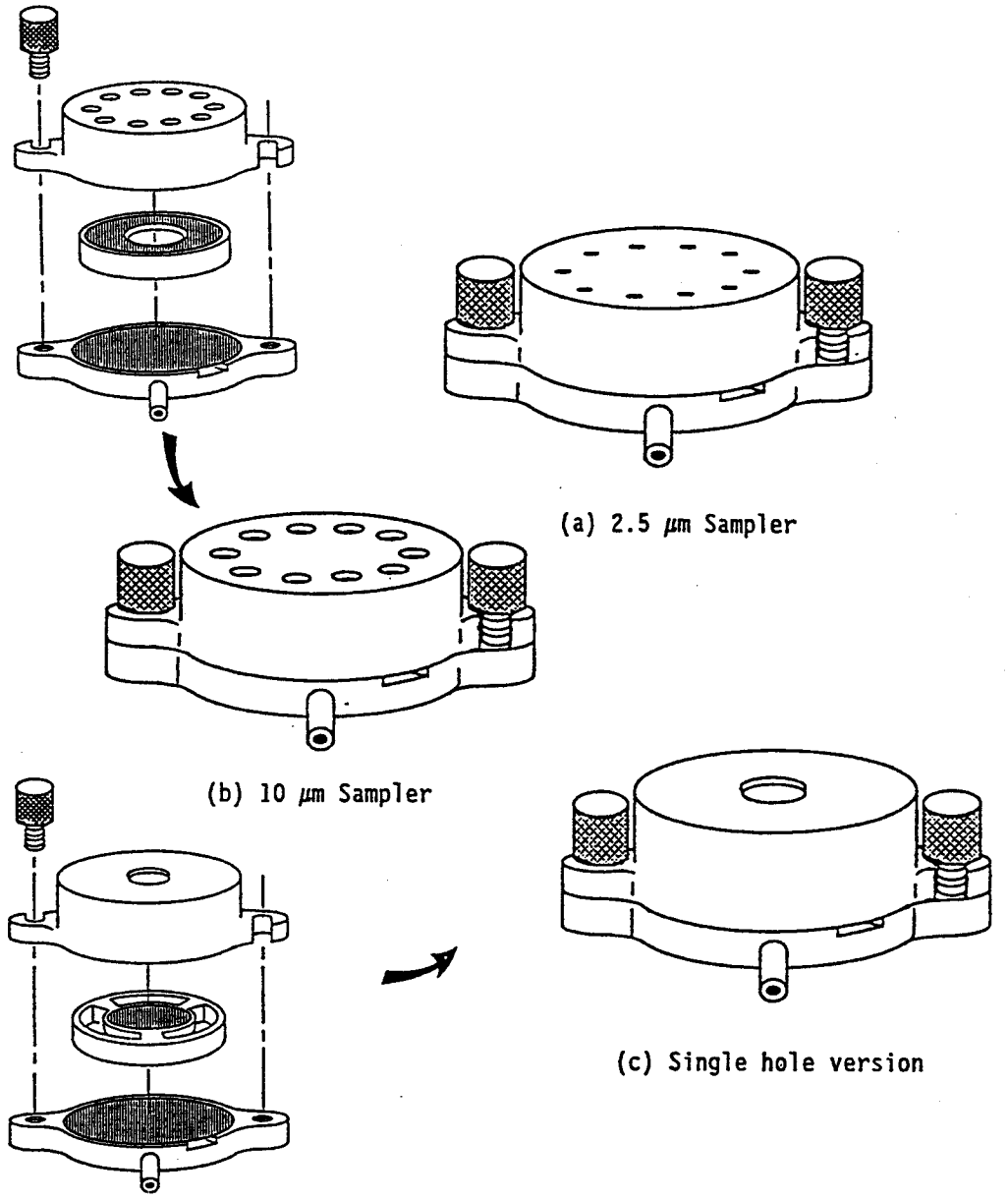

Figure 3. Schematic of Personal Exposure Monitor (PEMs)

[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

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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

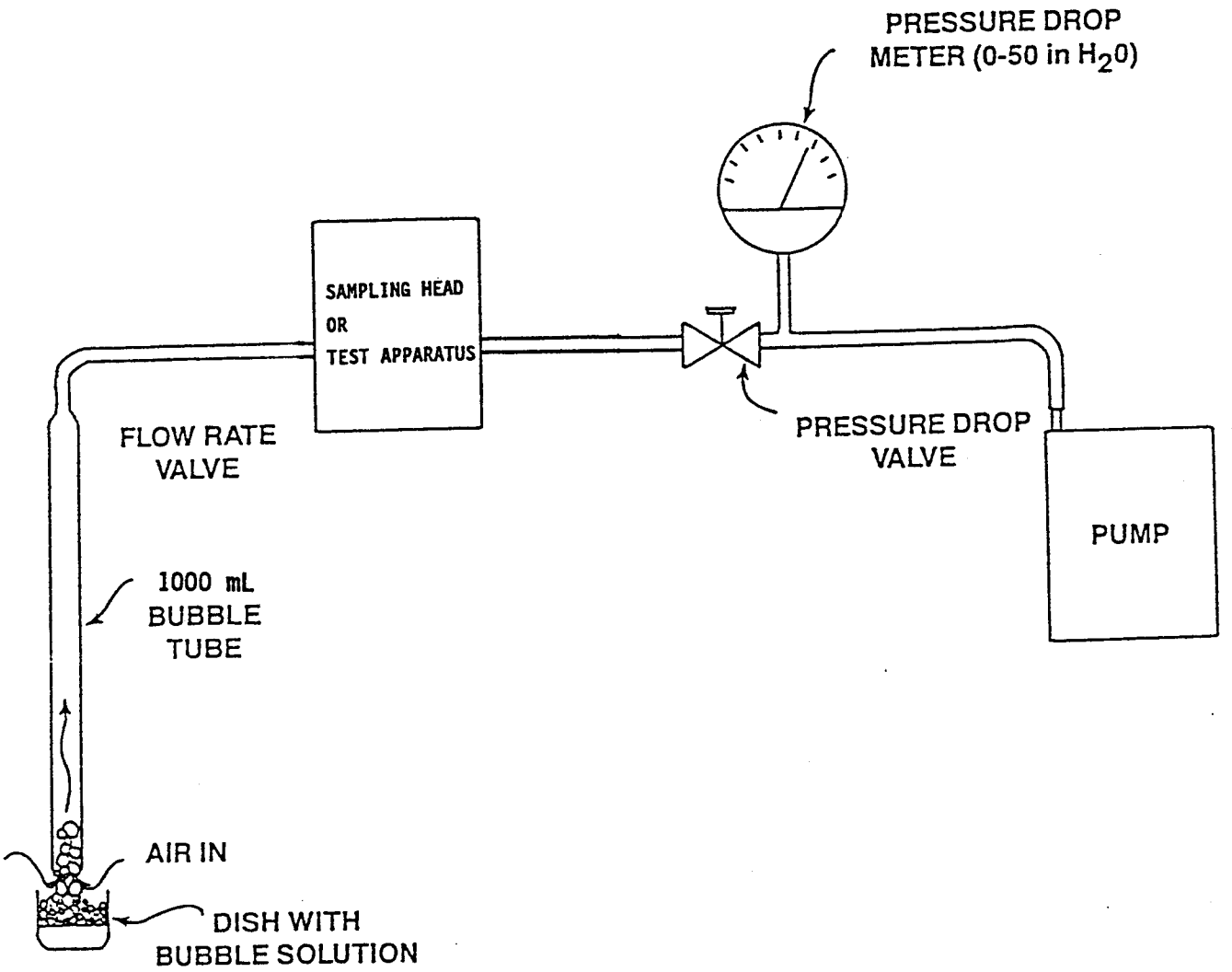

Figure 5. Calibration Assembly for Personal Sampling Pump

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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

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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

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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

1. Rupprecht & Patashnick Co., Inc., *TEOM® Hardware Manual (TEOMPLUS® Software Version 3)*, Albany, NY, April, 1988.

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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.

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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	DI00	Digital Input 0	With instrument in Automatic Setting, these inputs control operation
149	DI01	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.

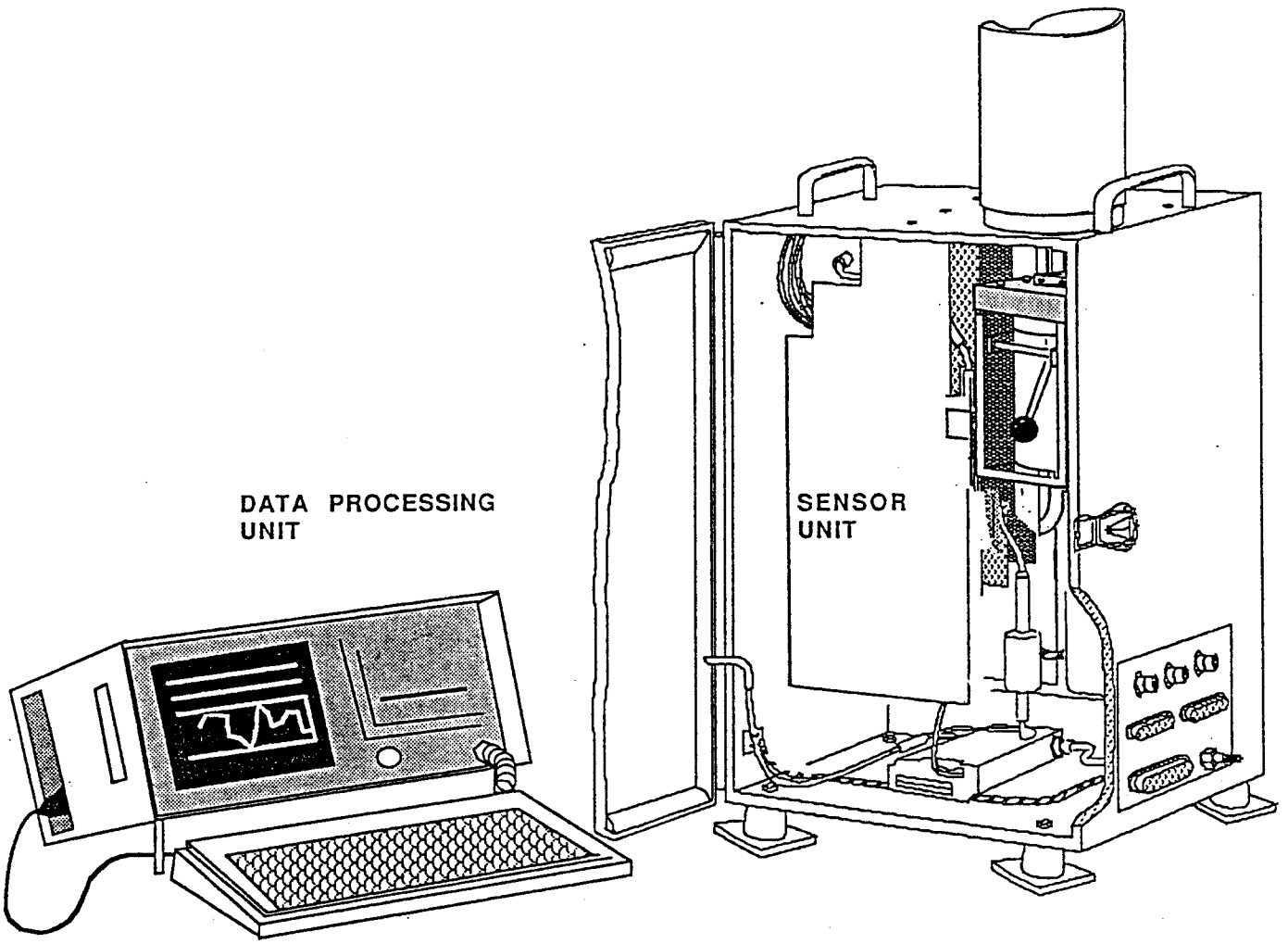

Figure 1. Assembled TOEM® Continuous Particulate Monitor

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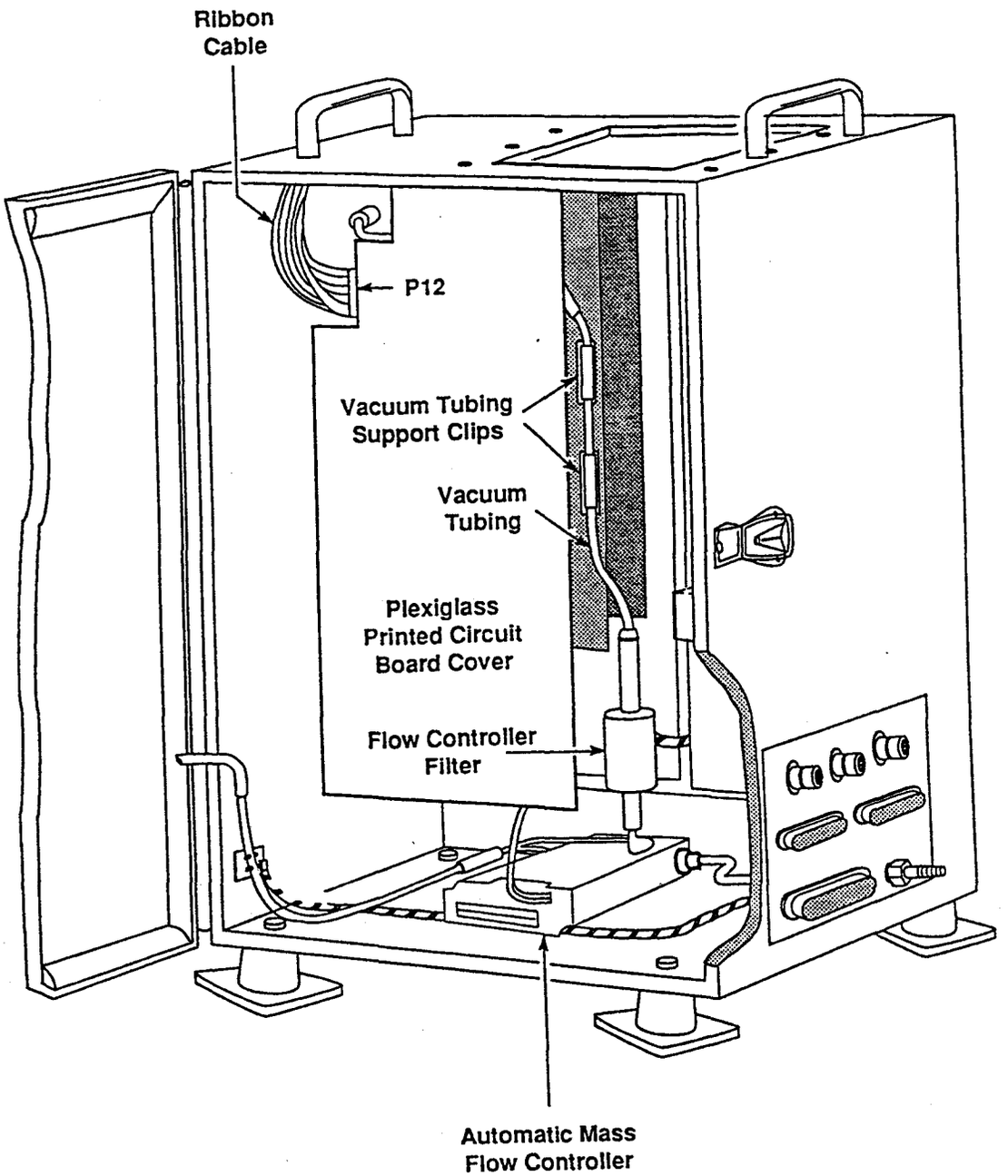

Figure 2. Enclosure Cabinet

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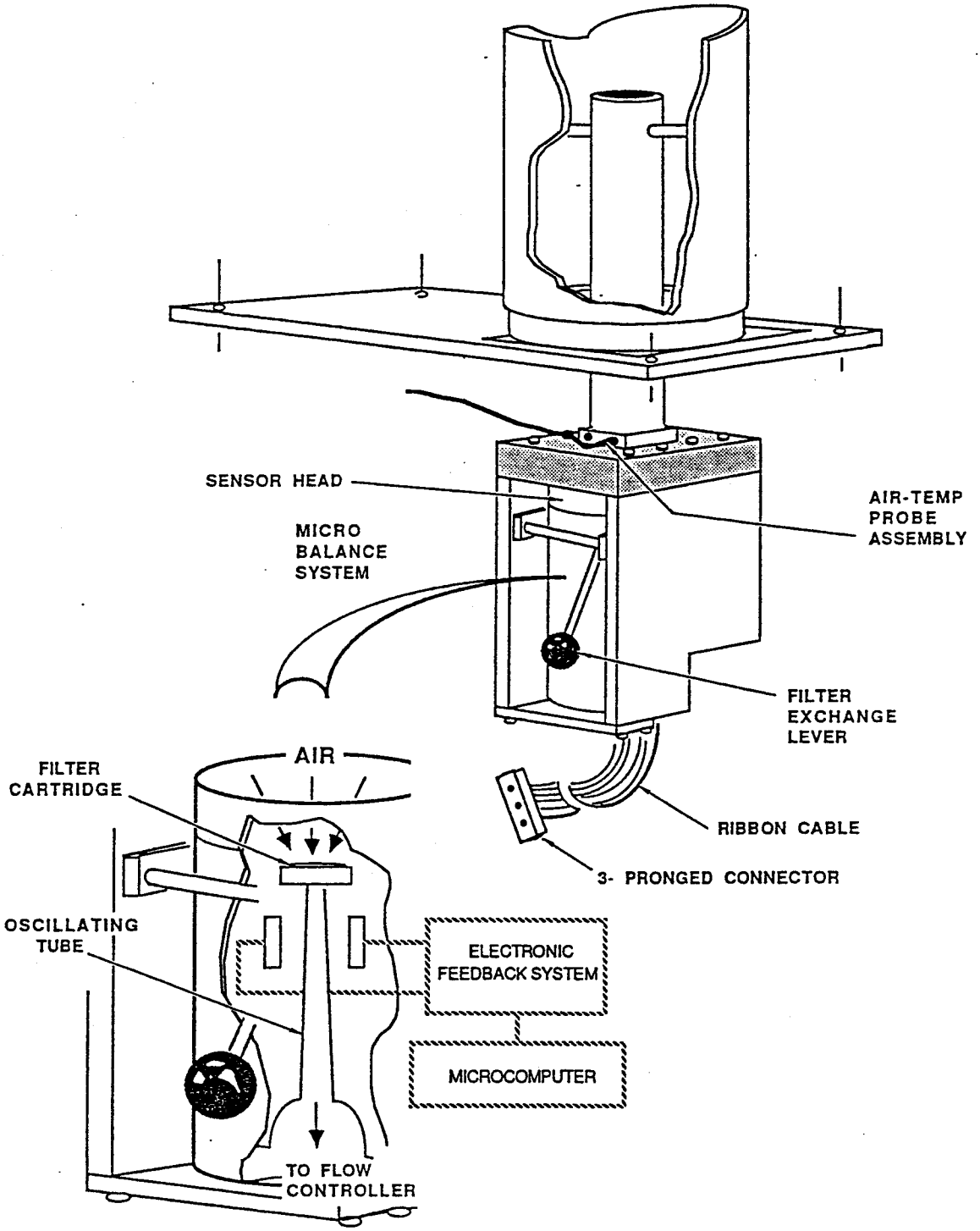

Figure 3. Sensor/Preheater Assembly

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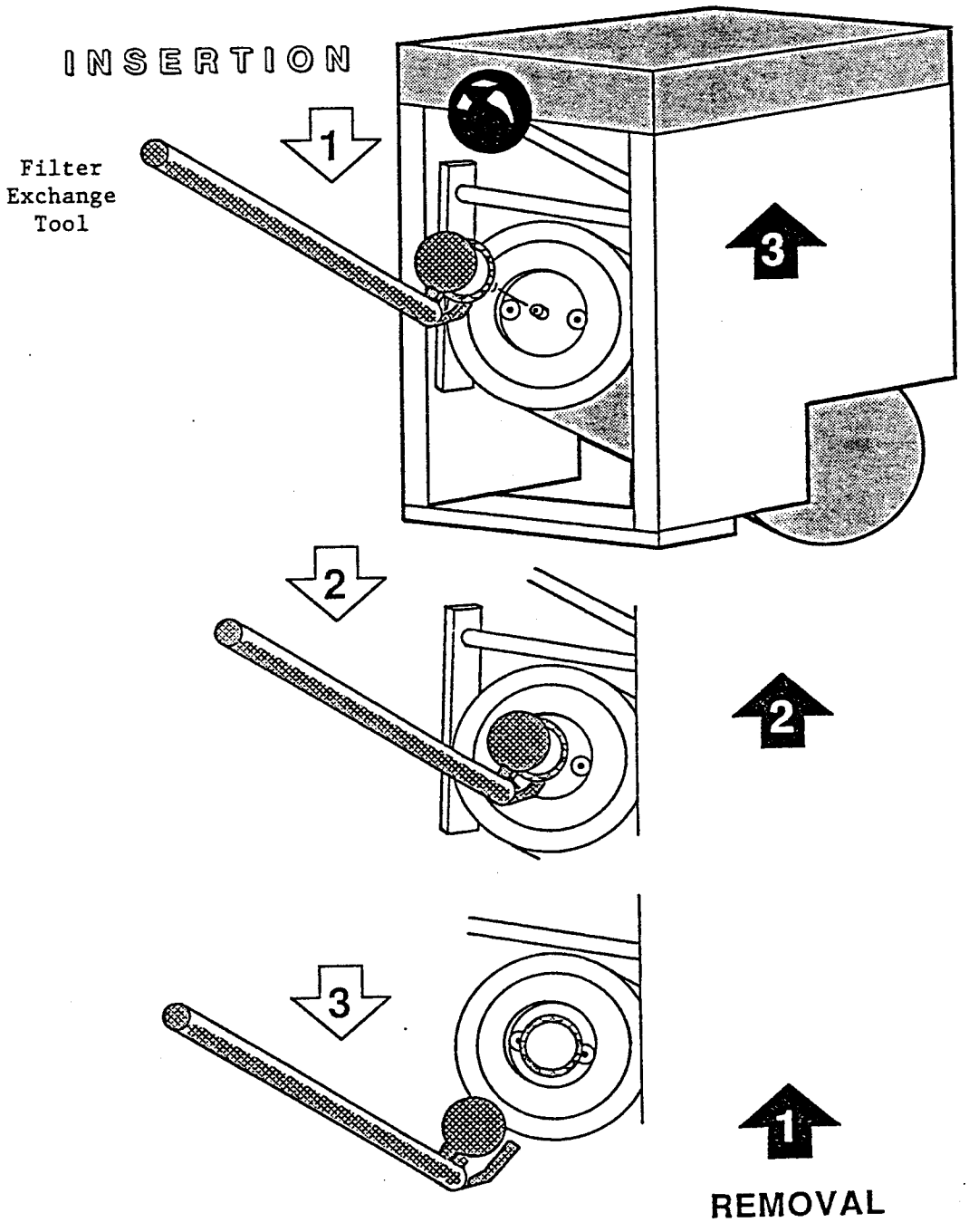

Figure 4. Loading/Removing Filter Cartridge Assembly

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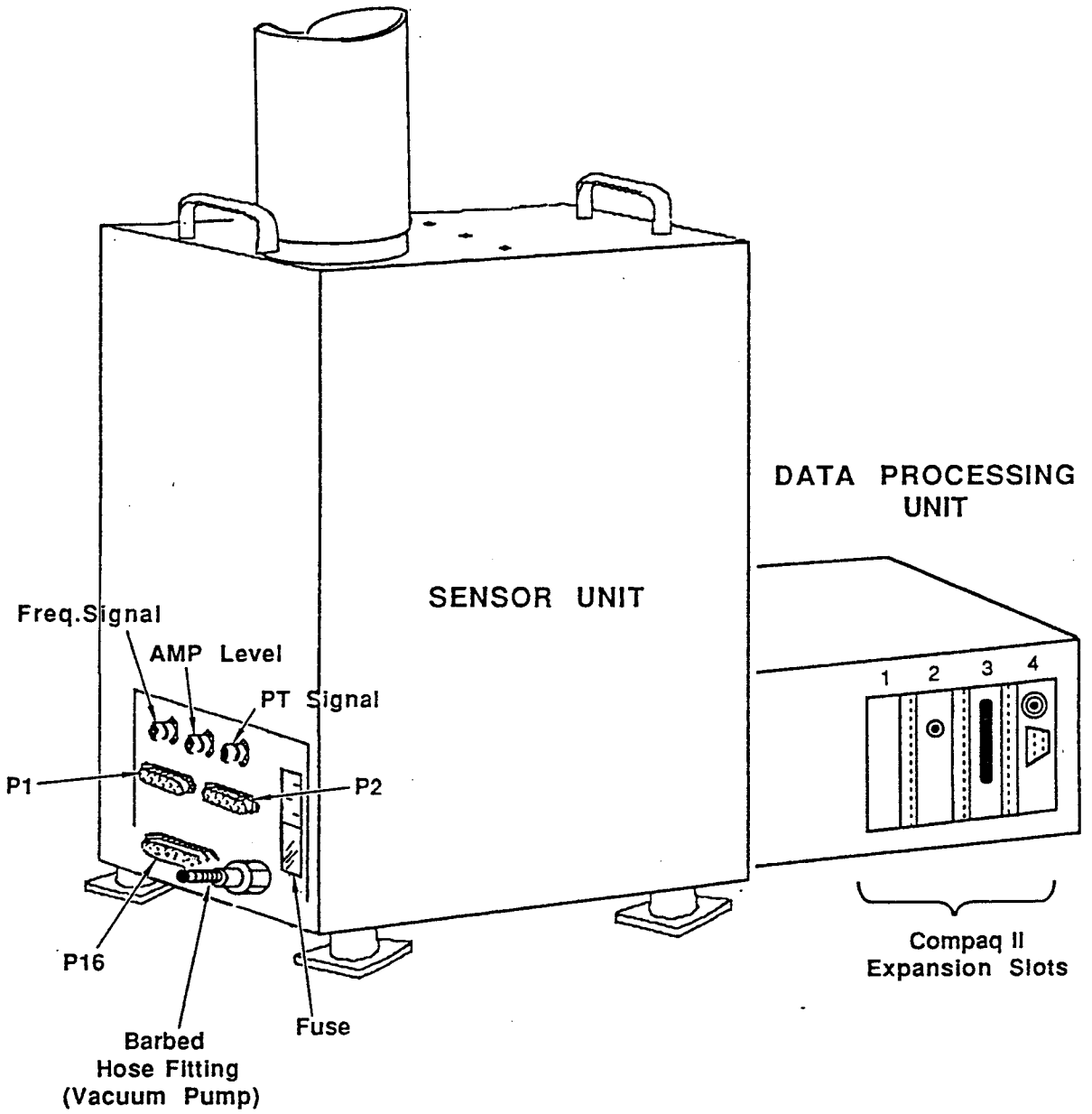

Figure 5. Electrical Connections Associated with the TEOM® Sensor Unit and Data Processing Unit

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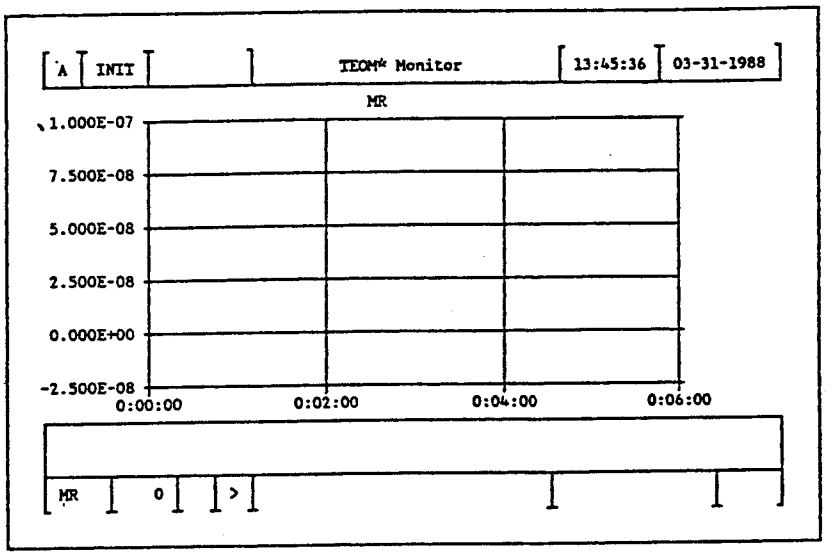
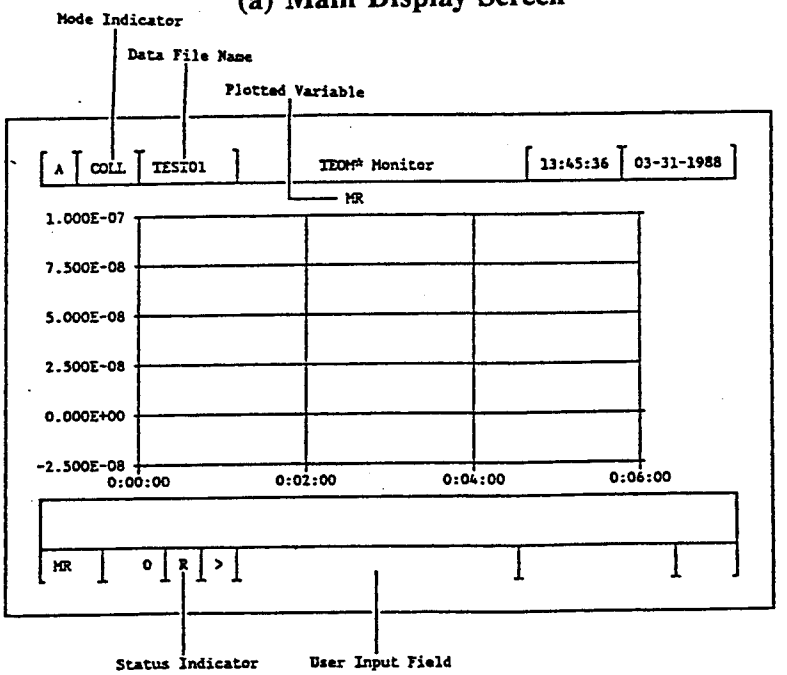


(a) Main Display Screen



(b) Components of the Main Display Screen

Figure 6. TEOM® Display Screen

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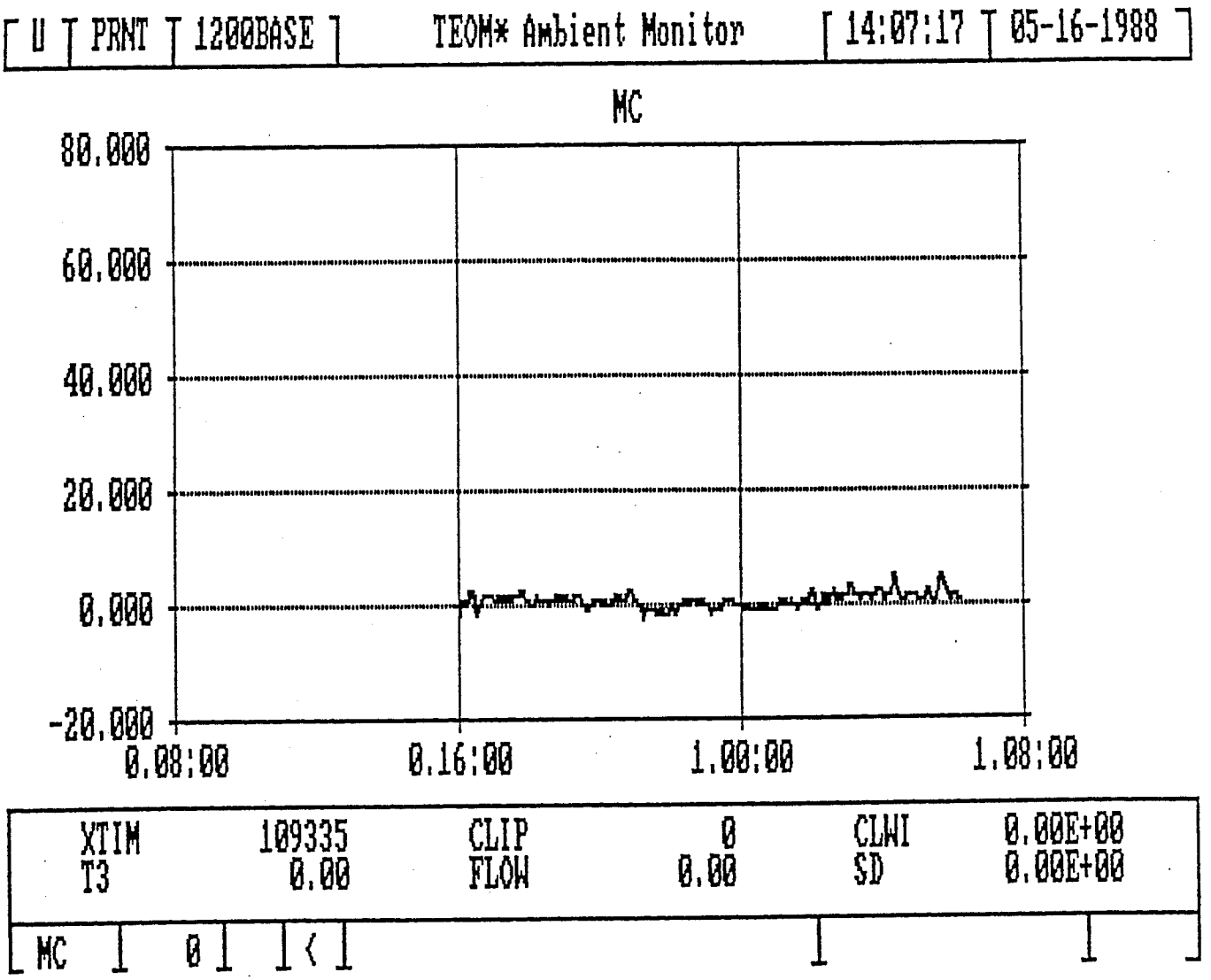

Figure 7. Baseline Performance of the TEOM® Monitor

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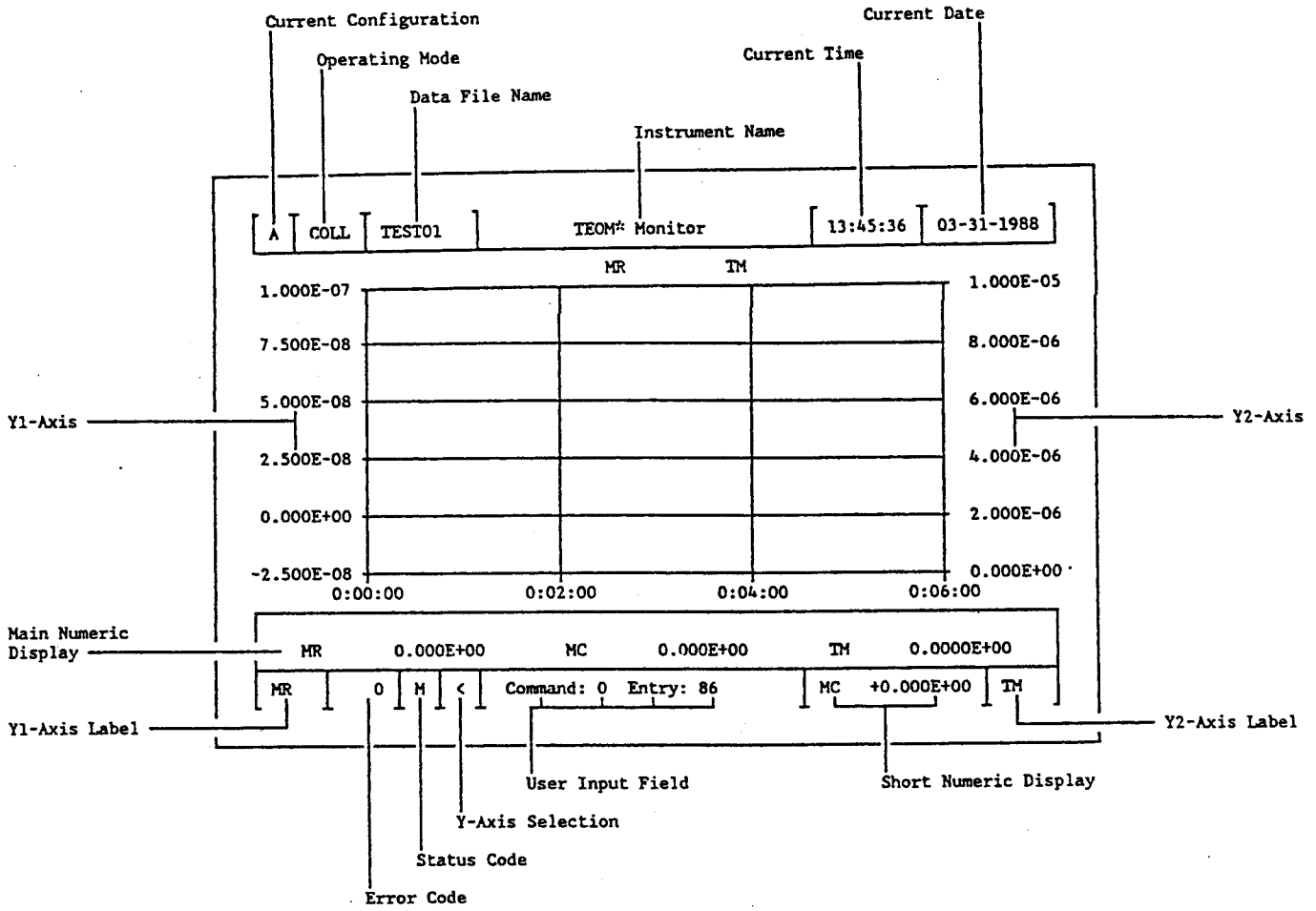

Figure 8. Components of the Main Display Screen of the TEOM® Particulate Monitor

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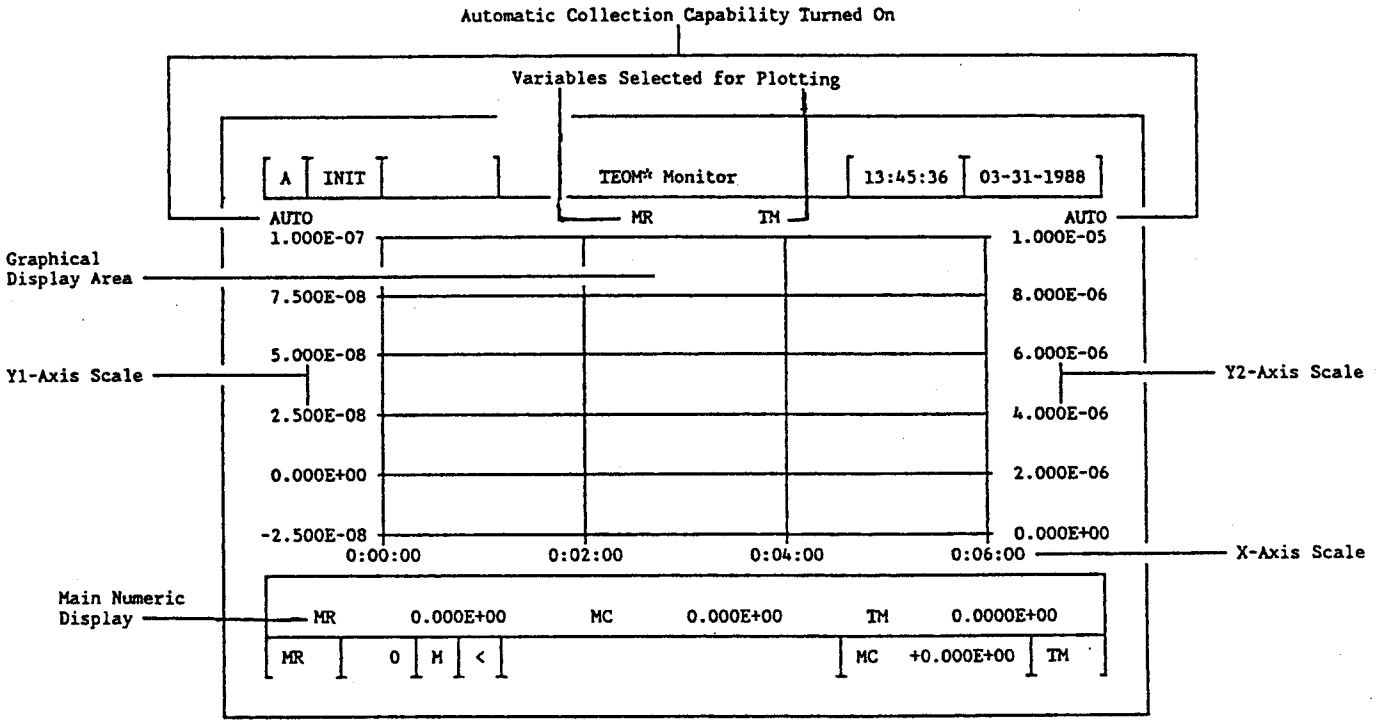

Figure 8. Components of the Main Display Screen of the TEOM® Particulate Monitor (cont'd)

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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.

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

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.

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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

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.

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.

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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).

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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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16. ABSTRACT

Determination of pollutants in indoor air is a complex task because of the wide variety of compounds of interest and the lack of standardized sampling and analysis procedures. To assist agencies and persons responsible for sampling and analysis of indoor pollutants, this methods compendium provides current, technically-reviewed sampling and analysis procedures in a standardized format for determination of selected pollutants of primary importance in indoor air. Each chapter contains one or more active or passive sampling procedures along with one or more appropriate analytical procedures. The ten chapters of the compendium cover determination of volatile organic compounds (VOCs), nicotine, carbon monoxide (CO) and carbon dioxide (CO_2), air exchange rate, nitrogen dioxide (NO_2), formaldehyde (CH_2O), benzo(a)pyrene and other polynuclear aromatic hydrocarbons, acid gases and aerosols, particulate matter, and pesticides. As further advancements are made, the procedures may be modified or updated, or additional methods may be added as appropriate.

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FOREWORD

The Atmospheric Research and Exposure Assessment Laboratory (AREAL) in Research Triangle Park is a research laboratory of the Environmental Protection Agency (EPA). It has an ongoing responsibility to assess environmental monitoring technologies and systems, to implement Agency-wide quality assurance programs for air pollution measurement systems, and to provide technical support to program offices in EPA and to other groups.

The recent emergence of indoor air pollution as a major environmental and public health concern has created the need for standardized monitoring and measurement methods of important indoor air contaminants. Such methods are useful in the conduct of research, in the development and implementation of policies and programs, and in the investigation of specific indoor air quality problems which can occur in all types of building environments.

AREAL has developed this compendium to assist federal, state and local agencies, and private sector organizations in the conduct of their indoor air pollution monitoring activities, and to promote the accurate determination and assessment of human exposure to indoor air pollution.

Gary J. Foley
Director
Atmospheric Research and Exposure Assessment Laboratory
Research Triangle Park, North Carolina 27711

INTRODUCTION

In recent years, greatly increased attention has been focused on the quality of indoor air. Most people spend a major portion of their time indoors, in living areas, offices or other workplaces, stores, restaurants, waiting rooms, public buildings, public or private transportation vehicles, etc. Obviously, then, exposure to indoor air pollutants can constitute an important fraction of a person's total exposure to air pollution.

In addition to penetration of outdoor pollutants into the indoor environment, indoor air pollutants may originate from many sources, including various indoor activities, use of many different types of appliances, tools, and substances, and outgassing of various types of construction and decoration materials. Indoor air pollutants include a wide variety of compounds and typically occur in concentrations and mixtures that generally vary greatly over time and from one area to another and are often episodic in nature. Consequently, human exposures are difficult to assess for both individuals and groups. This difficulty is further complicated by restrictions in the sampling and measurement techniques that can be used indoors due to limitations in the physical size, noise, air flow rates, power consumption, installation, etc. of the apparatus used. Not surprisingly, there has been a lack of standardized procedures for sampling and analysis of indoor air pollutants, particularly for very low concentrations of indoor air contaminants.

To date, little guidance has been available to state and local agencies or to other organizations concerned with the determination of indoor air pollutants. As a result, state and local agencies and others responding to indoor air pollution problems have had to develop their own monitoring strategies, including selection of monitoring methods, sampling plan design, and specific procedures for sampling, analysis, logistics, calibration, and quality control. For the most part, these procedures were based on professional judgments rather than adherence to any documented uniform guidelines. Many governmental agencies and professional or research organizations have developed indoor air monitoring methods and procedures, mostly to respond to specialized needs. But these methods and procedures have generally been neither standardized nor readily available to other agencies involved with indoor air monitoring.

This Compendium has been prepared to provide regional, state and local environmental regulatory agencies, as well as other interested parties, with specific guidance on the determination of selected air pollutants in indoor air. The ten chapters of the Compendium cover those contaminants (as well as ventilation rate) that are considered to be of primary interest in indoor air monitoring efforts. These ten chapters address:

- Volatile organic compounds (VOCs)
- Nicotine
- Carbon monoxide (CO) and Carbon dioxide (CO_2)
- Air exchange rate
- Nitrogen dioxide (NO_2)
- Formaldehyde (CH_2O)
- Benzo(a)pyrene and other polynuclear aromatic hydrocarbons

- Acid gases and aerosols (NO_x, SO_x, and NH_3)
- Particulate matter
- Pesticides

Each chapter contains one or more methods for measuring the parameter, including sampling and/or analysis techniques, calibration, quality assurance, and other pertinent topics. These methods have been compiled from the best elements of methods developed or used by various research or monitoring organizations. They are presented in a standardized format, and each has been extensively reviewed by several technical experts having expertise in the methodology used. However, the methods are not certified and should not be regarded as officially recommended or endorsed by EPA. As advancements are made in the methodology, the current methods for other contaminants may be added as such methods become available.

Each of the methods is self-contained (including pertinent literature citations) and can be used without the other portions of the Compendium. To the extent possible, the American Society for Testing and Materials (ASTM) standardized format has been used, since many potential users of these methods are familiar with that format. Each method has been identified with a revision date so that future modifications or updates to the methods can be identified.

Nearly all of the methods have some degree of flexibility in the procedure. Consequently, it is the user's responsibility to prepare certain standard operating procedures (SOPs) to be employed for the particular laboratory or organization using the method. Each method description indicates those operations for which SOPs are required. Some methods may present analytical options that can be used instead of, or in addition to, those specifically described. In such cases, the user is referred to other methods within the Compendium that contain the pertinent detailed analytical protocol.

Table 1 summarizes the methods currently contained in the Compendium and briefly indicates the application of each. Table 2 presents a listing of many of the indoor air pollutants that can be determined with one or more of the Compendium methods and identifies which method (or methods) are applicable. Some methods may be used to determine additional compounds, but the user must carefully evaluate the applicability of the method to such compounds before use.

As advancements are made, the current methods may be modified from time to time. In addition, new methods addressing new pollutants of concern will be added as methodology becomes available. Future consideration may include methodology for:

- Synthetic fibers
- Ethylene oxides
- Biological particles
- Asbestos
- Radon
- Metals

Table 1. List of Methods in the Compendium

Method Number	Description	Types of Compounds Determined
IP-1A	Stainless Steel Canister	Volatile organic compounds (VOCs) (e.g. aromatic hydrocarbons, chlorinated hydrocarbons) having boiling points in the range of 80° to 200°C.
IP-1B	Solid Adsorbent Tubes	
IP-2A	XAD-4 Sorbent Tube	Nicotine (gaseous and particulate)
IP-2B	Treated Filter Cassette	
IP-3A	Nondispersive Infrared (NDIR)	Carbon monoxide and/or carbon dioxide
IP-3B	Gas Filter Correlation (GFC)	
IP-3C	Electrochemical Oxidation	Carbon monoxide
IP-4A	Perfluorocarbon Tracer (PTF)	Air exchange rate
IP-4B	Tracer Gas	
IP-5A	Continuous Luminox Monitor	Nitrogen oxides
IP-5B	Palmes Diffusion Tube	
IP-5C	Passive Sampling Device	
IP-6A	Solid Adsorbent Cartridge	Formaldehyde (CH_2O) and other aldehydes/ketones
IP-6B	Continuous Colorimetric Analyzer	
IP-6C	Passive Sampling Device	
IP-7	Medium Volume PUF/XAD Sampler	Polynuclear aromatic hydrocarbons
IP-8	Low Volume PUF with GC/ECD	Pesticides (e.g. Organochlorine, Organophosphorus, Urea, Pyrethrin, Carbamate, and Triazine)
IP-9	Annular Denuder System	Acid Gases/Aerosols/Particles (e.g. nitrates, sulfates, and ammonia)
IP-10A	Size Specific Impaction	Particulate matter
IP-10B	Continuous Particulate Monitor	

Table 2. List of Compounds of Primary Interest

Volatile Organic Compounds
(Methods IP-1A, IP-1B)

Freon 12 (Dichlorodifluoromethane)
Methyl chloride (Chloromethane)
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)
Vinyl Chloride (Chloroethylene)
Methyl bromide (Bromomethane)
(Perchloroethylene)
Ethyl chloride (Chloroethane)
Freon 11 (Trichlorofluoromethane)
Vinylidene chloride (1,1-Dichloroethane)
Dichloromethane (Methylene chloride)
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)
Tribromomethane
cis-1,2-Dichloroethylene
Chloroform (Trichloromethane)
1,2-Dichloroethane (Ethylene dichloride)
Methyl chloroform (1,1,1-Trichloroethane)
Benzene (Cyclohexatriene)
Carbon tetrachloride (Tetrachloromethane)
1,2-Dichloropropane (Propylene dichloride)
Trichloroethylene (Trichloroethane)
cis-1,3-Dichloropropene
1,2-Dichloropropane
1,3-Dichloropropane
1,2,3-Trichloropropane
1-Bromo-3-chloropropane
3-Chloro-1-propene
1,2-Dibromopropane
2-Chlorobutane
1,3-Dichlorobutane
1,4-Dichlorobutane
Dichloropropylene
1,1,2-Trichloroethane (Vinyl trichloride)
1,1,2-Trichloroethane
Trichloroethene
2-Chloroethoxyethene
1,1,1,2-tetrachloroethane
1,1,2,2-tetrachloroethane
Toluene (Methyl benzene)
1,2-Dibromomethane (Ethylene dibromide)
Tetrachloroethylene
Chlorobenzene (Phenyl chloride)
Ethylbenzene
m-Xylene (1,3-Dimethylbenzene)
p-Xylene (1,4-Dimethylbenzene)
Styrene (Vinyl benzene)
1,1,2,2-Tetrachloroethane
o-Xylene (1,2-Dimethylbenzene)
4-Ethyltoluene
1,3,5-Trimethylbenzene (Mesitylene)
1,2,4-Trimethylbenzene (Pseudocumene)
m-Dichlorobenzene (1,3-Dichlorobenzene)
Benzyl chloride (α-Chlorotoluene)
o-Dichlorobezene (1,2-Dichlorobenzene)
p-Dichlorobenzene (1,4-Dichlorobenzene)
1,2,4-Trichlorobenzene
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3-butadiene)
(1-Methylethyl) benzene
Butylbenzene
1-Methyl-4-(1-methylethyl) Benzene
Bromobenzene
1-Ethyl-4-chlorobenzene
Bromochloromethane
Bromotrichloromethane
1-Chloropropane
2-Chloropropane
2,3-Dichlorobutane
1,4-Dichloro-2-Butane (cis)
3,4-Dichloro-1-Butane
Tetrahydrofuran
1,4-Dioxane
1-Chloro-2,3-Epoxypropane
Benzaldehyde
Benzonitrile
Pentachloroethane
Bromoethane
1-Phenylethanone
1,1-Dichloroethane (Ethylidene dichloride)

Table 2. List of Compounds of Primary Interest (Cont'd)

Pesticides
(Method IP-8)

Organochlorine

Aldrin
p,p,-DDT
p,p,-DDE
Dieldrin
Dicofol
2,4,5-Trichlorophenol
Pentachlorophenol
BHC (α- and ß-Hexachlorocyclohaxanes)
Captan
Chlordane, technical
Chlrorothalonil
2,4,-D esters

Organophosphorus
Chlorpyrifos
Diazinon
Dichlorvos (DDVP)
Ethylparathion
Malathion
Methyl parathion
Ronnel

Carbamates
Propuxur
Carbofuran
Bendicarb
Mexacarbate
Carbaryl

Triazine
Simazine
Atrazine
Propazine

Organochlorine

Methoxychlor
Mexacarbate
Mirex
trans-Nonachlor
Oxychlordane
Pentachlorobenzene
Folpet
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Lindane (and γ-BHC)

Ureas
Monuron
Diuron
Liuron
Terbuthiuron
Fluometuron
Chlortoluron

Pyrethrin
Pyrethrin I
Pyrethrin II
Allethrin
d-trans-Allethrin
Diocrotophos
Resmethrin
Fenvalerate

Inorganics
(Methods IP-3A, IP-3B, IP-3C, IP-5A, IP-5B, IP-5C, IP-9, IP-10A, IP-10B)

Ammonia (Ammonium)
Nitrogen dioxide
Nitric acid
Nitrous acid
Sulfuric acid
Sulfite
Sulfur dioxide
Carbon monoxide
Carbon dioxide
Particulate matter

Table 2. List of Compounds of Primary Interest (Cont'd)

Polynuclear Aromatic Hydrocarbons (PAHs)
(Method IP-7)

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

Environmental Tobacco Smoke (ETS)
(Methods IP-2A, IP-2B)

Nicotine (particle and gaseous)

Aldehydes and Ketones
(Methods IP-6A, IP-6B, IP-6C)

Formaldehyde
Acrolein
Propionaldehyde
Butyraldehyde
Isovaleraldehyde
o-Tolualdehyde
p-Tolualdehyde
2,5-Dimethylbenzaldehyde
Acetaldehyde
Acetone
Crotonaldehyde
Benzaldehyde
Valeraldehyde
m-Tolualdehyde
Hexanaldehyde

Chapter IP-1

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN INDOOR AIR

- **Method IP-1A - Stainless Steel Canisters**
- **Method IP-1B - Solid Adsorbent Tubes**

1. Scope

1.1 This document describes procedures for sampling and analysis of volatile organic compounds (VOCs) in indoor air. The methods are based on either collection of whole air samples in SUMMA® passivated stainless steel canisters or collection on solid adsorbent tubes. The VOCs are subsequently separated by gas chromatography and measured by mass-selective detector or multidetector techniques. Method IP-1A presents procedures for sampling VOCs into canisters to final pressure both above and below atmospheric pressure (respectively referred to as pressurized and subatmospheric pressure sampling), while Method IP-1B presents procedures for sampling VOCs using a solid adsorbent bod.

2. Significance

2.1 VOCs are emitted into the indoor atmosphere from a variety of sources including diffusion from outdoor sources, manufacturing processes, and use of various products, appliances, and building materials. Many of these VOC emissions are acutely toxic; therefore, their determination in indoor air is necessary to assess human health impacts.

2.2 Conventional methods for VOC determination use solid sorbent sampling techniques. The most widely used solid sorbent is Tenax®. An air sample is drawn through a Tenax®-filled cartridge where certain VOCs are trapped on the polymer. The sample cartridge is transferred to a laboratory and analyzed by GC-MS.

2.3 VOCs can also be successfully collected in stainless steel canisters. Collection of indoor air samples in canisters provides 1) convenient integration of indoor samples over a specific time period, (e.g., 24 hours), 2) remote sampling and central analysis, 3) ease of storing and shipping samples, 4) unattended sample collection, 5) analysis of samples from multiple sites with one analytical system, and 6) collection of sufficient sample volume to allow assessment of measurement precision and/or analysis of samples by several analytical systems. However, care must be exercised in selecting, cleaning, and handling sample canisters and sampling apparatus to avoid losses or contamination of the samples. Contamination is a critical issue with canister-based sampling because the canister is the last element in the sampling train.

Method IP-1A

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN INDOOR AIR USING STAINLESS STEEL CANISTERS

Method IP-1A

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN INDOOR AIR USING STAINLESS STEEL CANISTERS

1. Scope

1.1 This document describes a procedure for sampling and analysis of volatile organic compounds (VOCs) in indoor air. The method is based on collection of whole air samples in SUMMA® passivated stainless steel canisters. The VOCs are subsequently separated by gas chromatography and measured by mass-selective detector or multidetector techniques. This method presents procedures for sampling into canisters to final pressures both above and below atmospheric pressure (respectively referred to as pressurized and subatmospheric pressure sampling).

1.2 This method is applicable to specific VOCs that have been tested and determined to be stable when stored in pressurized and subatmospheric pressure canisters. Numerous compounds, many of which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters (1,2); however, minimal documentation is currently available demonstrating stability of VOCs in subatmospheric pressure canisters.

1.3 The organic compounds that have been successfully collected in pressurized canisters by this method are listed in Table 1. These compounds have been successfully measured at the parts per billion by volume (ppbv) level.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definition of Terms Related to Atmospheric Sampling and Analysis
E260 Recommended Practice for General Gas Chromatography Procedures
E355 Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

U.S. Environmental Protection Agency Technical Assistance Document (3)
Laboratory and Ambient Air Studies (4-17)

3. Summary of Method

3.1 Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister and a pump-ventilated sample line during sample collection. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of indoor air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into a pre-evacuated SUMMA® passivated canister.

3.2 After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to a predetermined laboratory for analysis.

3.3 Upon receipt at the laboratory, the canister tag data is recorded and the canister is attached to the analytical system. During analysis, water vapor is reduced in the gas stream by a Nafion® dryer (if applicable), and the VOCs are then concentrated by collection in a cryogenically-cooled trap. The cryogen is then removed and the temperature of the trap is raised. The VOCs originally collected in the trap are revolatilized, separated on a GC column, then detected by one or more detectors for identification and quantitation.

3.4 The analytical strategy for Method IP-1A involves using a high resolution gas chromatograph (GC) coupled to one or more appropriate GC detectors. Historically, detectors for a GC have been divided into two groups: non-specific detectors and specific detectors. The non-specific detectors include, but are not limited to, the nitrogen-phosphorus detector (NPD), the flame ionization detector (FID), the electron capture detector (ECD) and the photoionization detector (PID). The specific detectors include the mass spectrometer (MS) operating in either the selected ion monitoring (SIM) mode or the SCAN mode, or the ion trap detector. The use of these detectors or a combination of these detectors as part of an analytical scheme is determined by the required specificity and sensitivity of the application. While the nonspecific detectors are less expensive per analysis and in some cases more sensitive than the specific detector, they vary in specificity and sensitivity for a specific class of compounds. For instance, if multiple halogenated compounds are targeted, an ECD is usually chosen; if only compounds containing nitrogen or phosphorus are of interest, a NPD can be used; or, if a variety of hydrocarbon compounds are sought, the broad response of the FID or PID is appropriate. In each of these cases, however, the specific identification of the compound within the class is determined only by its retention time, which can be subject to shifts or to interference from other nontargeted compounds. When misidentification occurs, the error is generally a result of a cluttered chromatogram, making peak assignment difficult. In particular, the more volatile organics (chloroethanes, ethyltoluenes, dichlorobenzenes, and various freons) exhibit less well defined chromatographic peaks, leading to misidentification using non-specific detectors. Quantitative comparisons indicate that the FID is more subject to error than the ECD because the ECD is a much more selective detector for a smaller class of compounds which exhibits a stronger response. Identification errors, however, can be reduced by employing simultaneous detection by different detectors or correlating retention times from different GC columns for confirmation. In either case, interferences on the non-specific detectors can still cause error in identifying a complex sample. The non-specific detector system (GC-NPD-FID-ECD-PID), however, has been used for approximate quantitation of relatively clean samples. The non-specific detector system can provide a "snapshot" of the constituents in the sample, allowing determination of:

- Extent of misidentification due to overlapping peaks,
- Position of the VOCs within or not within the concentration range of anticipated further analysis by specific detectors (GC-MS-SCAN-SIM) (if not, the sample is further diluted), and
- Existence of unexpected peaks which need further identification by specific detectors.

On the other hand, the use of specific detectors (MS coupled to a GC) allows positive compound identification, thus lending itself to more specificity than the multidetector GC.

Operating in the SIM mode, the MS can readily approach the same sensitivity as the multidetector system, but its flexibility is limited. For SIM operation, the MS is programmed to acquire data for a limited number of targeted compounds while disregarding other acquired information. In the SCAN mode, however, the MS becomes a universal detector, often detecting compounds which are not detected by the multidetector approach. The GC-MS-SCAN will provide positive identification, while the GC-MS-SIM procedure provides quantitation of a restricted "target compound" list of VOCs. The analyst often must decide whether to use specific or nonspecific detectors by considering such factors as project objectives, desired detection limits, equipment availability, cost and personnel capability in developing an analytical strategy. A list of some of the advantages and disadvantages associated with non-specific and specific detectors may assist the analyst in the decision-making process.

Non-Specific Multidetector Analytical System

Advantages

- Somewhat lower equipment cost than GC-MS
- Less sample volume required for analysis
- More sensitive (ECD may be 1000 times more sensitive than GC-MS

Disadvantages

- Multiple detectors cost to calibrate
- Compound identification not positive
- Lengthy data interpretation (one hour each for analysis data reduction)
- Interference(s) from co-eluting compounds(s)
- Cannot identify unknown compounds outside range of calibration and without standards
- Does not differentiate targeted compounds from interfering compounds

Specific Detector Analytical System

GC-MS-SIM

Advantages	Disadvantages
• positive compound identification (ions)	• can't identify non-specified compounds
• greater sensitivity than GC-MS-SCAN	• somewhat greater equipment cost than multidetector GC
• less operator interpretation than for multidetector GC	• greater sample volume required than for multidetector GC
• resolve co-eluting peaks to achieve enhancement in sensitivity	• universality of detector sacrificed
• more specific than the multidetector GC	

GC-MS-SCAN

Advantages	Disadvantages
• positive compound identification	• lower sensitivity than GC-MS-SIM
• can identify all compounds for multidetector GC	• greater sample volume required than
• less operator interpretation than multidetector GC	• somewhat greater equipment cost
• can resolve co-eluting peaks	

The analytical finish for the measurement chosen by the analyst should provide a definitive identification and a precise quantitation of volatile organics. In a large part, the actual approach to these two objectives is subject to equipment availability. Figure 1 indicates some of the favorite options that are used as an analytical finish. The GC-MS-SCAN option uses a capillary column GC coupled to a MS operated in a scanning mode and supported by spectral library search routines. This option offers the nearest approximation to unambiguous identification and covers a wide range of compounds as defined by the completeness of the spectral library. GC-MS-SIM mode is limited to a set of target compounds which are user defined and is more sensitive than GC-MS-SCAN by virtue of the longer dwell times at the restricted number of m/z values. Both these techniques, but especially the GC-MS-SIM option, can use a supplemental general non-specific detector to verify/identify the presence of VOCs. Finally, the option labelled GC-multidetector system uses a combination of retention time and multiple general detector verification to

identify compounds. However, interference due to nearly identical retention times can affect system quantitation when using this option.
For the low concentration VOCs in indoor air, typically less than 4 parts per billion by volume (ppbv), along with their complicated chromatograms, Method IP-1 strongly recommends the specific detectors (GC-MS-SCAN-SIM) for positive identification and for primary quantitation to ensure that high-quality indoor data is acquired. For the experienced analyst whose analytical system is limited to the non-specific detectors, Section 10.3 does provide guidelines and example chromatograms showing typical retention times and calibration response factors, and utilizing the non-specific detectors (GC-FID-ECD-PID) analytical system as the primary quantitative technique.

4. Significance

4.1 VOCs are emitted into the indoor atmosphere from a variety of sources including diffusion from outdoor sources, manufacturing processes, and use of various products, appliances, and building materials. Many of these VOC emissions are acutely toxic; therefore, their determination in indoor air is necessary to assess human health impacts.

4.2 Conventional methods for VOC determination use solid sorbent sampling techniques. The most widely used solid sorbent is Tenax®. An air sample is drawn through a Tenax®-filled cartridge where certain VOCs are trapped on the polymer. The sample cartridge is transferred to a laboratory and analyzed by GC-MS.

4.3 VOCs can also be successfully collected in stainless steel canisters. Collection of indoor air samples in canisters provides: 1) convenient integration of indoor samples over a specific time period, (e.g., 24 hours), 2) remote sampling and central analysis, 3) ease of storing and shipping samples, 4) unattended sample collection, 5) analysis of samples from multiple sites with one analytical system, and 6) collection of sufficient sample volume to allow assessment of measurement precision and/or analysis of samples by several analytical systems. However, care must be exercised in selecting, cleaning, and handling sample canisters and sampling apparatus to avoid losses or contamination of the samples. Contamination is a critical issue with canister-based sampling because the canister is the last element in the sampling train.

4.4 Interior surfaces of the canisters are treated by the SUMMA® passivation process, in which a pure chrome-nickel oxide is formed on the surface. This type of vessel has been used in the past for sample collection and has demonstrated sample storage stability of many specific organic compounds.

4.5 This method can be applied to sampling and analysis of not only VOCs, but also some selected semivolatile organic compounds (SVOCs). The term "semivolatile organic compounds" is used to broadly describe organic compounds that are too volatile to be collected by filtration air sampling but not volatile enough for thermal desorption from solid sorbents. SVOCs can generally be classified as those with saturation vapor pressures at 25°C between 10^{-1} and 10^{-7} mm Hg. VOCs are generally classified as those organics having saturated vapor pressures at 25°C greater than 10^{-1} mm Hg.

5. Definitions

Note: Definitions used in this document and any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, E260, and E355. All pertinent abbreviations and symbols are defined within this document at point of use. Additional definitions, abbreviations, and symbols are located in Appendix A-I and B-2 of this Compendium.

5.1 Absolute canister pressure = Pg + Pa, where Pg = gauge pressure in the canister (kPa, psi) and Pa = barometric pressure (see Section 5.2).

5.2 Absolute pressure - Pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as kPa, mm Hg or psia.

5.3 Cryogen - A refrigerant used to obtain very low temperatures in the cryogenic trap of the analytical system. A typical cryogen is liquid oxygen (bp -183.0°C) or liquid argon (bp -185.7°C).

5.4 Dynamic calibration - Calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system in a manner very similar to the normal sampling or analytical process.

5.5 Gauge pressure - Pressure measured above ambient atmospheric pressure (as opposed to absolute pressure). Zero gauge pressure is equal to ambient atmospheric (barometric) pressure.

5.6 MS-SCAN - The GC is coupled to a MS programmed in the SCAN mode to scan all ions repeatedly during the GC run. As used in the current context, this procedure serves as a qualitative identification and characterization of the sample.

5.7 MS-SIM - The GC is coupled to a MS programmed to acquire data for only specified ions and to disregard all others. This is performed using SIM coupled to retention time discriminators. The GC-SIM analysis provides quantitative results for selected constituents of the sample gas as programmed by the user.

5.8 Megabore® column - Chromatographic column having an internal diameter (I.D.) greater than 0.50 mm. The Megabore® column is a trademark of the J&W Scientific Co. For purposes of this method, Megabore® refers to chromatographic columns with 0.53 mm I.D.

5.9 Pressurized sampling - Collection of an air sample in a canister with a (final) canister pressure above atmospheric pressure, using a sample pump.

5.10 Qualitative accuracy - The ability of an analytical system to correctly identify compounds.

5.11 Quantitative accuracy - The ability of an analytical system to correctly measure the concentration of an identified compound.

5.12 Static calibration - Calibration of an analytical system using standards in a form different than the samples to be analyzed. An example of a static calibration would be injecting a small volume of a high concentration standard directly onto a GC column, bypassing the sample extraction and preconcentration portion of the analytical system.

5.13 Subatmospheric sampling - Collection of an air sample in an evacuated canister at a (final) canister pressure below atmospheric pressure, without the assistance of a sampling pump. The canister is filled as the internal canister pressure increases to ambient or near ambient pressure. An auxiliary vacuum pump may be used as part of the sampling system to flush the inlet tubing prior to or during sample collection.

6. Interferences and Limitations

6.1 Interferences can occur in sample analysis if moisture accumulates in the dryer (see Section 10.1.1.2). An automated cleanup procedure that periodically heats the dryer to about 100°C while purging with zero air eliminates any moisture buildup. This procedure does not degrade sample integrity.

6.2 Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) should be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples. Instructions for cleaning the canisters and certifying the field sampling system are described in Sections 12.1 and 12.2, respectively.

6.3 Because the GC-MS analytical system employs a Nafion® permeable membrane dryer to remove water vapor selectively from the sample stream, polar organic compounds may permeate concurrent with the moisture molecule. Consequently, the analyst should quantitate his or her system with the specific organic constituents under examination.

7. Apparatus

7.1 Sample Collection

Note: Subatmospheric pressure and pressurized canister sampling systems are commercially available and have been used as part of U.S. Environmental Protection Agency's Toxics Air Monitoring Stations (TAMS), Urban Air Toxic Pollutant Program (UATP), and the non-methane organic compound (NMOC) sampling and analysis program.

7.1.1 Subatmospheric Pressure (see Figure 2 Without Metal Bellows Type Pump)

7.1.1.1 Sampling inlet line - stainless steel tubing to connect the sampler to the sample inlet.

7.1.1.2 Sample canister - leak-free stainless steel pressure vessels of desired volume (e.g., 6 L), with valve and SUMMA® passivated interior surfaces (Scientific Instrumentation Specialists, Inc., P.O. Box 8941, Moscow, ID 83843, or Anderson Samplers, Inc., 4215-C Wendell Dr., Atlanta, GA, 30336, or equivalent).

7.1.1.3 Stainless steel vacuum/pressure gauge - capable of measuring vacuum (-100 to 0 kPa or 0 to 30 in Hg) and pressure (0-206 kPa or 0-30 psig) in the sampling system

(Matheson, P.O. Box 136, Morrow, GA 30200, Model 63-3704, or equivalent). Gauges should be tested clean and leak tight.

7.1.1.4 Electronic mass flow controller - capable of maintaining a constant flow rate (± 10%) over a sampling period of up to 24 hours and under conditions of changing temperature (20-40°C) and humidity (Tylan Corp., 19220 S. Normandie Ave., Torrance, CA 90502, Model FC-260, or equivalent).

7.1.1.5 Particulate matter filter - 2 μm sintered stainless steel in-line filter (Nupro Co., 4800 E. 345th St., Willoughby, OH 44094, Model SS-2F-K4-2, or equivalent).

7.1.1.6 Electronic timer - for unattended sample collection (Paragon Elect. Co., 606 Parkway Blvd., P.O. Box 28, Twin Rivers, WI 54201, Model 7008-00, or equivalent).

7.1.1.7 Solenoid valve - electrically-operated, bi-stable solenoid valve (Skinner Magnelatch Valve, New Britain, CT, Model V5RAM49710, or equivalent) with Viton® seat and o-rings.

7.1.1.8 Chromatographic grade stainless steel tubing and fittings - for interconnections (Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015, Cat. #8125, or equivalent). All such materials in contact with sample, analyte, and support gases prior to analysis should be chromatographic grade stainless steel.

7.1.1.9 Thermostatically controlled heater - to maintain temperature inside insulated sampler enclosure above ambient temperature (Watlow Co., Pfafftown, NC, Part 04010080, or equivalent).

7.1.1.10 Heater thermostat - automatically regulates heater temperature (Elmwood Sensors, Inc., 500 Narragansett Park Dr., Pawtucket RI 02861, Model 3455-RC-01000222, or equivalent).

7.1.1.11 Fan - for cooling sampling system (EG&G Rotron, Woodstock, NY, Model SUZAI, or equivalent).

7.1.1.12 Fan thermostat - automatically regulates fan operation (Elmwood Sensors, Inc., Pawtucket, RI, Model 3455-RC-0100-0244, or equivalent).

7.1.1.13 Maximum-minimum thermometer - records highest and lowest temperatures during sampling period (Thomas Scientific, Brooklyn Thermometer Co., Inc., P/N 9327H30, or equivalent).

7.1.1.14 Nupro stainless steel shut-off valve - leak free, for vacuum/pressure gauge.

7.1.1.15 Auxiliary vacuum pump - continuously draws air to be sampled through the inlet manifold at 10 L/min. or higher flow rate. Sample is extracted from the manifold at a lower rate, and excess air is exhausted.

Note: The use of higher inlet flow rates dilutes any contamination present in the inlet and reduces the possibility of sample contamination as a result of contact with active adsorption sites on inlet walls.

7.1.1.16 Elapsed time meter - measures duration of sampling (Conrac, Cramer Div., Old Saybrook, CT, Type 6364, P/N 10082, or equivalent).

7.1.1.17 Optional fixed orifice, capillary, or adjustable micrometering valve - may be used in lieu of the electronic flow controller for grab samples or short duration time-integrated samples. Usually appropriate only in situations where screening samples are taken to assess future sampling activity.

7.1.2 Pressurized (see Figure 2 With Metal Bellows Type Pump and Figure 3)

7.1.2.1 Sample pump - stainless steel, metal bellows type (Metal Bellows Corp., 1075 Providence Highway, Sharon, MA 02067, Model MB-151, or equivalent), capable of 2 atmospheres output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds.

Note: An alternative sampling system has been developed by Dr. R. Rasmussen, The Oregon Graduate Center (18,19) and is illustrated in Figure 3. This flow system uses, in order, a pump, a mechanical flow regulator, and a mechanical compensating flow restrictive device. In this configuration the pump is purged with a large sample flow, thereby eliminating the need for an auxiliary vacuum pump to flush the sample inlet. Interferences using this configuration have been minimal.

7.1.2.2 Other supporting materials - all other components of the pressurized sampling system [Figure 2 (with metal bellows type pump) and Figure 3] are similar to components discussed in Sections 7.1.1.1 through 7.1.1.16.

7.2 Sample Analysis

7.2.1 GC-MS-SCAN Analytical System (see Figure 4)

7.2.1.1 The GC-MS-SCAN analytical system must be capable of acquiring and processing data in the MS-SCAN mode.

7.2.1.2 Gas chromatograph - capable of sub-ambient temperature programming for the oven, with other generally standard features such as gas flow regulators, automatic control of valves and integrator, etc. Flame ionization detector optional. (Hewlett Packard, Rt. 41, Avondale, PA 19311, Model 5880A, with oven temperature control and Level 4 BASIC programming, or equivalent.)

7.2.1.3 Chromatographic detector - mass-selective detector (Hewlett Packard, 3000-T Hanover St., 9B, Palo Alto, CA 94304, Model HP-5970 MS, or equivalent), equipped with computer and appropriate software (Hewlett Packard, 3000-T Hanover St., 9B, Palo Alto, CA 94304, HP-216 Computer, Quicksilver MS software, Pascal 3.0, mass storage 9133 HP Winchester with 3.5 inch floppy disk, or equivalent). The GC-MS is set in the SCAN mode, where the MS screens the sample for identification and quantitation of VOC species.

7.2.1.4 Cryogenic trap with temperature control assembly; refer to Section 10.1.1.3 for complete description of trap and temperature control assembly (Nutech Corporation, 2142 Geer St., Durham, NC, 27704, Model 320-01, or equivalent).

7.2.1.5 Electronic mass flow controllers (3) - maintain constant flow for carrier gas and sample gas) and to provide analog output to monitor flow anomalies (Tylan Model 260, 0-100 cm^3/min, or equivalent).

7.2.1.6 Vacuum pump - general purpose laboratory pump, capable of drawing the desired sample volume through the cryogenic trap (Thomas Industries, Inc., Sheboygan, WI, Model 107A20, or equivalent).

7.2.1.7 Chromatographic grade stainless steel tubing and stainless steel plumbing fittings - refer to Section 7.1.1.8 for description.

7.2.1.8 Chromatographic column - to provide compound separation such as shown in Table 5 (Hewlett Packard, Rt. 41, Avondale, PA 19311, OV-I capillary column, 0.32 mm x 50 m with 0.88 μm crosslinked methyl silicone coating, or equivalent).

7.2.1.9 Stainless steel vacuum/pressure gauge (optional) capable of measuring vacuum (-101.3 to 0 kPa) and pressure (0-206 kPa) in the sampling system (Matheson, P.O. Box 136, Morrow, GA 30200, Model 63-3704, or equivalent). Gauges should be tested clean and leak tight.

7.2.1.10 Stainless steel cylinder pressure regulators - standard, two-stage cylinder regulators with pressure gauges for helium, zero air and hydrogen gas cylinders.

7.2.1.11 Gas purifiers (3) - used to remove organic impurities and moisture from gas streams (Hewlett Packard, Rt. 41, Avondale, PA, 19311, P/N 19362 -60500, or equivalent).

7.2.1.12 Low dead-volume tee (optional) - used to split the exit flow from the GC column (Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015, Cat. #5839, or equivalent).

7.2.1.13 Nafion® dryer - consisting of Nafion® tubing coaxially mounted within larger tubing (Perma Pure Products, 8 Executive Drive, Toms River, NJ, 08753, Model MD-125-48, or equivalent). Refer to Section 10.1.1.2 for description.

7.2.1.14 Six-port gas chromatographic valve - (Seismograph Service Corp, Tulsa, OK, Seiscor Model VIII, or equivalent).

7.2.1.15 Chart recorder (optional) - compatible with the detector output signals to record optional FID detector response to the sample.

7.2.1.16 Electronic integrator (optional) - compatible with the detector output signal of the FID and capable of integrating the area of one or more response peaks and calculating peak areas corrected for baseline drift.

7.2.2 GC-MS-SIM Analytical System (see Figure 4)

7.2.2.1 The GC-MS-SIM analytical system must be capable of acquiring and processing data in the MS-SIM mode.

7.2.2.2 All components of the GC-MS-SIM system are identical to Sections 7.2.1.2 through 7.2.1.16.

7.2.3 GC-Multidetector Analytical System (see Figure 5 and Figure 6)

7.2.3.1 Gas chromatograph with flame ionization and electron capture detectors (photoionization detector optional) -capable of sub-ambient temperature programming for the oven and simultaneous operation of all detectors, and with other generally standard features such as gas flow regulators, automatic control of valves and integrator, etc. (Hewlett Packard, Rt. 41, Avondale, PA 19311, Model 5880A, with oven temperature control and Level 4 BASIC programming, or equivalent).

7.2.3.2 Chart recorders - compatible with the detector output signals to record detector response to the sample.

7.2.3.3 Electronic integrator - compatible with the detector output signals and capable of integrating the area of one or more response peaks and calculating peak areas corrected for baseline drift.

7.2.3.4 Six-port gas chromatographic valve - (Seismograph Service Corp, Tulsa, OK, Seiscor Model VIII, or equivalent).

7.2.3.5 Cryogenic trap with temperature control assembly refer to Section 10.1.1.3 for complete description of trap and temperature control assembly (Nutech Corporation, 2142 Geer St., Durham, NC 27704, Model 320-01, or equivalent).

7.2.3.6 Electronic mass flow controllers (3) - maintain constant flow (for carrier gas, nitrogen make-up gas and sample gas) and to provide analog output to monitor flow anomalies (Tylan Model 260, 0-100 cm^3/min, or equivalent).

7.2.3.7 Vacuum pump - general purpose laboratory pump, capable of drawing the desired sample volume through the cryogenic trap (see 7.2.1.6 for source and description).

7.2.3.8 Chromatographic grade stainless steel tubing and stainless steel plumbing fittings - refer to Section 7.1.1.8 for description.

7.2.3.9 Chromatographic column - to provide compound separation such as shown in Table 7. (Hewlett Packard, Rt. 41, Avondale, PA 19311, OV-I capillary column, 0.32 mm x 50 m with 0.88 μm crosslinked methyl silicone coating, or equivalent).

Note: Other columns (e.g., DB-624) can be used as long as the system meets user needs. The wider Megabore® column (i.e., 0.53 mm I.D.) is less susceptible to plugging as a result of trapped water, thus eliminating the need for a Nafion® dryer in the analytical system. The Megabore® column has sample capacity approaching that of a packed column, while retaining much of the peak resolution traits of narrower columns (i.e., 0.32 mm I.D.).

7.2.3.10 Vacuum/pressure gauges (3) - refer to Section 7.2.1.9 for description.

7.2.3.11 Cylinder pressure stainless steel regulators standard, two-stage cylinder regulators with pressure gauges for helium, zero air, nitrogen, and hydrogen gas cylinders.

7.2.3.12 Gas purifiers (4) - used to remove organic impurities and moisture from gas streams (Hewlett-Packard, Rt. 41, Avondale, PA, 19311, P/N 19362 60500, or equivalent).

7.2.3.13 Low dead-volume tee - used to split (50/50) the exit flow from the GC column (Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015, Cat. #5839, or equivalent).

7.3 Canister Cleaning System (see Figure 7)

7.3.1 Vacuum pump - capable of evacuating sample canister(s) to an absolute pressure of <0.05 mm Hg.

7.3.2 Manifold - stainless steel manifold with connections for simultaneously cleaning several canisters.

7.3.3 Shut-off valve(s) - seven (7) on-off toggle valves.

7.3.4 Stainless steel vacuum gauge - capable of measuring vacuum in the manifold to an absolute pressure of 0.05 mm Hg or less.

7.3.5 Cryogenic trap (2 required) - stainless steel U-shaped open tubular trap cooled with liquid oxygen or argon to prevent contamination from back diffusion of oil from vacuum pump and to provide clean, zero air to sample canister(s).

7.3.6 Stainless steel pressure gauges (2) - 0-345 kPa (0-50 psig) to monitor zero air pressure.

7.3.7 Stainless steel flow control valve - to regulate flow of zero air into canister(s).

7.3.8 Humidifier - pressurizable water bubbler containing high performance liquid chromatography (HPLC) grade deionized water or other system capable of providing moisture to the zero air supply.

7.3.9 Isothermal oven (optional) for heating canisters (Fisher Scientific, Pittsburgh, PA, Model 349, or equivalent).

7.4 Calibration System and Manifold (See Figure 8)

7.4.1 Calibration manifold - glass manifold, (1.25 cm I.D. x 66 cm) with sampling ports and internal baffles for flow disturbance to ensure proper mixing.

7.4.2 Humidifier - 500 mL impinger flask containing HPLC grade deionized water.

7.4.3 Electronic mass flow controllers - one 0 to 5 L/min and one 0 to 50 cm^3/min (Tylan Corporation, 23301-TS Wilmington Ave., Carson, CA, 90745, Model 2160, or equivalent).

7.4.4 Teflon® filter(s) - 47 mm Teflon® filter for particulate control, best source.

8. Reagents and Materials

8.1 Gas cylinders of helium, hydrogen, nitrogen, and zero air ultrahigh purity grade, best source.

8.2 Gas calibration standards - cylinder(s) containing approximately 10 ppmv of each of the following compounds of interest:

vinyl chloride
vinylidene chloride
1,1,2-trichloro-1,2,2-trifluoroethane
p-dichlorobenzene
chloroform
1,2-dichloroethane
benzenecarbon
toluene
Freon 12
methyl chloride
ethylbenzene
1,2,4-trichlorobenzene
methyl bromide
ethyl chloride
Freon 11
dichloromethane
1,1-dichloroethane
cis-1,2-dichloroethylene
1,2-dichloropropane
1,1,2-trichloroethane
1,2-dibromoethane
tetrachloroethylene
chlorobenzene
benzyl chloride
hexachloro-1,3-butadiene
methyl chloroform
tetrachloride
trichloroethylene
cis-1,3-dichloropropene
trans-1,3-dichloropropene
1,2-dichloro-1,1,2,2-tetrafluoroethane
o-dichlorobenzene
o-xylene
m-xylene
p-xylene
styrene
1,1,2,2-tetrachloroethane
1,3,5-trimethylbenzene
1,2,4-trimethylbenzene
m-dichlorobenzene

The cylinder(s) should be traceable to a National Bureau of Standards (NBS) Standard Reference Material (SRM) or to a NBS/EPA approved Certified Reference Material (CRM). The components may be purchased in one cylinder or may be separated into different cylinders. Refer to manufacturer's specification for guidance on purchasing and mixing VOCs in gas cylinders. Those compounds purchased should match one's own target list.

8.3 Cryogen - liquid oxygen (bp -183.0°C), or liquid argon (bp -185.7°C), best source.

8.4 Gas purifiers - connected in-line between hydrogen, nitrogen, and zero air gas cylinders and system inlet line, to remove moisture and organic impurities from gas streams (Alltech Associates, 2051 Waukegan Road, Deerfield, IL, 60015, or equivalent).

8.5 Deionized water - high performance liquid chromatography (HPLC) grade, ultrahigh purity (for humidifier), best source.

8.6 4-bromofluorobenzene - used for tuning GC-MS, best source.

8.7 Hexane - for cleaning sampling system components, reagent grade, best source.

8.8 Methanol - for cleaning sampling system components, reagent grade, best source.

9. Sampling System

9.1 System Description

9.1.1 Subatmospheric Pressure Sampling (see Figure 2 Without Metal Bellows Type Pump)

9.1.1.1 In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.05 mm Hg. When opened to the atmosphere containing the VOCs to be sampled, the differential pressure causes the sample to flow into the canister. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-integrated samples (duration of 12 to 24 hours) taken through a flow-restrictive inlet (e.g., mass flow controller, critical orifice).

9.1.1.2 With a critical orifice flow restrictor, there will be a decrease in the flow rate as the pressure approaches atmospheric. However, with a mass flow controller, the subatmospheric sampling system can maintain a constant flow rate from full vacuum to within about 7 kPa (1.0 psi) or less below ambient pressure.

9.1.2 Pressurized Sampling (see Figure 2 With Metal Bellows Type Pump)

9.1.2.1 Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. The sample is collected in a canister using a pump and flow control arrangement to achieve a typical 103-206 kPa (15-30 psig) final canister pressure. For example, a 6-liter evacuated canister can be filled at 10 cm^3/min for 24 hours to achieve a final pressure of about 144 kPa (21 psig).

9.1.2.2 In pressurized canister sampling, a metal bellows type pump draws in air from the sampling manifold to fill and pressurize the sample canister.

9.1.3 All Samplers

9.1.3.1 A flow control device is chosen to maintain a constant flow into the canister over the desired sample period. This flow rate is determined so the canister is filled (to about 88.1 kPa for subatmospheric pressure sampling or to about one atmosphere above ambient pressure for pressurized sampling) over the desired sample period. The flow rate can be calculated by:

$$F = (P \times V)/(T \times 60)$$

where:
F = flow rate, cm^3/min
P = final canister pressure, atmospheres absolute. P is approximately equal to:

$$[(kPa\ gauge)/101.2] + 1$$

V = volume of the canister, cm^3
T = sample period, hours

For example, if a 6 L canister is to be filled to 202 kPa (2 atmospheres) absolute pressure in 24 hours, the flow rate can be calculated by:

$$F = (2 \times 6000)/(24 \times 60) = 8.3\ cm^3/min$$

9.1.3.2 For automatic operation, the timer is wired to start and stop the pump at appropriate times for the desired sample period. The timer must also control the solenoid valve, to open the valve when starting the pump and close the valve when stopping the pump.

9.1.3.3 The use of the Skinner Magnelatch valve avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve that would have to be energized during the entire sample period. The temperature rise in the valve could cause outgassing of organic compounds from the Viton valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained either with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods, or with a conventional mechanical timer and a special pulse circuit. A simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer is illustrated in Figure 9(a). However, with this simple circuit, the valve may operate unreliably during brief power interruptions or if the timer is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 9(b).

9.1.3.4 The connecting lines between the sample inlet and the canister should be as short as possible to minimize their volume. The flow rate into the canister should remain relatively constant over the entire sampling period. If a critical orifice is used, some drop

in the flow rate may occur near the end of the sample period as the canister pressure approaches the final calculated pressure.

9.1.3.5 As an option, a second electronic timer (see Section 7.1.1.6) may be used to start the auxiliary pump several hours prior to the sampling period to flush and condition the inlet line.

9.1.3.6 Prior to use, each sampling system must pass a humid zero air certification (see Section 12.2.2). All plumbing should be checked carefully for leaks. The canisters must also pass a humid zero air certification before us (see Section 12.1).

9.2 Sampling Procedure

9.2.1 The sample canister should be cleaned and tested according to the procedure in Section 12.1.

9.2.2 A sample collection system is assembled as shown in Figure 2 (and Figure 3) and must meet certification requirements as outlined in Section 12.2.3.

Note: The sampling system should be contained in an appropriate enclosure.

9.2.3 Prior to locating the sampling system, the user may want to perform "screening analyses" using a portable GC system, as outlined in Appendix B, to determine potential volatile organics present and potential "hot spots." The information gathered from the portable GC screening analysis would be used in developing a monitoring protocol, which includes the sampling system location, based upon the "screening analysis" results.

9.2.4 After "screening analysis," the sampling system is located. Temperatures of indoor air and sampler box interior are recorded on canister sampling data sheet (see Figure 10).

Note: The following discussion is related to Figure 2.

9.2.5 To verify correct sample flow, a "practice" (evacuated) canister is used in the sampling system.

Note: For a subatmospheric sampler, the flow meter and practice canister are needed. For the pump-driven system, the practice canister is not needed, as the flow can be measured at the outlet of the system. A certified mass flow meter is attached to the inlet line of the manifold, just in front of the filter. The canister is opened. The sampler is turned on and the reading of the certified mass flow meter is compared to the sampler mass flow controller. The values should agree within ±10%. If not, the sampler mass flow meter needs to be recalibrated or there is a leak in the system. This should be investigated and corrected.

Note: Mass flow meter readings may drift. Check the zero reading carefully and add or subtract the zero reading when reading or adjusting the sampler flow rate, to compensate for any zero drift. After two minutes, the desired canister flow rate is adjusted to the proper value (as indicated by the certified mass flow meter) by the sampler flow control unit controller (e.g., 3.5 cm^3/min for 24 hr, 7.0 cm^3/min for 12 hr). Record final flow under "CANISTER FLOW RATE," Figure 10.

9.2.6 The sampler is turned off and the elapsed time meter is reset to 000.0.

Note: Any time the sampler is turned off, wait at least 30 seconds to turn the sampler back on.

9.2.7 The "practice" canister and certified mass flow meter are disconnected and a clean certified (see Section 12.1) canister is attached to the system.

9.2.8 The canister valve and vacuum/pressure gauge valve are opened.

9.2.9 Pressure/vacuum in the canister is recorded on the canister sampling field data sheet (see Figure 10) as indicated by the sampler vacuum/pressure gauge.

9.2.10 The vacuum/pressure gauge valve is closed and the maximum/minimum thermometer is reset to current temperature. Time of day and elapsed time meter readings are recorded on the canister sampling field data sheet.

9.2.11 The electronic timer is set to begin and stop the sampling period at the appropriate times. Sampling commences and stops by the programmed electronic timer.

9.2.12 After the desired sampling period, the maximum, minimum, current interior temperature and current indoor temperature are recorded on the sampling field data sheet. The current reading from the flow controller is recorded.

9.2.13 At the end of the sampling period, the vacuum/pressure gauge valve on the sampler is briefly opened and closed and the pressure/vacuum is recorded on the sampling data sheet. Pressure should be close to desired pressure.

Note: For a subatmospheric sampling system, if the canister is at atmospheric pressure when the final pressure check is performed, the sampling period may be suspect. This information should be noted on the sampling field data sheet. Time of day and elapsed time meter readings are also recorded.

9.2.14 The canister valve is closed. The sampling line is disconnected from the canister and the canister is removed from the.system. For a subatmospheric system, a certified mass flow meter is once again connected to the inlet manifold in front of the in-line filter and a "practice" canister is attached to the Magnelatch valve of the sampling system. The final flow rate is recorded on the canister sampling data sheet (see Figure 10).

Note: For a pressurized system, the final flow may be measured directly. The sampler is turned off.

9.2.15 An identification tag is attached to the canister. Canister serial number, sample number, location, and date are recorded on the tag.

10. Analytical System (see Figures 4, 5 and 6)

10.1 System Description

10.1.1 GC-MS-SCAN System

10.1.1.1 The analytical system is comprised of a GC equipped with a mass-selective detector set in the SCAN mode (see Figure 4). All ions are scanned by the MS repeatedly during the GC run. The system includes a computer and appropriate software for data acquisition, data reduction, and data reporting. A 400 cm^3 air sample is collected from the canister into the analytical system. The sample air is first passed through a Nafion® dryer, through the 6-port chromatographic valve, then routed into a cryogenic trap.

Note: While the GC-multidetector analytical system does not employ a Nafion® dryer for drying the sample gas stream, it is used here because the GC-MS system utilizes a larger sample volume and is far more sensitive to excessive moisture than the GC-multidetector

analytical system. Moisture can adversely affect detector precision. The Nafion® dryer also prevents freezing of moisture on the 0.32 mm internal diameter (I.D.) column, which may cause column blockage and possible breakage. The trap is heated (-160°C to 120°C in 60 sec) and the analyte is injected onto the OV-I capillary column (0.32 mm x 50 m).
Note: Rapid heating of the trap provides efficient transfer of the sample components onto the gas chromatographic column. Upon sample injection onto the column, the MS computer is signaled by the GC computer to begin detection of compounds which elute from the column. The gas stream from the GC is scanned within a preselected range of atomic mass units (amu). For detection of compounds in Table 1, the range should be 18 to 250 amu, resulting in a 1.5 Hz repetition rate. Six scans per eluting chromatographic peak are provided at this rate. The 10-15 largest peaks are chosen by an automated data reduction program, the three scans nearest the peak apex are averaged, and a background subtraction is performed. A library search is then performed and the top ten best matches for each peak are listed. A qualitative characterization of the sample is provided by this procedure. A typical chromatogram of VOCs determined by GC-MS-SCAN is illustrated in Figure 11(a).

10.1.1.2 A Nafion® permeable membrane dryer is used to remove water vapor selectively from the sample stream. The permeable membrane consists of Nafion® tubing (a copolymer of tetrafluoroethylene and fluorosulfonyl monomer) that is coaxially mounted within larger tubing. The sample stream is passed through the interior of the Nafion® tubing, allowing water (and other light, polar compounds) to permeate through the walls into a dry air purge stream flowing through the annular space between the Nafion® and outer tubing.
Note: To prevent excessive moisture build-up and any memory effects in the dryer, a cleanup procedure involving periodic heating of the dryer (100°C for 20 minutes) while purging with dry zero air (500 cm^3/min) should be implemented as part of the user's standard operating procedure (SOP) manual. The clean-up procedure is repeated during each analysis (see Section 14, reference 7). Recent studies have indicated no substantial loss of targeted VOCs utilizing the above clean-up procedure (7). This cleanup procedure is particularly useful when employing cryogenic preconcentration of VOCs with subsequent GC analysis using a 0.32 mm I.D. column because excess accumulated water can cause trap and column blockage and also adversely affect detector precision. In addition, the improvement in water removal from the sampling stream will allow analyses of much larger volumes of sample air in the event that greater system sensitivity is required for targeted compounds.

10.1.1.3 The packed metal tubing used for reduced temperature trapping of VOCs is shown in Figure 12. The cooling unit is comprised of a 0.32 cm outside diameter (O.D.) nickel tubing loop packed with 60-80 mesh Pyrex® beads (Nutech Model 320-01, or equivalent). The nickel tubing loop is wound onto a cylindrically formed tube heater (250 watt). A cartridge heater (25 watt) is sandwiched between pieces of aluminum plate at the trap inlet and outlet to provide additional heat to eliminate cold spots in the transfer tubing. During operation, the trap is inside a two-section stainless steel shell which is well insulated. Rapid heating (-150 to +100°C in 55 s) is accomplished by direct thermal contact

between the heater and the trap tubing. Cooling is achieved by vaporization of the cryogen. In the shell, efficient cooling (+120 to -150°C in 225 s) is facilitated by confining the vaporized cryogen to the small open volume surrounding the trap assembly. The trap assembly and chromatographic valve are mounted on a baseplate fitted into the injection and auxiliary zones of the GC on an insulated pad directly above the column oven when used with the Hewlett-Packard 5880 GC.

Note: Alternative trap assembly and connection to the GC may be used depending upon user's requirements. The carrier gas line is connected to the injection end of the analytical column with a zero-dead-volume fitting that is usually held in the heated zone above the GC oven. A 15 cm x 15 cm x 24 cm aluminum box is fitted over the sample handling elements to complete the package. Vaporized cryogen is vented through the top of the box.

10.1.1.4 As an option, the analyst may wish to split the gas stream exiting the column with a low dead-volume tee, passing one-third of the sample gas (1.0 mL/min) to the mass selective detector and the remaining two-thirds (2.0 mL/min) through a flame ionization detector, as illustrated as an option in Figure 4. The use of the specific detector (MS-SCAN) coupled with the nonspecific detector (FID) enables enhancement of data acquired from a single analysis. In particular, the FID provides the user:

- Semi-real time picture of the progress of the analytical scheme;
- Confirmation by the concurrent MS analysis of other labs that can provide only FID results; and
- Ability to compare GC-FID with other analytical laboratories with only GC-FID capability.

10.1.2 GC-MS-SIM System

10.1.2.1 The analytical system is comprised of a GC equipped with an OV-I capillary column (0.32 mm x 50 m) and a mass-selective detector set in the SIM mode (see Figure 4). The GC-MS is set up for automatic, repetitive analysis. The system is programmed to acquire data for only the target compounds and to disregard all others. The sensitivity is 0.1 ppbv for a 250 cm^3 air sample with analytical precision of about 5% relative standard deviation. Concentration of compounds based upon a previously installed calibration table is reported by an automated data reduction program. A Nafion® dryer is also employed by this analytical system prior to cryogenic preconcentration; therefore, many polar compounds are not identified by this procedure.

10.1.2.2 SIM analysis is based on a combination of retention times and relative abundances of selected ions (see Table 2). These qualifiers are stored on the hard disk of the GC-MS 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, except for vinyl chloride and methylene chloride, which is determined to be ± 25%. Three ions are measured for most of the forty compounds. When compound identification is made by the computer, any peak that fails any of the qualifying tests is flagged (e.g., with an *). All 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. A typical chromatogram of VOCs determined by GC-MS-SIM mode is illustrated in Figure 11(b).

10.1.3 GC-Multidetector (GC-FID-ECD) System with Optional PID

10.1.3.1 The analytical system (see Figure 5) is comprised of a gas chromatograph equipped with a capillary column and electron capture and flame ionization detectors (see Figure 5). In typical operation, sample air from pressurized canisters is vented past the inlet to the analytical system from the canister at a flow rate of 75 cm^3/min. For analysis, only 35 cm^3/min of sample gas is used, while excess is vented to the atmosphere. Sub-ambient pressure canisters are connected directly to the inlet. The sample gas stream is routed through a six port chromatographic valve and into the cryogenic trap for a total sample volume of 490 cm^3.

Note: This represents a 14 minute sampling period at a rate of 35 cm^3/min. The trap (see Section 10.1.1.3) is cooled to -150°C by controlled release of a cryogen. VOCs and SVOCs are condensed on the trap surface while N_2, O_2, and other sample components are passed to the pump. After the organic compounds are concentrated, the valve is switched and the trap is heated. The revolatilized compounds are transported by helium carrier gas at a rate of 4 cm^3/min to the head of the Megabore® OV-I capillary column (0.53 mm x 30 m). Since the column's initial temperature is at -50°C, the VOCs and SVOCs are cryofocussed on the head of the column. Then, the oven temperature is programmed to increase and the VOCs/SVOCs in the carrier gas are chromatographically separated. The carrier gas containing the separated VOCs/SVOCs is then directed to two parallel detectors at a flow rate of 2 cm^3/min each. The detectors sense the presence of the speciated VOCs/SVOCs, and the response is recorded by either a strip chart recorder or a data processing unit.

10.1.3.2 Typical chromatograms of VOCs determined by the GC-FID-ECD analytical system are illustrated in Figures 11(c) and 11(d), respectively.

10.1.3.3 Helium is used as the carrier gas (4 cm^3/min) to purge residual air from the trap at the end of the sampling phase and to carry the revolatilized VOCs through the Megabore® GC column. Moisture and organic impurities are removed from the helium gas stream by a chemical purifier installed in the GC (see Section 7.2.1.11). After exiting the OV-I Megabore® column, the carrier gas stream is split to the two detectors at rates of 2 cm^3/min each.

10.1.3.4 Gas scrubbers containing Drierite® or silica gel and 5A molecular sieve are used to remove moisture and organic impurities from the zero air, hydrogen, and nitrogen gas streams.

Note: Purity of gas purifiers is checked prior to use by passing humid zero air through the gas purifier and analyzing according to Section 12.2.2.

10.1.3.5 All lines should be kept as short as practical. All tubing used for the system should be chromatographic grade stainless steel connected with stainless steel fittings. After assembly, the system should be checked for leaks according to manufacturer's specifications.

10.1.3.6 The FID burner air, hydrogen, nitrogen (makeup), and helium (carrier) flow rates should be set according to the manufacturer's instructions to obtain an optimal FID response while maintaining a stable flame throughout the analysis. Typical flow rates are: burner air, 450 cm^3/min; hydrogen, 30 cm^3/min; nitrogen, 30 cm^3/min; helium, 2 cm^3/min.

10.1.3.7 The ECD nitrogen make-up gas and helium carrier flow rates should be set according to manufacturer's instructions to obtain an optimal ECD response. Typical flow rates are: nitrogen, 76 cm^3/min and helium, 2 cm^3/min.

10.1.3.8 The GC-FID-ECD could be modified to include a PID (see Figure 6) for increased sensitivity (20). In the photoionization process, a molecule is ionized by ultraviolet light as follows: R + hv --> R + e-, where R+ is the ionized species and a photon is represented by hv, with energy less than or equal to the ionization potential of the molecule. Generally all species with an ionization potential less than the ionization energy of the lamp are detected. Because the ionization potential of all major components of air (O_2, N_2, CO, CO_2, and H_2O) is greater than the ionization energy of lamps in general use, they are not detected. The sensor is comprised of an argon-filled, ultraviolet (UV) light source where a portion of the organic vapors is ionized in the gas stream. A pair of electrodes is contained in a chamber adjacent to the sensor. When a positive potential is applied to the electrodes, any ions formed by the absorption of UV light are driven by the created electronic field to the cathode, and the current (proportional to the organic vapor concentration) is measured. The PID is generally used for compounds having ionization potentials less than the ratings of the ultraviolet lamps. This detector is used for determination of most chlorinated and oxygenated hydrocarbons, aromatic compounds, and high molecular weight aliphatic compounds. Because the PID is insensitive to methane, ethane, carbon monoxide, carbon dioxide, and water vapor, it is an excellent detector. The electron volt rating is applied specifically to the wavelength of the most intense emission line of the lamp's output spectrum. Some compounds with ionization potentials above the lamp rating can still be detected due to the presence of small quantities of more intense light. A typical system configuration associated with the GC-FID-ECD-PID is illustrated in Figure 6. This system is currently being used in EPA's FY-89 Urban Air Toxics Monitoring Program.

10.2 GC-MS-SCAN-SIM System Performance Criteria

10.2.1 GC-MS System Operation

10.2.1.1 Prior to analysis, the GC-MS system is assembled and checked according to manufacturer's instructions.

10.2.1.2 Table 3.0 outlines general operating conditions for the GC-MS-SCAN-SIM system with optional FID.

10.2.1.3 The GC-MS system is first challenged with humid zero air (see Section 11.2.2).

10.2.1.4 The GC-MS and optional FID system is acceptable if it contains less than 0.2 ppbv of targeted VOCs.

10.2.2 Daily GC-MS Tuning (see Figure 13)

10.2.2.1 At the beginning of each day or prior to a calibration, the GC-MS system must be tuned to verify that acceptable performance criteria are achieved.

10.2.2.2 For tuning the GC-MS, a cylinder containing 4-bromofluorobenzene is introduced via a sample loop valve injection system.

Note: Some systems allow auto-tuning to facilitate this process. The key ions and ion abundance criteria that must be met are illustrated in Table 4. Analysis should not begin until all those criteria are met.

10.2.2.3 The GC-MS tuning standard could also be used to assess GC column performance (chromatographic check) and as an internal standard. Obtain a background correction mass spectra of 4-bromofluorobenzene 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.

10.2.2.4 The performance criteria must be achieved before any samples, blanks or standards are analyzed. If any key ion abundance observed for the daily 4-bromofluorobenzene 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 gases reanalyzed until the above condition is met.

10.2.3 GC-MS Calibration (see Figure 13)

Note: Initial and routine calibration procedures are illustrated in Figure 13.

10.2.3.1 Initial Calibration - Initially, a multipoint dynamic calibration (three levels plus humid zero air) is performed on the GC-MS system, before sample analysis, with the assistance of a calibration system (see Figure 8). The calibration system uses National Bureau of Standards (NBS) traceable standards or NBS/EPA CRMs in pressurized cylinders [containing a mixture of the targeted VOCs at nominal concentrations of 10 ppmv in nitrogen (Section 8.2)] as working standards to be diluted with humid zero air. The contents of the working standard cylinder(s) are metered (2 cm^3/min) into the heated mixing chamber where they are mixed with a 2 L/min humidified zero air gas stream to achieve a nominal 10 ppbv per compound calibration mixture (see Figure 8). This nominal 10 ppbv standard mixture is allowed to flow and equilibrate for a minimum of 30 minutes. After the equilibration period, the gas standard mixture is sampled and analyzed by the real-time GC.MS system [see Figure 8(a) and Section 7.2.1]. The results of the analyses are averaged, flow audits are performed on the mass flow meters and the calculated concentration compared to generated values. After the GC-MS is calibrated at three concentration levels, a second humid zero air sample is passed through the system and analyzed. The second humid zero air test is used to verify that the GC.MS system is certified clean (less than 0.2 ppbv of target compounds).

10.2.3.2 As an alternative, a multipoint humid static calibration (three levels plus zero humid air) can be performed on the GC-MS system. During the humid static calibration analyses, three (3) SUMMA® passivated canisters are filled each at a different concentration between 1-20 ppbv from the calibration manifold using a pump and mass flow control arrangement [see Figure 8(c)]. The canisters are then delivered to the GC-MS to serve as calibration standards. The canisters are analyzed by the MS in the SIM mode, each

analyzed twice. The expected retention time and ion abundance (see Table 2 and Table 5) are used to verify proper operation of the GC-MS system. A calibration response factor is determined for each analyte, as illustrated in Table 5, and the computer calibration table is updated with this information, as illustrated in Table 6.

10.2.3.3 Routine Calibration - The GC-MS system is calibrated daily (and before sample analysis) with a one point calibration. The GC-MS system is calibrated either with the dynamic calibration procedure [see Figure 8(a)] or with a 6 L SUMMA® passivated canister filled with humid calibration standards from the calibration manifold (see Section 10.2.3.2). After the single point calibration, the GC-MS analytical system is challenged with a humidified zero gas stream to insure the analytical system returns to specification (less than 0.2 ppbv of selective organics).

10.3 GC-FID-ECD System Performance Criteria (With Optional PID System) (See Figure 14)

10.3.1 Humid Zero Air Certification

10.3.1.1 Before system calibration and sample analysis, the GC-FID-ECD analytical system is assembled and checked according to manufacturer's instructions.

10.3.1.2 The GC-FID-ECD system is first challenged with humid zero air (see Section 12.2.2) and monitored.

10.3.1.3 Analytical systems contaminated with less than 0.2 ppbv of targeted VOCs are acceptable.

10.3.2 GC Retention Time Windows Determination (see Table 7)

10.3.2.1 Before analysis can be performed, the retention time windows must be established for each analyte.

10.3.2.2 Make sure the GC system is within optimum operating conditions.

10.3.2.3 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 every 72 hours during continuous operation.

10.3.2.4 Calculate the standard deviation of the three absolute retention times for each single component standard. The retention window is defined as the mean plus or minus three times the standard deviation of the individual retention times for each standard. In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a closely-eluting, similar compound to develop a valid retention time window.

10.3.2.5 The laboratory must calculate retention time windows for each standard (see Table 7) on each GC column, whenever a new GC column is installed or when major components of the GC are changed. 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.

10.3.3 GC Calibration

Note: Initial and routine calibration procedures are illustrated in Figure 14.

10.3.3.1 Initial Calibration - Initially, a multipoint dynamic calibration (three levels plus humid zero air) is performed on the GC-FID-ECD system, before sample analysis, with the assistance of a calibration system (see Figure 8). The calibration system uses NBS traceable standards or NBS/EPA CRMs in pressurized cylinders [containing a mixture of the targeted VOCs at nominal concentrations of 10 ppmv in nitrogen (Section 8.2)] as working standards to be diluted with humid zero air. The contents of the working standard cylinders are metered (2 cm^3/min) into the heated mixing chamber where they are mixed with a 2 L/min humidified zero air stream to achieve a nominal 10 ppbv per compound calibration mixture (see Figure 8). This nominal 10 ppbv standard mixture is allowed to flow and equilibrate for an appropriate amount of time. After the equilibration period, the gas standard mixture is sampled and analyzed by the GC-MS system [see Figure 8(a)]. The results of the analyses are averaged, flow audits are performed on the mass flow controllers used to generate the standards and the appropriate response factors (concentration/ area counts) are calculated for each compound, as illustrated in Table 5.
Note: GC-FIDs are linear in the 1-20 ppbv range and may not require repeated multipoint calibrations; whereas, the GC-ECD will require frequent linearity evaluation. Table 5 outlines typical calibration response factors and retention times for 40 VOCs. After the GC-FID-ECD is calibrated at the three concentration levels, a second humid zero air sample is passed through the system and analyzed. The second humid zero air test is used to verify that the GC-FID-ECD system is certified clean (less than 0.2 ppbv of target compounds).

10.3.3.2 Routine Calibration - A one point calibration is performed daily on the analytical system to verify the initial multipoint calibration (see Section 10.3.3.1). The analyzers (GC-FID-ECD) are calibrated (before sample analysis) using the static calibration procedures (see Section 10.2.3.2) involving pressurized gas cylinders containing low concentrations of the targeted VOCs (10 ppbv) in nitrogen. After calibration, humid zero air is once again passed through the analytical system to verify residual VOCs are not present.

10.3.4 GC-FID-ECD-PID System Performance Criteria

10.3.4.1 As an option, the user may wish to include a photoionization detector (PID) to assist in peak identification and increase sensitivity.

10.3.4.2 This analytical system is presently being used in U.S. Environmental Protection Agency's Urban Air Toxic Pollutant Program (UATP).

10.3.4.3 Preparation of the GC-FID-ECD-PID analytical system is identical to the GC-FID-ECD system (see Section 10.3).

10.3.4.4 Table 8 outlines typical retention times (minutes) for selected organics using the GC-FID-ECD-PID analytical system.

10.4 Analytical Procedures

10.4.1 Canister Receipt

10.4.1.1 The overall condition of each sample canister is observed. Each canister should be received with an attached sample identification tag.

10.4.1.2 Each canister is recorded in the dedicated laboratory logbook. Also noted on the identification tag are date received and initials of recipient.

10.4.1.3 The pressure of the canister is checked by attaching a pressure gauge to the canister inlet. The canister valve is opened briefly and the pressure (kPa, psig) is recorded. Note: If pressure is <83 kPa (<12 psig), the user may wish to pressurize the canisters, as an option, with zero grade nitrogen up to 137 kPa (20 psig) to ensure that enough sample is available for analysis. However, pressurizing the canister can introduce additional error, increase the minimum detection limit (MDL), and is time consuming. The user should weigh these limitations as part of his program objectives before pressurizing. Final cylinder pressure is recorded on canister sampling data sheet (see Figure 10).

10.4.1.4 If the canister pressure is increased, a dilution factor (DF) is calculated and recorded on the sampling data sheet:

$$DF = Y_a/X_a$$

where:
X_a = canister pressure absolute before dilution, kPa, psia
Y_a = canister pressure absolute after dilution, kPa, psia

After sample analysis, detected VOC concentrations are multiplied by the dilution factor to determine concentration in the sampled air.

10.4.2 GC-MS-SCAN Analysis (With Optional FID System)

10.4.2.1 The analytical system should be properly assembled, humid zero air certified (see Section 12.3), operated (see Table 3), and calibrated for accurate VOC determination.

10.4.2.2 The mass flow controllers are checked and adjusted to provide correct flow rates for the system.

10.4.2.3 The sample canister is connected to the inlet of the GC-MS-SCAN (with optional FID) analytical system. For pressurized samples, a mass flow controller is placed on the canister, the canister valve is opened and the canister flow is vented past a tee inlet to the analytical system at a flow of 75 cm^3/min so that 40 cm^3/min is pulled through the Nafion® dryer to the six-port chromatographic valve.
Note: Flow rate is not as important as acquiring sufficient sample volume. Sub-ambient pressure samples are connected directly to the inlet.

10.4.2.4 The GC oven and cryogenic trap (inject position) are cooled to their set points of -50°C and -160°C, respectively.

10.4.2.5 As soon as the cryogenic trap reaches its lower set point of -160.C, the six-port chromatographic valve is turned to its fill position to initiate sample collection.

10.4.2.6 A ten minute collection period of canister sample is utilized.

Note: 40 cm^3/min x 10 min = 400 cm^3 sampled canister contents.

10.4.2.7 After the sample is preconcentrated in the cryogenic trap, the GC sampling valve is cycled to the inject position and the cryogenic trap is heated. The trapped analytes are thermally desorbed onto the head of the OV-I capillary column (0.31 mm I.D. x 50 m length). The GC oven is programmed to start at -50°C and after 2 min to heat to 150°C at a rate of 8°C per minute.

10.4.2.8 Upon sample injection onto the column, the MS is signaled by the computer to scan the eluting carrier gas from 18 to 250 amu, resulting in a 1.5 Hz repetition rate. This corresponds to about 6 scans per eluting chromatographic peak.

10.4.2.9 Primary identification is based upon retention time and relative abundance of eluting ions as compared to the spectral library stored on the hard disk of the GC-MS data computer.

10.4.2.10 The concentration (ppbv) is calculated using the previously established response factors (see Section 10.2.3.2), as illustrated in Table 5.

Note: If the canister is diluted before analysis, an appropriate multiplier is applied to correct for the volume dilution of the canister (Section 10.4.1.4).

10.4.2.11 The optional FID trace allows the analyst to record the progress of the analysis.

10.4.3 GC-MS-SIM Analysis (With Optional FID System)

10.4.3.1 When the MS is placed in the SIM mode of operation, the MS monitors only preselected ions, rather than scanning all masses continuously between two mass limits.

10.4.3.2 As a result, increased sensitivity and improved quantitative analysis can be achieved.

10.4.3.3 Similar to the GC-MS-SCAN configuration, the GC-MS-SIM analysis is based on a combination of retention times and relative abundances of selected ions (see Table 2 and Table 5). These qualifiers are stored on the hard disk of the GC-MS computer and are applied for identification of each chromatographic peak. Once the GC-MS-SIM has identified the peak, a calibration response factor is used to determine the analyte's concentration.

10.4.3.4 The individual analyses are handled in three phases: data acquisition, data reduction, and data reporting. The data acquisition software is set in the SIM mode, where specific compound fragments are monitored by the MS at specific times in the analytical run. Data reduction is coordinated by the postprocessing macro program that is automatically accessed after data acquisition is completed at the end of the GC run. Resulting ion profiles are extracted, peaks are identified and integrated, and an internal integration report is generated by the program. A reconstructed ion chromatogram for hardcopy reference is prepared by the program and various parameters of interest such as time, date, and integration constants are printed. At the completion of the macro program, the data reporting software is accessed. The appropriate calibration table (see Table 9) is retrieved by the data reporting program from the computer's hard disk storage and the proper retention time and response factor parameters are applied to the macro program's integration file. With reference to certain pre-set acceptance criteria, peaks are

automatically identified and quantified and a final summary report is prepared, as illustrated in Table 10.

10.4.4 GC-FID-ECD Analysis (With Optional PID System)

10.4.4.1 The analytical system should be properly assembled, humid zero air certified (see Section 12.2) and calibrated through a dynamic standard calibration procedure (see Section 10.3.2). The FID detector is lit and allowed to stabilize.

10.4.4.2 Sixty-four minutes are required for each sample analysis, 15 for system initialization, 14 for sample collection, 30 for analysis, and 5 for post-time, during which a report is printed.

Note: This may vary depending upon system configuration and programming.

10.4.4.3 The helium and sample mass flow controllers are checked and adjusted to provide correct flow rates for the system. Helium is used to purge residual air from the trap at the end of the sampling phase and to carry the revolatilized VOCs from the trap onto the GC column and into the FID-ECD. The hydrogen, burner air, and nitrogen flow rates should also be checked. The cryogenic trap is connected and verified to be operating properly while flowing cryogen through the system.

10.4.4.4 The sample canister is connected to the inlet of the GC-FID-ECD analytical system. The canister valve is opened and the canister flow is vented past a tee inlet to the analytical system at 75 cm^3/min using a 0-500 cm^3/min Tylan mass flow controller. During analysis, 40 cm^3/min of sample gas is pulled through the six-port chromatographic valve and routed through the trap at the appropriate time while the extra sample is vented. The VOCs are condensed in the trap while the excess flow is exhausted through an exhaust vent, which assures that the sample air flowing through the trap is at atmospheric pressure.

10.4.4.5 The six-port valve is switched to the inject position and the canister valve is closed.

10.4.4.6 The electronic integrator is started.

10.4.4.7 After the sample is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. Since the column is at -50°C, the VOCs are cryofocussed on the column. Then, the oven temperature (programmed) increases and the VOCs elute from the column to the parallel FID-ECD assembly.

10.4.4.8 The peaks eluting from the detectors are identified by retention time (see Table 7 and Table 8), while peak areas are recorded in area counts. Figures 15 and 16 illustrate typical response of the FID and ECD, respectively, for the forty (40) targeted VOCs.

Note: Refer to Table 7 for peak number and identification.

10.4.4.9 The response factors (see Section 10.3.3.1) are multiplied by the area counts for each peak to calculate ppbv estimates for the unknown sample. If the canister is diluted before analysis, an appropriate dilution multiplier (DF) is applied to correct for the volume dilution of the canister (see Section 10.4.1.4).

10.4.4.10 Depending on the number of canisters to be analyzed, each canister is analyzed twice and the final concentrations for each analyte are the averages of the two analyses.

10.4.4.11 However, if the GC-FID-ECD analytical system discovers unexpected peaks which need further identification and attention or overlapping peaks are discovered, eliminating possible quantitation, the sample should then be subjected to a GC-MS-SCAN for positive identification and quantitation.

11. Cleaning and Certification Program

11.1 Canister Cleaning and Certification

11.1.1 All canisters must be clean and free of any contaminants before sample collection.

11.1.2 All canisters are leak tested by pressurizing them to approximately 206 kPa (30 psig) with zero air.

Note: The canister cleaning system in Figure 7 can be used for this task.
The initial pressure is measured, the canister valve is closed, and the final pressure is checked after 24 hours. If leak tight, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period.

11.1.3 A canister cleaning system may be assembled as illustrated in Figure 7. Cryogen is added to both the vacuum pump and zero air supply traps. The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The vacuum pump is started and the vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) are evacuated to < 0.05 mm Hg (for at least one hour).

Note: On a daily basis or more often if necessary, the cryogenic traps should be purged with zero air to remove any trapped water from previous canister cleaning cycles.

11.1.4 The vacuum and vacuum/pressure gauge shut-off valves are closed and the zero air shut-off valve is opened to pressurize the canister(s) with humid zero air to approximately 206 kPa (30 psig). If a zero gas generator system is used, the flow rate may need to be limited to maintain the zero air quality.

11.1.5 The zero shut-off valve is closed and the canister(s) is allowed to vent down to atmospheric pressure through the vent shut-off valve. The vent shut-off valve is closed. Steps 11.1.3 through 11.1.5 are repeated two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

11.1.6 At the end of the evacuation/pressurization cycle, the canister is pressurized to 206 kPa (30 psig) with humid zero air. The canister is then analyzed by a GC-MS or GC-FID-ECD analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.2 ppbv of targeted VOCs) should not be used. As a "blank" check of the canister(s) and cleanup procedure, the final humid zero air fill of 100% of the canisters is analyzed until the cleanup system and canisters are proven reliable (less than 0.2 ppbv of target VOCs). The check can then be reduced to a lower percentage of canisters.

11.1.7 The canister is reattached to the cleaning manifold and is then reevacuated to <0.05 mm Hg and remains in this condition until used. The canister valve is closed. The

canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting. The canister is now ready for collection of an air sample. An identification tag is attached to the neck of each canister for field notes and chain-of-custody purposes.

11.1.8 As an option to the humid zero air cleaning procedures, the canisters could be heated in an isothermal oven to 100°C during Section 11.1.3 to ensure that lower molecular weight compounds (C_2-C_8) are not retained on the walls of the canister.

Note: For sampling heavier, more complex VOC mixtures, the canisters should be heated to 250°C during Section 11.1.3.7. Once heated, the canisters are evacuated to 0.05 mm Hg. At the end of the heated/evacuated cycle, the canisters are pressurized with humid zero air and analyzed by the GC-FID-ECD system. Any canister that has not tested clean (less than 0.2 ppbv of targeted compounds) should not be used. Once tested clean, the canisters are reevacuated to 0.05 mm Hg and remain in the evacuated state until used.

11.2 Sampling System Cleaning and Certification

11.2.1 Cleaning Sampling System Components

11.2.1.1 Sample components are disassembled and cleaned before the sampler is assembled. Nonmetallic parts are rinsed with HPLC grade deionized water and dried in a vacuum oven at 50°C. Typically, stainless steel parts and fittings are cleaned by placing them in a beaker of methanol in an ultrasonic bath for 15 minutes. This procedure is repeated with hexane as the solvent.

11.2.1.2 The parts are then rinsed with HPLC grade deionized water and dried in a vacuum oven at 100°C for 12 to 24 hours.

11.2.1.3 Once the sampler is assembled, the entire system is purged with humid zero air for 24 hours.

11.2.2 Humid Zero Air Certification

Note: In the following sections, "certification" is defined as evaluating the sampling system with humid zero air and humid calibration gases that pass through all active components of the sampling system. The system is "certified" if no significant additions or deletions (less than 0.2 ppbv of targeted compounds) have occurred when challenged with the test gas stream.

11.2.2.1 The cleanliness of the sampling system is determined by testing the sampler with humid zero air without an evacuated gas cylinder, as follows.

11.2.2.2 The calibration system and manifold are assembled as illustrated in Figure 8. The sampler (without an evacuated gas cylinder) is connected to the manifold and the zero air cylinder activated to generate a humid gas stream (2 L/min) to the calibration manifold [see Figure 8 (b)].

11.2.2.3 The humid zero gas stream passes through the calibration manifold, through the sampling system (without an evacuated canister) to a GC-FID-ECD analytical system at 75 cm^3/min so that 40 cm^3/min is pulled through the six port valve and routed through

the cryogenic trap (see Section 10.2.2.1) at the appropriate time while the extra sample is vented.
Note: The exit of the sampling system (without the canister) replaces the canister in Figure 4.
After the sample (400 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. Since the column is at -50°C, the VOCs are cryofocussed on the column. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC-MS (see Section 10.2) or the GC-FID-ECD (see Section 10.3). The analytical system should not detect greater than 0.2 ppbv of targeted VOCs in order for the sampling system to pass the humid zero air certification test. Chromatograms of a certified sampler and contaminated sampler are illustrated in Figures 17(a) and (b), respectively. If the sampler passes the humid zero air test, it is then tested with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling (e.g., 0.5 to 2 ppbv) as outlined in Section 11.2.3.

11.2.3 Sampler System Certification with Humid Calibration Gas Standards

11.2.3.1 Assemble the dynamic calibration system and manifold as illustrated in Figure 8.

11.2.3.2 Verify that the calibration system is clean (less than 0.2 ppbv of targeted compounds) by sampling a humidified gas stream, without gas calibration standards, with a previously certified clean canister (see Section 12.1).

11.2.3.3 The assembled dynamic calibration system is certified clean if less than 0.2 ppbv of targeted compounds are found.

11.2.3.4 For generating the humidified calibration standards, the calibration gas cylinder(s) (see Section 8.2) containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs are attached to the calibration system, as outlined in Section 10.2.3.1. The gas cylinders are opened and the gas mixtures are passed through 0 to 10 cm^3/min certified mass flow controllers to generate ppb levels of calibration standards.

11.2.3.5 After the appropriate equilibrium period, attach the sampling system (containing a certified evacuated canister) to the manifold, as illustrated in Figure 8(a).

11.2.3.6 Sample the dynamic calibration gas stream with the sampling system according to Section 9.2.1.
Note: To conserve generated calibration gas, bypass the canister sampling system manifold and attach the sampling system to the calibration gas stream at the inlet of the in-line filter of the sampling system so the flow will be less than 500 cm^3/min.

11.2.3.7 Concurrent with the sampling system operation, real time monitoring of the calibration gas stream is accomplished by the on-line GC-MS or GC-multidetector analytical system [see Figure 8(b)] to provide reference concentrations of generated VOCs.

11.2.3.8 At the end of the sampling period (normally same time period used for anticipated sampling), the sampling system canister is analyzed and compared to the reference GC-MS or GC-multidetector analytical system to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system.

11.2.3.9 A recovery of between 90% and 110% is expected for all targeted VOCs.

12. Performance Criteria and Quality Assurance

12.1 Standard Operating Procedures (SOPs)

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

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

12.2 Method Relative Accuracy and Linearity

12.2.1 Accuracy can be determined by injecting VOC standards (see Section 8.2) from an audit cylinder into a sampler. The contents are then analyzed for the components contained in the audit canister. Percent relative accuracy is calculated:

$$\% \text{ Relative Accuracy} = (X-Y)/X \times 100$$

where:
Y = Concentration of the targeted compound recovered from sampler
X = Concentration of VOC targeted compound in the NBS-SRM or EPA-CRM audit cylinders

12.2.2 If the relative accuracy does not fall between 90 and 110 percent, the sampler should be removed from use, cleaned, and recertified according to initial certification procedures outlined in Section 11.2.2 and Section 11.2.3. Historically, concentrations of carbon tetrachloride, tetrachloroethylene, and hexachlorobutadiene have sometimes been detected at lower concentrations when using parallel ECD and FID detectors. When these three compounds are present at concentrations close to calibration levels, both detectors usually agree on the reported concentrations. At concentrations below 4 ppbv, there is a problem with non-linearity of the ECD. Plots of concentration versus peak area for calibration compounds detected by the ECD have shown that the curves are nonlinear for carbon tetrachloride, tetrachloroethylene, and hexachlorobutadiene, as illustrated in Figures 18(a) through 18(c). Other targeted ECD and FID compounds scaled linearly for the range 0 to 8 ppbv, as shown for chloroform in Figure 18(d). For compounds that are not linear over the calibration range, area counts generally roll off between 3 and 4 ppbv. To correct for the nonlinearity of these compounds, an additional calibration step is performed. An evacuated stainless steel canister is pressurized with calibration gas at a nominal concentration of 8 ppbv. The sample is then diluted to approximately 3.5 ppbv with zero air and analyzed. The instrument response factor (ppbv/area) of the ECD for each of the three compounds is calculated for the 3.5 ppbv sample. Then, both the 3.5 ppbv and the 8 ppbv response factors are entered into the ECD calibration table. The software for the

Hewlett-Packard 5880 level 4 GC is designed to accommodate multilevel calibration entries, so the correct response factors are automatically calculated for concentrations in this range.

12.3 Method Modification

12.3.1 Sampling

12.3.1.1 The sampling system for pressurized canister sampling could be modified to use a lighter, more compact pump. The pump currently being used weighs about 16 kilograms (35 lbs). Commercially available pumps that could be used as alternatives to the prescribed sampler pump are described below. Metal Bellows MB-41 pump: These pumps are cleaned at the factory; however, some precaution should be taken with the circular (4.8 cm diameter) Teflon® and stainless steel part directly under the flange. It is often dirty when received and should be cleaned before use. This part is cleaned by removing it from the pump, manually cleaning with deionized water, and placing in a vacuum oven at 100°C for at least 12 hours. Exposed parts of the pump head are also cleaned with swabs and allowed to air dry. These pumps have proven to be very reliable; however, they are only useful up to an outlet pressure of about 137 kPa (20 psig). Neuberger Pump: Viton gaskets or seals must be specified with this pump. The "factory direct" pump is received contaminated and leaky. The pump is cleaned by disassembling the pump head (which consists of three stainless steel parts and two gaskets), cleaning the gaskets with deionized water and drying in a vacuum oven, and remachining (or manually lapping) the sealing surfaces of the stainless steel parts. The stainless steel parts are then cleaned with methanol, hexane, deionized water and heated in a vacuum oven. The cause for most of the problems with this pump has been scratches on the metal parts of the pump head. Once this rework procedure is performed, the pump is considered clean and can be used up to about 240 kPa (35 psig) output pressure. This pump is utilized in the sampling system illustrated in Figure 3.

12.3.1.2 Urban Air Toxics Sampler - The sampling system described in this method can be modified like the sampler in EPA's FY-89 Urban Air Toxics Pollutant Program. This particular sampler is described in Appendix C (see Figure 19).

12.3.2 Analysis

12.3.2.1 Inlet tubing from the calibration manifold could be heated to 50°C (same temperature as the calibration manifold) to prevent condensation on the internal walls of the system.

12.3.2.2 The analytical strategy for Method IP-1A involves positive identification and quantitation by GC-MS-SCAN-SIM mode of operation with optional FID. This is a highly specific and sensitive detection technique. Because a specific detector system (GC-MS-SCAN-SIM) is more complicated and expensive than the use of non-specific detectors (GC-FID-ECD-PID), the analyst may want to perform a screening analysis and preliminary quantitation of VOC species in the sample, including any polar compounds, by utilizing the GC-multidetector (GC-FID-ECD-PID) analytical system prior to GC-MS analysis. This

system can be used for approximate quantitation. The GC-FID-ECD-PID provides a "snapshot" of the constituents in the sample, allowing the analyst to determine:

- Extent of misidentification due to overlapping peaks,
- Whether the constituents are within the calibration range of the anticipated GC-MS-SCAN-SIM analysis or does the sample require further dilution, and
- Are there unexpected peaks which need further identification through GC-MS-SCAN or are there peaks of interest needing attention?

If unusual peaks are observed from the GC-FID-ECD-PID system, the analyst then performs a GC-MS-SCAN analysis. The GC-MS-SCAN will provide positive identification of suspect peaks from the GC-FID-ECD-PID system. If no unusual peaks are identified and only a select number of VOCs are of concern, the analyst can then proceed to GC-MS-SIM. The GC-MS-SIM is used for final quantitation of selected VOCs. Polar compounds, however, cannot be identified by the GC-MS-SIM due to the use of a Nafion® dryer to remove water from the sample prior to analysis. The dryer removes polar compounds along with the water. The analyst often has to make this decision incorporating project objectives, detection limits, equipment availability, cost and personnel capability in developing an analytical strategy. Figure 20 outlines the use of the GC-FID-ECD-PID as a "screening" approach, with the GC-MS-SCAN-SIM for final identification and quantitation.

12.4 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.

12.5 Quality Assurance (See Figure 21)

12.5.1 Sampling System

12.5.1.1 Section 9.2 suggests that a portable GC system be used as a "screening analysis" prior to locating fixed-site samplers (pressurized or subatmospheric).

12.5.1.2 Section 9.2 requires pre-and post-sampling measurements with a certified mass flow controller for flow verification of sampling system.

12.5.1.3 Section 11.1 requires all canisters to be pressure tested to 206 kPa ± 14 kPa (30 psig ± 2 psig) over a period of 24 hours.

12.5.1.4 Section 11.1 requires that all canisters be certified clean (containing less than 0.2 ppbv of targeted VOCs) through a humid zero air certification program.

12.5.1.5 Section 11.2.2 requires all sampling systems to be certified initially clean (containing less than 0.2 ppbv of targeted VOCs) through a humid zero air certification program.

12.5.1.6 Section 11.2.3 requires all sampling systems to pass an initial humidified calibration gas certification [at VOC concentration levels expected in the field (e.g., 0.5 to 2 ppbv)] with a percent recovery of greater than 90.

12.5.2 GC-MS-SCAN-SIM System Performance Criteria

12.5.2.1 Section 10.2.1 requires the GC-MS analytical system to be certified clean (less than 0.2 ppbv of targeted VOCs) prior to sample analysis, through a humid zero air certification.

12.5.2.2 Section 10.2.2 requires the tuning of the GC-MS with 4-bromofluorobenzene (4-BFB) and that it meet the key ions and ion abundance criteria (10%) outlined in Table 5.

12.5.2.3 Section 10.2.3 requires both an initial multipoint humid static calibration (three levels plus humid zero air) and a daily calibration (one point) of the GC-MS analytical system.

12.5.3 GC-Multidetector System Performance Criteria

12.5.3.1 Section 10.3.1 requires the GC-FID-ECD analytical system, prior to analysis, to be certified clean (less than 0.2 ppbv of targeted VOCs) through a humid zero air certification.

12.5.3.2 Section 10.3.2 requires that the GC-FID-ECD analytical system establish retention time windows for each analyte prior to sample analysis, when a new GC column is installed, or major components of the GC system altered since the previous determination.

12.5.3.3 Section 8.2 requires that all calibration gases be traceable to a National Bureau of Standards (NBS) Standard Reference Material (CRM).

12.5.3.4 Section 10.3.2 requires that the retention time window be established throughout the course of a 72-hr analytical period.

12.5.3.5 Section 10.3.3 requires both an initial multipoint calibration (three levels plus humid zero air) and a daily calibration (one point) of the GC-FID-ECD analytical system with zero gas dilution of NBS traceable or NBS/EPA CRMs gases.

Note: Gas cylinders of VOCs at the ppm and ppb level are available for audits from the USEPA, Atmospheric Research and Exposure Assessment Laboratory, Quality Assurance Division, MD-77B, Research Triangle Park, NC 27711, (919)541-4531. Appendix A outlines five groups of audit gas cylinders available from USEPA.

13. Acknowledgements

The determination of volatile and some semi-volatile organic compounds in indoor air is a complex task, primarily because of the wide variety of compounds of interest and the lack of standardized sampling and analytical procedures. While there are numerous procedures for sampling and analyzing VOCs/SVOCs in indoor air, this method draws upon the best aspects of each one and combines 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. Volatile Organic Compound Data Sheet

COMPOUND (SYNONYM)	FORMULA	MOLECULAR WEIGHT	BOILING POINT (°C)	MELTING POINT (°C)	CAS NUMBER
Freon 12 (Dichlorodifluoromethane)	Cl_2CF_2	120.91	-29.8	-158.0	
Methyl chloride (Chloromethane)	CH_3Cl	50.49	-24.2	-97.1	74-87-3
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	$ClCF_2CClF_2$	170.93	4.1	-94.0	
Vinyl chloride (Chloroethylene)	$CH_2=CHCl$	62.50	-13.4	-1538.0	75-01-4
Methyl bromide (Bromomethane)	CH_3Br	94.94	3.6	-93.6	74-83-9
Ethyl chloride (Chloroethane)	CH_3CH_2Cl	64.52	12.3	-136.4	75-00-3
Freon 11 (Trichlorofluoromethane)	CCl_3F	137.38	23.7	-111.0	
Vinylidene chloride (1,1-Dichloroethene)	$C_2H_2Cl_2$	96.95	31.7	-122.5	75-35-4
Dichloromethane (Methylene chloride)	CH_2Cl_2	84.94	39.8	-95.1	75-09-2
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	CF_2ClCCl_2F	187.38	47.7	-36.4	
1,1-Dichloroethane (Ethylidene chloride)	CH_3CHCl_2	98.96	57.3	-97.0	74-34-3
cis-1,2-Dichloroethylene	$CHCl=CHCl$	96.94	60.3	-80.5	
Chloroform (Trichloromethane)	$CHCl_3$	119.38	61.7	-63.5	67-66-3
1,2-Dichloroethane (Ethylene dichloride)	$ClCH_2CH_2Cl$	98.96	83.5	-35.3	107-06-2
Methyl chloroform (1,1,1-Trichloroethane)	CH_3CCl_3	133.41	74.1	-30.4	71-55-6
Benzene (Cyclohexatriene)	C_6H_6	78.12	80.1	5.5	71-43-2
Carbon tetrachloride (Tetrachloromethane)	CCl_4	153.82	76.5	-23.0	56-23-5
1,2-Dichloropropane (Propylene dichloride)	$CH_3CHClCH_2Cl$	112.99	96.4	-100.4	78-87-5
Trichloroethylene (Trichloroethene)	$ClCH=CCl_2$	131.29	87	-73.0	79-01-6
cis-1,3-Dichloropropene (cis-1,3-dichloropropylene)	$CH_3CCl=CHCl$	110.97	76		
trans-1,3-Dichloropropene (cis-1,3-Dichloropropylene)	$ClCH_2CH=CHCl$	110.97	112.0		
1,1,2-Trichloroethane (Vinyl trichloride)	$CH_2ClCHCl_2$	133.41	113.8	-36.5	79-00-5
Toluene (Methyl benzene)	$C_6H_5CH_3$	92.15	110.6	-95.0	108-88-3
1,2-Dibromoethane (Ethylene dibromide)	$BrCH_2CH_2Br$	187.88	131.3	9.8	106-93-4
Tetrachloroethylene (Perchloroethylene)	$Cl_2C=CCl_2$	165.83	121.1	-19.0	127-18-4
Chlorobenzene (Phenyl chloride)	C_6H_5Cl	112.56	132.0	-45.6	108-90-7
Ethylbenzene	$C_6H_5C_2H_5$	106.17	136.2	-95.0	100-41-4
m-Xylene (1,3-Dimethylbenzene)	$1,3-(CH_3)_2C_6H_4$	106.17	139.1	-47.9	
p-Xylene (1,4-Dimethylxylene)	$1,4-(CH_3)_2C_6H_4$	106.17	138.3	13.3	
Styrene (Vinyl benzene)	$C_6H_5CH=CH_2$	104.16	145.2	-30.6	100-42-5
1,1,2,2-Tetrachloroethane	$CHCl_2CHCl_2$	167.85	146.2	-36.0	79-34-5
o-Xylene (1,2-Dimethylbenzene)	$1,2-(CH_3)_2C_6H_4$	106.17	144.4	-25.2	
1,3,5-Trimethylbenzene (Mesitylene)	$1,3,5-(CH_3)_3C_6H_6$	120.20	164.7	-44.7	108-67-8
1,2,4-Trimethylbenzene (Pseudocumene)	$1,2,4-(CH_3)_3C_6H_6$	120.20	169.3	-43.8	95-63-6
m-Dichlorobenzene (1,3-Dichlorobenzene)	$1,3-Cl_2C_6H_4$	147.01	173.0	-24.7	541-73-1
Benzyl chloride (α-Chlorotoluene)	$C_6H_5CH_2Cl$	126.59	179.3	-39.0	100-44-7
o-Dichlorobenzene (1,2-Dichlorobenzene)	$1,2-Cl_2C_6H_4$	147.01	180.5	-17.0	95-50-1
p-Dichlorobenzene (1,4-Dichlorobenzene)	$1,4-Cl_2C_6H_4$	147.01	174.0	53.1	106-46-7
1,2,4-Trichlorobenzene	$1,2,4-Cl_3C_6H_3$	181.45	213.5	17.0	120-82-1
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3-butadiene)					

Table 2. Ion/Abundance and Expected Retention Time for Selected VOCs Analyzed by GC-MS-SIM

Compound	Ion/Abundance (amu/% base peak)	Expected Retention Time (minutes)
Freon 12 (Dichlorodifluoromethane)	85/100 87/ 31	5.01
Methyl chloride (Chloromethane)	50/100 52/ 34	5.69
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	85/100 135/ 56 87/ 33	6.55
Vinyl chloride (Chloroethene)	62/100 27/125 64/ 32	6.71
Methyl bromide (Bromomethane)	94/100 96/ 85	7.83
Ethyl chloride (Chloroethane)	64/100 29/140 27/140	8.43
Freon 11 (Trichlorofluoromethane)	101/100 103/ 67	9.97
Vinylidene chloride (1,1-Dichloroethylene)	61/100 96/ 55 63/ 31	10.93
Dichloromethane thylene chloride)	49/100 84/ 65 86/ 45	11.21
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	151/100 101/140 103/ 90	11.60
1,1-Dichloroethane (Ethylidene dichloride)	63/100 27/ 64 65/ 33	12.50
cis-1,2-Dichloroethylene	61/100 96/ 60 98/ 44	13.40
Chloroform (Trichloromethane)	83/100 85/ 65 47/ 35	13.75
1,2-Dichloroethane (Ethylene dichloride)	62/100 27/ 70 64/ 31	14.39
Methyl chloroform (1,1,1-Trichloroethane)	97/100 99/ 64 61/ 61	14.62

Table 2. (cont.)

Compound	Ion/Abundance (amu/% base peak)	Expected Retention Time (minutes)
Benzene (Cyclohexatriene)	78/100 77/ 25 50/ 35	15.04
Carbon tetrachloride (Tetrachloromethane)	117/100 119/ 97	15.18
1,2-Dichloropropane (Propylene dichloride)	63/100 41/ 90 62/ 70	15.83
Trichroethylene (Trichloroethene)	130/100 132/ 92 95/ 87	16.10
cis-1,3-Dichloropropene	75/100 39/ 70 77/ 30	16.96
trans-1,3-Dichloropropene (1,3-dichloro-1-propene)	75/100 39/ 70 77/ 30	17.49
1,1,2-Trichloroethane (Vinyl trichloride)	97/100 83/ 90 61/ 82	17.61
Toluene (Methyl benzene)	91/100 92/ 57	17.86
1,2-Dibromoethane (Ethylene dibromide)	107/100 109/ 96 27/115	18.48
Tetrachloroethylene (Perchloroethylene)	166/100 164/ 74 131/ 60	19.01
Chlorobenzene (Benzene chloride)	112/100 77/ 62 114/ 32	19.73
Ethylbenzene	91/100 106/ 28	20.20
m,p-Xylene(1,3/1,4-dimethylbenzene)	91/100 106/ 40	20.41
Styrene (Vinyl benzene)	104/100 78/ 60 103/ 49	20.81
1,1,2,2-Tetrachloroethane (Tetrachloroethane)	83/100 85/ 64	20.92
o-Xylene (1,2-Dimethylbenzene)	91/100 106/ 40	20.92

Table 2. (cont.)

Compound	Ion/Abundance (amu/% base peak)	Expected Retention Time (minutes)
4-Ethyltoluene	105/100 120/ 29	22.53
1,3,5-Trimethylbenzene (Mesitylene)	105/100 120/ 42	22.65
1,2,4-Trimethylbenzene (Pseudocumene)	105/100 120/ 42	23.18
m-Dichlorobenzene (1,3-Dichlorobenzene)	146/100 148/ 65 111/ 40	23.31
Benzyl chloride (α-Chlorotoluene)	91/100 126/ 26	23.32
p-Dichlorobenzene (1,4-Dichlorobenzene)	146/100 148/ 65 111/ 40	23.41
o-Dichlorobenzene (1,2-Dichlorobenzene)	146/100 148/ 65 111/ 40	23.88
1,2,4-Trichlorobenzene	180/100 182/ 98 184/ 30	26.71
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3-butadiene)	225/100 227/ 66 223/ 60	27.68

Table 3. General GC and MS Operating Conditions

Chromatography

Column	Hewlett-Packard OV-1 crosslinked methyl silicone (50 m x 0.31-mm I.D., 17 μm film thickness), or equivalent
Carrier Gas	Helium (2.0 cm^3/min at 250°C)
Injection Volume	Constant (1-3 μL)
Injection Mode	Splitless

Temperature Program

Initial Column Temperature	-50°C
Initial Hold Time	2 min
Program	8°C/min to 150°C
Final Hold Time	15 min

Mass Spectrometer

Mass Range	18 to 250 amu
Scan Time	1 sec/scan
EI Condition	70 eV
Mass Scan	Follow manufacturer's instruction for selecting mass selective (MS) detector and selected ion monitoring (SIM) mode
Detector Mode	Multiple ion detection

FID System (Optional)

Hydrogen Flow	30 cm^3/minute
Carrier Flow	30 cm^3/minute
Burner Air	400 cm^3/minute

Table 4. 4-Bromofluorobenzene Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but <101% of mass 174
177	5 to 9% of mass 176

Table 5. Response Factors (ppbv/area count) and Expected Retention Time for GC-MS-SIM Analytical Configuration

Compound	Response Factor (ppbv/area count)	Expected Retention Time (minutes)
Freon 12	0.6705	5.01
Methyl chloride	4.093	5.64
Freon 114	0.4928	6.55
Vinyl chloride	2.343	6.71
Methyl bromide	2.647	7.83
Ethyl chloride	2.954	8.43
Freon 11	0.5145	9.87
Vinylidene chloride	1.037	10.93
Dichloromethane	2.255	11.21
Trichlorotri fluoroethane	0.9031	11.60
1,1-Dichloroethane	1.273	12.50
cis-1,2-1.363 Dichloroethylene	13.40	
Chloroform	0.7911	13.75
1,2-Dichloroethane	1.017	14.39
Methyl chloroform	0.7078	14.62
Benzene	1.236	15.04
Carbon tetrachloride	0.5880	15.18
1,2-Dichloropropane	2.400	15.83
Trichloroethylene	1.383	16.10
cis-1,3- Dichloropropene	1.877	16.96
trans-1,3- Dichloropropene	1.338	17.49
1,1,2-Trichloroethane	1.891	17.61
Toluene	0.9406	17.86
1,2-Dibromoethane (EBD)	0.8662	18.48
Tetrachloroethylene	0.7357	19.01
Chlorobenzene	0.8558	19.73
Ethylbenzene	0.6243	20.20
m,p-Xylene	0.7367	20.41
Styrene	1.888	20.80
1,1,2,2- Tetrachloroethane	1.035	20.92
o-Xylene	0.7498	20.92
4-Ethyltoluene	0.6181	22.53
1,3,5-Trimethyl- benzene	0.7088	22.65

Table 5. (cont.)

Compound	Response Factor (ppbv/area count)	Expected Retention Time (minutes)
1,2,4-Trimethyl-benzene	0.7536	23.18
m-Dichlorobenzene	0.9643	23.31
Benzyl chloride	1.420	23.32
p-Dichlorobenzene	0.8912	23.41
o-Dichlorobenzene	1.004	23.88
1,2,4-Trichloro-benzene	2.150	26.71
Hexachlorobutadiene	0.4117	27.68

Table 6. GC-MS-SIM Calibration Table

*** External Standard ***

Operator: JDF 8 Jan 87 10:02 am
Sample Info : SYR 1
Misc Info:
Integration File Name : DATA:SYR2A02A.I
Sequence Index: 1 Bottle Number : 2

Last Update: 8 Jan 87 8:13 am
Reference Peak Window: 5.00 Absolute Minutes
Non-Reference Peak Window: 0.40 Absolute Minutes
Sample Amount: 0.000 Uncalibrated Peak RF: 0.000 Multiplier: 1.667

Peak Num	Peak Type	Int Type	Ret Time	Signal Description		Compound Name	Area	Amount	
1		1	PP	5.020	Mass 85.00 amu	FREON 12	12893	4011 pptv	
2		1	PP	5.654	Mass 50.00 amu	METHYLCHLORI	4445	2586 pptv	
3		1	BP	6.525	Mass 85.00 amu	FREON 114	7067	1215 pptv	
4		1	PB	6.650	Mass 62.00 amu	VINYLCHLORID	2892	1929 pptv	*
5		1	BP	7.818	Mass 94.00 amu	METHYLBROMID	2401	1729 pptv	
6		1	BB	8.421	Mass 64.00 amu	ETHYLCHLORID	2134	2769 pptv	*
7		1	BV	9.940	Mass 101.00 amu	FREON 11	25069	6460 pptv	
8		1	BP	10.869	Mass 61.00 amu	VINDENECHLOR	5034	1700 pptv	
9		1	BP	11.187	Mass 49.00 amu	DICHLOROMETH	4803	2348 pptv	
10		1	PP	11.225	Mass 41.00 amu	ALLYLCHLORID	761	8247 pptv	*
11		1	BP	11.578	Mass 151.00 amu	3CHL3FLUETHA	5477	1672 pptv	
12		1	BP	12.492	Mass 63.00 amu	1,1DICHLOETH	5052	1738 pptv	#
13		1	VP	13.394	Mass 61.00 amu	c-1,2DICHLET	4761	1970 pptv	
14		1	PH	13.713	Mass 83.00 amu	CHLOROFORM	5327	1678 pptv	
15		1	BP	14.378	Mass 62.00 amu	1,2DICHLETHA	5009	2263 pptv	
16		1	PB	14.394	Mass 97.00 amu	METHCHLOROFO	6656	2334 pptv	
17		1	VP	15.009	Mass 78.00 amu	BENZENE	8352	2167 pptv	
18		1	VP	15.154	Mass 117.00 amu	CARBONTETRAC	5868	1915 pptv	
19		1	BB	15.821	Mass 63.00 amu	1,2DICHLPROP	3263	1799 pptv	*
20		1	BB	16.067	Mass 130.00 amu	TRICHLETHENE	4386	2109 pptv	
21		1	PB	16.941	Mass 75.00 amu	c-1,3DICHLPR	2228	987.3 pptv	
22		1	BP	17.475	Mass 75.00 amu	t-1,3DICHLPR	1626	689.2 pptv	
23		1	BB	17.594	Mass 97.00 amu	1,1,2CHLETHA	2721	1772 pptv	
24		1	BV	17.844	Mass 91.00 amu	TOLUENE	14417	2733 pptv	
25		1	PB	18.463	Mass 107.00 amu	EDB	4070	1365 pptv	*
26		1	PH	18.989	Mass 166.00 amu	TETRACHLETHE	6874	2065 pptv	
27		1	PB	19.705	Mass 112.00 amu	CHLOROBENZEN	5648	1524 pptv	
28		1	BP	20.168	Mass 91.00 amu	ETHYLBENZENE	11084	1842 pptv	
29		1	PB	20.372	Mass 91.00 amu	m,p-XYLENE	17989	3790 pptv	
30		1	BV	20.778	Mass 104.00 amu	STYRENE	3145	1695 pptv	
31		1	BH	20.887	Mass 83.00 amu	TETRACHLETHA	4531	1376 pptv	
32		1	BP	20.892	Mass 91.00 amu	o-XYLENE	9798	2010 pptv	
33		1	VV	22.488	Mass 105.00 amu	4-ETHYLTOLUE	7694	1481 pptv	
34		1	VB	22.609	Mass 105.00 amu	1,3,5METHBEN	6781	1705 pptv	
35		1	BB	23.144	Mass 105.00 amu	1,2,4METHBEN	7892	2095 pptv	
36		1	BV	23.273	Mass 146.00 amu	m-DICHLBENZE	3046	1119 pptv	
37		1	VV	23.279	Mass 91.00 amu	BENZYLCHLORI	3880	1006 pptv	
38		1	VB	23.378	Mass 146.00 amu	p-DICHLBENZE	6090	2164 pptv	
39		1	BP	23.850	Mass 146.00 amu	o-DICHLBENZE	2896	1249 pptv	
40		1	BB	26.673	Mass 180.00 amu	1,2,4CHLBENZ	562	767.1 pptv	
41		1	BB	27.637	Mass 225.00 amu	HEXACHLBUTAD	6309	1789 pptv	

Table 7. Typical Retention Time (min) and Calibration Response Factors (ppbv/area count) for Targeted VOCs Associated with FID and ECD Analytical System

Peak Number[1]	Compound	Retention Time (RT), minutes	FID Response Factor (RF) (ppbv/area count)	ECD Response Factor (ppbv/area count x 10^{-5})
1	Freon 12	3.65	3.465	13.89
2	Methyl chloride	4.30	0.693	
3	Freon 114	5.13	0.578	22.32
4	Vinyl chloride	5.28	0.406	
5	Methyl bromide	6.44		26.34
6	Ethyl chloride	7.06	0.413	
7	Freon 11	8.60	6.367	1.367
8	Vinylidene chloride	9.51	0.347	
9	Dichloromethane	9.84	0.903	
10	Trichlorotrifluoroethane	10.22	0.374	3.955
11	1,1-Dichloroethane	11.10	0.359	
12	cis-1,2-Dichloroethylene	11.99	0.368	
13	Chloroform	12.30	1.059	11.14
14	1,2-Dichloroethane	12.92	0.409	
15	Methyl chloroform	13.12	0.325	3.258
16	Benzene	13.51	0.117	
17	Carbon tetrachloride	13.64	1.451	1.077
18	1,2-Dichloropropane	14.26	0.214	
19	Trichloroethylene	14.50	0.327	8.910
20	cis-1,3-Dichloropropene	15.31		
21	trans-1,3-Dichloropropene	15.83		
22	1,1,2-Trichloroethane	15.93	0.336	
23	Toluene	16.17	0.092	
24	1,2-Dibromoethane (EDB)	16.78	0.366	5.137
25	Tetrachloroethylene	17.31	0.324	1.449

Table 7. (cont.)

Peak Number[1]	Compound	Retention Time (RT), minutes	FID Response Factor (RF) (ppbv/area count)	ECD Response Factor (ppbv/area count x 10^{-5})
26	Chlorobenzene	18.03	0.120	
27	Ethylbenzene	18.51	0.092	
28	m,p-Xylene	18.72	0.095	
29	Styrene	19.12	0.143	
30	1,1,2,2-Tetrachloroethane	19.20	9.856	
31	o-Xylene	19.23		
32	4-Ethyltoluene	20.82	0.100	
33	1,3,5-Trimethylbenzene	20.94	0.109	
34	1,2,4-Trimethylbenzene	21.46	0.111	
35	m-Dichlorobenzene	21.50		
36	Benzyl chloride	21.56		
37	p-Dichlorobenzene	21.67	0.188	
38	o-Dichlorobenzene	22.12	0.188	
39	1,2,4-Trichlorobenzene	24.88	0.667	
40	Hexachlorobitatadiene	25.82	0.305	1.055

[1] Refer to Figures 15 and 16 for peak location

Table 8. Typical Retention Time (minutes) for Selected Organics Using GC-FID-ECD-PID* Analytical System

Compound	Retention Time (minutes) FID	ECD	PID
Acetylene	2.984	----	----
1,3-Butadiene	3.599	----	3.594
Vinyl chloride	3.790	----	3.781
Chloromethane	5.137	----	----
Chloroethane	5.738	----	----
Bromoethane	8.154	----	----
Methylene Chloride	9.232	----	9.218
trans-1,2-Dichloroethylene	10.077	----	10.065
1,1-Dichloroethane	11.190	----	----
Chloroprene	11.502	----	11.491
Perfluorobenzene	13.077	13.078	13.069
Bromochloromethane	13.397	13.396	13.403
Chloroform	13.768	13.767	13.771
1,1,1-Trichloroethane	14.151	14.153	14.158
Carbon Tetrachloride	14.642	14.667	14.686
Benzene/1,2-Dichloroethane	15.128	----	15.114
Perfluortoluene	15.420	15.425	15.412
Trichloroethylene	17.022	17.024	17.014
1,2-Dichloropropene	17.491	17.805	17.522
Bromodichloromethane	18.369	----	----
trans-1,3-Dichloropropylene	19.694	19.693	19.688
Toluene	20.658	----	20.653
cis-1,3-Dichloropropylene	21.461	21.357	21.357
1,1,2-Trichloroethane	21.823	----	----
Tetrachloroethylene	22.340	22.346	22.335
Dibromochloromethane	22.955	22.959	22.952
Chlorobenzene	24.866	----	24.861
m/p-Xylene	25.763	----	25.757
Styrene/o-Xylene	27.036	----	27.030
Bromofluorobenzene	28.665	28.663	28.660
1,1,2,2-Tetrachloroethane	29.225	29.227	29.228
m-Dichlorobenzene	32.347	32.345	32.342
p-Dichlorobenzene	32.671	32.669	32.666
o-Dichlorobenzene	33.885	33.883	33.880

* Varian® 3700 GC equipped with J & W Megabore® DB 624 Capillary Column (30 m X 0.53 I.D. mm) using helium carrier gas.

Table 9. GC-MS-SIM Calibration Table

Last Update: 18 Dec 86 7:54 am
Reference Peak Window: 5.00 Absolute Minutes
Non-Reference Peak Window: 0.40 Absolute Minutes
Sample Amount: 0.000 Uncalibrated Peak RF: 0.000 Multiplier: 1.000

Ret Time	Pk#	Signal	Descr	Amt pptv	Lvl	[Area]	Pk-Type	Partial Name
5.008	1	Mass	85.00 amu	13620	1	72974	1	FREON 12
5.690	2	Mass	50.00 amu	12720	1	36447	1	METHYLCHLORID
6.552	3	Mass	85.00 amu	8380	1	81251	1	FREON 114
6.709	4	Mass	62.00 amu	8050	1	20118	1	VINYLCHLORIDE
7.831	5	Mass	94.00 amu	12210	1	28265	1	METHYLBROMIDE
8.431	6	Mass	64.00 amu	12574	1	16149	1	ETHYLCHLORIDE
9.970	7	Mass	101.00 amu	12380	1	80088	1	FREON 11
10.927	8	Mass	61.00 amu	7890	1	38954	1	VINDENECHLORI
11.209	9	Mass	49.00 amu	12760	1	43507	1	DICHLOROMETHA
11.331	10	Mass	41.00 amu	12650	1	1945	1	ALLYLCHLORIDE
11.595	11	Mass	151.00 amu	7420	1	40530	1	3CHL3FLUETHAN
12.502	12	Mass	63.00 amu	12710	1	61595	1	1,1DICHLOETHA
13.403	13	Mass	61.00 amu	12630	1	50900	1	c-1,2DICHLETH
13.747	14	Mass	83.00 amu	7670	1	40585	1	CHLOROFORM
14.387	15	Mass	62.00 amu	9040	1	33356	1	1,2DICHLETHAN
14.623	16	Mass	97.00 amu	8100	1	38503	1	METHCHLOROFOR
15.038	17	Mass	78.00 amu	10760	1	69119	1	BENZENE
15.183	18	Mass	117.00 amu	8340	1	42737	1	CARBONTETRACH
15.829	19	Mass	63.00 amu	12780	1	38875	1	1,2DICHLPROPA
16.096	20	Mass	130.00 amu	8750	1	30331	1	TRICHLETHENE
16.956	21	Mass	75.00 amu	4540	1	17078	1	c-1,3DICHLPRO
17.492	22	Mass	75.00 amu	3380	1	13294	1	t-1,3DICHLPRO
17.610	23	Mass	97.00 amu	12690	1	32480	1	1,1,2CHLETHAN
17.862	24	Mass	91.00 amu	10010	1	88036	1	TOLUENE
18.485	25	Mass	107.00 amu	6710	1	33350	1	EDB
19.012	26	Mass	166.00 amu	7830	1	43454	1	TETRACHLETHEN
19.729	27	Mass	112.00 amu	7160	1	44224	1	CHLOROBENZENE
20.195	28	Mass	91.00 amu	12740	1	127767	1	ETHYLBENZENE
20.407	29	Mass	91.00 amu	25400	1	200973	1	m,p-XYLENE
20.806	30	Mass	104.00 amu	12390	1	38332	1	STYRENE
20.916	31	Mass	83.00 amu	11690	1	64162	1	TETRACHLETHAN
20.921	32	Mass	91.00 amu	11085	1	90096	1	o-XYLENE
22.528	33	Mass	105.00 amu	12560	1	108747	1	4-ETHYLTOLUEN
22.648	34	Mass	105.00 amu	12620	1	83666	1	1,3,5METHBENZ
23.179	35	Mass	105.00 amu	12710	1	79833	1	1,2,4METHBENZ
23.307	36	Mass	146.00 amu	12650	1	57409	1	m-DICHLBENZEN
23.317	37	Mass	91.00 amu	7900	1	50774	1	BENZYLCHLORID
23.413	38	Mass	146.00 amu	12390	1	58127	1	p-DICHLBENZEN
23.885	39	Mass	146.00 amu	13510	1	52233	1	o-DICHLBENZEN
26.714	40	Mass	180.00 amu	15520	1	18967	1	1,2,4CHLBENZE
27.680	41	Mass	225.00 amu	7470	1	43920	1	HEXACHLBUTADI

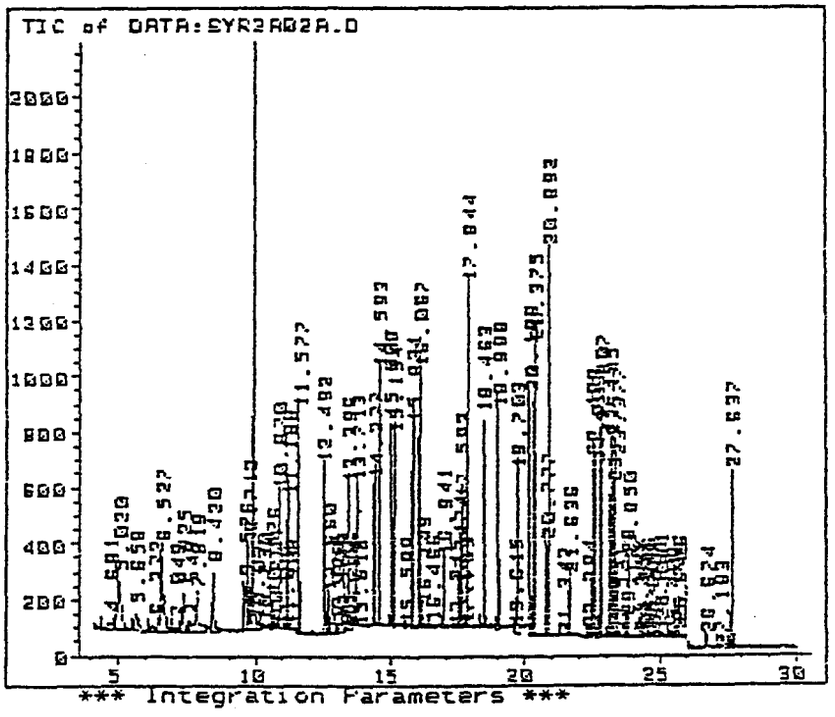
Table 10. Example of Hard-Copy of GC-MS-SIM Analysis

```
Data file: DATA:SYR2A02A.D
File type: GC / MS DATA FILE

Name Info: SYR 1
Misc Info:
Operator : JDP

Date     :  8 Jan 87  10:02 am
Instrment: MS_5970
Inlet    : GC

Sequence index :     1
Als bottle num :     2
Replicate num  :     1
```




```
FALSE : Shoulder Detection Enabled
0.020 : Expected Peak Width (Min)
   11 : Initial Peak Detection Threshold

4.000  THRESHOLD     5.000
4.000  PEAK_WIDTH     0.200
9.800  PEAK_WIDTH     0.060
```

Table 10. (cont.)

Operator: JDF 8 Jan 87 10:02 am
Sample Info : SYR 1
Misc Info:
Integration File Name : DATA:SYR2A02A.I
Sequence Index: 1 Bottle Number : 2

Last Update: 8 Jan 87 8:13 am
Reference Peak Window: 5.00 Absolute Minutes
Non-Reference Peak Window: 0.40 Absolute Minutes
Sample Amount: 0.000 Uncalibrated Peak RF: 0.000 Multiplier: 1.667

Peak Num	Peak Type	Int Type	Ret Time	Signal Description			Compound Name	Area	Amount	
1		1	PP	5.020	Mass	85.00 amu	FREON 12	12893	4011 pptv	
2		1	PP	5.654	Mass	50.00 amu	METHYLCHLORI	4445	2586 pptv	
3		1	BP	6.525	Mass	85.00 amu	FREON 114	7067	1215 pptv	
4		1	PB	6.650	Mass	62.00 amu	VINYLCHLORID	2892	1929 pptv	*
5		1	BP	7.818	Mass	94.00 amu	METHYLBROMID	2401	1729 pptv	
6		1	BB	8.421	Mass	64.00 amu	ETHYLCHLORID	2134	2769 pptv	*
7		1	BV	9.940	Mass	101.00 amu	FREON 11	25069	6460 pptv	
8		1	BP	10.869	Mass	61.00 amu	VINDENECHLOR	5034	1700 pptv	
9		1	BP	11.187	Mass	49.00 amu	DICHLOROMETH	4803	2348 pptv	
10		1	PP	11.225	Mass	41.00 amu	ALLYLCHLORID	761	8247 pptv	*
11		1	BP	11.578	Mass	151.00 amu	3CHL3FLUETHA	5477	1672 pptv	
12		1	BP	12.492	Mass	63.00 amu	1,1DICHLOETH	5052	1738 pptv	*
13		1	VP	13.394	Mass	61.00 amu	c-1,2DICHLET	4761	1970 pptv	
14		1	PH	13.713	Mass	83.00 amu	CHLOROFORM	5327	1678 pptv	
15		1	BP	14.378	Mass	62.00 amu	1,2DICHLETHA	5009	2263 pptv	
16		1	PB	14.594	Mass	97.00 amu	METHCHLOROFO	6656	2334 pptv	
17		1	VP	15.009	Mass	78.00 amu	BENZENE	8352	2167 pptv	
18		1	VP	15.154	Mass	117.00 amu	CARBONTETRAC	5888	1915 pptv	
19		1	BB	15.821	Mass	63.00 amu	1,2DICHLPROP	3263	1799 pptv	*
20		1	BB	16.067	Mass	130.00 amu	TRICHLETHENE	4386	2109 pptv	
21		1	PB	16.941	Mass	75.00 amu	c-1,3DICHLPR	2228	967.3 pptv	
22		1	BP	17.475	Mass	75.00 amu	t-1,3DICHLPR	1626	689.2 pptv	
23		1	BB	17.594	Mass	97.00 amu	1,1,2CHLETHA	2721	1772 pptv	
24		1	BV	17.844	Mass	91.00 amu	TOLUENE	14417	2733 pptv	
25		1	PB	18.463	Mass	107.00 amu	EDB	4070	1365 pptv	*
26		1	PH	18.989	Mass	166.00 amu	TETRACHLETHE	6674	2065 pptv	
27		1	PB	19.705	Mass	112.00 amu	CHLOROBENZEN	5648	1524 pptv	
28		1	BP	20.168	Mass	91.00 amu	ETHYLBENZENE	11084	1842 pptv	
29		1	PB	20.372	Mass	91.00 amu	m,p-XYLENE	17989	3790 pptv	
30		1	BV	20.778	Mass	104.00 amu	STYRENE	3145	1695 pptv	
31		1	BH	20.887	Mass	83.00 amu	TETRACHLETHA	4531	1376 pptv	
32		1	BP	20.892	Mass	91.00 amu	o-XYLENE	9798	2010 pptv	
33		1	VV	22.488	Mass	105.00 amu	4-ETHYLTOLUE	7694	1481 pptv	
34		1	VB	22.609	Mass	105.00 amu	1,3,5METHBEN	6781	1705 pptv	
35		1	BB	23.144	Mass	105.00 amu	1,2,4METHBEN	7892	2095 pptv	
36		1	BV	23.273	Mass	146.00 amu	m-DICHLBENZE	3046	1119 pptv	
37		1	VV	23.279	Mass	91.00 amu	BENZYLCHLORI	3880	1006 pptv	
38		1	VB	23.378	Mass	146.00 amu	p-DICHLBENZE	6090	2164 pptv	
39		1	BP	23.850	Mass	146.00 amu	o-DICHLBENZE	2896	1249 pptv	
40		1	BB	26.673	Mass	180.00 amu	1,2,4CHLBENZ	562	767.1 pptv	
41		1	BB	27.637	Mass	225.00 amu	HEXACHLBUTAD	6309	1789 pptv	

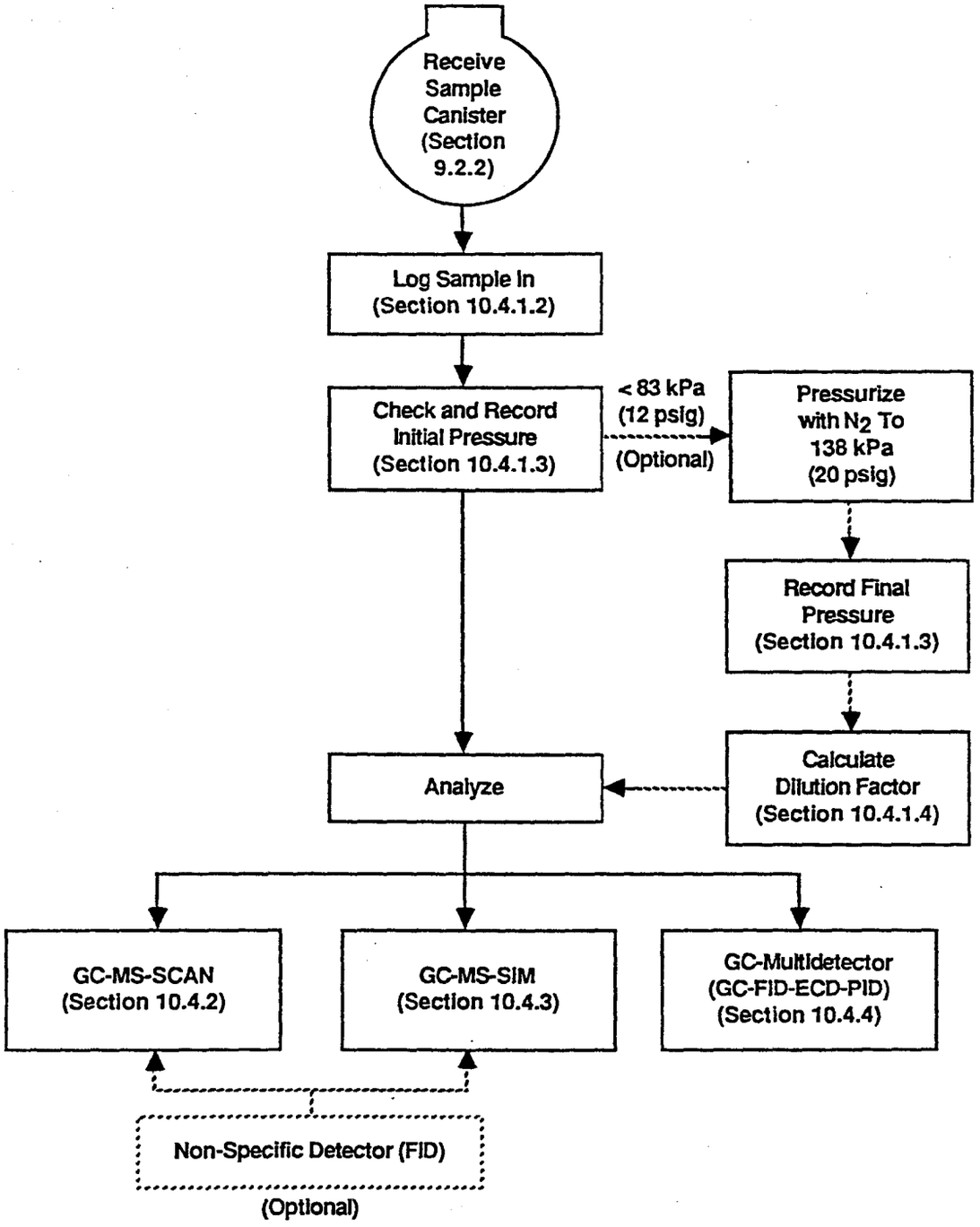


Figure 1. Analytical Systems Available for Canister VOC Identification and Quantitation

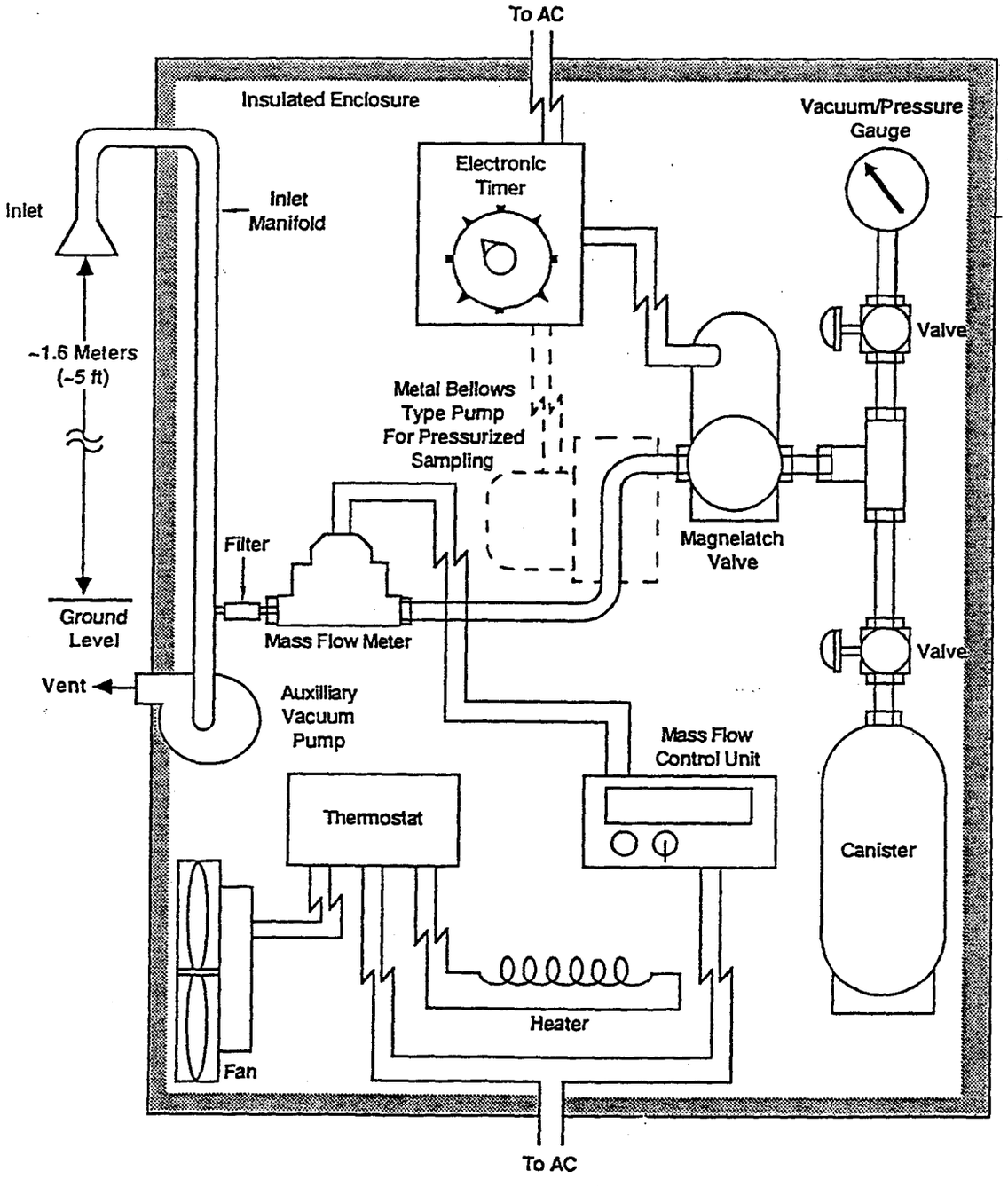


Figure 2. Sampler Configuration for Subatomic Pressure or Pressurized Canister Sampling

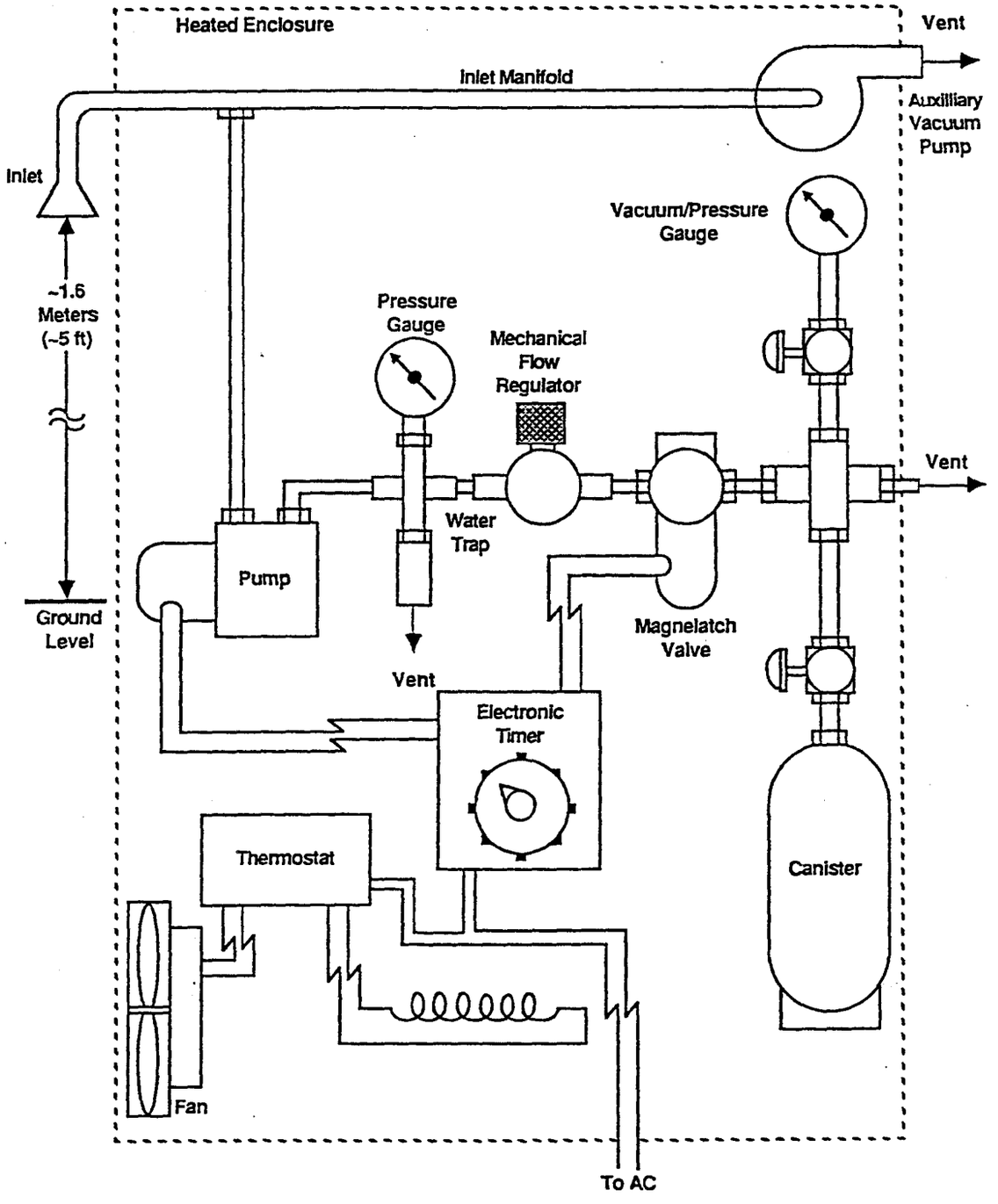


Figure 3. Alternative Sampler Configuration for Pressurized Canister Sampling

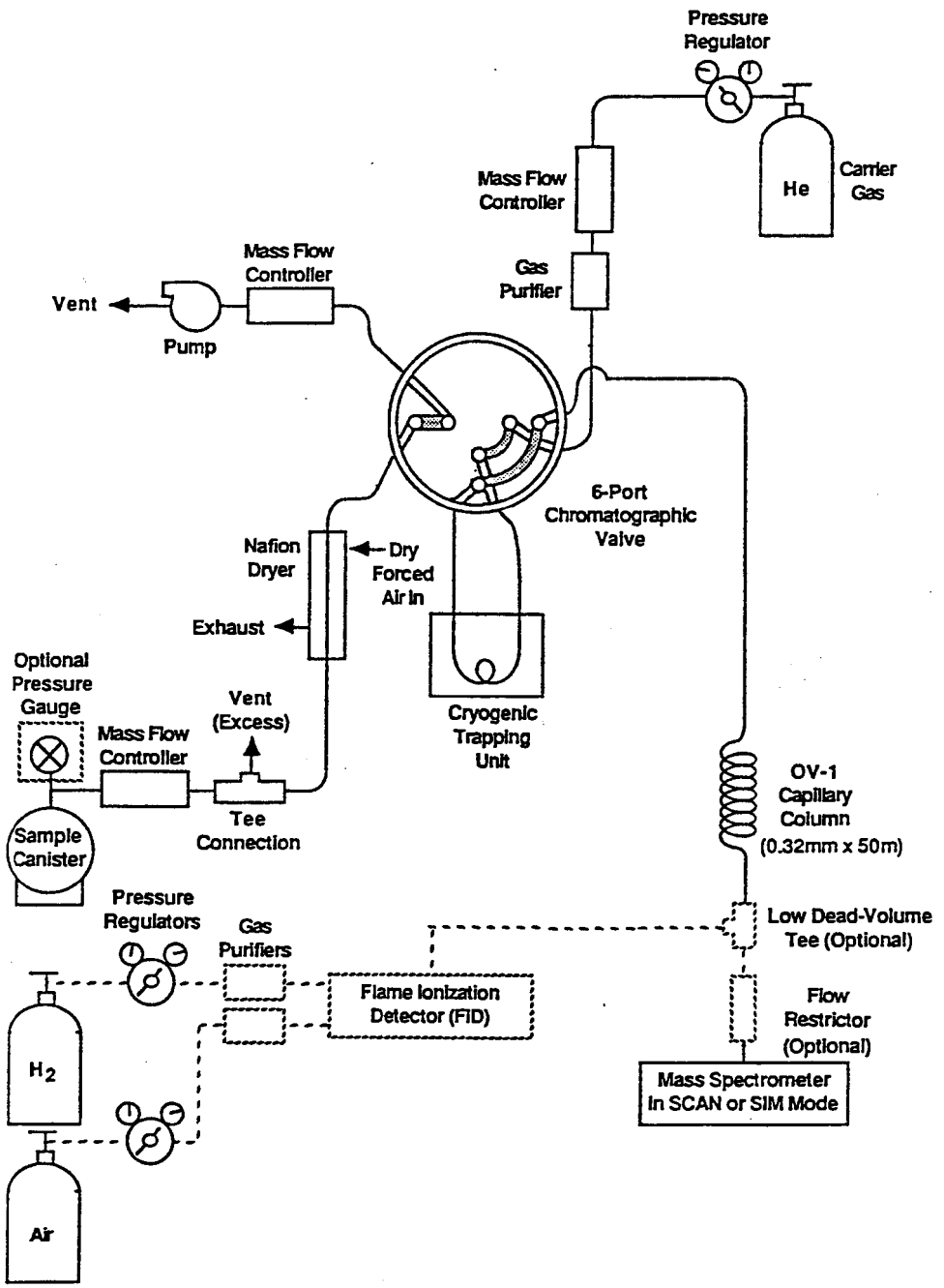


Figure 4. Canister Analysis Utilizing GC-MS-SCAN-SIM Analytical System with Optional Flame Ionization Detector with the 6-Port Chromatographic Valve in the Sample Desorption Mode

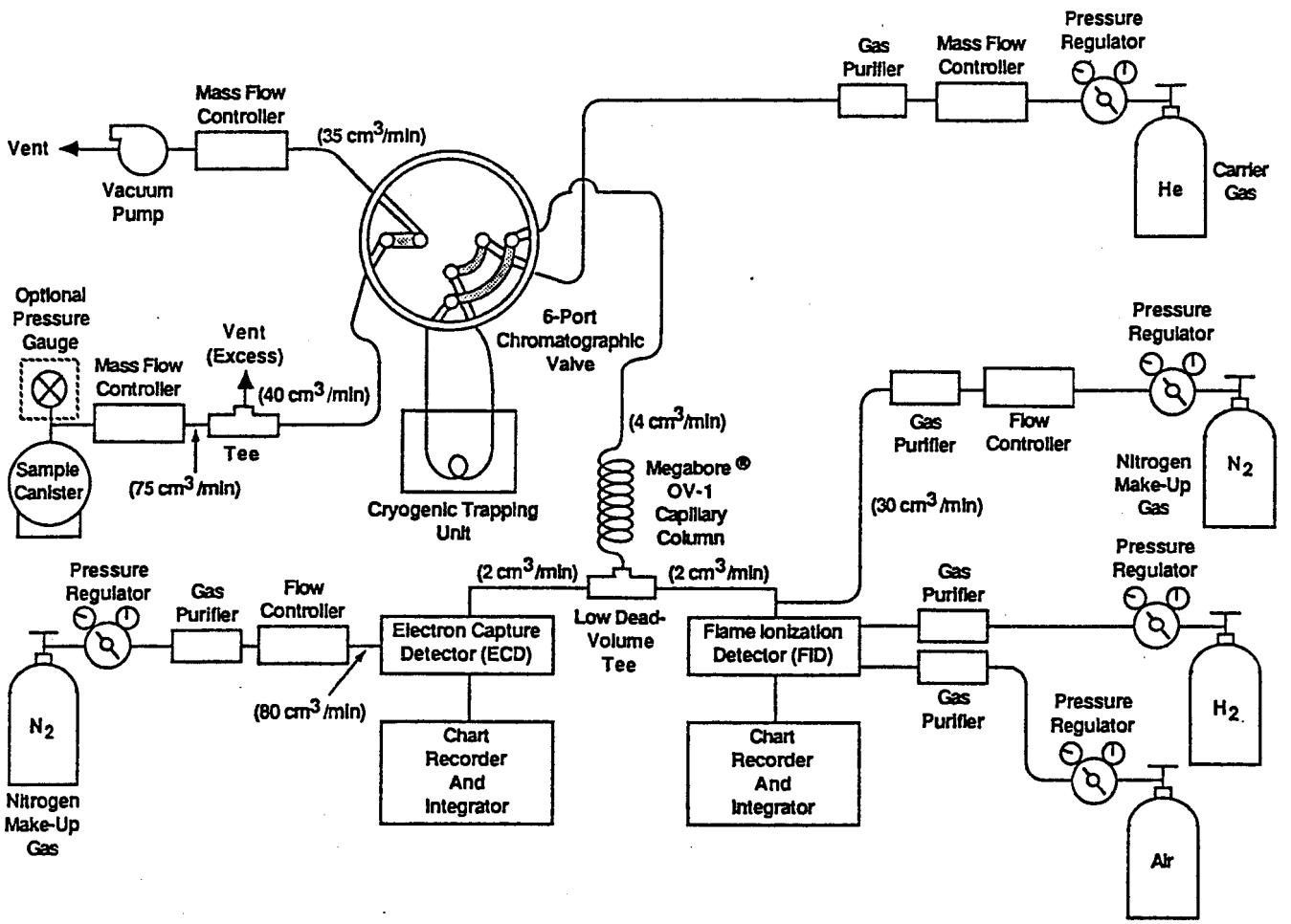


Figure 5. GC-FID-ECD Analytical System with the 6-Port Chromatographic Valve in the Sample Desorption Mode

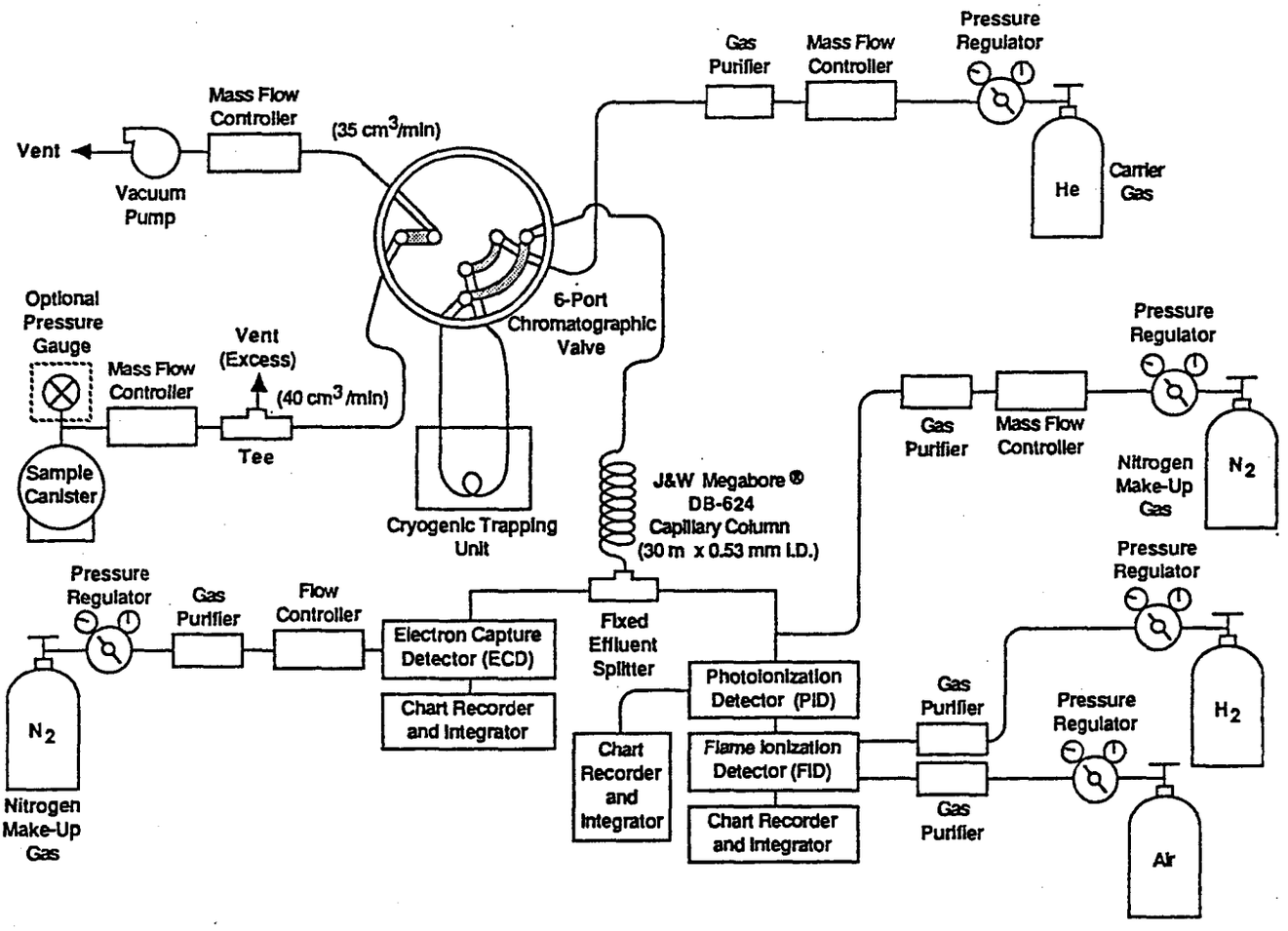


Figure 6. System Configuration Associated with the GC-FID-ECD-PID Analytical System with the 6-Port Chromatographic Valve in the Sample Desorption Mode

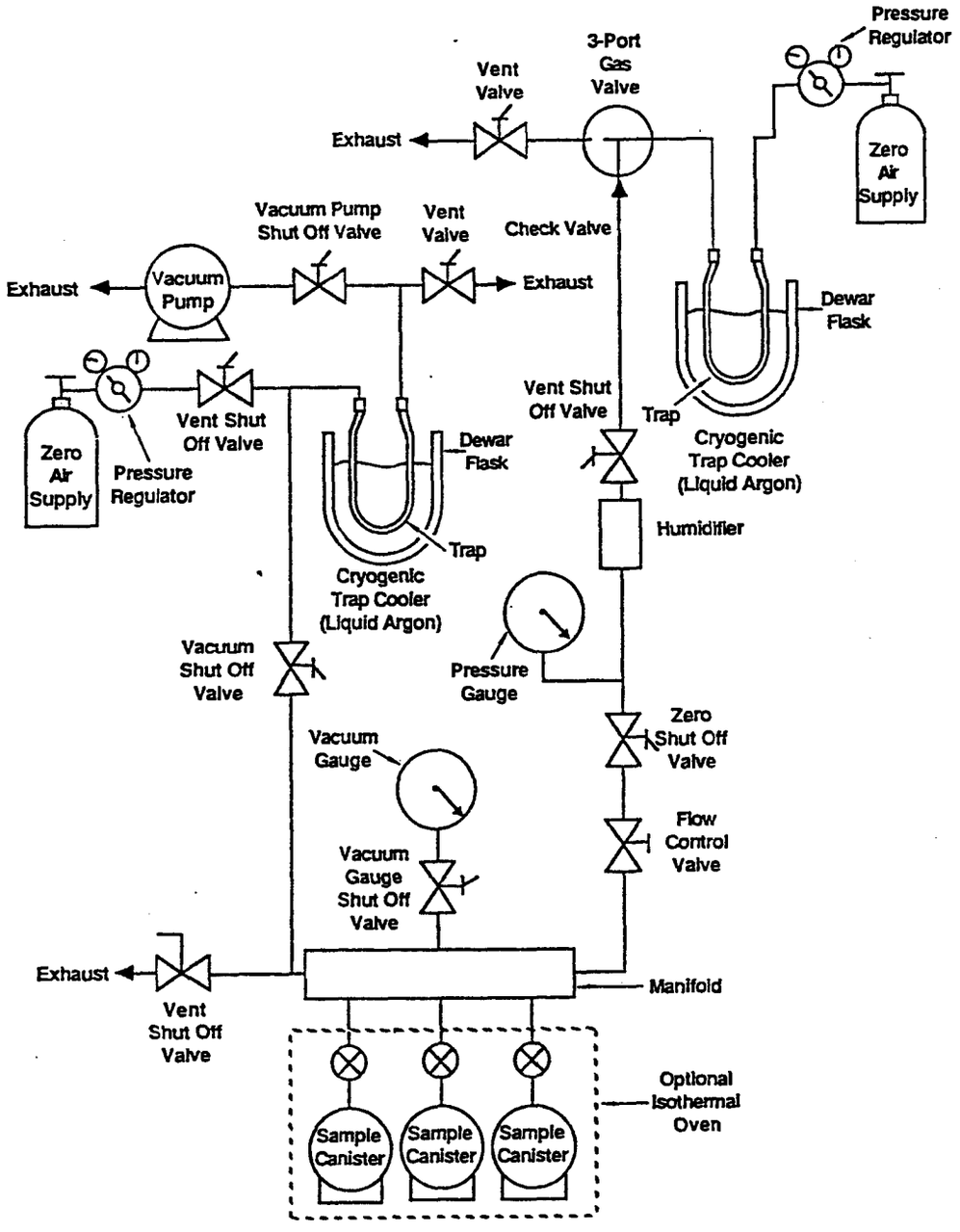


Figure 7. Canister Cleaning System

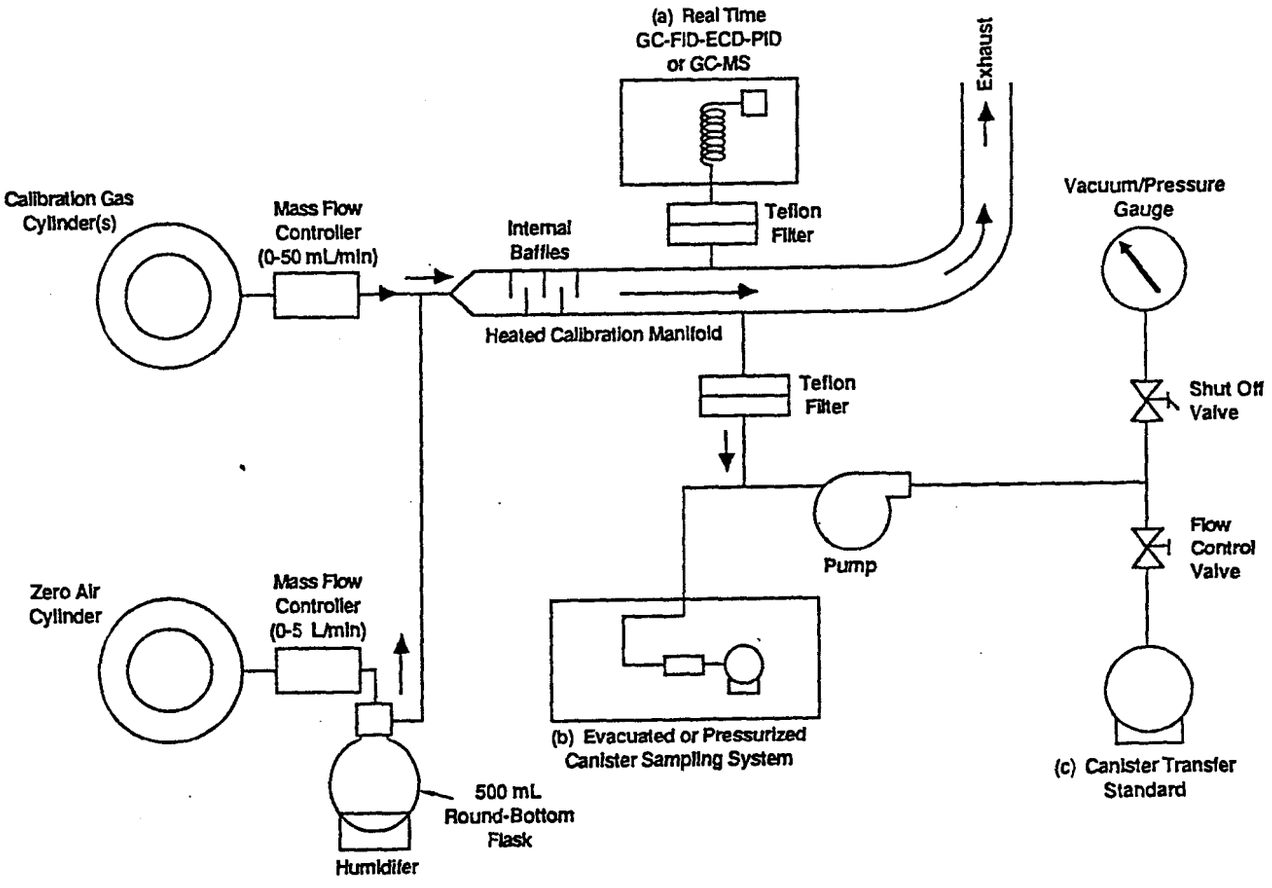
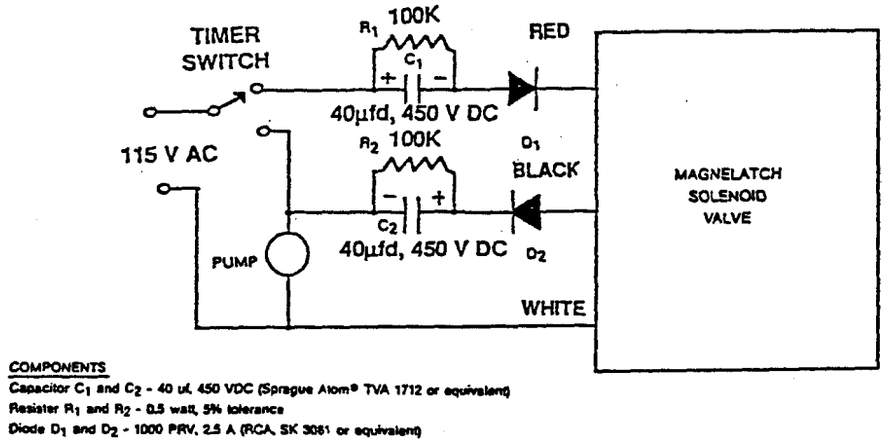


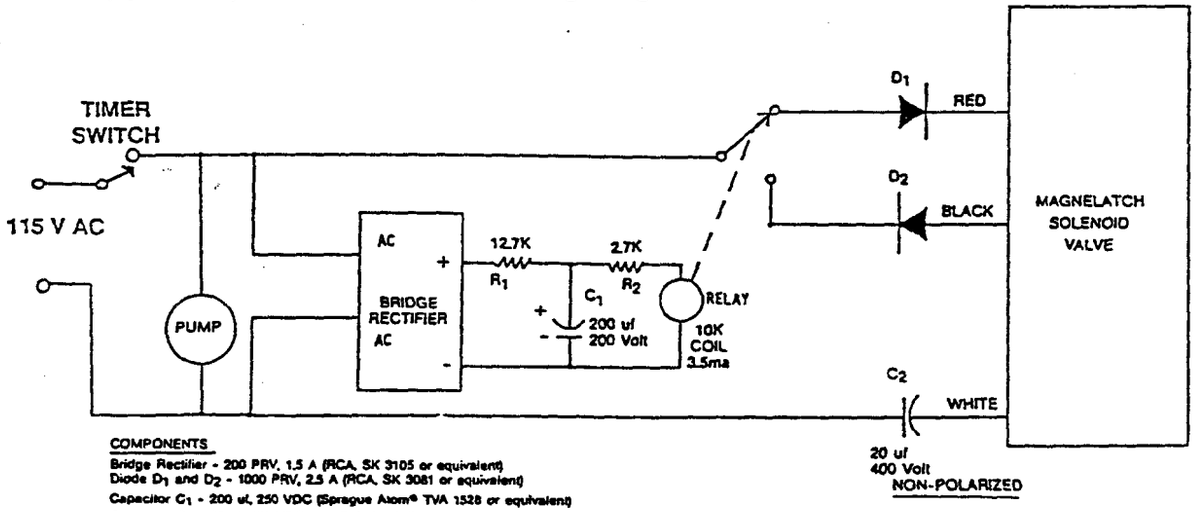
Figure 8. Schematic of Calibration System and Manifold for a) Analytical System Calibration, b) Testing Canister Sampling System and c) Preparing Canister Transfer Standards



COMPONENTS

Capacitor C_1 and C_2 - 40 uf, 450 VDC (Sprague Atom® TVA 1712 or equivalent)
Resister R_1 and R_2 - 0.5 watt, 5% tolerance
Diode D_1 and D_2 - 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)

(a). Simple Circuit For Operating Magnelatch Valve



COMPONENTS

Bridge Rectifier - 200 PRV, 1.5 A (RCA, SK 3105 or equivalent)
Diode D_1 and D_2 - 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)
Capacitor C_1 - 200 uf, 250 VDC (Sprague Atom® TVA 1528 or equivalent)
Capacitor C_2 - 20 uf, 400 VDC Non-Polarized (Sprague Atom® TVAN 1652 or equivalent)
Relay - 10,000 ohm coil, 3.5 ma (AMF Potter and Brumfield, KCP 5, or equivalent)
Resister R_1 and R_2 - 0.5 watt, 5% tolerance

(b). Improved Circuit Designed To Handle Power Interruptions

Figure 9. Electrical Pulse Circuits for Driving Skinner Magnelatch Solenoid Valve with a Mechanical Timer

CANISTER SAMPLING FIELD DATA SHEET

A. GENERAL INFORMATION

SITE LOCATION: _____
SITE ADDRESS: _____
_____
_____
SAMPLING DATE: _____

SHIPPING DATE: _____
CANISTER SERIAL NO. _____
SAMPLER ID: _____
OPERATOR: _____
CANISTER LEAK CHECK DATE: _____

B. SAMPLING INFORMATION

TEMPERATURE

	INTERIOR	AMBIENT	MAXIMUM	MINIMUM
START				
STOP				

PRESSURE

CANISTER PRESSURE	

SAMPLING TIMES

	LOCAL TIME	ELAPSED TIME METER READING
START		
STOP		

FLOW RATES

MANIFOLD FLOW RATE	CANISTER FLOW RATE	FLOW CONTROLLER READOUT

SAMPLING SYSTEM CERTIFICATION DATE: _____
QUARTERLY RECERTIFICATION DATE: _____

C. LABORATORY INFORMATION

DATE RECEIVED: _____
RECEIVED BY: _____
INITIAL PRESSURE: _____
FINAL PRESSURE: _____
DILUTION FACTOR: _____
ANALYSIS
GC-FID-ECD DATE: _____
GC-MSD-SCAN DATE: _____
GC-MSD-SIM DATE: _____
RESULTS*: _____
_____
GC-FID-ECD: _____
GC-MSD-SCAN: _____
GC-MSD-SIM: _____

_____
SIGNATURE/TITLE

* ATTACH DATA SHEETS

Figure 10. Canister Sampling Field Data Sheet

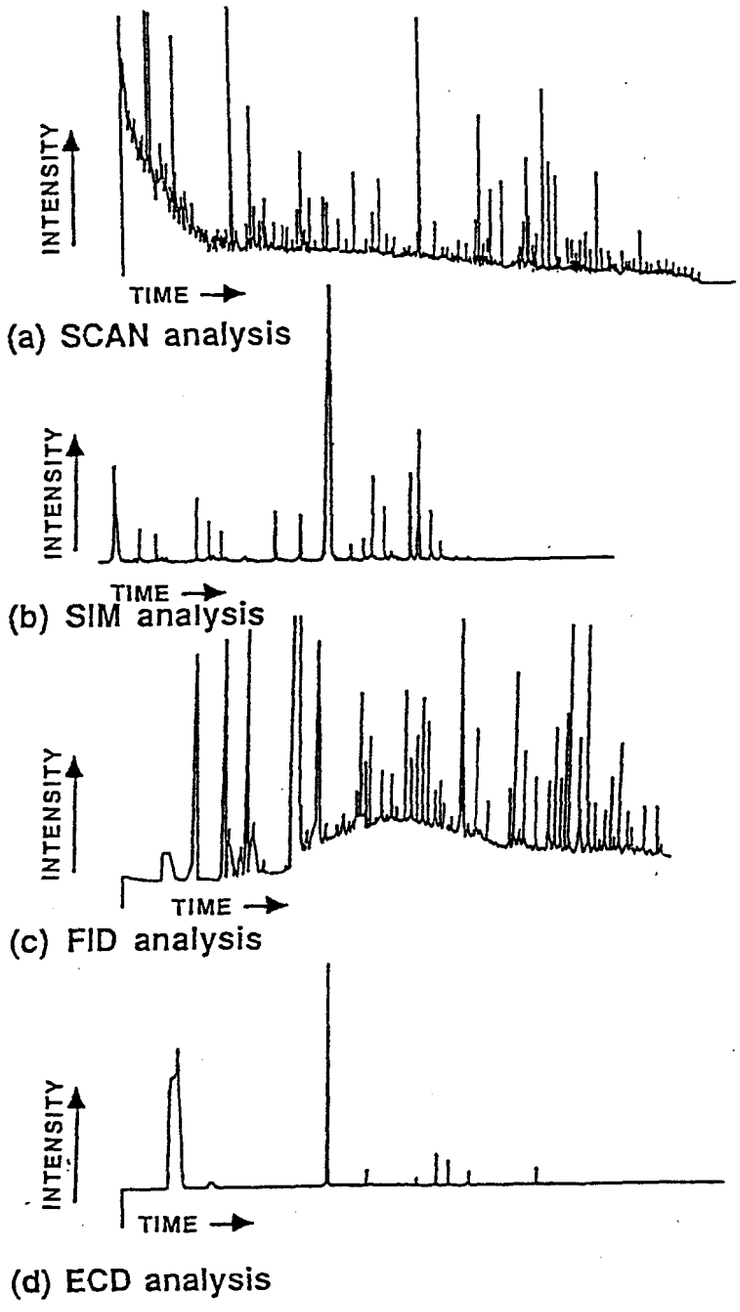


Figure 11. Typical Chromatograms of a VOC Sample Analyzed by GC-MS-SCAN-SIM Mode and GC-Multidetector Mode

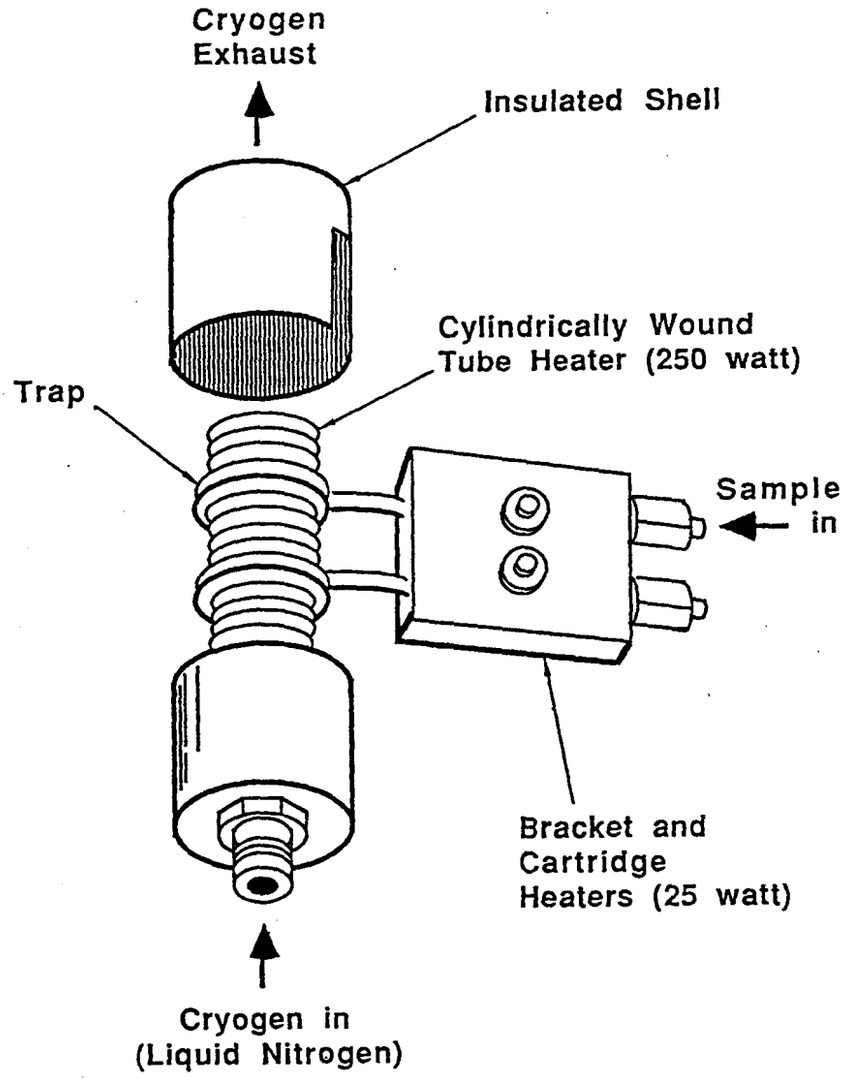


Figure 12. Cryogenic Trapping Unit

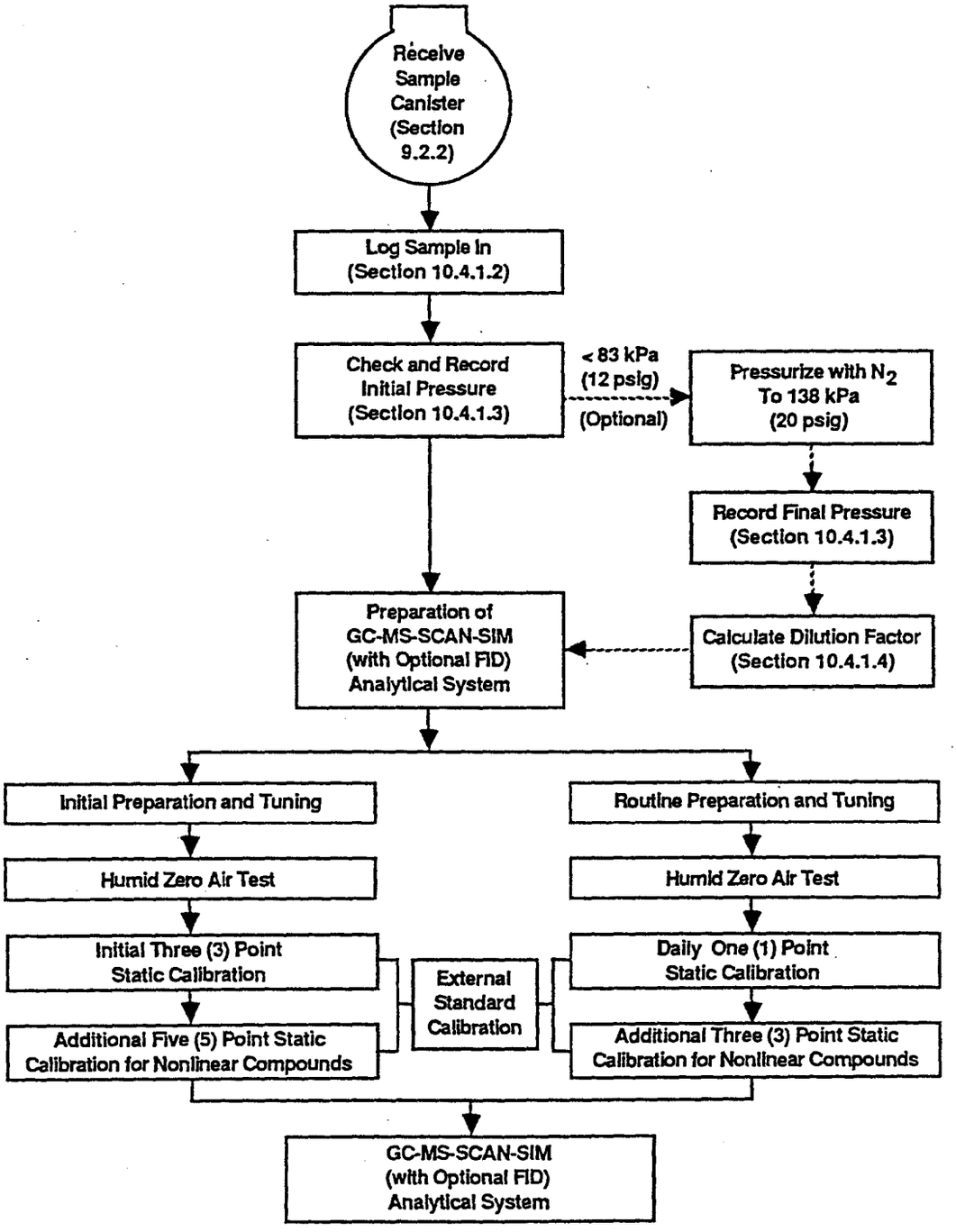


Figure 13. Flowchart of GC-MS-SCAN-SIM Analytical System Preparation (with Optional FID System)

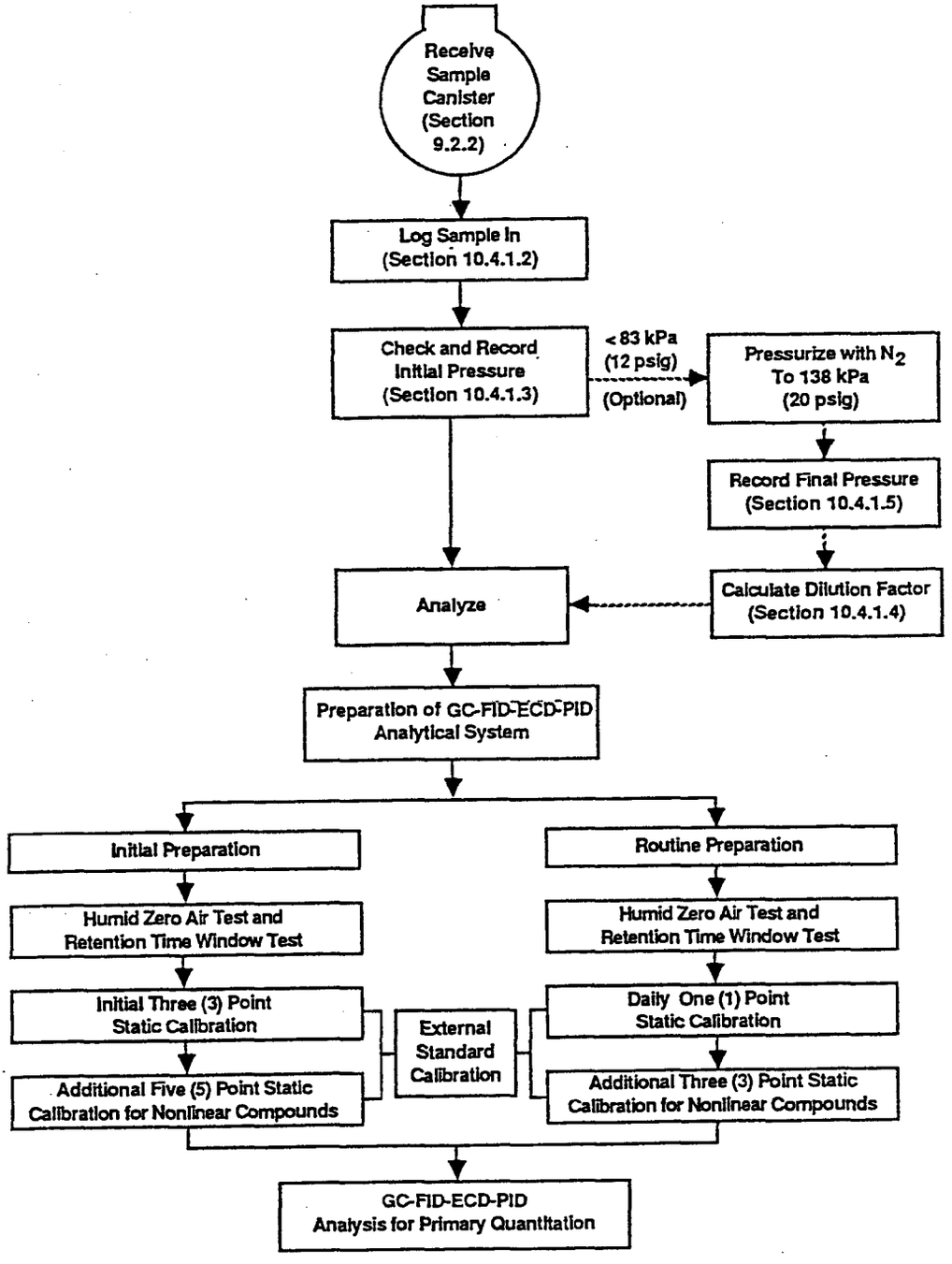


Figure 14. Flowchart of GC-FID-ECD-PID Analytical System Preparation

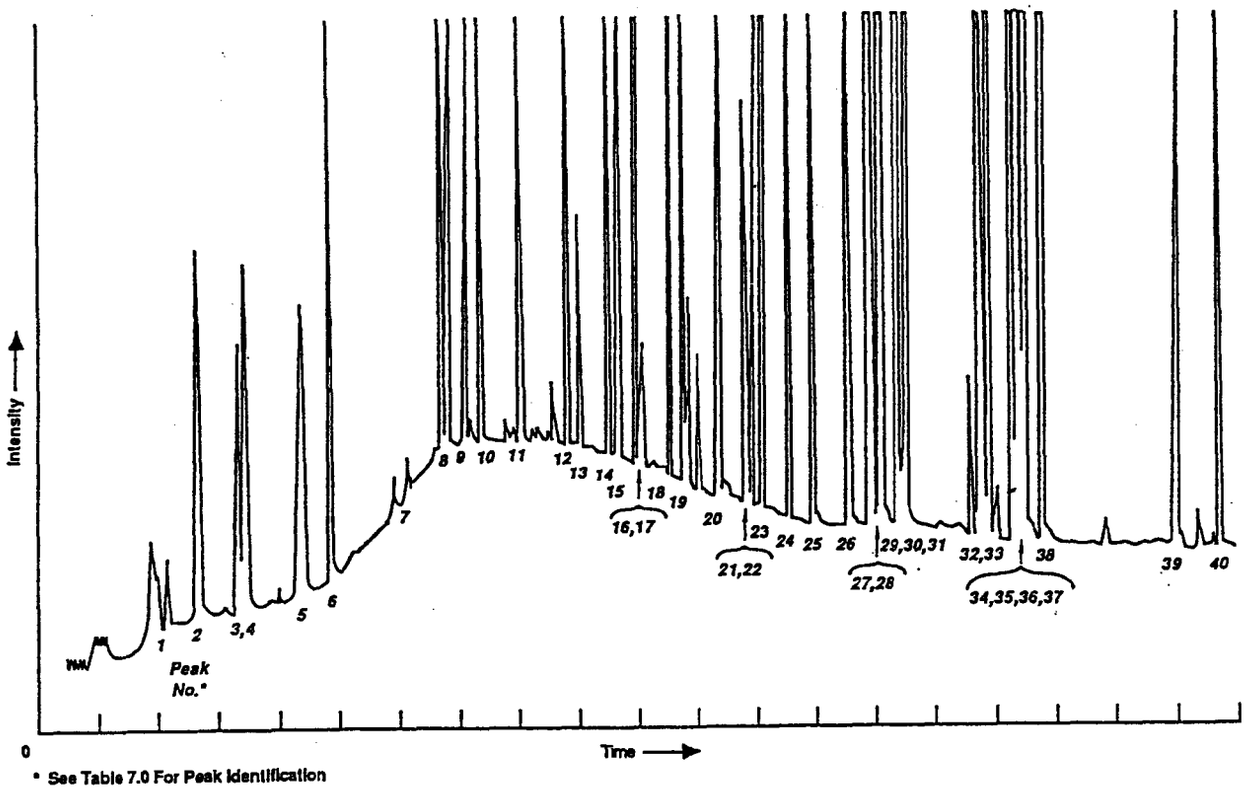


Figure 15. Typical FID Response to Selective VOCs

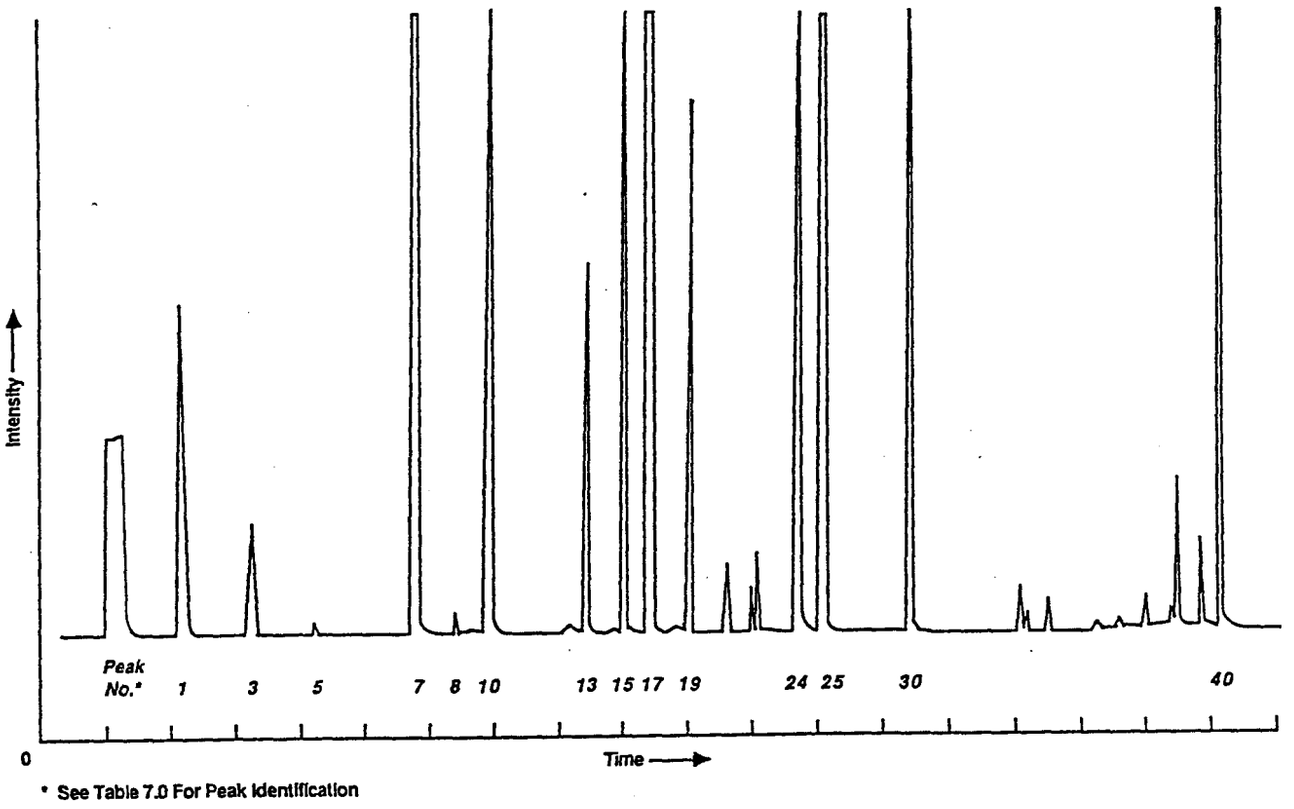
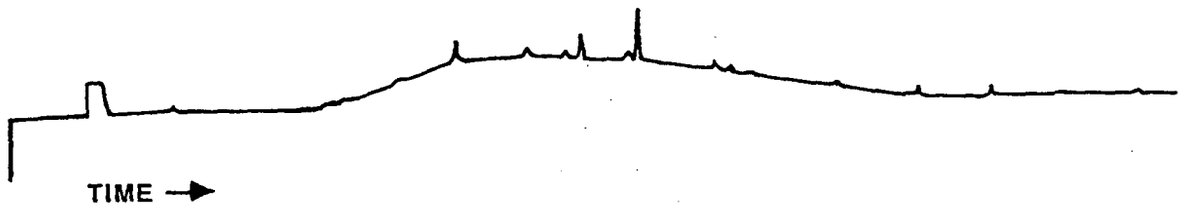
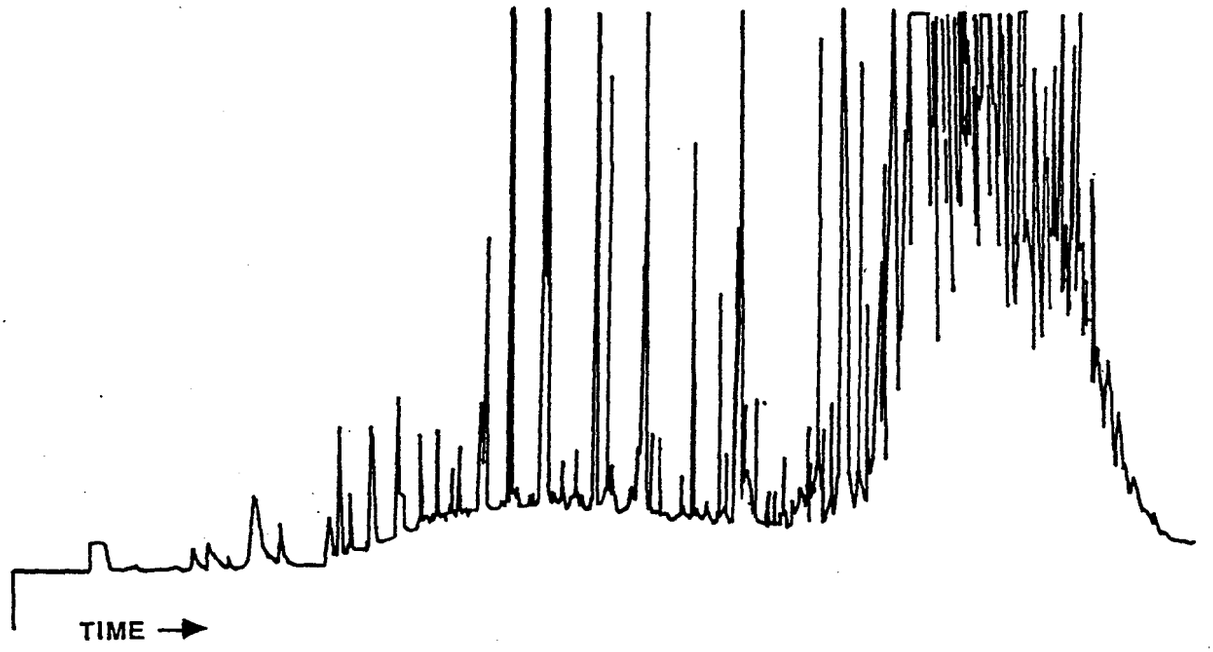


Figure 16. Typical ECD Response to Selective VOCs



(a). Certified Sampler



(b). Contaminated Sampler

Figure 17. Example of Humid Zero Air Test Results for a Clean Sampler (a) and a Contaminated Sampler (b)

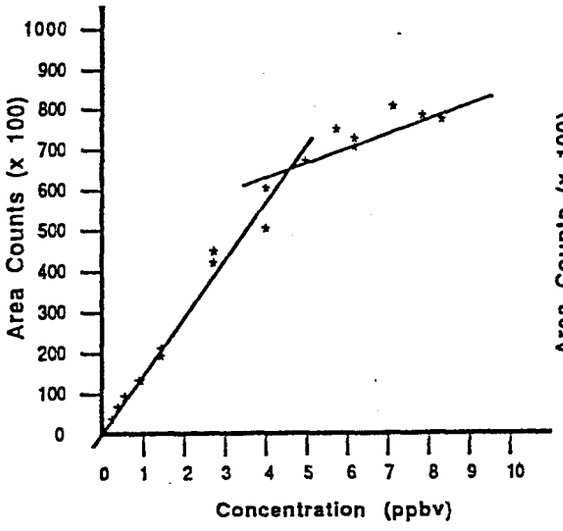


FIGURE 18(a). NONLINEAR RESPONSE OF TETRACHLOROETHYLENE ON THE ECD

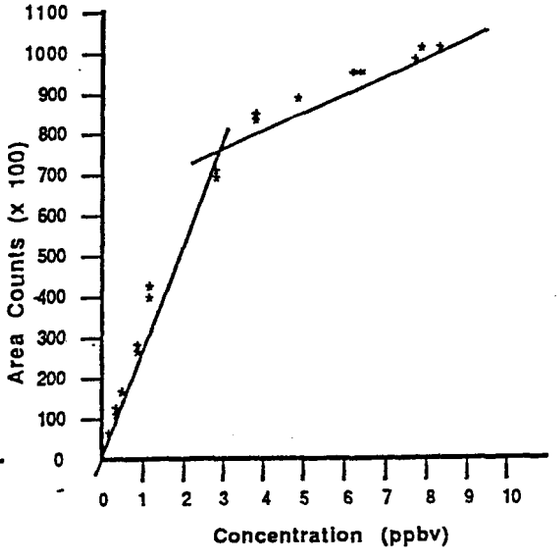


FIGURE 18(b). NONLINEAR RESPONSE OF CARBON TETRACHLORIDE ON THE ECD

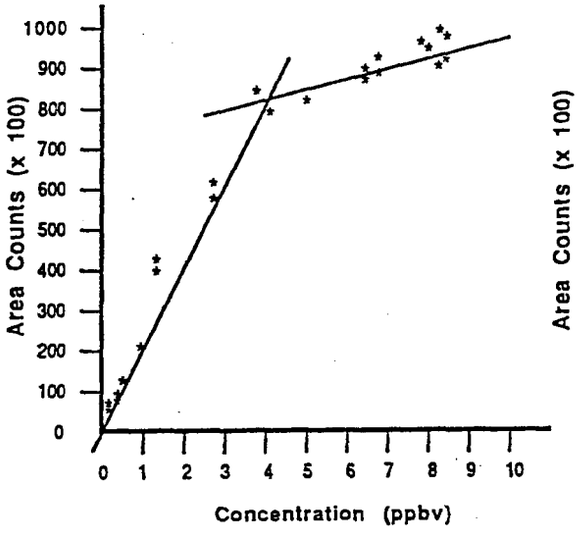


FIGURE 18(c). NONLINEAR RESPONSE OF HEXACHLOROBUTADIENE ON THE ECD

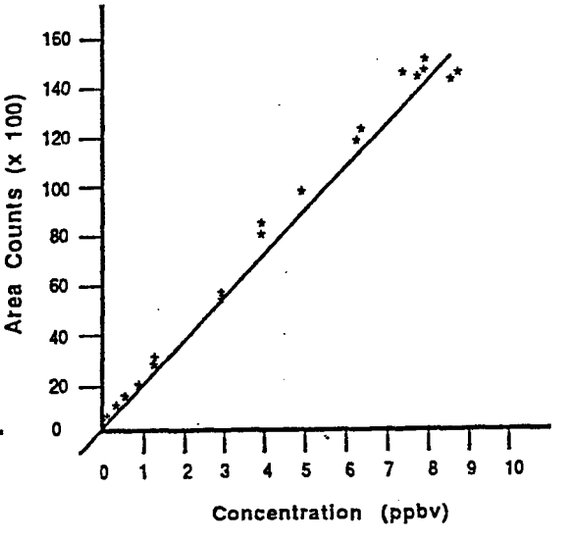


FIGURE 18(d). LINEAR RESPONSE OF CHLOROFORM ON THE ECD

Figure 18. Response of ECD to Various VOCs

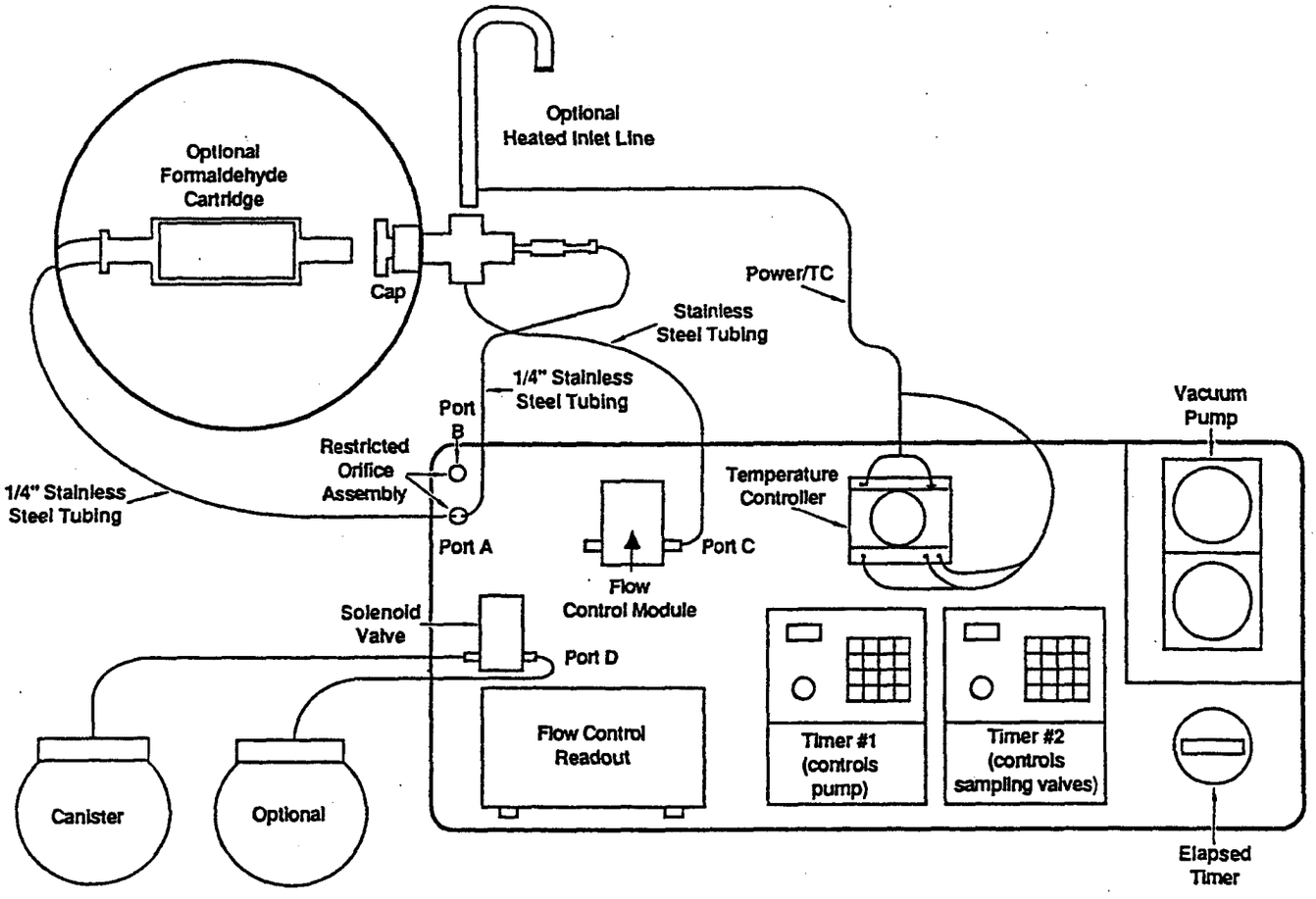


Figure 19. U.S. Environmental Protection Agency UTAP, Schematic of Sample Inlet Connections Sampler

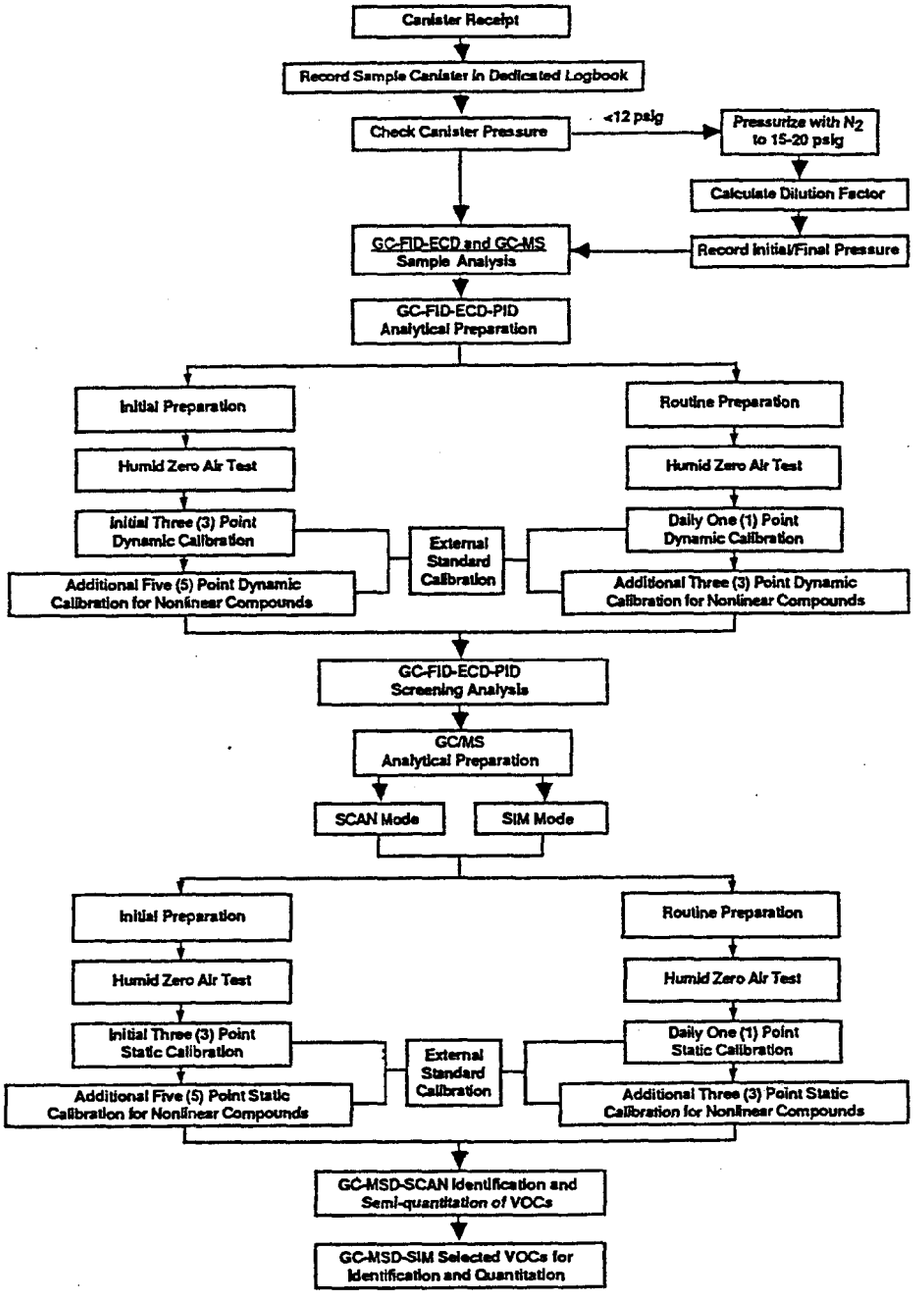


Figure 20. Flowchart of Analytical Systems Preparation

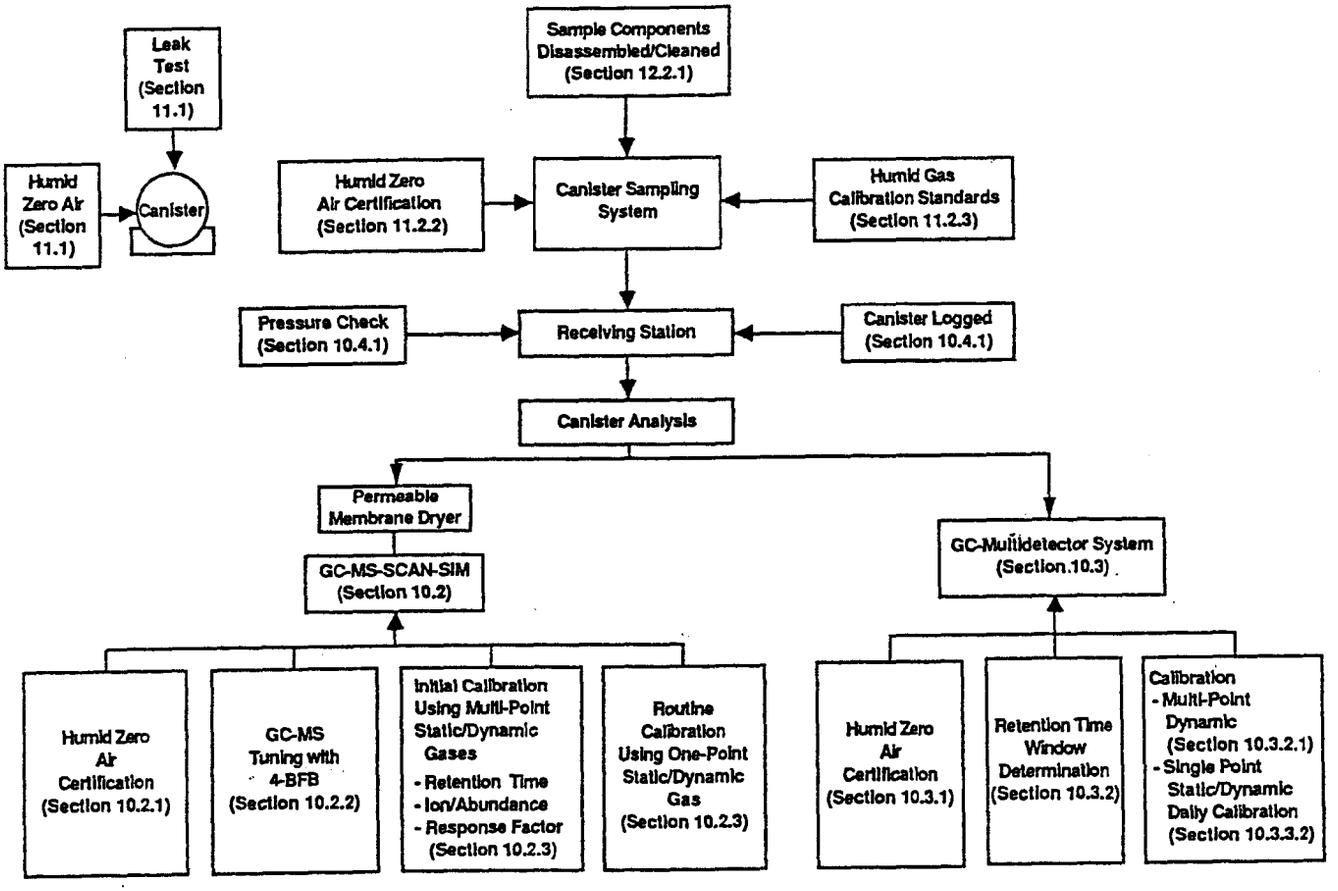


Figure 21. System Quality Assurance/Quality Control (QA/QC) Activities Associated with Various Analytical Systems

AVAILABILITY OF AUDIT CYLINDERS FROM UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (USEPA) PROGRAMS/REGIONAL OFFICES, STATE AND LOCAL AGENCIES AND THEIR CONTRACTORS

1. Availability of Audit Cylinders

1.1 The USEPA has available, at no charge, cylinder gas standards of hazardous organic compounds at the ppb level that may be used to audit the performance of indoor air source measurement systems.

1.2 Each audit cylinder contains 5 to 18 hazardous organic compounds in a balance of N_2 gas. Audit cylinders are available in several concentration ranges. The concentration of each organic compound in the audit cylinder is within the range illustrated in Table A-1.

2. Audit Cylinder Certification

2.1 All audit cylinders are periodically analyzed to assure that cylinder concentrations have remained stable.

2.2 All stability analyses include quality control analyses of ppb hazardous organic gas standards prepared by the National Bureau of Standards for USEPA.

3. Audit Cylinder Acquisition

3.1 USEPA program/regional offices, State/local agencies, and their contractors may obtain audit cylinders (and an audit gas delivery system, if applicable) for performance audits during:

- RCRA Hazardous Waste Trial Burns For PHOCs, and
- Ambient/Indoor Air Measurement of Toxic Organics.

3.2 The audit cylinders may be acquired by contacting:

Robert L. Lampe
U.S. Environmental Protection Agency
Quality Assurance Division
MD-77B
Research Triangle Park, NC 27711
919-541-4531

Table A-1. Available USEPA Performance Audit Cylinders

Group I Compounds	Group II Compounds	Group III Compounds
Carbon tetrachloride	Trichloroethylene	Pyridine (Pyridine in Group III cylinders but certified analysis not available)
Chloroform	1,2-dichloroethan	
Perchloroethylene	1,2-dibromoethane	
Vinyl chloride	Trichlorofluoromethane (Freon-11)	Vinylidene chloride
Benzene		1,1,2-trichloro-1,2,2 trifluoroethane (Freon-113)
	Dichlorodifluoromethane (Freon-12)	1,2-dichloro-1,1,2,2 tetrafluoroethane (Freon-114)
	Bromomethane	Acetone
	Methyl ethyl ketone	1-4 Dioxane
	1,1,1-trichloroethane	Toluene
		Chlorobenzene

Group I Ranges	Group II Ranges	Group III Ranges
7 to 90 ppb	7 to 90 ppb	7 to 90 ppb
90 to 430 ppb	90 to 430 ppb	90 to 430 ppb
430 to 10,000 ppb		

Group IV Compounds	Group V Compounds	
Acrylonitrile	Carbon tetrachloride	Methylene chloride
1,3-butadiene	Chloroform	Trichlorofluoromethane (Freon-11)
Ethylene oxide	Perchloroethylene	Bromomethane
Methylene chloride	Vinyl chloride	Toluene
Propylene oxide	Benzene	Chlorobenzene
o-xylene	Trichloroethylene	1,3-Butadiene
	1,2-dichloroethane	o-xylene
	1,2-dibromoethane	Ethyl benzene 1,2-dichloropropane
	1,1,1-trichloroethane	

Group IV Ranges	Group V Ranges
7 to 90 ppb	1 to 40 ppb
430 to 10,000 ppb	

OPERATING PROCEDURES FOR A PORTABLE GAS CHROMATOGRAPH EQUIPPED WITH A PHOTOIONIZATION DETECTOR

1. Scope

This procedure is intended to screen indoor air environments for volatile organic compounds. Screening is accomplished by collection of VOC samples within an area and analysis on-site using a portable gas chromatograph/integrator (Photovac Models 10S10, 10S50) or equivalent. This procedure is not intended to yield quantitative or definite qualitative information regarding the substances detected. Rather, it provides a chromatographic "profile" of the occurrence and intensity of unknown volatile compounds which assists in placement of fixed-site samplers.

2. Applicable Documents

2.1 ASTM Standards

E260 Recommended Practice for General Gas Chromatography Procedures
E355 Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

Portable Instruments User's Manual for Monitoring VOC Sources, EPA-34011-86-015, U.S. Environmental Protection Agency, Washington, DC, June, 1986.

3. Summary of Method

3.1 An air sample is extracted directly from indoor air and analyzed on-site by a portable GC.

3.2 Analysis is accomplished by drawing an accurate volume of indoor air through a sampling port and into a concentrator, then the sample air is transported by carrier gas onto a packed column and into a PID, resulting in response peak(s). Retention times are compared with those in a standard chromatogram to predict the probable identity of the sample components.

4. Significance

4.1 VOCs are emitted into the indoor atmosphere from a variety of sources including diffusion from outdoor sources, manufacturing processes, and use of various products, appliances, and building materials. Many of these VOC emissions are acutely toxic; therefore, their determination in indoor air is necessary to assess human health impacts.

4.2 Conventional methods for VOC determination use solid sorbent and canister sampling techniques.

4.3 Collection of indoor air samples in canisters provides: 1) convenient integration of indoor samples over a specific time period (e.g, 2 hours); 2) remote sampling and central analysis; 3) ease of storing and shipping samples, if necessary; 4) unattended sample

collection; 5) analysis of samples from multiple sites with one analytical system; and 6) collection of sufficient sample volume to allow assessment of measurement precision and/or analysis of samples by several analytical systems.

4.4 The use of portable GC equipped with multidetectors has assisted air toxics programs by using the portable GC as a "screening tool" to determine "hot spots," potential interferences, and semiquantitation of VOCs/SVOCs, prior to locating more traditional fixed-site samplers.

5. Definitions

Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D1356 and E355. Abbreviations and symbols pertinent to this method are defined at point of use. Additional abbreviations and symbols are provided in Appendices A-1 and B-2 of this method.

6. Interferences

6.1 The most significant interferences result from extreme differences in limits of detection (LOD) among the target VOCs (Table B-1). Limitations in resolution associated with indoor temperature, chromatography and the relatively large number of chemicals result in coelution of many of the target components. Coelution of compounds with significantly different PID sensitivities will mask compounds with more modest sensitivities. This will be most dramatic in interferences from benzene and toluene.

6.2 A typical chromatogram and peak assignments of a standard mixture of target VOCs (under the prescribed analytical conditions of this method) are illustrated in Figure B-1. Samples which contain a highly complex mixture of components and/or interfering levels of benzene and toluene are analyzed on a second, longer chromatographic column. The same liquid phase in the primary column is contained in the alternate column but at a higher percent loading.

6.3 Recent designs in commercially available GCs (Table B-2) have pre-concentrator capabilities for sampling lower concentrations of VOCs, pre-column detection with back-flush capability for shorter analytical time, constant column temperature for method precision and accuracy and multidetector (PID, ECD, and FID) capability for versatility. Many of these newer features address the weaknesses and interferences mentioned above.

7. Apparatus

7.1 Gas Chromatograph - A GC (Photovac Inc., 739 B Parks Ave, Huntington, NY, 11743, Model 10S10 or 10S50), or equivalent used for surveying indoor air environments (which could employ a multidetector) for sensing numerous VOCs compounds eluting from a packed column at room temperatures. This particular portable GC procedure is written employing the photoionization detector as its major sensing device, as part of the Photovac Model 10S10 portable GC survey tool. Chromatograms are developed on a column of 3% SP-2100 on 100/120 Supelcoport (0.66 m x 3.2 mm I.D.) with a flow of 30 cm^3/min air.

7.2 GC accessories - In addition to the basic gas chromatograph, several other pieces of equipment are required to execute the survey sampling. Those include gas-tight syringes for standard injection, alternate carrier gas supplies, high pressure connections for filling the internal carrier gas reservoir, and if the Model 10S10 is used, a recording integrator (Hewlett Packard, Avondale, PA, Model 3390A), or equivalent.

8. Reagents and Materials

8.1 Carrier Gas - "Zero" air [<0.1 ppm total hydrocarbon (THC)] is used as the carrier gas. This gas is conveniently contained in 0.84 m^3 (30 ft^3) aluminum cylinders. Carrier gas of poorer quality may result in spurious peaks in sample chromatograms. A Brooks, Type 1355-00FIAAA rotameter (or equivalent) with an R-215-AAA tube and glass float is used to set column flow.

8.2 System Performance Mixture - A mixture of three target compounds (e.g., benzene, trichloroethylene, and styrene) in nitrogen is used for monitoring instrument performance. The approximate concentration for each of the compounds in this mixture is 10 parts per billion (ppb). This mixture is manufactured in small, disposable gas cylinders [at 275 kPa (40 psi)] from Scott Specialty Gases, or equivalent.

8.3 Reagent Grade Nitrogen Gas - A small disposable cylinder of high purity nitrogen gas is used for blank injections.

8.4 Sampling Syringes - Gas-tight syringes, without attached shut-off valves (Hamilton Model 1002LT), or equivalent are used to introduce accurate sample volumes into the high pressure injectors on the portable gas chromatograph. Gas syringes with shut-off valves are not recommended because of memory problems associated with the valves. For samples suspected of containing high concentrations of volatile compounds, disposable glass syringes (e.g, Glaspak, or equivalent) with stainless steel/Teflon® hub needles are used.

8.5 High Pressure Filler - An adapter (Photovac SA101, or equivalent) for filling the internal carrier gas reservoir on the portable GC is used to deliver "zero" air.

9. Procedure

9.1 Instrument Setup

9.1.1 The portable gas chromatograph must be prepared prior to use in the indoor survey sampling. The pre-sampling activities consist of filling the internal carrier gas cylinder, charging the internal power supply, adjusting individual column carrier gas flows, and stabilizing the photoionization detector.

9.1.2 The internal reservoir is filled with "zero" air. The internal 12V, 6AH lead/acid battery can be recharged to provide up to eight hours of operation. A battery which is discharged will automatically cause the power to the instrument to be shut down and will require an overnight charge. During AC operation, the batteries will automatically be trickle-charged or in a standby mode.

9.1.3 The portable GC should be operated (using the internal battery power supply) at least forty minutes prior to collection of the first sample to insure that the

photoionization detector has stabilized. Upon arriving at the area to be sampled, the unit should be connected to AC power, if available.

9.2 Sample Collection

9.2.1 After the portable gas chromatograph is located and connected to 110V AC, the carrier gas flows must be adjusted. Flows to the 1.22 meter, 5% SE-30 and 0.66 meter, 3% SP2100 columns are adjusted with needle valves. Flows of 60 cm^3/min (5% SE-30) and 30 cm^3/min (3% SP2100) are adjusted by means of a calibrated rotameter. Switching between the two columns is accomplished by turning the valve located beneath the electronic module. During long periods of inactivity, the flows to both columns should be reduced to conserve pressure in the internal carrier gas supply. The baseline on the recorder/integrator is set to 20% full scale.

9.2.2 Prior to analysis of actual samples, an injection of the performance evaluation mixture must be made to verify chromatographic and detector performance. This is accomplished by withdrawing 1.0 mL samples of this mixture from the calibration cylinder and injecting it onto the 3% SP2100 column. The next sample analyzed should be a blank, consisting of reagent grade nitrogen.

9.2.3 Indoor air samples are injected onto the 3% SP2100 column. The chromatogram is developed for 15 minutes. Samples which produce particularly complex chromatograms, especially for early eluting components, are reinjected on the 5% SE-30 column.
Note: In no instance should a syringe which has been used for the injection of the calibrant/system performance mixture be used for the acquisition and collection of samples, or vice versa.

9.2.4 Samples have generally been collected from the indoor air at sites which are near suspected sources of VOCs and SVOCs and compared with those which are not. Typically, selection of sample locations is based on the presence of chemical odors. Samples collected in areas without detectable odors have not shown significant PID responses. Therefore, sampling efforts should be initially concentrated on "suspect" environments (i.e., those which have appreciable odors). The objective of the sampling is to locate sources of the target compounds. Ultimately, samples should be collected throughout the entire location, but with particular attention given to areas of high or frequent occupation.

9.3 Sample Analysis

9.3.1 Qualitative Analysis - Positive identification of sample components is not the objective of this "screening" procedure. Visual comparison of retention times to those in a standard chromatogram (Figure B-1) are used only to predict the probable sample component types.

9.3.2 Estimation of Levels - As with qualitative analysis, estimates of component concentrations are extremely tentative and are based on instrument responses to the calibrant species (e.g., benzene, trichloroethylene, styrene), the proposed component identification, and the difference in response between sample component and calibrant. For purposes of locating pollutant emission sources, roughly estimated concentrations and suspected compound types are considered sufficient.

10. Performance Criteria and Quality Assurance

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

10.1 Standard Operating Procedures

10.1.1 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 portable GC sampling system and equipment used; 2) preparation, storage, shipment, and handling of the portable GC sampler; 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.

10.1.2 Specific step-wise instructions should be provided in the SOPs and should be readily available to and understood by the personnel conducting the survey work.

10.2 Quality Assurance Program

10.2.1 Reagent and Materials Control - The carrier gas employed with the portable GC is "zero air" containing less than 0.1 ppm VOCs. System performance mixtures are certified standard mixtures purchased from Scott Specialty Gases, or equivalent.

10.2.2 Sampling Protocol and Chain of Custody - Sampling protocol sheets must be completed for each sample. Specifics of the sample with regard to sampling location, sample volume, analysis conditions, and supporting calibration and visual inspection information are detailed by these documents. An example form is exhibited in Table B-3.

10.2.3 Blanks, Duplicates, and System Performance Samples

10.2.3.1 Blanks and Duplicates - Ten percent of all injections made to the portable GC are blanks, where the blank is reagent grade nitrogen gas. This is the second injection in each sampling location. An additional 10% of all injections made are duplicate injections. This will enhance the probability that the chromatogram of a sample reflects only the composition of that sample and not any previous injection. Blank injections showing a significant amount of contaminants will be cause for remedial action.

10.2.3.2 System Performance Mixture - An injection of the system performance mixture will be made at the beginning of a visit to a particular sampling location (i.e., the first injection). The range of acceptable chromatographic system performance criteria and detector response is shown in Table B-4. These criteria are selected with regard to the intended application of this protocol and the limited availability of standard mixtures in this area. Corrective action should be taken with the column or PID before sample injections are made if the performance is deemed out-of-range. Under this regimen of blanks and system performance samples, approximately eight samples can be collected and analyzed in a three hour visit to each sampling location.

10.3 Method Precision and Accuracy

The purpose of the analytical approach outlined in this method is to provide presumptive information regarding the presence of selected VOCs and SVOCs emissions. In this context precision and accuracy are to be determined. However, quality assurance criteria are described in Section 10.2 which insure the samples collected represent the indoor environment.

10.4 Range and Limits of Detection

The range and limits of detection of this method are highly compound-dependent due to large differences in response of the portable GCs photoionization detector to the various target compounds. Aromatic compounds and olefinic halogenated compounds will be detected at lower levels than the halomethanes or aliphatic hydrocarbons. The concentration range of application of this method is approximately two orders of magnitude.

Table B-1. Estimated Limits of Detection (LOD) for Selected VOCs Based on 1 μL Sample Volume

Compound	LOD (ng)	LOD (ppb)
Chloroform[a]	2	450
1,1,1-Trichloroethane[a]	2	450
Carbon tetrachloride[a]	2	450
Benzene	0.006	2
1,2-Dichloroethane[b]	0.05	14
Trichloroethylene[b]	0.05	14
Tetrachloroethylene[b]	0.05	14
1,2-Dibromoethane	0.02	2
p-Xylene[c]	0.02	4
m-Xylene[c]	0.02	4
o-Xylene[d]	0.01	3
Styrene[d]	0.01	3

[a]Chloroform, 1,1,1-Trichloroethane, and Carbon tetrachloride coelute on 0.66 m 3% SP2100.

[b]1,2-Dichloroethane, Trichloroethylene, and Tetrachloroethylene coelute on 0.66 m 3% SP2100.

[c]p-Xylene and m-Xylene coelute on 0.66 m 3% SP2100.

[d]Styrene and o-Xylene coelute on 0.66 m 3% SP2100.

Table B-2. Commercially Available Portable VOC Detection Instruments

Monitor	Detection principle	Range, ppm	Sensitivity	Response time, s	Accessories	Calibration Techniques	Weaknesses	Service Rate	Lack of Response	Cost,$	Samp Rate L/m
550,551 555,580 (AID, Inc.	PID, FID	0-200, 0-2000, 0-10,000	0.1 ppm at 0-200 ppm	<5		o Bag Sampling	o Umbilical cord too short o Digital readout hard to read o Flame out frequently	8 hrs		4,300	1.5
OVA 108, 128 Century Systems, Inc. (Foxboro)	FID	0-10, 0-100, 0-1000, 0-10,000, 0-100,000	0.2 ppm (Model 128) 0.5 ppm (Model 108)	2 2	o Thermal Desorbers available o Optional GC available	o Hand Space o Direct Injection o Bag Samp.	o Battery failure o Sample line kinks o Compounds containing O_2/N give low response o Neg. resp. to CO/CO_2	8 hrs		6,300	
PI-101 (HNu Systems, Inc)	PID	1 1-20 1-200 1-2000	0.1 ppm Low molecular weights aromatics	<5	o Three lamps available o 9.5 (aromatics) o 10.2 (2-4 compounds) o 11.7 (halocarbons)	o External Gas Cyl. o Bag Samp.	o Three lamps - may miss something	10 hrs	o Cl hydrocarbons o CH_4	4,955	0.5
TLV Sniffer (Bacharach)	Catalytic combustion	0-500 0-5000 0-50,000	2.0 ppm	5		o Bag Samp. o Head Space				900	
Ecolyzer 400 (Energetics Science)	Catalytic combustion	0-100% LFL	1% LFL	15		o Bag Samp.	o Changes in gas temp/ humidity affects response				
Miran 1A (Foxboro)	IR	ppm to %	1 ppm	1,4,10 and 40						9,500	
Miran 1B (Foxboro)	IR	ppm to %								12,500	
Scentor (Sentex)	GC/EC, Argon Ionization PID		0.01 ppb Cl organics	2	Preconcentrator Thermal Desoprtion GC Columns Auto Cal. from Integral Gas Cylinder	o Internal gas cyl. o Preconcentrator o GC Column				12,950	
Photovac Standard Automatic Computer Auto Comp. Communication	PID (UV Light)	0	0.1 ppb Benzene with signal-to-noise ratio 4:1, Good for aromatics	2	o Dual Column o Manual/Auto Injection o Column Cond. o Pre-flush o Auto Dial Modem o Programmable		o Column operates at ambient temp. o STD in lab, then to field at diff. temp o Can't inject liquid samp. o Light fractions interfere		o H_2O o O_2	6,995 8,995 10,500 10,955 12,955	
Photovac Tip	PID	0-2000 ppm	0.05 ppm Benzene	3							

Table B-3. Portable Gas Chromatograph Sampling Data Sheet

DATE: LOCATION: TIME:

CHROMATOGRAPHIC CONDITIONS:

COLUMN 1: COLUMN TYPE:

I.D. (mm):_____ LENGTH (mm):_____ FLOW (mL/min):_____

COLUMN 2: COLUMN TYPE:

I.D. (mm):_____ LENGTH (mm):_____ FLOW (mL/min):_____

INJ. NO.	INJ. VOL.	COLUMN NO.	SETTING

SITE PLAN (indicate sampling locations):

_____ _____

DATE SIGNATURE

Table B-4. System Performance Criteria for Portable GC[a]

Criteria	Test Compound	Acceptable Range	Suggested Corrective Action
PID Response	Trichloroethylene	$\geq 10^8$ μV-sec/ng	Re-tune or replace lamp
Elution Time	Styrene	2.65 ± 0.15 min adjust carrier flow	Inspect for leaks,
Resolution[b]	Benzene/Trichloro-ethylene	≥ 1.4	Replace column

[a]Based on analysis of a vapor mixture of benzene, styrene, and trichloroethylene.

[b]Define by: $R + = 2d/(W_1+W_2)$; where d = distance between the peaks and W = peak width at base.

Peak Assignments For Standard Mixture

Peak No.	Compound(s) [a]
1	Benzene; Chloroform; 1,1,1-Trichloroethane; Carbon Tetrachloride
2	1,2-Dichloroethane; Trichloroethylene
3	Tetrachloroethylene; 1,2-Dibromoethane
4	Ethylbenzene
5	m,p- Xylene
6	o- Xylene; Styrene

[a] Toluene (not listed) elutes between peaks 1 and 2.

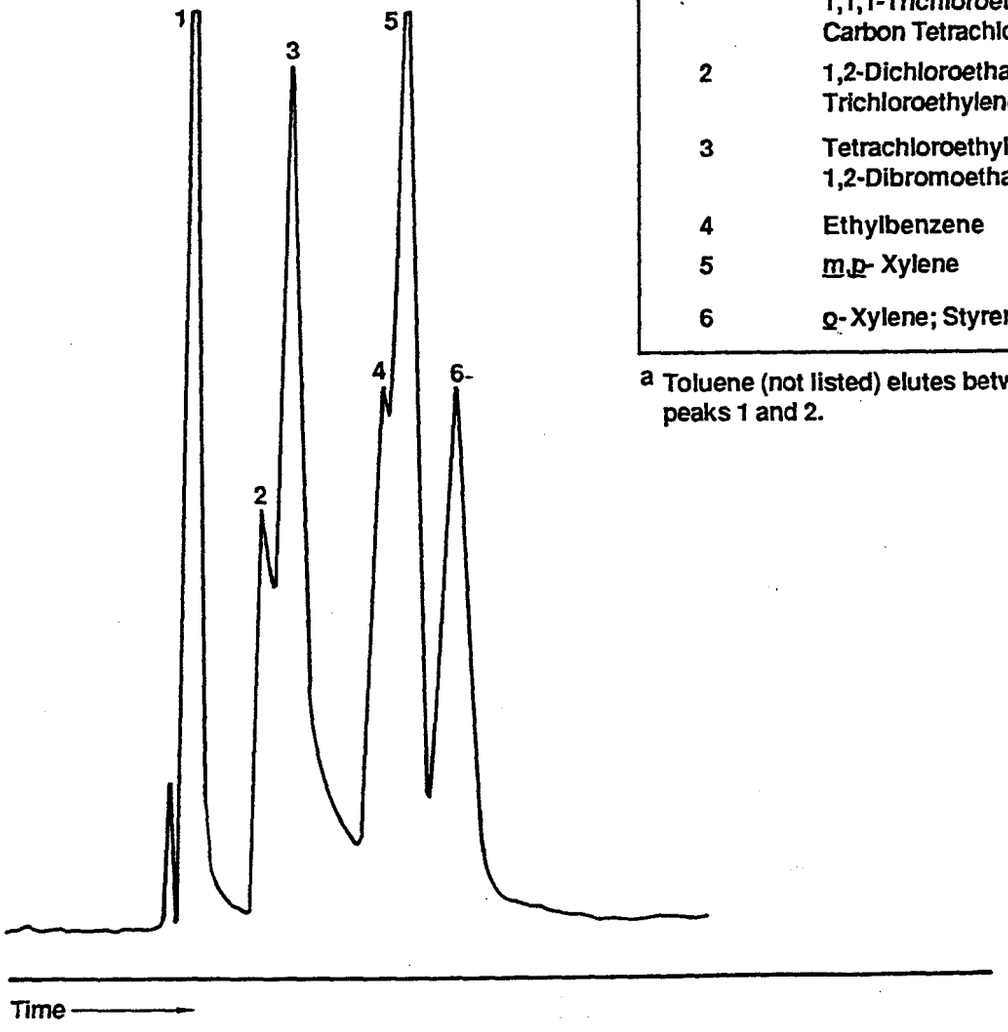


Figure B-1. Typical Chromatogram of VOCs Determined by a Portable GC

INSTALLATION AND OPERATION PROCEDURES FOR U.S. ENVIRONMENTAL PROTECTION AGENCY'S URBAN AIR TOXIC POLLUTANT PROGRAM SAMPLER

1. Scope

1.1 The subatmospheric sampling system described in this method has been modified and redesigned specifically for use in USEPA's Urban Air Toxic Pollutant Program (UATP), a joint project of USEPA's Office of Air Quality Planning and Standards, the Environmental Monitoring Systems Laboratory, and the participating state air pollution control agencies. The purpose of UATP is to provide analytical support to the states in their assessment of potential health risks from certain toxic organic compounds that may be present in urban atmospheres. The sampler is described in the paper, "Automatic Sampler for Collection of 24-Hour Integrated Whole-Air Samples for Organic Analysis," presented at the 1988 Annual Meeting of APCA, Dallas, TX, June, 1988 (Paper No. 88-150.3).

1.2 The sampler is based on the collection of whole air samples in 6 liter, SUMMA® passivated stainless steel canisters. The sampler features electronic timer for ease, accuracy and flexibility of sample period programming, an independently settable presample warmup and air purge period, protection from loss of sample due to power interruptions, and a self-contained configuration housed in an all-metal portable case, as illustrated in Figure C-1.

1.3 The design of the sampler is pumpless, using an evacuated canister to draw the indoor sample air into itself at a fixed flow rate (3-5 cm^3/min) controlled by an electronic mass flow controller. Because of the relatively low sample flow rates necessary for the integration periods, auxiliary flushing of the sample inlet line is provided by a small, general-purpose vacuum pump (not in contact with the sample air stream). Further, experience has shown that inlet lines and surfaces sometimes build up or accumulate substantial concentrations of organic materials under stagnant (zero flow rate) conditions. Therefore such lines and surfaces need to be purged and equilibrated to the sample air for some time prior to the beginning of the actual sample collection period. For this reason, the sampler includes dual timers, one of which is set to start the pump several hours prior to the specified start of the sample period to purge the inlet lines and surfaces. As illustrated in Figure C-1, sample air drawn into the canister passes through only four components: the heated inlet line, a 2 micron particulate filter, the electronic flow controller, and the latching solenoid valve.

2. Summary of Method

2.1 In operation, timer 1 is set to start the pump about 6 hours before the scheduled sample period. The pump draws sample air in through the sample inlet and particulate filter to purge and equilibrate these components, at a flow rate limited by the capillary to approximately 100 cm^3/min. Timer 1 also energizes the heated inlet line to allow it to come up to its controlled temperature of 65 to 70 degrees C, and turns on the flow controller to allow it to stabilize. The pump draws additional sample air through the flow controller by way of the normally open port of the 3 way solenoid valve. This flow purges

the flow controller and allows it to achieve a stable controlled flow at the specified sample flow rate prior to the sample period.

2.2 At the scheduled start of the sample period, timer 2 is set to activate both solenoid valves. When activated, the 3 way solenoid valve closes its normally open port to stop the flow controller purge flow and opens its normally closed port to start flow through the aldehyde sample cartridges. Simultaneously, the latching solenoid valve opens to start sample flow into the canister.

2.3 At the end of the sample period, timer 2 closes the latching solenoid valve to stop the sample flow and seal the sample in the canister and also de-energizes the pump, flow controller, 3 way solenoid, and heated inlet line. During operation, the pump and sampler are located external to the sampler.

3. Sampler Installation

3.1 The sampler must be operated indoors with the temperature between 20-32°C (68 to 90°F). The sampler case should be located conveniently on a table, shelf, or other flat surface. Access to a source of 115 vac line power (500 watts min) is also required. The pump is removed from the sampler case and located remotely from the sampler (connected with 1/4 inch O.D. extension tubing and a suitable electrical extension cord).

3.2 Electrical Connections (Figure C-1)

3.2.1 The sampler cover is removed. The sampler is not plugged into the 115 vac power until all other electrical connections are completed.

3.2.2 The pump is plugged into its power connector (if not already connected) and the battery connectors are snapped onto the battery packs on the covers of both timers.

3.2.3 The sampler power plug is inserted into a 115 VAC line grounded receptacle. The sampler must be grounded for operator safety. The electrical wires are routed and tied so they remain out of the way.

3.3 Pneumatic Connections

3.3.1 The length of 1/16 inch O.D. stainless steel tubing is connected from port A of the sampler (on the right side of the flow controller module) to the air inlet line.

3.3.2 The pump is connected to the sampler with 1/4 inch O.D. plastic tubing. This tubing may be up to 7 meters (20 feet) long. A short length of tubing is installed to reduce pump noise. All tubing is conveniently routed and, if necessary, tied in place.

4. Sampler Preparation

4.1 Canister

4.1.1 The sample canister is installed no more than 2 days before the scheduled sampling day.

4.1.2 With timer #1 ON, the flow controller is allowed to warm up for at least 15 minutes, longer if possible.

4.1.3 An evacuated canister is connected to one of the short lengths of 1/8 inch O.D. stainless steel tubing from port B (solenoid valve) of the sampler. The canister valve is left closed. The Swagelok fitting on the canister must not be cross-threaded. The connection is tightened snugly with a wrench.

4.1.4 The end of the other length of stainless steel tubing from port B (solenoid valve) is connected with a Swagelok plug.

4.1.5 If duplicate canisters are to be sampled, the plug is removed from the second 1/8 inch O.D. stainless steel tubing from port B (solenoid valve) and the second canister is connected. The canister valve is left closed.

4.1.6 The ON button of timer #2 is pressed. The flow through the flow controller should be stopped by this action.

4.1.7 The flow controller switch is turned to "READ" and the zero flow reading is obtained. If this reading is not stable, wait until the reading is stabilized.

4.1.8 The flow controller switch is turned to "SET" and the flow setting is adjusted to the algebraic SUM of the most recent entry on Table C-1 and the zero reading obtained in step 4.1.7 (if the zero reading is negative, SUBTRACT the zero reading from the Table C-1 value). Be sure to use the correct Table C-1 flow value for one or two canisters, as appropriate.

Note: If the analytical laboratory determines that the canister sample pressure is too low or too high, a new flow setting or settings will be issued for the sampler. The new flow setting should be recorded in Table C-1 and used until superseded by new settings.

4.1.9 Timer #2 is turned OFF to again start the flow through the flow controller. With the pump (timer #1) ON and the sampling valve (timer #2) OFF, the flow controller is turned to "READ" and the flow is verified to be the same as the flow setting made in step 4.1.8. If not, the flow setting is rechecked in step 4.1.8 and the flow setting is readjusted if necessary.

4.1.10 The OFF button of timer #1 is pressed to stop the pump.

4.1.11 The canister valve(s) are fully opened.

4.2 Timers

4.2.1 Timer #2 is set to turn ON at the scheduled ON time for the sample period, and OFF at the scheduled OFF time. (See the subsequent section on setting the timers.) Normal ON time: 12:00 AM on the scheduled sampling day. Normal OFF time: 11:59 PM on the scheduled sampling day. (The OFF time is 11:59 PM instead of 12:00 AM so that the day number for the OFF time is the same as the day number for the ON time.) Be sure to set the correct day number.

4.2.2 Timer #1 is set to turn ON six (6) hours before the beginning of the scheduled sample period and OFF at the scheduled OFF time for the sample period (same OFF time as for timer #2). (See the subsequent section on setting the timers.) Normal ON time: 06:00 PM on the day prior to the scheduled sampling day. Normal OFF time: 11:59 PM on the scheduled sampling day.

Note: The timers are wired so that the pump will be on whenever either timer is on. Thus the pump will run if timer #2 is ON even if timer #1 is OFF.

4.2.3 The elapsed time meter is set to 0.

4.3 Sampler Check

4.3.1 The following must be verified before leaving the sampling site:

4.3.1.1 Canister(s) is (are) connected properly and the unused connection is capped if only one canister is used.

4.3.1.2 Canister valve(s) is (are) opened.

4.3.1.3 Both timers are programmed correctly for the scheduled sample period.

4.3.1.4 Both timers are set to "AUTO".

4.3.1.5 Both timers are initially OFF.

4.3.1.6 Both timers are set to the correct current time of day and day number.

4.3.1.7 Elapsed time meter is set to 0.

4.4 Sampler Recovery (Post Sampling)

4.4.1 The valve on the canister is closed.

4.4.2 The canister is disconnected from the sampler, the sample data sheet is completed, and the canister is prepared for shipment to the analytical laboratory.

4.4.3 If two canisters were sampled, step 2.4.2 is repeated for the other canister.

5. Timer Setting

5.1 Since the timers are 7-day timers, the days of the week are numbered from 1 to 7. The assignment of day numbers to days of the week is indicated on the timer keypad: 1 = Sunday, 2 = Monday, 3 = Tuesday, 4 = Wednesday, 5 = Thursday, 6 = Friday, and 7 = Saturday. This programming is quite simple, but some timers may malfunction or operate erratically if not programmed exactly right. To assure correct operation, the timers should be reset and completely reprogrammed "from scratch" for each sample. The correct current time of day is re-entered to reprogram the timer. Any program in the timer's memory is erased by resetting the timer (pressing the reset button). The timer is set by the following:

5.1.1 Pressing the reset button,

5.1.2 Entering the correct day number and time of day,

5.1.3 Entering the ON and OFF times for the sample period, and

5.1.4 Verifying that the ON and OFF time settings are correct.

5.2 Timer Reset

The timer reset button is pressed, which is recessed in a small hole located just above the LED (light emitting diode) indicator light. A small object that will fit through the hole, such as a pencil, match, or pen is used to press the timer. After reset, the timer display should show |1| |10:00|.

Note: The timers may operate erratically when the batteries are discharged, which happens when the sampler is unplugged or without power for several hours. When the sampler is again powered up, several hours may be required to recharge the batteries. To avoid

discharging the batteries, the battery pack should be disconnected from the timer when the sampler is unplugged.

5.3 Date and Time Entry

The selector switch is turned to SET and the number button corresponding to the day number is pressed. (For example, a "2" is pressed for Monday.) The current time of day is entered. (For example, if the time is 9:00 AM, 900 is pressed.) AM or PM is pressed as applicable. (Display should show |2| |'9:00| for 9:00 AM Monday.)
Note: ' indicates AM and , indicates PM.
The CLOCK button is pressed. (Display should show |-| |--:--|.) If an error is made, |E| |EE:EE| is shown on the display. The CLEAR button is pressed and the above steps are repeated. The selector switch is turned to AUTO or MAN to verify correct time setting.

5.4 ON and OFF Entry

The selector switch is turned to SET. The ON and OFF program is entered in the following order: day, number, time, AM or PM, ON or OFF. (Example: To turn ON at 12:00 AM on day 5 (Thursday); 5. 1200, AM, ON is entered). (Example: To turn OFF at 11:59 PM on day 5 (Thursday), 5. 11:59. PM. OFF is entered.) If the display indicates an error (|E| |EE:EE|), the timer is reset. The selector switch is turned to AUTO.

5.5 ON and OFF Verification

5.5.1 The selector switch is turned to REVIEW. The number of the scheduled sample day is pressed. ON is pressed. The display should show the time of the beginning of the sample period (for example, |5| |'12:00|). [' indicates AM.] ON is pressed again. The display should show |5| |--:--|, indicating no other ON times are programmed.

5.5.2 OFF is pressed. The display should show the time of the end of the sample period, (for example, |5| |, 11:59|). PM is indicated by the "," mark before the time. OFF is pressed again. The display should show |5| |--:--|, indicating no other OFF times are programmed. The selector is switched to AUTO. If anything is incorrect, the timer is reset and reprogrammed.

Table C-1. Net Flow Controller Setting

DATE	1 CANISTER	2 CANISTERS

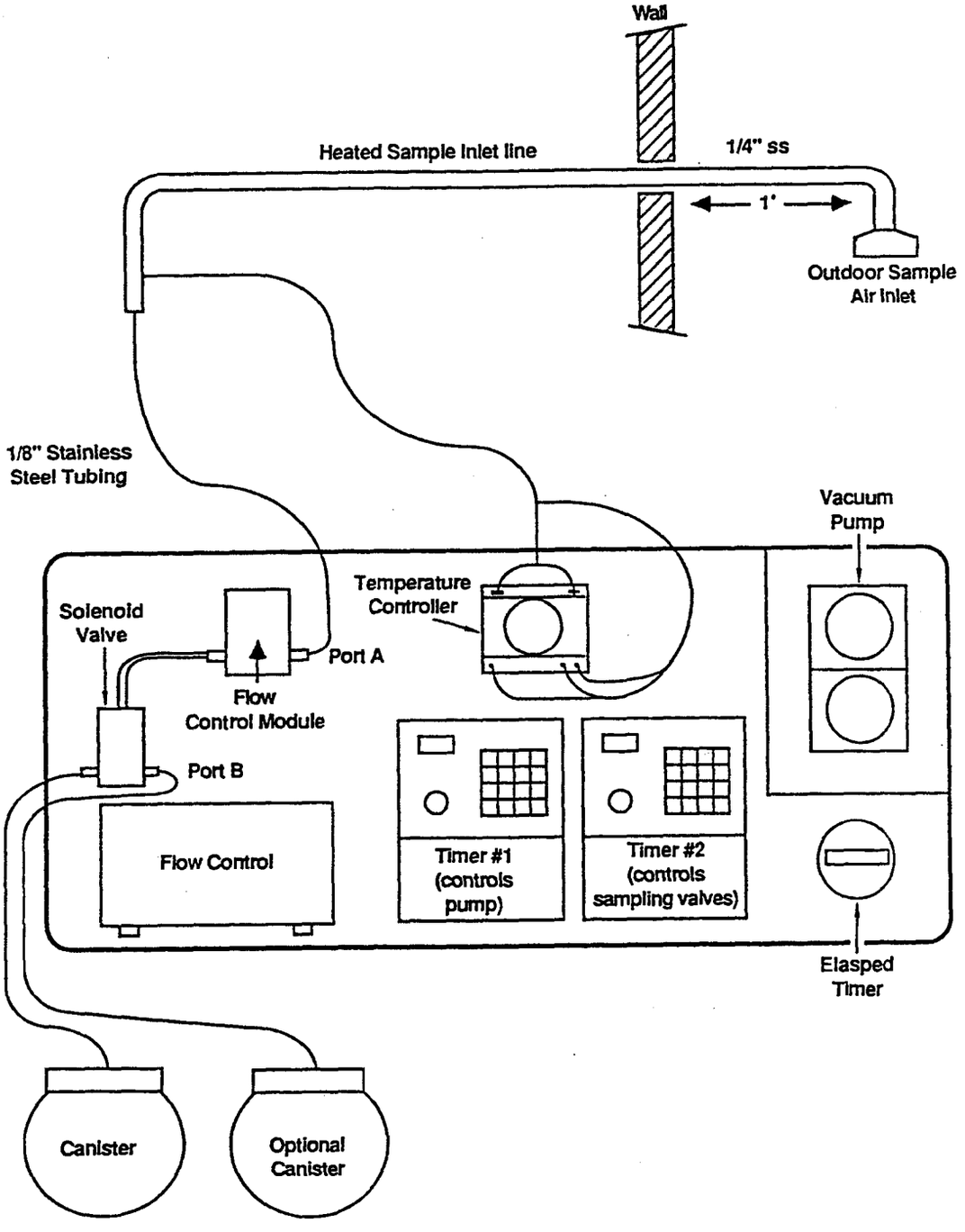


Figure C-1. Alternative 24-Hour Air Toxic Sampling System

Method IP-1B

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN INDOOR AIR USING SOLID ADSORBENT TUBES

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Method IP-1B

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN INDOOR AIR USING SOLID ADSORBENT TUBES

1. Scope

1.1 This document describes a procedure for sampling and analysis of volatile organic compounds (VOCs) in indoor air. The method is based on the collection of VOCs on Tenax® solid adsorbent [poly (2,6-diphenyl phenylene oxide)]. The collected VOCs are thermally desorbed and subsequently speciated by gas chromatography (GC) and identified by mass spectroscopy (MS). Specific approaches using these techniques are described in the literature (1-29).

1.2 This method is similar to Compendium Method IP-1A entitled: "Determination of Volatile Organic Compounds (VOCs) in Indoor Air Using Stainless Steel Canisters" in that the same analytical finish (GC-MS-DS) is used. Compendium Method IP-1A uses Summa® polished canisters as the collection mechanism and has only been validated for approximately thirty-two selected organics (30-38). While Compendium Method IP-1B has been validated for a larger number of VOCs, it must be used knowing and understanding its many limitations.

1.3 This protocol is designed to allow some flexibility in order to accommodate procedures currently in use. However, such flexibility also results in placement of considerable responsibility with the user to document that such procedures give acceptable results (i.e. documentation of method performance within each laboratory situation is required). Each user must generate standard operating procedures (SOPs) describing specific stepwise instructions for the sampling and analytical systems and should be readily available to be understood by all personnel. Types of documents required are described in the literature (39-46).

1.4 This method is based upon those procedures developed by the U.S. Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, as outlined in "Standard Operating Procedure for the GC-MS Determination of Volatile Organic Compounds Collectors on Tenax®." Compounds which can be determined by this method are nonpolar organics having boiling points in the range of approximately 80 - 200°C. However, not all compounds falling into this category can be determined. Table 1 presents a listing of compounds with detection limits for which the method has been used. Other compounds (semi-polar) may yield satisfactory results but validation by the individual user is required.

2. Referenced Documents

2.1 ASTM Standards

D1356 Standard Definitions of Terms Relating to Atmospheric Sampling and Analysis
D3609 Standard Practice for Calibration Techniques Using Permeation Tubes
D3686 Standard Practice for Sampling Atmospheres to Collect Organic Compound Vapors. Activated Charcoal Tube Adsorption Method

E260 Recommended Practice for General Gas Chromatography Procedures
E355 Standard Practice for Gas Chromatography Terms and Relationships
D1605-60 Standard Recommended Practice for Sampling Atmospheres for Analysis of Gases and Vapors

2.2 Other Documents

U.S. Environmental Protection Agency Technical Assistance Document (7)
Laboratory and Ambient Air Studies (47-54)

3. Summary of Protocol

3.1 Ambient air is drawn through an adsorbent cartridge containing approximately 1-2 grams of Tenax®. While highly volatile organic compounds and most inorganic atmospheric constituents pass through the cartridge, certain organic compounds are trapped on the resin bed.

3.2 After the organics are trapped on the resin bed, the cartridge is tagged and transported back to the lab for analysis.

3.3 Upon receipt at the laboratory, the cartridge is logged into the lab book and the chain-of-custody form completed. The cartridges are stored under refrigeration until analysis.

3.4 The cartridge is then submitted for analysis by capillary gas chromatography/mass spectroscopy/data system. During analysis, the cartridge is removed from the refrigerator, an internal standard is added to permit quantitative analysis, and the organics trapped on the Tenax® are thermally desorbed. The organic vapors are removed from the Tenax® by heating the sample cartridge to 275°C under a flow of helium. The desorbed vapors are collected in a cryogenic trap which is cooled to liquid nitrogen temperature. The use of the cryogenic trap allows the carrier gas flow, needed for the GC/MS, to be balanced.

3.5 The cryogenic trap containing the organics is then heated to transfer the sample to the head of the capillary GC column which is cooled to liquid nitrogen temperatures. This step is essential to focus the organic compounds and allow their application to the head of the capillary column in a discrete band.

3.6 The scan of the mass spectrometer is initiated and the analytical procedure is begun. Under a flow of helium, the GC column is programmed to a temperature to allow the elution of all of the organic compounds while the mass spectrometer is scanning. Data are recorded by the computer for subsequent processing. Quantitation is performed by the method of relative response factors, where the proportionate system responses for analyte and standard are determined prior to the analysis of the sample and this relative system response is used to determine the quantity of compound present on the sample cartridge.

3.7 Component identification is normally accomplished, using a library search routine, on the basis of the GC retention time and mass spectral characteristics. Less sophisticated

detectors (e.g., electron capture or flame ionization) may be used for certain applications but their suitability for a given application must be verified by the user.

3.8 The quantitative analysis is performed by a combination of manual and computerized procedures: the computer is instructed to seek characteristic ions in a previously determined retention window. At this point the operator intervenes to determine if the compound of interest has been located correctly. If the compound identification is correct, the computer then performs the quantitative calculation using the method of relative response factors. Data are reported as ng/cartridge, and can be subsequently converted to whatever units are desired.

3.9 Quality control procedures are followed in order to determine that the column is performing within acceptable limits, the mass spectrometer is tuned correctly and performing acceptably, and chromatography criteria are being met. A chromatogram (actually reconstructed ion chromatogram) is obtained for each analysis and entered into the laboratory project notebook. The quantitation report from the computer is also entered into the laboratory notebook. Standard Chain-of-Custody procedures are followed for every sample analyzed.

3.10 Due to the complexity of ambient air samples only high resolution (i.e. capillary) GC techniques are considered to be acceptable in this protocol.

4. Significance and Use

4.1 While much attention has been given in previous years to sources of VOCs in outdoor programs, that attention is now being focused on indoor VOC sources due to their human health impact. Many of these VOC compounds are toxic; hence, knowledge of the levels of such materials in the indoor atmosphere is required in order to determine human health impacts (16,17).

4.2 In recent indoor studies (12,15), VOCs have been found in building materials, decorating materials, and a variety of consumer products. Principle indoor sources of these compounds include solvents, furnishings, and other consumer products such as aerosols and coatings. Various indoor activities such as cooking, smoking, and arts and crafts also generate emissions of volatile organics. Concentrations of these pollutants vary widely from home to home, depending on source, strength, rate of ventilation and other factors. Limited data on indoor and outdoor concentrations exist, but studies show that indoor concentrations exceed outdoor levels.

4.3 Various techniques have been used to collect VOCs in indoor air. Compendium Method IP-1A utilizes Summa® polished stainless steel canisters (both pressurized and sub-atmospheric) for sampling, with subsequent analysis using a high-resolution gas chromatograph coupled to one or more appropriated GC detectors. Collection of indoor air samples in Summa® polished canisters, followed by GC-multidetection analysis, provides many attractive options to an indoor monitoring program. They are: 1) convenient integration of ambient samples over a specific time period (e.g., 24 hours), 2) remote sampling and central analysis, 3) ease of storing and shipping samples, if necessary, 4)

unattended sample collection, 5) analysis of samples from multiple sites with one analytical system, and 6) collection of sufficient sample volume to allow assessment of measurement precision and/or analysis of samples by several analytical systems. However, care must be exercised in selecting, cleaning,and handling sample canisters and sampling apparatus to avoid losses or contamination of the samples.

4.4 Conventional methods, however, for VOC determination in indoor air have relied on solid sorbent techniques, specifically carbon adsorption techniques. Specifically, the U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health base many of their sampling procedures on the use of carbon adsorption techniques. As with many solid adsorbents, there are many limitations to their use. The more significant problems in utilizing solid adsorbents are listed below.

- Formation of artifacts has been noted on several adsorbents (55-56), especially Tenax® in the presence of NO_x. This is especially true of the oxidation of amines to form nitrosoamines, yielding false positive results.
- Sorbents can be easily contaminated during manufacturing, shipping, or storage. Rigorous cleanup steps are generally needed to insure that the sorbent is free from interfering compounds. Tenax®, for instance, is generally contaminated with benzene and toluene as a result of manufacture, requiring an intensive cleanup involving Soxhlet extraction and thermal conditioning. Once prepared, the sampling cartridges must be further protected from contamination during handling prior to and after sampling.
- Breakthrough volumes of certain compounds, such as vinyl chloride, on some sorbent resins are so small that quantitative collection is prevented.
- While breakthrough volumes for charcoal are generally higher than the resin sorbents, irreversible adsorption of the analytes onto the charcoal may occur, causing less than quantitative (although frequently reproducible) recovery of the analyte.
- Solvent extraction technique, as applied to carbon adsorption, is generally applicable to semivolatile and non-volatile compounds. Similarly, solvent extraction dilutes the analyte of interest, thus allowing only a small portion, typically 1-5% of the sample, to be introduced into the GC-MS-DS. Typical ambient air concentrations of these compounds require a more sensitive approach. The thermal desorption process, wherein the entire sample is introduced into the analytical system, fulfills this need for enhanced sensitivity.

More specifically, the basic limitations for several solid adsorbent are outlined below. They are:

Charcoal

- high surface area causes artifact formation during sampling
- high background contamination if using thermal desorption
- high affinity for water
- high catalytic activity
- incomplete sample recovery
- impurities in solvent extraction may be high
- solvent extraction causes dilution of sample

Silica Gel

- limited use in humid areas
- thermal breakdown if using thermal desorption
- solvent extraction causes dilution of sample

XAD-2

- thermal stability questionable
- compounds below C_7 lost/breakthrough extensive

Tenax®

- poor desorption of highly polar (alcohol) compounds
- possibly retains O_2 which leads to sample oxidation
- limited to some volatile compounds
- high benzene background
- low breakthrough volume for some organics

Carbon Molecular Sieve

- holds onto very volatile compounds
- solvent extraction
- desorption efficiency decreases with B.P. > 100°C

Although sorbent techniques demonstrate problems, several advantages can be gained through their use. First, integrated sampling over a period of 8 to 12 hours is easily performed. Because of the small size and portability of the sample tubes and pumps, they are easily located in many indoor sampling applications.

4.5 Consequently, Compendium Method IP-1B, entitled "Determination of Volatile Organic Compounds (VOCs) in Indoor Air Using Solid Adsorbent Tubes" is applicable to the qualitative and quantitative analysis of volatile organic compounds in indoor air. The method is not applicable as herein described to the analysis of permanent gases present in the atmosphere. Thermal desorption of Tenax® followed by cryofocusing of the organic vapors, with subsequent capillary gas chromatography-mass spectrometry-data system analysis has been applied to adsorbed volatile organic compounds collected from exterior and interior air, personal air, air collected in the workplace, breath, and volatile organics transferred to Tenax® from other adsorptive media. The basic method is adaptable to any gas chromatograph-mass spectrometer-computer system upon construction of a suitable thermal desorption unit. A certain amount of flexibility in the analytical method from instrument to instrument is tolerable in order to optimize the operation parameters of any given instrument. Data handling procedures may also follow a wide range (from completely computerized to entirely manual) and still produce data within the criteria for acceptability.

5. Definitions

Note: Definitions used in this test method and any user-prepared SOPs should be consistent with ASTM Test Methods D1356, B260, and E355. All abbreviations and symbols are defined within this document at the point of use.

5.1 Cryogen - A substance used to obtain very low temperatures in the cryogenic trap of the analytical system. A typical cryogen is liquid nitrogen.

5.2 Dynamic calibration - Calibration of an analytical system with calibration gas concentrations that are generated in a dynamic, flowing system, by metering known volumetric flow rates of concentrated gas standards and zero gas into a common inlet line to the system.

5.3 Gauge pressure - Pressure measured above ambient atmospheric pressure (as opposed to absolute pressure). Zero gauge pressure (0 psig) is equal to ambient atmospheric pressure, which at standard conditions is 14.7 psia (101 kPa).

5.4 MSD-SIM - The gas chromatograph (GC) is coupled to a mass selective detector where the instrument is programmed to acquire data for only the target compounds and to disregard all others. This is performed using selected ion monitoring (SIM) coupled to retention time discriminators. The SIM analysis provides quantitative results.

5.5 Deuterated chemicals - Those chemicals which contain deuterium (hydrogen isotope that is twice the mass of hydrogen) used as tracers for system quality assurance.

5.6 Static calibration - Calibration of an analytical system with known concentrations of calibrations gas, obtained from a source such as gas cylinders or prepared from standard stock solutions.

5.7 Retention time (RT) - The time to elute a specific chemical from a chromatographic column for a specific carrier gas flow rate, measured from the time the chemical is injected into the gas stream until its maximum concentration appears at the detector.

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

5.9 Breakthrough volume (V_B) - Sample volume at which point a particular component will be initially detected in the eluate from the Tenax® sample cartridge.

5.10 Molar response (MR) - Total corrected ion count measured per molar concentration of the analyte in the standard.

5.11 Relative molar response (RMR) - The molar response (MR) measured for a particular analyte divided by the MR determined for an internal standard.

5.13 Sample recovery (SR) - The quantity of a component measured in a sample as compared to a known quantity of an isotopically labeled compound injected directly onto the same Tenax® cartridge.

6. Interferences and Limitations

6.1 Gas chromatographic separations are extremely susceptible to component overlap or coelution of more than one component. The use of high-resolution capillary columns of two different polarities may eliminate this problem.

6.2 In the use of porous polymer sorbents, artifacts can arise from chemical reactions due to oxidants in the sample, degradation of the polymer material, or thermal alterations of certain volatile organic compounds. This can usually be resolved by running blank and control samples prior to analysis and using multiple sampling volumes.

6.3 Breakthrough volumes of the compounds of interest must be known or determined prior to quantitative analysis. Section 11.3 contains calculations for breakthrough volumes.

6.4 Excessive concentrations of water vapor on high humidity days may cause some changes in retention properties of the sorbent media. In general, this can be minimized by multiple sampling volumes, smaller sampling volumes, and the use of desiccants in the culture tubes used for storage.

6.5 Contamination of the Tenax® adsorbent with the compound(s) of interest is a commonly encountered problem in the method. The user must be extremely careful in the preparation, storage, and handling of the cartridges throughout the entire sampling and analysis process to minimize this problem. Otherwise, false positive detection of chloroform, toluene, benzene, and other volatile organics may occur. Precautions should be taken for sampling caustic atmospheres which contain levels of NO_x and molecular halogens greater than 2-5 ppm and 25 ppb, respectively.

7. Range/Limits of Detection and Reproducibility

7.1 The linear range for the analysis of volatile organic compounds depends upon two factors. First, it is a function of the breakthrough volume of each specific compound which is trapped on the Tenax® GC sampling cartridge and second, it is related to the limits of detection of the mass spectrometer for each analyte. Thus, the range and limit of detection are a direct function of each compound which is present in the sampled air. The nominal linear range for quantitation using a capillary gas chromatograph/mass spectrometer/computer (GC-MS-DS) system is generally three orders of magnitude [5-5,000 ng]. Table 1 lists the detection limits for some volatile organics based on the limits of detection of the mass spectrometer. Absolute limit of detection may vary from 0.1 ng to about 50 ng. Curvature of the calibration plot may begin at levels as low as 1000 ng and must be determined for each compound.

7.2 The reproducibility of this method is generally ±10 - 30%, but depends on the chemical and physical nature of each analyte. The inherent analytical errors are a function of several factors: 1) the ability to accurately determine the breakthrough volume and its

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relation to field sampling conditions for each of the organic compounds identified, 2) the accurate measurement of sample volume, 3) the percent recovery of the organic from the sampling cartridge after a period of storage, 4) the reproducibility of thermal desorption for a compound from the cartridge and its introduction into the analytical system, 5) the accuracy of determining the response factor ratios between the identified substance and the quantitation standard used for calibrating the analytical system, 6) the reproducibility of transmitting the sample through the high resolution gas chromatographic column, and 7) the day-to-day reliability of the GC-MS-DS system. More specifically, the method written herein assumes the user has basic knowledge of solid adsorbent technology and more importantly, is intimately familiar with the operations and validation techniques associated with the capillary gas chromatography and mass spectrometer system delineated in the procedure. This required familiarity will insure the reporting of precise and accurate data, enabling a higher degree of confidence.

7.3 Accuracy is unknown. Precision depends greatly on the substance and method of introduction. Direct gas injections typically are repeatable to ± 20% at a 300 ng level. Repeatability of thermal desorptions may be ± 30% at a 300 ng level.

8. Apparatus

8.1 Sample Collection

8.1.1 Sample cartridge - sampling cartridges consist of 13.5 x 99 mm borosilicate glass with polished-flat end surfaces. One end is etched with an I (inlet) and the other with an E (exit). Figure 1 illustrates common designs of available adsorbent cartridge. Stainless steel cartridges may also be used. However, cartridges must be adaptable to the thermal desorption unit. User prepared.

8.1.2 Constant flow samplers - DuPont Environment Systems, Model P-125A, Concord Plaza 9, Wilmington, DE, 19898, 302-772-5042.

8.1.3 Bubble flow meter - 25mL, best source.

8.1.4 Stopwatch/calculator, best source.

8.1.5 Tenax® sampling trains - Nutech Corp., 2806 Check Rd., Durham, NC, 27704, 919-682-0402.

8.1.6 Glass fiber filters, 25 mm - Gelman Sciences, 600 S. Wagner Rd, Ann Arbor, MI, 48106, 800-521-1520.

8.1.7 Forceps, best source.

8.1.8 Kimwipes®, best source.

8.1.9 Sampling vests (optional) - user prepared.

8.1.10 Mercury thermometer - to record ambient temperature, best source.

8.1.11 Filter holder - stainless steel or aluminum (to accommodate 1 inch diameter filter). Other sizes may be used if desired (optional).

8.1.12 Barometer, best source.

8.1.13 Polyester gloves - for handling Tenax® cartridges, best source.

8.1.14 Sampling flow system - capable of accurately and precisely drawing an airflow of 10-1,000 mL/min through the Tenax® sampling cartridge.

8.2 Sample Analysis

8.2.1 Sample Desorption/Injection Unit - designed for thermally heating a Tenax® sample cartridge (glass or stainless steel) for sample transfer into a suitable GC-MS-DS system for analysis. The configuration of the thermal desorption unit should permit the enclosure and heating of the Tenax® cartridge from room temperature to approximately 250°C, rapidly while purging with an inert gas (helium) into a cryogenically cooled (liquid nitrogen) trap. The cryogenically cooled sample must then be rapidly heated to a preselected temperature (200-250°C) and a helium gas supply allowed to sweep the sample from the trap onto the gas chromatographic column. A schematic diagram of a typical thermal desorption unit is identified in Figure 2.

8.2.2 Gas Chromatograph/Mass Spectrometer - should be capable of subambient temperature programming, exhibit unit mass resolution up to 800 amu, and capable of scanning a 30-440 amu region every 1-2 seconds. Equipped with data system for instrument control as well as data acquisition, data processing using spectral enhancement algorithms, and historical library screening and storage. A schematic diagram of a typical GC-MS-DS unit is illustrated in Figure 3.

8.2.3 GC column - glass capillary or fused silica, 0.3 mm ID x 50 m, SE-30 or OV-1 coating.

8.3 Tenax® Cleaning

8.3.1 Extraction thimbles - cellulose (60 mm x 180 mm), best source.

8.3.2 Soxhlet extraction apparatus - extraction flask and 60/180 mm extraction thimbles (see Figure 4) - Fisher Scientific, 711 Forbes Avenue, Pittsburgh, PA, 15219, 412-562-8300.

8.3.3 Condenser, best source.

8.3.4 Tweezers, best source.

8.3.5 Beaker - 100 mL, best source.

8.3.6 Variable transformer, best source.

8.3.7 Heating mantle for 1,000 mL flask, best source.

8.3.8 Mettler balance - type H15 for weighing Tenax® powder, Fisher Scientific, 711 Forbes Avenue, Pittsburgh, PA, 15219, 412-562-8300.

Note: All glassware must be cleaned by soaking for at least one hour in Amway SA-8 laundry compound, or equivalent, followed by several rinses with deionized water; finally, baking for a minimum of four hours at 500-550°C.

8.4 Drying the Tenax®

8.4.1 Desiccator with gas connectors - Drierite ($CaSO_4$), best source.

8.4.2 Jar, wide mouth amber, best source.

8.4.3 Crystallizing dish, Kimax®, best source.

8.4.4 Vacuum oven equipped with a dry ice trap and connected to water apparatus vacuum supply - Fisher Scientific, 711 Forbes Avenue, Pittsburgh, PA, 15219, 412-562-8300.

8.4.5 Aluminum foil, best source.

8.4.6 Funnel, best source.

8.4.7 Pyrex disks - for drying Tenax®, best source.

8.5 Sieving of Tenax®

8.5.1 Cotton gloves, best source.
8.5.2 Sieves - 40 and 60 mesh, best source.
8.5.3 Glass funnel, best source.

8.6 Packing of Tenax® Tubes

8.6.1 Cotton gloves, best source.
8.6.2 Pre-washed glass wool - unsilanized, best source.
8.6.3 Aluminum shipping cylinder - 17.8 cm x 1.6 cm O.D., TEKMAR Co., P.O. Box 371856, Cincinnati, OH 45222, 800-543-4461.
8.6.4 Teflon cap liners - 24 mm, best source.
8.6.5 Stainless steel tweezers, best source.
8.6.6 Screw caps - 24 mm, best source.
8.6.7 Silicone septa - Teflon®-backed, best source.
8.6.8 One gallon metal paint cans - to hold clean Tenax® cartridges, best source.
8.6.9 Stainless steel tubes, 10 cm x 1.6 cm O.D., TEKMAR Co., P.O. Box 371856, Cincinnati, OH 45222, 800-543-4461.
8.6.10 Glass jar - capped with Teflon®-lined screw cap. For storage of purified Tenax®.

8.7 Desorption

8.7.1 Desorption chambers - TEKMAR Co., P.O. Box 371856, Cincinnati, OH 45222 or NuTech Co., 2806 Check Rd., Durham, NC 27704, 919-682-0402.
8.7.2 Helium - certified 99.995%, with regulator, best source.
8.7.3 Tweezers, best source.

8.8 Calibration of DuPont Pump

8.8.1 Constant flow sampler and operations manual - E. I. DuPont De Nemours, Applied Technology Division, Wilmington, DE, 1989, Model P-125A.
8.8.2 Bubble flow meter - 25 mL, best source.
8.8.3 Stopwatch/calculator, best source.
8.8.4 Small flat screwdriver, best source.
8.8.5 Allen keys (5/64"), best source.
8.8.6 110 volt, 60 Mz battery charger, best source.
8.8.7 Tygon® tubing (1/8" I.D.), best source.

8.9 Standard Preparation

8.9.1 Static Dilution Bottle

8.9.1.1 Two-liter round-bottom flask containing 30 3-mm diameter glass beads and a l-in. Teflon®-coated magnetic stirring bar - the flask is modified to accept a screw-on Mininert septum cap, TEKMAR Co., P.O. Box 371856, Cincinnati, OH 45222, 800-543-4461.

8.9.1.2 Gas-tight glass microsyringes - ranges of 10, 25, 50, 100, 500, 1000, and 2500 µL, best source.

8.9.1.3 Laboratory oven - large enough to contain at least two dilution bottles and capable of maintaining 60 ± 5°C, best source.

8.9.1.4 Drying oven capable of 300°C, best source.

8.9.1.5 Helium cylinder and pressure regulator connected to a length of flexible tubing, best source.

8.9.1.6 Vacuum syringe cleaner, best source.

8.9.1.7 Magnetic stirrer, best source.

8.9.1.8 Heat gun, best source.

8.9.1.9 50 mL vial fitted with a septum cap, best source.

8.9.2 Flash Vaporization

8.9.2.1 Flash vaporization unit (see Figure 5), best source.

8.9.2.2 Liquid microsyringes - ranges of 5, 10, 50, and 100 µL for injecting neat liquid standards into flash vaporization system, best source.

8.9.2.3 Volumetric flasks - 25, 50, 100, 250 mL, best source.

8.9.2.4 Helium cylinder and pressure regulator and needle valves for controlling flow rate, best source.

8.9.2.5 Soap bubble, flow meter, best source.

8.9.2.6 Thermal conductivity detector, best source.

8.9.2.7 Vacuum syringe cleaner, best source.

8.9.3 Permeation Tube System

8.9.3.1 Permeation system

8.9.3.2 Nitrogen gas (99.995% purity), best source.

8.9.3.3 Nylon gloves, best source.

8.9.3.4 Long glass hook (for retrieving permeation tubes), best source.

8.9.3.5 Permeation tubes, best source.

8.9.3.6 Kimwipes®, best source.

8.9.3.7 Stopwatch, best source.

9. Reagents and Materials

9.1 Granular activated charcoal - for preventing contamination of Tenax® cartridges during storage.

9.2 Tenax® Cleaning

9.2.1 Acetone - pesticide quality or equivalent, best source.

9.2.2 Methanol - distilled in glass, best source.

9.2.3 n-Pentane - distilled in glass, best source.

9.2.4 Glass wool, silanized, best source.

9.2.5 Tenax®, 60/80 mesh (2,6-diphenylphenylene oxide polymer), GC or TA - Alltech Associates, Inc., 2051 Waukegan Road, Deerfield, IL 60015, 312-948-8600.

9.3 Standard Preparation

Note: Individual chemicals to be used for standards should have a manufacturer's determined purity ≥98% or better, and isotopic standards should have ≥98% purity. Purity should be checked by NMR and direct probe MS. Each chemical received by the laboratory is checked by injection of an aliquot into a GC, using a 50-m SE-30 WCOT glass capillary bonded (cross-linked) column and FID. The resulting chromatogram is examined for extraneous peaks. If such peaks are observed and amount to more than 2% of the standard peak, the standard is unacceptable. Chemicals are also screened by GC-MS to confirm the identity of the compound by the examination of the mass spectra.

9.3.1 Standards of compounds to be used in calibration. Standards should be ≥98% pure, isotopic standards should be ≥ chemical and isotopic purity. Purity should be checked by NMR and direct probe MS.

9.3.2 Spectrograde methanol and acetone - distilled in glass, best source.

10. Cartridge Construction and Preparation

10.1 Cartridge Design

10.1.1 Several cartridge designs have been reported in the literature (1-3). The most common is shown in Figure 1(a). This design minimizes contact of the sample with metal surfaces, which can lead to decomposition in certain cases. However, a disadvantage of this design is the need to rigorously avoid contamination of the outside portion of the cartridge since the entire surface is subjected to the purge gas stream during the desorption process. Clean cotton gloves must be worn at all times when handling such cartridges and exposure of the open cartridge to ambient air must be minimized.

10.1.2 A second common type of design is shown in Figure 1(b). While this design uses a metal (stainless steel) construction, it eliminates the need to avoid direct contact with the exterior surface since only the interior of the cartridge is purged.

10.1.3 Finally, a third design has been developed by Supelco, as illustrated in Figure 1(c). The tube contains three adsorbent beds to capture the more volatile organics which Tenax® cannot retain.

10.1.4 The thermal desorption module and sampling system must be selected to be compatible with the particular cartridge design chosen. Typical module designs are shown in Figures 2(a) and b. These designs are suitable for the cartridge designs shown in Figures 1(a) and 1(b), respectively.

10.2 Adsorbent Purification

All Tenax®, whether new or recycled, must be purified through solvent extraction and thermal treatment before it is used for sample collection of organic compounds. The following routine shall be followed (as illustrated in Figure 6) when Tenax® is cleaned and packed into cartridges: 1) selection of the Tenax® to be used, 2) solvent extraction, 3) drying the Tenax®, 4) sieving the Tenax®, 5) packing the Tenax® into glass cartridges, 6) thermally desorbing the Tenax® cartridges, 7) ensuring the integrity of the cleaning and desorbing procedure, and 8) packing and storing the cartridges. All glassware used in

Tenax® purification as well as cartridge materials should be thoroughly cleaned by water rinsing followed by an acetone rinse and dried in an oven at 250°C.

10.2.1 Tenax® Selection

10.2.1.1 To the batch of Tenax®, assign a unique number and record on the Tenax® Clean-up Worksheet, as illustrated in Figure 7. If possible, new Tenax® should be taken from a single batch that has been certified clean by the manufacturer.

10.2.1.2 If the Tenax® is new, also record batch number on the Worksheet. If the Tenax® is used, record previous Tenax® blank value and matrix in which Tenax® was used (i.e., fixed-site monitoring, breath or personal air). Enter the complete history on the Worksheet.

10.2.2 Tenax® Cleaning Procedure

Note: The following adsorbent purification procedure is based on U.S. Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory (AREAL), Research Triangle Park, NC, Standard Operating Procedure (SOP) manual entitled "SOP for Preparation of Clean Tenax® Cartridges" (43). Deviations from this procedure should be thoroughly verified before implementation into the user prepared SOP.

10.2.2.1 In a hood, set up a sufficient number of Soxhlet extraction units, each with a 1000 mL round flask and a water cooled condenser (see Figure 4).

10.2.2.2 Load approximately 50 g of Tenax® into each thimble.

10.2.2.3 Cover the Tenax® with approximately two centimeters of unsilanized glass wool.

10.2.2.4 Place the thimble in the Soxhlet.

10.2.2.5 Add 600 mL of methanol to the 1000 mL flask.

10.2.2.6 Carefully pour an additional 300 mL of methanol onto the Tenax®.

Note: The 300 mL of extra methanol are added directly onto the Tenax® to ensure sufficient solvent for the extraction process after the initial adsorption of solvent.

10.2.2.7 Turn on the water to the condenser.

10.2.2.8 Turn on the Variac controlled heating mantle.

10.2.2.9 After the first extraction cycle, adjust the temperature with the variable transformer to obtain five cycles per hour.

10.2.2.10 Record on the Tenax® Worksheet the date and time the extraction was started.

10.2.2.11 Continue the extraction for 48 hours.

10.2.2.12 Check the extraction units twice daily and enter the information on the Worksheet.

Note: To avoid solvent losses, ensure that sufficient water is flowing to cool the condensers.

10.2.2.13 After 48 hours, cool the system and discard the methanol.

10.2.2.14 With a pair of tweezers carefully pull out the thimble and let it drain in a 100 mL beaker for 10 minutes.

10.2.2.15 Rinse the thimble with 50 mL of clean pentane. Repeat the rinse twice and then return the thimble to the Soxhlet. Discard the pentane.

Note: To avoid contamination do not handle the thimble with your hands.

10.2.2.16 Transfer 700 mL of clean pentane to the flask. Reposition the Soxhlet and heat to reflux.

10.2.2.17 After the first cycle, adjust the temperature to obtain five cycles per hour.

10.2.2.18 Record in the Worksheet the date and time that the pentane extraction began.

10.2.2.19 Complete the information on the Worksheet for this Tenax® batch.

10.2.2.20 Continue the extraction for 48 hours.

10.2.2.21 Check the extraction units twice daily and enter the information on the Worksheet.

10.2.2.22 After 48 hours of extraction, cool the system to room temperature.

10.2.2.23 Remove the thimble from the Soxhlet with a pair of tweezers.

10.2.2.24 Discard the pentane.

10.2.3 Drying Tenax®

10.2.3.1 Place the beakers containing the thimbles in the desiccator at room temperature under a slow "house" nitrogen flow (i.e., 25 mL/min) that contains a cryogenic trap to remove residual organics.

10.2.3.2 The following day transfer the contents of the two thimbles to a large crystallizing dish.

10.2.3.3 Transfer the rest of the Tenax® to a wide mouth jar and label it indicating that it has not been dried.

10.2.3.4 Cover the dish loosely with aluminum foil.

10.2.3.5 Set the dish in the vacuum oven.

10.2.3.6 Place dry ice/isopropanol in the vacuum trap.

10.2.3.7 Dry the Tenax® overnight at 100°C and 29 inches of water.

10.2.3.8 The following day turn off the heater and allow the oven to reach room temperature before opening the oven.

Note: The oven needs approximately 3 hours to cool to room temperature.

10.2.3.9 To open the vacuum oven, first close off the valve leading to the pump.

10.2.3.10 Connect the "house" nitrogen line to the other valve connector on the vacuum oven.

10.2.3.11 Slowly turn on the nitrogen flow with one hand while opening the valve with the other hand.

Note: This procedure allows the oven to reach normal pressure under a nitrogen atmosphere.

Note: Ensure that the nitrogen is vented out the oven through an activated charcoal tube.

10.2.3.12 Record every operation on the Tenax® Clean-up Worksheet.

10.2.3.13 Remove the Tenax® from the vacuum oven.

10.2.3.14 Open the valve leading to the pump and then immediately turn the vacuum pump off.

10.2.3.15 Carry the Tenax® to the "clean room" and store it, protected from the light, in a clean wide mouth jar with Teflon-lined cap.

10.2.3.16 Dry the rest of the Tenax® batch following Sections 10.2.3.2 to 10.2.3.15.

10.2.4 Sieving of Tenax®

10.2.4.1 Combine the contents of the jars containing Tenax® from the same batch.
10.2.4.2 Sieve the material and collect the contents in the 40/60 mesh range.
10.2.4.3 Return the contents to the jar. Label the jar "sieved" and indicate the date.
10.2.4.4 Record this operation on the Worksheet.

10.3 Cartridge Preparation

10.3.1 Place the Teflon® liners in a beaker and sonicate them in methanol for 10 minutes.
10.3.2 Rinse the liners with fresh methanol.
10.3.3 Repeat Sections 10.3.1 and 10.3.2 with pentane instead of methanol.
10.3.4 Dry the Teflon® liners in the vacuum oven for five hours at 100°C and 29 inches of water.
10.3.5 Store the liners in a wide mouth jar in the "clean room."
Note: To avoid contamination of the Tenax®, always use a pair of tweezers to handle the liners.
10.3.6 Follow Sections 10.3.1 to 10.3.5 to clean the silicone septa.
10.3.7 Soak the 24-mm screw caps in methanol for 30 minutes.
10.3.8 Remove the paper-lined foil from the caps with a spatula.
10.3.9 Rinse the caps in clean methanol and dry them in the vacuum oven overnight at 100°C.
10.3.10 Wrap the Kimax® culture tube with aluminum foil and secure it with clear tape.
10.3.11 Place a 2-cm glass wool plug at the bottom of the culture tube.
10.3.12 Place a silicone septum in the screw cap. Cover the septum with a cleaned Teflon-liner.
10.3.13 Loosely close the culture tube with the screw cap.

10.4 Cartridge Packing

10.4.1 Carefully inspect the tubes before packing. Discard any tube with rough ends or cracks, if glass.
10.4.2 Set the tubes in a rack.
10.4.3 Insert a 1-cm glass wool plug into one end of the tube and press with a dowel.
10.4.4 Transfer 6 cm of Tenax® to the tube, using a glass funnel.
10.4.5 Insert another 1-cm glass wool plug into the other end of the tube (see Figure 1). Lightly compress it with a dowel.
Note: A 10-cm tube (stainless steel or glass) packed with Tenax® is referred to as a Tenax® cartridge.
10.4.6 Store the Tenax® cartridges in the prepared culture tubes until desorption.

10.5 Cartridge Pretreatment

10.5.1 Place adsorbent cartridges into conditioning unit.

10.5.2 Turn on the helium tank. This allows oxygen to be purged from the cartridge before heating. Now turn on the desorption unit to 300°C.

10.5.3 Place liquid nitrogen in the cryogenic trap.

10.5.4 Open the helium line to the desorption chambers.

Note: Insure that a cryogenic trap has been placed in the helium line to remove residual organics.

10.5.5 Adjust the helium flow under each chamber to approximately 15 mL/min.

10.5.6 After all the cartridges are in place, recheck the flows from each chamber.

Note: To avoid contamination of the Tenax®, ensure that helium is flowing through every cartridge.

10.5.7 Desorb the Tenax® cartridges for five hours at 300°C.

10.5.8 Refill the cryogenic trap with liquid nitrogen every hour, or when the level of liquid nitrogen is less than one-third full.

Note: If liquid nitrogen in the trap is depleted all the impurities trapped in the line will be transported to the Tenax®.

10.5.9 Record all pertinent information on the Tenax® Cleanup Worksheet for specific Tenax® batch.

10.5.10 Recheck the helium flow every two hours and before removing the cartridges. Allow cartridges to cool to room temperature under the helium flow.

10.5.11 Remove each cartridge with a pair of tweezers and immediately place the hot cartridge in a shipping container.

10.5.12 Seal the tube.

10.5.13 Label the screw cap with the Tenax® batch number and the culture tube with the desorption date.

10.5.14 The cartridges are labeled and placed in a tightly sealed friction-top container. For cartridges of the type shown in Figure 1(a), the culture tube, not the cartridge, is labeled.

10.5.15 Cartridges should be used for sampling within two weeks after preparation and analyzed within two weeks after sampling. If possible, the cartridges should be stored at -20°C in a clean freezer (i.e., no solvent extracts or other sources of volatile organics contained in the freezer).

10.5.16 Each batch of Tenax® cartridges prepared should be checked for contamination (<10 ng per cartridge) by analyzing one cartridge immediately after preparation by GC-MS, according to Section 12.

10.6 Cartridge Spiking

10.6.1 Each sample cartridge is quantitatively spiked with 100 µL of perfluorotoluene (PFT), $toluene_{d8}$ and 1,2-dichlorobenzene prepared from a static dilution bottle technique (see Section 15.3). PFT serves as an initial internal marker for the MS, $toluene_{d8}$ serves as a transfer standard and 1,2-dichlorobenzene serves as the final internal marker for the MS.

10.6.2 As a quality assurance indicator, 10% of Tenax® cartridges should be spiked with deuterated compounds (~100 ng) as indicator of performance during sampling and analysis. The deuterated compounds used as pre-sample spikes or internal standards can be added to the adsorbent cartridge by either the flash vaporization (see Section 15.2), the static dilution (see Section 15.3) or by the permeation gas generator (see Section 15.4) technique. They are:

- chlorobenzene$_{d5}$
- 1,4-dichlorobenzene$_{d4}$

11. Sample Collection

11.1 Description of Sampling Apparatus

11.1.1 As discussed in Section 4.4, adsorbent sampling is a difficult and lengthy process containing much uncertainty. The sampling approach should facilitate and improve interpretation of the data and sort the complicating factors of 1) breakthrough volumes, 2) high background contamination and 3) artifact formation.

11.1.2 To address the above complicating factors, U.S. Environmental Protection Agency initiated the distributed air volume (55) approach in their Toxics Air Monitoring System (TAMS). In the TAMS, four adsorbent tubes are exposed to the same air parcel, but sample very different air volumes. The TAMS (57) adsorbent sampler is illustrated in Figure 8.

11.1.3 The underlying idea is that at any fixed sampling rate, the amount of a substance adsorbed will be a linear function of the volume sampled. This is true even if input composition varies. Since the proportionality constant for any useful adsorbent is the average concentration of the input gas, apparent concentrations are independent of volume sampled. Analytical results are then simply sorted into a group where all apparent concentrations of a given substance are indistinguishable over the set and a second group where they are dependent on the volume sampled. Dependence on air volume guarantees the presence of unspecified complicating factors. Their identity cannot be deduced from the data if gathered through a single or tandem sampling configuration (see Figure 9). Lack of dependence of volume is presumptive evidence of results describing the atmosphere sampled. In contrast, one tandem sample or occasionally duplicates are collected in the usual tandem bed sampling approach. The lack of independence of the air volumes in the tandem beds and the total absence of a distribution prevents the uncovering of any different functional dependencies. Tandem beds are, therefore, inherently weaker for this kind of data evaluation.

11.1.4 The distributive air volume approach does not point to any one reason for a problem, only indicates a problem associated with 1) breakthrough volume, 2) high background contamination and 3) artifact formation during sampling. The distributive air volume approach is a stringent diagnostic test and tool to confirm the integrity of the sample to the ambient air sample.

11.1.5 The traditional sampling train has consisted of an adsorbent tube, a flow controller (needle valve or mass flow controller), an oilless pump and if required, a means of measuring the total volume of air sampled. Figure 10(a) illustrates the traditional

sampling train utilizing mass flow controllers, while Figure 10(b) illustrates the use of needle valves and dry test meter in conjunction with the adsorbent tube.

11.1.6 While the traditional sampling configuration cannot evaluate the effect of artifact formation and background contamination as effectively as the distributing air volume approach, the user must therefore evaluate these uncertainties on a case-by-case basis.

11.1.7 The traditional configuration lends itself more to outdoor sampling than indoors. Because the adsorbent bed does not demonstrate a high pressure drop, the traditional pumps can be replaced with personal pumps, as illustrated in Figure 11. Figure 11 illustrates a stationary approach, while Figure 12 demonstrates a personal monitoring approach.

11.2 Breakthrough Volume Determination

11.2.1 The question of quantitative breakthrough volume by the adsorbent must be answered for each substance in every sample. Generalized 'safe sampling volumes' based on limited fundamental information but accompanied by warning of significant limitations have been suggested and published (58). They can be used as guides to prevent significant adsorbate loss due to exceeding the capacity of the adsorbent. However, for any given sampling bed and flow rate, breakthrough volumes are functions of temperature and gas phase composition, as illustrated in both laboratory and field studies (59-64). Breakthrough volumes, however, only give estimates of sampling volume to be used in a monitoring protocol.

11.2.2 The sample capacity of a sorbent is the maximum amount of an analyte that a sorbent will retain. For sample streams with a high concentration of organic vapors the pores of the sorbent trap will become filled and the trap will overflow. For low concentrations of organic vapors the holding power of the sorbent will be exceeded by the flow of the sample stream and the species of interest will be stripped out of the trap. The volume of gas containing the analyte, which can be sampled before some fraction of the analyte reaches the outlet, is the breakthrough volume. This fraction has been defined as 100%, 50%, or 1% in the literature. For this reason widely varying breakthrough volumes for a given compound have appeared in the literature. The larger the breakthrough volume, the greater the sample volume that can be used, and the greater the enrichment factor. Breakthrough volume of an analyte depends on the affinity of the analyte for the sorbent, the efficiency of the sorbent trap measured in theoretical plates, and the trapping temperature. Within experimental limits, the breakthrough volume of a compound is independent of normal variations in humidity and of concentrations of analytes in air below 100 ppm. The specific retention volume of an analyte on a sorbent is an excellent approximation of the analyte's breakthrough volume at a given temperature. An approximately linear relationship exists between the logarithm of the specific retention volume of a substance and column temperature, as illustrated in Figure 13. The breakthrough volume of an analyte can be measured at several column temperatures, and the value of the breakthrough volume at a given temperature can be obtained through extrapolation. Table 2 outlines typical breakthrough volumes and safe-sample volumes for some common adsorbents. The breakthrough volume data are supplied only as a rough

guide and are subject to considerable variability, depending on cartridge design as well as sampling parameters and atmospheric conditions. A second tube, placed in series with the primary adsorbent tube, may be used to monitor breakthrough (see Figure 9).

11.2.3 Calculate the "safe sample volume" of air which is to be sampled, using the following equation:

$$V_{MAX} = (V_b \times W)/1.5$$

where:

V_{MAX} = the calculated maximum total volume (safe sample volume), L

V_b = the breakthrough volume for the least retained compound of interest, L/g of Tenax®

W = the weight of Tenax® in the cartridge, g

Note: 1.5 is a dimensionless safety factor to allow for variability in atmospheric conditions to calculate a safe sample volume. This factor is appropriate for temperatures in the range of 25-30°C. If higher temperatures are encountered the factor should be increased (i.e., maximum total volume decreased).

11.2.4 Calculate maximum flow rate to be used by the following equation:

$$Q_{MAX} = (V_{MAX} \times 100)/t$$

where:

Q_{MAX} = calculated maximum flow rate, mL/min

t = desired sampling time, min. Times greater than 24 hours (1440 minutes) generally are unsuitable because the flow rate required is too low to be accurately maintained

The maximum flow rate Q_{MAX} should yield a linear flow velocity of 35-300 cm/minute. Calculate the linear velocity corresponding to the maximum flow rate using the following equation:

$$B = Q_{MAX}/\pi r^2$$

where:

B = linear flow velocity, cm/min

r = internal radius of the cartridge, centimeters

Linear velocity should be 35-300 cm/min. If B is greater than 500 centimeters per minute either the total sample volume (V_{MAX}) should be reduced or the sample flow rate (Q_{MAX}) should be reduced by increasing the collection time. If B is less than 50 centimeters per minute the sampling rate (Q_{MAX}) should be increased by reducing the sampling time. The total sample volume (V_{MAX}) cannot be increased due to component breakthrough.

11.2.5 The flow rate calculated as described above defines the maximum flow rate allowed. In general, one should collect additional samples in parallel, for the same time period but at lower flow rates. This practice yields a measure of quality control. In general, flow rates 2 to 4 fold lower than the maximum flow rate should be employed for the parallel samples. In all cases a constant flow rate should be achieved for each cartridge

since accurate integration of the analyte concentration requires that the flow be constant over the sampling period.

11.3 Collection of Samples

11.3.1 Prepare the Chain-of-Custody and Field Data Sheet for all samples to be collected (see Figures 14 and 15, respectively).

11.3.2 Remove and label the appropriate number of Tenax® cartridges required from the Tenax® storage area.

11.3.3 Store all of the labeled Tenax® cartridges in the Tenax® storage area until needed.

Note: If more than one Tenax® batch number has been assigned per matrix, use Tenax® from same batch for all the field and duplicate samples.

11.3.4 Prior to sampling, calibrate the personal sampling pump (see Section 16).

Note: The ideal air sample volume is 20 ± 3% liters (17-23 L). A pumping rate should be used which will give a sample volume in this range over the collection period and be within the safe sample volume outlined in Table 2. If the anticipated collection time is between approximately 11 and 13 hours, any flow rate in the range of 12-30 mL/min will be adequate. If the collection period will be less than 11 hours, use a pump with a correspondingly higher flow rate (30-60 mL/min). Do not use a flow rate less than 12 mL/min.

11.3.5 Assemble the sampling train as illustrated in Figure 12. If sampling is to be performed in a high particulate area, then an optional filter may be adapted to the adsorbent cartridge, as illustrated in Figure 16. However, prefilters have the potential of removing organics during sampling. If a prefilter is to be used as part of the sampling protocol, it must be demonstrated that it does not affect the integrity of the sample.

11.3.6 Remove the Tenax® cartridges from the Tenax® storage area and place into a field collection can.

Note: Remove only those cartridges which will be exposed during the appointment. The additional cartridges should remain in the Tenax® storage area until needed.

11.3.7 Attach the sampling train to the inlet (top) barb of the personnel sampler pump.

11.3.8 If a glass fiber filter is used, place in the top filter holder of the sampling train.

Note: Filters are replaced at the beginning of each new 24-hour sampling period or more frequently if the filters appear damaged or soiled.

11.3.9 Record the sampler number, flow rate, and time on the Sample Field Data Sheet (see Figure 15).

11.3.10 Remove the Tenax® cartridge from the field collection can and reseal the can.

11.3.11 Using forceps, remove the top pad of glass wool from the culture tube and place it on a clean Kimwipe®.

11.3.12 Using cotton gloves, remove the Tenax® cartridge from the culture tube.

11.3.13 Install the Tenax cartridge in the sampling train.

Note: Do not allow the Tenax® cartridge to touch the hands or other material. Contamination may result. Install the cartridge in the proper orientation with the exit (E) end nearest the DuPont sampler.

11.3.14 Using forceps replace the glass wool pad.

11.3.15 Return the empty culture tube to the field collection can and reseal the can.

11.3.16 Start the pump and record the following parameters on the Field Sampling Data Sheet (see Figure 15): data, sampling location, time, ambient temperature, barometric pressure, relative humidity, dry gas meter reading (if applicable), flow rate, rotameter reading (if applicable), and cartridge number.

11.3.17 The flow rate should be checked before and after each sample collection. If the sampling interval exceeds 4 h, the flow rate should be checked at an intermediate point during sampling as well.

11.3.18 Allow the sampler to operate for the desired time, periodically recording the variables listed above. Check flow rate at the midpoint of the sampling interval if longer than four hours. At the end of the sampling period record the parameters listed in Section 11.3.16 and check the flow rate and record the value. If the flows at the beginning and end of the sampling period differ by more than 10% the cartridge should be marked as suspect. Note: Changes in temperature and humidity during sampling may change flow through adsorbent tube. One may want to check flow rate more frequently under these situations.

11.3.19 Remove the cartridges (one at a time) and place in the original container (use gloves for glass cartridges). Seal the cartridges or culture tubes in the friction-top can containing a layer of charcoal and package for immediate shipment under dry ice to the laboratory for analysis. Store cartridges at reduced temperature (e.g., -20°C) before analysis, if possible, to maximize storage stability.

11.3.20 Calculate and record the average sample rate for each cartridge according to the following equation:

$$Q_A = (Q_1 + Q_2 + ...Q_N)/N$$

where:

Q_A = average flow rate, mL/min

$Q_1, Q_2, ...Q_N$ = flow rates determined at beginning, end, and intermediate points during sampling, mL/min

N = number of points averaged

11.3.21 Calculate and record the total volumetric flow for each cartridge using the following equation:

$$V_m = (T \times Q_A)/1000$$

where:

V_m = total volume sampled at measured temperature and pressure, L

T_2 = stop time

T_1 = start time

T = sampling time = $T_2 - T_1$, minutes

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:
P_A = average barometric pressure, mm Hg
t_A = average ambient temperature, °C

12. GC-MS-DS Analysis

12.1 Description of Analytical Apparatus

12.1.1 The analytical system (see Figure 3) is comprised of a GC equipped with a mass spectrometer set in the full scan mode. The GC-MS-DS is setup for automatic, repetitive analysis. The system is programmed to acquire data for the target compounds. The sensitivity is ~0.3-0.5 μg in the full scan mode with an analytical precision of about 5% relative standard deviation. Concentration of compounds based upon a previously installed calibration table is reported by an automated data reduction program. Primary quantitation is provided by this analysis. The analyst has the option of operating the mass spectrometer in either the scan or SIM mode. In the SIM mode, the spectrometer requires data for only those target ions which it has been programed to see, thus disregarding all others. Some of the positive aspects in operating in the SIM mode are:

- increased sensitivity because more time is spent on selected ions,
- able to look at each fragment longer, and
- date interpretation contains less uncertainty.

The negative aspects of operating in the SIM mode are:

- reliability of identification is low because looking only at one or two key ions, and
- loose spectral information because looking only at selected ions.

The mass spectrometer operated in the SIM mode should be used in a clearly defined monitoring program that provides a clearly defined chemical. For an unknown atmosphere, it is suggested that the mass spectrometer be operated in the scan mode to acquire as much spectral data about the sample as possible.
Note: Considerable variation from one laboratory to another is expected in terms of instrument configuration. Therefore, each laboratory must be responsible for verifying that their particular system yields satisfactory results. Section 17 discusses specific performance criteria which should be met.

12.1.2 GC-MS-DS is based on a combination of retention times and relative abundances of target ions. These qualifiers are stored on the hard disk of the GC-MS-DS 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 each compound. When compound identification is made by the computer, any peak that fails any of the qualifying tests is flagged (e.g., with an *). All the data is 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 is also performed to verify concentrations outside the expected range.

12.1.3 A block diagram of the typical GC-MS-DS system required for analysis of Tenax® cartridges is depicted in Figure 3. The thermal desorption module (see Table 3) must be designed to accommodate the specific cartridge configuration used in the sampling protocol. Steel or nickel metal surfaces should be employed. The volume of tubing and fittings leading from the cartridge to the GC column must be minimized and all areas must be well-swept by helium carrier gas.

12.1.4 The GC column inlet should be capable of being cooled to -70°C and subsequently increased rapidly to approximately 30°C. This can be most readily accomplished using a GC equipped with an automated subambient cooling capability (liquid nitrogen), although other approaches such as manually cooling the inlet of the column with a cotton swab containing liquid nitrogen may be acceptable.

12.1.5 The specific GC column and temperature program employed will be dependent on the specific compounds of interest. Appropriate conditions are described in the literature (44). In general a nonpolar stationary phase (e.g., SE-30, OV-1) temperature programmed from 30 to 245°C at 4°/min will be suitable. Fused silica bonded phase columns are preferable to glass columns since they are more rugged and can be inserted directly into the MS ion source, thereby eliminating the need for a GC-MS transfer line.

12.1.6 Capillary column dimensions of 0.3 mm ID and 50 meters long are generally appropriate although shorter lengths may be sufficient in many cases.

12.2 Initial Start-Up

12.2.1 Prior to instrument calibration or sample analysis, the GC-MS system is assembled as shown in Figure 3. Helium purge flows (through the desorption unit) and carrier flow are set at approximately 10 mL/min and 1-2 mL/min respectively. If applicable the injector sweep flow is set at 2-4 mL/min.

12.2.2 Once the column and other system components are assembled and the various flows established, the column temperature is increased to 250°C for approximately four hours (or overnight if desired) to condition the column.

12.2.3 The MS and data system are set according to the manufacturer's instructions. Electron impact ionization (70 eV) and an electron multiplier gain of approximately 5×10^4 should be employed. The mass range should be from 35 to 320 amu, the scan timer should be at least five scans per peak and not to exceed one second per scan. Table 4 outlines general operating conditions for the GC-MS-DS system.

12.2.4 Once the entire GC-MS system has been setup, the user should prepare a detailed standard operating procedure describing the operation of the specific instrument being used.

12.2.5 Turn on the power to the Tylan mass-flow controllers.

12.2.6 Turn on the following gases and set line pressures:

- Helium 60 psig
- Compressed Air 40 psig
- Nitrogen 30 psig

12.2.7 Typical flow rates for the thermal desorption and GC system are:

- Carrier flow through thermal desorption unit 1.2 mL/min

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- Carrier through injector 1.2 mL/min
- Injector septum purge 2.6 mL/min
- Thermal desorption unit purge 10.0 mL/min

12.2.8 Turn on the master power switch to the chromatograph.

12.2.9 Set manifold temperature to 105 ± 5°C.

12.2.10 Set ionization temperature to 260°C.

12.2.11 Turn on the power to the thermal desorption unit. Set the following temperatures for the valve, trap, and transfer line on the vernier dials on the control box of the thermal desorption unit:

- Valves 275°C
- Trap 190°C
- Line 210°C

12.2.12 Tune the radio frequency of the mass spectrometer using the manufacturer's procedures.

12.2.13 Set the zero of the mass spectrometer according to manufacturer's instructions.

12.3 Tuning the Mass Spectrometer with p-Bromofluorobenzene (BFB)

12.3.1 Tuning and mass standardization of the MS system is performed according to manufacturer's instructions and relevant information from the user-prepared SOP.

12.3.2 It is necessary to establish that a given GC-MS meets the standard mass spectral abundance criteria prior to initiating any on-going data collection. This is accomplished through the analysis of p-bromofluorobenzene (BFB).

12.3.3 Each GC-MS used for analysis must be hardware tuned daily or once per each twelve hour time period of operation, whichever is most frequent, to meet the technical acceptance criteria for BFB. Also, whenever corrective action which could change or affect the tuning for BFB (e.g., ion source cleaning or repair, column replacement, etc.), the tune must be verified immediately irrespective of the twelve-hour daily tuning requirement.

12.3.4 Prepare a 25 ng/μL solution of BFB in methanol. Prepare fresh BFB solution every six months or sooner if the solution has degraded or evaporated.

Note: The 25 ng/μL concentration is used with a 2 μL injection volume. The laboratory may prepare a 50 ng/μL solution of BFB if a 1 μL injection volume is used.

12.3.5 Inject 50 ng/μL BFB sample into the GC-MS.

12.3.6 Set time and parameters for the acquisition of the data and initiate data acquisition by following instructions in the operator's manual.

12.3.7 The instrumental parameters (e.g., lens voltages, resolution) should be adjusted to give the relative ion abundances shown in Table 5 as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria. These alternate values, however, must be repeatable on a day-to-day basis.

12.3.8 Typical criteria for an acceptable standardization as specified by manufacturer procedures and recommendation are:

- Base Peak Fit ≤15
- Mass Range ≤50 to ≥414
- Projection Error (MMU) < +75 to > -75
- Fit Error (MMU) ≤1.5%

Note: If the standardization is rejected because of total ion intensity, it can probably be corrected by slight adjustment of the "calibration" gas metering valve, followed by restandardization. If standardization is rejected because of the diagnostics, the percent relative abundances, or the ion intensities, the instrument must be returned and restandardized.

12.3.9 The abundance criteria listed in Table 5 must be met for a 50 ng injection of BFB.

12.4 Performance Specifications of the GC-MS with Perfluorotoluene (PFT)

Note: The initial tuning of the mass spectrometer to the manufacturer's criteria for an acceptable tune using BFB does not guarantee that an acceptable mass spectrum for perfluorotoluene (PFT) will be obtained.

12.4.1 Control of the percent relative abundances of ions of perfluorotoluene, the compound selected as the tuning standard for the analysis of volatile organic compounds from Tenax® cartridges, is essential for obtaining data of the desired quality. The relative abundances (RA) of the ions of perfluorotoluene should be reproducible within a specific range established by an historical data base from day-to-day.

12.4.2 Check the appearance of the mass spectrum of PFT by injecting a 50 ng/μL sample into the GC-MS.

12.4.3 When PFT is present in the ion source, set the oscilloscope in SINGLE mode and set the first Mass Control for mass 50 and the Last Mass for mass 250.

12.4.4 Observe all the major ions of the PFT mass spectrum on the oscilloscope.

12.4.5 Set up data acquisition and acquire several scans of the PFT mass spectrum.

12.4.6 Select one scan to check the % RA.

Note: The spectrum of PFT obtained by introduction of PFT into the GC-MS using the syringe inlet will differ slightly from the PFT mass spectrum obtained by thermal desorption of the PFT from a Tenax® cartridge and introduction to the mass spectrometer through the GC column, but the appearance of the mass spectrum should be a very good indication of whether the tune will meet the criteria for acceptable analysis.

12.4.7 Tuning criteria set for the major ions of the mass spectrum of PFT are as follows:

Ion	% RA of Base Peak
69	29
79	7
93	15
117	39
167	12
186	59
217	100
236	75

Ideally, the % RA should not vary by more than 10%.

12.4.8 If the mass spectrum of PFT does not meet the criteria for instrument operation, retune the instrument to meet these criteria.

12.5 Calibration of the GC-MS-DS System

12.5.1 External Standard Calibration Procedure

12.5.1.1 After the mass standardization and tuning process has been completed and the appropriate values entered into the data system, the user must calibrate the entire system daily by introducing known quantities of the standard components of interest into the system. Two suggested procedures may be employed for the external calibration process. They are: 1) direct syringe injection of dilute vapor phase standards, prepared in a dilution bottle, onto the GC column and 2) spiking of dilute vapor phase standards onto a Tenax® cartridge, then analysis by thermal desorption to the GC-MS-DS. The standards preparation procedures for each of these approaches are described in Section 15.3. The following paragraphs describe the instrument calibration process for each of these approaches.

12.5.1.2 If the instrument is to be calibrated by the external standard calibration mixture approach by direct injection of a 50 µL gaseous standards (see Table 1 asterisk compounds), the standards are prepared in a dilution bottle as described in Section 15.3. The GC column is cooled to -70°C (or, alternately, a portion of the column inlet is manually cooled with liquid nitrogen). The MS and data system is set up for acquisition as described in the relevant user SOP. The ionization filament should be turned off during the initial 2-3 minutes of the run to allow oxygen and other highly volatile components to elute. An appropriate volume (less than 1 mL) of the gaseous standard is injected onto the GC system using an accurately calibrated gas tight syringe. The system clock is started and the column is maintained at -70°C (or liquid nitrogen inlet cooling) for 2 minutes. The column temperature is rapidly increased to the desired initial temperature (e.g., 30°C). The temperature program is started at a consistent time (e.g., four minutes) after injection. Simultaneously the ionization filament is turned on and data acquisition is initiated. After the last component of interest has eluted, data acquisition is terminated and a calibration curve for each compound can be generated or RF evaluated according to Section 12.7.1.8.

12.5.1.3 If the system is to be calibrated by analysis of spiked Tenax® cartridges, a set of spiked cartridges are prepared as described in Sections 15.2 or 15.4. Prior to analysis the cartridges are stored as described in Section 10.5. If glass cartridges [Figure 1(a)] are employed care must be taken to avoid direct contact, as described earlier. The GC column is cooled to -70°C, the collection loop is immersed in liquid nitrogen and the desorption module is maintained at 250°C. The inlet valve is placed in the desorb mode and the standard spiked cartridge is placed in the desorption module, making certain that no leakage of purge gas occurs. The cartridge is purged for 10 minutes and then the inlet valve is placed in the inject mode and the liquid nitrogen source removed from the collection trap. The GC column is maintained at -70°C for two minutes and subsequent steps are taken as described in Section 12.7.1.2. After the process is complete the cartridge

is removed from the desorption module and stored for subsequent use as described in Section 10.5.

12.5.1.4 Data processing for instrument calibration involves determining retention times, and integrated characteristic ion intensities for each of the compounds of interest. A calibration curve for each compound can be generated or RF evaluated according to Section 12.7.1.8. In addition, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectra to ensure proper instrumental performance. Since the steps involved in data processing are highly instrument specific, the user should prepare a SOP describing the process for individual use. Overall performance criteria for instrument calibration are provided in Section 17. If these criteria are not achieved the user should refine the instrumental parameters and/or operating procedures to meet these criteria.

12.5.1.5 Calibration and quantitation of volatile organic compounds by GC-MS-DS can be performed by the Response Factor (RF) technique.

12.5.1.6 A RF is determined for each compound of interest.

12.5.1.7 To establish a RF data base for the target compounds prior to analysis of field sample cartridges, analyze a series of at least three cartridges by thermal desorption with the GC-MS-DS containing the target compounds applied to them by flash vaporization (see Section 15.2) technique. Table 6 outlines typical target compounds and number of nanograms/cartridge used in the RF determination.

12.5.1.8 Calculate three sets of RFs for each ion of interest for each target compound by the following equation:

$$\text{Response Factor (RF)} = A_i/C_i$$

where:
A_i = area counts for most intense ion, and
C_i = nanograms of standard deposited on cartridge

12.5.1.9 Tabulate these RFs.

12.5.1.10 If several RFs in a particular assay can be identified as outliers by their lack of correspondence to the other values obtained, discard that set of RFs.

12.5.1.11 If the ratio of response to concentration is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio of RF can be used in place of a calibration curve.

12.5.1.12 If the set of three RFs does not appear to be consistent, immediately check the desorption unit, gas chromatograph, and mass spectrometer for the presence of an air leak or some other problem, rectify the problem, and repeat the series of three cartridges. Note: If substantial nonlinearity is present in the calibration curve a nonlinear least squares fit (e.g., quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where:
Y = peak, area counts

X = quantity of component, ng
A, B, and C are coefficients in the equation

12.5.1.13 Initiate quantitation of the calculated RFs for target compounds and creation of the library in the data system to obtain ion peak areas and scan numbers automatically for each ion of each compound.

Note: The data system should include information about compound ions, the scan number at which the compound should be sought, and the Method file. The Method file contains information needed to designate a mass range in which to search for ions of the target compounds and establishes parameters required for peak area quantitation.

12.5.1.14 Create a library file for the target compounds within the data system.

12.5.1.15 Verify the correctness of all information entered (RFs, amount added to cartridge, etc.) for the ion of a compound by inspecting the terminal display.

12.5.1.16 When both a Quantitation List and a Library have been created, obtain calculated Response Factors by making a correlation between the ion of the compound and a library entry number.

12.5.1.17 Correlate all ions to a library entry.

12.5.1.18 Store RFs in a Response list of the computer.

Note: The computer, using a QUAN program, will automatically calculate ng/cartridge for targeted compounds.

12.5.1.19 Transfer all data acquired to a nine-track magnetic tape for archiving and possible further reference.

12.5.2 Internal Standard Technique Using Relative Response Factors (RRFs)

12.5.2.1 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 standards can be suggested that is applicable to all samples. The compounds recommended for use as surrogate spikes have been also used successfully as internal standards, because of their generally unique retention times.

12.5.2.2 Prepare five calibration standards, containing all the target compounds, spiked on clean Tenax® tubes as outlined in Section 15.3.

12.5.2.3 To each of these tubes, add a known concentration of an internal standard, as outlined in Section 10.6.2.

12.5.2.4 Analyze each tube according to Section 12.5.

12.5.2.5 Tabulate peak height or area responses against concentration for each compound and internal standard. Calculate relative response factors (RRF) for each target compound and the internal standard using the following equation.

Note: Table 1 contains primary quantitation ions to be used for each target compound and internal standard.

$$RRF = (A_x/A_{is})(C_{is}/C_x)$$

where:
A_x = area response for the compound to be measured
A_{is} = area response ion for the internal standard
C_{is} = concentration of the internal standard, ng
C_x = concentration of the compound to be measured, ng

12.5.2.6 Initiate quantitation of the RRFs for the target compounds and creation of the library in the data system.

12.5.2.7 If the RRF value over the working range is constant (< 10% RSD), the RRF can be assumed to be invariant and the average RRF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RRF.

13. Receipt of Samples

13.1 Receive all Tenax® cartridge tubes in a sealed can with the appropriate Chain-of-Custody sheet after standards have been loaded on them.

13.2 Match the Chain-of-Custody Sheet with the corresponding sample to ensure no mixup has occurred.

13.3 Check each Chain-of-Custody Sheet carefully for the following items: 1) a signature of a person relinquishing custody, 2) the amounts of standards loaded on the cartridge, 3) the temperature and volume collected amounts, and 4) the Tenax® batch number.

13.4 Do not analyze any sample that has no Chain-of-Custody sheet or is missing any of the above information.

13.5 Put all cans of samples in the cartridge freezer when received.

13.6 Log each sample in the appropriate notebook as received.

13.7 Place each Chain-of-Custody sheet in the project notebook (with all other information regarding that particular sample) after signing and dating it.

13.8 Store any used cartridges in sealed cans so they can be recycled, cleaned, and used again.

14. GC-MS-DS Analysis of Tenax® Adsorbent Tubes by Thermal Desorption

14.1 Description of Analytical Process

14.1.1 The instrumental conditions for the analysis of volatile organics on Tenax® sampling cartridge are outlined in Table 4. The thermal desorption chamber and the six port Valco valve are maintained at 275°C during analysis. The mass spectrometer is set to scan the mass range from approximately 35-350. The helium purge gas through the desorption chamber should be 10 mL/min. The nickel capillary trap on the inlet manifold should be cooled with liquid nitrogen.

14.1.2 Initially, the thermal desorption unit is cold while the Tenax® traps are placed inside while flowing helium through them. This allows oxygen to be purged from the trap, reducing oxidative degradation of Tenax®.

14.1.3 Then, during the thermal desorption cycle, helium gas continues to flow through the cartridge to purge the organic vapors on the Tenax® into the liquid nitrogen capillary trap.

14.1.4 After the desorption has been completed, the six-port valve is rotated and the temperature on the capillary loop is rapidly raised (greater than 100°C/min); the carrier gas then introduces the vapors onto the high resolution GC column. The bonded phase fused silica capillary column is temperature programmed from 40°C (5 min hold) to 240°C at 4°C/min and held at the upper limit for a minimum of 15 min.

14.1.5 The column is programmed to a temperature to allow the elution of all of the organic compounds while the mass spectrometer is scanning. Data are recorded by the computer for subsequent processing. Quantitation is performed by the method of response factors (see Section 12.5), where the proportionate system responses for analyte and standard are determined prior to the analysis of the sample and this relative system response is used to determine the quantity of compound present on the sample cartridge.

14.1.6 The quantitative analysis is performed by a combination of manual and computerized procedures: the computer is instructed to seek characteristic ions in a previously determined retention window. At this point the operator intervenes to determine if the compound of interest has been located correctly. If the compound identification is correct, the computer then performs the quantitative calculation using the method of relative response factors. Data are reported as ng/cartridge, and can be subsequently converted to whatever units are desired.

14.2 Desorption Process

Note: The following outlines typical steps associated with thermal desorption using the NuTech device. They are presented as a guideline to follow when using general equipment.

14.2.1 Remove the sealed paint can containing the desired cartridge from the freezer. Note: Use the freezer in the laboratory designated for cartridge storage ONLY for this purpose. Inadvertent storage of containers of solvent in this freezer will result in contamination of all cartridges stored in the freezer and will compromise the analysis, since organic solvents are frequently target compounds for quantitative analysis. Verify that the laboratory personnel are not involved in any process which requires the presence of open containers of organic solvents as the fumes of organic solvents will hopelessly contaminate a Tenax® cartridge exposed to this atmosphere for only a few seconds, thus compromising the quantitative and/or qualitative assay.

14.2.2 Open the sealed lid of the paint can, using a flat-bladed screwdriver, beverage can opener, or other convenient tool for this purpose.

Note: The cartridge will be in a stainless steel culture tube with a Teflon-lined screw cap.

14.2.3 Remove a single culture tube from the paint can and place in the wooden cartridge holder in front of the gas chromatograph.

14.2.4 Seal the paint can and replace in the freezer.

14.2.5 Release the Teflon cap of the desorption chamber.

14.2.6 Remove the cartridge from the culture tube using forceps.

Note: DO NOT TOUCH THE CARTRIDGE WITH YOUR HANDS! The slightest trace of organic compounds present on the fingertips can be sufficient to compromise the analysis. If the cartridge is inadvertently touched, make careful note of the circumstances in both the instrument log and the project notebook.

14.2.7 Insert the cartridge immediately into the desorption chamber.

14.2.8 Close the Teflon cap of the desorption chamber.

14.2.9 Initiate the timing of the eight-minute desorption cycle.

14.3 Injection Procedure

14.3.1 At the end of the eight-minute desorption cycle, turn the desorption unit valve to the INJECT mode (down).

Note: The following sets are automatic on some commercially available instruments.

14.3.2 Initiate heating of the nickel trap.

14.3.3 Begin acquisition of data system.

14.3.4 Turn off the trap after it has heated to 240°C.

14.3.5 Press the "start run" key on the GC microprocessor simultaneously with the <CR> key on the data-system terminal. This starts the GC temperature program and the data acquisition program.

14.3.6 Turn the thermal desorption unit valve back to desorb and remove the Tenax® cartridge.

14.3.7 At the end of the run, the GC will recycle and cool to 30°C, and the data acquisition will stop automatically after 4500 scans have been acquired.

14.3.8 The analysis may be stopped before 4500 scans by pressing the "stop run" key on the GC microprocessor. The data acquisition may then be stopped by typing [<CTRL>D] on the data system terminal and then typing [E<CR>STOP<CR>].

14.3.9 Repeat this procedure for each Tenax® cartridge to be analyzed.

14.4 Data Tabulation and Storage

14.4.1 Data from GC-MS runs are normally processed by the data system in an automated program which locates the compounds of interest in the data set, quantifies those compounds for which calibration data are available, and prints a report. A typical report will present the quantification parameters and result for those compounds present and quantifiable. The report will typically list those compounds which were searched for in the sample, indicate which ones were not found, print the identifying characteristics and quantification results for those which were found, and present comments for the operator's benefit, such as the criteria which caused a peak to be rejected or the center scan for any search which failed. The information in the report can also be saved in a DS file for archival storage and DS transfer purposes.

14.4.2 The library in the data system should contain a file composed of one entry for each compound of interest. For each entry, the library contains the compound name, its mass spectrum from the Mass Spectral Data Base, its absolute retention time, and its

retention time relative to perfluorotoluene, the retention time marker, as determined from authentic standards. Response lists (RL) are compound specific DS files containing the quantitative calibration data for each of the target compounds.

14.4.3 The automated procedure attempts to locate chromatographic peaks corresponding to target compounds by a reverse library search using the following criteria for scan window:

- for internal standards: ± 100 scans from library scan number
- for single compounds: ± 20 scans from the calculated scan
- for isomer groups: -20 and +20 scans from the calculated scans for the earliest and latest eluting members of the group, respectively
- Peak identification: peak 1/2-width ≥ 5 scans, purity ≥200, fit ≥700
- Peak selection: the scan list is partitioned in order of increasing distance from the center of the scan window, except for isomer groups

14.4.4 The automated procedure begins by attempting to locate the two retention time markers (PFT and 1,2-dichlorobenzene) and the internal standards ($toluene_{d8}$). If the early eluting standard, PFT, is not located a warning message is printed and the procedure is terminated. If only the late eluting internal standard is not found, the procedure uses the scan number calculated from the library retention time for this standard as a default value. Note: Alternatively, the operator may specify scan numbers for the internal standards and then initiate the remainder of the automated procedure. The procedure cycles through the compounds in the library list attempting to locate each compound in turn.

14.4.5 If one or more peaks are identified in the search for a target compound, the resulting scan list is partitioned to order the scans in increasing distance from the center of the search window. The mass spectra in the partitioned list are sequentially compared to the library entry for the target compound in order to the mass weighted purity, fit and rfit. The following ratio ranges are tested:

- Fit/purity: >0.99, <1.30
- Rfit/purity: >0.99, <1.05

If rfit/purity passes but fit/purity exceeds 1.29 the spectrum is enhanced, reprocessed through the library comparison, and tested against the above criteria.

14.4.6 If the mass spectrum at the peak maximum passes either of the above tests, the procedure attempts to quantify the peak. If the target is a single compound, only the first peak to pass the qualitative criteria is processed further. If the target is an isomer group, all peaks detected by the search are processed through the qualitative filters and all that pass these filters are quantified. If no peaks are found by the search or pass through the qualitative filters, a "not found" entry is placed in the report.

Note: The failure of a peak to satisfy these criteria does not necessarily prove the absence of the compound in the sample. Interfering compounds or low levels of the compound of interest may cause the test values to fall outside of the acceptance range. It is also possible to obtain acceptable values for fit/purity and rfit/purity, but have a questionable identification. If the absence of a particular compound is of crucial importance and the DS procedure fails to locate the compound, or for any compound which has a fit, purity, or rfit

less than 700, manual inspection of the data by a person skilled in the interpretation of GC-MS data is necessary for confirmation.

14.5 Qualitative Peak Identification

14.5.1 Relative intensities of major ions in the reference spectrum (ions greater than 25% of the most abundant ion) should be present in the sample spectrum.

14.5.2 The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% of the standard spectra, the corresponding sample ion abundance must be between 30 and 70%).

14.5.3 Molecular ions present in reference spectrum should be present in sample spectrum.

14.5.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

14.5.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

14.5.6 If in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (e.g., unknown aromatic, unknown hydrocarbon, unknown chlorinated compound). If a probable molecular weight can be distinguished, include it.

14.6 Peak Quantification

The procedure attempts to quantify peaks which have been qualitatively identified. Quantification is based on integration of the extracted ion current profile (EICP) of a quantitation mass or ion for the compound. This mass has been previously selected for each compound based on its spectral uniqueness, intensity, and lack of potential interferences from known coeluting compounds. Currently used masses are listed in Table 1.

14.7 Sample Quantitation

14.7.1 Sample quantitation is performed by the data processing system for all desired ions of all target compounds.

14.7.2 Utilizing the QUAN package of the data system involving compound identification and response factor to obtain quantitation data of the target compounds by the following equation:

$$X_A = [(A_A)(\mu g_{STD})]/[A_{STD})(RRF)]$$

where:

X_A = amount of target compound, μg
A_A = area of ion of analyte, counts
μg_{STD} = mass of standard applied to tube, μg

A_{STD} = area of standard, counts
RRF = relative response factor (see Section 12.5.2)

14.7.3 The computer, upon request, will print out peak number, m/e, scan, time, relative retention time, area and amount.

14.7.4 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = [(X_A - B_A)(1000\ L)]/[(m^3)(V_S)(R_A)]$$

where:
C_A = calculated concentration of target compound, ng/L
X_A = defined in Section 14.7.2
B_A = amount of target compound on blank, μg
V_S = calculated in Section 11.3.21
R_A = recovery factor, if applicable

15. Generation of Known Concentrations Procedures

15.1 Three procedures are discussed for generating known concentrations of targeted VOCs to be used for direct injection into the GC-MS-DS for calibration or depositing upon Tenax® tubes to be used in calibration of the entire GC-MS-DS analytical system. They are: 1) preparation of known concentrations utilizing static dilution bottles, 2) use of flash vaporization technique for loading targeted VOC standards upon Tenax® tubes and 3) use of permeation tube system for generating known concentrations of VOC standards upon Tenax® tubes. The standards preparation procedures are based on U.S. Environmental Protection Agency SOPs (41,45).

15.2 Flash Vaporization (see Figure 5)

15.2.1 Principle

15.2.1.1 A dilute solution of one or more organic compounds in methanol is injected into a heated zone in a helium stream. The methanol and the solute compounds are rapidly vaporized and then swept onto a sorbent cartridge. Methanol has little affinity for Tenax® sorbent and is rapidly eluted from the cartridge.

15.2.1.2 The solute compounds remain in the sorbent bed when the cartridge is removed from the flow system, and may subsequently be desorbed from the cartridge and delivered to an analytical instrument for analysis.

15.2.1.3 Since the quantity of each compound in the cartridge can be determined from its concentration in the solution and the volume of solution injected, this method may be used to spike quantitative standards on sorbent cartridges.

15.2.2 Interferences

15.2.2.1 Contamination of the methanol solvent with compounds to be calibrated, or with compounds producing similar instrumental responses, will result in false high or false positive responses.

15.2.2.2 Contamination of a compound used as a standard will result in a decreased response. Contamination of one compound with another one to be used in the same solution will result in incorrect responses for both compounds.

15.2.2.3 Chemical reaction between two compounds in a standard mixture will result in low responses for both. Absorption of a compound into the matrix of sorbent particles will probably result in part of it being retained in the cartridge during desorption, with consequent decreased response.

15.2.3 Flash Vaporization Assembly

15.2.3.1 Assemble the flash vaporization unit, as illustrated in Figure 5.

15.2.3.2 Adjust the helium flow to 30 mL/min and the heating mantle to 310 ± 10°C.

15.2.3.3 Allow the helium to flow for approximately 30 minutes to equilibrate the system.

15.2.4 Syringe Cleaning

15.2.4.1 Rinse individual syringe with methanol and acetone.

15.2.4.2 Dry in a vacuum syringe cleaner for ~30 seconds. (A heat gun is used to heat the barrel of the syringe during vacuum drying).

Note: Syringes must be rigorously cleaned after each injection to remove traces of sample. Even if more than one injection is needed from any given source a freshly cleaned syringe must be used for each injection. Failure to do so will probably result in erratic responses.

15.2.5 Helium Volume Required

15.2.5.1 The volume of helium required to elute methanol from a sorbent cartridge is determined by using a thermal conductivity detector.

15.2.5.2 Several different flow rates are tried to find one which results in as sharp a methanol peak as possible without sweeping volatile solutes out of the cartridge before it can be removed from the system.

15.2.6 Preparation of Standard Gas Concentration

15.2.6.1 Set the helium flow to 30 mL/min and the heater to 310° ± 10°C.

15.2.6.2 Place a clean (see Section 10.2) Tenax® cartridge in line.

15.2.6.3 Pass helium through the cartridge for a period of 5 minutes.

15.2.6.4 Using a heated syringe retrieve from the individual standard flask an aliquot by the following procedure:

15.2.6.4.1 Pull a 1 µL sample of methanol into the syringe.

15.2.6.4.2 Next draw a 1 µL plug of air.

15.2.6.4.3 Then pull the calculated quantity of standard solution into the syringe.

15.2.6.4.4 Finally, continue to pull another 1 µL plug of air.

Note: This insures that the sample solution is flushed completely out of the needle by the methanol plug during injection.

15.2.6.5 With the aliquot of the standard in the syringe, inject smoothly, at the standard injection point, the syringe contents over a period of about 5 seconds.

15.2.6.6 Allow the helium containing the injection standard to pass through the cartridge for 50 minutes or until 1500 mL of helium has passed.

15.2.6.7 Remove the cartridge from the system, cap and store at 5°C.

15.2.7 Calculation of Deliverable Concentration

15.2.7.1 The approximate volume of solution to be injected is calculated by working backward from the size of the spike to be placed in the sorbent cartridge.

15.2.7.2 For example, if a 500 ng spike is needed, it could be done by injecting 10 µL of methanol containing 50 ng/µL of solute. Therefore, 10 µL x 50 ng/µL solution = 500 ng.

15.2.7.3 A solution containing 50 ng/µL of solute is prepared by dissolving 5 mg of neat compound in a 100 mL volumetric flask and diluting to mark with methanol.

15.2.7.4 If the density of the neat compound is 0.9726 g/mL (0.9726 mg/µL), then the measured neat compound would be

$$5 \text{ mg}/(0.9726 \text{ mg}/\mu\text{L}) = 5.14 \ \mu\text{L}$$

15.2.7.5 Therefore, 5.14 µL of solute measured with a syringe would produce 50 ng/µL solution when diluted to 100 mL with methanol.

15.2.7.6 It is not practical to measure fractions of microliters, so usual practice would be to dissolve 5 µL of sample in 100 mL of methanol to produce a concentration of

$$(0.9726 \text{ mg}/\mu\text{L} \times 5 \ \mu\text{L})/100 \text{ mL} = 0.0486 \text{ mg/mL} = 48.63 \text{ ng}/\mu\text{L}$$

A 10 µL aliquot of this solution would contain 486.3 ng.

15.2.7.7 No correction for impurities in the neat sample is needed if manufacturer's determined purity is 98% or better.

15.2.7.8 As an example, a typical column evaluation mixture can be prepared as follows:

Standard	Density, g/mL	Volume, µL	Weight, mg	Deliverable Volume, µl	Spiked on Cartridges, ng
Ethylbenzene	0.867	11.0	9.54	3	286
p-Xylene	0.861	12.0	10.33	3	310
Acetophenone	1.028	10.0	10.28	3	308
2-Nonanone	0.821	12.0	9.85	3	296

These compounds should be 98% pure or better, and purity should be checked by capillary GC. Each compound is measured into a 100 mL volumetric flask using a microsyringe. The flasks are filled to the mark with spectrographic grade methanol and the contents mixed thoroughly. The solution must be used within half a day. Three microliters of those solutions, when injected into the flash vaporization unit in the manner specified above, will

deposit approximately 300 ng of each compound on a sorbent cartridge as shown in the table above.

15.3 Static Dilution Bottle

15.3.1 Principle

15.3.1.1 A quantity of liquid organic compound is injected into a two-liter round bottom helium-filled flask through a septum cap. After injections are completed, the flask is agitated and heated to achieve complete vaporization.

15.3.1.2 Aliquots of the resulting vapor are then delivered to sorbent cartridges or analytical instruments. The weight of each compound delivered is calculated from 1) the density of the liquid, 2) the volume of liquid injected into the known volume of the bottle, and 3) the volume of the vapor aliquot removed.

Note: The quantity of any compound injected into the dilution flask must be substantially less than that which would result in a partial pressure equal to its vapor pressure at ambient temperature. Vaporization of liquid aliquots injected into the bottle must not result in a large positive pressure, and removal of vapor aliquots from the flask must not result in a substantial vacuum. If these precautions are not taken erratic responses will occur.

15.3.2 Interferences

15.3.2.1 Contamination of a compound used as a standard will result in decreased response. Contamination of one compound with another one used in the same vapor mixture will result in an incorrect response for both compounds.

15.3.2.2 Adsorption of vapor molecules on the walls of the bottle or on the septum will result in loss of material, with a consequent decrease in response. This is especially likely when new, freshly annealed bottles are used. Contamination of apparatus can result in adsorption loss or provide unexpected sources of compounds in a mixture.

15.3.2.3 Chemical reactions between compounds can deplete them from the mixture and might also result in unexpected reaction products. Use of a syringe for consecutive injections from the same bottle without cleaning after each injection will probably result in erratic responses due to buildup of sample residues in the syringe.

15.3.3 Applicability

15.3.3.1 The static dilution bottle technique for preparing standards has been validated for the following 22 substances:

Acetophenone	3,4-Dichloro-1-butene
Benzonitrile	Perfluorotoluene
1,1,1,2-Tetrachloroethane	Fluoroiodobenzene
1,4-Dioxane	1-Ethenyl-4-chlorobenzene
1-Chloro-2,3-epoxypropane	3-Chloro-1-propene
1,3-Dichlorobutane	1,4-Dichlorobutane
1,4-Dichlorobenzene	1,2,3-Trichloropropane
cis-1,4-Dichloro-2-butene	1,1-Dichloroethane

2-Chlorobutane	1-Methyl-4-(1-Methyl-ethyl)-benzene
2-Chloroethoxyethene	Butylbenzene
1-Methylethylbenzene	1,3,5-Trimethylbenzene

15.3.3.2 Amounts used have ranged between 0.3 and 4 μL of liquid samples. Repeatability of daily injections of a mixture of the 22 compounds into the GC-MS is about ± 10% relative standard deviation. Precision depends on the substance introduced, the skill of the individual producing the flask standard, and the skill of the operator of the instrument used to analyze the flask contents. Accuracy has not been established.

15.3.4 Flask Cleaning

15.3.4.1 Wash the two-liter flask with detergent and water.
15.3.4.2 Rinse several times with deionized water.
15.3.4.3 Dry in an oven at 300°C for 4 hours.

15.3.5 Syringe Cleaning

15.3.5.1 Rinse individual syringes with methanol and acetone.
15.3.5.2 Dry in a vacuum syringe cleaner for ~30 seconds. (A heat gun is used to heat the barrel of the syringe during vacuum drying.)
Note: Syringes must be rigorously cleaned after each injection to remove traces of sample. Even if more than one injection is needed from any given source a freshly cleaned syringe must be used for each injection. Failure to do so will probably result in erratic responses.

15.3.6 Flask Calibration

15.3.6.1 Place 30 3-mm glass beads inside the flask and weigh on an analytical balance to an accuracy of 0.01 g.
15.3.6.2 Fill the flask with deionized water to the level of the septum cap.
15.3.6.3 Weigh the flask containing the glass beads and water on an analytical balance to an accuracy of 0.01 g.
15.3.6.4 The weight of the water required to fill the bottle is the difference between the two weights, as calculated below:

$$V_f = (Wt_f - Wt_i)$$

where:
V_f = volume of flask, mL
Wt_f = final weight of flask with beads and water, g
Wt_i = initial weight of flask with beads, g

15.3.7 Preparation of a Standard Gas Solution in a Flask

15.3.7.1 Two methods have been used to load the dilution flask with organic components for standards: 1) direct injection of each compound separately into the flask and 2) a single direct injection of a previously prepared mixture of compounds.

Note: These methods have been shown to produce indistinguishable results.

15.3.7.2 The first method involves injecting each compound (one at a time) into the flask. The flask is inverted after each injection with the syringe in place through the septum, in order for the beads to remove any liquid remaining on the syringe needle. The second method involves preparing a master solution by injecting 1 mL of each component into a culture vial fitted with a septum cap. After all the compounds have been added, the vial is agitated to produce a homogeneous liquid mixture. The vial is then recapped with a new septum. Aliquots of this master solution are removed and injected into the dilution flask as needed in the same manner as indicated above.

15.3.7.3 Retrieve a clean, dry two liter flask containing 70 3 mm glass beads.

15.3.7.4 Flush the flask with helium for a period of five minutes.

15.3.7.5 At the end of the flushing process, immediately cap with a Mininert septum cap.

15.3.7.6 Place the two liter flask on a magnetic stirring apparatus and set at the maximum speed.

15.3.7.7 Using the syringes, inject the calculated volume of each compound (one at a time) or from the mixture solution into the flask while the glass beads are agitated by the stirring bar at the maximum setting of the magnetic stirrer.

15.3.7.8 Invert the flask after each injection with the syringe in place through the septum, in order for the beads to remove any liquid remaining on the syringe needle.

15.3.7.9 After all substances have been introduced, place the flask in the oven at 60°C for 30 minutes to equilibrate.

15.3.7.10 Store the flask in the oven at 60°C until needed. Bottles are stable for one week after preparation.

Note: The technique of injecting a solution of targeted compounds rather than individual injection of specific compounds is preferred if many substances are involved, because it is more rapid, and the master solution can be used over a long period if it is refrigerated at 0°C. Before use, the refrigerated solution is allowed to sit at room temperature for about an hour. It is recommended that a total less than 90 µL of liquid be injected and a total less than 20,000 µL of gas be removed.

15.3.8 Withdrawal of an Aliquot

15.3.8.1 Remove the flask from the oven and place on the magnetic stirrer for approximately 15 seconds.

15.3.8.2 Place the syringe to be used in the extraction procedure in the oven at 60°C to prevent condensation in the syringe during delivery.

15.3.8.3 Using the heated syringe, insert its needle through the septum and pump three times slowly.

15.3.8.4 After the third pump, fill the syringe to approximately 25% greater volume than needed.

15.3.8.5 After a 5-second pause, withdraw the needle from the Mininert septum valve.

15.3.8.6 Flush the excess sample from the syringe, then draw a small quantity of air into the syringe to retard diffusion of sample through the syringe tip.

15.3.8.7 The aliquot sample must be used immediately.

15.3.9 Delivery of an Aliquot

15.3.9.1 If the sample is to be injected into a clean sorbent cartridge, the tip of the needle is inserted to the center of the sorbent bed. Then the plunger is depressed over a 10 second period while the needle tip is being withdrawn about half the distance to the end of the bed.

15.3.9.2 If the sample is injected directly into the analytical instrument, injection is made in the normal manner unless column-head freeze-trapping (cryofocusing) is being employed, in which case the plunger is depressed over about a 10 second period.

15.3.9.3 If a sample is too large to be injected in one step, two or more injections may be made. This causes no complication for injection into a sorbent cartridge, but cryofocusing must be employed when multiple injections are made directly into a gas chromatograph.

15.3.10 Calculation of Deliverable Concentration

15.3.10.1 Volumes to be introduced into the 2 liter flask are calculated by working backwards from the quantity of material to be delivered.

15.3.10.2 For example, if a 500 ng delivery is needed, it could conveniently be accomplished by using a 50 µL syringe containing 10 ng/µL of compound. Therefore,

$$50\ \mu L \text{ syringe} \times 10\ ng/\mu L \text{ solution} = 500\ ng$$

15.3.10.3 If the typical volume of the flask is 2.065 L, then to get that concentration (10 ng/µL) in the flask, one would have to add 20.65 mg of liquid compound to the flask. The calculation would therefore involve:

10 ng/µL x 2.065 L = quantity of liquid needed to develop a flask concentration of 10 ng/µL.

$$10\ ng/\mu L \times 2.065\ L = 20.65\ mg$$

15.3.10.4 If the density of the solution was 0.9726 g/mL (or 0.9726 mg/µL), then the volume of solution needed to add to the flask to maintain a concentration of 10 ng/µL or a deliverable of 500 ng would be 21.23 µL, as calculated:

$$20.65\ mg/(0.9726\ mg/\mu L) = 21.23\ \mu L$$

15.3.10.5 It is not practical to deliver and measure fractions of a microliter, so, in practice, 21 µL would be used. Therefore, the deliverable would be calculated:

$$(21\ \mu L \times 0.9726\ mg/\mu L)/2065\ mL = 0.00989\ mg/mL = 0.00989\ \mu g/\mu L$$

15.3.10.6 This is equivalent to 9.89 ng/µL, so a 50-µL injection of the vapor compound from the static dilution flask would contain:

$$9.89\ ng/\mu L \times 50\ \mu L = 494.5\ ng \text{ of compound delivered}$$

15.3.10.7 No correction for impurities in the neat sample is needed if manufacturer's determined purity is ≥98% or better.

15.4 Permeation Calibration Generator (see Figure 18)

15.4.1 Principle

15.4.1.1 A permeation calibration generator is designed to allow the permeation of gas through Teflon® or other plastic material at a constant rate in a water bath at constant temperature to generate test atmospheres.

15.4.1.2 The permeation tube is made by sealing a liquid chemical in a tube made of some permeable material. It is essential that the chemical be in the liquid state for the permeation tube to operate properly. In many cases the chemical is a gas at atmospheric pressure, but is maintained in the liquid state under its own saturation vapor pressure in the permeation tube. The tube is sealed at both ends with a non-permeable plug.

15.4.1.3 Permeation of the pollutant vapor within the tube occurs through the exposed sidewalls because of the concentration gradient that exists between the inner and outer tube walls. By passing different flows of diluent gas over the tube, gases of varying concentration can be generated. If the tube is held at a constant temperature, the permeation rate will remain constant. By measuring the weight loss at this constant temperature over a given period of time, the permeation rate may be determined. The output rate of the tube will remain essentially constant until nearly all of the liquid in the tube has permeated through the walls. In general, permeation tubes can be used to generate known pollutant concentration between 0.7 to 200 ppbv.

15.4.1.4 Before a permeation device can be used in the laboratory or in the field, its permeation rate must be determined. The permeation rate, R, is determined gravimetrically. In essence, the tube is weighed, then placed in a temperature bath (±1°C) for a period of time. The tube is removed and reweighed. This process is repeated over several days to calculate a permeation rate at that specific temperature. The difference between initial and recorded weight (ng), divided by time (min) determines the permeation rate at that specific temperature.

$$R = W/T$$

where:
R = permeation rate, ng/min
W = weight change, ng
T = time, minutes

The permeation rate can be calculated either manually, as shown in the above equation, or recorded automatically. At different temperatures, different permeation rates can be calculated.

15.4.1.5 Permeation tubes should be kept at the temperature specified by the manufacturer and at a constant temperature (±0.05°C) during calibration procedures. Changes in temperature as small as 0.1°C can significantly affect the permeation rate.

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Tubes should initially be allowed to equilibrate for 24 hours. After small changes in temperature (1 to 5°C), the tube should be allowed to equilibrate for at least half an hour.

15.4.2 Applicability

15.4.2.1 A permeation tube system has been developed for application of loading known standards onto Tenax® cartridges for use in determining the relative response factor and the column performance evaluation (CPMX) of the GC-MS-COMP system in conjunction with the flash vaporization system.

15.4.2.2 In addition, the permeation tube system is used for generating external standards [perfluorobenzene (PFB) and perfluorotoluene (PFT)] to be loaded by syringe onto the Tenax® tube to determine relative retention times, relative response factors and stability of the GC-MS-DS system and for generating deuterated standards used in the evaluation of breakthrough volumes associated with Tenax®.

15.4.3 Permeation Generator Assembly

15.4.3.1 A permeation system consists of four main parts (see Figure 18): 1) a temperature-controlled chamber containing permeation tubes, 2) a mixing chamber, and 3) permeation tube storage chamber. A stream of nitrogen flows through the system. The amounts of compounds transported downstream remain constant once the system has become equilibrated with the compounds to be loaded. The amount of compounds can be determined by measuring the time and the gas flow through the cartridge.

15.4.3.2 The permeation system may be used to load any volatile compound that will permeate at a constant rate under controlled conditions, and to inject a calibration standard onto a sorbent via syringe.

15.4.4 Preparation of Standard Gas Concentration

Note: The following routine should be followed when Tenax® cartridges are loaded with deuterated standards via a permeation system: 1) determine the number of cartridges to be loaded, 2) select the permeation tubes, 3) determine the loading conditions to be used, 4) equilibrate the system, 5) load the cartridges, 6) calculate the amounts of compounds loaded, 7) ensure the integrity of the loading procedure, and 8) pack and store the cartridges.

15.4.4.1 Determination of the Number of Cartridges to be Loaded

15.4.4.1.1 Obtain a copy of the field sampling schedule from the Monitoring Coordinator or Program Manager.

15.4.4.1.2 Determine the number of deuterated standards and external standards required to satisfy the sampling objectives.

15.4.4.2 Selection of the Permeation Tubes

15.4.4.2.1 Check the permeation notebooks (located in the laboratory) to see which permeation tubes are available for the needed standards.

15.4.4.2.2 Select only the permeation tubes whose permeation rates are stable.

Note: A permeation rate is considered stable when the mean permeation rate has a coefficient of variation (CV) of less than 10%. The mean permeation rate is calculated using the last five individual permeation rates. Do not use permeation tubes with permeation rates below 100 ng/min or above 1×10^5 ng/min.

15.4.4.2.3 In a bound notebook assigned for the specific project, prepare a table including: 1) the numbers of the tubes to be used, 2) the names of the compounds, and 3) the corresponding mean permeation rates.

15.4.4.3 Determination of the Permeation System Conditions

15.4.4.3.1 For any compound, calculate the amounts needed to be loaded onto a Tenax® cartridge using the following formula:

$$G = (P)(t)[F_1/(F_1 + F_2)]$$

where:
G = amount loaded of compound onto Tenax® tube, ng
P = permeation rate of specific compound, ng/min
t = total time of loading of compound onto Tenax® tube, minutes
F_1 = flow rate through the Tenax® cartridge, mL/min
F_2 = exhaust flow rate, mL/min
Note: The four variables G, t, F_1, and F_2 determine the loading conditions. Any three may be fixed and the fourth one calculated from the equation.

15.4.4.3.2 The following restrictions must be followed to minimize error: 1) do not load for less than two minutes, 2) do not load with a cartridge flow below 50 mL/min or above 150 mL/min, 3) do not operate the system with a total flow below 250 mL/min.

15.4.4.3.3 If the GC-MS-DS system needs to operate in the range of 200-500 ng per analyte, then the analyst must generate standards concurrent with that range. Fixing three of the four variables of the above equation will enable calculation of the needed loading onto the Tenax® tube.

15.4.4.3.4 As an example, the following calculations are provided to assist the user in determining operating parameters of the permeation tube system in generating standards on QA/QC checks.

OBJECTIVE: To load chlorobenzene and chloroform onto a cartridge in the range of 200-500 per analyte.

GIVEN: G = 200 ng per analyte
F_1 = 80 mL/min
t = 4 min
P = 270 ng/min for chlorobenzene
= 520 ng/min for chloroform

Chlorobenzene

$$G = (P)(t)[F_1/(F_1+F_2)]$$

$$200 \text{ ng} = (270 \text{ ng/min})(4 \text{ min})[(80 \text{ mL/min})/(80 \text{ mL/min} + F_2)]$$

$$F_2 = \{[(270 \text{ ng/min})(4 \text{ min})(80 \text{ mL/min})]/200 \text{ ng}\} - 80 \text{ mL/min}$$

$$F_2 = 352 \text{ mL/min}$$

Now, since all tubes are in the permeation device together, the flow (F_2) for chloroform will be 352 mL/min. Therefore, the loading on the Tenax® tube for chloroform must be calculated to verify that it falls within the 200-500 ng per tube loading.

Chloroform

$$G = (P)(t)[F_1/(F_1 + F_2)]$$

$$G = (520 \text{ ng/min})(4 \text{ min})[(80 \text{ mL/min})/(80 \text{ mL/min} + 352 \text{ mL/min})]$$

$$G = 385 \text{ ng}$$

All values obtained are within the acceptable range.

15.4.4.4 Equilibration of the Permeation System

15.4.4.4.1 Locate the chambers in which the selected permeation tubes are stored.

15.4.4.4.2 With a long glass hook, remove the selected permeation tubes from the storage chamber and transfer immediately to the loading chamber of the permeation system.

Note: Failure to wear nylon gloves when handling permeation tubes may result in skin damage and/or contamination of the permeation tubes.

Note: Perform this operation as quickly as possible. The tubes contain toxic materials, some of which are cancer suspect agents.

15.4.4.4.3 Direct nitrogen flow to the side where the Tenax® cartridge will be loaded.

Note: When a cartridge is not being loaded, a dummy cartridge is placed in the loading position.

15.4.4.4.4 Allow the system to equilibrate for 90 minutes before loading cartridges with the generated test atmospheres.

15.4.4.5 Loading of the Tenax® Cartridges

Note: Be sure the background of the Tenax® cartridges is acceptable before loading them.

15.4.4.5.1 Divert the nitrogen flow to the side that will not be used for loading cartridges.

15.4.4.5.2 Insert the Tenax® cartridge into the chamber.

15.4.4.5.3 Direct the test atmospheres gas flow through the cartridge.

15.4.4.5.4 Concurrently, start the stopwatch.

15.4.4.5.5 Calculate the time needed to load the amounts desired as follows:

$$t = (G/P) \times [(F_1 + F_2)/F_1]$$

Do the calculation based only on the compound whose permeation tube has the highest or lowest permeation rate.

15.4.4.5.6 At the calculated time rotate the two stopcocks to direct gas flow away from the cartridge being loaded.

15.4.4.5.7 Handling the cartridge with a Kimwipe®, remove the cartridge and return it to its culture tube. Seal the tube.

15.4.4.5.8 Label the tube. Include the following information: 1) project number, 2) deuterated standard mixture followed by a number indicating the order of loading, and 3) the date.

15.4.4.5.9 Prepare a Chain-of-Custody sheet with the information concerning amount loaded on the tube.

15.4.4.6 Storage of the Deuterated Standard Cartridges

15.4.4.6.1 Secure the cartridge inside the Kimax® tube with a glass wool plug to avoid breakage during transport.

15.4.4.6.2 Label the top of the screw cap with the following symbol: D*.

Note: * The star indicates that deuterated standards have been loaded onto the cartridge. This symbol will also be added to the participant's code.

15.4.4.6.3 Store the cartridges in a sealed paint can in the freezer until they are ready to be sent to the field.

15.4.4.7 Calculations of the Amounts Loaded

15.4.4.7.1 For every compound, calculate the amount loaded onto a cartridge using the general formula:

$$G = (P)(t)[F_1/(F_1 + F_2)]$$

15.4.4.7.2 Deliver the loaded permeation tubes to the GC-MS-DS for use in the quality assurance program.

16. Calibration of Personal Sampling Pump

16.1 The pump is calibrated so the flow controller is set at the desired sampling rate at standard conditions for the Tenax® sorbent sampling tube.

16.2 Sampling pumps are calibrated at the beginning and at the conclusion of each sampling period. To ensure quality volumetric results, pump calibration is recommended at random points throughout each study.

16.3 Assemble the personal sampling pump calibration system (see Figure 19). Connect a soap-film flowmeter of suitable volume (typically 1 liter) with Tygon tubing to the back-end of the active sampler, as illustrated in Figure 19.

Note: With higher sampling rates, a considerable pressure drop through the tube can result. To minimize this effect, a larger capacity pump would be necessary for higher sampling rates (i.e., >5 L/min).

16.4 Record the barometric pressure and ambient temperature on the sampling data sheet.

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16.5 Thoroughly wet the surface of the flowmeter before any measurements are recorded. Measure the time for a soap-film bubble to travel a known volume with a stopwatch. Perform five replicate measurements and compute the average time. Calculate the standard volume (V_S) in liters from the equation:

$$V_S = (V_a \times P_b \times 298)/[(T + 273) \times 760]$$

where:
V_S = volume corrected to standard conditions of 298°K and 760 torr, L
V_a = actual volume measured with the soap-film flowmeter, L
T = temperature at calibration, °C
P_b = barometric pressure at calibration, torr
760 = standard pressure, torr
298 = standard temperature, °K

16.6 The standard flow rate (Q_S) is then calculated with the equation:

$$Q_S = V_S/R$$

where:
Q_S = standard flow rate, L/min
V_S = volume corrected to standard conditions, L
R = average time obtained from soap-film measurement, minutes

16.7 Once the flow has been set, record calibration date in laboratory logbook.
Note: Set flow rate of pump and indicate flow rate on a sticker attached to the pump.

17. Performance Criteria and Quality Assurance

17.1 This section summarizes quality assurance (QA) measure and provides guidance concerning performance criteria which should be achieved within each laboratory. In many cases the specific QA procedures have been described within the appropriate sections of this protocol. Figure 20 summarizes these performance criteria discussed in this protocol.

17.2 Standard Operating Procedures (SOPs)

17.2.1 Each user should generate SOPs describing the following activities as they are performed in their laboratory: 1) assembly, calibration, and operation of the sampling system, 2) preparation, handling and storage of Tenax® cartridges, 3) assembly and operation of GC-MS system including the thermal desorption apparatus and data system, and 4) all aspects of data recording and processing.

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

17.3 Tenax® Cartridge Preparation

17.3.1 Each batch of Tenax® cartridges prepared should be checked for contamination by analyzing one cartridge immediately after preparation. While analysis can be

accomplished by GC-MS, many laboratories may choose to use GC-FID due to logistical and cost considerations.

17.3.2 Analysis by GC-FID is accomplished as described for GC-MS except for use of FID detection.

17.3.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria the entire lot should be rejected.

17.4 Sample Collection

17.4.1 During each sampling event at least 10% of all field samples should accompany the samples to the field and back to the laboratory, without being used for sampling, to serve as a field blank. The average amount of material found on the field blank cartridge may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data for that component must be identified as suspect.

17.4.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) will be collected, preferably at different flow rates. If agreement between parallel samples is not generally within ± 25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples one should consider using a reduced flow rate and longer sampling interval if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest may be required.

17.4.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 20% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater. The frequency of use of backup cartridges should be increased if increased flow rate is shown to yield reduced component levels for parallel sampling. This practice will help to identify problems arising from breakthrough of the component of interest during sampling.

17.5 GC-MS Analysis

17.5.1 Performance criteria for MS tuning and mass calibration have been discussed. Additional criteria may be used by the laboratory if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC-MS system.

17.5.2 Chromatographic efficiency should be evaluated using spiked Tenax® cartridges since this practice tests the entire system. In general, a reference compound such as perfluorotoluene should be spiked onto a cartridge at the 100 nanogram level. The cartridge is then analyzed by GC-MS. The perfluorotoluene (or other reference compound)

peak is then plotted on an expanded time scale so that its width at 10% of the peak can be calculated. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The asymmetry factor should be between 0.8 and 2.0. The asymmetry factor for any polar or reactive compound should be determined using the process described above. If peaks are observed that exceed the peak width or asymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings and is necessary. Some laboratories may choose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature. Such schemes cannot be conducted by placing the substances onto Tenax® because many of the compounds (e.g., acids, bases, alcohols) contained in the test mix are not retained, or degrade, on Tenax®.

17.5.3 The system detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where:

DL = calculated detection limit injected, ng
A = the intercept of the slope
S = the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required)

In general, the detection limit should be 20 nanograms or less and for many applications detection limits of 1-5 nanograms may be required. The lowest level standard should yield a signal to noise ratio, from the total ion current response, of approximately 5.

17.5.4 The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation should be 25% or less.

17.5.5 A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present in ambient air (e.g., perfluorotoluene). The integrated ion intensity for this compound helps to identify problems with a specific sample. In general the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any sample giving a value greater than ±2 standard deviations from the mean (calculated excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

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Table 1. Compounds Identified and Quantified by Automated GC-MS-DS Procedure with Typical Detection Limits in Full Scan Mode

Compound	Quantitation Mass (m/z)	Detection Limits (ng)
perfluorotoluene (internal standard)*	217	0.3
benzene*	78	2.6
methylbenzene*	91	2.0
1,2-dimethylbenzene*	106	0.5
1,3,5-trimethylbenzene	120	2.5
ethylbenzene*	91	1.6
ethylbenzene*	104	1.7
(1-methylethyl) benzene	105	1.1
butylbenzene	91	0.7
1-methyl-4-(1-methylethyl) benzene	119	4.0
chlorobenzene*	112	1.7
bromobenzene	156	14.1
1,2-dichlorobenzene*	146	12.4
1-ethenyl-4-chlorobenzene	138	2.0
trichloromethane	83	2.7
tetrachloromethane*	82	2.1
bromochloromethane*	130	2.1
bromotrichloromethane*	163	1.6
dibromomethane*	174	4.5
tribromomethane*	171	8.5
1,1-dichloroethane*	63	5.7
1,2-dichloroethane	62	3.8
1,1,1-trichloroethane*	99	1.7
1,1,2-trichloroethane*	85	2.1
1,1,1,2-tetrachloroethane	31	0.9
1,1,2,2-tetrachloroethane	83	6.5
pentachloroethane*	167	1.8
1,1-dichloroethane*	961	6.9
trichloroethene*	132	0.8
tetrachloroethene	166	2.6
bromoethane*	108	7.8
1,2-dibromoethane*	107	3.3
1-chloropropane*	42	1.7
2-chloropropane*	43	3.4
1,2-dichloropropane	63	4.0
1,3-dichloropropane	76	9.6
1,2,3-trichloropropane	753	4.7
1-bromo-3-chloropropane	158	1.6
3-chloro-1-propene	41	1.6

Table 1 (cont'd)

Compound	Quantitation Mass (m/z)	Detection Limits (ng)
1,2-dibromopropane*	121	14.4
2-chlorobutane	57	3.5
1,3-dichlorobutane	55	0.5
1,4-dichlorobutane	55	8.2
2-3-dichlorobutane*	90	5.1
1,4-dichloro-2-butane (cis)	752	1.9
3,4-dichloro-1-butane	75	6.5
tetrahydrofuran	72	1.2
1,4-dioxane	88	3.9
1-chloro-2,3-epoxypropane	71	8.1
2-chloroethoxyethene	631	8.2
benzaldehyde*	77	5.9
acetophenone	105	2.9
benzonitrile	103	1.3
ISOMER GROUPS		
1,3- & OR 1,4-dimethylbenzene	106	0.5
1,2- & OR 1,3-dichlorobenzene*	146	1.3
2- & OR 3- & OR 4-chloro-1-methylbenzene*	126	0.5
SURROGATE GROUPS AND INTERNAL STANDARDS		
4-bromofluorobenzene (BFB)	95	
chlorobenzene-d_5	117	
1,4-dichlorobenzene	150	
1,4-difluorobenzene	114	

* Compounds used to calibrate GC-MS-DS on a daily basis either by direct injection or on spiked adsorbent tubes.

Table[a] 2. Breakthrough Volumes[b] and Safe Sampling Volumes[b] for Tenax-GC and Tenax-TA

	Tenax-GC breakthrough volume[b]	Tenax-TA breakthrough volume[b]		Tenax-GC safe sampling volume[c]	Tenax-TA safe sampling volume[c]	
	38°C	20°C	35°C	38°C	20°C	35°C
Acetaldehyde	0.6	0.6	0	0.3	<1	<1
Acrolein	4	5	2	1.7	2	<1
Acrylonitrile	-	8	3	-	3	1
Allyl chloride	-	8	3	-	3	1
Benzene	19	36	15	8.2	14	6
Benzyl chloride	300	440	200	130	175	80
Bromobenzene	300			130		
Carbon tetrachloride	8	27	13	3.5	11	5
Chlorobenzene	150	184	75	6.5	5	2
Chloroform	8	13	5	4	5	2
Chloroprene	-	26	12	-	10	5
Cresol	440	570	240	191	230	95
p-Dichlorobenzene	510	820	330	221	290	130
1,4-Dioxane	-	58	24	87	23	10
Ethylene dibromide	60	77	35	26	30	14
Ethylene dichloride	-	29	12	-	12	5
Ethylene oxide	-	0.5	0.3	-	<1	<1
Formaldehyde	-	0.6	0.2	-	<1	<1
Hexachlorocyclo-pentadiene	-	2000	900	-	800	360
Methyl bromide	0.8	0.8	0.4	0.4	<1	<1
Methyl chloroform	-	9	4	-	3	2
Methylene chloride	3	5	2	1.5	2	<1
Nitrobenzene	-	520	240	-	200	95
Perchloroethylene	-	100	45	-	40	18
Phenol	-	300	140	-	120	55
Propylene oxide	3	3	1	1.5	1	<1
Trichloroethylene	21	45	17	8.5	18	7
Vinyl chloride	0.6	.06	.03	.03	<1	<1
Vinylidene chloride	-	4	2	-	2	<1
Xylene	200	177	79	89	70	32

[a]See Section 18, reference 58.
[b]Breakthrough volumes expressed as liters/gram of sorbent.
[c]Safe sampling volume = {[Breakthrough volume (L/g)]/1.5} x 0.65 grams of sorbent.
[d]Breakthrough volumes for other chemicals can be extrapolated on the basis of boiling points for chemicals in the same chemical class.

Table 3. Commercially Available Thermal Desorption Units

Company	Address	Number	Model Comments
Tekmar Co.	PO Box 371856 Cincinnati, OH 45222-1856 (800) 543-4461	5010GT	1. 1/4 or 5/8 in. tubes 3 to 7-inches long, glass or metal. 2. Desorption temperatures to 420°C.
Nutech Corp.	2806 Cheek Rd. Durham, NC 27704 (919 682-0402	320	1. Uses glass sorbent tubes.
Chrompack	1130 Rt. 202 South Raritan, NJ 08869 (800) 526-3687	TCT	1. Desorption temperatures to 300°C. 2. 1/4-in. OD x 3.0 in.
Chemical Data Sys., Inc.	7000 Limestone Rd. Oxford, PA 19363 (215) 932-3636	330	1. Desorption temperature to 350°C. 2. 1/4-in. OD x 3-in. long or 1/2 in.
Perkin-Elmer	2772 N. Garey Ave. Pomona, CA 91767 (714) 593-3581	ATD-50	1. Desorption temperatures to 250°C. 2. 1/4-in. OD x 3-in. long tubes. 3. Up to 50 samples processed automatically.
Envirochem, Inc.	Box 180 Kemblesville, PA 19347 (212) 255-4474		1. Desorption temperatures to 300°C. 2. 6-mm OD x 11.5-cm long tubes.

Table 4. Typical Operating Conditions for a GC-MS-DS

Thermal Desorption Unit - NuTech Model 320 or Tekman Model 5000 or equivalent

Purge Gas	Helium @ 1.2 mL/min
Desorption Cycle	8 Minutes
Initial Desorption Temperature	25°C
Final Desorption Temperature	190°C
Thermal Desorption Unit Purge	10 mL/min

Gas Chromatography

Injection/Detector Temperature	200°C
Initial Column Temperature	30°C
Initial Hold Time	0.1 minutes
Program	4°C/min to 240°C
Final Hold Temperature	240°C
Final Hold Time	0.1 minutes
Maximum Over Temperature	245°C
Carrier Gas	Helium velocity 20 cm^3/sec at 250°C
GC-MS Interface	Direct coupling or glass jet
Sample Injection to MS	Direct Probe
Column	Hewlett-Packard OV-1 glass capillary crosslinked methyl silicone (50 m x 0.3 mm, 0.17 μm film thickness) Scientific Glass Engineering SE-30 glass capillary crosslinked methyl silicone (50 m x 0.5 mm, 0.80 μm film thickness)

Mass Spectrometer - Quadrupole Spectrometer, Electron Impact (EI)

Mass Range	35 to 320 amu
Scan Time	1 sec-10 min over entire range
EI Condition	70 eV
Mass Scan and Detector Mode	Follow manufacturer instruction for select mass selective detector (MS) and selected ion monitoring (SIM) mode
Routine Tuning	p-bromofluorobenzene
Preamp Sensitivity	10^{-7}
Emission Current	-0.45
Electron Multiplier Voltage	1000 to 1500
Mass Filter	10 amu/sec
Filter	x 100
Total Ion Current Sensitivity	1
Resolution	Normal
Display	TIC
Response	Fast

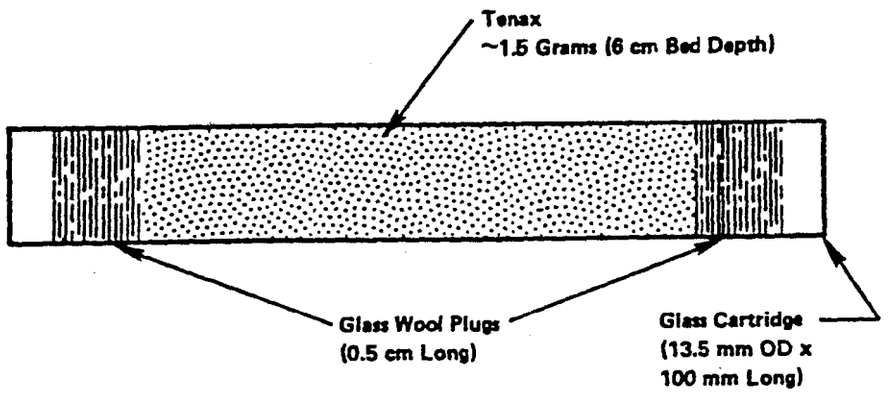
Table 5. Suggested BFB Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	15-40% of the base peak
75	30-60% of the base peak
95	base peak, 100% relative abundance
96	5-9% of the base peak
173	<2% of mass 174
174	>50% of the base peak
175	5-9% of mass 174
176	>95% but <101% of mass 174
177	5-9% of mass 176

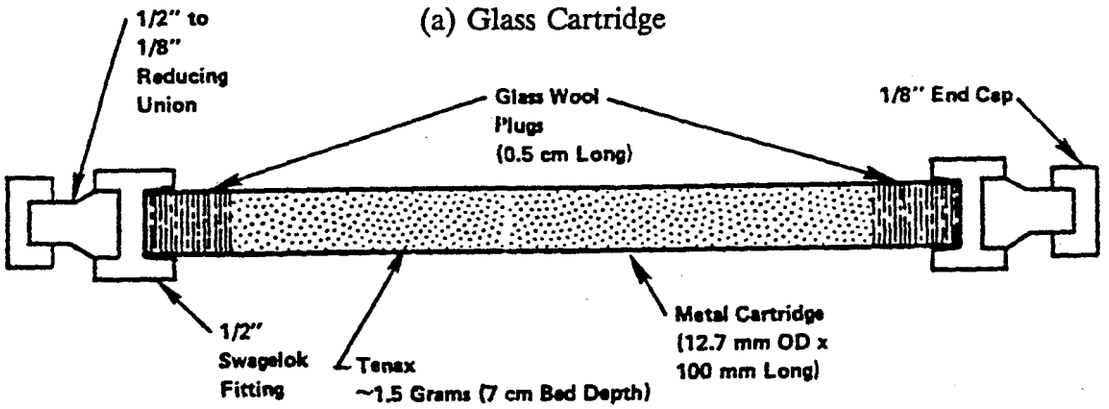
Table 6. Target Compound List Used in Response Factor (RF) Determination with Specific Mass Loading onto Spiked Cartridge

Compound	ng Loaded
Benzene	304
Chloroform	114
1,1,1-Trichloroethane	174
Carbon Tetrachloride	201
1,2-Dichloroethane	329
Trichloroethylene	403
1,1,2,2-Tetrachloroethane	409
Chlorobenzene	140
Tetrachloroethylene	323
Ethylbenzene	346
p-Xylene	344
o-Xylene	352
Styrene	362
o-Dichlorobenzene	260
p-Dichlorobenzene	260
n-Octane	288
n-Decane	292
5-Nonanone*	328
Acetophenone*	411
2,6-Dimethylphenol*	294
2,6-Dimethylaniline*	391
1-Octanol*	330
Perfluorobenzene	125
Perfluorotoluene	130

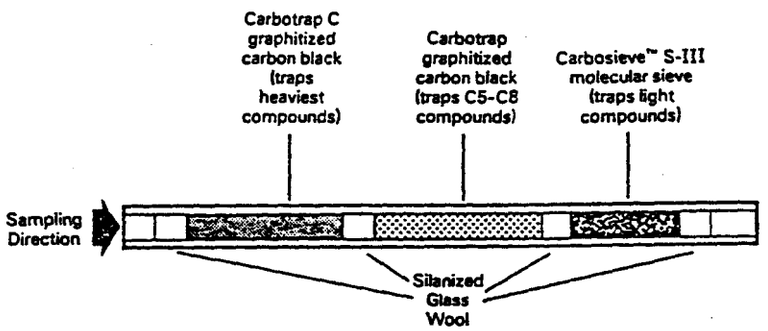
*Used in the calculation of column performance parameters; not a target compound.



(a) Glass Cartridge

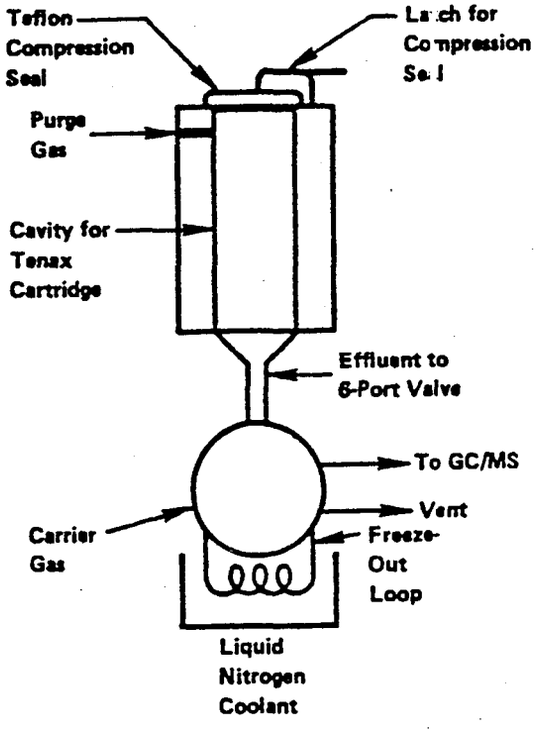


(b) Metal Cartridge

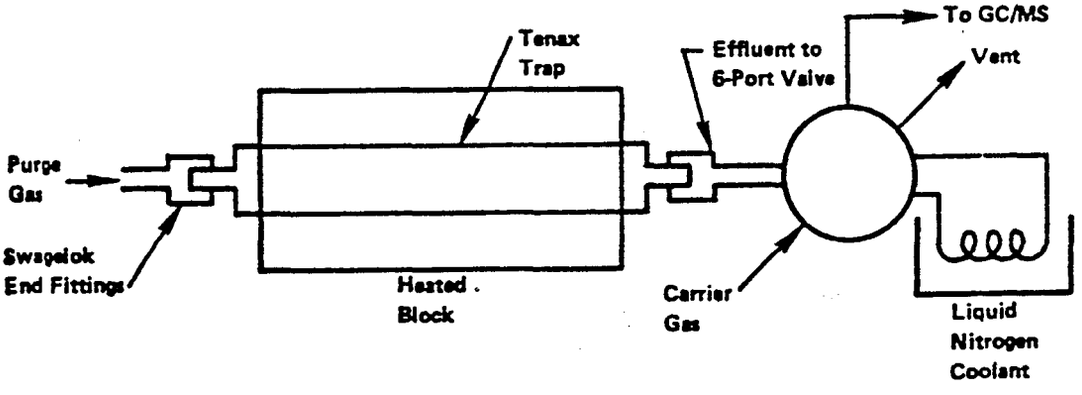


(c) Multibed Adsorbent Tube

Figure 1. Common Designs of Adsorbent Cartridges



(a) Glass Cartridges (Compression Fit)



(b) Metal Cartridges (Swagelok Fittings)

Figure 2. Tenax® Cartridge Desorption Modules

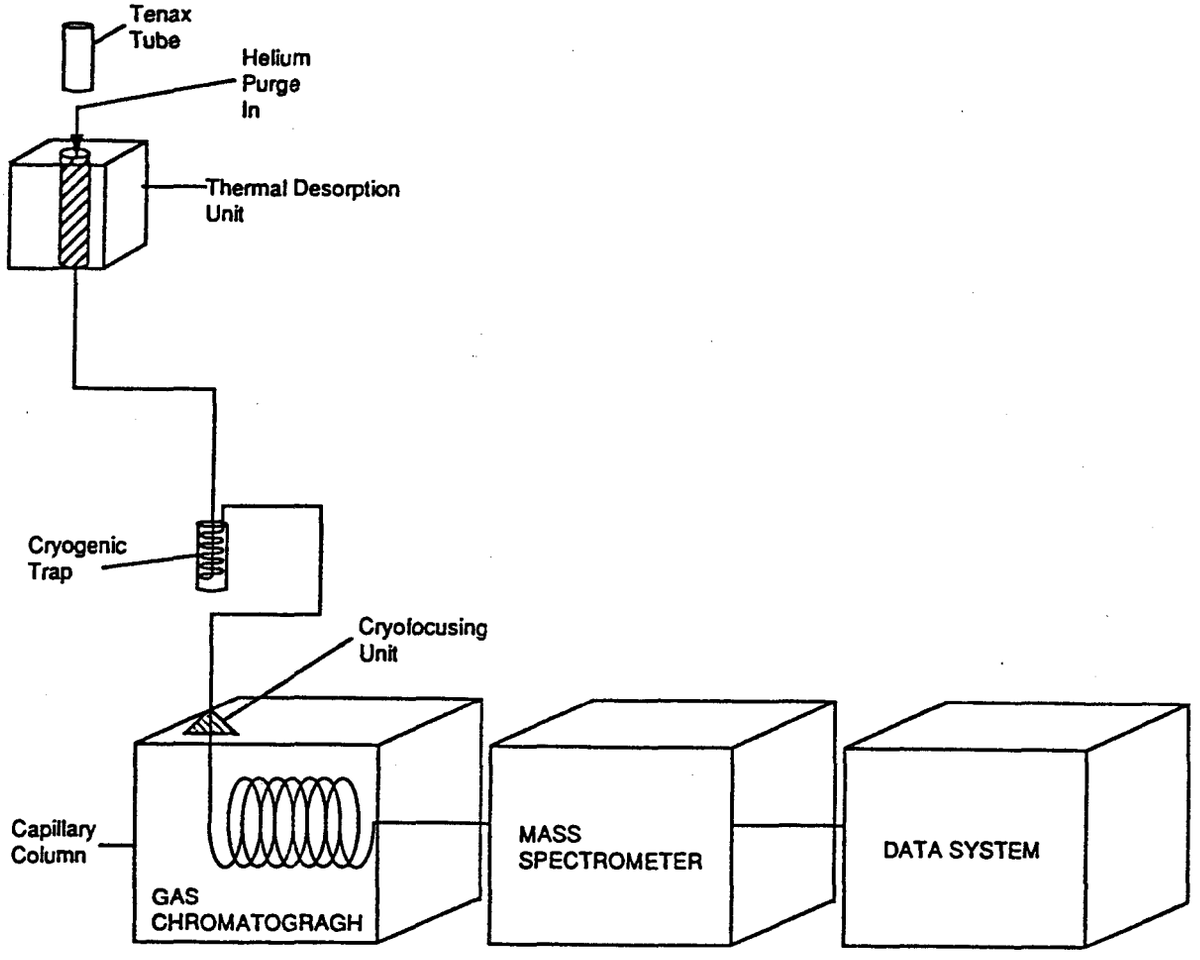


Figure 3. Typical Desorption GC-MS-DS Configuration

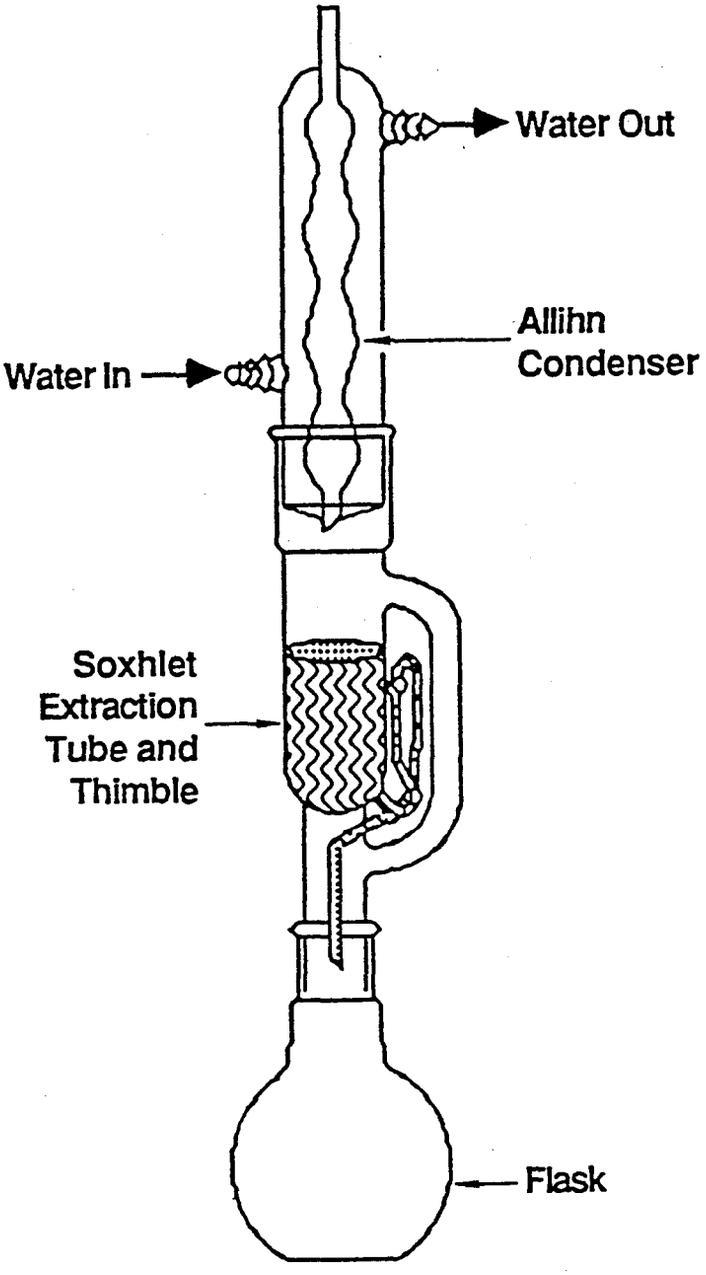


Figure 4. Soxhlet Extraction Apparatus with Allihn Condenser

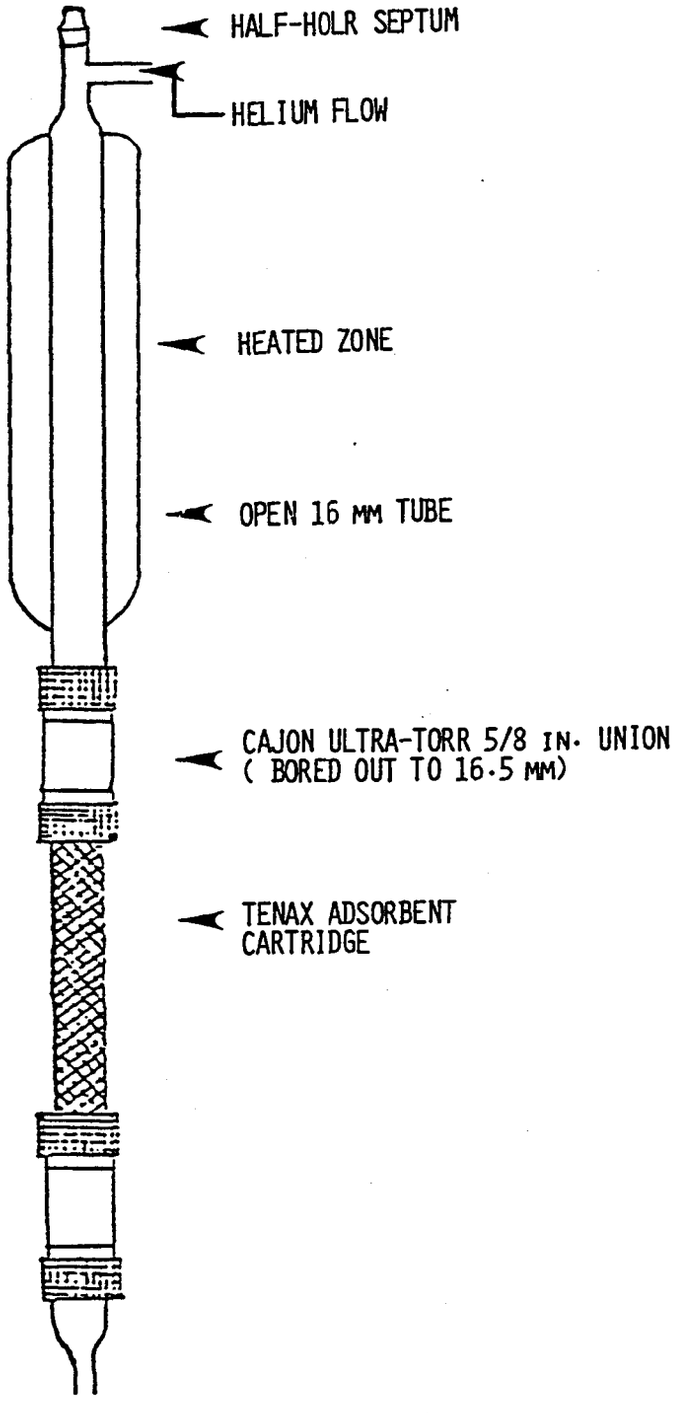


Figure 5. Flash Evaporation Unit

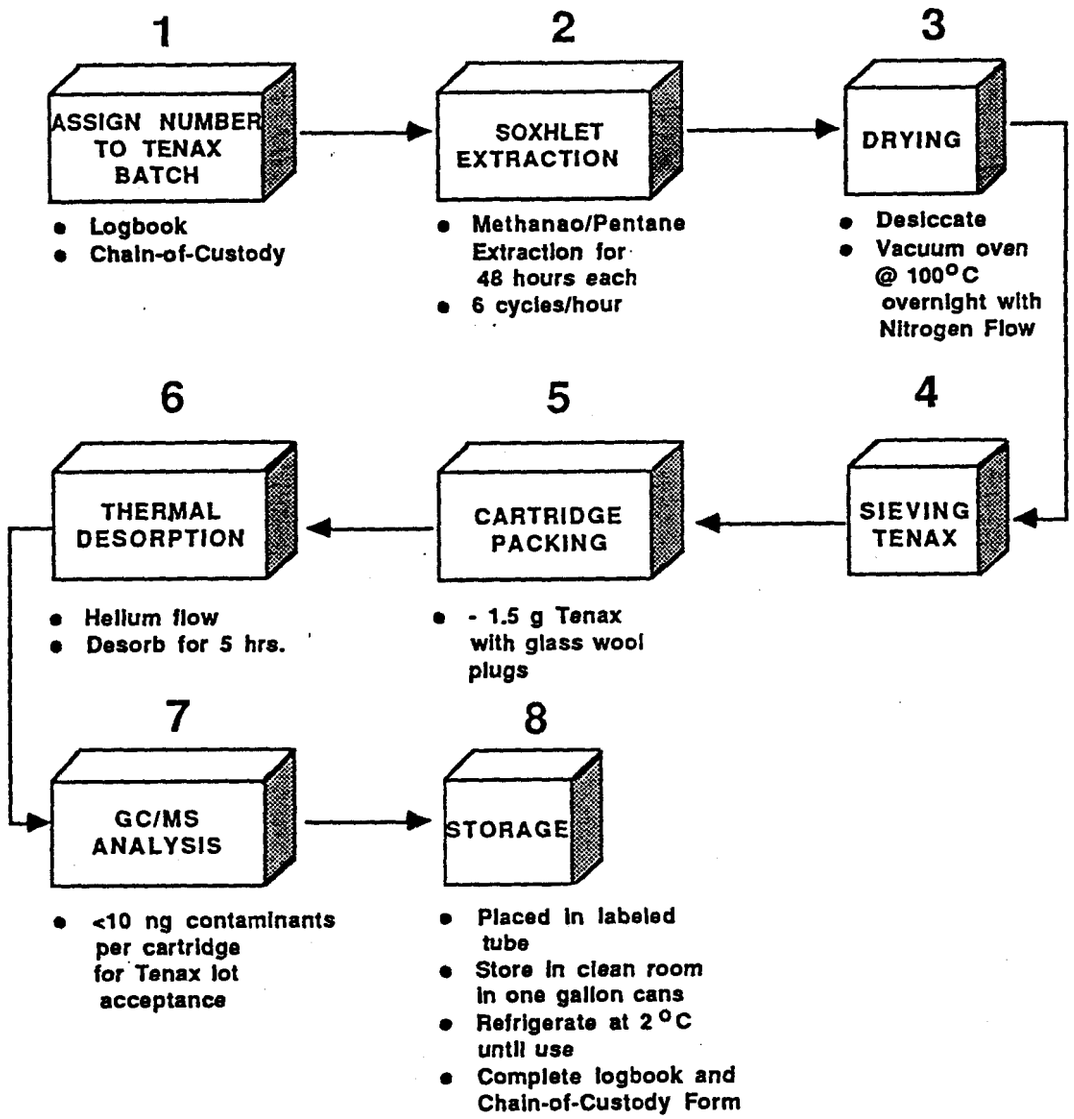


Figure 6. Tenax® Clean-Up Scheme

TENAX CLEANUP WORKSHEET

Tenax Batch No. _____ Projected Use _____
Virgin/Recycled. Recycled Source _____ No. of Cartridges _____

Extraction

Number of Soxhlet Units (circle one): 1 2 3 4 5

Methanol Extraction: Date (Hours)

Siphon Rate

Pentane Extraction: Date (Hours)

Siphon Rate

Drying

Nitrogen Chamber: Date (Hours)

Approx. Flowrate

Vacuum Oven: Date (Hours)

Pump Trap

Cooldown (Hours)

N_2 Vent Thru Act. C

Sieving/Packing

Sieve (40/60) Date:

Packing Date(s):

Cleanup

Teflon Septum; Date:

Teflon Liner; Date:

Figure 7. Tenax® Clean-Up Worksheet

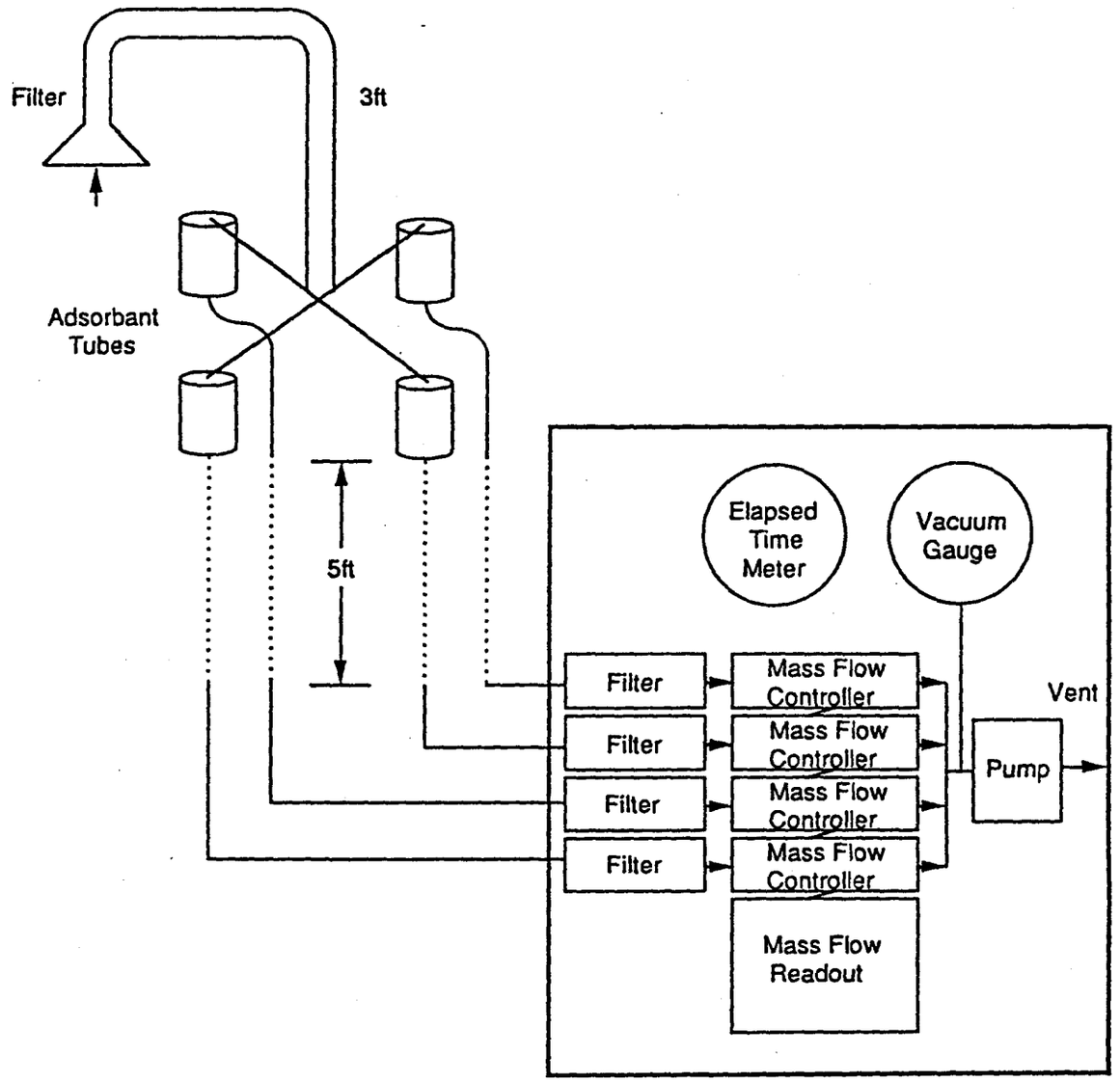


Figure 8. Flow Diagram for TAMS Toxic Air Sampler

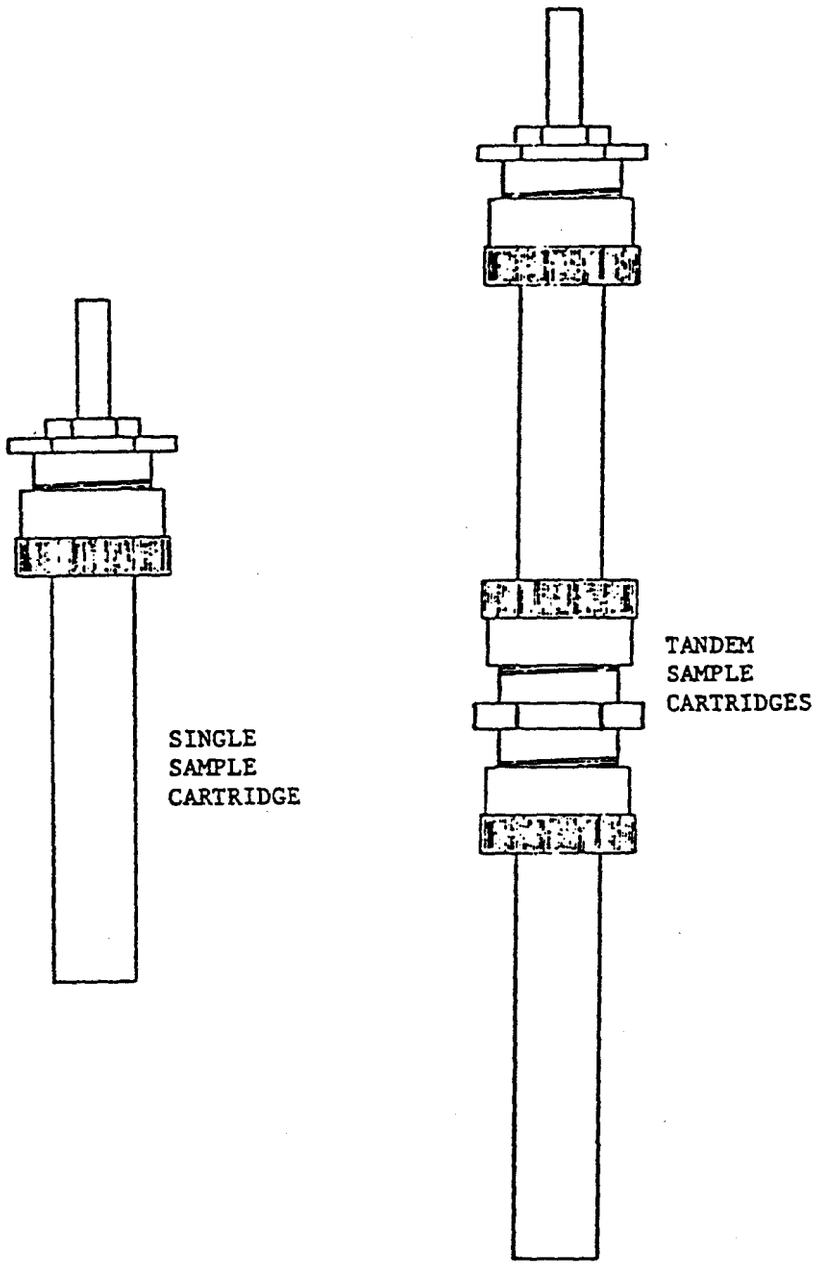
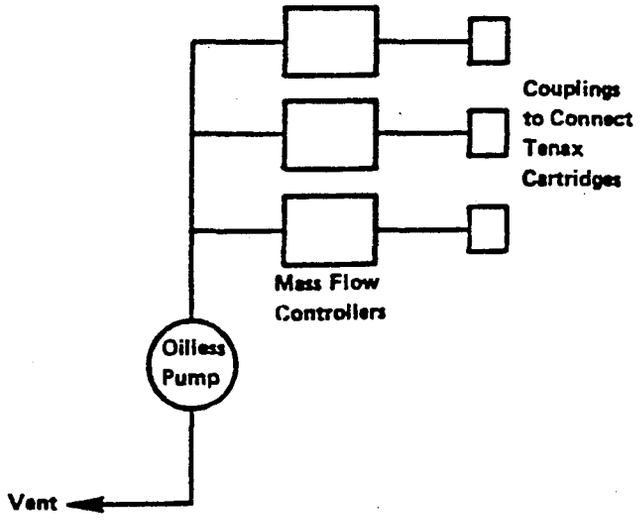
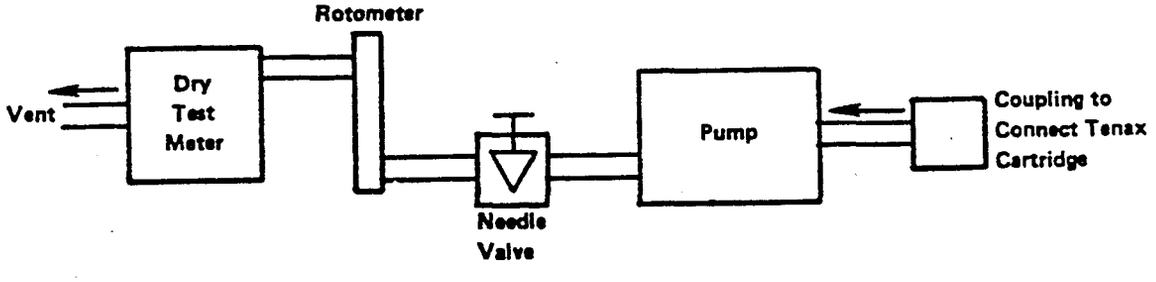


Figure 9. Single and Tandem Sample Cartridges



(a) Mass Flow Control



(b) Needle Valve Control

Figure 10. Typical Sampling System Configurations

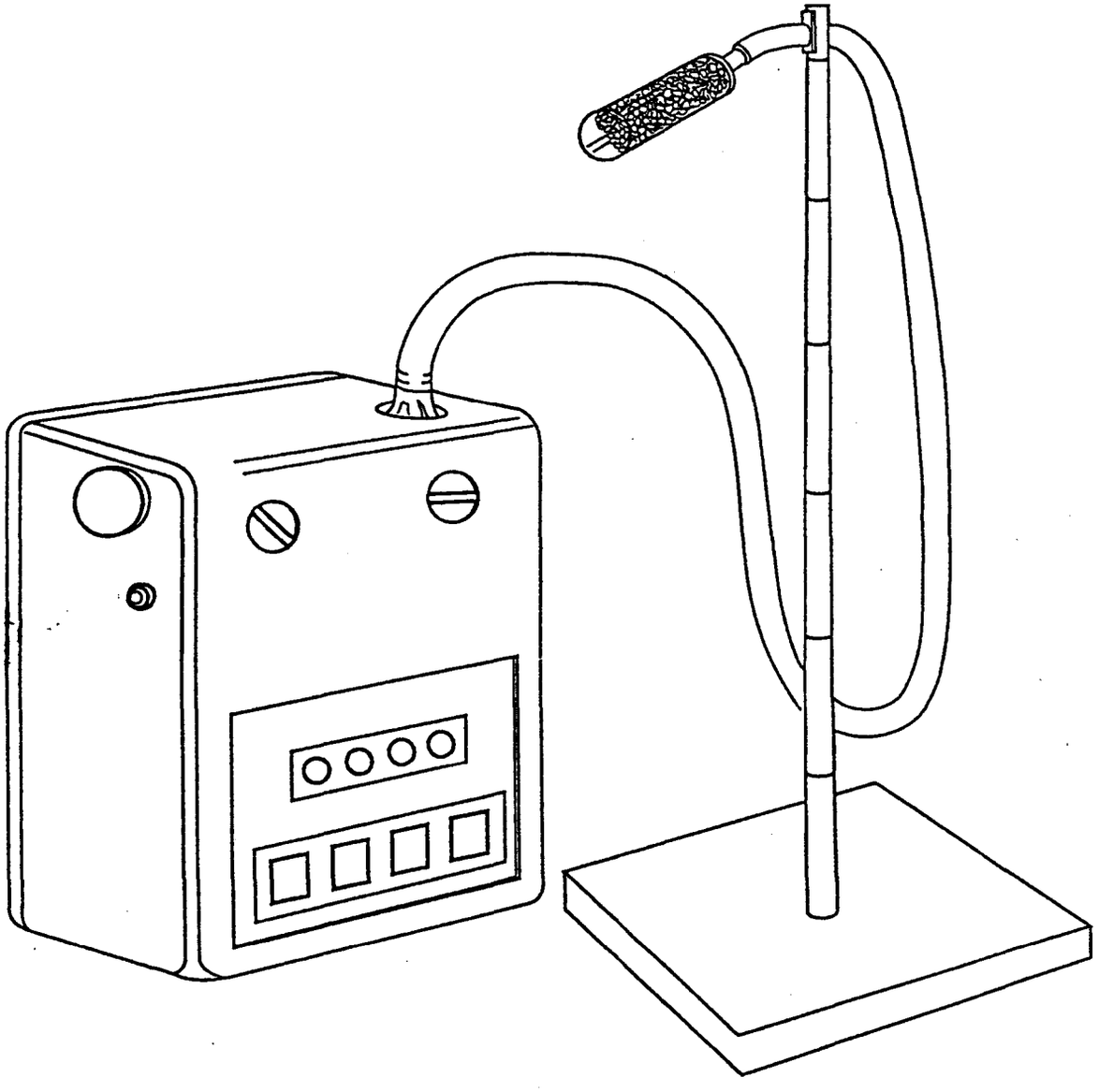


Figure 11. Adsorbent Cartridge Attached to Personal Pump

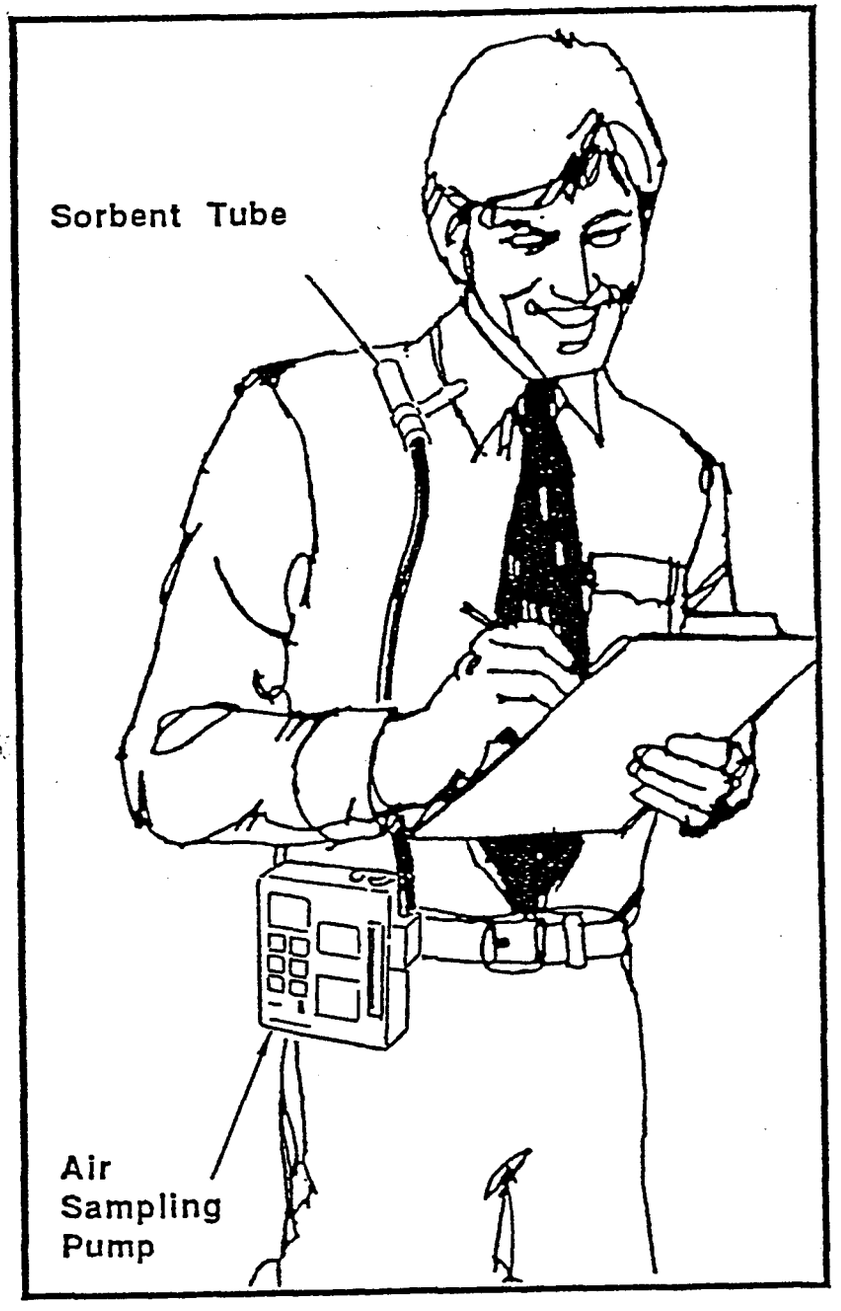


Figure 12. Personal Monitoring

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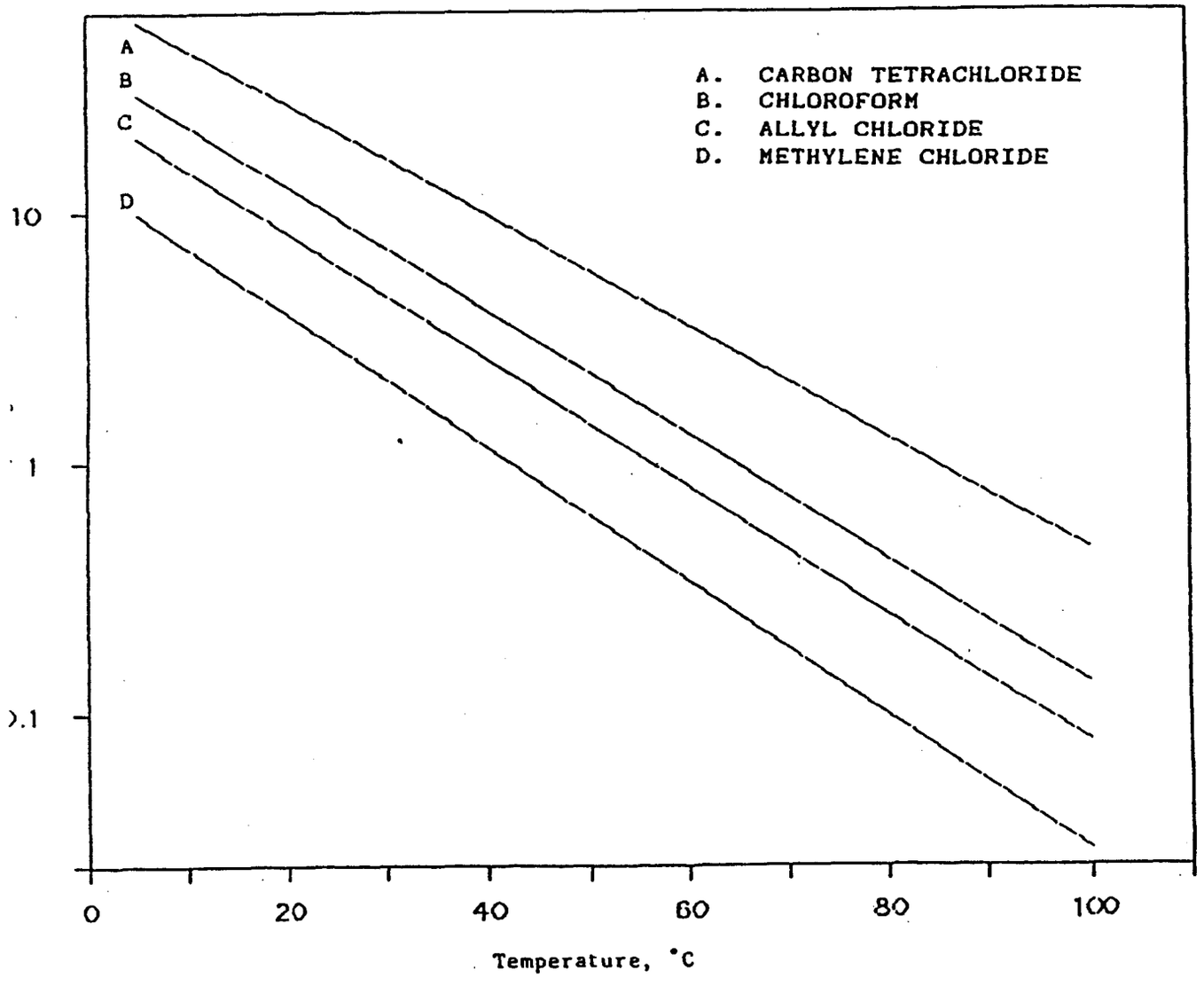

Figure 13. Breakthrough Curves for Carbon Tetrachloride, Chloroform, Allyl Chloride, and Methylene Chloride on Tenax®

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CHAIN-OF-CUSTODY FORM
(One Sample per Custody Sheet)

GENERAL:
Project: _____
Site: _____
Location: _____
Instrument Model #: _____
Pump Serial #: _____
Pump Calibration Date: _____
Sample Code: _____
Sample Type: _____

Date(s) Sampled: _____
Time Period Sampled: _____
Operator: _____
Calibrated by: _____
Breakthrough volume for most volatile compound: _____
Safe-sample volume for most volatile compound: _____

TENAX® DATA:
Tube #: _____
Batch #: _____
Certification Clean Date: _____

SAMPLING DATA:
Volume Collected: _____

TUBE HISTORY:

RELIN-QUISHED BY	REC'D BY	TIME	DATE	OPERATION PERFORMED

Figure 14. Chain-of-Custody Form

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FIELD SAMPLING DATA SHEET
(One Sample Per Data Sheet)

GENERAL:

PROJECT: _____
SITE: _____
LOCATION: _____
INSTRUMENT MODEL NO: _____
PUMP SERIAL NO: _____

PUMP CALIBRATION DATE: _____

DATE(S) SAMPLED: _____
TIME PERIOD SAMPLED: _____
OPERATOR: _____
CALIBRATED BY: _____
BREAKTHROUGH VOLUME FOR MOST VOLATILE COMPOUND: _____
SAFE-SAMPLE VOLUME FOR MOST VOLATILE COMPOUND: _____

TENAX® DATA:

TUBE NUMBER: _____
BATCH NUMBER: _____
CERTIFICATION CLEAN DATE: _____

SAMPLING DATA:

START TIME: _____ STOP TIME: _____

TIME	ROTAMETER READ	FLOW RATE (Q) mL/min	AMBIENT TEMPERATURE °C	BAROMETRIC PRESSURE mm Hg	RELATIVE HUMIDITY %	COMMENTS
1)						
2)						
3)						
4)						
5)						

TOTAL VOLUME DATA

$$V_m = \frac{Q_1 + Q_2 + Q_3 \ldots . Q_N}{N} \times \frac{1}{1000 \times (\text{sampling time in minutes})} = \_\_\_\_\_ \text{ L}$$

Flow rate from rotameter or soap bubble calibrator (specify which).

Figure 15. Field Sampling Data Sheet

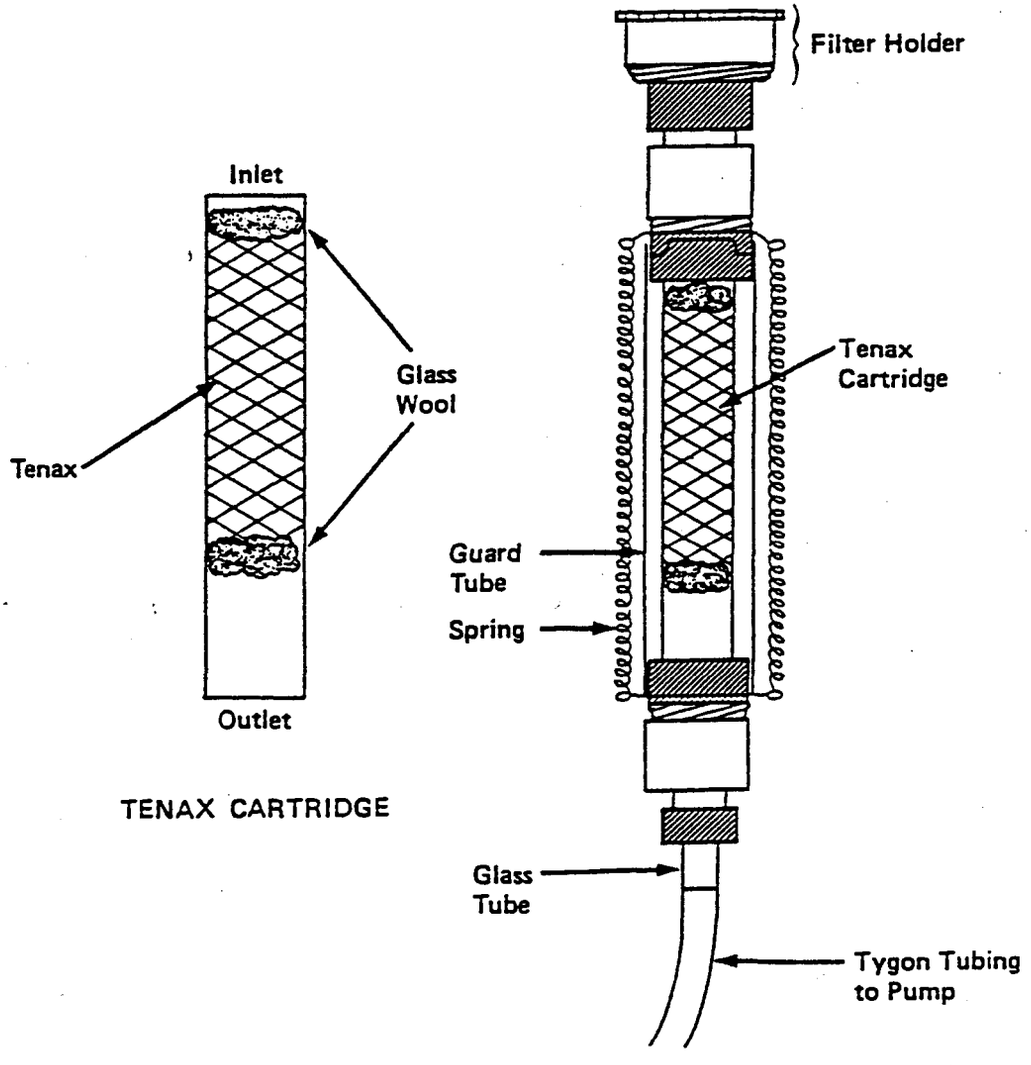

Figure 16. Optional Particulate Filter Assembly Attached to Adsorbent Cartridge

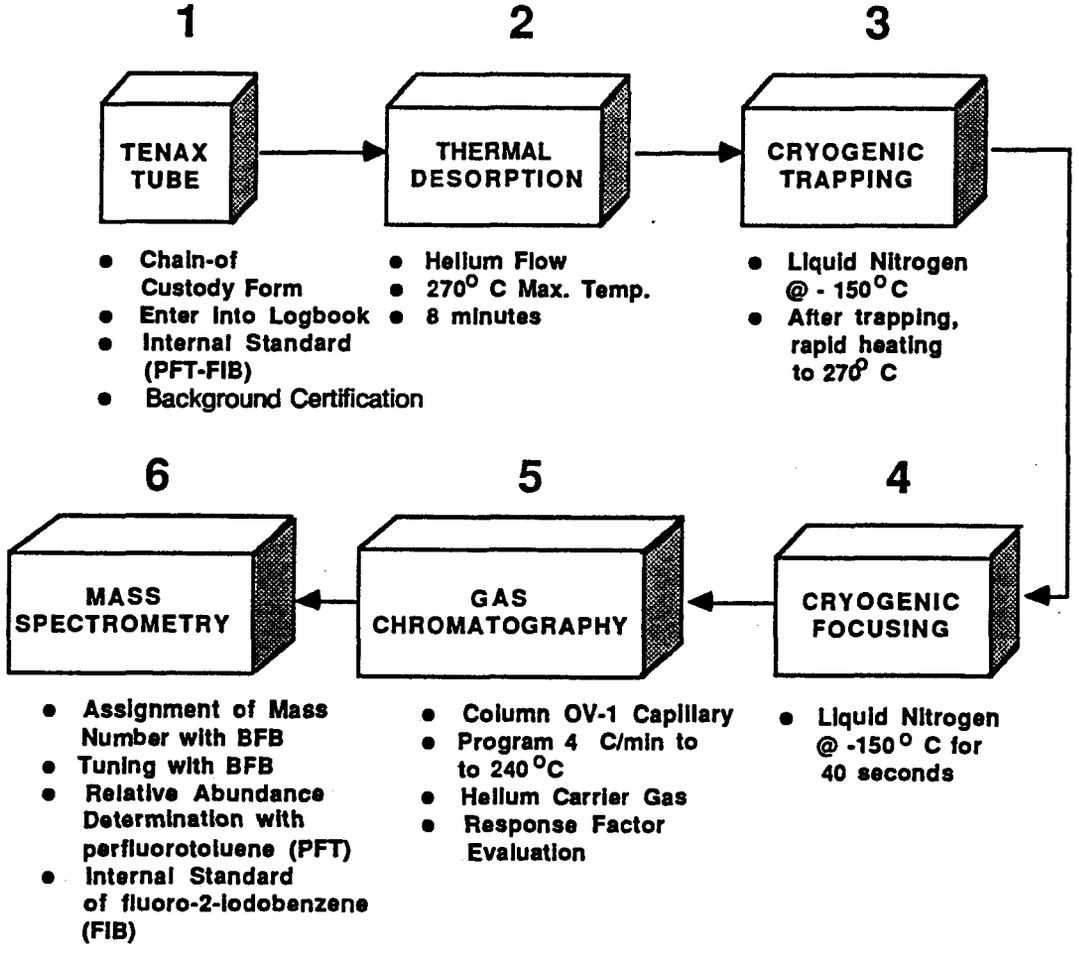

Figure 17. Specific Activities Associated with the GC-MS-DS

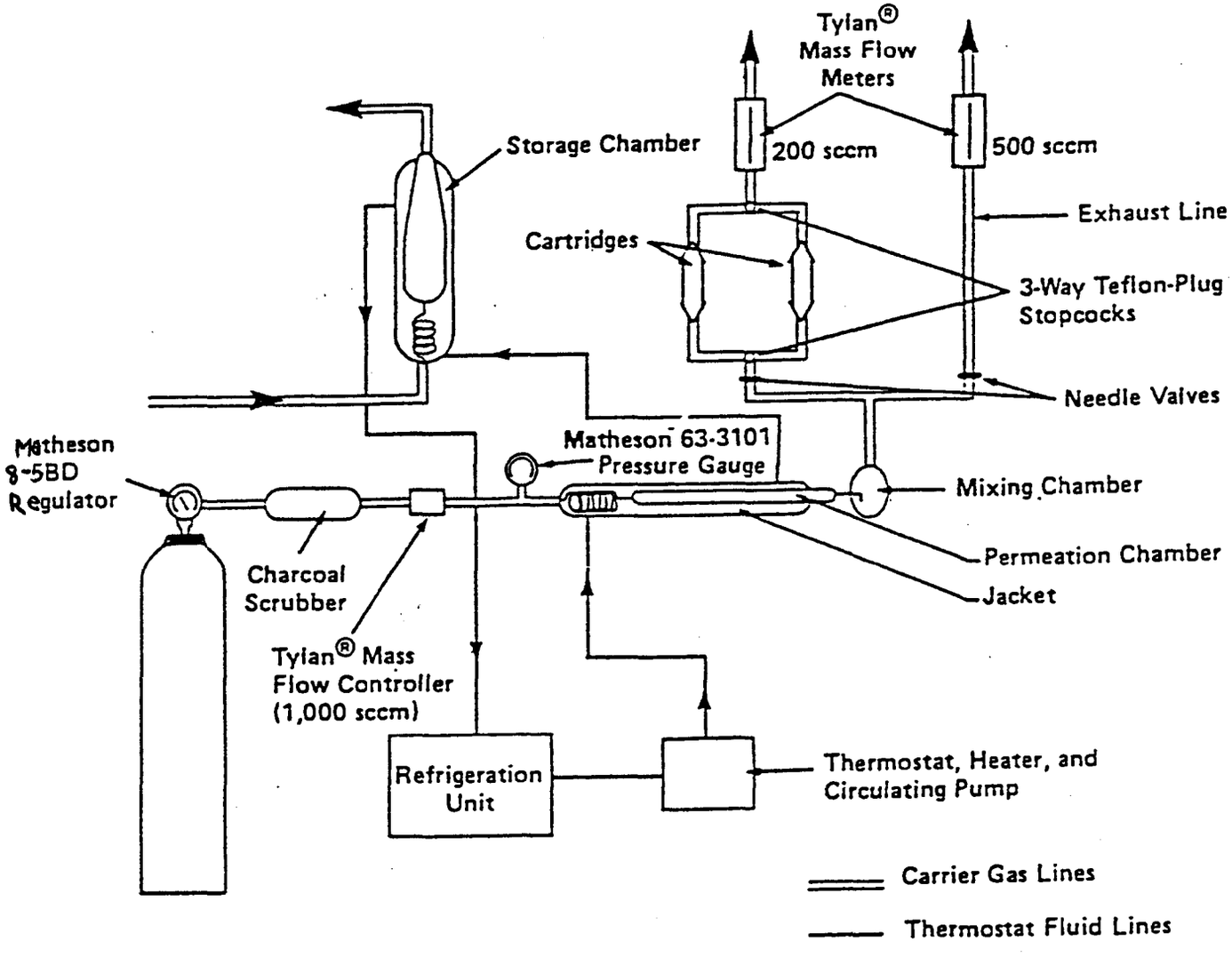

Figure 18. Permeation Tube System for Generating Standard Gas Atmospheres

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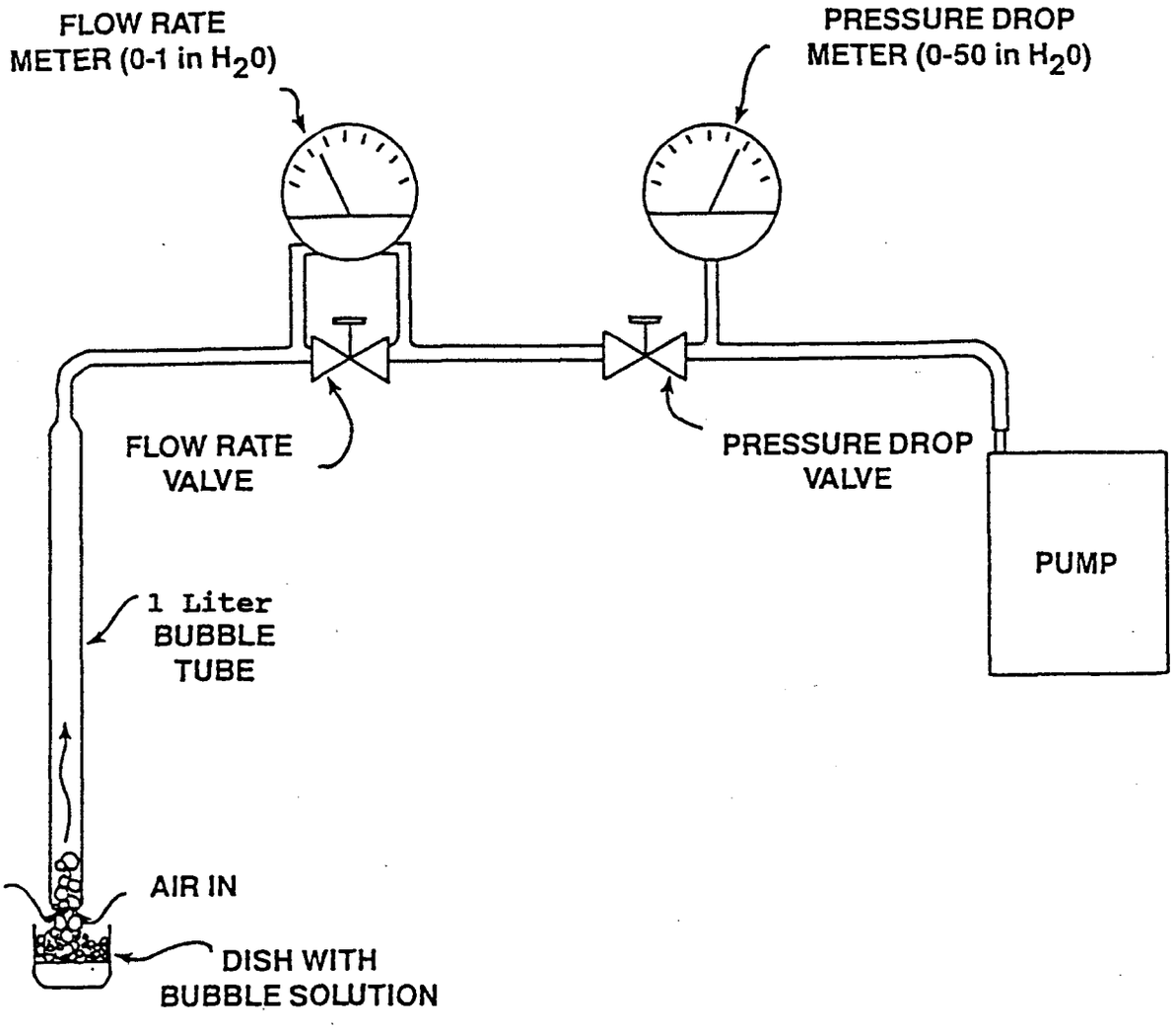

Figure 19. Calibration Assembly for Personal Sampling Pump

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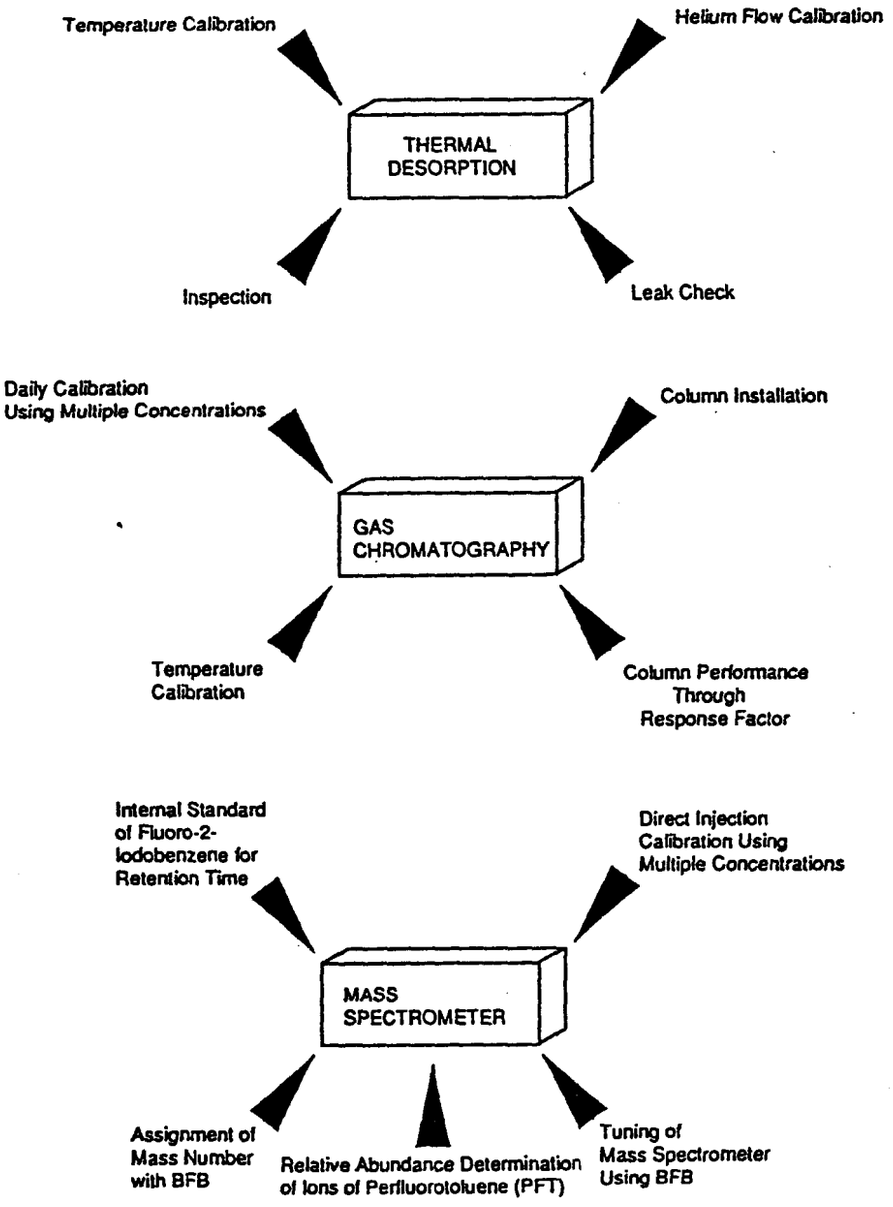

Figure 20. Performance Criteria Associated with the GC-MS-DS

AVAILABILITY OF AUDIT CYLINDERS FROM UNITED STATES ENVIRONMENTAL PROTECTION AGENCY USEPA PROGRAMS/ REGIONAL OFFICES, STATE AND LOCAL AGENCIES AND THEIR CONTRACTORS

1. Availability of Audit Cylinders

1.1 The USEPA has available, at no charge, cylinder gas standards of hazardous organic compounds at the ppb level that may be used to audit the performance of indoor air source measurement systems.

1.2 Each audit cylinder contains 5 to 18 hazardous organic compounds in a balance of N_2 gas. Audit cylinders are available in several concentration ranges. The concentration of each organic compound in the audit cylinder is within the range illustrated in Table A-1.

2. Audit Cylinder Certification

2.1 All audit cylinders are periodically analyzed to assure that cylinder concentrations have remained stable.

2.2 All stability analyses include quality control analyses of ppb hazardous organic gas standards prepared by the National Bureau of Standards for USEPA.

3. Audit Cylinder Acquisition

3.1 USEPA program/regional offices, state/local agencies, and their contractors may obtain audit cylinders (and an audit gas delivery system, if applicable) for performance audits during:

- RCRA Hazardous Waste Trial Burns For PHOC's; and
- Ambient/Indoor Air Measurement of Toxic Organics.

3.2 The audit cylinders may be acquired by contacting:

Robert L. Lampe
U.S. Environmental Protection Agency
Atmospheric Research and Exposure Assessment Laboratory
Quality Assurance Division
MD-77B
Research Triangle Park, NC 27711
919-541-4531

AVAILABLE USEPA PERFORMANCE AUDIT CYLINDERS

Group I Compounds	Group II Compounds	Group III Compounds
Carbon tetrachloride	Trichloroethylene	Pyridine (Pyridine in Group III cylinders but certified analysis not available)
Chloroform	1,2-dichloroethane	Vinylidene chloride
Perchloroethylene	1,2-dibromoethane	1,1,2-trichloro-1,2,2 trifluoroethane (Freon-113)
Vinyl chloride	Acetonitrile	1,2-dichloro-1,1,2,2 tetrafluoroethane (Freon-114)
Benzene	Trichlorofluoromethane (Freon-11)	Acetone
	Dichlorodifluoromethane (Freon-12)	1-4 Dioxane
	Bromomethane	Toluene
	Methyl ethyl ketone	Chlorobenzene
	1,1,1-trichloroethane	

Group I Ranges	Group II Ranges	Group III Ranges
7 to 90 ppb	7 to 90 ppb	7 to 90 ppb
90 to 430 ppb	90 to 430 ppb	90 to 430 ppb
430 to 10,000 ppb		

Group IV	Group V	
Acrylonitrile	Carbon tetrachloride	Methylene chloride
1,3-butadiene	Chloroform	Trichlorofluoromethane (Freon-11)
Ethylene oxide	Perchloroethylene	Bromomethane
Methylene chloride	Vinyl chloride	Toluene
Propylene oxide	Benzene	Chlorobenzene
o-xylene	Trichloroethylene	1,3-Butadiene
	1,2-dichloroethane	o-xylene
	1,2-dibromoethane	Ethyl benzene 1,2-dichloropropane
	1,1,1-trichloroethane	

Group IV Ranges	Group V Ranges
7 to 90 ppb	1 to 40 ppb
430 to 10,000 ppb	

Chapter IP-2

DETERMINATION OF NICOTINE IN INDOOR AIR

- **Method IP-2A - XAD-4 Sorbent Tubes**
- **Method IP-2B - Treated Filter Cassette**

1. Scope

This document describes two methods for sampling and analysis of nicotine in indoor air. The methods are based upon collection of nicotine by adsorption on a sorbent resin or acidic surface. Gas chromatographic separation with nitrogen-selective detection (NSD) is employed for analysis. Two active samplers and one passive sampler are described. The active samplers consist of an XAD-4 sorbent tube or a treated filter cassette attached to a personal sampling pump. The XAD-4 sorbent tube method is a modification of the NIOSH Method S293. The passive sampler consists of a modified treated filter cassette used in active sampling.

2. Applicability

2.1 Nicotine is the major alkaloid in tobacco. During cigarette smoking, burned tobacco emits nicotine to the atmosphere. In indoor environments, nicotine is found as a main constituent of environmental tobacco smoke (ETS). ETS is a mixture of exhaled cigarette smoke, smoke from the burning tip of a cigarette and smoke that diffuses to the air through the paper of a cigarette. Because nicotine is characteristic of ETS, it is frequently used as a marker for ETS.

2.2 Studies show that more than 90% of nicotine in indoor air is found in the vapor phase. However, the following methods quantify total nicotine from indoor air samples. The methods are not able to sample and analyze for the distinct phases of nicotine because particulate phase nicotine has the ability to volatilize after initial impact on a filter or other collection surface.

2.3 Concentrations of 1.8-83.0 $\mu g/m^3$ nicotine have been found in various indoor environments. Because such low concentrations of nicotine are encountered, sophisticated analytical procedures and equipment are used for determining nicotine in indoor air.

2.4 These methods are still under development, but have been tested in several field studies and laboratories. The active methods employ a personal sampling pump with a sorbent sampling tube or a treated filter cassette. The passive method employs a treated filter cassette. Analysis employs solvent extraction and GC/NSD determination. XAD-4 sorbent tubes are commercially available, enabling ease and uniformity in the sampling procedure. In addition, older model GCs (equipped with packed or Megabore® columns) can be adapted with a split/splitless injector to use with capillary columns.

Method IP-2A

DETERMINATION OF NICOTINE IN INDOOR AIR USING XAD-4 SORBENT TUBES

Method IP-2A

DETERMINATION OF NICOTINE IN INDOOR AIR USING XAD-4 SORBENT TUBES

1. Scope

1.1 This method describes a procedure for sampling and determination of nicotine in indoor air. The method is based upon collection of nicotine by adsorption on a sorbent resin. Gas chromatographic separation with nitrogen-selective detection is employed for analysis.

1.2 The active sampler consists of an XAD-4 sorbent tube (1-2) attached to a personal sampling pump. The XAD-4 sorbent tube method is a modification of the NIOSH Method S293 (3).

1.3 Nicotine is the major alkaloid in tobacco. During cigarette smoking, burned tobacco emits nicotine to the atmosphere. In indoor environments, nicotine is found as a main constituent of environmental tobacco smoke (ETS). ETS is a mixture of exhaled cigarette smoke, smoke from the burning tip of a cigarette and smoke that diffuses to the air through the paper of a cigarette. Because nicotine is characteristic of ETS, it is frequently used as a marker for ETS.

1.4 Studies show that more than 90% of nicotine in indoor air is found in the vapor phase (4,5). However, the following method quantifies total nicotine from indoor air samples. The method is not able to sample and analyze for the distinct phases of nicotine because particulate phase nicotine has the ability to volatilize after initial impact on a filter or other collection surface.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis
E260 Recommended Practice for General Gas Chromatography Procedures
E355 Practice for Gas Chromatography Terms and Relationships D4185 - Annex Procedure to Calibrate Small Volume Air Pumps

2.2 Other Documents

U.S. EPA Technical Assistance Document (6)
Laboratory and Ambient/Indoor Air Studies (7-12)
General Guidelines for Indoor Air Studies (13-15)

3. Summary of Method

3.1 An indoor air sample is collected using a personal sampling pump. The pump draws air at a rate of 1.0 L/min through a 7 cm long, 6 mm O.D., 4 mm I.D. glass tube containing XAD-4 sorbent as seen in Figure 1. The method has been evaluated for sampling periods from one to eight hours with a limit of detection of 0.17 $\mu g/m^3$ for a

one hour sample and 0.02 $\mu g/m^3$ for an eight hour sample (1). During sampling, vapor phase nicotine is adsorbed onto the sorbent.

3.2 For sample recovery, the XAD-4 is transferred to a sample vial where it is desorbed with ethyl acetate. The ethyl acetate is modified with 0.01% triethylamine to prevent adsorption of nicotine onto the glass walls of the sample vial.

3.3 Analysis employs a gas chromatograph (GC) equipped with a fused silica capillary column and a nitrogen-selective detector (NSD). The internal standard method of quantitation is used with quinoline serving as the internal standard. Figure 2 outlines the steps associated with the sampling/analysis of nicotine utilizing XAD-4 sorbent tubes.

4. Significance

4.1 Nicotine emissions result primarily from the combustion of tobacco, e.g., cigarette smoking. Nicotine is toxic when inhaled causing excessive stress to the circulatory and nervous systems and has been linked to increased susceptibility for developing cancer (16). Because smokers and nonsmokers are both exposed to ETS, accurate measurements of nicotine in indoor environments are important in assessing human health impacts as a marker for ETS (which contains other toxic compounds) and controlling indoor air pollution.

4.2 Concentrations of 1.8-83.0 $\mu g/m^3$ nicotine have been found in various indoor environments (17). Because such low concentrations of nicotine are encountered, sophisticated analytical procedures and equipment are used for determining nicotine in indoor air.

4.3 Method IP-2A is still under development, but has been tested in several field studies and laboratories (2,10,18). XAD-4 sorbent tubes are commercially available, enabling ease and uniformity in the sampling procedure. In addition, older model GCs (equipped with packed or column injectors) can be adapted for use with Megabore® columns or a GC equipped with a split/splitless injector to use with capillary columns.

4.4 The XAD-4 sorbent tube method described here is the approved Interim First Action Method of the Association of Official Analytical Chemists (AOAC).

5. Definitions

Note: Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D1356, E620, E355 and D4185. All pertinent abbreviations and symbols are defined within this document at point of use. Additional definitions, abbreviations, and symbols are located in Appendix A-1 and B-2 of this Compendium.

5.1 Autosampler - an automatic injection device whereby a mechanical syringe withdraws an aliquot of sample and injects the sample into the instrument for analysis.

5.2 Capillary column - small diameter open tube (typically fused silica) that is specially coated on the inner wall to enable separation of compounds in a GC. A polymer

coating allows the column to be coiled inside the GC oven, hence capillary columns can be of unlimited length (typically 15-60 m).

5.3 Coefficient of variation - a measure of precision calculated as the standard deviation of a series of values divided by their average. It is usually multiplied by 100 and expressed as a percentage.

5.4 Environmental tobacco smoke (ETS) - a composite of exhaled cigarette smoke, smoke from the tip of a burning cigarette and smoke which diffuses through the paper of the cigarette.

5.5 GC terminal - data system and strip chart recorder integrated with a GC. These components are available as a whole package with some GCs.

5.6 Nitrogen-selective detector (NSD) - a highly sensitive detector selective for detection of nitrogen and phosphorus, whereby the detector gas propagates surface ionization on an alkali-salt bead.

5.7 Personal sampling pump - pump with a capacity of 1-5 L/min sampling rate used in personal monitoring.

5.8 Split/splitless injector - a type of injector on a GC to enable sample to enter a capillary column.

6. Interferences

Using packed columns in GCs may result in readings lower than expected because nicotine can adsorb onto undeactivated glass, metal, and solid support particles. Using a fused silica capillary column and modified solvent prescribed here can circumvent this problem. The following describes potential problems that may occur with sample collection and analysis:

- calibration curves defined with a correlation coefficient below 0.990.
- sampling at levels below the sensitivity of the method.
- using glass columns (such as packed columns) in GCs may result in readings lower than expected because nicotine can adsorb onto glass. Using a fused silica capillary column and modified solvent prescribed here can circumvent this problem.
- spiking XAD-4 sorbent tubes with large volumes of nicotine solution when preparing blind samples can result in abnormally low nicotine concentrations because nicotine can adhere to the glass walls of the tube.
- incorrect identification and recording of retention times, nicotine peaks, and associated peak areas.
- neglecting to use consistent significant figures when constructing calibration curves and calculating nicotine content in samples.

7. Apparatus

7.1 Sampling System

7.1.1 XAD-4 sorbent tube sampler - glass tube with both ends flame-sealed, approximately 7 cm long with 6 mm outside diameter (O.D.) and 4 mm inside diameter (I.D.), containing two sections of 20/40 mesh XAD-4 resin (SKC, Inc., 334 Valley View Rd., Eighty Four, PA 15330-9614, Cat. No. 226-30-11-04, or equivalent; buyer should specify glass wool spacers instead of foam for nicotine sampling). The front section contains 80 mg of resin and the back-up section contains 40 mg of resin. A glass wool plug is located at each end of the tube and in between the front and back-up sections. The front plug is held in place with a metal lockspring as illustrated in Figure 1.

7.1.2 Tube holder with clip attachment - for attaching tube to clothing or objects (SKC, Inc., Cat. No. 224-28A, or equivalent).

7.1.3 Tube breaker/capper - to break sealed ends off sample tubes (SKC, Inc., Cat. No. 222-3-50, or equivalent).

7.1.4 NIOSH-approved plastic caps - for capping tubes after sampling.

7.1.5 Barometer, thermometer and stopwatch - for calibrating sampling pumps and taking pressure and temperature readings during sampling.

7.1.6 Personal sampling pump - calibrated for a flow rate of 1 L/min at standard conditions (SKC, Inc., Model No. 224, or equivalent).

7.1.7 Tubing - Tygon 1/4 inch I.D. to connect sampler to pump (SKC, Inc., Cat. No. 225-13-4, or equivalent).

7.2 Analytical System

7.2.1 Tool - for breaking open tubes (SKC, Inc. Cat. No. 222-3-50, or equivalent).

7.2.2 Glass cutter - for opening tubes, optional.

7.2.3 Vial-rack SKC, Inc., Cat. No. 226-04, or equivalent.

7.2.4 Vibrator - for solvent extraction (SKC, Inc., Cat. No. 226D-03, or equivalent).

7.2.5 Gas chromatograph with a nitrogen-selective detector and GC terminal with electronic peak integration and temperature programming capability (Hewlett-Packard, Rte. 41, Avondale, PA 19311, Model 5880A, or equivalent) and autosampler (Hewlett-Packard, Model 7673A, or equivalent).

7.2.6 GC column - either a 30 m x 0.53 mm I.D. fused silica capillary column, coated with a 1.5 um film of 5% phenyl methylpolysiloxane (DB-5) (J&W Scientific, Inc., 3781 Scientific Park Dr., Rancho Cordova, CA 95670, Cat. No. 125-5032) or a 30 m x 0.32 mm I.D. fused silica capillary column, coated with a 1.0 um film of DB-5 (J&W Scientific, Inc., 3781 Scientific Park Dr., Rancho Cordova, CA 95670, Cat. No. 1235033) or equivalent.

7.2.7 Sample containers - 2-mL autosampler vials with Teflon®-lined closures.

7.2.8 Dispensing pipets - 1.0 mL.

7.2.9 Volumetric flasks - 100 mL for making standard solutions.

7.2.10 Microliter syringes - 25, 50, 100 µL for making standard solutions.

7.2.11 Forceps - for transferring XAD-4 resin from tube to sample vial (SKC, Inc., 334 Valley View Road, Eighty Four, PA 15330, Cat. No. 225-15-1, or equivalent).

8. Reagents and Materials

8.1 Helium cylinders - for detector and/or carrier gas, 99.9995% grade.

8.2 Hydrogen cylinders - for detector gas, 99.9995% grade.

8.3 Air - for detector gas (<0.1 ppm hydrocarbon).

8.4 Volumetric flasks - 100 mL or convenient sizes for making internal standards.

8.5 Nicotine - reagent grade (Eastman Kodak Co., Dept. 412-L-236, 343 State St., Rochester, NY, Cat. No. 112 4973, or equivalent).

8.6 Quinoline (internal standard) >99% A.C.S. reagent, Gold Label (Aldrich Chemical Co., Inc., Dept. T, P.O. Box 355, Milwaukee, WI 53201, Cat. No. 25, 401-01, or equivalent).

8.7 Nicotine salicylate - reagent grade (Eastman Kodak Co., Dept. 412-L-236, 343 State St., Rochester, NY).

8.8 Ethyl acetate - chromatographic quality.

8.9 Triethylamine (solvent modifier) >99% Gold Label (Aldrich Chemical Co., Cat. No 23, 962-3, or equivalent).

8.10 Empty vials - to hold wastes from the wash-pump cycle on the GC autosampler or injection procedure.

9. System Description

9.1 Sampling System

9.1.1 The active sampling system consists of a sampler and personal sampling pump. In active sampling the pump draws a volume of air through either an XAD-4 sorbent tube or a treated filter cassette to adsorb any nicotine present.

9.1.2 The sampling systems are portable and can be used effectively in several setups. A sampling case resembling a briefcase is recommended for active sampling in public areas (7). A typical briefcase sampler is illustrated in Figure 3. Disguising the apparatus ensures unobtrusive sampling and reduces interferences caused by curious, smoking onlookers who may be encouraged to increase or decrease smoking upon seeing the sampling system.

9.1.3 Alternately, the active sampling systems can be attached to a person for personal monitoring. In this setup, the pump is attached to a belt and Tygon tubing connects the sampler to the pump. The sampler is then clipped onto clothing near the breathing zone. Figure 4(a) illustrates the briefcase sampler, while Figure 4(b) depicts the personal monitoring arrangement.

9.1.4 In a third setup, the active sampler may be located on a stationary surface for area monitoring in any indoor environment.

9.2 Analytical System

9.2.1 Analysis is performed using a GC equipped with an autosampler, a nitrogen-selective detector, and injectors equipped either for split/splitless injection (0.32 mm I.D.) or on-column/direct injection (0.53 mm I.D.). Recommended modes of injection are split (ratio 10:1) for 0.32 mm I.D. columns and direct for 0.53 mm I.D. columns.

9.2.2 The GC column is a fused silica capillary column (30 m x 0.53 mm or 0.32 mm I.D.) with a film of 1.5 or 1.0 μm DB-5, respectively.

9.2.3 Helium is the carrier gas.

9.2.4 Hydrogen and air are detector gases with helium as detector make-up gas.

9.2.5 The oven temperature is programmed from 150°C to 180°C at a rate of 5°C/min with a total run time of 6 minutes.

9.2.6 The autosampler uses default settings for the injection sequence. A 1 or 2 μL sample is injected for analysis.

9.2.7 Parameters concerning sample and injection integrity should include 5 prewashes with sample, 5 pumps with sample, and 10 postwashes with solvent.
Note: Settings for the GC analysis are summarized in Table 1.

10. Sampling Procedure

10.1 XAD-4 sampling tubes are prepared immediately before sampling. Both ends of the sealed sorbent tube are broken off using a tube breaker/capper tool. The opening should measure at least 2 mm in diameter.

10.2 The back-up section of the XAD-4 sorbent tube is positioned near the pump and connected to the pump with Tygon tubing. The inlet end of the tube is located in the sampler housing so the front section of the tube end is directly exposed to the atmosphere (i.e., the air being sampled is not passed through any hose or tubing before entering the XAD-4 sorbent tube). The tube is either put into a safety casing in the personal sampling setup as in Figure 4(b) and attached accordingly to clothing, or placed in the sampling port of the briefcase setup as in Figure 4(a).

10.3 After the XAD-4 sorbent tube is correctly inserted and positioned, the power switch for the pump is turned on and the sampling begins.
Note: Newer pumps have microprocessing capabilities for preset sampling periods. The elapsed-time meter is activated and the start time recorded. The pumps are checked during the sampling process and any abnormal conditions discovered are recorded on the Field Sampling Data Sheet as in Figure 5.

10.4 Record on the Field Sampling Data Sheet the temperature and pressure of the atmosphere being sampled.

10.5 At the end of the desired sampling period the pump is turned off.

10.6 Record the time elapsed during sampling.

10.7 Immediately after sampling, remove the XAD-4 sorbent tubes from their casing, detach from the pump, cap with plastic caps, and label.

10.8 Three tubes are handled in the same manner as the sample tubes (break, seal, and transport) except that no air is sampled through these tubes. These tubes are labeled and processed as "sample blanks".

10.9 Transport capped XAD-4 sorbent tubes to the laboratory for analysis.
Note: If the samples are not prepared and analyzed immediately, they should be stored at 0°C or lower until analysis. All XAD-4 samples should be analyzed within two weeks after arrival in the laboratory. However, no absolute time limit has been documented.

11. Analytical Procedure

The analytical procedure for nicotine is performed by extraction of the XAD-4 resin followed by GC/NSD analysis. Ethyl acetate extracts nicotine from the XAD-4 beads; however, the solvent is modified with 0.01% v/v triethylamine to prevent any adsorption of nicotine on the glass walls of the vials. To modify the ethyl acetate solvent, add 0.5 mL of neat triethylamine to a freshly opened 4 L bottle of ethyl acetate and agitate for several minutes. ("Solvent" henceforth will refer to this modified ethyl acetate solvent.)
Note: Because of the sensitivity of the nitrogen selective detector and the possibility of hour to hour variations in response to standard solutions, the use of an internal standard is prescribed as an integral part of the analysis. For this method, quinoline performs very well as an internal standard.

11.1 Propagation of Calibration Standards and Internal Standard

11.1.1 Preparation of standard solutions - clean all volumetric flasks used for preparation of standard samples with detergent, thoroughly rinse with tap water and distilled water, and allow to air dry. Prepare a primary standard (1 mg/mL) of nicotine each month by weighing 100 mg of nicotine directly into a 100 mL volumetric flask, diluting to the mark with solvent, and shaking for several minutes. Prepare a secondary standard (10 µg/mL) of nicotine daily by transferring 1.0 mL of the primary standard to another 100 mL volumetric flask, diluting to the mark with solvent, and shaking for several minutes. A primary standard of quinoline is prepared in exactly the same manner as for nicotine. For the quinoline secondary standard, transfer 10.0 mL of the primary quinoline standard to a 100 mL volumetric flask and dilute to the mark with solvent. Store all standards in a freezer when not in use. Fresh primary standards are prepared from neat nicotine and quinoline once each month. Fresh secondary standards are prepared from the primary standards once each week.

11.1.2 Preparation of calibration standards - sets of five calibration standards covering the expected range of nicotine concentrations in the samples are prepared fresh each day from the individual secondary standards in the following way. Add 50 µL of the secondary quinoline stock solution to each of the prepared five autosampler vials with a microliter syringe. Add various volumes of the secondary nicotine stock solution

to the same five autosampler vials to yield final nicotine concentrations which cover the expected range of the samples. Typical volumes used are 10, 20, 50, 100, and 200 µL (dispensed with appropriate volume syringes) which give nicotine standards of 0.1 µg, 0.2 µg, 0.5 µg, 1.0 µg, and 2.0 µg, respectively. Next, add 1 mL of solvent to each vial. Cap and tightly seal the vials. The vials containing standards will be analyzed along with the sample vials. All solutions stored in the freezer are allowed to warm to room temperature before use. A minimum equilibration time of 1 hour is observed.

11.2 Extraction, Desorption and Analysis of XAD-4 Sample Cartridges

11.2.1 In preparation for analysis, the analyst should thoroughly wash his/her hands with soap and water immediately prior to handling the samples and refrain from smoking or otherwise contacting a known nicotine-containing environment until all samples and standards have been prepared and loaded in the autosampler tray.

11.2.2 Extraction/desorption of the XAD-4 requires transferring the contents of each section of the tube to the autosampler vials for extraction.

11.2.3 Break open the tubes at the back end to empty the contents more easily. The front section and back-up section are transferred to separate vials.

11.2.4 Starting from the back end of the tube, use forceps to transfer the glass wool, resin, and center glass wool plug to a 2-mL vial. Transfer the front section of resin along with the inlet glass wool plug to a second 2-mL vial.

Note: If the resin beads cling to the glass walls of the tube, push them out using the glass wool. If this does not work, flush them out of the tube with a stream of air.

11.2.5 Label each vial. Add 50 µL of the secondary quinoline stock solution along with 1 mL solvent to each vial containing the XAD-4 sample.

11.2.6 Solvent blanks should be prepared in a similar way such that vials without nicotine can be analyzed along with samples. Cap the vials tightly and place them in a holding tray.

11.2.7 After all samples and standards have been prepared, transfer the trays to the vibrator. Turn on the vibrator and let the samples desorb under agitation for 30 minutes.

11.2.8 When loading the autosampler, load the solvent blank in position number one in the tray. Its purpose is to verify correct operation of the gas chromatograph in terms of peak location and detector sensitivity. Load the 5 nicotine standards conveniently in the tray following the solvent blank. These will be used to construct the calibration curve. Next, load all the samples in the autosampler tray in random order. Finish loading the tray with another set of 5 standards.

Note: In the event that more than 25 sample vials are loaded after the first 5 standards, additional sets of standards should be loaded within the tray, so that no more than 25 samples are analyzed between standards. Place the same number of samples before and after the middle set of calibration standards. Load the injection tray with wash and waste vials.

Note: In the HP 7673A model, this is a small rotating tray (housed in the bottom of the autosampler containing the injection syringe) which has positions for wash and waste

vials, and one position dedicated for a sample vial. Before each sample is injected, pre-wash the syringe 5 times with sample; and then pump 5 times with sample. Wash the syringe 10 times with solvent after injection.

11.2.9 The operating conditions for the GC are listed in Table 1. Typical retention times for quinoline and nicotine under these GC conditions are approximately:

RETENTION TIMES

Capillary Column I.D.	Quinoline	Nicotine
0.53 mm	1.9 min	2.6 min
0.32 mm	3.3 min	4.2 min

11.2.10 Begin analysis of the standards and sample. The areas of the peaks are measured electronically by the GC terminal or integrator. Figure 6 illustrates typical chromatograms of an ETS sample. The areas of the sample peaks are compared to calibration standards and concentrations of nicotine are calculated using the calibration curve. Figures 7 and 8 depict typical calibration standards and the associated calibration curve, respectively.

11.3 Constructing the Calibration Curve

11.3.1 For the internal standard method of quantitation, construct a plot of the ratio of nicotine peak area divided by quinoline peak area (y-axis) versus the weight of nicotine in the calibration standards (x-axis). Plot the area ratios of nicotine to quinoline by using the average of all calibration standards prepared and analyzed at a given level, as illustrated in Figure 8.

11.3.2 Fit the data to either a linear or a second-order polynomial regression model, whichever is deemed more appropriate. In most cases, a second-order regression model shows clearly superior results and should be used.

11.3.2.1 The linear regression analysis yields the A and B parameters (slope and y-intercept, respectively) of the function $y = Ax + B$. For the internal standard method, the area ratios of nicotine to quinoline are converted to micrograms of nicotine by the equation:

$$\mu g \text{ nicotine} = [\text{Area ratio} - (\text{y-intercept})]/\text{slope}$$

Note: When not using an internal standard, the absolute nicotine area is used rather than an area ratio.

11.3.2.2 When fitting data to a second-order polynomial regression model, the coefficients A, B, C of the polynomial $y = A + Bx + Cx^2$ are found. In this analysis, y represents the weight of nicotine. A typical calibration curve is depicted in Figure 8.

11.3.2.3 The correlation coefficient (R^2) of either fitted line is expected to be at least 0.990 for the XAD-4 method and 0.998 for the cassette methods. A significantly

lower value indicates unusual scattering in the data points defining the calibration curve and preparation and analysis of additional standards should be carried out.

11.4 System Performance Criteria

11.4.1 Retention times for quinoline and nicotine at conditions set forth in Table 1 are approximately:

RETENTION TIMES

Capillary Column I.D.	Quinoline	Nicotine
0.53 mm	1.9 min	2.6 min
0.32 mm	3.3 min	4.2 min

11.4.2 Desorption efficiency should be determined for each analysis and is expected to be at least 95% at all concentrations of nicotine to ensure accuracy of the test results. Failure to calculate the desorption efficiency and adjust results may impair the accuracy of the test.

11.4.3 Breakthrough (>5% of tube contents found in backup resin section) can occur after collecting approximately 300 μg of nicotine in a single XAD-4 tube. A shorter sampling time is necessary if sample concentration and duration of sampling suggests a breakthrough occurrence.

12. Calculations

12.1 Determination of Desorption Efficiency

Note: The decimal fraction of nicotine recovered in the desorption process should be determined for every batch of XAD-4 sorbent tubes that are received.

12.1.1 Break open twenty XAD-4 sorbent tubes and transfer the XAD-4 constituting the front section of each tube together with the glass wool plug to one of twenty 2-mL autosampler vials. Dope three sets of five vials with nicotine to correspond to the three low calibration standards prepared in Section 11.2. For the first set, add 10 μL of the secondary nicotine stock solution directly to the XAD-4 resin in each of five vials. For the second set, add 20 μL of the secondary nicotine stock solution to each of five vials. For the third set, add 50 μL of the secondary nicotine stock solution to each of five vials. The fourth set of five vials are not doped with nicotine and are treated as blanks.

12.1.2 Cap all vials and store in a manner resembling conditions actual samples will experience. This normally entails storage in a freezer overnight for samples collected locally or storage in a dark area at room temperature for 24-48 hours for samples requiring overnight transportation. Since the desorption efficiency may be dependent on the length of time the tubes are stored, the storage time of tubes used in determining desorption efficiency is chosen as the average time required to analyze field samples. If samples are stored longer than 48 hours, perform additional desorption efficiency determinations in the same manner with appropriate storage time before analysis.

12.1.3 Add equal amounts of internal standard to each spiked sample and calibration standard, then desorb and analyze as described in Section 11.2.8.

12.1.4 Prepare ten calibration standards from the secondary nicotine stock solution as described in Section 11.2.

12.1.5 The desorption efficiency (DE) is defined as the average weight of nicotine recovered from the tube divided by the weight of nicotine added to the tube:

desorption efficiency (DE) = [Avg. wt. (μg) recovered/wt. (μg) added] x 100

12.1.6 The desorption efficiency may be dependent on the amount of nicotine collected on the XAD-4 resin. If so, construct a plot of desorption efficiency versus weight of nicotine found experimentally (not the amount added).

12.1.7 For most cases the desorption efficiency is 100% over the range of 0.1 to 2.0 μg nicotine (12).

12.2 Calculating Nicotine Concentrations

12.2.1 Read the weight in μg corresponding to each peak area from the standard curve.

12.2.2 Make corrections for the sample blank for each sample with the equation:

μg nicotine = (μg sample) - (avg. μg blank)

where:
μg sample = nicotine found in front section of sample tube or on filter, μg
avg. μg blank = nicotine found in front section of sample blank tubes or on filter, μg
Note: Follow a similar procedure for the back-up section of the XAD-4 sample tube.

12.2.3 To determine the total weight of nicotine in the sample, add the quantities of nicotine present in the front and back-up sections of the same XAD-4 sorbent tube after correcting them for their respective blanks.

12.2.4 If the desorption efficiency is less than 100%, read the desorption efficiency from the curve generated in Section 12.1.1 or if no curve was generated, use the simple arithmetic mean (if less than 100%). Determine the total weight of nicotine by dividing the weight of nicotine by the desorption efficiency (DE):

corrected μg/sample = [total nicotine weight]/[desorption efficiency (DE)] x 100

12.2.5 Convert the amount of nicotine found to micrograms per cubic meter of air by the equation:

$\mu g/m^3$ = [corrected μg x 1000 (L/m^3)]/[air volume sampled (L)]

12.2.6 If desired, adjust the nicotine concentration found in the sampled air to standard conditions of temperature and pressure by the equation:

corrected $\mu g/m^3$ = $\mu g/m^3$ x 760/P x (T + 273)/298

where:
P = barometric pressure of air sampled, torr
T = temperature of air sampled, °C
760 = standard pressure, torr
298 = standard temperature, °K

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

13.1.1 Users should generate SOPs describing and documenting 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 samples,
- assembly, leak-check, calibration, and operation of the analytical system, addressing the specific equipment used,
- sampler storage and transport, and
- 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 Calibration of Personal Sampling Pump

13.2.1 The pump is calibrated so the flow controller is set at a sampling rate of 1 L/min at standard conditions for the XAD-4 sorbent sampling tube.

13.2.2 Sampling pumps are calibrated at the beginning and at the conclusion of each sample study. To ensure quality volumetric results, pump calibration is recommended at random points throughout each study.

13.2.3 Connect a soap-film flow meter of suitable volume with Tygon tubing to the front end of the active sampler, as illustrated in Figure 9.

Note: With higher sampling rates, a considerable pressure drop through the XAD-4 sampling tube can result. To minimize this effect, a larger capacity pump would be necessary for higher sampling rates (i.e., >5 L/min).

13.2.4 Record the barometric pressure and ambient temperature on the Field Sampling Data Sheet.

13.2.5 Thoroughly wet the surface of the flowmeter before any measurements are recorded. Measure the time for a soap-film bubble to travel a known volume with a stopwatch. Perform five replicate measurements and compute the average time. Correct the volume (liters) to standard conditions from the equation:

$$V_s = [V_a \times P_b \times 298]/[(T + 273) \times 760]$$

where:
V_s = volume corrected to standard conditions of 298°K and 760 torr, L
V_a = actual volume measured with the soap-film flowmeter, L
T = temperature at calibration, °C
P_b = barometric pressure at calibration, torr
760 = standard pressure, torr
298 = standard temperature,°K

13.2.6 The standard flow rate (Q_s) is then calculated with the equation:

$$Q_s = V_s/R$$

where:
Q_s = standard flow rate, L/min
V_s = volume corrected to standard conditions, L
R = average time obtained from soap-film measurement, min

13.3 Method Sensitivity, Precision and Linearity

13.3.1 The sensitivity of the method is specified by a limit of detection of 0.17 $\mu g/m^3$ for one hour sampling. The XAD-4 sorbent tube method described here is the approved Interim First Action Method of the AOAC (13).

13.3.2 Determining desorption efficiency (see Section 12.1), repeatability and reproducibility ensures method precision.

Note: Coefficients of variation of repeatability and reproducibility were calculated for the XAD-4 method in a collaborative study involving six labs (18).
The method uses a 0.53 mm wide-bore capillary column in the GC with the prescribed sampling analysis. Combining spiked sample and ETS sample results showed acceptable margins of a variation by a 2-way analysis of variance (ANOVA as described in "Statistical Manual of the Association of Official Analytical Chemists"). The coefficient of variation of repeatability was found in the range 4.2-13.2% and the coefficient of variation of reproducibility was found in the range 7.0-14.5%.

13.3.3 Non-linearity in the calibration curve or desorption efficiency curve may occur at concentrations near the limit of detection for the method or at high concentrations near the breakthrough limit of 300 μg nicotine per tube.

13.4 Method Modification

13.4.1 General

13.4.1.1 The sampling time described in the XAD-4 method (up to one hour) may be increased up to eight hour periods.

13.4.1.2 To perform eight hour sampling, modifications in the analysis might involve diluting the sample by using additional solvent in the analysis or adjusting the calibration standards and constructing a calibration curve with a higher range of nicotine concentrations.

13.4.1.3 Flow rate of air through the XAD-4 tube may be increased up to 1.5 L/min.

13.4.1.4 Capabilities of the method may be extended to determine other organic compounds. Semi-volatile and nonvolatile organics containing nitrogen with appreciable carbon content (six carbons or more) may be detected by the prescribed sampling and analysis with GC separation and NSD determination.

13.4.1.5 There is an alternate procedure for adding the internal standard to the autosampler vials. Instead of adding the quinoline after the addition of the resin beads and the extraction solvent, the quinoline could be added to a batch of the modified solvent and added with the solvent.

13.4.2 Standard Preparation with Nicotine Salicylate

Note: Because nicotine is extremely toxic and readily absorbed through the skin, direct contact with the reagent should be avoided. Using a solid reagent (subsequently dissolved in a solvent) reduces the amount of initial contact with nicotine already in a liquid form. The following provides a procedure for preparing primary nicotine standard solutions with nicotine salicylate, which is more easily handled and less hazardous if spilled.

13.4.2.1 Weigh 0.1851 g nicotine salicylate. Add to 100 mL volumetric flask partially filled with ultra high purity water. Bring to 100 mL mark. This is the stock 1000 ppm nicotine solution (aqueous).

13.4.2.2 Place a clean magnetic stirring bar into a clean 50 mL Erlenmeyer flask.

13.4.2.3 Accurately pipet 10 mL of 1000 ppm nicotine stock solution into this flask.

13.4.2.4 Add 10 mL of 10 N NaOH to flask. Stir gently for approximately two minutes.

13.4.2.5 Add 10 mL of ammoniated heptane to the flask and stir an additional five minutes.

13.4.2.6 Carefully transfer the supernatant (heptane) to a 100 mL volumetric flask using a pipet.

13.4.2.7 Add an additional 10 mL ammoniated heptane, stir 2 minutes, transfer to a 100 mL volumetric flask.

13.4.2.8 Repeat Section 13.4.2.7 two more times.

13.4.2.9 Dilute the 100 mL volumetric flask to volume with ammoniated heptane and label "100 ppm nicotine".

13.4.2.10 Pipet 0.5, 1.0, 2.0, 5.0, and 10.0 mL of the 100 ppm nicotine into labelled volumetric flasks and dilute to 100 mL with ammoniated heptane. Resulting concentrations are 0.5, 1.0, 2.0, 5.0, and 10.0 ppm nicotine respectively.

Note: Use freshly ammoniated heptane.

14. Safety

14.1 If spilling of nicotine reagent or solvent occurs, take quick and appropriate clean up action.

14.2 When preparing standards, as with handling any chemicals, protective gloves, lab coats and safety glasses should always be worn to avoid contact with skin and eyes. Particular caution should be taken with nicotine because it is quite toxic, (TLV = 0.5 mg/m^3) and easily absorbed through the skin.

14.3 Use an efficient tube breaking tool when breaking open sealed ends of the XAD-4 tube and when breaking tubes open to transfer contents for analysis. This should prevent injury from raw glass edges of the tube.

15. Acknowledgements

The determination of nicotine in indoor air is a complex task, primarily because of the lack of standardized sampling and analysis procedures. Compendium Method IP-2 is an effort to address these difficulties. While there are numerous procedures for sampling and analyzing nicotine in indoor air, this method draws upon the best aspects of each one and combines them into 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. GC/NSD Settings

Column	*(1) 30 m x 0.53 mm I.D., fused silica capillary 1.50 μm film DB-5 (2) 30 m x 0.32 mm I.D., fused silica capillary 1.00 μm, film DB-5
Temps	
Injector	250°C
Oven	Initial 150° Increase 5°C/min Final 180°C
Detector	300°C
NPD Bead Current	10-20 units to give 0 offset (S/N > 50 for 0.1 μg/mL Standard)
Gas Flows	
He, carrier	(1) 15 mL/min (12 psig) (2) 4 mL/min (15 psig)
H_2, detector	3 mL/min
Air, detector	75 mL/min
He, makeup	15 mL/min
Auto Sampler	
Prewashes	5 with sample
Rinses	5 with sample
Postwashes	10 with solvent
Injection	2 μL
Settings	"Default"
Calibration Standards	5 point check at beginning, middle and end of tray
Integration Parameters	
Threshold	0
Peak width	0.04
Retention Time	(1) 1.9 min for Quinoline 2.6 min for Nicotine (2) 3.3 min for Quinoline 4.2 min for Nicotine

*Note: (1) and (2) designate different settings according to column type. Where no number designation exists, setting accounts for both column types.

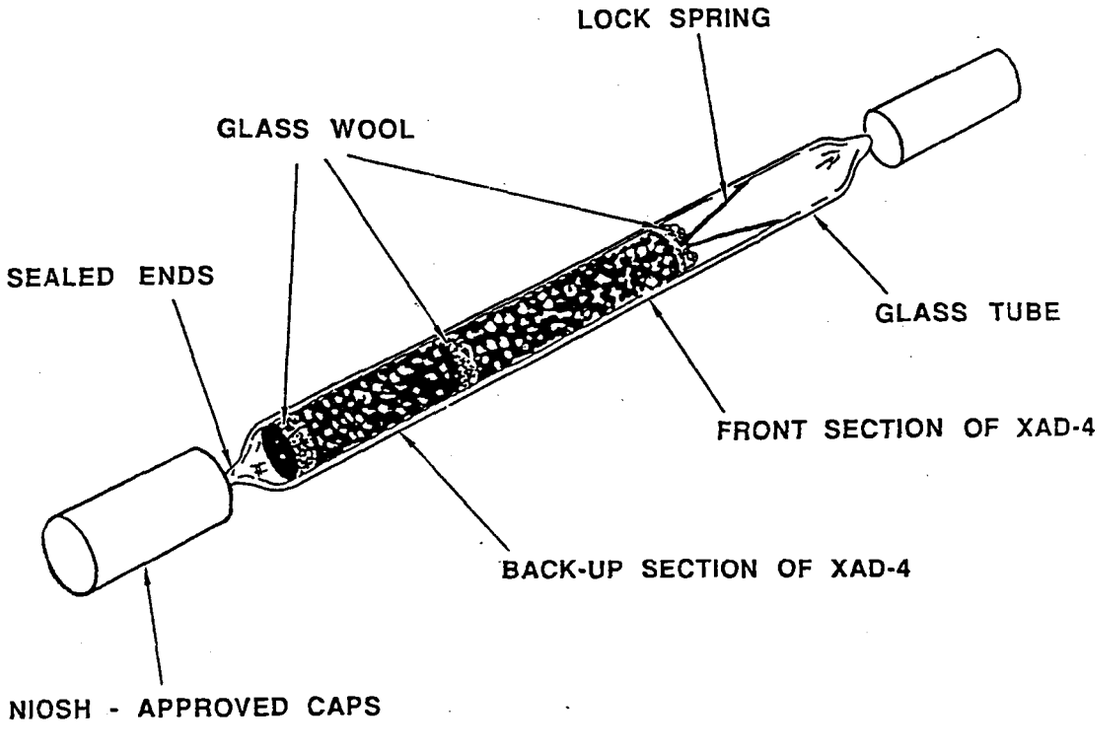

Figure 1. XAD-4 Sorbent Tube

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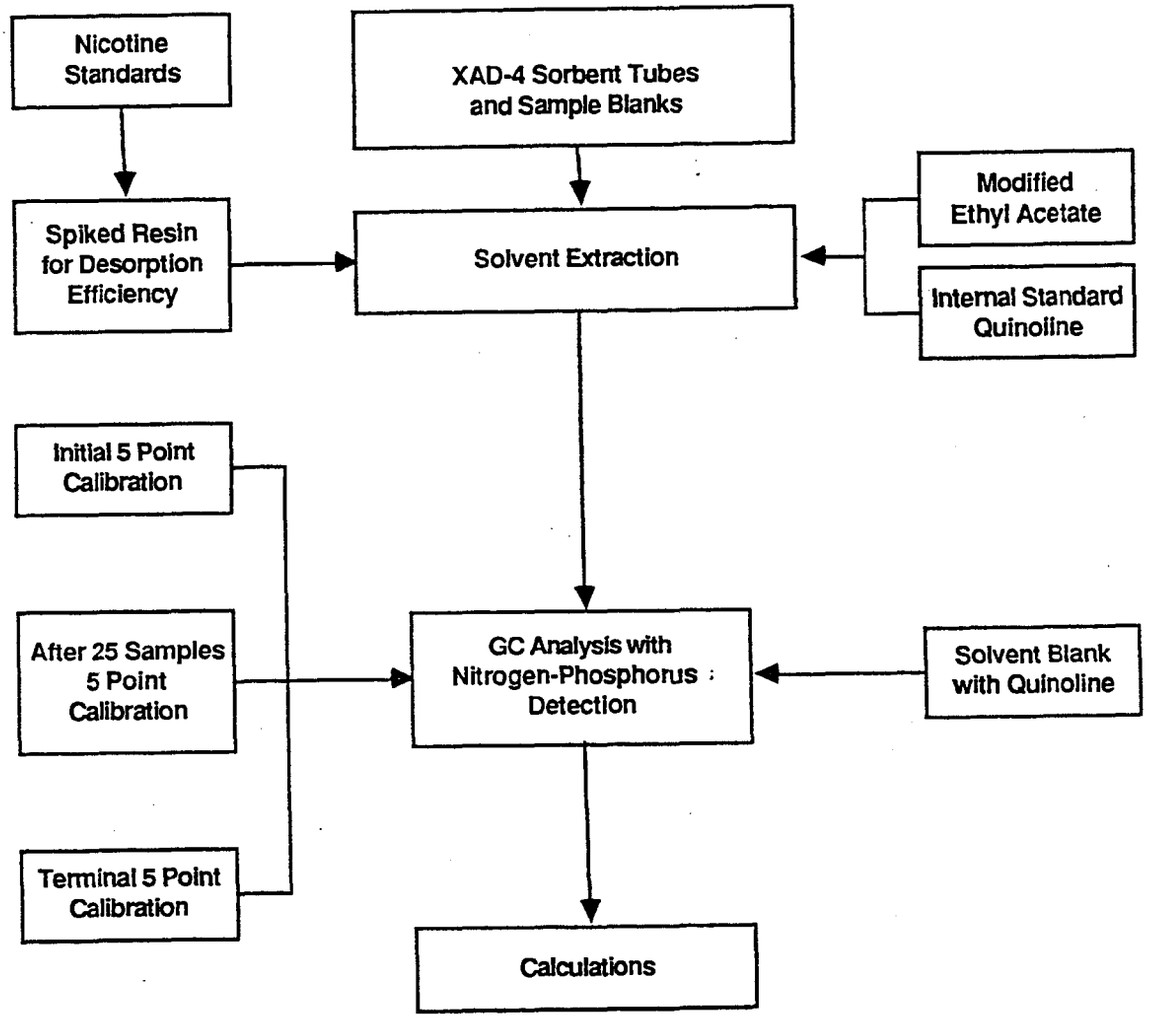


Figure 2. Sampling/Analysis Using XAD-4 Sorbent Tubes

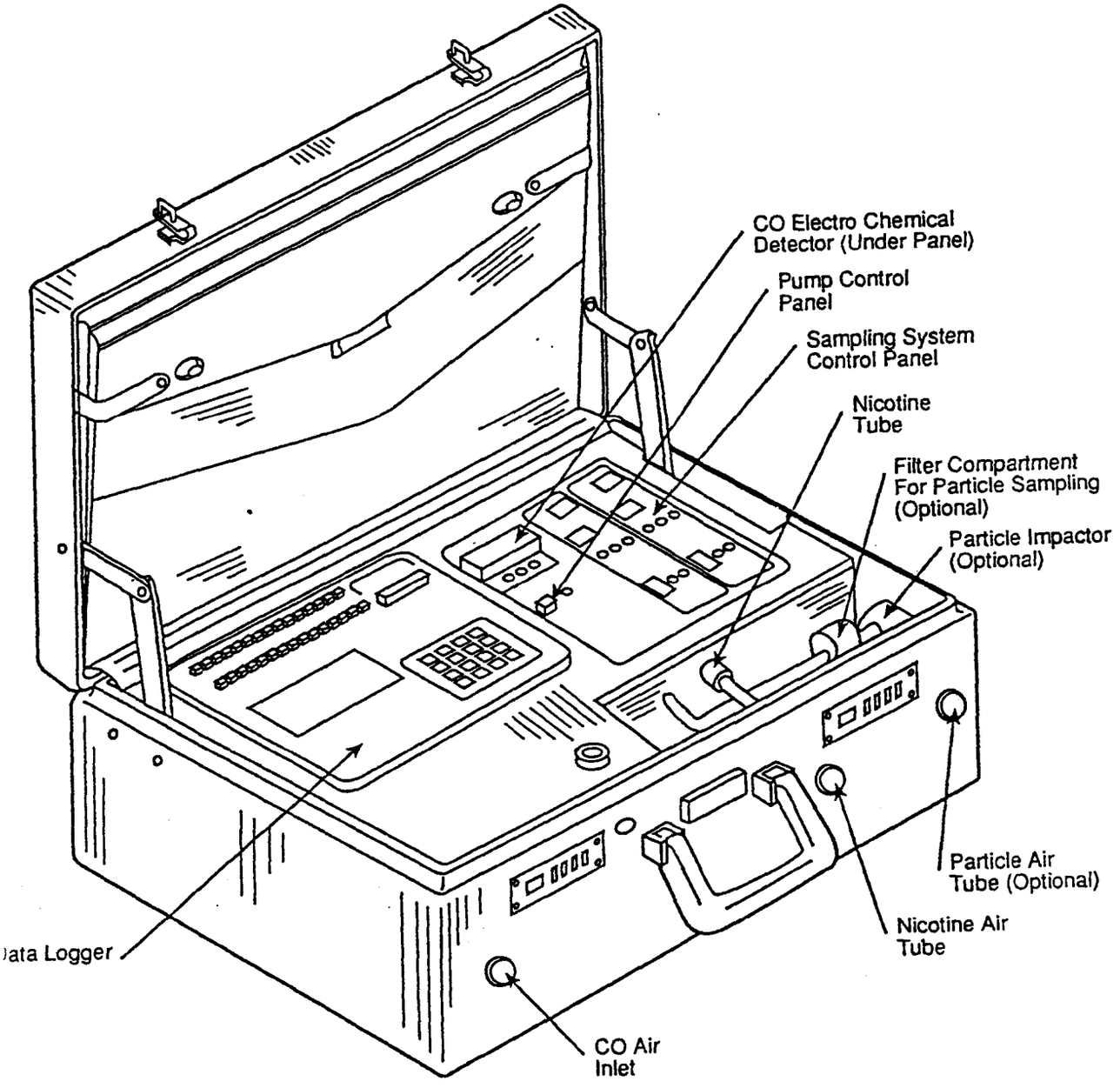
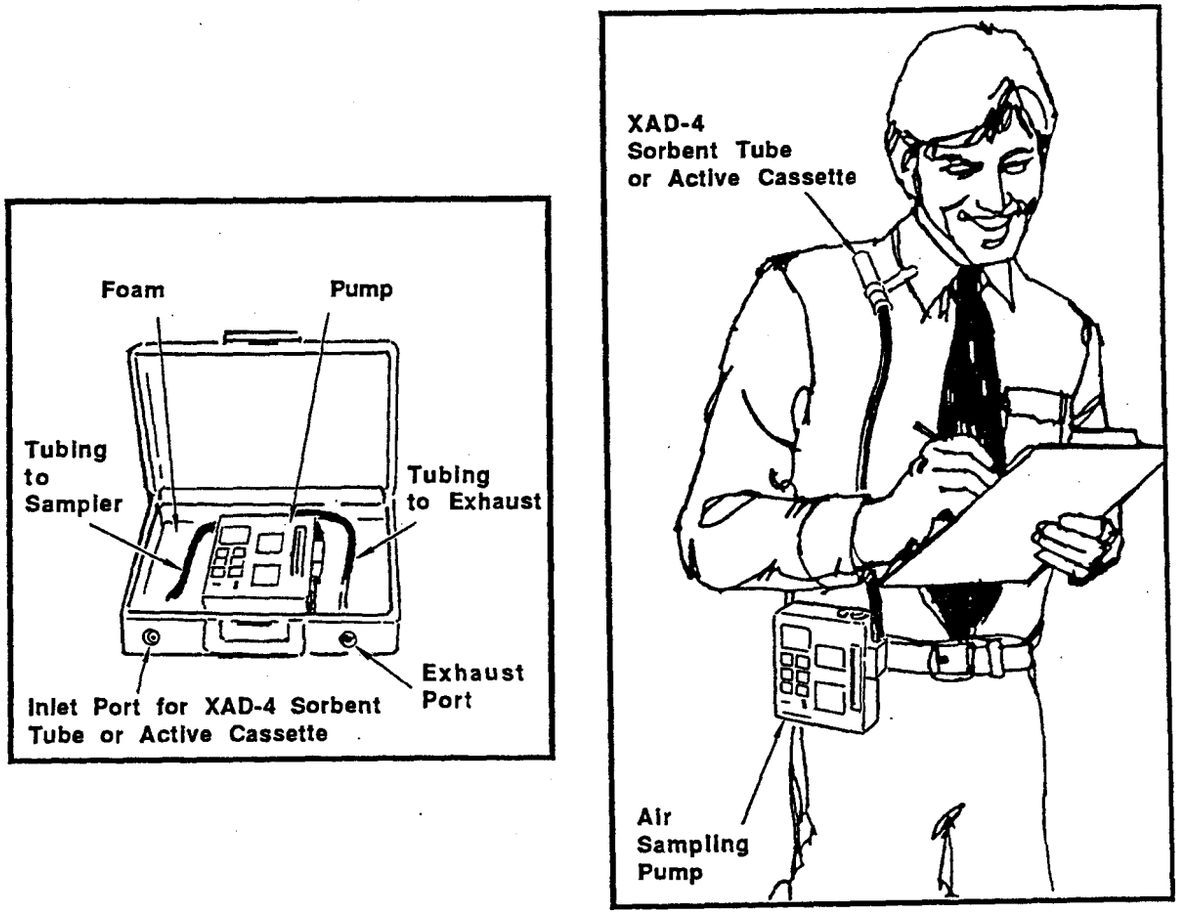


Figure 3. Briefcase Sampling System Containing Nicotine Adsorbent Tube Sampler with Optional Particulate and CO Capabilities



(a) Briefcase Sampling (b) Personal Monitoring

Figure 4. Sampling Setup

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SAMPLING DATA SHEET
(One Sample per Data Sheet)

PROJECT: _____
SITE: _____
LOCATION: _____
INSTRUMENT MODEL NO.: _____
PUMP SERIAL NO.: _____

DATE(S) SAMPLED: _____
TIME PERIOD SAMPLED: _____
OPERATOR: _____
CALIBRATED BY: _____

ADSORBENT CARTRIDGE INFORMATION:
Type: _____
Adsorbent: _____

Serial Number: _____
Sample Number: _____

SAMPLING DATA:

Type of Samplers Active, or Passive	Sampling Location	Temp. F°	Pressure in Hg	Flow Rate (Q) mL/min.	Sampling Period		Total Sampling Time, min.	Total Sample Volume, Liters
					Start	Stop		

Checked by _____

Date _____

* Flow rate from soap bubble calibrator

Figure 5. Nicotine Field Sampling Data Sheet

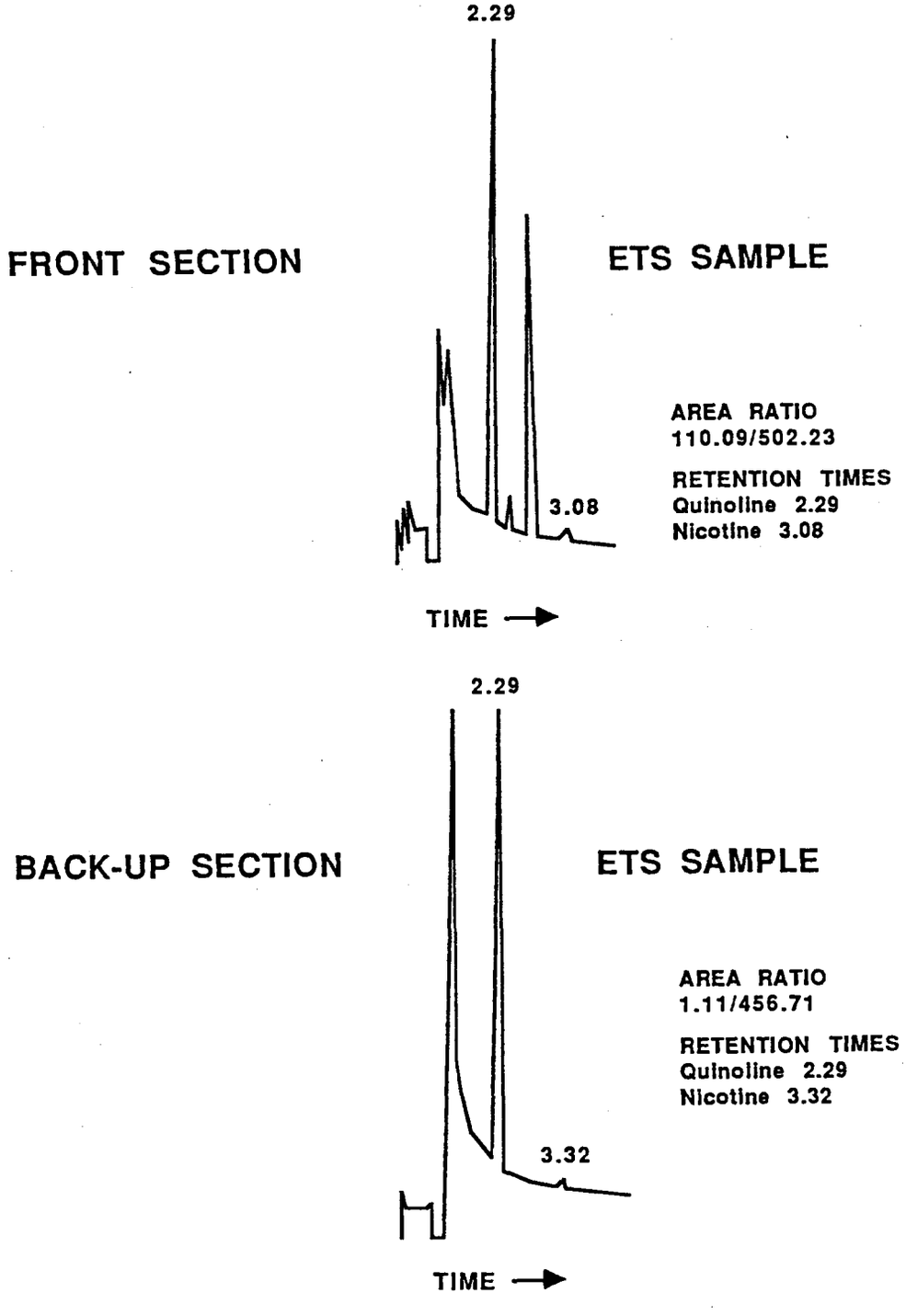
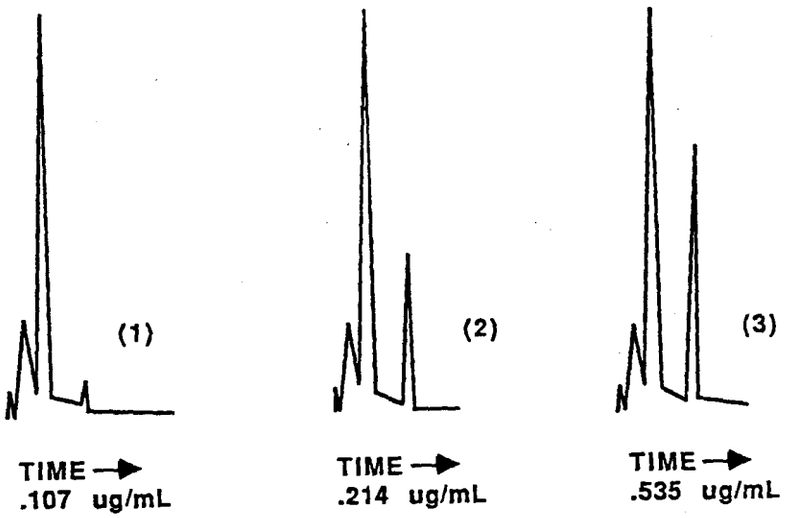
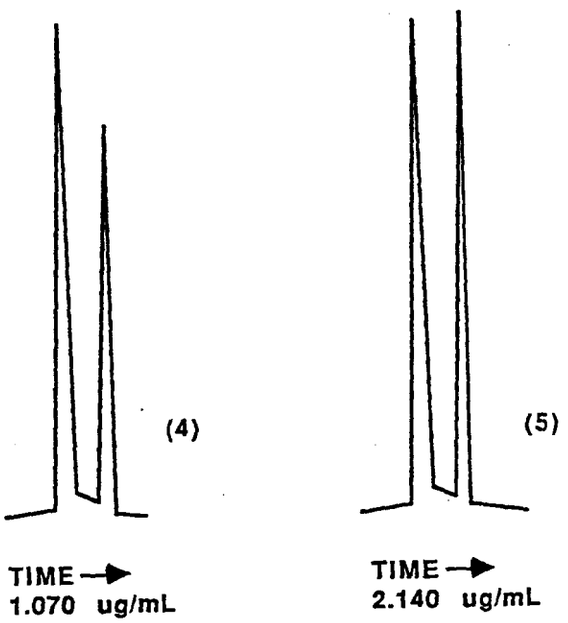


Figure 6. Chromatograms of an ETS Sample



OPERATING PARAMETERS FOR THE GC

Flow Rate: Helium carrier gas - 15 mL/min.
Column: 30 m x .53 mm I.D. fused silica capillary, 1.5 um film of DB-5
Oven: 150°C, program rate increase of 5°C to 180° C
Detector: Nitrogen-Phosphorus operating, at 300° C
Detector Gas Flow Rates: Hydrogen - 3mL/min., Air - 75 mL/min.
Helium Make Up Gas: 15 mL/min.
Injector Temperature: 250°C
Injection: 2 uL direct
Retention Times: 2.29 min. for Quinoline, 3.08 min. for Nicotine



CONC	RATIOS
.107 ug/mL	9.29/466.25
.214 ug/mL	36.91/437.42
.535 ug/mL	106.48/462.95
1.070 ug/mL	237.42/529.03
2.140 ug/mL	453.63/478.30

Figure 7. Chromatograms of Nicotine Calibration Standards

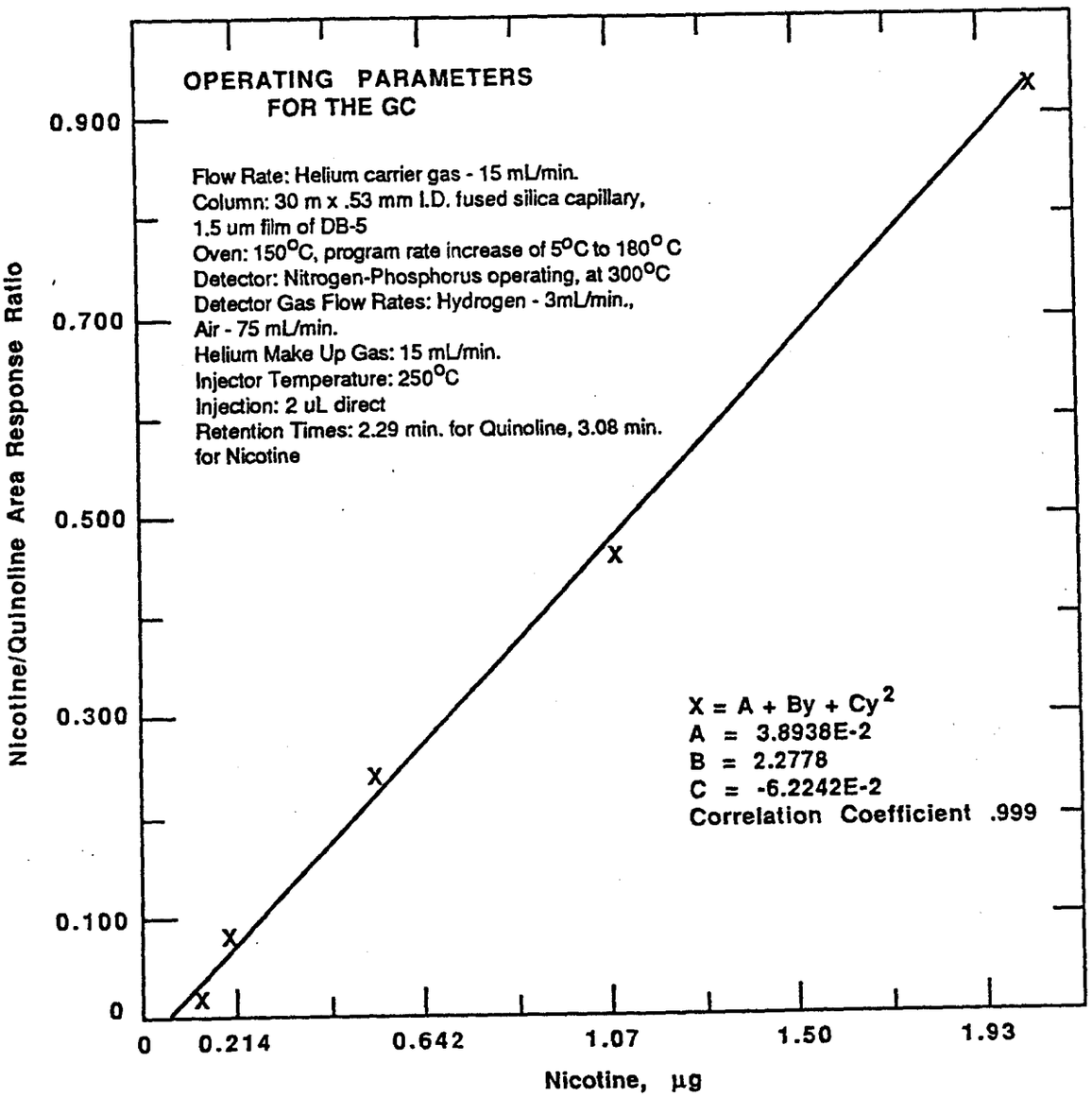


Figure 8. Nicotine Calibration Curve

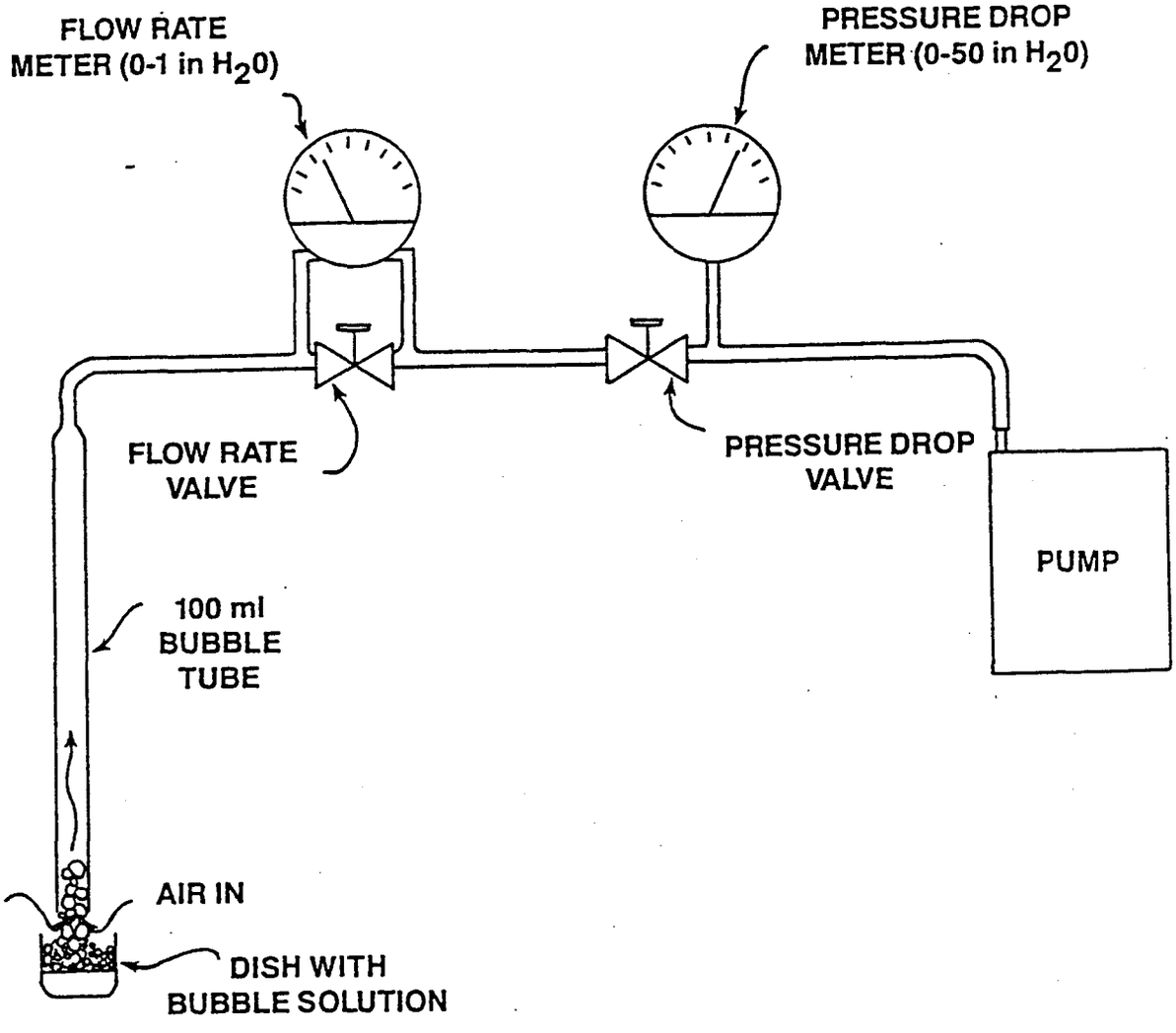


Figure 9. Calibration Assembly for Personal Sampling Pump

Method IP-2B

DETERMINATION OF NICOTINE IN INDOOR AIR USING TREATED FILTER CASSETTES

Method IP-2B

DETERMINATION OF NICOTINE IN INDOOR AIR USING TREATED FILTER CASSETTES

1. Scope

1.1 This method describes two variations for sampling and determination of nicotine in indoor air using treated filter cassettes. The method is based upon collection of nicotine by adsorption on an acidic surface. Gas chromatographic separation with nitrogen-selective detection is employed for analysis.

1.2 One active sampler and one passive sampler are described. The active samplers consist of a treated filter cassette (1) attached to a personal sampling pump. The passive sampler consists of a modification of the treated filter cassette used in active sampling (2).

1.3 Nicotine is the major alkaloid in tobacco. During cigarette smoking, burned tobacco emits nicotine to the atmosphere. In indoor environments, nicotine is found as a main constituent of environmental tobacco smoke (ETS). ETS is a mixture of exhaled cigarette smoke, smoke from the burning tip of a cigarette and smoke that diffuses to the air through the paper of a cigarette. Because nicotine is characteristic of ETS, it is frequently used as a marker for ETS.

1.4 Studies show that more than 90% of nicotine in indoor air is found in the vapor phase (3,4). The following method quantifies total nicotine from indoor air samples. They are not able to sample and analyze for the distinct phases of nicotine since particulate phase nicotine has the ability to volatilize after initial impact on a filter or other collection surface.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis
E260 Recommended Practice for General Gas Chromatography Procedures
E355 Practice for Gas Chromatography Terms and Relationships
D4185 Annex A1 Procedure to Calibrate Small Volume Air Pumps

2.2 Other Documents

U.S. EPA Technical Assistance Document (5)
Laboratory and Ambient/Indoor Air Studies (6-11)
General Guidelines for Indoor Air Studies (12-14)

3. Summary of Method

3.1 Active Sampling Using Treated Filter Cassettes

3.1.1 An indoor air sample is collected using a personal sampling pump. The pump draws air at a rate of 1.7 to 3 L/min through a cassette containing a particulate filter and a filter treated with sodium bisulfate. The method has been evaluated for an eight hour sampling period at a rate of 1.7 L/min with a limit of detection of 0.1 $\mu g/m^3$ and at a rate

of 3 L/min with a limit of detection of 0.03 $\mu g/m^3$ (1). It has also shown a limit of detection of 0.5 $\mu g/m^3$ for a one hour sampling period at a sampling rate of 1.7 L/min. Figure 1 illustrates the active cassette approach.

3.1.2 For analysis, the filters are transferred to test tubes and extracted. The particulate filter is extracted using dichloromethane and the nicotine is concentrated into ammoniated heptane. The dichloromethane is then evaporated from the sample. The treated filter is extracted with a 5% ethanol solution. Sodium hydroxide is added to deprotonate the nicotine and the solution is concentrated into ammoniated heptane for analysis. Ammoniated heptane prevents adsorption of nicotine to the glass walls of the test tubes and sample vials.

3.1.3 Analysis employs gas chromatographic separation with nitrogen-selective detection and a packed column rather than a capillary column. Figure 2 outlines the analytical sequence employing the active treated filter cassette technique.

3.2 Passive Sampling Using Treated Filter Cassettes

3.2.1 Passive sampling requires no pump, and functions on the basis of molecular diffusion. Ideally, the sampling rate follows Fick's First Law of Diffusion and was determined to be 25 mL/min. The passive cassette has been evaluated for a 4-5 hour sampling period with a limit of detection of 16 $\mu g/m^3$ and for a one-week sampling period with a limit of detection of 0.2 $\mu g/m^3$ (2). Figure 3 shows the passive cassette containing a filter treated with sodium bisulfate behind a windscreen which limits mass transport to diffusion.

3.2.2 Analysis of the treated filter is the same as the analysis of the treated filter used in the active cassette. Figure 4 outlines the steps associated with the sampling/analysis of nicotine utilizing the passive filter cassette technique.

4. Significance

4.1 Nicotine emissions result primarily from the combustion of tobacco, e.g., cigarette smoking. Nicotine is toxic when inhaled causing excessive stress to the circulatory and nervous systems and has been linked to increased susceptibility for developing cancer (15). Because smokers and nonsmokers are both exposed to ETS which contains other toxic compounds, accurate measurements of nicotine in indoor environments are important in assessing human health impacts and controlling indoor air pollution.

4.2 Concentrations of 1.8-83.0 $\mu g/m^3$ nicotine have been found in various indoor environments (16). Because such low concentrations of nicotine are encountered, sophisticated analytical procedures and equipment are used for determining nicotine in indoor air.

4.3 These methods are still under development, but have been tested in several field studies and laboratories (1,9,17). The active method employs a personal sampling pump with a treated filter cassette. The passive method employs a treated filter cassette and windscreen for sampling. Analysis employs solvent extraction and gas chromatography separation followed by nitrogen-selective detection.

5. Definitions

Note: Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D1356, E620, E355 and D4185. All pertinent abbreviations and symbols are defined within this document at point of use. Additional definitions, abbreviations, and symbols are located in Appendix A-1 and B-2 of this Compendium.

5.1 Autosampler - an automatic injection device whereby a mechanical syringe withdraws an aliquot of sample and injects the sample into the instrument for analysis.

5.2 Coefficient of variation - a measure of precision calculated as the standard deviation of a series of values divided by their average. It is usually multiplied by 100 and expressed as a percentage.

5.3 Environmental tobacco smoke (ETS) - a composite of exhaled cigarette smoke, smoke from the tip of a burning cigarette and smoke which diffuses through the paper of the cigarette.

5.4 GC terminal - data system and strip chart recorder integrated with a GC. These components are available as a whole package with some GCs.

5.5 Nitrogen-selective detector (NSD) - a highly sensitive detector selective for detection of nitrogen and phosphorus, whereby the detector gas propagates surface ionization on an alkali-salt bead.

5.6 Personal sampling pump - pump with a capacity of 1-5 L/min sampling rate used in personal monitoring.

6. Interferences

Using packed columns in GCs may result in readings lower than expected because nicotine can adsorb onto undeactivated glass, metal, and solid support particles. The following describes potential problems that may occur with sample collection and analysis:

- calibration curves defined with a correlation coefficient below 0.990.
- sampling at levels below the sensitivity of the method.
- using glass columns (such as packed columns) in GCs may result in readings lower than expected because nicotine can adsorb onto glass. Using a modified solvent prescribed here can circumvent this problem.
- incorrect identification and recording of retention times, nicotine peaks, and associated peak areas.
- neglecting to use consistent significant figures when constructing calibration curves and calculating nicotine content in samples.

7. Apparatus

7.1 Sample Collection

7.1.1 Active Cassette Technique

7.1.1.1 37-mm Teflon®-coated glass fiber filters (Pallflex Products Co., Kennedy Dr., Putnam, CT 06260, Type TX40H120WW, or equivalent).

7.1.1.2 37-mm diameter polystyrene air sampling cassette (SKC, Inc., Cat. No. 225-3-03) or equivalent.

7.1.1.3 Support pad (Millipore Corp., 80 Ashby Rd., Bedford, MA 01730, Cat. No. AP10 03700, or equivalent).

7.1.1.4 O-ring - to separate filters in active samplers.

7.1.1.5 Stainless steel screen (Supelco, Inc., Supelco Park, Bellefonte, PA 16823-0048, or equivalent).

7.1.1.6 Sealing bands - to wrap around cassette connections (SKC, Inc., Cat. No. 225-25-01, or equivalent).

7.1.1.7 Tubing - Tygon 1/4 inch I.D. (SKC, Inc., Cat. No. 225-13-4, or equivalent).

7.1.2 Passive Cassette Technique

7.1.2.1 Windscreen (15-um pore) - 37-mm membrane filter (Schleicher and Schuell, Inc., Keene, NH 03431, Product #TE39, or equivalent).

7.1.2.2 37-mm Teflon®-coated glass fiber filters - refer to Section 7.1.1.1 for description and source.

7.1.2.3 37-mm polystyrene air sampling cassette-refer to Section 7.1.1.2 for description and source.

7.1.2.4 Support pad - refer to Section 7.1.1.3 for description and source.

7.2 Analytical System

7.2.1 Watch glasses.

7.2.2 13 x 100 mm borosilicate glass disposable test tubes.

7.2.3 Aluminum foil - used as surface for drying treated filters.

7.2.4 Gas chromatograph with nitrogen-selective detector (Hewlett-Packard, Rt. 41, Avondale, PA 19311, Model 5890A, or equivalent) and integrator (Hewlett-Packard, Model 3391A, or equivalent); sampler event-control module (Hewlett-Packard, Model 19405A, or equivalent); autosampler (Hewlett-Packard, Model HP 7673A, or equivalent); and precision sampling syringe with 10-uL reinforced plunger 23 gauge needle.

7.2.5 GC column - 2% KOH on Carbowax 20M, 2 mmid, 6 ft glass.

7.2.6 Vortex mixer - for extraction.

7.2.7 Sample containers - 2-mL and 300-mL autosampler vials with Teflon®-lined crimp-cap closures.

7.2.8 Crimp-cap sealer.

7.2.9 Dispensing pipets - 1.00 mL.

7.2.10 Volumetric flasks - 100 mL for making standard solutions.

7.2.11 Microliter pipets - 25, 50, 100 and 1000 µL, for making solutions.

7.2.12 Forceps - for handling treated filters and for assembling cassettes (SKC, Inc., 334 Valley View Road, Eighty Four, PA 15330 Cat. No. 225-15-1, or equivalent).

8. Reagents and Materials

8.1 General

8.1.1 Helium cylinders - for detector and/or carrier gas, 99.9995% grade.
8.1.2 Hydrogen cylinders - for detector gas, 99.9995% grade.
8.1.3 Air - for detector gas (<0.1 ppm hydrocarbon).
8.1.4 Volumetric flasks - 100 mL or convenient sizes for making internal standards.
8.1.5 Nicotine - reagent grade (Eastman Kodak Co., Dept. 412-L-236, 343 State St., Rochester, NY, Cat. No. 112 4973, or equivalent).
8.1.6 Quinoline (internal standard) >99% A.C.S. reagent, Gold Label (Aldrich Chemical Co., Inc., Dept. T, P.O. Box 355, Milwaukee, WI 53201, Cat. No. 25, 401-01, or equivalent).
8.1.7 Nicotine salicylate - reagent grade (Eastman Kodak Co., Dept. 412-L-236, 343 State St., Rochester, NY).

8.2 Active and Passive Cassettes

8.2.1 Absolute ethanol - USP or reagent grade used in treated filters extraction.
8.2.2 Sodium bisulfate - monohydrate, reagent grade.
8.2.3 Heptane - HPLC grade, ultra high purity (J. T. Baker Chemical Co., 222 Red School Lane, Phillipsburg, NJ, or equivalent).
8.2.4 High quality water - deionized, double-distilled.
8.2.5 Sodium hydroxide pellets - reagent grade, used in treated filters extraction.
8.2.6 Ammonia - anhydrous, bubbled through heptane and used in extraction.
8.2.7 Dichloromethane - reagent grade, used for extraction of particulate filter in active sampling only.

9. Sampling System

9.1 System Description

9.1.1 Active Cassette Sampling System

9.1.1.1 The active sampling system consists of a sampler and personal sampling pump. In active sampling the pump draws a volume of air through a treated filter cassette to adsorb any nicotine present.

9.1.1.2 The sampling systems are portable and can be used effectively in several setups.

9.1.1.3 The active sampling system can be attached to a person for personal monitoring. In this setup, the pump is attached to a belt and Tygon tubing connects the sampler to the pump. The sampler is then clipped onto clothing near the breathing zone as in Figure 5.

9.1.1.4 The active sampler may be located on a stationary surface for area monitoring in any indoor environment as in Figure 6.

9.1.2 Passive Cassette Sampling System

9.1.2.1 For passive sampling, the sampling system consists of a modified treated filter cassette without a pump. The cassette is simply attached to clothing, with the windscreen exposed to the atmosphere.

9.1.2.2 In passive sampling, nicotine diffuses to a modified treated filter inside a cassette.

9.2 Preparation of Filters for Active and Passive Cassettes

9.2.1 Filter Treatment

9.2.1.1 Fill a watchglass with an aqueous solution of 4% sodium bisulfate and 5% ethanol.

9.2.1.2 With forceps transfer a filter to the watchglass. Soak filter in the solution. Note: It will become saturated in a few seconds.

9.2.1.3 Remove filters to aluminum foil and allow them to dry. Caution should be taken during the drying process to ensure the absence of possible nicotine contamination. Note: The sodium bisulfate solution should coat 7-10 mg sodium bisulfate onto the filter surface.

9.2.2 Assembling Active Filter Cassette

Note: Active cassette sampling collects particulates on a Teflon®-coated glass fiber filter and vapor phase nicotine on a treated filter. Assembly must be performed in a nicotine-free environment. Gloves and clean lab coats should be worn. Place the components into the cassette in the same sequence as shown in Figure 1.

9.2.2.1 Place a support pad into the bottom half of the cassette.

9.2.2.2 Using forceps, place a treated filter on top of the support pad.

9.2.2.3 Place an o-ring (or spacer section of the cassette) on top of the treated filter, followed with a stainless steel screen and an untreated filter on top.

9.2.2.4 Push the top half of the cassette over the bottom as in Figure 1.

Note: A spacer section placed between the two halves can be substituted for the o-ring to hold the stainless steel screen and particulate filter in place.

9.2.2.5 Wrap connection with sealing bands so cassette is air tight.

9.2.2.6 Cap at both ends and label cassette for sampling.

9.2.3 Assembling Passive Filter Cassette

Note: Assembly must be performed in a nicotine-free environment. Gloves and clean lab coats should be worn. Prior to assembling the modified treated filter cassette for passive sampling, a windscreen must be made to distribute air over the entire face of the cassette, subsequently distributing the air being sampled over the entire surface area of the treated filter. In passive sampling, nicotine diffuses through the windscreen and is chemically adsorpted on the treated filter.

9.2.3.1 To prepare the windscreen, take a cassette spacer (see note below) and remove the outer rim from one side. This is usually done by a machine shop. This alteration should expose the inner diameter of the spacer and provide a flat surface for attachment of a membrane filter.

Note: A spacer is generally used in between the top and bottom halves of a cassette to separate a series of filters. In passive sampling, the spacer is converted to a top half of the cassette as in Figure 3. Swab a TE39 membrane filter with methylene chloride and stick the edges of the filter to the edges of the spacer.

9.2.3.2 Referring to Figure 3, place a support pad into the bottom of a cassette, then place a treated filter on top of the support pad. This assembly comprises the top half of the cassette.

9.2.3.3 Remove the small plastic cap from the bottom half of the cassette. Removing the cap prevents a vacuum from forming which can damage the windscreen. Push the top half of the cassette into the bottom half of the cassette.

9.2.3.4 Recap the bottom and immediately put sampler in a clean, airtight container until needed for sampling.

9.3 Sampling Procedure

9.3.1 Active Cassette Technique

9.3.1.1 The active sampling cassette is connected to the calibrated pump and arranged in either the stationary sampling setup or situated for personal monitoring (see Figures 5 or 6, respectively).

9.3.1.2 Record on the Field Sampling Data Sheet as in Figure 7, the temperature and pressure of the atmosphere being sampled.

9.3.1.3 After the cassette is correctly situated for sampling the power switch is turned on and sampling begins. Sample at a rate of 1.7 L/min for the duration of the sampling period.

9.3.1.4 At the end of the desired sampling period the pump is turned off.

9.3.1.5 Record the time elapsed during sampling.

9.3.1.6 Immediately after sampling, remove the cassette, detach from the pump, cap each half of the cassette with plastic caps, and label. Record pertinent information on the Field Sampling Data Sheet.

9.3.1.7 Two or three cassettes are handled in the same manner as the sample cassette except that no air is sampled through these cassettes. These cassettes are labeled and processed as "sample blanks".

9.3.1.8 Transport capped treated filter cassettes to the laboratory for analysis. Samples are stable at room temperature for at least six months after collection.

9.3.2 Passive Cassette Technique

9.3.2.1 The passive cassette should be transported to the sampling site in an air tight container made of glass or metal; plastic is not acceptable.

9.3.2.2 The cassettes should be located on a stationary surface or attached to a person for sampling.

Note: As soon as the cassette is removed from the air tight container, sampling begins.

9.3.3.3 Immediately record on the Field Sampling Data Sheet the start time.

9.3.3.4 At the end of the sampling period, record the stop time and transfer the passive cassette to a clean, airtight container until analysis is performed.

10. Analytical System

10.1 System Description

10.1.1 Analysis is performed using a GC with a nitrogen-selective detector. The analytical system also includes an autosampler, integrator, and system sampler-event-control module. A chromatogram from an ETS sample is shown in Figure 8. Figure 9 depicts chromatograms of varying nicotine concentrations and lists GC operating parameters.

Note: Settings for the GC analysis are summarized in Table 1.

10.1.2 The GC column is a 6 ft glass packed column (2 mmid): 2% KOH on 10° Carbowax 20M held at a constant temperature of 140°C.

10.1.3 A 3-μL sample is injected for analysis.

10.2 System Performance Criteria

10.2.1 To check reproducibility of the GC system, duplicate injections for all calibration standards should agree within 5%.

10.2.2 The calibration curve should have a correlation coefficient of at least 0.998.

10.2.3 Spiked samples should show a recovery of at least 90% ± 5% before proceeding with sample preparation.

10.3 Analytical Procedure

10.3.1 Preparation of Reagents

10.3.1.1 Prepare ammoniated heptane daily by bubbling ammonia through 100 mL heptane for 2 minutes to saturate.

10.3.1.2 When preparing standards, use ammoniated heptane for all dilutions. Prepare 5% ethanol in water daily by measuring 5 mL of ethanol into a 250-mL Erlenmeyer flask and diluting to 100 mL with water.

10.3.1.3 All water is deionized, double-distilled or equivalent. Prepare 10 N NaOH weekly by placing 40 grams NaOH pellets in a 250 mL Erlenmeyer flask and diluting to 100 mL with water or use reagent grade 10 N NaOH solution.

10.3.2 Preparation of Standard Solutions

10.3.2.1 Prepare a primary nicotine stock solution (1 mg/mL) every month by the following procedure: Add about 50 mL ammoniated heptane to a 100-mL volumetric flask. Measure 100 μL of nicotine with a syringe and add to the heptane. Dilute to the mark with heptane and mix well. Place aliquots into four crimp top vials and seal. Label each vial with concentration and date.

10.3.2.2 Store in a freezer at -20°C or less. (One vial will be used each week to prepare calibration standards.)

10.3.2.3 Prepare a secondary nicotine stock solution (100 µg/mL) daily. Use a 1 mL positive displacement autopipet with fresh tip to measure 1 mL of the primary stock solution into a 10 mL volumetric flask. Dilute to the mark with ammoniated heptane.

Note: Due to nicotine's extreme toxicity, caution should be employed when handling the reagent. SOPs should be developed for using nicotine when preparing standard solutions.

Note: An alternative procedure for making the primary nicotine standard is provided in Section 12.4. The alternative procedure uses nicotine salicylate, which is a crystalline salt.

10.3.3 Preparation of Calibration Standards

10.3.3.1 Calibration standards should cover a tenfold range of concentration. For high concentration samples, prepare standards from 5 µg/mL to 50 µg/mL. For low concentration samples and passive sampling, prepare standards from 0.05 µg/mL to 5 µg/mL.

10.3.3.2 Prepare all standards daily as follows: For a 50 µg/mL standard, measure 1 mL of 100 µg/mL primary standard of nicotine into a 10 mL volumetric flask and dilute with ammoniated heptane to 2 mL. Similarly prepare the other standards using the following quantities of nicotine standards and ammoniated heptane:

10.0 µg/mL:	1 mL of 100 µg/mL diluted to 10 mL
5.0 µg/mL:	1 mL of 10 µg/mL diluted to 2 mL
1.0 µg/mL:	1 mL of 10 µg/mL diluted to 10 mL
0.5 µg/mL:	1 mL of 1 µg/mL diluted to 2 mL
0.1 µg/mL:	1 mL of 1 µg/mL diluted to 10 mL
0.05 µg/mL:	1 mL of 1 µg/mL diluted to 20 mL

Note: If an internal standard is desired, quinoline has been used in nicotine analysis using gas chromatography with nitrogen selective detection. (Refer to Method IP-2A of this Compendium, Determination of Nicotine in Indoor Air Using XAD-4 Sorbent Tubes.)

10.3.4 Extraction/Desorption for Active Cassette

Note: Analysis of the active cassette sample requires extraction of the treated filter and the particulate filter.

10.3.4.1 Extract the nicotine from the treated filter and the support pad by the following steps.

10.3.4.1.1 Transfer the treated filter and support pad to separate 13 x 100 mm test tubes.

10.3.4.1.2 Add 2 mL of 5% ethanol solution to the test tube containing the support pad and vortex 1 minute. Draw off liquid and add to the test tube containing the filter.

10.3.4.1.3 Add 1 mL of 5% ethanol solution to test tube support pad and vortex 15 seconds. Transfer liquid to the test tube containing the filter.

10.3.4.1.4 Vortex the test tube containing the filter one minute. Add 2 mL 10 N NaOH and vortex 1 minute. Add 250 µL ammoniated heptane (measured with positive displacement pipet) and vortex 1 minute.

10.3.4.1.5 Draw off top layer of prepared sample and transfer to sample vial. Cap with crimp top. Inject manually or load into autosampler.

10.3.4.2 Extract the nicotine from the particulate filter by the following steps.

10.3.4.2.1 Transfer the particulate filter to a 13 x 100 mm test tube. Add about 2 mL dichloromethane (or enough to cover the filter) to test tube and ultrasonically desorb.

10.3.4.2.2 Add 200 µL heptane to the test tube and evaporate the dichloromethane from the sample.

Note: This step is necessary because chlorinated solvents should not be used with nitrogen-selective detectors.

10.3.4.2.3 Transfer an aliquot from the test tube to a sample vial. Cap with crimp top. Inject manually or load into autosampler for injection into the GC and run samples according to settings listed in Table 1.

10.3.5 Extraction/Desorption for Passive Cassette

10.3.5.1 Transfer the treated filter to a 13 x 100 mm test tube. Add 2 mL 5% ethanol solution to test tube and vortex 1 minute.

10.3.5.2 Add 2 mL 10 N NaOH and vortex 1 minute.

10.3.5.3 Add 250 mL ammoniated heptane and vortex 1 minute.

10.3.5.4 Draw off top layer of prepared sample and transfer to sample vial. Cap with crimp top. Inject manually or load into autosampler.

10.3.6 Loading the Autosampler

10.3.6.1 Run a set of standards to establish linear response of the detector.

10.3.6.2 Intersperse the samples with blank heptane and standards so that there are no more than four samples between standards.

10.3.6.3 Run the samples at the conditions set forth in Table 1.

10.3.6.4 At the end of each day, replace the septum on the GC injector.

11. Calculations

11.1 Determination of Desorption Efficiency For Treated Filters

The decimal fraction of nicotine recovered in the desorption of nicotine from treated filters is determined as follows:

11.1.1 Prepare several treated filters in the manner described in Section 9.1.2.

11.1.2 Spike the filters with nicotine in dichloromethane creating a range of concentrations of nicotine. For active samples, spike with 1 to 50 µg of nicotine. For passive samples, spike with 0.1 to 5 µg of nicotine.

11.1.3 Let the filters dry for a time equivalent to sampling period (at least 24 hours).

11.1.4 Desorb the spiked treated filters as described in Section 10.3.1.

11.1.5 The desorption efficiency is defined as the weight of nicotine recovered from the filter divided by the weight of nicotine added to the filter.

11.1.6 The desorption efficiency may be dependent on the amount of nicotine collected on the filter. If so, construct a plot of desorption efficiency versus weight of nicotine found experimentally.

11.2 Determination of the Extraction Efficiency For Treated Filters

Note: The extraction efficiency for the liquid/liquid extraction from the aqueous solution to the heptane layer should be performed at the beginning of each study and should show no loss of nicotine.

11.2.1 Add a known amount of nicotine to 2 mL water containing 200 µL of 4% sodium bisulfate.

11.2.2 Extract as described in Section 10.3.4.1.

11.3 Determination of the Extraction Efficiency For Particulate Filters

Note: The extraction efficiency for the evaporation of dichloromethane from heptane should be performed at the beginning of each study and should show no loss of nicotine.

11.3.1 Measure 200 µL of heptane and 1 mL dichloromethane into a test tube.

11.3.2 Add a known amount of nicotine to the test tube.

11.3.3 Evaporate the dichloromethane from the heptane as described in Section 10.3.4.2.

Note: Heptane always refers to ammoniated heptane.

11.4 Constructing the Calibration Curve

11.4.1 The linear regression analysis yields the A and B parameters (slope and y-intercept, respectively) of the function $y = Ax + B$. For the internal standard method, the area ratios of nicotine to quinoline are converted to micrograms of nicotine by the equation:

$$\mu g \text{ nicotine} = [\text{Area ratio} - (\text{y-intercept})]/\text{slope}$$

Note: When not using an internal standard, the absolute nicotine area is used rather than an area ratio.

11.4.2 When fitting data to a second-order polynomial regression model, the coefficients A, B, C of the polynomial $y = A + Bx + Cx^2$ are found. In this analysis, y represents the weight of nicotine. A typical calibration curve is depicted in Figure 7.

11.4.3 The correlation coefficient (R^2) of either fitted line is expected to be at least 0.998 for the cassette methods. A significantly lower value indicates unusual scattering in the data points defining the calibration curve and preparation and analysis of additional standards should be carried out.

11.5 Calculating Nicotine Concentrations

11.5.1 Read the weight in µg corresponding to each peak area from the standard curve.

11.5.2 Make corrections for the sample blank for each sample with the equation:

$$\mu g \text{ nicotine} = (\mu g \text{ sample}) - (\text{avg. } \mu g \text{ blank})$$

where:
μg sample = μg nicotine found on filters
avg. μg blank = average μg nicotine found in front section of sample blank filter

11.5.3 To determine the total weight of nicotine in the sample, add the quantities of nicotine present in the front and back-up sections of the treated and particulate filters from the active cassette, after correcting them for their respective blanks. For passive sampling, the amount of nicotine from the treated filter is used.

11.5.4 If the desorption efficiency is less than 100%, read the desorption efficiency from the curve generated in Section 11.1, or if no curve was generated, use the simple arithmetic mean (if less than 100%). Determine the total weight of nicotine by dividing the weight of nicotine by the desorption efficiency (DE):

$$\text{corrected } \mu g/\text{sample} = [\text{total nicotine weight}/\text{desorption efficiency (DE)}] \times 100$$

11.5.5 Convert the amount of nicotine found to micrograms per cubic meter of air by the equation:

$$\mu g/m^3 = [\text{corrected } \mu g \times 1000 \text{ (L/m}^3)]/[\text{air volume sampled (L)}]$$

Note: In passive sampling the air volume sampled is calculated from:

$$\text{sampling rate} = \text{mass collected}/[(\text{conc.})(\text{time})] = DA/L$$

where:
D = diffusion coefficient
A = cross-sectional area of sampler
L = length of sampler (distance between windscreen and treated filter)
Note: For this sampler, A = 8.11 cm^2, L = 1.17 cm, and D = 0.063 cm^2/s, with a resulting theoretical sampling rate equal to 25 mL/min. This sampling rate has been confirmed experimentally (3).

11.5.6 Adjust the nicotine concentration found in the sampled air to standard conditions of temperature and pressure by the equation:

$$\text{corrected } \mu g/m^3 = \mu g/m^3 \times 760/P \times [(T + 273)/298]$$

where:
P = barometric pressure of air sampled, torr
T = temperature of air sampled, °C
760 = standard pressure, torr
298 = standard temperature, °K

12. 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.

12.1 Standard Operating Procedures

12.1.1 Users should generate SOPs describing and documenting 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 samples
- assembly, leak-check, calibration, and operation of the analytical system, addressing the specific equipment used
- sampler storage and transport
- 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 Calibration of Personal Sampling Pump

12.2.1 The pump is calibrated so the flow controller is set at a sampling rate of 1.7 L/min for the treated filter cassette.

12.2.2 Sampling pumps are calibrated at the beginning and at the conclusion of each sample study. To ensure quality volumetric results, pump calibration is recommended at random points throughout each study.

12.2.3 Connect a soap-film flow meter of suitable volume with Tygon tubing to the front end of the active sampler, as illustrated in Figure 11.

12.2.4 Record the barometric pressure and ambient temperature on the Field Sampling Data Sheet.

12.2.5 Thoroughly wet the surface of the flowmeter before any measurements are recorded. Measure the time for a soap-film bubble to travel a known volume with a stopwatch. Perform five replicate measurements and compute the average time. Correct

$$V_s = (V_a \times P_b \times 298)/[(T + 273) \times 760]$$

where:

V_s = volume corrected to standard conditions of 298°K and 760 torr, L
V_a = actual volume measured with the soap-film flowmeter, L
T = temperature at calibration, °C
P_b = barometric pressure at calibration, torr
760 = standard pressure, torr
298 = standard temperature,°K

12.2.6 The standard flow rate (Q_s) is then calculated with the equation:

$$Q_s = V_s/R$$

where:
Q_s = standard flow rate, L/min
V_s = volume corrected to standard conditions, L
R = average time obtained from soap-film measurement, min

12.3 Method Sensitivity, Precision and Linearity

12.3.1 The sensitivity of the active sampling technique has a limit of detection of 0.1 $\mu g/m^3$ over an eight hour period and 0.5 $\mu g/m^3$ over a one hour sampling period at a sampling rate of 1.7 L/min. The sensitivity of the passive sampling technique is specified by a limit of detection of 16 $\mu g/m^3$ over a five hour period and 0.2 $\mu g/m^3$ over a one week period at a sampling rate of 1.7 L/min.

12.3.2 Determining desorption efficiency (see Section 11.1), repeatability and reproducibility ensures method precision.

12.3.3 Non-linearity in the calibration curve or desorption efficiency curve may occur at concentrations near the limit of detection of the method or at high concentrations near the saturation limit of 100 μg nicotine per treated filter.

12.4 Method Modification

Note: Because nicotine is extremely toxic and readily absorbed through the skin, direct contact with the reagent should be avoided. Using a solid reagent (subsequently dissolved in a solvent) reduces the amount of initial contact with nicotine already in a liquid form. The following provides a procedure for preparing primary nicotine standard solutions with nicotine salicylate, which is more easily handled and less hazardous if spilled.

12.4.1 Weigh 0.1851 g nicotine salicylate. Add to 100 mL volumetric flask partially filled with ultra high purity water. Bring to 100 mL mark. This is the stock 1000 ppm nicotine solution (aqueous).

12.4.2 Place a clean magnetic stirring bar into a clean 50 mL Erlenmeyer flask.

12.4.3 Accurately pipet 10 mL of 1000 ppm nicotine stock solution into this flask.

12.4.4 Add 10 mL of 10 N NaOH to flask. Stir gently for approximately two minutes.

12.4.5 Add 10 mL of ammoniated heptane to the flask and stir an additional five minutes.

12.4.6 Carefully transfer the supernatant (heptane) to a 100 mL volumetric flask using a pipet.

12.4.7 Add an additional 10 mL ammoniated heptane, stir 2 minutes, transfer to a 100 mL volumetric flask.

12.4.8 Repeat Section 12.4.7 two more times.

12.4.9 Dilute the 100 mL volumetric flask to volume with ammoniated heptane and label "100 ppm nicotine".

12.4.10 Pipet 0.5, 1.0, 2.0, 5.0, and 10.0 mL of the 100 ppm nicotine into labelled volumetric flasks and dilute to 100 mL with ammoniated heptane. Resulting concentrations are 0.5, 1.0, 2.0, 5.0, and 10.0 ppm nicotine respectively.

Note: Use freshly ammoniated heptane.

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12.5 Safety

12.5.1 If spilling of nicotine reagent or solvent occurs, take quick and appropriate clean up action.

12.5.2 When preparing standards, as with handling any chemicals, protective gloves, lab coats and safety glasses should always be worn to avoid contact with skin and eyes. Particular caution should be taken with nicotine because it is quite toxic, (TLV = 0.5 mg/m^3) and easily absorbed through the skin.

13. Acknowledgements

The determination of nicotine in indoor air is a complex task, primarily because of the lack of standardized sampling and analysis procedures. Compendium Method IP-2 is an effort to address these difficulties. While there are numerous procedures for sampling and analyzing nicotine in indoor air, this method draws upon the best aspects of each one and combines them into 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. GC/NPD Settings

	Treated Filter Cassette
Column	2% KOH on 10% Carbowax 20M 6 ft. glass (2 mmid)
Temps	
Injector	225°C
Oven	140°C (isothermal)
Detector NPD Bead	250°C
Gas Flows	
He, carrier	15 mL/min
H_2 , detector	1 mL/min
Air, detector	115 mL/min
Injection	3 µl

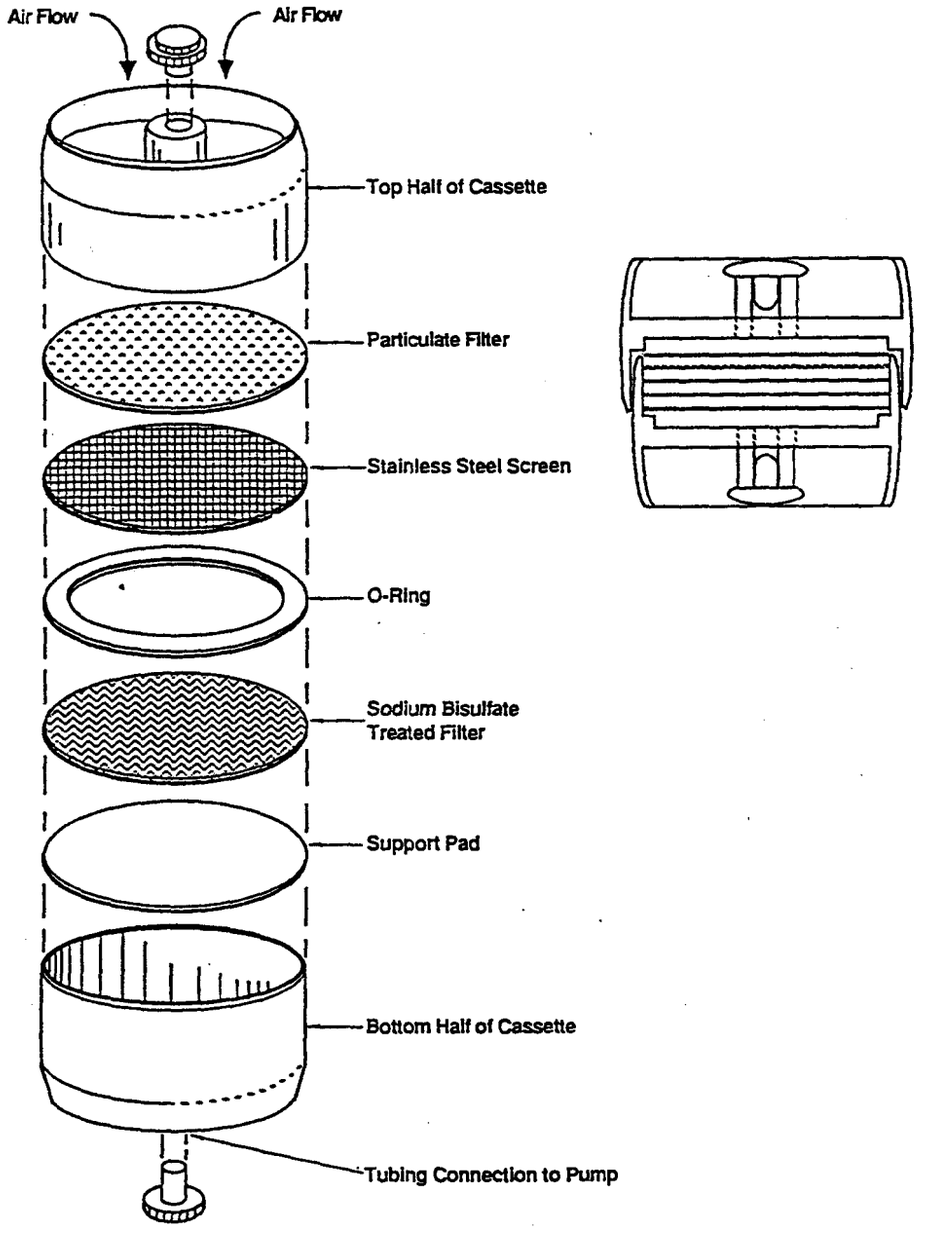

Figure 1. Filter Cassette Used for Active Sampling

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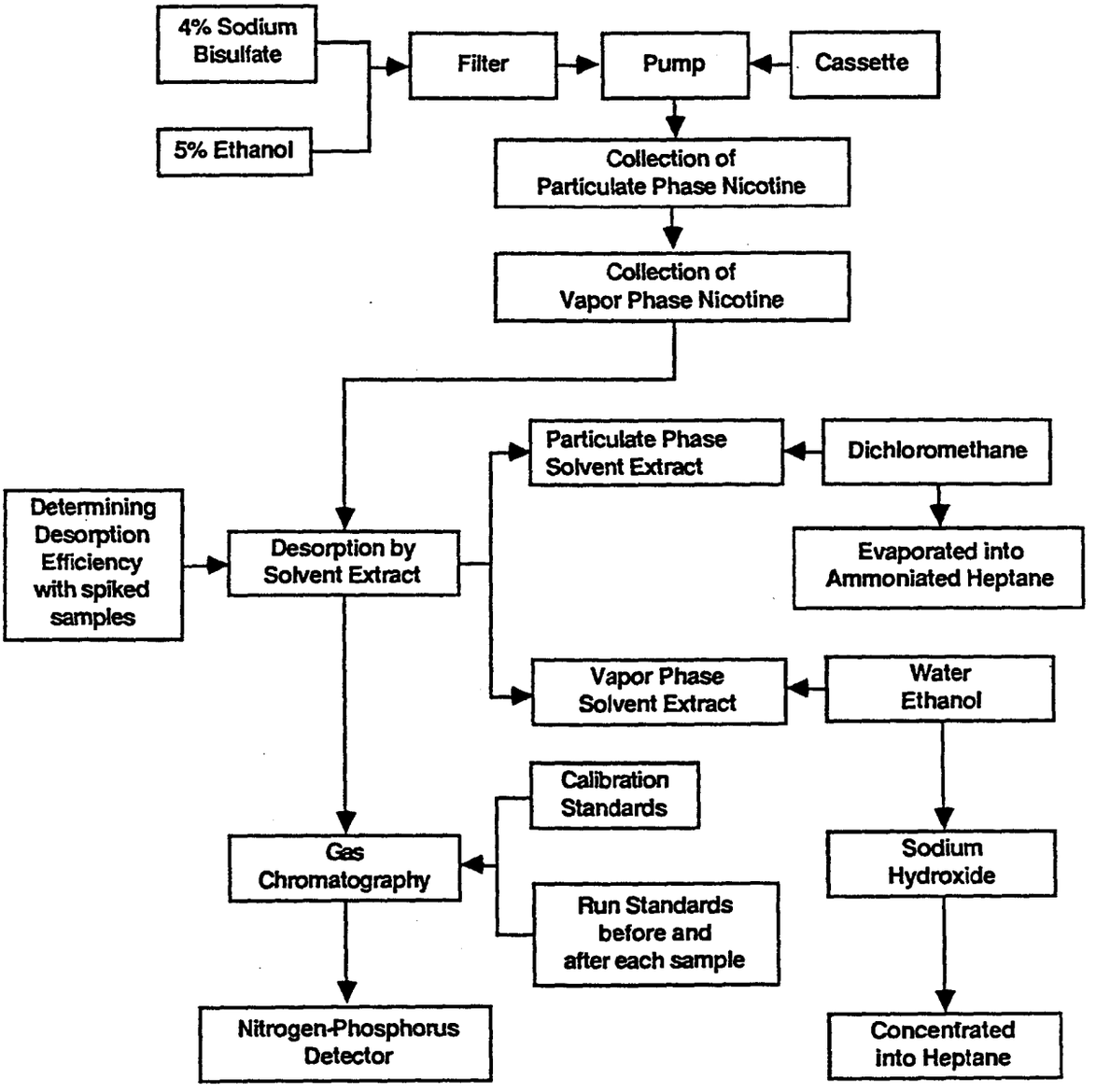

Figure 2. Sampling/Analysis for Active Sampling Using a Filter Cassette

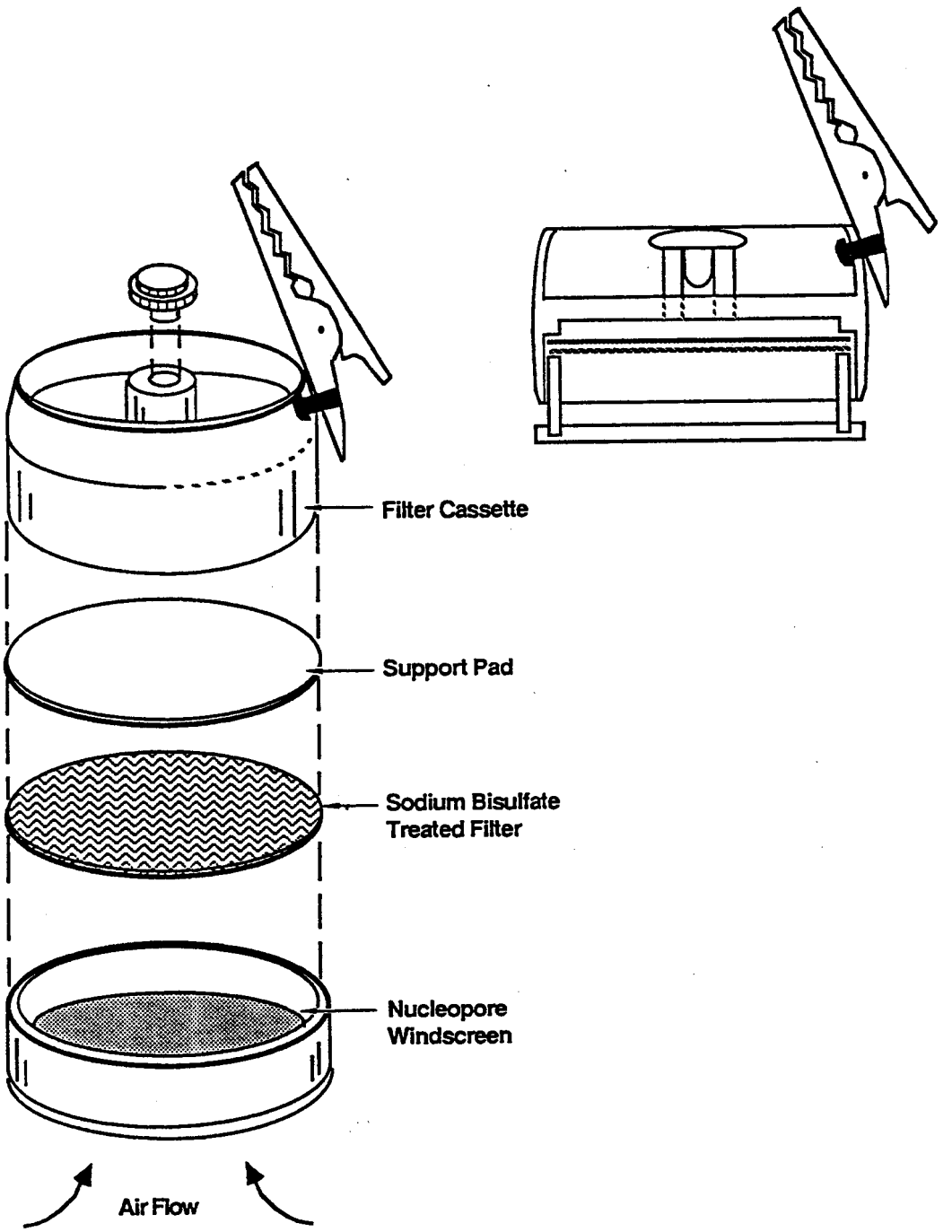

Figure 3. Filter Cassette Used for Passive Sampling

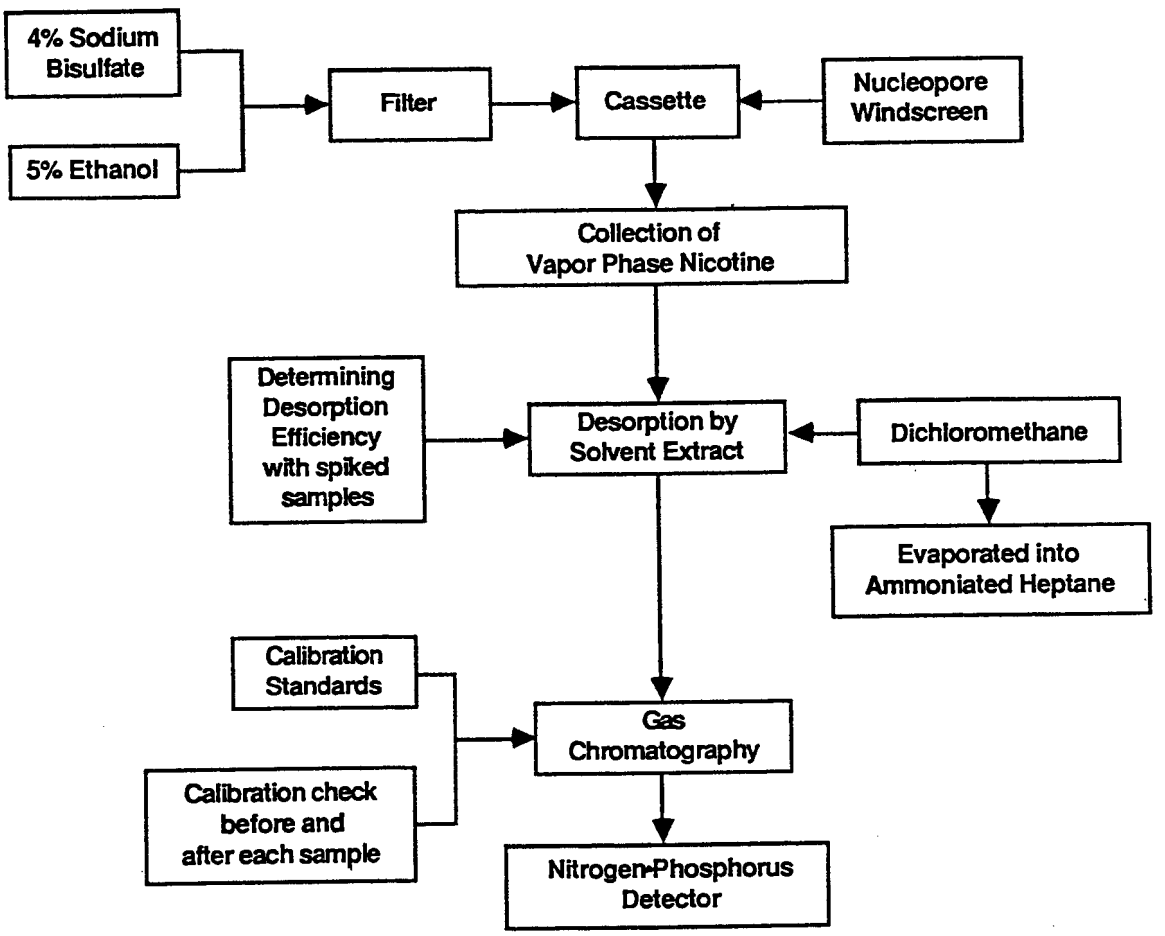

Figure 4. Sampling/Analysis for Passive Sampling Using a Filter Cassette

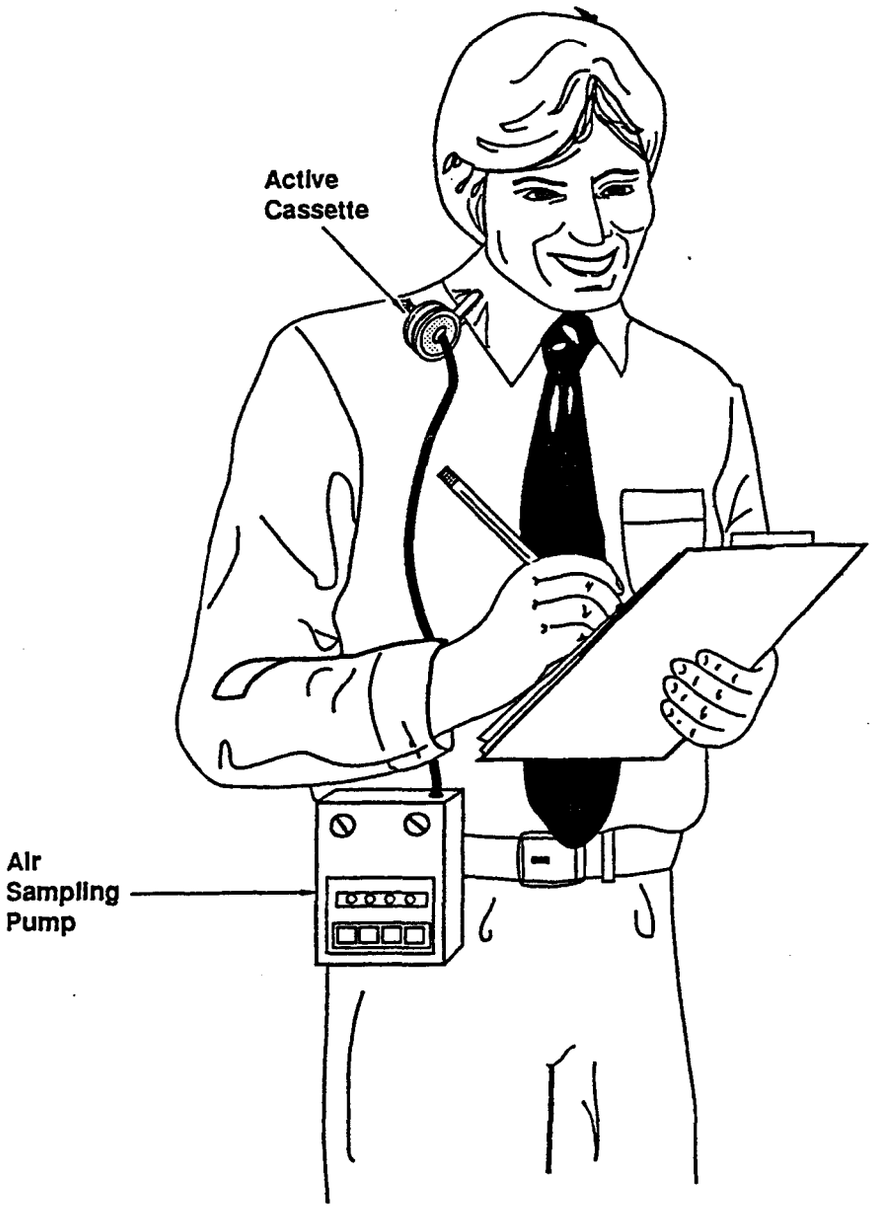

Figure 5. Sampling Setup for Personal Monitoring

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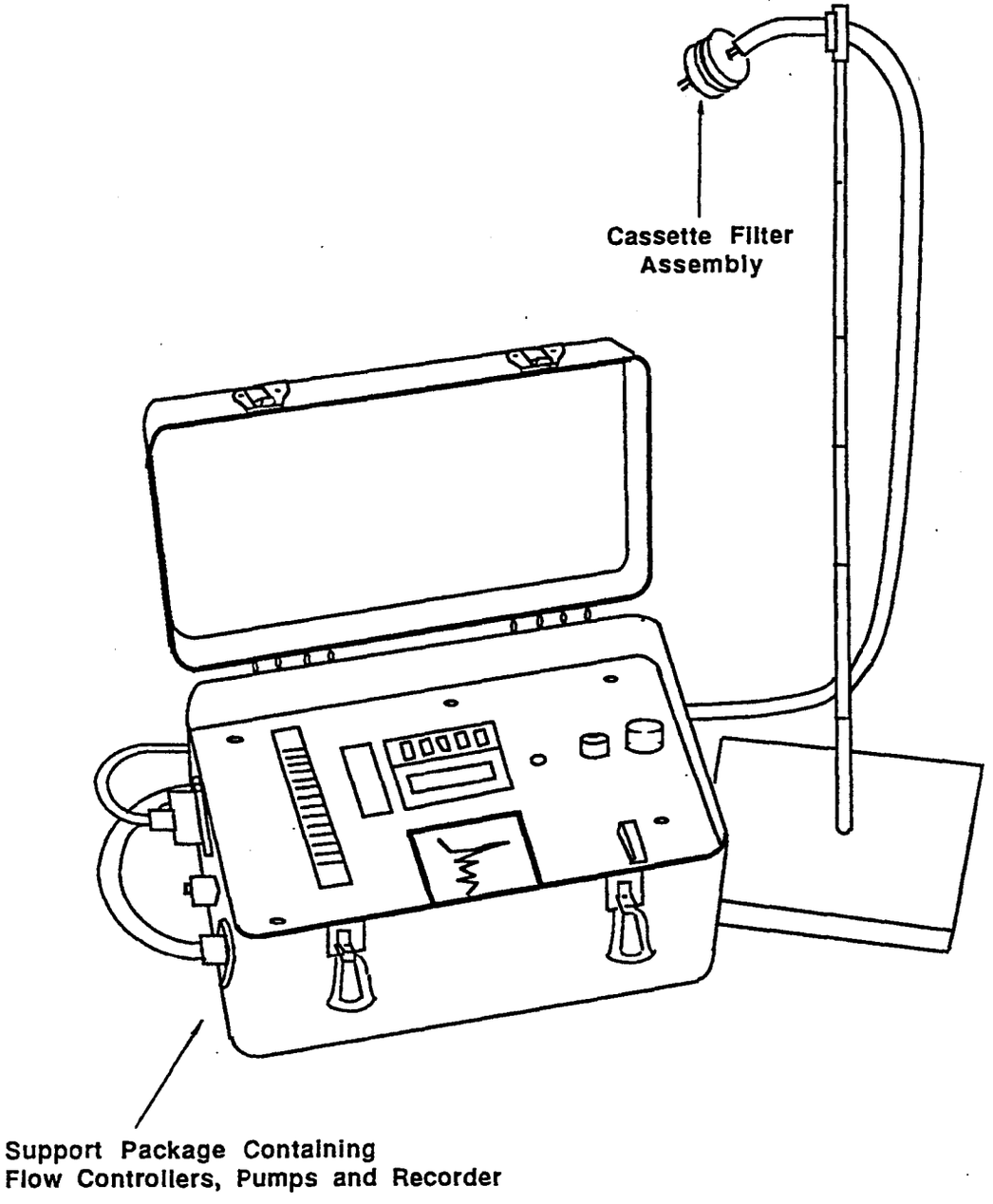

Figure 6. Sampling Setup for Stationary Sampling

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FIELD SAMPLING DATA SHEET
(One Sample per Data Sheet)

PROJECT: _____
SITE: _____
LOCATION: _____
INSTRUMENT MODEL NO.: _____
PUMP SERIAL NO.: _____

DATE(S) SAMPLED: _____
TIME PERIOD SAMPLED: _____
OPERATOR: _____
CALIBRATED BY: _____

ADSORBENT CASSETTE INFORMATION:
Type: _____
Adsorbent: _____

Serial Number: _____
Sample Number: _____

SAMPLING DATA:

Type of Samplers Active, or Passive	Sampling Location	Temp. F°	Pressure in Hg	Flow Rate (Q) mL/min.	Sampling Period		Total Sampling Time, min.	Total Sample Volume, Liters
					Start	Stop		

Checked by _____

Date _____

* Flow rate from soap bubble calibrator

Figure 7. Nicotine Field Sampling Data Sheet

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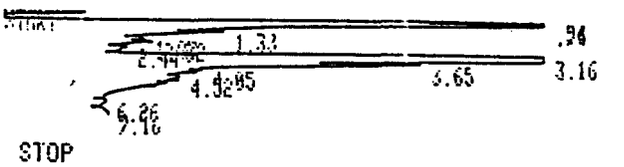

Operating Parameters for the GC

Flow Rate: Helium carrier, 15 ml/min
Column: 2 mm 6 foot 2% KOH on 10% Carbowax 20 M
Oven: 140°C
Detector: 250°C
Detector Gas Flow Rates: Hydrogen 1 mL/min; Air 115 mL/min
Injector: 225°C
Injection: 3 µl
Retention Time: ~3.16 min for Nicotine

RUN # 47

AREA%

RT	AREA	TYPE	AREA%	AREA%
0.56	2771700	PH	0.128	2.265
0.74	2.1823E+07	SHH	0.213	17.836
1.33	213810	DTBP	0.166	0.175
1.83	81123	TPV	0.131	0.066
2.02	143970	TVV	0.173	0.118
2.44	69636	TPB	0.245	0.057
3.16	9.6244E+07	ISHH	0.202	78.661
3.65	809480	TBP	0.195	0.662
4.05	39248	DTPV	0.177	0.032
4.52	108820	TPV	0.254	0.089
6.26	32536	TBP	0.268	0.027
7.16	15755	ITPB	0.245	0.013

TOTAL AREA= 1.2235E+08
MUL FACTOR= 1.0000E+00

Figure 8. Chromatograms from an ETS Sample

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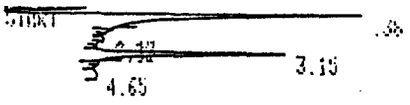
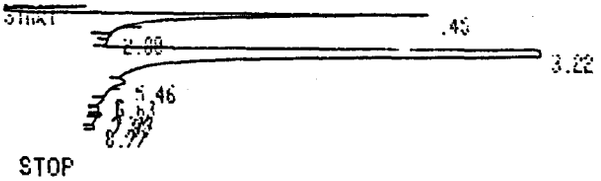


RUN # 6

AREA%

RT	AREA	TYPE	HT	AREA%
0.38	4639600	PB	0.374	76.321
2.13	19440	PV	0.139	0.320
2.32	18262	D VP	0.127	0.300
3.15	1370600	PB	0.238	22.547
4.65	31098	PV	0.413	0.512

TOTAL AREA= 6079100
MUL FACTOR= 1.0000E+00

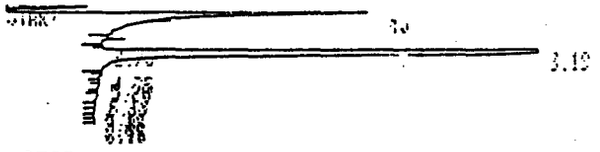


RUN # 10

AREA%

RT	AREA	TYPE	HT	AREA%
0.45	5857400	PB	0.467	4.016
2.00	8661	D BP	0.148	0.006
3.22	1.3977E+08	†SPB	0.209	95.824
5.46	130970	TBB	0.429	0.090
6.63	28151	BP	0.369	0.019
7.79	30109	D VV	0.145	0.021
7.99	31492	D VP	0.139	0.022
8.77	3925	PP	0.143	0.003

TOTAL AREA= 1.4586E+08
MUL FACTOR= 1.0000E+00



RUN # 8

AREA%

RT	AREA	TYPE	HT	AREA%
0.45	3433200	PB	0.293	19.035
2.73	4444	PP	0.096	0.025
3.19	1.4425E+07	PB	0.828	80.192
4.75	13831	VP	0.170	0.077
5.20	15217	PV	0.169	0.085
6.19	41916	VP	0.506	0.233
6.82	19103	PV	0.219	0.106
7.19	15959	VP	0.179	0.089
7.64	5992	PV	0.193	0.033
7.92	12210	VP	0.183	0.068
8.15	1317	I PP	0.349	0.007

TOTAL AREA= 1.7989E+07
MUL FACTOR= 1.0000E+00

Operating Parameters for the GC

Flow Rate: Helium carrier, 15 mL/min
Column: 2 mm 6 foot 2% KOH on 10% Carbowax 20 M
Oven: 140°C
Detector: 250°C
Detector Gas Flow Rates: Hydrogen 1 mL/min; Air 115 mL/min
Injector: 225°C
Injection: 3 µL
Retention Time: ~3.16 min for Nicotine
Run #6 = 1 µg/mL
Run #8 = 10 µg/mL
Run #10 = 100 µg/mL

Figure 9. GC Chromatograms of Varying Nicotine Concentrations

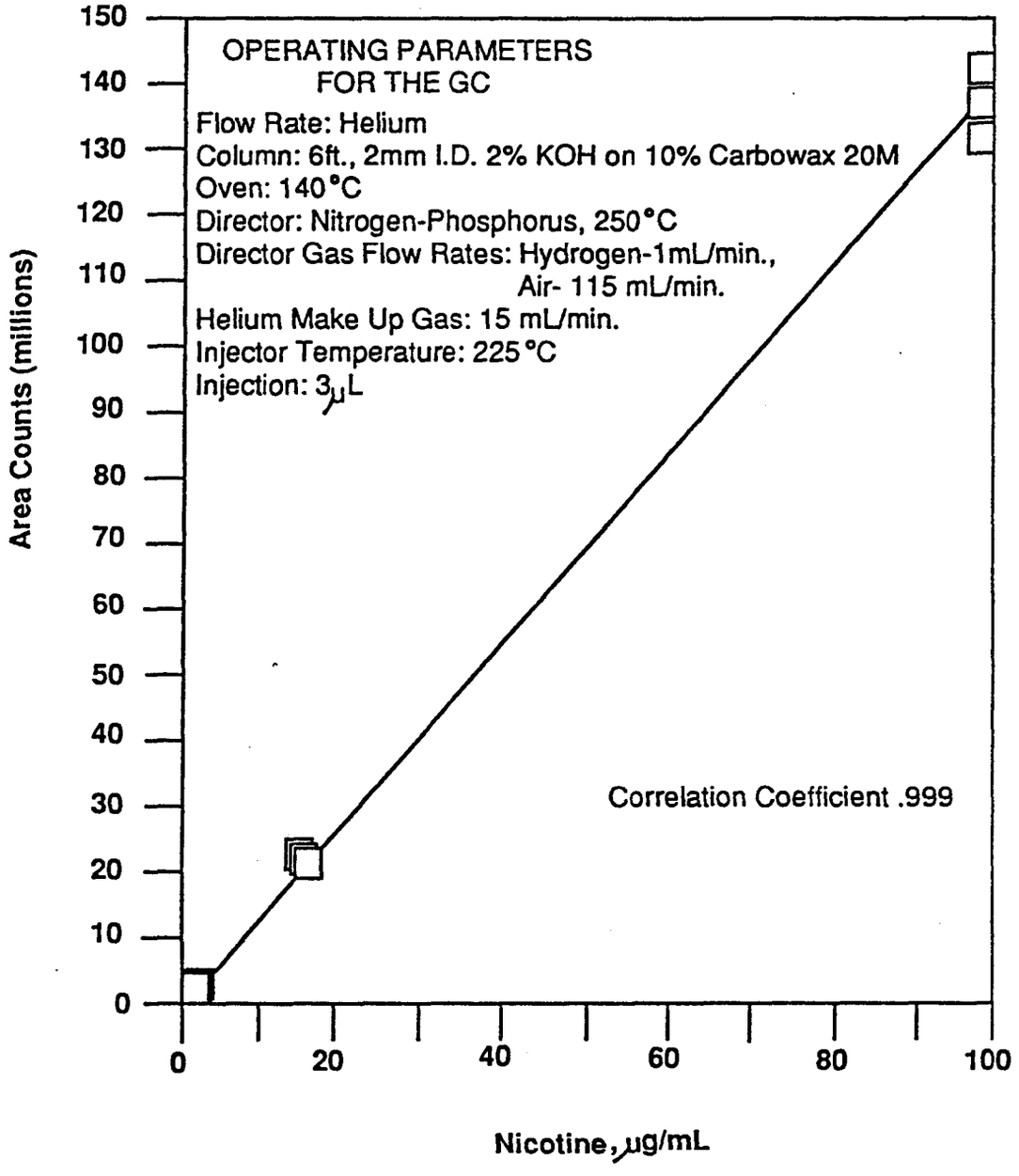


Figure 10. Nicotine Calibration Curve

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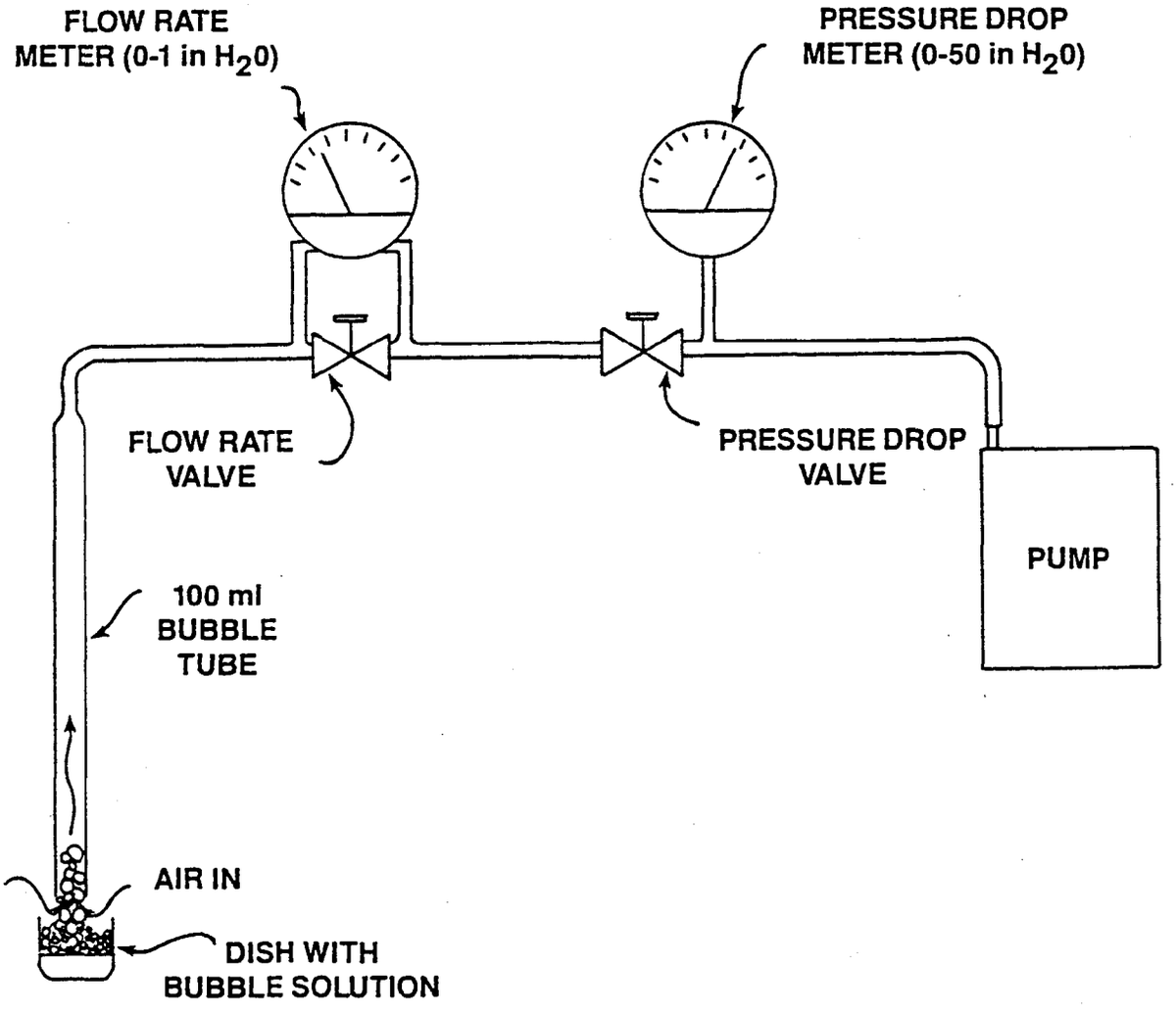

Figure 11. Calibration Assembly for Personal Sampling Pump

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Chapter IP-3

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO_2) IN INDOOR AIR

- **Method IP-3A - Nondispersive Infrared (NDIR)**
- **Method IP-3B - Gas Filter Correlation (GFC)**
- **Method IP-3C - Electrochemical Oxidation**

1. Scope

This document provides three methods for determination of CO or CO_2 in indoor air. The first method (IP-3A) employs nondispersive infrared (NDIR) spectrometry for fixed-site monitoring using a real-time continuous monitor. The second method (IP-3B) presents the use of the gas filter correlation (GFC) technique for determination of CO or CO_2 in indoor air. Method IP-3B utilizes GFC analyzers that are located at fixed sites within the monitoring area. The third method (IP-3C) utilizes electrochemical oxidation principles to determine CO in indoor air. An Appendix to Method IP-3C describes a specific portable air sampling system (PASS) using electrochemical techniques.

2. Applicability

2.1 Indoor air quality has become a significant environmental health issue because most people spend the majority of their time indoors. As with outdoor air quality and occupational exposure, monitoring pollutant concentrations indoors is essential to evaluate potential health threats and identify proper abatement approaches. Indoor CO/CO_2 emissions contribute to poor indoor air quality. With the presence of these pollutants in indoor air, there is a need to assess human exposure and at least meet ambient air and occupational standards.

2.2 Indoor CO emissions are mostly due to incomplete fuel combustion in unvented cooking and heating appliances and from consumption of tobacco products. Vehicular exhaust originating in attached or underground garages may also be a major contributor. CO is essentially nonreactive, and in the absence of indoor sources, average indoor CO concentrations are comparative to outdoor concentrations. However, when indoor sources are present, indoor levels can be much higher than those outdoors. Indoor levels can exceed the 8-hour ambient standard when indoor sources are substantial. The National Ambient Air Quality Standards (NAAQS) for CO are 9 ppm (10 mg/m^3) for an 8 hour period and 35 ppm (40 mg/m^3) for a 1 hour period.

2.3 Carbon dioxide is a colorless, odorless, and tasteless gas than can produce a debilitating effect on humans, including impaired breathing and unconsciousness. This gas is heavier than air and it seeks the lowest levels, displacing normal air. CO_2 is produced by human metabolic activity and exhaled through the lungs. The amount of CO_2 produced is a function of an individual's activity level and composition of food consumed. The average amount of CO_2 normally exhaled by an adult with an activity level equivalent to an office worker is approximately 200 mL/min.

2.4 In addition to being a product of human respiration, CO_2 is also an indicator of inadequately vented combustion processes such as gas or oil-fired space and hot water heaters. Individuals exposed to 1.5% CO_2 for prolonged periods of time experience mild metabolic stress, while exposure to 7-10% CO_2 results in unconsciousness within a few minutes. Ventilation standards have historically been set to maintain CO_2 indoor concentrations $\leq$ 0.5%, a level which appears not to adversely affect persons with normal health. Under standards newly adopted by the American Society of Heating, Refrigeration, and Air Conditioning Engineers (ASHRAE) utilizing a 20 cfm/person fresh air intake rate, CO_2 indoor concentrations should be maintained below 0.08%.

Method IP-3A

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO_2) IN INDOOR AIR USING NONDISPERSIVE INFRARED (NDIR)

Method IP-3A

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO_2) IN INDOOR AIR USING NONDISPERSIVE INFRARED (NDIR)

1. Scope

1.1 This document describes a combined method for determination of CO or CO_2 in indoor air using nondispersive infrared spectrometry. This method makes use of a commercially available nondispersive infrared (NDIR) analyzer that is located at a fixed site for continuous measurement of CO or CO_2 in indoor atmospheres.

1.2 The NDIR method described herein is based on ASTM Standard Procedure D3162-78 and 40 CFR Part 50, Appendix C. This procedure has a detection limit of approximately 0.5 ppm (0.6 mg/m^3) CO in air. NDIR analyzers are relatively insensitive to flow rate, require no wet chemicals, are sensitive over wide concentration ranges, and have short response times.

1.3 While nondispersive infrared analyzers are the most commonly used continuous, automated devices for measuring ambient level CO concentrations, other instruments have been developed and tested.

1.4 Galvanic and coulometric analyzers are two other instruments commercially available for continuously measuring CO concentrations. The function of both instruments depends on the oxidation of CO by iodine pentoxide (I_2O_5). These instruments are flow- and temperature-dependent and suffer from multiple interferences; consequently, they have not been widely used.

1.5 A mercury vapor analyzer, which depends on the liberation of mercury vapor when CO is passed over hot mercuric oxide, has been used as a portable, continuous-monitoring analyzer. Though especially adaptable for measuring low CO concentrations 0.25 ppm (0.29 mg/m^3), this instrument does not appear suitable for routine air monitoring because of numerous interferences and electronic instability.

1.6 A recently developed automated gas chromatographic system operates by quantitatively converting CO to methane (CH_4), which is subsequently semi-continuously measured by a flame ionization detector. This arrangement shows considerable promise as a monitoring device. Concentrations of from 0.1 to 1,000 ppm (0.1 to 1,150 mg/m^3) may be determined, and instrument output over this range is linear for both CO and CH_4.

1.7 The NDIR systems have several advantages over these monitoring techniques. They are:

- Insensitive to flow rates,
- Require no wet chemicals,
- Independent of room temperature change,
- Sensitive over a wide concentration range,
- Quick responding, and
- Operatable by non-technical personnel.

1.8 Consequently, this method is based upon the NDIR principle of detection of CO and CO_2 in indoor air.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definition of Terms Relating to Atmospheric Sampling and Analysis
D1357 Recommended Practice for Planning the Sampling of the Atmosphere
D3195 Recommended Practice for Rotameter Calibration
D1914 Recommended Practice for Conversion Units and Factors Relating to Atmospheric Analysis
D3249 Recommended Practice for General Ambient Air Analyzer Procedures
E1 Specification for ASTM Thermometers
E180 Recommended Practice for Development of Precision Data for ASTM Methods for Analysis and Testing of Industrial Chemicals
D3162-78 Standard Test Method for Carbon Monoxide in the Atmosphere (Continuous Measurement by Nondispersive Infrared Spectrometry)

2.2 Other Documents

Laboratory and Indoor/Ambient Air Studies (1-5)
U.S. Environmental Protection Agency Technical Assistance Document (6)
U.S. Environmental Protection Agency Quality Assurance Handbook (7)

3. Summary of Detection

3.1 Nondispersive infrared analyzers have been developed to monitor not only CO or CO_2, but also SO_2, NO_x, hydrocarbons and other gases that absorb in the infrared region of the electromagnetic spectrum. The term "nondispersive" is used to describe the fact that no prisms or grating are used in the monitor to disperse the infrared energy source into component wavelengths. Rather the measurement gas itself (i.e. CO or CO_2) is used in the detector to detect wavelength, and hence species, specificity.

3.2 A broad wavelength band of infrared emission is used instead of employing monochromatic filters or diffraction gratings to isolate one particular wavelength (8). As illustrated in Figure 1A, a gas will have characteristic absorption peaks centered at specific wavelengths (λ_0) in the infrared spectrum when exposed to broad band infrared radiation (λ). The center of these absorption peaks are specific for individual compounds, as illustrated in Figure 1B.

3.3 An NDIR analyzer operates on the principle that CO (or CO_2) has a sufficiently characteristic infrared absorption spectrum such that the absorption of infrared radiation by the CO molecule can be used as a measure of CO concentration in the presence of other gases that may occur in indoor air. Although the size, shape, sensitivity, and range of these instruments vary with manufacturer, basic components and configurations are similar. Most commercially available instruments include a hot filament source of infrared radiation, a

rotating sector (chopper), a sample cell, a reference cell, and a detector, as illustrated in Figure 2.

3.4 In operation, broad band infrared radiation is emitted from the infrared source and passes through the chopper wheel into the compartments containing the reference and sample cells. The reference cell is filled with a non-absorbing inert gas such as nitrogen or argon. The sample cell is a flow-through design enabling the passing of the gas stream of interest. Equal amounts of infrared energy enter both the sample and reference cells. If no CO or CO_2 is present in the gas stream, then the amount of radiation exiting the sample cell compartment will be equal to that exiting the reference cell. If, however, the gas stream contains molecules of CO or CO_2, then the infrared energy exiting the sample cell will be less than that exiting the reference cell because of molecular absorption.
Note: Recent models have included a distribution cell (containing 100% CO_2) and a flow-through design for the reference cell. In this design, a CO-CO_2 converter consisting of a temperature-controlled cartridge containing platinum-coated aluminum trioxide beads converts the sample gas CO to CO_2 on the reference cell side. At the same time, sample gas containing CO, but not converted to CO_2, flows through the sample cell. the CO-CO_2 converter causes no other change to the sample gas, thus the only difference between the sample and reference gases is the CO content. Since only the CO has been removed from the reference gas, and due to the distribution cell, all the CO_2 wavelength IR energy has been removed from both beams, then the only difference between the IR energy emanating from the sample cell and reference cell is that caused by CO wavelength absorption in the sample cell. Because all the CO_2 wavelength energy has been absorbed in the distribution cell, there can be no further absorption from the increased CO_2 concentration in the "reference" cell. All other interferents, such as water, exist similarly in both cells and do not contribute to the difference. The distinct advantage of this system over systems using cylinder reference gas or static reference cells is that all interferents, known and unknown, are similarly present in the sample and reference cells and thus their effect is cancelled.

3.5 A mathematical relationship exists between the amount of CO or CO_2 in the sample and the amount of absorption or energy attenuation. The mathematical relationship is known as the Beer-Lambert Law and is used to determine the concentration of CO or CO_2 in an air sample. The law states that the transmittance of light through a medium that absorbs light is decreased exponentially by the product αcl. The Beer-Lambert Law is defined by the following equation:

$$T = I/I_o = e^{-\alpha c l}$$

where:
T = transmittance of light through sample gas
I_o = intensity of light entering the sample gas
I = intensity of light leaving the gas
c = concentration of the pollutant, mol/liter
l = distance light beam travels through sample gas, path length, cm
α = attenuation coefficient, liter/mol-cm

3.6 The attenuation coefficient, α, is dependent upon the wavelength of the radiation and also upon the properties of the molecule. The coefficient tells how much a gas species will absorb light energy at a given wavelength. If no absorption occurs, α will be zero, and the transmittance of IR energy would equal 100%. If an electronic or vibrational-rotational transition occurs in the gas at some wavelength, α will be some value, and the reduction of light energy across the path will depend upon the pollutant concentration and the original intensity, I_o, of the light beam. I_o is determined by taking a reading from the detector when no pollutant gas is in the sample cell. The concentration is obtained from the Beer-Lambert Law if α and ℓ are known. Generally, a calibration curve is generated with known gas concentrations rather than using a theoretical value for α.

3.7 The resultant IR energy exiting both the sample and reference cells now strike the detector compartment.

3.8 The uniqueness of commercially available NDIR monitors lies within the detection of the remaining IR radiation. More specifically, the detector consists of two compartments filled with equal concentrations (%) of the pollutant being monitored, i.e. CO or CO_2. Because the pollutant absorbs at discrete wavelengths, its specificity enables it to be an excellent detector for monitoring the change in IR energy entering the detector system caused by the same pollutant gas in the sample cell.

3.9 As illustrated in Figure 2, the detector compartments, containing similar concentrations of specific pollutant of interest, are separated by a thin diaphragm whose movement is detected by an induction tranceducer.

3.10 The resultant infrared signal from the reference cell strikes one compartment of the detector cell, while the resultant infrared energy from the sample cell strikes the other side of the detector cell (1). The detector functions in the following manner: when the molecules of CO or CO_2 in the detector compartments absorb infrared radiation, they absorb the energy of that radiation. This increase in energy results in the CO or CO_2 molecule becoming more active (it begins to vibrate and move more rapidly). This increase in molecular activity causes the CO or CO_2 gas to expand. However, because the gas is contained in a rigid compartment, expansion results in an increase in the pressure of the CO or CO_2 gas within the cell. The compartment receiving the reference signal receives more infrared energy and subsequently more energy is absorbed by the CO or CO_2 molecules contained within that cell. This results in a higher gaseous pressure on the reference side of the detector relative to the sample side of the detector. The thin metal diaphragm naturally bends toward the area of lower pressure (the sample side), and the amount of this deflection is measured by means of the induction transducer. This signal is then amplified and used to determine the concentration utilizing the Beer-Lambert Law. The use of CO or CO_2 in the detector compartments limits the measured absorption to one or more of the characteristic wavelengths at which CO strongly absorbs, thus providing specificity of the detector for that gas.

3.11 Because the diaphragm detector is sensitive to vibrations, the micro-flow® detector was developed. Similar to the diaphragm detector, it also contained two detector cells filled

with CO. However, the two cells are separated by a passage way which allows gas to flow between detector reference and sample cells. The flow of gas is monitored by a mini-flowmeter. In operation, the two detector cells filled with CO absorb the unequal infrared energy. This energy is absorbed in the CO-filled detector cell, raising the gas temperature and thus its pressure. The unequal pressure rise in the detector cells, due to the unequal IR energy striking the detector cells, causes a flow from the reference detector to the sample detector cell which is measured by the micro-flow® mini-flowmeter in the connecting passage. The detector cell gas flow continues from "reference" to "sample" until the chopper blade obscures the IR energy source. At that time the transmitted energy goes to zero, the reference detector cell temperature falls to approach the temperature of the sample cell and the detector cell flow reverses to re-equalize the detector cell pressures. At the chopping rate of 10 cycles per second (8.33 for a 50 Hz installation), the micro-flow® sensor generates an alternating signal whose amplitude is proportional to CO concentration in the sample cell. The alternating micro-flow® signals are fed to an AC differential amplifier and the output fed to a synchronous rectifier phased with the chopper. The DC output of the rectifier is then filtered and amplified, then linearized and presented to the output voltage terminals as % CO.

4. Significance

4.1 CO is absorbed by the lung and reacts primarily with hemoproteins and most notably with the hemoglobin of the circulating blood (9). The absorption of CO is associated with a reduction in the oxygen-carrying capacity of blood and in the readiness with which the blood gives up its available oxygen to the tissues. The affinity of hemoglobin for CO is over 200 times that for oxygen, indicating that carboxyhemoglobin (COHb) is a more stable compound than oxyhemoglobin (O_2Hb). About 20% of an absorbed dose of CO is found outside of the vascular system, presumably in combination with myoglobin and heme-containing enzymes.

4.2 The magnitude of absorption of CO increases with the concentration, the duration of exposure, and the ventilatory rate. With fixed concentrations and with exposures of sufficient duration, an equilibrium is reached; the equilibrium is reasonably predictable from partial-pressure ratios of oxygen to CO.

4.3 Long-term exposures to sufficiently high CO concentrations can produce structural changes in the heart and brain. It has not been shown that ordinary ambient exposures will produce this. The lowest exposure producing any such changes has been 50 ppm (58 mg/m^3) continuously for 6 weeks. The recommended American Conference of Government Industrial Hygienists (ACGIH) permissible exposure limit for CO is 35 ppm for a 10-hour time weighted average (TWA) with a 200 ppm ceiling (10).

4.4 Consequently, due to the reliability and accuracy needed, this method recommends NDIR analyzers that have performance specifications similar to those for EPA designated reference methods (11) as outlined in Table 1 and Table 2. For monitoring ambient CO to determine compliance with the National Ambient Air Quality Standards (NAAQS), analyzers designated as reference methods are required. Portable NDIRs can be used to

screen residential environments, workplace, etc. for the presence and intensity of CO or CO_2. Use of portable NDIRs may not yield defensible quantitative information regarding CO or CO_2 concentrations. Rather, they can be used to provide a "profile" of intensity of CO or CO_2 and to assist in the placement of indoor fixed site monitors. Rigorous sampling strategy using fixed site NDIR (EPA reference models as listed in Table 2) can subsequently be instituted at specific locations based on this screening. This method will not attempt to detail the operation of portable NDIRs, which can be found in specific models users manuals.

5. Definitions

Note: Definitions used in this document and any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, E260, and E355. All abbreviations and symbols are defined within this method at point of use. Additional definitions, abbreviations, and symbols are located in Appendices A-1 and B-2 of this Compendium.

5.1 Range - The minimum and maximum measurement limits of a monitor.

5.2 Output - Electrical signal which is proportional to the measurement; intended for connection to data recording or data processing devices. Usually expressed as millivolts or milliamps full scale.

5.3 Full scale - The maximum measuring limit for a given range of a monitor.

5.4 Minimum detectable sensitivity - The smallest amount of input concentration that can be detected as the concentration approaches zero.

5.5 Accuracy - The degree of agreement between a measured value and the true value; usually expressed as ± percent of full scale.

5.6 Lag time - The time interval from a step change in input concentration at the instrument inlet to the first corresponding change in the instrument output.

5.7 Time to 90% response - The time interval from a step change in the input concentration at the instrument inlet to a reading of 90% of the ultimate recorded concentration.

5.8 Rise time (90%) - The interval between initial response time and time to 90% of the final response after a step increase in the inlet concentration (90% response-lag time).

5.9 Fall time (90%) - The interval between initial response time and time to 90% of final response change after a step decrease in the inlet concentration to zero.

5.10 Zero drift - The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is zero; usually expressed as percent full scale.

5.11 Span drift - The change instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is a stated upscale value; usually expressed as percent.

5.12 Precision - The degree of agreement between repeated measurements of the same concentration, expressed as the standard deviation.

5.13 Operational period - The period of time over which the instrument can be expected to operated unattended within specifications.

5.14 Noise - Spontaneous deviations in measured concentrations from the mean not caused by input concentration changes.

5.15 Interference - An undesired positive or negative response caused by a substance other than the one being measured.

5.16 Interference equivalent - Quantitative interference response, measured as equivalent concentration units of the gas being measured.

5.17 Operating temperature range - The range of ambient temperatures over which the instrument will meet all performance specifications.

5.18 Operating humidity range - The range of ambient relative humidity over which the instrument will meet all performance specifications.

5.19 Linearity - The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between upper and lower calibration points.

5.20 NDIR - This measuring technique is based on absorption by a gaseous pollutant of radiation in the infrared region. This technique is termed nondispersive because no prism or grating is used to disperse the infrared radiation. Uniqueness of this approach is that compound specificity is achieved by using the pollutant being measured (CO or CO_2) in the detector compartments in a differential absorption application to discriminate the discrete wavelengths characteristic of that pollutant.

5.21 Discrimination ratio - Discrimination ratio equals the concentration of an interferent required to produce an instrument response equivalent to unit concentration of the gas being measured.

6. Interferences (8)

6.1 The degree of interference varies with individual NDIR analyzers. Manufacturer's specifications should be consulted to determine if possible interferences render the analyzer unsuitable for proposed use.

6.2 Interference may arise from gases that absorb infrared radiation in wave length bands that overlap that of carbon monoxide or carbon dioxide. Some of the possible interferents are organics, water vapor, methane, and ethane. Carbon dioxide (for CO monitors) and water vapor (for both CO and CO_2 monitors) pose the major interference problems due to

their common occurrence in the atmosphere, and also due to their relatively much higher concentrations than typical CO concentrations.
Note: Concentrations of carbon dioxide found in ambient air (approximately 400 ppm) normally do not interfere with CO measurements, provided the calibration gas contains about the same concentration of CO_2. However, in air grossly contaminated with combustion products, CO_2 (in excess of 1,000 ppm) could result in positive interferences of 1 ppm or higher.

6.3 Water vapor absorbs infrared radiation to a varying degree throughout the infrared region. Its presence can be a primary positive interference in NDIR type instruments. With no correction, error from the moisture interference could be as great as 10 ppm (11 mg/m^3) CO.

6.4 Various measures may be taken to minimize moisture interference. The most obvious is a drying device in the sample inlet section of the analyzer. One device is a tube filled with silica gel or other suitable desiccant such as Drierite®. The sample air is passed over the desiccant before it enters the absorption cell. Another technique includes passing the sample air through a water saturator maintained at a constant temperature. The saturator maintains a constant humidity level in the sample gas stream. This constant humidity is also added to the calibration gases, thereby negating the moisture effects on concentration readings.

6.5 Refrigeration units in the sampling inlet systems are often used in commercial analyzers to maintain a constant, low humidity level. By cooling the sampled air, the moisture is condensed and subsequently removed from the air stream.
Note: Moisture-eliminating devices and constant humidity systems, when employed, should be used on all gases entering the analyzer - calibration, zero, and span gases as well as air samples.

6.6 Two other methods commonly employed to remove water vapor interference involve correcting the action of water vapor on the absorption phenomenon. Narrow band-pass optical filters can be used to remove those wavelengths most sensitive to water vapor from the irradiating beam. In a similar manner an "interference cell" containing water vapor and other principal interferents can be placed in line, between the infrared sources and the sample cell. The interference cell absorbs and reduces those wavelengths which overlap the CO absorption band. This reduces the interference effect of water vapor on the detector.

6.7 Another method of alleviating the interferences due to both CO_2 and water vapor (as well as other interferents) is designing the detector to contain a front and rear measuring chamber, each containing CO or CO_2, as illustrated in Figure 3. In this detector design, the infrared beams from both the reference and sample cells are geometrically combined into a single path into the detector, although the two beams are still separate due to the alternating action of the optical chopper. The front chamber is shorter than the longer rear chamber. The concentrations of pollutant gas in the two chambers are such that overall absorption, and hence the gas pressure, is equal in the two chambers (with no pollutant gas in the sample cell). Due to the peaked absorption characteristic of the detector gas,

absorption in the front chamber is substantially greater at the center wavelengths than at the side wavelengths. In the rear chamber, however, absorption is greater at the side wavelengths because the center wavelengths have been greatly attenuated by the front chamber. This differential absorption in the two chambers helps to compensate for interference from compounds whose absorption spectra overlap that of the detector gas.

6.8 Hydrocarbons at indoor levels should not cause interferences because of the specificity of the NDIR for the component of interest's spectrum. Effects of specific hydrocarbons on the analyzer are routinely provided by the manufacturer.

7. Apparatus

7.1 Analyzer

7.1.1 Continuous CO or CO_2 monitoring system - NDIR CO or CO_2 analyzer equipped with IR source, sample and reference gas cells, sample preconditioner (if needed), detector capable of sensing differences between infrared energy levels in the sample and reference cells, adequate power supply, amplifier/ control unit, meter, and recording system. The analyzer must meet or exceed manufacturer's specifications. Table 1 contains a listing of commercially available CO analyzers. The table lists reference method analyzers from U.S. EPA's List of Designated Reference and Equivalent Methods and also includes a sampling of portable CO or CO_2 analyzers available. Those monitors designated by U.S. EPA as reference methods generally meet or exceed the suggested performance specification listed in Table 2.

7.1.2 Pump - used to flow sample air into the analytical system, if required.

7.1.3 Flow control valve - used to control sample flow rate through the analytical system.

7.1.4 Flowmeter - used to measure sample flow rate through the analyzer.

7.1.5 Moisture control system - for analytical systems that require constant humidity control, refrigeration units are available with some commercial instruments. Drying tubes (with sufficient capacity to operate for 72 hours) containing silica gel (or equivalent drying agent) may be used for short-term sampling.

7.1.6 Particulate matter filter (inline) - used to remove particulate matter from sample flow and to keep sample cell clean. Filter porosity should be 2 to 10 microns.

7.2 Calibration

7.2.1 Pressure regulator(s) - Regulators must have a nonreactive diaphragm and suitable delivery pressure. A two-stage regulator with inlet and delivery pressure gauges is recommended.

7.2.2 Flow controller - The flow controller can be any device capable of adjusting and regulating the flow from the calibration standard. If the dilution method is to be used for calibration (see Section 9.2), a second flow controller will be required for the zero-air. For dilution, the controllers must be capable of regulating the flow to ± 1%.

7.2.3 Flow meter - A calibrated flow meter capable of measuring and monitoring the calibration standard flow rate will be required. If the dilution method is used, a second

flow meter will be required for the zero-air flow. For dilution, the flow meters must be capable of measuring the flow with an accuracy of ± 2%.

7.2.4 Mixing chamber - A mixing chamber is required only if the calibrator concentrations are generated by dynamic dilution of a CO standard. The chamber should be designed to provide thorough mixing of CO and zero-air.

7.2.5 Output manifold - The output manifold should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

7.2.6 Tubing - Polypropylene tubing to connect analyzer to gas cylinders when calibrating, zeroing, and spanning the instrument.

7.2.7 Thermometer - used to measure monitoring area temperature.

7.2.8 Barometer - capable of measuring barometric pressure of monitoring area.

8. Reagents and Materials

8.1 Zero-air source - A source of dry zero-air that is verified to be free of contaminants that could cause detectable responses from the CO analyzer will be needed. The zero-air must contain <0.1 ppm CO; some air cylinders sold as ultrapure may actually contain 1 to 2 ppm CO. The use of a catalytic oxidizing agent such as Hopcalite on any zero-air source would be prudent.

Note: Zero air and calibration gases for CO analyzers should contain about 350 ppm CO_2 to simulate normal ambient concentrations. If synthetic air is used, CO_2 may have to be added.

8.2 Calibration standard - CO standards must be traceable (12) to a National Institute of Standards and Technology - Standard Reference Material (NIST-SRM) or a NIST/EPA approved commercially available Certified Reference Material (CRM). The CO standards must be in air unless the dilution method is used. For dilution, CO in nitrogen may be used if the zero-air dilution ratio is not less than 100:1. An acceptable protocol for demonstrating the traceability of commercial cylinder gas to an NITS-SRM or CRM cylinder gas is provided in Section 12, reference 13. In order to establish a calibration curve and determine linearity of the NDIR analyzer, the calibration gases should correspond to approximately 10, 20, 40, 60, and 80% of full scale value.

8.3 Span gas - pressurized cylinder containing CO or CO_2 concentration corresponding to 80% of full scale, best source.

9. NDIR Analyzer Operation

9.1 Installation

9.1.1 Prior to locating the fixed site NDIR sampling system, the user may want to perform "screening analyses" using a portable CO detection system, such as the PASS as outlined in Method IP-3C, Appendix, or using a portable NDIR system, examples listed in Table 2, to determine presence of CO and variances in concentration. The information gathered from the portable screening analysis would be used in developing a monitoring

protocol, which includes the sampling system location based upon the screening analysis. After screening analysis is performed and sampling site(s) are determined, the fixed site NDIR sampling system is located.

9.1.2 Generally, CO or CO_2 fixed-site NDIR continuous monitors are designed for benchtop operation or installation into a rack. The instrument should be placed in an area that is relatively free of vibration. Appendix C-3 of this Compendium, Placement of Stationary Active Monitors, and Section 13, reference 4 gives further guidelines for monitor placement. If the analyzer is mounted on a rack, plumbing connections should be made on the rear of the cabinet for sample intake, span gas intake, zero gas intake, sample bypass and vent. Usually, on the table top analyzers, these intakes are connected to the front panel by quick-disconnect fittings. Additionally, for typical installation, primary power and recorder signal connections are also made. Portable NDIR monitors allow for much greater flexibility of employment. Some portable models are battery powered, allowing up to 8 hours of continuous operation or can be used continuously with an outside power source.

9.1.3 The manufacturer's operating instructions should include further instructions on the following: receiving inspection, typical/general installation, installation equipment required, and plumbing/electrical connections.

9.2 Operation

9.2.1 Turn-On Procedure and Initial Inspection

9.2.1.1 Turn on and inspect in accordance with specific model's user manual.

9.2.1.2 Ensure that indicators are illuminated, flow meters and pressure gauges are operational and flow meter is adjusted to obtain desired flow rate through the sample cell.

9.2.1.3 Allow the analyzer to stabilize as per user manual instructions (e.g., a minimum of two hours) prior to zeroing and spanning the instrument.

Note: Best performance can be expected if analyzer is left on continuously.

9.2.2 Manual Zero and Span Calibration

9.2.2.1 Prior to operating the analyzer, an initial calibration must be performed. The following provides procedures to measure CO or CO_2 concentrations in indoor air using the CO or CO_2 continuous monitor.

Note: Follow the manufacturer's detailed instructions when calibrating a specific analyzer.

9.2.2.2 Assemble the analyzer as illustrated in Figure 4.

9.2.2.3 Turn the power on and let the analyzer warm up. This usually requires several hours (2 hours minimum) depending on individual analyzers.

9.2.2.4 Connect zero gas to the analyzer.

9.2.2.5 Open the gas cylinder pressure valve (see Figure 4).

9.2.2.6 Adjust the secondary pressure valve until the secondary pressure gauge reads approximately (5 psi) more than the desired sample cell pressure.

Caution: Do not exceed the pressure limit of the sample cell.

9.2.2.7 Set the sample flow rate as read by the rotameter (read the widest part of the float) to the value that is to be used during sampling.

9.2.2.8 Let the zero gas flow long enough to establish a stable trace. Allow at least 5 minutes for the analyzer to stabilize.

9.2.2.9 Adjust the zero control knob until the trace corresponds to the line representing 5% of the strip chart width above the chart zero or baseline. The above is to allow for possible negative zero drift. If the strip chart already has an elevated baseline, use it as the zero setting.

9.2.2.10 Let the zero gas flow long enough to establish a stable trace. Allow at least 5 minutes for this. Mark the strip chart trace as adjusted zero and record on Multipoint Calibration Data Sheet, Figure 5.

9.2.2.11 Disconnect the zero gas.

9.2.2.12 Connect the span gas with a concentration corresponding to approximately 80% of full scale.

9.2.2.13 Open the gas cylinder pressure valve (see Figure 4). Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired sample cell pressure.

9.2.2.14 Set the sample flow rate, as read by the rotameter, to the value that is to be used during sampling.

9.2.2.15 Let the span gas flow until the analyzer stabilizes.

9.2.2.16 Adjust the span control until the deflection corresponds to the correct percentage of chart as computed by:

$$\text{Correct percentage of chart} = [C_s(\text{ppm})]/[C_f(\text{ppm})] \times 100 + 5\ \%\ \text{zero offset}$$

where:
C_s = concentration of span gas, ppm
C_f = full scale reading of analyzer, ppm

As an example where the percent zero offset is 5 and the correct percentage of chart for the span gas of 40 ppm would be:

$$40\ \text{ppm}/50\ \text{ppm} \times 100 + 5 = 85$$

9.2.2.17 Allow the span gas to flow until a stable trace is observed. Allow at least 5 minutes. Mark the strip chart trace as adjusted span and give concentration of span gas in ppm.

9.2.2.18 Disconnect the span gas.

9.2.2.19 Repeat Section 9.2.2.9 through Section 9.2.2.18 and if no readjustment is required, go to Section 9.2.3. If a readjustment greater than 1 ppm is required, repeat Section 9.2.2.9 through Section 9.2.2.10.

9.2.2.20 Lock the zero and span controls.

9.2.3 Multipoint Calibration

9.2.3.1 A multipoint calibration is required when the analyzer is first purchased, the analyzer has had maintenance which could affect its response characteristics, or when results from the auditing process show that the desired performance standards are not being met.

9.2.3.2 A multipoint calibration required calibration gases with concentrations corresponding to approximately 10, 20, 40, 60, and 80% of full scale and a zero gas containing less than 0.1 ppm CO (see Section 8).
Note: Zero air and calibration gases for CO analyzers should contain about 350 ppm CO_2 to simulate normal ambient concentrations. If synthetic air is used, CO_2 may have to be added.
The calibration gases should be certified to be within ± 2% of the stated value and purchased in high pressure cylinders with inside surfaces of a chromium-molybdenum alloy of low iron content or other appropriate linings. The cylinders should be stored in areas not subject to extreme temperature changes nor exposed to direct sunlight. There are two acceptable methods for obtaining multipoint calibration standard concentrations. They are:

- the use of individual certified standard cylinders of CO for each concentration needed, and
- the use of one certified standard cylinder of CO, diluted as necessary with zero-air, to obtain the various calibration concentrations needed.

The equipment needed for calibration can be purchased commercially, or can be assembled by the user as illustrated in Figure 6. When a calibrator or its components are being purchased, certain factors must be considered:

- traceability of the certified calibration gases to an NIST-SRM (12) or a NIST/EPA-approved commercially available Certified Reference Manual (see Section 8),
- accuracy of the flow-measuring device or devices (rotameter, mass flow meter, bubble meter),
- maximum and minimum flows of dilution air and calibration gases, and
- ease of transporting the calibration equipment from site to site.

9.2.3.3 For an individual cylinder multipoint calibration, assemble the monitor and calibration system as illustrated in Figure 4.

9.2.3.4 Perform a manual zero and span calibration as in Section 9.2.2 and record the adjusted zero and span concentrations and their respective chart values on the Multipoint Calibration Data Sheet, Figure 5.

9.2.3.5 Connect the span gas with a concentration value corresponding to 80% of full scale, to the analyzer system.

9.2.3.6 Open the gas cylinder pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired sample cell pressure.

9.2.3.7 Set the sample flow rate as read by the rotameter (read the widest part of the float) to the value to be used when sampling.

9.2.3.8 Let the span gas flow long enough to establish a stable trace on the strip chart recorder; allow a least 5 minutes. Mark the chart trace as an unadjusted span. Record unadjusted span reading in ppm on the Multipoint Calibration Data Sheet, Figure 5.
Note: No adjustments are made at this point.

9.2.3.9 Disconnect the span gas.

9.2.3.10 Connect zero gas to the analyzer.

9.2.3.11 Open the gas cylinder pressure valve and adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired sample cell pressure.

9.2.3.12 Set the sample flow rate as read by the rotameter to the value that is used when sampling.

9.2.3.13 Let the zero gas flow long enough to establish a stable zero trace on the strip chart recorder; allow at least 5 minutes. Mark the chart trace as an unadjusted zero. Record the unadjusted zero reading in ppm on the Multipoint Calibration Data Sheet, Figure 5.

9.2.3.14 Repeat Section 9.2.3.5 through Section 9.2.3.13 for each of the calibration gases with concentrations corresponding to approximately 60, 40, 20 and 10% of full scale in that order.

9.2.3.15 Fill in the information required on the Multipoint Calibration Data Sheet and construct a calibration curve of analyzer response as percent of chart versus concentration in ppm as illustrated in Figure 7. Draw a best fit, smooth curve passing through zero and minimizing the deviation of the four remaining upscale points from the curve. The calibration curve should have no inflection points, i.e., it should either be a straight line or bowed in one direction only. Curve fitting techniques may be used in constructing the calibration curve by applying appropriate constraints to force the curve through the zero. This procedure becomes quite involved; however, the most frequently used technique is to graph the curve (see Section 9.2.3.28 through Section 9.2.3.30).

9.2.3.16 Recheck any calibration point deviating more than ± 1.0 ppm CO from the smooth calibration curve. If the recheck gives the same results, have the calibration gas reanalyzed. Use the best fit curve as the calibration curve.

9.2.3.17 For a dynamic dilution multipoint calibration, assemble the analyzer and dynamic dilution system as illustrated in Figure 6.

9.2.3.18 Perform a manual zero and span calibration as in Section 9.2.2 and record the adjusted zero and span concentrations and their respective chart values on the Multipoint Calibration Data Sheet, Figure 5.

9.2.3.19 Now produce the zero air flow from the dilution system to the analyzer. The flow must exceed the total demand of the analyzer connected to the output manifold to ensure that no ambient air is pulled into the manifold vent.

Note: In lieu of connecting analyzer to manifold, one may fill Tedlar® bags with generated standards to be sampled by the NDIR.

9.2.3.20 Allow the analyzer to sample the zero air until a stable response is obtained; adjust the analyzer zero control to within ± 0.5 ppm of zero base line; and record the stable zero-air response (% scale) on the Multipoint Calibration Data Sheet.

Note: Offsetting the analyzer zero adjustment to +5% of scale is recommended to facilitate observing negative zero drift. On most analyzers this should be done by offsetting the recorder zero.

9.2.3.21 Determine the 80% of monitor full scale. Example: For an analyzer with an operating range of 0 to 50 ppm, the 80% value would be:

$$0.80 \times 50 = 40 \text{ ppm}$$

9.2.3.22 Adjust the CO flow from the standard CO cylinder to generate a CO concentration of approximately 80% of the monitor full scale. Measure the CO flow, and record on the Multipoint Calibration Data Sheet.

9.2.3.23 Calculate the generated CO standard by the following equation:

$$(CO)_{gen} = [(CO)_{std}(Q_{co})]/[Q_{dil} + Q_{co}]$$

where:
$(CO)_{gen}$ = concentration of CO generated, by dilution, ppm
$(CO)_{std}$ = concentration of NITS-SRM or CRM CO gas standard, ppm
Q_{co} = flow rate of CO standard, L/min
Q_{dil} = flow rate of dilution air, L/min

Note: If wet test meter or bubble meter is used for flow measurement, the vapor pressure of water at the temperature of the meter must be subtracted from the barometric pressure.

Note: If both the CO and the zero-air flow rates are measured with the same type of flow meter (e.g. bubble flow meter, rotameter, mass flow meter, wet test meter, etc.), correction to standard temperature and pressure (STP) is not necessary. However, if this is not the case, then the flows of CO gas and dilution gas must be corrected to STP by the following equation:

$$Q_{co} = (Q_1)\,[(P_{bar}/760)(298/T + 273)]$$

where:
Q_{co} = flow rate of CO standard corrected to STP, L/min
Q_1 = uncorrected flow rate of CO standard, L/min
P_{bar} = barometric pressure, mm Hg
T = temperature of gas being measured, °C

9.2.3.24 Allow the analyzer to sample until the response is stable; adjust the analyzer span until the required response is obtained, and record the CO recorder response on the Multipoint Calibration Data Sheet. After the zero and 80% points have been set, without further adjusting the instrument, generate four approximately evenly spaced points between zero and 80% by increasing the dilution flow (Q_{dil}) or by decreasing the CO flow (Q_{co}). For each concentration generated, calculate the CO concentrations and record the results for each point under the appropriate column on the data sheet.

Note: If substantial adjustments of the span control are necessary, recheck the zero and span adjustments by repeating Section 9.2.2.

9.2.3.25 Fill in the information required on the Multipoint Calibration Data Sheet and construct a calibration curve of analyzer response as percent of chart versus concentration in ppm, as illustrated in Figure 7. Draw a best fit, smooth curve passing through the zero and minimizing the deviation of the remaining upscale points from the curve. The calibration curve should have no inflection points, i.e., it should either be a straight line or bowed in one direction only. Curve fitting techniques may be used in

constructing the calibration curve by applying appropriate constraints to force the curve through the zero. This procedure becomes quite involved; however, the most frequently used technique is to graph the curve.

9.2.3.26 Recheck any calibration point deviating more than $\pm$ 1.0 + 0.02 C_c ppm from the smooth calibration curve. If the recheck gives the same results, have that calibration gas reanalyzed. Use the best fit curve as the calibration curve.

10. Systems Maintenance

10.1 Periodic Maintenance

Proper maintenance is necessary for successful monitor performance. Periodic maintenance should be performed to reduce equipment failure and maintain calibration integrity of the instrument as illustrated in Table 3. Instrument calibration should be checked on a schedule established after the analyzer has operated for a period of time. The sensitivity and linearity should also be checked. These instrument checks should be done at least on an annual basis. However, when any optical component (i.e., detector, cell or source) is changed, the linearity and selectivity of the instrument should be confirmed. The settings of the zero and span controls of instruments which operate continuously should be checked as often as required. A log of these settings and a service and repair log should be kept to assist in evaluating maintenance difficulties. Figure 8 illustrates a monthly maintenance check sheet for a typical NDIR analyzer.

10.2 Routine Maintenance

Regular checks of the instrument and its operation are mandatory. Even though a system may provide excellent quality data initially, without routine maintenance and system checks the quality of the data will degenerate with time. Table 3 provides a routine servicing schedule for a typical NDIR analyzer. Follow all routine maintenance procedures specified in the manufacturer's instruction manual.

10.2.1 Sampling system - The sampling system to which the analyzer is connected must be checked at regular intervals according to a maintenance schedule based on the components used in the specific application. Sampling system maintenance normally includes the following steps:

- checking the entire system for leaks and proper flow rates,
- cleaning and/or renewing sample system components,
- ensuring that calibration cylinders are shut off when not in use,
- ordering filled and assayed cylinders at intervals which include ample lead time to ensure continuous supply of calibration gas,
- checking operation of pumps, recorders, motors, timers and other commercial components by referring to manufacturer's instructions,
- checking and/or cleaning the entire sampling system, including the sample cell in the analyzer, when abnormal sample conditions occur, such as when slugs of water, dirt or oil are introduced, or high temperature or pressure conditions arise.

10.2.2 Daily servicing - Automatic 80% full scale span (40 ppm) and zero precision checks should be performed utilizing the instrument's automatic zero/span standardization feature (if so equipped) and individual secondary standard gases of CO in air with the above concentrations.

10.2.3 Each visit servicing - Verify that the zero and span potentiometer settings are at the proper position. Likewise, verify that the sample cell flow is reading correctly and at the proper setting. Plot the daily zero, precision check, and span values on their respective days on the Maintenance Check Sheet. If any of the zero and span values exceed 5% of stated value, perform a manual zero and span check and adjust the analyzer to the correct zero and span values using the front panel zero and span potentiometer, respectively. If there is insufficient range in the span potentiometer, a multipoint calibration must be performed. Record the adjusted ppm values and zero and span potentiometer settings on the monthly Maintenance Check Sheet (see Figure 8).

10.2.4 Weekly servicing - At least once per week replace the Teflon® sample inlet particulate filter. Note the filter cleanliness and vary the replacement frequency accordingly. Change the filter even if only a slight particulate coating or discoloration is visible. Perform a leak check weekly and whenever the loosening or tightening of a fitting is involved in maintenance procedures. Using an individual cylinder, introduce a 20% of full scale (10 ppm) intermediate span gas at ambient pressure upstream of the sample pump as a precision check. Maintain the same excess flow each time the manual precision check is performed. The manual precision check should be within 10% of value. If not, investigate the cause and initiate repairs.

10.2.5 Monthly servicing - Inspect the water trap filter for particulate loading and replace if necessary. Note the filter cleanliness and adjust the replacement frequency accordingly. Check the span gas solenoid valve for leakage. Replace valve if necessary. Record the results and the date of the check on the Monthly Maintenance Check Sheet. An analyzer multipoint calibration should be performed monthly.

10.2.6 Quarterly servicing - Inspect and clean the filters downstream of the sample and reference flow meters. Note the filter cleanliness and adjust the cleaning frequency accordingly.

10.2.7 Semi-annual servicing - Perform an electronic bias adjustment utilizing the procedures outlined in the manufacturer's instruction manual. Perform a source balance adjustment utilizing the procedures outlined in the manufacturer's instruction manual.

10.2.8 Cell walls and windows - Inspect cell walls and windows for cleanliness and clean if necessary utilizing the procedures outlined in the manufacturer's instruction manual. Do not clean with cloth or paper towel; cleaning should be performed using distilled water followed by isopropyl alcohol and air drying.

10.3 Preventive Maintenance

The preventive maintenance section of the manufacturer's instruction manual of the NDIR monitoring system should contain a trouble shooting guide and diagnostic chart to assist operators in identifying and correcting instrument problems.

10.4 Troubleshooting the Analyzer

10.4.1 The manufacturer's instruction manual generally contains troubleshooting guidelines that cover most troubles which may occur. Table 4 illustrates typical NDIR monitor problems as outlined in a manufacturer's instruction manual.

10.4.2 The troubleshooting guidelines should be used only after the analyzer cannot be calibrated or aligned according to manufacturers' specifications or cannot be operated properly.

10.4.3 If the recording instrument indicates an incorrect value when a sample which contains a low concentration of the component of interest is measured, check the alignment and calibration of the analyzer for optical balance. If the meter does not deflect upscale when span gas is passed through the analyzer and the power indicator is on, check the output circuit. If the power indicator is off, check the power connections. If these or other problems cannot be located or corrected using the specified guidelines, contact the manufacturer for assistance.

11. 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.

11.1 Standard Operating Procedures (SOPs)

11.1.1 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.

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

11.2 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 and operation procedures in Section 9.2, and maintenance procedures in Section 10.3 of this method and the manufacturer's instruction manual should be followed and included in the QA program, as outlined in Table 5. Additional QA measures (e.g., trouble shooting) as well as further guidance in maintaining the sampling system should be provided by the manufacturer.

11.2.1 Precision Check

11.2.1.1 A periodic precision check is used to assess the quality of the data. A one-point check on the analyzer is carried out at least once every 2 weeks at a CO concentration between 8 and 10 ppm.

11.2.1.2 The analyzer must be operated in its normal sampling mode, and the precision test gas must pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling. The standards from which the precision check test concentrations are obtained must be traceable to a NITS-SRM or a commercially available CRM; the same standards used for calibration may be used for the precision check. They must conform to specifications outlined in Section 8.1 and Section 8.2.

Note: All gas standards used for precision or daily zero and span check should contain about 350 ppm CO_2 to simulate normal ambient concentrations.

11.2.1.3 Connect the analyzer's sample inlet line to a precision gas source that has a concentration between 8 and 10 ppm CO and that is traceable to a NITS-SRM or a CRM as illustrated in Section 9.2.3 and Figure 4. If a precision check is made in conjunction with a zero/span check, it must be made prior to any zero and span adjustments.

11.2.1.4 Allow the analyzer to sample the precision gas for a least 5 min or until a stable recorder trace is obtained.

11.2.1.5 Record this value on the Monthly Maintenance Check Sheet and mark the chart as "unadjusted" precision check.

11.2.1.6 The expected response of the NDIR analyzer should be within 10% of the precision calibration gas standard.

11.2.2 Performance Audit

11.2.2.1 An audit is an independent assessment of the accuracy of data generated by an analyzer.

11.2.2.2 Independence is achieved by having the audit performed by an operator other than the one conducting the routine field measurements and by using audit standards, reference materials, and equipment different from those routinely used in monitoring.

11.2.2.3 The audit should be an assessment of the measurement process under normal operations, that is, without any special preparation or adjustment of the system. Routine quality assurance checks conducted by the operator are necessary for obtaining and reporting good quality data, but they are not to be considered part of the auditing procedure.

11.2.2.4 Proper implementation of an auditing program will ensure the integrity of the data and assess the accuracy of the data.

11.2.2.5 A performance audit consists of challenging the continuous analyzer with known concentrations of CO within the measurement range of the analyzer. Known concentrations of CO can be generated by using individual cylinders for each concentration (see Section 9.2.3.3) or by using one cylinder of a high CO concentration and diluting it to the desired levels with zero-air (see Section 9.2.3.17). In either case, the gases used must by traceable to a NITS-SRM or a commercially available CRM and contain about 350 ppm CO_2 to simulate normal ambient concentrations.

11.2.2.6 A dynamic dilution system must be capable of measuring and controlling flow rates to within ± 2% of the required flow. Flow meters must be calibrated under the conditions of use against a reliable standard such as a soap bubble meter or a wet test meter; all volumetric flow rates should be corrected to STP at 25°C (77°F) and 760 mm Hg (29.92 in Hg); but if both the CO and the zero air flow rates are measured with the same type device at the same temperature and pressure, the STP correction factor in the audit equations can be disregarded.

11.2.2.7 The analyzer should be challenged with at least one audit gas of known concentration from each of the following concentrations within the measurement range of the analyzer being audited:

Audit Point	CO Concentration Range, ppm
1	3 to 7
2	8 to 12
3	18 to 22
4	28 to 32
5	33 to 42

The difference in CO concentration (ppm) between the audit value and the measured value is used to calculate the accuracy of the analyzer.

11.2.2.8 All measurements of audit concentrations should fall within ± 10% of the audit value.

12. 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.

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11. List of Designated Reference and Equivalent Methods, U.S. Environmental Protection Agency, Office of Research and Development, Atmospheric Research and Exposure Assessment Laboratory (AREAL), Research Triangle Park, NC, 27711, April, 1988.

12. National Institute of Standards and Technology (NIST) Catalog of Standard Reference Materials, NIST Special Publication, 1989 Edition, NIST, Gaithersburg, MD.

13. *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II - Ambient Air Specific Methods* - Section 2.0.7, U.S. Environmental Protection Agency, Quality Assurance Division, Research Triangle Park, NC, 27711, EPA-600/4-77-0272, May, 1987.

Table 1. Commercially Available NDIR CO Analyzers Designated by U.S. EPA as References Methods and Other Commercially Available CO and CO_2 Analyzers

Identification	Manufacturer	Fed. Register Notice Vol.	Page	Date
Bendix or Combustion Engineering Model 8501-5CA Infrared CO Analyzer, operated on the 0-50 ppm range and with a time constant setting between 5 and 16 seconds.	Combustion Engineering, Inc. Process Analytics P.O. Box 831 Lewisburg, WV 24901	41	7450	2/18/76
Beckman Model 866 Ambient CO Monitoring System, consisting of the following components: Pump/Sample-Handling Module, Gas Control Panel, Model 865-17 Analyzer Unit, Automatic Zero/Span Standardizer; operated with a 0-50 ppm range, a 13 second electronic response time.	Beckman Instruments, Inc. Process Instruments Div. 2500 Harbor Boulevard Fullerton, CA 92634	41	36245	8/27/76
LIRA Model 202A Air Quality Carbon Monoxide Analyzer System, consisting of a LIRA Model 202S optical bench (P/N 459839), a regenerative dryer (P/N 464084), and rack-mounted sampling system; operated on a 0-50 ppm range, with the slow response amplifier.	Mine Safety Appliances Co. 600 Penn Center Blvd. Pittsburgh, PA 15208	42	5748	1/31/77
Horiba Models AQM-10, AQM-11, and AQM-12 Ambient CO Monitoring Systems, operated on the 0-50 ppm range, with a response time setting of 15.5 seconds.	Horiba Instruments, Inc. 1021 Duryea Ave. Irvine Industrial Complex Irvine, CA 92714	43	58429	12/14/78
Monitor Labs Model 8310 CO Analyzer, operated on the 0-50 ppm range, with a sample inlet filter.	Monitor Labs, Inc. 10180 Scripps Ranch Blvd. San Diego, CA 92131	44 45	54545 2700	9/20/79 1/14/80

Table 1. Commercially Available NDIR CO Analyzers Designated by U.S. EPA as References Methods and Other Commerically Available CO and CO_2 Analyzers (Cont'd)

Identification	Manufacturer	Fed. Register Notice Vol.	Page	Date
Horiba Model APMA-300 Ambient Carbon Monoxide Monitoring System, operated on the 0-20/ 50/100 ppm range with a time constant switch setting of #5. The monitoring system may be operated at temperatures between 10-40°C.	Horiba Instruments, Inc. 1021 Duryea Ave. Irvine Industrial Complex Irvine, CA 92714	45	72774	11/03/80

Other Commercially Available NDIR CO Analyzers

Model #	Manufacturer	Portability
Gas Analyzer Model RI-550A	CEA Instruments Box 303 Emerson, NJ 07630 (201)967-5660	Portable

Commercially Available NDIR CO_2 Analyzers

Model #	Manufacturer	Portability
Gas Analyzer Model 8000	Automated Custom Sys., Inc. 1238 West Grove Ave. Orange, CA 92665 (714)974-5560	Stationary
Gas Analyzer Model RI-411A	CEA Instruments Box 303 Emerson, NJ 07630 (201)967-5660	Portable
Closed Room Monitor Model 4776	Gastech, Inc. 8445 Central Ave. Newark, CA 94560 (415)794-6200	Portable
Gas Analyzer Model APBA-210	Horiba Instruments 1021 Duryea Ave. Irvine Industrial Complex Irvine, CA 92714 (800)556-7422	Portable

Table 1. Commercially Available NDIR CO Analyzers Designated by U.S. EPA as References Methods and Other Commerically Available CO and CO_2 Analyzers (Cont'd)

Commercially Available NDIR CO_2 Analyzers (Cont'd)

Model #	Manufacturer	Portability
LIRA 3200	MSA Instrument Div. Box 427 Pittsburgh, PA 15230 (800)672-4678	Stationary

Table 2. Suggested Performance Specifications for NDIR CO Analyzers

Analyzer Parameter	Specification
Range (minimum)	0-50 ppm (0-58 mg/m^3)
Lower detection limit (LDL)	1.0 ppm (0.6 mg/m^3)
Lag time (maximum)	20 seconds
Rise time, (95% maximum)	15 minutes
Fall time, (95% maximum)	15 minutes
Zero drift (maximum)	± 1% per day and ± 2% per 3 days
Span drift (maximum)	± 1% per day and ± 2% per 3 days
Precision (maximum)	± 0.5%
Operational period (maximum)	3 days
Noise (maximum)	± 0.5%
Interference equivalent (maximum)	1% of full scale
Operating temperature range	5-40°C
Operating temperature fluctuation	± 5%
Linearity (maximum)	1%
Operating humidity range (maximum)	10-100%

Table 3. Typical NDIR Carbon Monoxide/Carbon Dioxide Analyzer Routine Servicing Schedule

Service	Frequency
Zero/span/precision checks	Daily
Zero/span/potentiometer settings	Daily
Range position checks	Each Visit
Sample & reference flow check	Each Visit
Replace sample inlet particulate filter	Weekly
Leak check system	Weekly
Manual precision check	Weekly
Inspect water removal system	Monthly
Inspect span gas solenoid valve	Monthly
Multipoint calibration	Monthly
Clean sample/reference filters	Quarterly
Electronic bias adjustment	Semi-Annually
Source balance adjustment	Semi-Annually
Cell wall & window inspection	Annually
CO_2 interference test	Annually
H_2O interference	Annually

Table 4. Typical NDIR Monitor Problems

Observation	Possible Cause	Diagnostic Check
CO level too low	Reference infrared source source failing	Run span gas check
	Sample lines clogged	Check with flow meter
	Decreased pressure in sample compartment of detector	Check after inspection of infrared source
	Vacuum pump failure	Inspect pump
	Amplifier failing	Completely check-out electronics system
CO level too high	Sample infrared source failing	Run span gas check
	Sample cell optics dirty	Inspect and clean if necessary
	Decreased pressure in reference compartment of detector	Run span gas check after inspection of infrared source
	Amplifier failing	Completely check-out electronics system
Abnormal positive zero drift	Moisture elimination devices inoperative	Recharge silica gel; check refrigeration unit
	Dirty optical surfaces	Clean cells as necessary; check particulate filter
	Amplifier failing	Check-out electronics system completely
		Run span check

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Table 5. QA/QC Operational Parameters

QA/QC Parameters	Actions
Calibration gas on concentration	Measurement of control samples as part of the auditing program.
Data processing errors	Data processing checks performed as a part of the auditing program.
Zero drift	Zero check and adjustment before each sampling period as part of routine operating procedure.
Span drift	Span check and adjustment before each sampling period as part of routine operating procedure.
System noise	Check of strip chart record trace for signs of noise after each sampling period as part of routine operating procedure.
Sample cell pressure variation	Reading and recording sample cell pressure at the beginning and end of a sampling period as part of routine operating procedure.
Temperature variation	Minimum-maximum thermometer placed near the analyzer, or any other temperature-indicating device, read periodically throughout the sampling period. This would usually be done as a special check.
Voltage variation	A.C. voltmeter measuring the voltage to the analyzer and read periodically throughout the sampling period. This would usually be done as a special check.

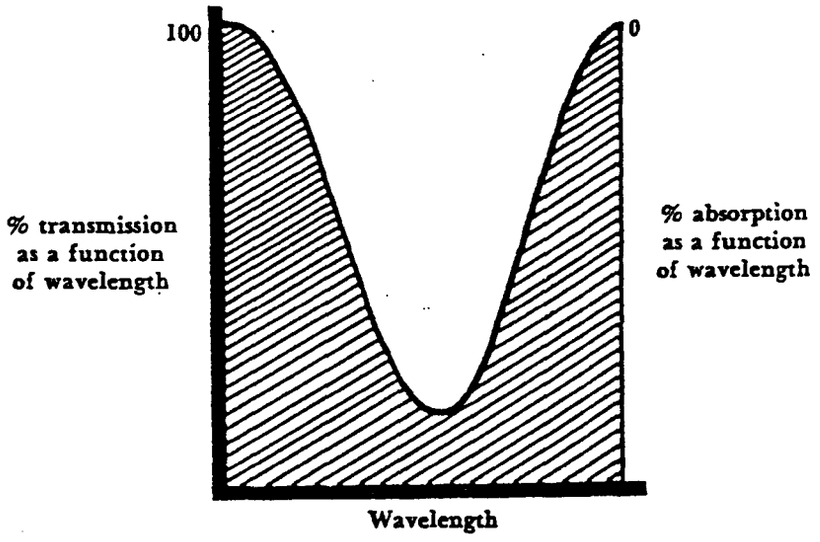

Figure 1A. Typical Absorption Curve in the IR

Gas	Location of band centers (μm)	Wave number (cm^{-1})
NO	5.0-5.5	1800-2000
NO_2	5.5-20	500-1800
SO_2	8-14	700-1250
H_2O	3.1	1000-1400
	5.0-5.5	1800-2000
	7.1-10	5200
CO	2.3	2200
	4.6	4500
CO_2	2.7	850-1250
	5.2	1900
	8-12	5700
NH_3	10.5	950
CH_4	3.3	1500
	7.7	5000
Aldehyde	3.4-3.9	2550-2950

Figure 1B. Infrared Band Centers of Some Common Gases

Figure 1. Typical Absorption Curve (Figure 1A) in the IR and Infrared Band Centers (Figure 1B) of Some Common Gases

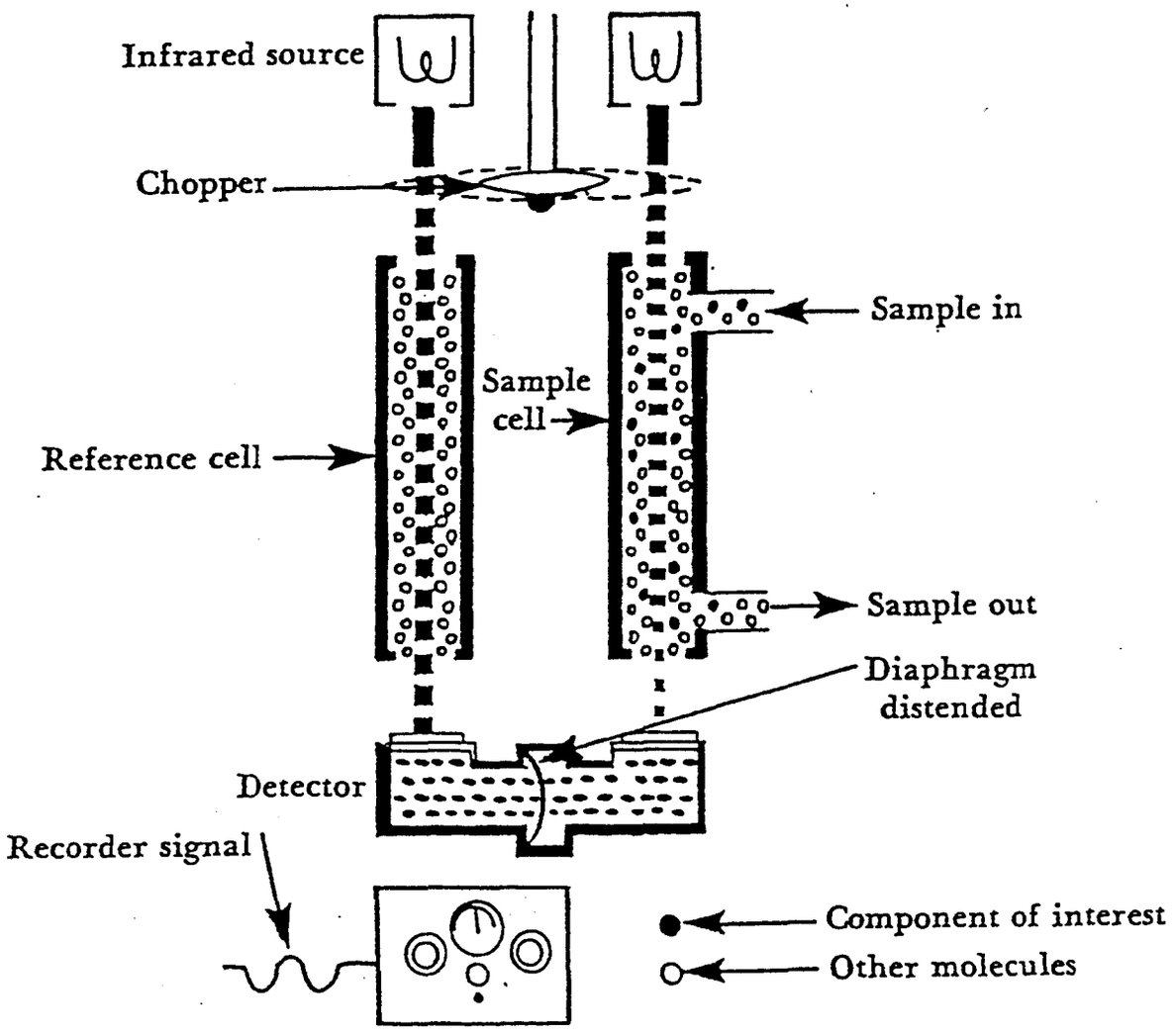

Figure 2. Major Components of a Commercially Available NDIR Instrument

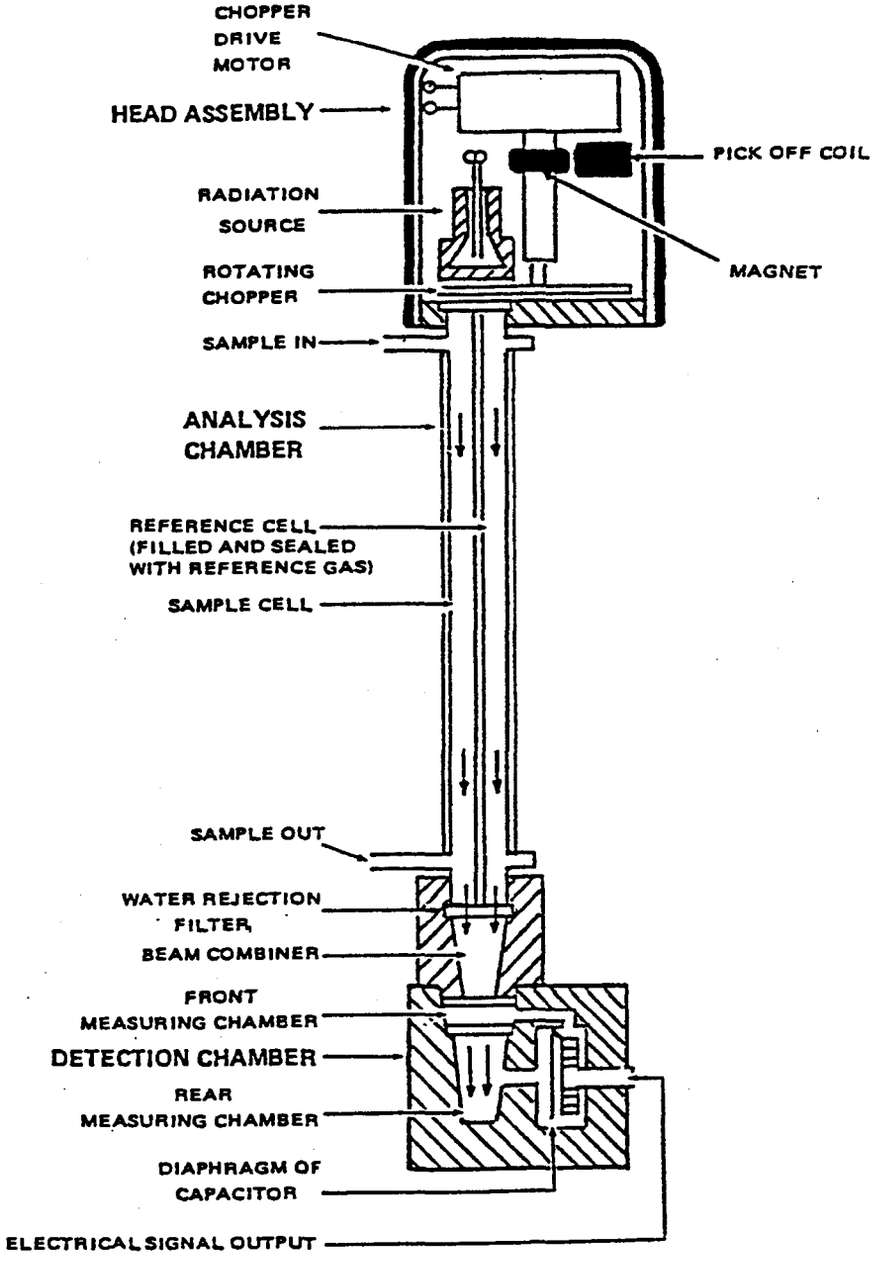

Figure 3. Front/Rear Chamber Detector Design

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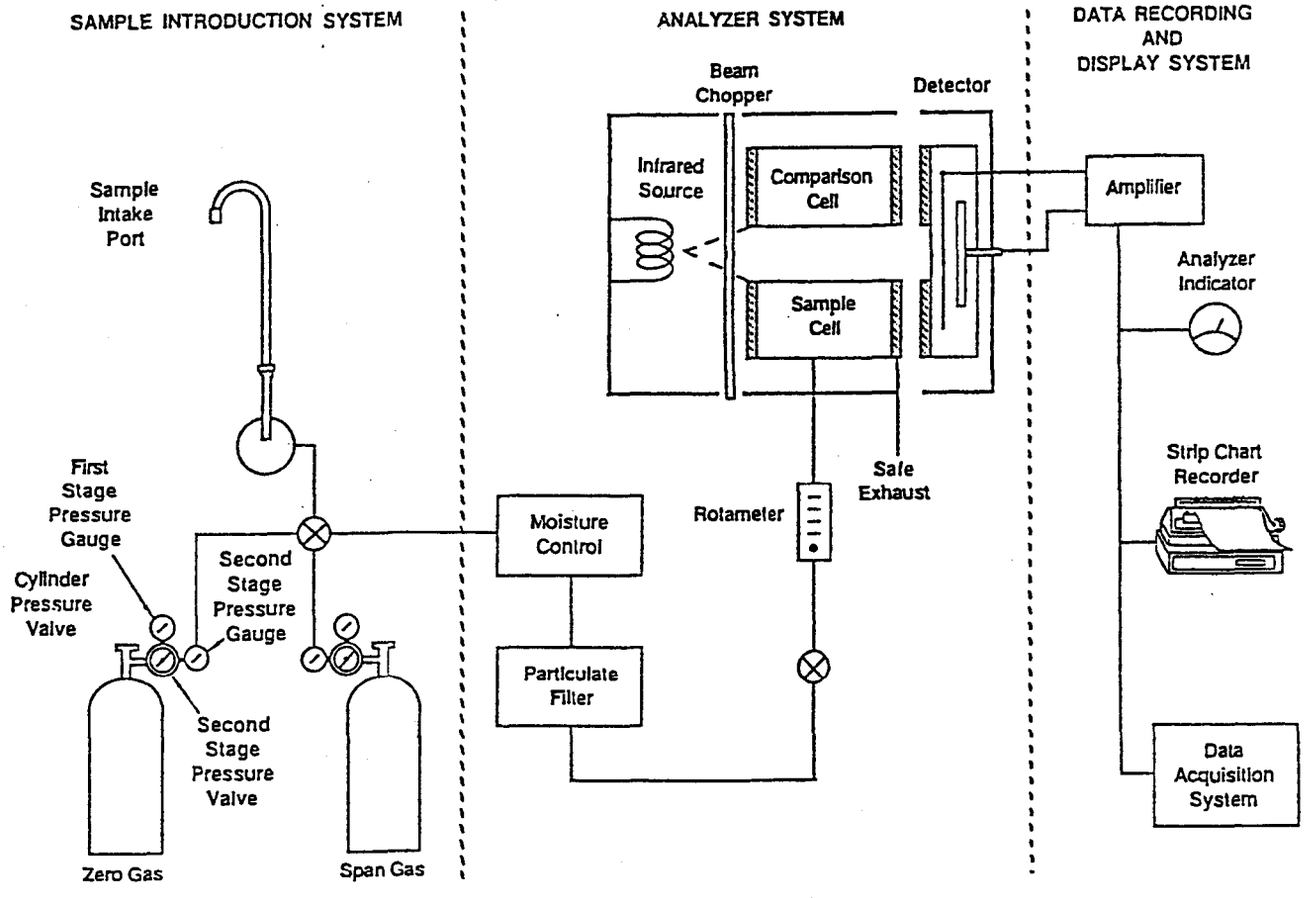

Figure 4. NDIR Calibration and Detector System

ADJUSTED ZERO AND SPAN VALUES			ANALYZER CALIBRATED
	% CHART	PPM	
ADJ. ZERO			LOCATION _____
ADJ. SPAN			S/N _____ SITE NO. _____
			DATE _____
TEMP. _____ °C	PRESS _____ "Hg		DATE LAST CALIBRATED _____
RANGE _____	TIME CONSTANT _____		

INPUT		ANALYZER RESPONSE	
ppm	% CHART	%CHART	ppm

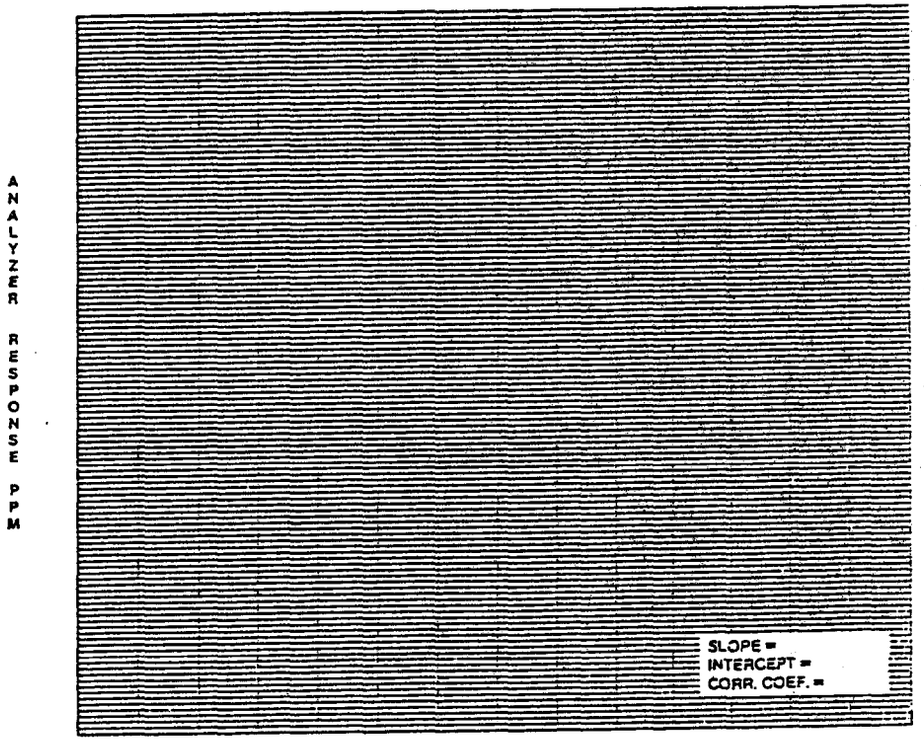

Figure 5. Multipoint Calibration Data Sheet

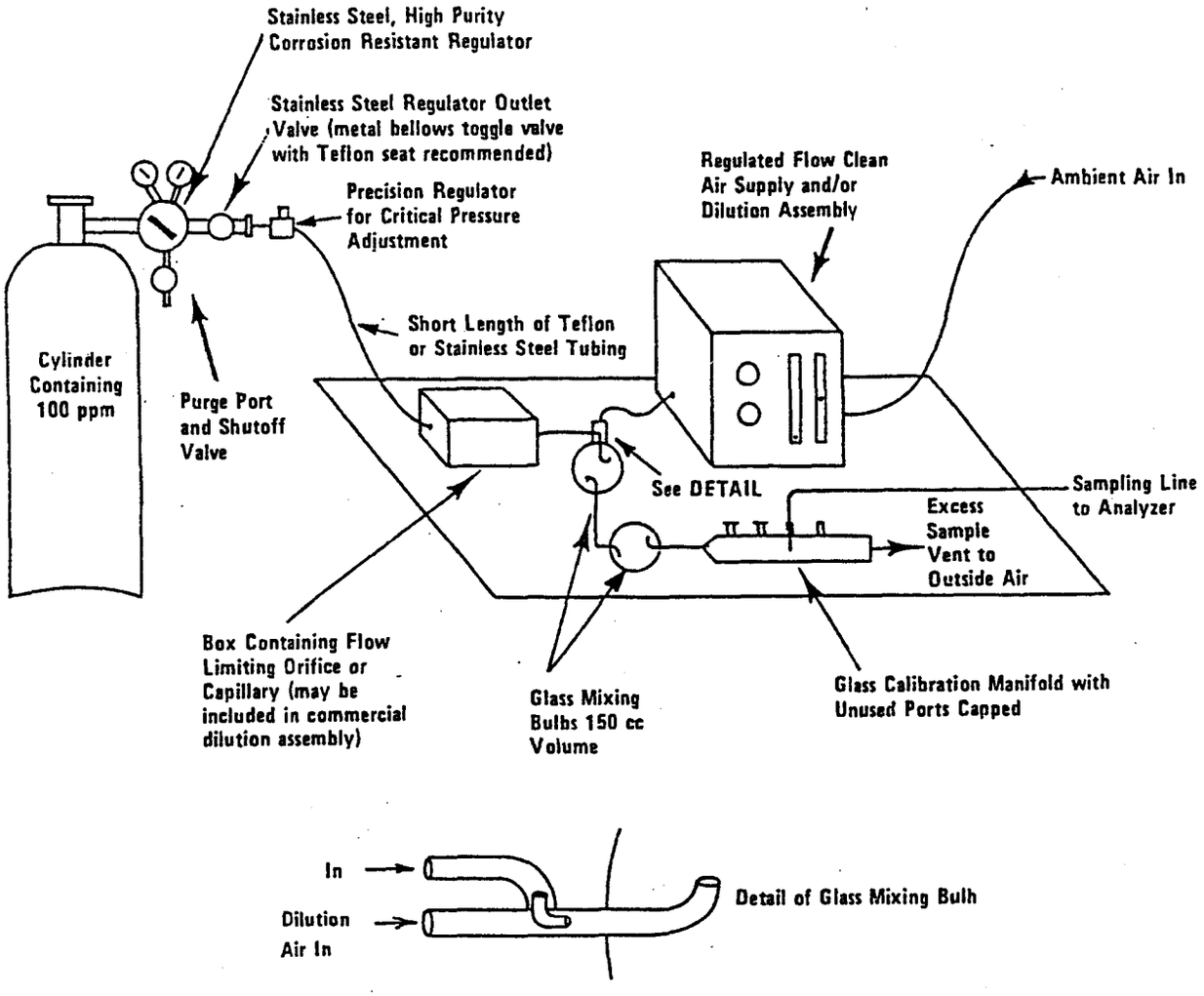

Figure 6. Assembly for Dilution of CO from Cylinder for Use in Calibration or Span Check

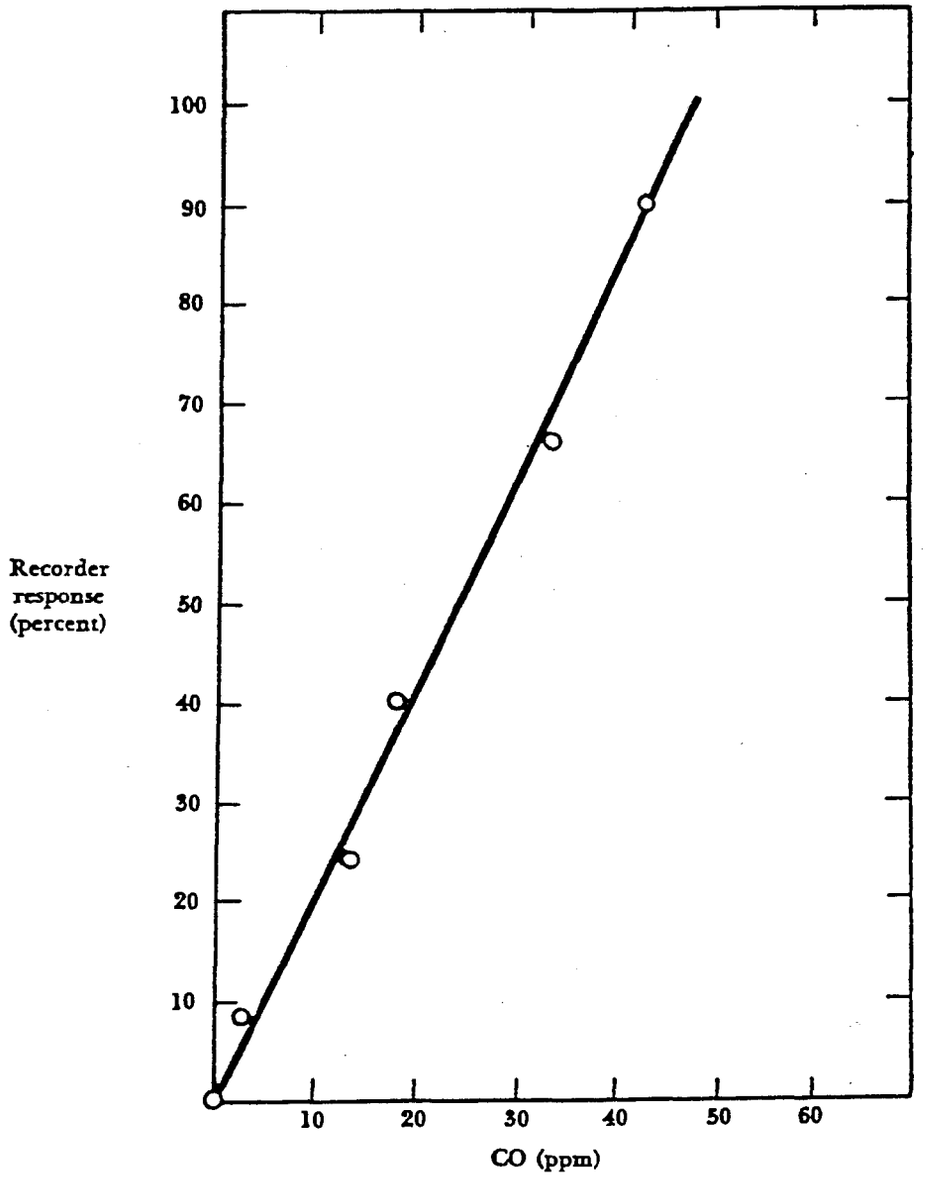

Figure 7. NDIR Calibration Curve

Monthly Maintenance Check List

SITE NUMBER _____ TECHNICIAN _____

ANALYZER S/N _____

DATE	READING: DIAL/CHART (ppm)				FLOW SETTING					CYL PRESSURE	
	ZERO		SPAN		SAMPLE		REFERENCE		PARTIC-ULATE FILTER	ZERO	SPAN
	UNADJ.	ADJ.	UNADJ.	ADJ.	UNADJ.	ADJ.	UNADJ.	ADJ		#	#

OPERATOR INSTRUCTIONS:

1. DAILY: ZERO/SPAN/PRECISION CHECK
2. EACH VISIT: CHECK FLOW SETTING;
   CHART TRACE
3. WEEKLY: REPLACE PARTICULATE FILTER;
4. MONTHLY: INSPECT WATER TRAP FILTER;
   INSPECT SPAN GAS SOLENOID VALVE - DATE LAST CHECKED _____
   ZERO AIR _____ ZERO AIR WITH SPAN GAS _____
5. QUARTERLY: CLEAN SAMPLE/REFERENCE FILTERS; MULTI POINT CALIBRATION.
   SPAN GAS TO SPAN GAS INLET _____ SPAN GAS TO SAMPLE INLET _____
6. SEMI-ANNUALLY: ELECTRONIC BIAS ADJUSTMENT - DATE LAST CHECKED _____
   SOURCE BALANCE ADJUSTMENT - DATE LAST CHECKED _____
7. ANNUAL: INSPECT CELL WALLS AND WINDOWS - DATE LAST CHECKED _____
   CO_2 INTERFERENCE TEST - DATE LAST CONDUCTED _____
   H_2O INTERFERENCE TEST - DATE LAST CONDUCTED _____

DATE	COMMENTS OR MAINTENANCE PERFORMED

Figure 8. Monthly Maintenance Check Sheet

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Method IP-3B

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO_2) IN INDOOR AIR USING GAS FILTER CORRELATION (GFC)

Method IP-3B

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO_2) IN INDOOR AIR USING GAS FILTER CORRELATION

1. Scope

This document describes a procedure for determination of CO and CO_2 concentrations in indoor air using gas filter correlation (GFC). This procedure provides automatic and continuous measurement of CO and CO_2 in indoor atmospheres. Analyzers employing the GFC measurement principle rely on the properties of CO and CO_2 to absorb infrared energy at distinctive wavelengths (i.e., 4.7 μ and 2.0 μ, respectively).

2. Applicable Documents

2.1 ASTM Standards

D1356 Definition of Terms Relating to Atmospheric Sampling and Analysis
D1357 Recommended Practice for Planning the Sampling of the Atmosphere
D3195 Recommended Practice for Rotameter Calibration
D1914 Recommended Practice for Conversion Units and Factors Relating to Atmosphere Analysis
D3249 Recommended Practice for General Ambient Air Analyzer Procedures
E1 Specification for ASTM Thermometers
E180 Recommended Practice for Development of Precision Data for ASTM Methods for Analysis and Testing of Industrial Chemicals

2.2 Other Documents

Laboratory and Indoor/Ambient Air Studies (1-10)
U.S. Environmental Protection Agency Technical Assistance Document (11)

3. Summary of Method

3.1 GFC spectrometry is based upon comparison of the detailed structure of the infrared absorption spectrum of the measured gas to that of other gases also present in the sample being analyzed. The technique is implemented by using a high concentration sample of the measured gas, i.e., CO and CO_2, as a filter for the infrared radiation transmitted through the analyzer, hence the term GFC.

3.2 The basic components of the GFC CO/CO_2 spectrometer are shown in Figure 1. Radiation from an IR source is chopped and then passed through a gas filter alternating between CO and N_2 due to rotation of the filter wheel. The radiation then passes through a narrow bandpass interference filter and enters a multiple optical pass cell where absorption by the sample gas occurs. The IR radiation then exits the sample cell and falls on an IR detector.

3.3 The CO/CO_2 gas filter acts to produce a reference beam which cannot be further attenuated by CO and CO_2 in the sample cell. The N_2 side of the filter wheel is transparent to the IR radiation and therefore produces a measure beam which can be

absorbed by CO and CO_2 in the cell. The chopped detector signal is modulated by the alternation between the two gas filters with an amplitude proportional to the concentration of CO and CO_2 in the sample cell. Other gases do not cause modulation of the detector signal since they absorb the reference and measure beams equally. Thus the GFC system responds specifically to CO and CO_2.

3.4 With the improved rejection of interferences afforded by the GFC technique, it is possible to increase the sensitivity of the analyzer. This is achieved by the multiple pass optics (white cell) used in the sample cell which leads to a large path length, and thus an improved sensitivity, in a small physical space. This allows full scale sensitivity down to 1 ppm CO with a lower detectable limit (LDL) of 0.020 ppm CO to be achieved.

4. Significance

4.1 The GFC method of measuring CO/CO_2 offers improved specificity and sensitivity over conventional NDIR techniques. The GFC analyzers provide a wide dynamic range with a reported sensitivity of 0.1 ppm CO. This technique employs the reference principle and affords the lower sensitivities needed for indoor air monitoring.

4.2 There are several GFC analyzers available for measuring CO or CO_2. The GFC analyzer described in this method is the Thermo Environmental Corp. (TECO) model 48 GFC CO Analyzer, (Thermo Environmental Corp., Instruments Division, 108 S. Street, Hopkinton, MA 01748). This analyzer meets the specifications as outlined in Table 1. The specific information is provided as guidance to be referred to in addition to specific model users manuals.

5. Definitions

Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with applicable ASTM procedures. 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.

6. Interferences

6.1 The microcomputer circuitry upon which the GFC analyzer described herein (Thermo Environmental Corp., Model 48 GFC CO Analyzer) is based eliminates many disadvantages inherent in analog systems and provides for increased stability, accuracy, and flexibility. Digital computations are insensitive to drift with time or temperature, therefore sources of instrument drift or error due to the electronics are minimized.

6.2 Because infrared absorption is a non-linear measurement technique, it is necessary for the instrument electronics to transform the basic analyzer signal into a linear output. In instruments employing analog electronics, this is accomplished with an additional circuit which generates a function approximating the basic analyzer's calibration curve over a limited range of gas concentrations. With the analyzer, approximations are not necessary since the exact calibration curve is stored in the computer's memory and is used to

accurately linearize the instrument output over any desired range. The analyzer is linearized in this way up to a CO concentration of 1000 ppm.

6.3 The analyzer is designed to perform a variety of tasks by using appropriate information stored in the instrument's program memory. For example, the microcomputer is used to process signals from both a pressure and temperature transducer to make corrections to the instrument output, resulting in concentration measurements which are unaffected by changes in the temperature or pressure of the gas being sampled.

7. Apparatus

7.1 Commercially available GFC CO analyzer - For measurement of CO, the analyzer should be EPA reference or equivalent monitor using GFC and provide a continuous CO monitoring system equipped with IR source, sample and reference gas cells, detector, adequate power supply, amplifier/control unit, meter, and recording system. The analyzer must meet or exceed manufacturer's specifications. See Table 2 for a listing of commercially available GFC CO analyzers. The listing is an excerpt from U.S. EPA's list of designated Reference and Equivalent Methods.

7.2 Commercially available GFC CO_2 analyzer - Analyzer should provide a continuous CO_2 monitoring system equipped with IR source, sample and reference gas cells, detector, adequate power supply, amplifier/control unit, meter, and recording system. The analyzer must meet or exceed manufacturer's specifications. Table 2 also includes commercially available GFC CO_2 analyzers.

7.3 Teflon® particulate filter - 5-10 μm pore size, 2" diameter Teflon® element.

7.4 Flowmeters and controllers - In order to obtain an accurate dilution ratio, in the dilution method used for calibration, the flow rates must be regulated to 1%, and be measured to an accuracy of at least 2%. The meter and controller can be two separate devices, or combined in one device. The users manual for the meter should be consulted for calibration information. Additional information on the calibration of flow devices can be found in the Quality Assurance Handbook (1). It should be noted that all flows should be corrected to 25° C and 760 mm Hg, and that care should be exercised in correcting for water vapor content.

7.5 Mixing chambers - A chamber constructed of glass, Teflon®, or other nonreactive material, and designed to provide thorough mixing of CO or CO_2 and diluent air for the dilution method.

7.6 Output manifold - The output manifold should be constructed of glass, Teflon®, or other nonreactive material, and should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent indoor air from entering the manifold.

8. Reagents and Materials

8.1 CO or CO_2 concentration standard - Cylinder of CO or CO_2 (depending on monitoring needs) in air containing an appropriate concentration of CO or CO_2 suitable for the selected operating range of the analyzer under calibration. The assay of the cylinder must be traceable either to a National Bureau of Standards (NBS) CO or CO_2 in Air Standard Reference Material (SRM) or an NBS/EPA approved gas manufacturer's Certified Reference Material (CRM). A recommended protocol for certifying CO or CO_2 gas cylinders against a CO or CO_2 SRM or CRM is given in the Quality Assurance Handbook (1). The gas cylinder should be recertified on a regular basis (best source).

8.2 Dilution gas (zero air) - Air, free of contaminants which will cause a detectable response on the CO or CO_2 analyzers. The zero air should contain <0.1 ppm CO/CO_2 (best source). Since the analyzer is virtually interference free, it is only necessary to insure that CO/CO_2 has been removed. It should be noted that zero air as supplied in cylinders from commercial suppliers typically contains CO/CO_2 concentrations in the 0.1 - 0.3 ppm range. Thus, cylinder air should be scrubbed of the residual CO/CO_2 prior to its use in the analyzer as a dilution gas or a zero standard. Room air which has been scrubbed of CO/CO_2 can be used as the zero air source. It is not necessary to remove SO_2, NO, NO_2, CO_2, water vapor, or hydrocarbons, since the analyzer does not respond to these molecules. If water vapor is not removed, it might be necessary to correct the flow measurement data when calculating the dilution ratio of the span CO/CO_2 reference. (A platinum on alumina catalyst, operated at 250°C, has been found to be a convenient oxidizer to convert CO to CO_2. If it is desired to remove water vapor, SO_2, etc., a photolytic ozone generator can be used to convert NO to NO_2. This can be followed by a heatless air drier to remove water vapor, NO_2, SO_2, hydrocarbons, and ozone. The oxidizer should then be used to remove the CO. An alternative to the heatless air drier could be Perma-Pure® Drier, followed by silica gel, followed by activated charcoal. It has also been reported that a substance sold as Purafil is successful in removing NO, and can be substituted for the ozonator.)

8.3 Pressure regulators for CO/CO_2 standard cylinders - The regulator used must have a nonreactive diaphragm and internal parts, as well as a suitable delivery pressure, best source.

8.4 Sampling line - Teflon®, borosilicate glass or similar tubing with an O.D. of 1/4" and a minimum I.D. of 1/8" is required for all sampling lines, best source.

9. Systems Maintenance

This chapter describes the periodic maintenance procedures that should be performed on the analyzer to ensure proper, uninterrupted operation. Certain components such as the sample pump, solenoid valves, and source have a limited life and should be checked on a regular calendar basis and replaced if necessary. Other operations, such as cleaning the optics and checking the calibration of the pressure and temperature transducers should also be performed on a regular basis. What follows is a check and/or cleaning procedure for

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these elements. Replacement procedures for components found to be defective by these checks are given in the manufacturer's instruction manual.

9.1 Cleaning the Optics

Best results will be obtained if the optics are cleaned prior to recalibration. The cleanliness of the mirrors should also be checked any time the Test INT intensity frequencies give a result less than 10,000 Hz, since one source of low output is light attenuation due to dirt on the mirrors. The procedure for cleaning the mirrors is outlined here.

9.1.1 Turn off power and disconnect power line.

9.1.2 Remove field mirror, (the field mirror is the rear mirror), by removing the four allen head screws holding it to the main bench (use a 9/64 allen wrench). Remove the relay mirror (the relay mirror is the front mirror, accessible through the front door), by removing the three allen head screws holding it to the main bench (use a 9/64 allen wrench).

9.1.3 Carefully clean each mirror using a "Q-tip" and methanol. Rinse with distilled or ionized water. Dry by blowing clean dry air over the mirror.

9.1.4 Reassemble following the above procedure in reverse. It is not necessary to realign any mirror following cleaning.

9.1.5 Calibrate following the procedure of Section 10.

9.2 Source Replacement

The source control system of the analyzer has been designed to operate the wire wound resister source conservatively in order to increase its life. Nevertheless, the source does have a finite life. Since the source is relatively inexpensive and easily replaced, it is recommended that the source be replaced after one (1) year of continuous use. This will prevent loss of data due to source failure. If a source is to be replaced on an "as needed" basis, it should be replaced when any one of the following conditions occurs.

9.2.1 The source should be replaced if there is no light output.

9.2.2 The source should be replaced if after cleaning the optics, the Test INT (intensity) frequencies remain below 10,000 Hz.

Note: Since the analyzer is a ratio instrument, and since replacing the sources does not affect the calibration, it is not necessary to recalibrate the analyzer every time the source is replaced.

9.3 Detector Frequencies

The analyzer measures intensity ratios and not absolute values. Therefore a large range of detector output frequencies are acceptable for proper operation of the instrument. The nominal values are between 10,000 and 30,000 Hz. These frequencies can be monitored by energizing the Test INT pushbutton. Degradation of detector frequencies below the acceptable range indicates either a dirty mirror or a weak source. If cleaning the mirrors does not increase the detector frequencies to their proper range, replace the source.

9.4 Pressure Transducer

By energizing the Test P/T (pressure/temperature) pushbutton, the LED display will show the pressure in mm Hg as determined by the pressure transducer. The pressure transducer has a zero and span adjust. The zero can be adjusted by disconnecting the tubing from the pressure transducer and connecting a vacuum pump known to produce a vacuum less than 1 mm Hg. The zero potentiometer is then adjusted for a reading of zero mm Hg. If the pump is then disconnected, but the transducer not connected to the bench, the display should read the current local barometric pressure. If this valve does not agree with a known accurate barometer, adjust the span potentiometer. Note that if the expected pressure changes are small (i.e., the only changes expected are barometric weather changes and not altitude changes) an error in the zero setting will not introduce a measurable error if the span is adjusted correctly. Thus if only a barometer is available, and not a vacuum pump, only adjust the span. If a barometer is not available, a rough check could be made as follows. Obtain the current barometric pressure from the local weather station or airport. Since these pressures are usually reported corrected to sea level, it might be necessary to correct to local pressure by subtracting .027 mm Hg per foot of altitude. Do not try to calibrate the pressure transducer unless the pressure is known accurately. Note that it is possible for the atmospheric barometric pressure from room to room or in a building to be different from the outside atmospheric pressure as a result of the positive pressure developed by the air-conditioning and/or heating systems.

9.5 Temperature Transducer

By energizing the Test P/T pushbutton twice, the LED display will show the temperature in °C. The transducer used is a thermistor. In order to calibrate the temperature transducer, remove it from the bench and tape it to a calibrated thermometer. Adjust the temperature adjustment potentiometer so that the LED displayed value agrees with the value on the calibrated thermometer. Since the thermistors used on the analyzer are interchangeable to an accuracy of ± .2°C, and have a value of 10K ohms at 25°C, an alternative procedure is to hook up an accurately known 10K resistor to the thermistor input on the mother board, and adjust for a reading of 25°C on the digital display. Note that a 1°C change corresponds to a ± 5% change in resistance, thus this alternative procedure can be quite accurate as a check; however, it clearly is not NBS traceable.

9.6 System Leaks and Pump Check Out

There are two major types of leaks, external leaks, and leaks across the solenoid seals.

9.6.1 External leaks - In order to test for the presence of leaks around the fittings, disconnect the sample input line and plug the sample fitting. The flow as read on the rotameter should slowly decrease to zero. The pressure as read on the LED display should drop to below 250 mm Hg. If the pump diaphragm is in good condition and the capillary not blocked, it should take less than one minute from the time the inlet is plugged to the time the reading below 250 mm Hg is obtained.

9.6.2 Leaks across the solenoid valve - In order to check for leaks across the solenoid valves, plug in the span inlet line, engage the "Run-Span" pushbutton, and check the leaks according to the procedure in Section 9.6.1. If the pressure drops below 250 mm Hg, the valve associated with the span line is okay. Next plug the zero inlet in, engage the "Run-Zero" pushbutton, and check the leaks according to the procedure in Section 9.6.1. If this pressure also drops below 250 mm Hg, the valve associated with the zero line is okay.

9.7 Digital to Analog Converter Test

By energizing the Test DAC (digital to analog converter) pushbutton, the analog outputs will track the digital output from -23 ppm to 1000 ppm going from -2.3% full scale to +100% full scale. If a recorder trace is made, giving a straight line, the analog outputs are operating properly. Any excursions from a straight line indicate a probable lost bit or bad recorder.

9.7.1 To adjust the zero on a recording device, enter the Test Z/FS (zero/full scale) mode. This will output zero volts on the analog outputs. To adjust the span on recording device, engage the button a second time. This will output the full scale voltage (10.000 V unless otherwise specified) on the analog outputs.

9.7.2 To adjust the zero and span on the D/A board, monitor the analog output with an accurate voltmeter. Enter the Test Z/FS mode and adjust (for analog output #1) on the D/A board for zero volts, or any small offset voltage desired. Do the same for analog output #2. Now engage the Test Z/FS pushbutton a second time and adjust (analog output #1) for 10.000 volts (or for 10.000 volts plus the zero offset). Do the same for analog output #2.

10. Analyzer Calibration

Prior to calibration, the analyzer is allowed to stabilize for one hour. Perform the service checks recommended by the manufacturer. Figure 2 provides a flow schematic for calibration of the analyzer.

10.1 Analyzer Connection

Connect the analyzer and the equipment of Section 7 as shown in Figure 2. If an optional sample line filter is used, the calibration must be performed through this filter. Insure that the flowrate into the output manifold is greater than the total flow required by the analyzer, and any other flow demand connected to the manifold.

10.2 Zero Adjust

10.2.1 Allow sufficient time for the analyzer to warm up and stabilize.

10.2.2 Adjust the dilution system of Figure 2 so that zero air alone is present in the output manifold. Since not all flow controllers have a positive shut off, it might be necessary to disconnect the CO/CO_2 input line and cap it. Allow the analyzer to sample zero air until a stable reading is obtained and adjust the zero using the ZERO thumbwheel switches. Adjust for an average reading of zero.

10.2.3 If a strip chart recorder is used to obtain a record of the analog output, it is recommended that the system (i.e., either the analyzer or the recorder) be adjusted to obtain a zero trace at 5% of scale. This is to allow observation of zero drift and/or zero noise. This offset can be achieved by using the zero offset capability of the recorder or by adjusting the analog output of the analyzer to obtain the desired offset.

10.2.4 Record the stable zero air response as Z.

10.3 Span Adjust

Note: The following discusses the span adjustment and concentration of CO, this also applies to span adjustment and concentration when sampling for CO_2 using the Thermo Environmental CO_2 GFC Analyzer, 41/41 H.

10.3.1 Select the operating range of the analyzer. The full scale analog outputs of the analyzer are given in Section 11.3.7.

10.3.2 Adjust the zero air flow and the CO flow from the standard CO cylinder to provide a diluted CO concentration of approximately 80% of the upper range limit (URL) of the analyzer. The total air flow must exceed the total demand of the analyzer connected to the output manifold to insure that no indoor air is pulled into the manifold vent. Allow the analyzer to sample this CO concentration standard until stable response is obtained. The exact CO concentration is calculated from:

$$[CO]out = ([CO]std \times Fco)/(Fd + Fco)$$

where:
[CO]out = diluted CO concentration at the output manifold ppm.
[CO]std = concentration of the undiluted CO standard ppm.
Fco = flow rate of the CO standard corrected to 25°C and 760 mm Hg, liters per minute.
Fd = flow rate of the dilution air corrected to 25°C and 760 mm Hg, liters per minute.

10.3.3 Adjust the analyzer SPAN thumbwheels to obtain a recorder response as indicated from:

$$\text{Recorder Response (percent scale)} = (([CO]out \times 100)/URL) + Zco$$

where:
URL = nominal upper range limit of the analyzer's operating range.
Zco = analyzer's response to zero air, % scale.
Note: If the instrument is zeroed first, use of the span switches will not affect the zero setting.

10.3.4 Record the CO concentration and the analyzer's response.

10.4 Additional Concentration Standards

Generate several additional concentrations (at least five others are suggested) by decreasing Fco or increasing Fd. Be sure the total flow exceeds the analyzer's total flow demand. For each concentration generated, calculate the exact CO concentration using the equation in

Section 10.3.2. Record the concentration and the analyzer's response for each concentration.

10.5 Calibration Curve

Plot the analyzer's response versus the corresponding CO concentrations. Connect the experimental points using a straight line, preferably determined by linear regression techniques. The calibration curve is used to reduce subsequent sampling data.

10.6 Frequency of Calibration

In order to generate data of the highest confidence it is recommended that a multipoint calibration be performed every three (3) months, any time any major disassembly of components is performed, or any time the zero or span checks give results outside the limits described in Section 10.7 below.

10.7 Periodic Zero and Span Checks

In order to achieve data of the highest confidence, it is suggested that periodic zero and span checks be performed.

10.7.1 Periodically challenge the analyzer with zero air. The output of the zero air supply should be greater than the flow demand of the analyzer. In addition, an atmospheric dump bypass should be utilized to ensure that the zero air gas flow is being delivered at atmospheric pressure. Record the analyzer's response in percent of scale as Ao. Compute the zero drift from the following equation:

$$\text{Zero Drift } \% = Ao - Z$$

Z = recorder response at the calibration for zero air, % scale.
Note: For convenience, zero air can be plumbed directly to the zero air input bulkhead port, and the zero check performed by engaging the "Run-Zero" pushbutton.

10.7.2 Periodically challenge the analyzer with a CO level of approximately 80% of the URL. The 80% URL level may be obtained by dilution of a higher level of CO using a system similar to that of Figure 4, or by using a low level cylinder of CO containing CO in air at a concentration of approximately 80% of the URL. In either case, the cylinder of CO should be checked against a National Bureau of Standards (NBS) CO in Air Standard Reference Material (SRM) or a NBS/EPA approved gas manufacturer's Certified Reference Material (CRM). It should also be rechecked periodically to check for stability. This is especially true for a cylinder of low level CO. The Quality Assurance Handbook should be referred to for the procedure of checking the cylinders. Record the analyzer's response in % of scale as A80. Compute the span error from the following equation:

$$\text{Span Error, } \% = ([A80 - Z)URL/100] - [CO]) \times 100/[CO]$$

where:
Z = Recorder response obtained at the last calibration for zero air, % scale
[CO] = Span concentration
URl = Nominal upper range limit of analyzer's operating range

Note: For user convenience, the span gas can be plumbed directly to the span input bulkhead fitting. By engaging the "Run-Span" pushbutton, span gas will flow into the instrument.

10.7.3 The latest copy of the Quality Assurance Handbook for Air Pollution Measurement Systems should be consulted to determine the level of acceptance of zero and span errors.

10.7.4 For detailed guidance in setting up a quality assurance program, the user is referred to the Code of Federal Regulations and the EPA Handbook on Quality Assurance.

11. Analyzer Operation

11.1 Analyzer Description

As illustrated in Figure 3, the instrument can be most conveniently discussed by separating it into the following operational components.

- Optical bench
- Correlation wheel and chopper motor
- Source and source power supply
- Detector, preamplifier, and bias supplies
- Input signal conditioning board
- DC power supply
- Microcomputer
- Temperature controller
- Flow components (pump, valves, flowmeter, and plumbing)
- Temperature and pressure transducers

11.1.1 Optical Bench - The optical bench is of the white cell design. The use of the white cell multipass optical bench allows one to achieve a long path length, with a large acceptance angle, in a small physical package. The bench has been designed for easy disassembly for cleaning. The source, detector, correlation wheel, and chopper motor mount rigidly to the bench. No realignment should be necessary after routine cleaning.

11.1.2 Correlation Wheel and Chopper Motor - The correlation wheel consists of two hemispherical cells, one fitted with CO (or CO_2 when using the Model 41/41H analyzer) and the other with N_2. Integral with the correlation wheel is the chopper pattern necessary to produce the high frequency (360 Hz) chop necessary for the infrared detector. The correlation wheel is rotated by a synchronous motor.

11.1.3 Source and Power Supply - The infrared source is a special wire wound resistor. It is heated by passing a highly regulated DC voltage through the resistor. Replacement, when necessary, is straightforward.

11.1.4 Detector, Preamplifier, and Bias Supply - The detector used on the analyzers (Model 48 and 41/41H) is a solid state device with an integral cooler. It is mounted directly onto the optical bench. The output of the detector is fed into a preamplifier prior to its transmission to the input signal conditioning board. The bias voltage necessary to operate the detector is generated by a separate bias voltage power supply. Table 2 outlines specifications for the GFC CO analyzer.

11.1.5 Input Signal Conditioning Board - The input signal conditioning board takes the output signal from the preamplifier, and separates the signal into two components, one component being the signal coming from the CO half of the correlation cell, the other due to the N_2 half of the correlation cell. This board includes the sensors and associated circuitry for determination of the wheel position, as well as an AGC (automatic gain control) circuit. Finally, it contains two V-F's (voltage to frequency) converters to digitize the two signals.

11.1.6 DC Power Supplies - The DC power supply board generates the necessary regulated DC voltages. In addition, it contains the driving circuitry for the solenoids.

11.1.7 Microcomputer - In the analyzed microcomputer the pulse train outputs of the input signal conditioning board feed directly into computer controlled counters. In addition, the pulse train output of the pressure transducer and the temperature transducer system are fed directly into the same computer controlled counter. The software operates on this information to determine the sample concentration, to output diagnostic data, and to output the computed sample concentration to the front panel digital display and rear panel analog recorder jacks. The software contains sophisticated algorithm to minimize noise, increase sensitivity, insure that the output is linear, to correct for changes in temperature and pressure, and to check for information.

11.1.8 Temperature Controller - The analyzer contains a temperature transducer to measure the temperature and to correct for temperature changes. However, in order to insure that the optical bench is above the dew point to avoid water condensation, the optical bench is operated at a temperature slightly above ambient. Meaningful output data will be generated even if the bench has not stabilized.

11.1.9 Flow Components - The analyzer operates at nominal atmospheric pressure. Figure 4 summarizes the flow schematic. A downstream pump and capillary control the sample flow through the optical bench, which is monitored by a rotameter. The nominal flow is 1 liter per minute, with valves between 1/2 - 2 liters per minute. The span, zero, and sample solenoids are operated by successive engagements of the RUN pushbutton on the front panel. The control signals for the solenoids go through the microcomputer.

11.1.10 Temperature and Pressure Transducer - Temperature and pressure must be measured if one wants to compensate for changes in atmospheric values. The pressure is measured by a strain gauge pressure transducer. The temperature is measured by a thermistor.

11.2 Analyzer Installation

The installation of the analyzer includes unpacking the instrument, connecting sample, zero, span, and exhaust lines to the instrument, and attaching the dual analog outputs to a suitable recording device. Installation should always be followed by a multipoint calibration using the procedure outlined in Section 11.4. See Appendix C-3 of this Compendium, Placement of Stationary Active Monitors, for a discussion of factors regarding monitor placement.

11.2.1 Unpacking the Analyzer - The analyzer is shipped complete in one container. In addition to the basic analyzer, a six-foot line cord and an instruction manual are included in the shipping container.

11.2.1.1 Remove the analyzer from the shipping container and set it on a table or bench which will allow easy access to both the front and rear of the instrument.

11.2.1.2 Snap open latches holding the cover to the instrument. Remove the cover from the main frame of the instrument to expose the internal components.

11.2.1.3 Check for possible damage during shipment.

11.2.1.4 Check that the printed circuit boards are tightly inserted in their connectors.

11.2.2 Assembling the Analyzer

11.2.2.1 Connect the sample air to be measured to the bulkhead connector labeled "SAMPLE" on the rear panel of the instrument. Care should be taken to ensure that the sample is not contaminated by dirty, wet, or incompatible materials in the sample lines. Teflon®, borosilicate glass, or similar tubing with an O.D. of 1/4" and a minimum I.D. of 1/8" is required for all sampling lines. The length of the tubing should be held to a minimum. For best results, the tubing between the manifold and the analyzer should be less than ten feet. [CAUTION: Sample gas should be delivered to the instrument at atmospheric pressure. It may be necessary to employ an atmospheric dump bypass plumbing arrangement to accomplish this.]

11.2.2.2 Connect a source of gas of interest free air to the bulkhead labeled "ZERO" on the rear panel of the instrument. Generation of CO/CO_2 free air is discussed in Section 8.2.

11.2.2.3 Connect a source of CO span gas (i.e., use CO_2 span gas for CO_2 analyzer) to the bulkhead connector labeled "SPAN" on the rear panel of the instrument.

11.2.2.4 Connect the rear panel bulkhead labeled "EXHAUST" to a suitable vent. take care to verify that there is no restriction on this line.

11.2.2.5 Connect a recording device to the output channels of the instrument. Unless otherwise specified, the recorder signals are 0-10 VDC.

11.2.2.6 Install the power cord to the rear of the instrument. Plug the male end into an appropriate outlet. Check for proper voltage requirements.

11.2.2.7 The analyzer can be operated either with or without a particulate filter. If a filter is used, it should be a Teflon® filter-holder with a 5-10 micron Teflon® filter. In order to satisfy all EPA requirements for precision and level 1 span checks (see reference 2), it is recommended that the filter be installed between the sample-span solenoid and the optical bench. The flow scheme of the analyzer has been designed to allow for this type installation.

11.3 Analyzer Operation

Analyzer operation is illustrated in the flow diagram provided in Figure 4. A description of the controls follows.

11.3.1 Power Switch - Controls power to the electronic circuits, pump, chopper motor, and solenoid valves. When turned on, the power "ON" light integral with the switch will be lit; there also should be an audible sound from the pump. The instrument automatically goes into the startup mode.

11.3.2 Sample Flowmeter - The flowmeter shows the flow rate through the optical bench. The meter should read between 1/2 to 2 liters per minute (1-4 scfh). The flow rate is set by a capillary. It can only be changed by using a different sized capillary.

11.3.3 LED Display - Depending upon the mode of operation, the display will show the CO concentration in PPM, O, or FSCALE, DAC ramp, detector frequencies, temperature in degrees Celsius, pressure in millimeters Hg, various status diagnostics, or the previous hourly average CO concentration.

11.3.4 CO Run and Test Mode Entry Pushbuttons - Allows the operator to change the mode of operation of the instrument. A LED (light emitting diode) above the pushbutton indicates the active mode. There are eight (8) pushbuttons.

11.3.4.1 Remote Mode - This pushbutton is used to engage (LED above the "ON") or disengage (LED above the pushbutton "OFF") the remote options if installed.

11.3.4.2 Test Z/FS (Zero/Full Scale) - First actuation into this mode sets the instrument to digital zero. The recorder output levels may then be adjusted to O V or to some offset level. Engaging the pushbutton a second time sets the instrument to digital full scale. The full scale levels of the recorder outputs can then be adjusted.

11.3.4.3 Test DAC (Digital to Analog Converter) - This function is used to test for proper operation of the analog outputs and any recorder which may be connected. Actuation of this pushbutton results in the generation of a "ramp" on the analog outputs. Initial entry into this mode displays -23 ppm and outputs -2.3% full scale on the analog outputs for 30 seconds. The DAC is then caused to change its output sequentially through all its possible states causing the digital display to count from -23 to +1000 ppm while the analog outputs change from -2.3% full scale to +100% full scale in steps of 0.1% FS. This process takes approximately seven minutes for completion. A straight line ramp on the recorder chart indicates proper functioning of both the instrument and recorder. Both the digital display and analog output ramp can be stopped at any intermediate value by engaging the pushbutton a second time. Engaging the pushbutton a third time causes the ramp to continue. This allows calibration of the recorder at any of the intermediate values.

11.3.4.4 Test INT (Intensity) - Actuation of this button causes the instrument to display the infrared light intensity in Hz measured by the IR detector. The initial actuation displays the intensity as digitized by the first V-F (voltage to frequency) converter. The second engagement displays the intensity as digitized by the second V-F converter. Both readings should be nominally the same, reading at least 10,000 Hz. A low reading is an indicator of either a weak IR source or of low reflectance of the mirrors in the optical bench. Therefore, the need to clean the optics and the status of the V-F converters can be ascertained without dismantling any part of the instrument.

11.3.4.5 Test P/T (Pressure/Temperature) - Initial entry into this mode caused the pressure to be displayed in millimeters Hg. If this pushbutton is engaged a second time, the temperature in degrees Celsius will be displayed.

11.3.4.6 Test STAT (Status) - This function allows the user to determine which options have been selected by the internal circuit board switches without the need to open the instrument and interpret the switch settings. Successive engagement of the pushbutton indicates the full scale ranges in ppm of analog outputs #1 and #2, the time responses of analog outputs, the status (whether on or off) of the eight internal switches, and additional status functions if in the troubleshooting mode.

11.3.4.7 Test H.A. (Hourly Average) - First actuation of this button displays the average CO concentration for the previous hour whether the hourly average analog output interrupts are engaged or not. The second actuation displays the minutes past the hour presently assumed by the instrument. If the pushbutton is then held in, the time will increment, allowing the user to set the beginning time of the average.

11.3.4.8 RUN - This pushbutton cancels all test diagnostic modes and puts the instruments into the sample monitoring mode. If no diagnostic tests are desired, use of this button is all that is required to "drive" the instrument. The digital display shows the CO concentration in ppm. There are three RUN modes, indicated by lights and labels in the display, and operated by successive engagements of the pushbutton:

11.3.4.9 Run-Zero - The solenoids switch so that zero gas flows into the optical bench.

11.3.4.10 Run-Span - The solenoids switch so that span gas flows into the optical bench.

11.3.4.11 Run-Sample - The solenoids switch so that sample gas flows into the optical bench. Note that "Run-Sample" is the default mode. Thus when the instrument is first turned on (or when power comes on again after a power failure) the instrument automatically goes into the "Run-Sample" mode. If the analyzer is inadvertently left in a diagnostic or calibration mode, data will be lost for only one hour, since the instrument will automatically default to the "Run-Sample" mode one hour after the last actuation of any switch.

11.3.5 Zero - When calibrating the instrument, three thumbwheel switches are used to set the zero reading of the analyzer.

11.3.6 Span - Three thumbwheel switches are used to set the instrument to the concentration of a span gas source. If the instrument is zeroed first, use of the span switches will not affect the zero setting.

11.3.7 Range - The analyzer has two independent analog outputs with independently selectable ranges and time responses. The first range thumbwheel switch selects the range for output #1 (the upper terminals on the rear panel), while the second switch selects the range for output #2. The selected full scale ranges can be displayed by use of the Test STAT function. The number code on the thumbwheel switches correspond to the following ranges:

Switch Setting	Full Scale Range (PPM)
0	1
1	2
2	5
3	10
4	20

Switch Setting	Full Scale Range (PPM) (cont.)
5	50
6	100
7	200
8	500
9	1000

11.3.8 Time - These two thumbwheel switches select the time response/hourly averaging options for analog outputs #1 and #2 respectively. The selected time responses for analog outputs #1 and #2 can be displayed by use of the Test STAT function. The number code on the thumbwheel switches corresponds to the following:

Setting	Time Response (60 Hz)	Time Response (50 Hz)
0	10 sec. CO average	12 sec. CO average
1	20 sec. CO running average	24 sec. CO running average
2	30 sec. CO running average	36 sec. CO running average
3	60 sec. CO running average	60 sec. CO running average
4	90 sec. CO running average	96 sec. CO running average
5	120 sec. CO running average	120 sec. CO running average
6	300 sec. CO running average	300 sec. CO running average
7	1 hr. CO continuous average (c.H.A.)	1 hr. CO continuous average (c.H.A.)
8	1 hr. & 60 sec. integrated CO averages, time multiplexed, 60 sec. averages periodically blanked (b.H.A.)	1 hr. & 60 sec. integrated CO averages, time multiplexed, 60 sec. averages periodically blanked (b.H.A.)
9	1 hr. & 60 sec. integrated CO averages, time multiplexed 60 sec. averages delayed (d.H.A.)	1 hr. & 60 sec. integrated CO averages, time multiplexed 60 sec. averages (d.H.A.)

11.3.8.1 For time switch settings 0 through 6, the analog output updates every 10 seconds (12 seconds for 50 Hz). If the switch setting is 7, the analog output gives the average for the previous hour setting at the time when the minute time (as displayed upon second actuation of the Test H.A. pushbutton) is equal to one.

11.3.8.2 If the switch setting is 8, the analog output gives during the first 10 minutes of every hour, the CO average for the previous hour, and during the remaining 50 minutes, updating every 60 seconds, the current 60 second CO integrated average.

11.3.8.3 If the switch setting is 9, the analog output gives during the first 10 minutes of every hour, the CO average for the previous hour, and during the remaining 50 minutes, sixty (60) second integrated CO averages for the present hour, time compressed in the ratio 5:6. Therefore, even while the hourly average is being output, the analyzer continues to monitor CO and stores the 60 second averages to be updated every 50 seconds for the remaining 50 minutes of the hour. The hourly average routines are discussed more fully in the manufacturer's instruction manual.

11.3.8.4 The digital display indicates the CO average corresponding to the time specified by switch settings 0 through 6 for analog output #1, updating every 10 seconds (12 seconds for 50 Hz) as indicated by a blinking decimal point. If the time switch for analog output #1 is set to 7, 8, or 9, the digital display indicates 60 second running averages updating every 10 seconds (12 seconds for 50 Hz).

11.4 Analyzer Startup

11.4.1 The source turns on, all electronics are turned on, the detector cooler goes on, the chopper motor and sample pump go on, the heater in the pressure transducer goes on, the program initializes itself.

11.4.2 During the few minutes it takes for the source etc. to stabilize observe that the power switch is energized, the LED display first displays the word "HELLO" followed by the word "CO" (during this time, approximately 2 minutes, the analog outputs will give 0 volts.) The instrument will then automatically go into the "RUN SAMPLE" mode.

11.4.3 The analyzer has been designed so that the Test diagnostic modes can be utilized without disturbing the analog outputs. Therefore, if one enters the Test STAT of H.A. modes, the instrument continues to output the CO values at the analog outputs. Entering the Test Z/FS or DAC modes does affect the outputs, however, the microcomputer continues to store the CO data for use when returning to the RUN mode. If one enters the Test INT or P/T modes, the analyzer "latches" onto the current CO value and continues to output that value until the instrument is returned to the RUN mode. The analyzer then enters a wait period of approximately 25 seconds before updating to the current CO value.

11.5 Analyzer Shutdown

De-energize the power switch on the front panel. The analyzer is now powered down.

11.6 Loss of Power

If a power failure occurs or if the analyzer is turned off momentarily, the instrument automatically goes into the start-up mode upon resumption of power. Note that if any of the hourly average modes are being used, upon power up the timer will be reset to zero, thus the average will not necessarily be in synchronization.

11.7 Analyzer Electronics and Microcomputer System

In order to understand the operation of the analyzer, a general knowledge of the electronics and software is necessary. The electronics can conveniently be broken down into the following components:

- DC power supply and solenoid driver
- Bias source and cooler power supply
- Detector and preamplifier
- Input signal conditioning board
- Digital electronics
- Temperature controller

11.7.1 DC Power Supplies - The DC power supply outputs the regulated and unregulated DC voltages necessary to operate the digital electronics, the bias supply, the detector and preamplifier, the input signal conditioning board, and the temperature controller. The transformer used is field jumpable for 110 and 220 volt service. It outputs +24 volts unregulated and ±15 volts and +5 volts regulated. Regulation is achieved by use of monolithic voltage regulators. The DC board also contains the driving circuit necessary to energize the solenoids. The logic on/off signals are received from the microcomputer.

11.7.2 Bias, Source and Cooler Power Supplies - The solid state detector used needs a bias voltage of approximately -100 volts DC. Both the cooler and source need a high current, low voltage source. The bias supply contains a high current 18 volt regulated power supply. This 18 volts is also used for an oscillator, the output of which goes to a step-up transformer to generate the high voltage. This high voltage then passes through a rectifying circuit to form the -100 volt bias needed for the detector.

11.7.3 Detector and Preamplifier - The detector used is a photo conductive, lead-selenide (PbSe) device, with an internal thermo-electric cooler. The PbSe detector operates through use of the internal photoelectric effect. That is, its conductivity is proportional to the high intensity hitting it. One characteristic of this device is that it has a high conductivity even with no light. The background conductivity increases with increasing temperature. Thus in order to reduce the background conductivity, the detector is cooled. In order to distinguish the signal from background, the source is chopped. Thus the output of the detector includes an AC component due to the background conductivity. It should be noted that the AC component is very small compared to the DC component. The output of the detector passes through a coupling capacitor which only passes the AC component. The AC component is then amplified. The output signal is an AC signal, with a low frequency component and a high frequency component. The low frequency component is at 30 Hz, and is due to the 30 Hz rotation of the correlation wheel. The high frequency component is at 360 Hz and is due to the mask on the correlation wheel which divides the wheel into 12 sectors. The output of the preamplifier is fed through a shielded cable to the input signal conditioning board.

11.7.4 Input Signal Conditioning Board - The input signal conditioning board contains the circuitry necessary to operate the AGC (automatic gain control), the rectifier, and the demodulation circuitry. In addition, it includes the necessary components to digitize the signal output.

11.7.5 Microcomputer System - The microcomputer system is a multiboard system interconnected by use of a mother board. A detailed discussion of these boards is provided in the manufacturer's Instruction Manual. The boards are broken up into functional forms as follows:

- Microprocessor
- Memory
- Counter
- Peripheral Interface
- Display Driver
- Digital/Analog

- Switch
- Span-Zero Buffer Board
- General Purpose Interface

11.7.6 Temperature Controller - Two 50 watt 100 ohm resistors (400 ohm for 220 V) mounted on the optical bench are used to heat the optical bench above the dew point, to avoid moisture condensation on the mirrors. A thermistor is used to determine the bench temperature, with op-amp and the solid state relay used as the control elements to control the current into the heaters.

12. 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.

13. 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.

13.1 Standard Operating Procedures (SOPs)

13.1.1 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.

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

13.2 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. Maintenance procedures provided in Section 9, calibration procedures in Section 10, and operation procedures in Section 11 of the method and the manufacturer's instruction manual should be followed and included in the QA program. Additional QA measures (i.e., trouble-shooting) are provided by the manufacturer as well as further guidance in maintaining the sampling system which is beyond the scope of this document.

14. References

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Table 1. Specifications for GFC CO Analyzer

Ranges	0-1, 2, 5, 10, 20, 50, 100, 200, 500, 1000 ppm
Noise	0.05 ppm RMS - with time constant = 30 seconds
Minimum Detectable Limit	0.10 ppm
Zero Drift, 24 hours	± 0.2 ppm
Span Drift	± 1% Full Scale
Rise, Fall Times (0-95%) (at 1 lpm flow, 30 second response time)	1 minute
Precision	± 0.1 ppm
Linearity	± 1%
Flow Rate	0.5 - 2 lpm
Rejection Ratio	Negligible interference from water and CO_2
Operating Temperature	Performance specifications maintained over the range 15-35°C (may be operated safely over the range 5-45°C)
Power Requirements	105 - 125 VAC, 60 Hz 220 - 240 VAC, 50 Hz 100 Watts
Physical Dimensions	17"W x 8 3/4"H x 23"D
Weight	45 lbs.
Dual Outputs (Standard)	Individually selectable to 0-10mv, 0-100mv, 0-1V, 0-5V, 0-10V; digital display; 1 hour integrated value. Other outputs available upon request (4-20ma, IEEE488)

Table 2. Commercially Available GFC CO Analyzers
Designated by U.S. EPA as Reference Methods

Identification	Manufacturer	Fed. Vol.	Reg. Pg.	Notice Date
Dasibi Model 3003 Gas Filter Correlation CO Analyzer, operated on the 0-50 ppm range, with a sample particulate filter installed on the sample inlet line.	Dasibi Environmental Corp. 515 West Colorado St. Glendale, CA 91204	46	20773	4/07/81
Thermo Electron Model 48 Gas Filter Correlation Ambient CO Analyzer, operated on the 0-50 ppm range, with a time constant setting of 30 seconds.	Thermo Electron Instruments, Inc. 8 West Forge Parkway Franklin, MA 02038	46	47002	9/23/81
Monitor Labs 8830 CO Analyzer operated on the 0-50 ppm range, with a five micron Teflon® filter element installed in the rear-panel filter assembly.	Monitor Labs, Inc. 10180 Scripps Ranch Blvd. San Diego, CA 92131	53	7233	3/07/88
Dasibi Model 3008 Gas Filter Correlation CO Analyzer, operated on the 0-50 ppm range, with a time constant setting of 60 seconds, a particulate filter installed in the analyzer sample inlet line, with or without use of the auto zero or auto zero/span feature.	Dasibi Environmental Corp. 515 West Colorado St. Glendale, CA 91204	53	12073	4/12/88

Commercially Available GFC CO Detection Devices

Detection Device I.D.	Manufacturer	Portability
Gas Analyzer DEFOR	Westinghouse Elec. Process & Environmental Measuring Technology Orrville, OH 44667 (800)628-1200	Stationary
CO_2 Analyzer Model 41/41H	Thermo Environmental Instruments, Inc. 8 West Forge Pkwy. Franklin, MA 02038 (508)520-0430	Stationary

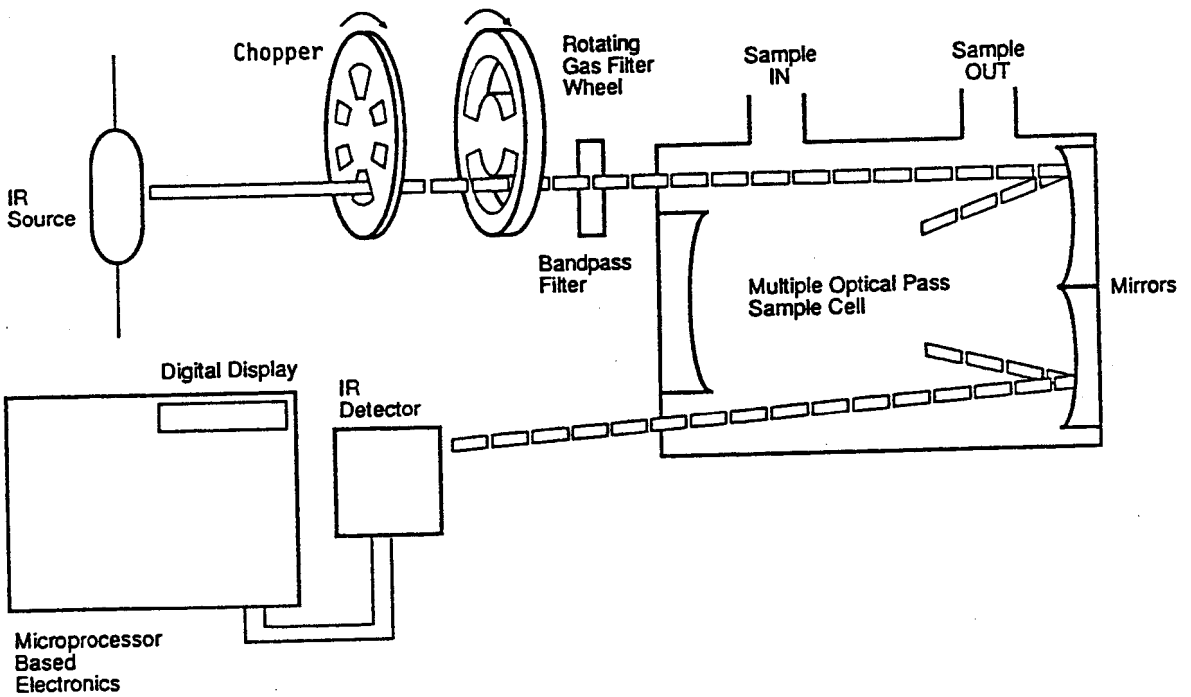

Figure 1. Gas Filter Correlation Basic Components

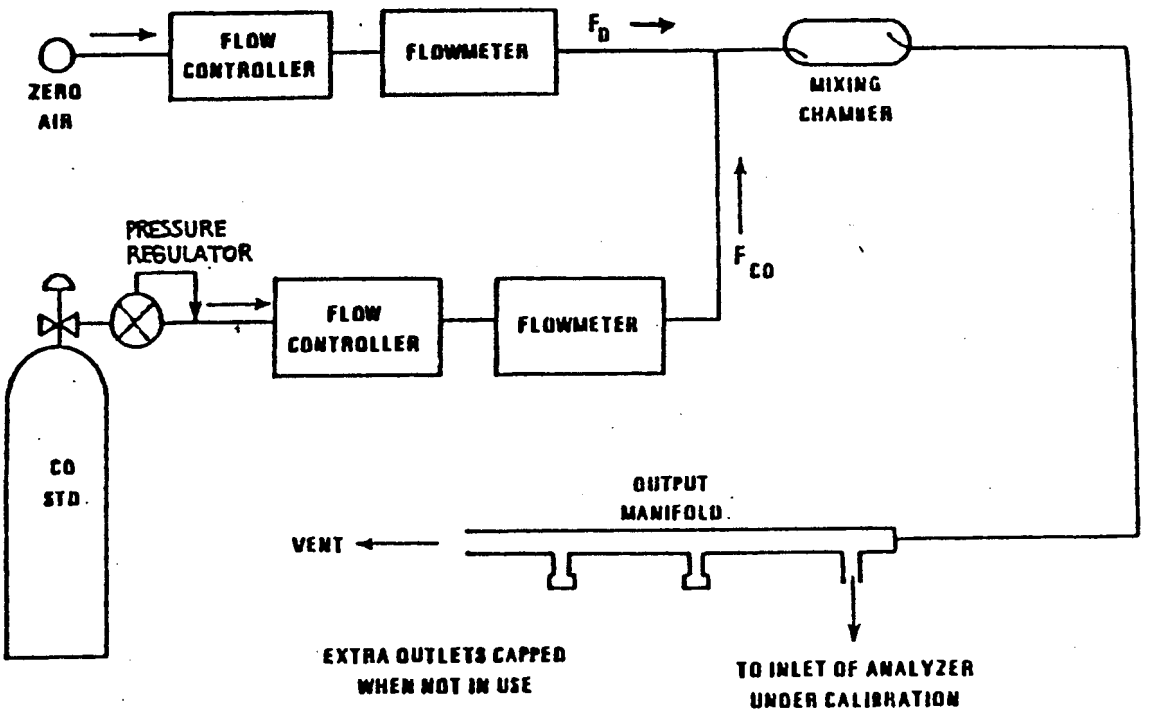

Figure 2. Flow Schematic of Calibration System

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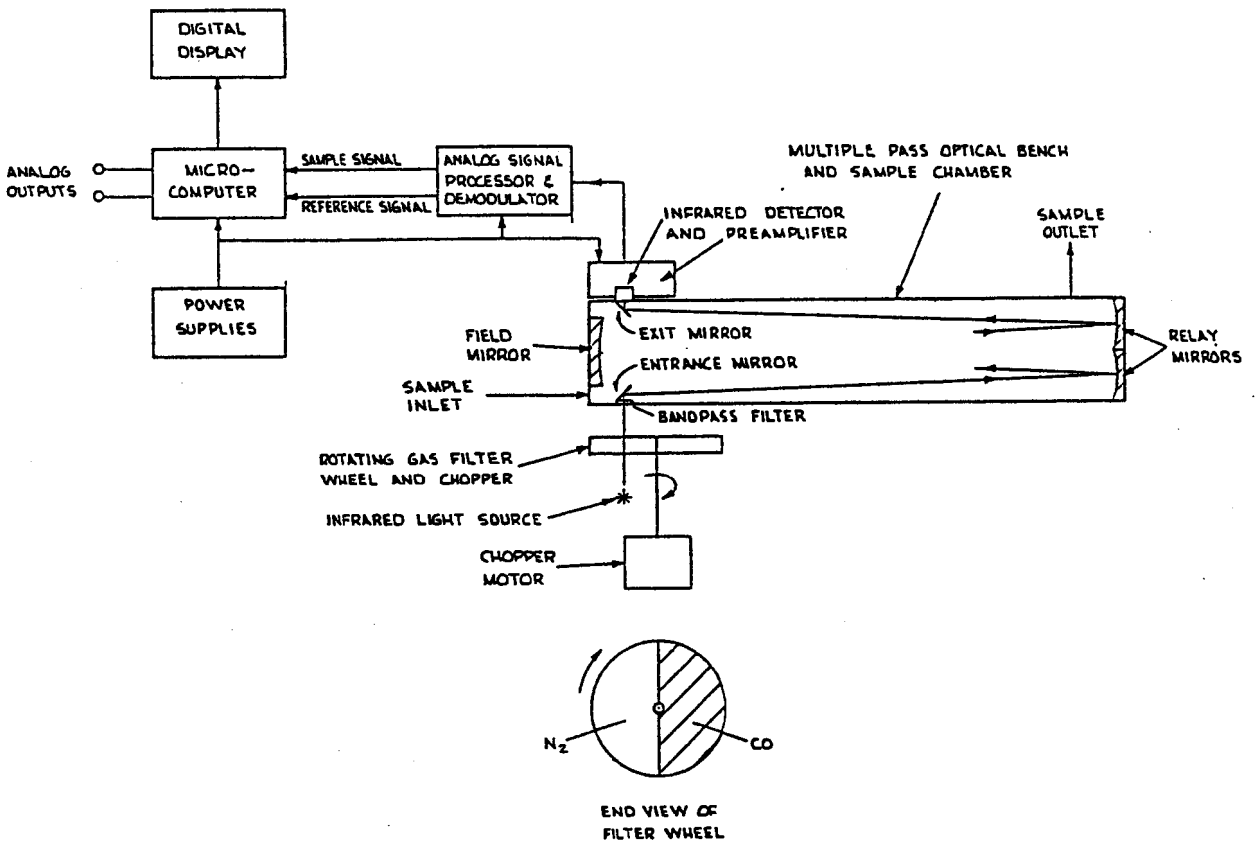

Figure 3. Block Diagram of a Gas Filter Correlation Spectrometer

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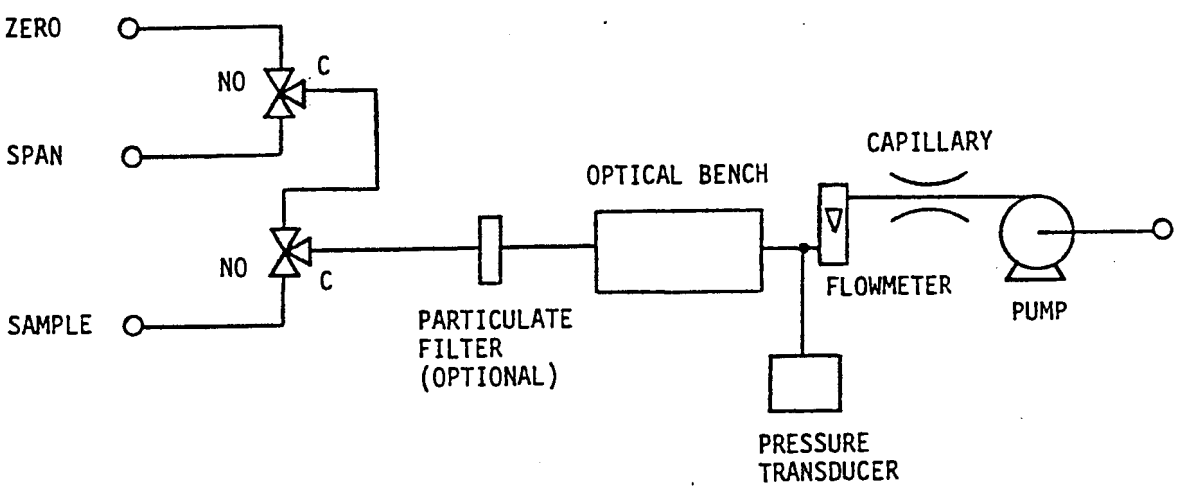

Figure 4. Flow Schematic for Calibration of GFC Analyzer

Method IP-3C

DETERMINATION OF CARBON MONOXIDE (CO) IN INDOOR AIR USING ELECTROCHEMICAL OXIDATION

Method IP-3C

DETERMINATION OF CARBON MONOXIDE (CO) IN INDOOR AIR USING ELECTROCHEMICAL OXIDATION

1. Scope

1.1 This document describes a method for determination of CO only, employing electrochemical oxidation. This method utilizes a small, portable, personal exposure monitor (PEM) which can be attached to an individual (i.e., to directly assess exposure levels). With the PEMs, CO levels are measured in an individual's breathing zone, on a continuous real-time basis. Electrochemical CO monitors can also be used as area monitors.

1.2 Measurement of CO by electrochemical oxidation relies on oxidation of CO to CO_2 to produce an electrical signal related to the CO concentration in sample air.

1.3 An Appendix detailing the use of a portable air sampling system (PASS) for the determination of CO is also included.

2. Applicable Documents

2.1 ASTM Standards

D1356	Definition of Terms Relating to Atmospheric Sampling and Analysis
D1357	Recommended Practice for Planning the Sampling of the Atmosphere
D3195	Recommended Practice for Rotameter Calibration
D1914	Recommended Practice for Conversion Units and Factors Relating to Atmospheric Analysis
D3249	Recommended Practice for General Ambient Air Analyzer Procedures
E1	Specification for ASTM Thermometers
E180	Recommended Practice for Development of Precision Data for ASTM Methods for Analysis and Testing of Industrial Chemicals
D3162-78	Standard Test Method for Carbon Monoxide in the Atmosphere (Continuous Measurement by Nondispersive Infrared Spectrometry)

2.2 Other Documents

Laboratory and Indoor/Ambient Air Studies (1-11)
U.S. Environmental Protection Agency Technical Assistance Document (12)

3. Summary of Method

3.1 The electrochemical CO monitor samples either by diffusion or by use of a small diaphragm type pump which maintains a constant flow rate. The monitor employs an electrochemical measuring principle in which CO is converted to CO_2 in a liquid cell, thus freeing electrons to generate a small electrical current that is amplified, measured, and recorded. Figure 1 provides a schematic of a standard CO PEM.

3.2 In the monitor, the sample is transported to an electrochemical cell where CO is oxidized to CO_2. Oxidation of CO produces a current and subsequent signal that are

proportional to the CO concentration in the sample air. The electrical signal can be displayed directly or integrated inside the instrument to give readings in parts per million. This process is illustrated in Figure 2.

3.3 Signal integrators and data loggers can be used to record data from the personal exposure monitors. The monitors generally operate over a range of 0-1000 ppm.

3.4 The following information details the operating principles of a CO PEM manufactured by General Electric (GE) Co. (1,2) and discusses basic principles of determining CO by electrochemical oxidation.

3.4.1 The GE monitor employed solid polymer electrolyte (SPE) technology (formerly patented by GE) using a membrane with deionized water stored on one side. Figure 2 provides a complete illustration of the GE CO monitor. The deionized water was stored in a plastic reservoir cell. The sample containing CO was continuously pumped past the other side of the membrane. The pump operated up to 40 hours with a precision of 2 ppm with zero and span checks performed before and after field service. When the sample entered the 100% relative humidity environment of the saturated membrane, CO (present in the sample) combined with water in the following reaction:

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$$

3.4.2 The resulting hydrogen ions ($2H^+$) passed through the membrane freeing up electrons ($2e^-$). A sensor electrode was mounted on the sampling side of the membrane and a counter electrode was mounted on the water reservoir side of the membrane. The electrons freed by the above reaction moved from the sensor electrode to the counter electrode through an external circuit, generating an electric current that was amplified. At the water reservoir side of the membrane, the hydrogen ions and electrons combined to form water as shown in the following reaction:

$$2H^+ + 2e^- + 1/2\ O_2 \rightarrow H_2O$$

3.4.3 When both of the reactions in Section 3.4.1 and Section 3.4.2 are combined, the following reaction occurred, causing CO in the sample to be oxidized to CO_2:

$$CO + 1/2\ O_2 \rightarrow CO_2$$

For each CO molecule oxidized, two electrons traveled through the external circuit. The resulting current generated was directly proportional to the CO concentration present in the sample.

3.4.4 After amplification, the CO concentration was read directly in parts per million by a liquid crystal display (LCD) system. The continuous electrical signal was recorded in internal memory of the GE monitor configured as discussed in Section 4.2.

3.4.5 The reaction was affected by temperature. A thermistor mounted in the sensing cell altered the gain of the amplifier circuitry, forming a temperature compensation network. Chemical interferents (e.g., nitrogen dioxide) were removed from the sample with a chemical filter consisting of an oxidant (e.g., potassium permanganate on activated alumina) before entering the sensing cell.

3.4.6 Although the GE CO PEMs are no longer manufactured, the information provided may be helpful in understanding the electrochemical oxidation process of CO to CO_2. Additionally, one could use the technology to develop a CO PEM or modify an existing one to meet specific monitoring needs.

4. Significance

4.1 Over the last decade, various small, portable personal monitors capable of measuring air pollution exposures of people as they go about their daily lives have been introduced. Several manufacturers offer light-weight personal monitors for carbon monoxide that are hand-held, belt-mounted, or can be carried on a shoulder strap like a camera or portable radio. Passive CO detectors also have been developed by several companies. However, minimal data concerning the performance and evaluation of these monitors are available. The sections describing the CO monitors have been generalized into standard procedures applicable to most of the currently available instruments. For use in the Compendium, the authors have relied on information provided from manufacturer's operating and instructional manuals.

4.2 At this writing, there is little documentation (i.e., research/test data, human exposure studies, etc.) available for CO monitors used for personal monitoring in non-industrial atmospheres except for the CO PEM manufactured by the Aircraft Division of General Electric (GE) Co. (1,2) from 1978 to 1984. The GE Co. Monitor is no longer produced. The GE CO detector was evaluated in two studies conducted by the U.S. Environmental Protection Agency (1,2). As part of the study, the GE CO sensing systems were adapted with microprocessor data loggers. The data loggers were used to automatically manipulate and store numerical data from the instruments for later examination and retrieval. For the study, the CO monitors were termed "COED" monitors for carbon monoxide exposure dosimeters. The COED monitors were used in Denver, Colorado and Washington, DC for human exposure studies conducted 1982-1983. The COED-I, which consisted of the GE monitor and a Magus Group microprocessor-based data logging and control package, was used successfully to obtain more than 1600 24 hour human CO exposures in these two cities. The COED-II, which consisted of the GE monitor and a HP41CV programmable calculator and interfacing electronics, was evaluated briefly, but data was not published due to problems with some instruments. The tests proved that the GE monitor was suitable for personal monitoring applications (1,2).

4.3 Although the GE monitors are no longer produced, the technology behind the CO monitor provides a means to adequately determine indoor CO concentrations. Table 1 provides the GE monitor's performance characteristics. Other small, portable electrochemical CO monitors are available. Though research validating other models' applicability to this method has not been conducted, additional models that may be usable are included in Table 2.

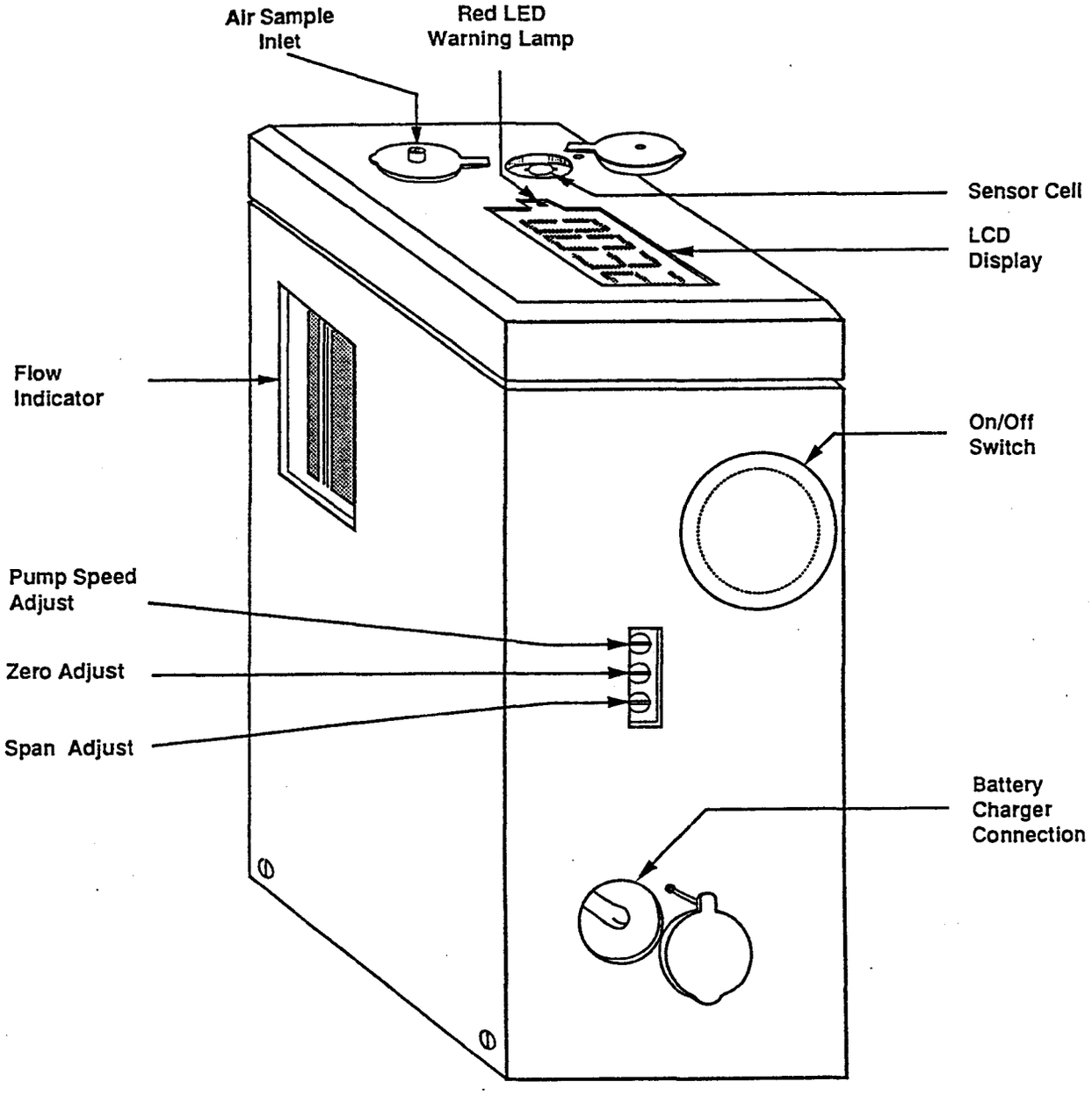

Figure 1. CO Personal Exposure Monitor

Note: Some models report erroneous zero when sensor cell is exposed to nitrogen for more than a few minutes. Users manual will specify zero procedure and what zero gas is recommended for that model.

8.2 Calibration and span gases - pressurized cylinders with CO concentrations corresponding to the CO dosimeter range of operation. Some models have available calibration kits with calibration gases, connecting tubing, and pressure regulators. The cylinders should be traceable to a NBS/SRM or to a NBS/CRM.

8.3 Multistage pressure regulators - standard, two-stage, stainless steel diaphragm regulators with pressure gauges for gas cylinders.

8.4 Battery charger - capable of recharging the CO monitor.

8.5 Thermometer - used to measure area monitoring temperature.

8.6 Barometer - used to measure barometric pressure of monitoring area.

9. Systems Maintenance

All necessary maintenance activities are included in the manufacturer's operating instructions. Because a majority of the CO monitors produced may not be uniform (e.g., pump/pumpless, filter/no filter, etc.), the maintenance practices vary from one monitor to the next. However, the following provides a brief summary of general maintenance practices standard for all CO monitors.

9.1 Periodic Maintenance

The CO monitor should be properly maintained to ensure successful operation. Periodic maintenance is conducted to reduce system failures and maintain calibration integrity of the monitor. Periodic maintenance should include inspection of the battery pack, filter (optional), pump (if applicable), and the important support equipment. As with the NDIR analyzer, instrument calibration should be checked on a schedule established after the monitor has operated for a period of time. The sensitivity and linearity should also be checked. These instrument checks should be done at least on an annual basis. However, when any major component is changed the linearity and selectivity of the instrument should be confirmed. A log of these settings and a service and repair log should be kept to assist in evaluating maintenance difficulties.

9.2 Routine Maintenance

Regular checks of the instrument and its operation are mandatory. Even though a system may provide excellent quality data initially, without routine maintenance and system checks the quality of the data will degenerate with time.

9.3 Preventive Maintenance

The preventive maintenance program of the CO monitoring system should contain a troubleshooting guide and diagnostic chart to assist operators in identifying and correcting instrument problems.

9.4 Troubleshooting the Monitor

9.4.1 The manufacturer's instruction manual generally contains troubleshooting guidelines that cover most troubles which may occur.

9.4.2 The troubleshooting guidelines should only be used after the analyzer cannot be calibrated or aligned according to manufacturers' specifications or cannot be operated properly.

9.4.3 The manufacturer's troubleshooting guide provides the user with a logical sequence to follow while investigating problems

10. CO Monitor Calibration

It is essential that zero, span and multipoint calibrations be performed frequently. Daily zero and span checks and weekly multipoint calibration is recommended. Proper calibration is vital to this equipment's accuracy. The instrument is calibrated by introducing into it a known concentration of gas being monitored, and adjusting the span control to correspond to the known analysis of the gas. The operator should not attempt to calibrate or use the instrument until the operating manual is thoroughly read. The CO monitor should be calibrated when the instrument is received, any maintenance is performed and any components are replaced. The following information refers to the GE COED and is provided as guidance in addition to specific model's users manuals.

10.1 CO Monitor Zero Calibration

10.1.1 Ensure that the cell assembly is stabilized and the batteries are charged and functioning properly.

10.1.2 Place the battery switch to on position and pump switch (if applicable) to off position.

10.1.3 Connect zero gas supply to CO monitor. Do not connect gas supply directly to monitor. Use appropriate tubing (i.e., Teflon®, Tygon®, or polyproylene tubing) and tee fittings for interconnections.

10.1.4 Start the zero gas flow from the cylinder into the monitor by turning the pressure regulator. For pump-fitted models, flow is generally maintained at approximately 100 mL/min at cylinder pressures greater than 50 psig.

10.1.5 Place the monitor pump switch to ON position (if applicable). The battery switch is still in the ON position. The monitor self-test (warning lights and audible alarm activated) may occur momentarily.

10.1.6 If the monitor reads 0 to 2 ppm after about three minutes, it is zeroed properly. If the reading is not in the 0-2 ppm range, adjust the dosimeter potentiometer for 0 ppm.

10.1.7 Release the pressure regulator to stop flow of the zero air calibration gas. Disconnect tubing and fittings.

10.2 CO Monitor Span Calibration

10.2.1 For span calibration of the CO monitor place the battery switch to ON position and the pump switch (if applicable) to the ON position. Connect span gas cylinder to instrument with appropriate tubing and fittings.

10.2.2 Start the span gas flow into the monitor. Note the CO concentration as written on the analysis tag attached to the cylinder (nominally 50-60 ppm CO).

10.2.3 After approximately three minutes, adjust the span potentiometer to achieve the same ppm CO reading as that of the span gas.

10.2.4 Release pressure regulator to stop flow of span calibration gas. Disconnect tubing and the fittings from the CO dosimeter and gas cylinder, and battery switches.

10.3 CO Monitor Multipoint Calibration

10.3.1 A multipoint calibration should be conducted on initial use, on a weekly basis and whenever maintenance which affects the monitor is performed.

10.3.2 Perform a manual zero and span calibration as in Sections 10.1 and 10.2.

10.3.3 Introduce intermediate span gases with concentrations of 20%, 40% and 60% of full scale in succession. A stable reading at each intermediate span point should be reached before proceeding to the next one. Intermediate span points will be introduced from individual cylinders.

10.3.4 Plot the monitor's response versus the corresponding CO concentrations. Connect the experimental points using a straight line, preferably determined by linear regression techniques. The calibration curve is used to reduce subsequent sampling data.

11. CO Monitor Operation

11.1 Once the monitor has been properly zeroed and the span checked, it is ready to analyze indoor CO concentration. Figure 2 provides a flowchart on CO monitor operation. The following information refers to the GE COED and is provided as guidance in addition to a specific model's users manuals.

11.2 Place the pump switch (if applicable) on. If the instrument is equipped with a self-test feature, lights/alarms will be activated when the monitor is started.

11.3 Verify sample flow (i.e., flowrate recommended by the manufacturer) on flow indicator scale. Adjust monitor as required to obtain proper flow rate.

11.4 Place CO monitor in shirt/pocket or secure to user's clothing. If CO monitor is to be used as an area monitor, see Appendix C-3 of this Compendium, Placement of Stationary Passive Monitors, for a discussion of factors regarding monitor placement.

11.5 After the desired sample period, turn the pump switch off. Recharge the battery after each sampling period to prevent damage.

12. 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.

13. 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.

13.1 Standard Operating Procedures (SOPs)

13.1.1 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.

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

13.2 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 10, operation procedures in Section 11, and maintenance procedures in Section 9 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.

13.2.1 The latest copy of the Quality Assurance Handbook for Air Pollution Measurement Systems (13) should be consulted to determine the level of acceptance of zero and span errors.

13.2.2 For detailed guidance in setting up a quality assurance program, the user is referred to the code of Rederal Regulations (14) and the EPA Handbook on Quality Assurance.

14. References

1. Turlington, C. F., Bostick, J. K., Abel, C. W., Weant, C. G., and Holland, J. C., "Evaluation of COED-1 and COED-2 Portable Carbon Monoxide Personal Exposure

Monitors," EPA Contract No. 68-02-4035, Research Triangle Park, NC, Northrop Services, Inc. - Environmental Sciences, 1984.

2. Ott, W., Williams, C., Rodes, C. E., Drago, R. J., and Burmann, F. J., "Automated Data-Logging Personal Exposure Monitors for Carbon Monoxide," *J. Air Poll. Contr. Assoc.*, Vol. 36:883-887, 1986.

3. Winberry, W. T., and Murphy, N. T., *Supplement to EPA-600/4-84-041: Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-87-006, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1986.

4. Nagda, N. L., et al., *Guidelines for Monitoring Indoor Air Quality*, ISBN: 0-89116-385-9, Hemisphere Publishing Co., New York, NY, 1987.

5. Wilson, M. L., Durham, O. G., Jr., and Elias, D. F., "Draft: APTI Course 435 Atmospheric Sampling," U.S. Environmental Protection Agency, Research Triangle Park, NC, March, 1979.

6. Wadden, R. A., and Scheff, P. A., *Indoor Air Pollution: Characterization, Prediction, and Control*, ISBN: 0-471-87673-9, Wiley Interscience Publishing Co., New York, NY, 1983.

7. Riggin, R. M., *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-84-041, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1986.

8. "Operations and Maintenance Instructions for the SPE Carbon Monoxide Dosimeter Models 15ECS1C02, 15ECS3C03, 15ECS1CO1 and 15ECS1CO1A," General Electric Aircraft Equipment Division, Cincinnati, OH, 1981.

9. "Instruction Manuals for 4000 and 5000 Series CO Personal Exposure Monitors," Interscan Corporation, Chatsworth, CA, 1988.

10. "Application Notes for Neotronics Exotox and Neotox CO Personal Exposure Monitors," Neotronics, Gainesville, GA, 1988.

11. List of Designated Reference and Equivalent Methods, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, April 12, 1988.

12. Riggin, R. M., *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.

13. *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II--Ambient Air Specific Methods*, EPA 600/4-77-0272, May 1977.

14. 40 CFR Part 58, Appendix A, B.

Table 1. Performance Characteristics of the GE CO Montior

Useful ranges: 0 to 1000 ppm CO

Lower detectable limit: 1 ppm CO

Accuracy: LCD direct readout; 0-500 ppm ± 10%

Warm-up time: 15 seconds (after full battery charge)

Response time: within 2 minutes to 90%

Operating temperature with specified accuracy: 1-40°C (34-104°F)

Attitude: within 45° of vertical

Relative humidity range: 0-95%

Span drift: less than ± 10% (1 week)

Zero drift: less than ± 2 ppm (10 hours)

Table 2. Commercially Available Electrochemical CO Monitors

Identification	Manufacturer	Data Logger
Neotox	Neotronics of NA Inc. Box 370 Gainesville, GA 30503 (800)535-0606	not available
Exotox 550FHC or 550FCS Multi-gas Monitor	Neotronics of NA Inc. Box 370 Gainesville, GA 30503 (800)535-0606	included
CO-82	GASTECH 8445 Central Ave. Newark, CA 94560-3431 (415)794-6200	optional
1140 or 4140 CO Analyzer Series or 5100 Series PEM	Interscan Box 2496 Chatsworth, CA 91313 (800)458-6153	optional
Model 170 CO Indicator	MSA Instrument Division Box 427 Pittsburgh, PA 15230 (800)672-4678	included
Tritector Model CGS-100	ENMET 2308 S. Industrial Highway P.O. Box 979 Ann Arbor, MI 48106 (313)761-1270	not available
Model 190 Personal CO Monitor	National Draeger, Inc. 101 Technology Dr. Box 120 Pittsburgh, PA 15230 (412)787-8383	included

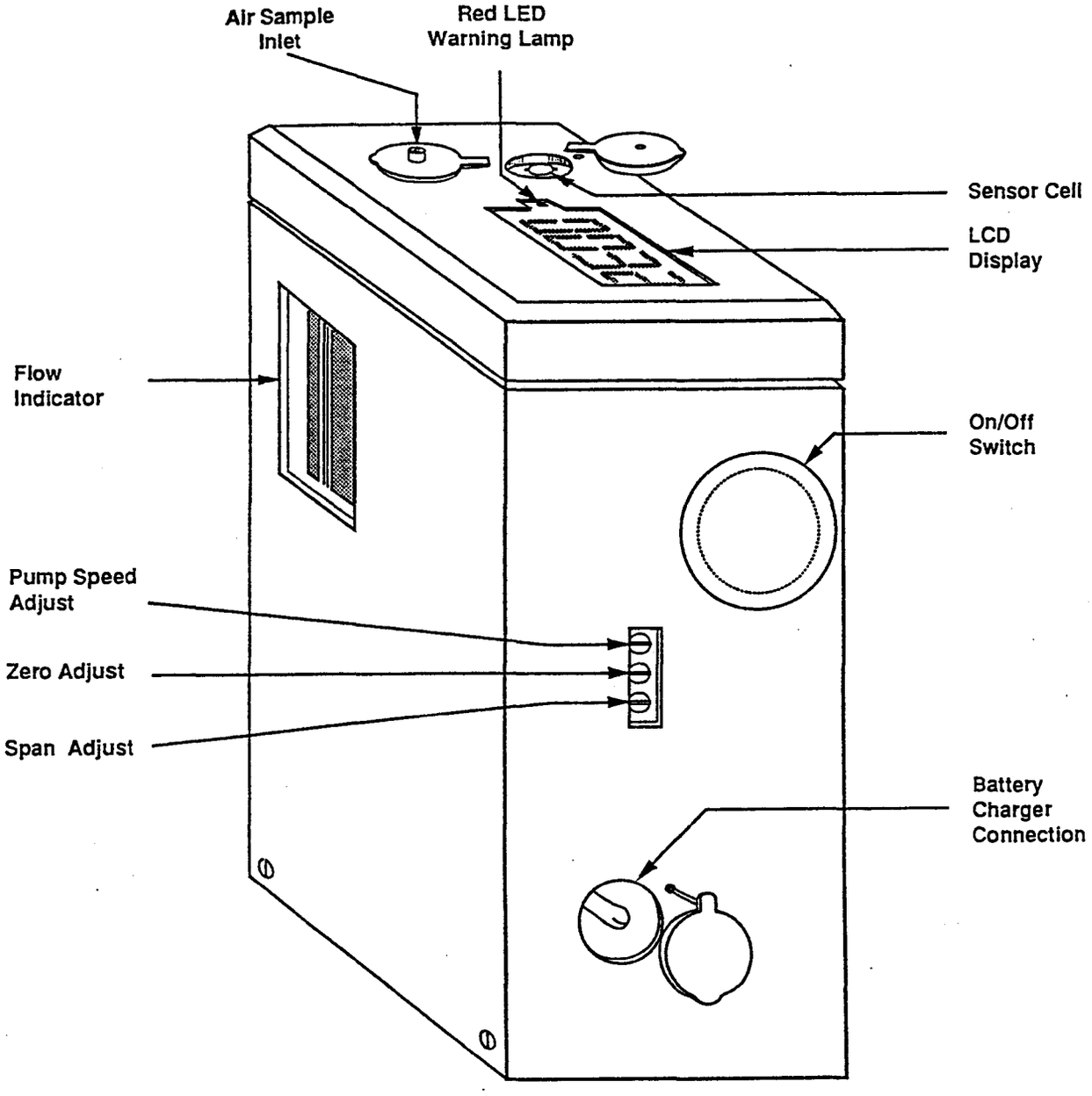

Figure 1. CO Personal Exposure Monitor

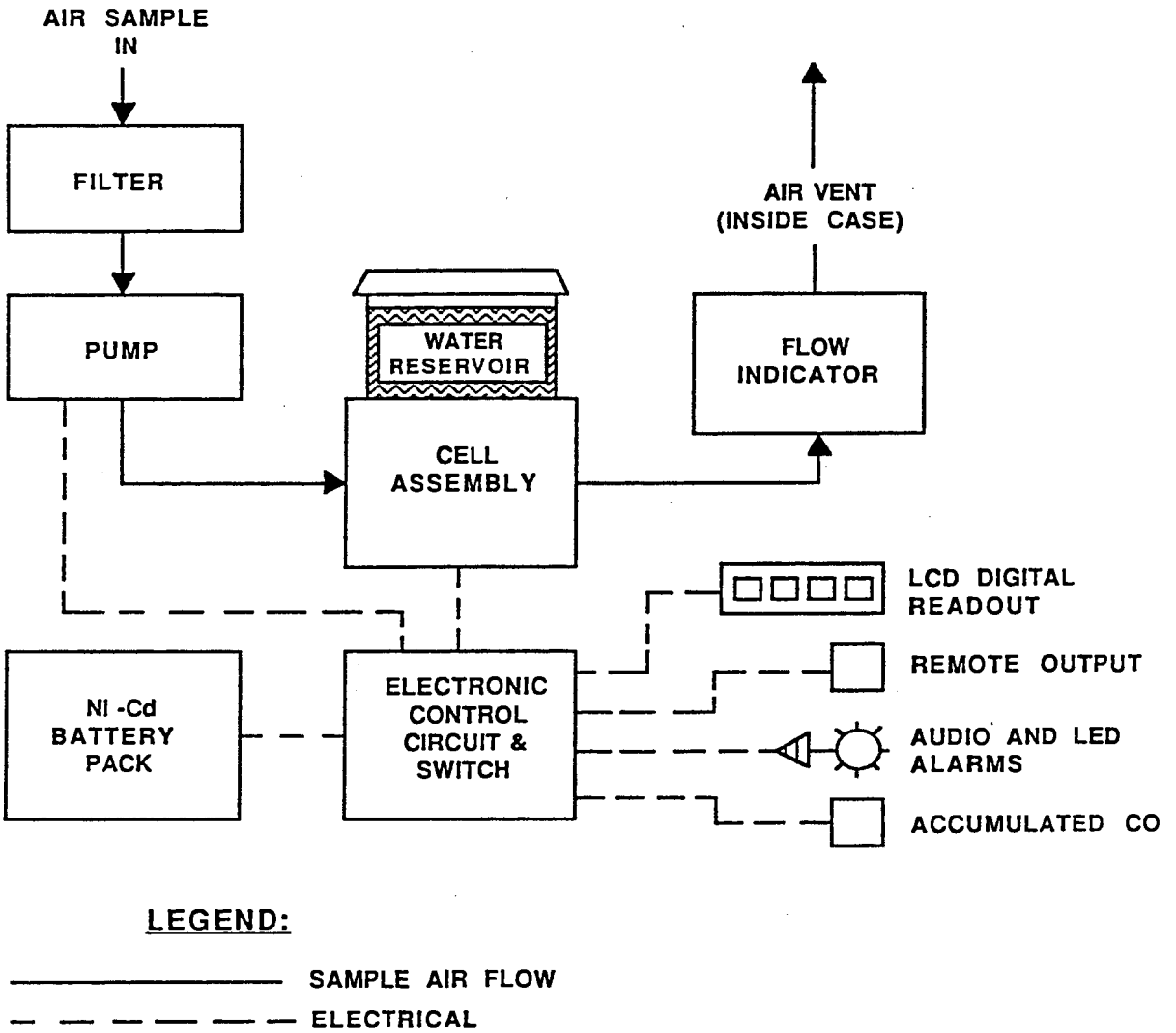

Figure 2. CO Monitor Functional Schematic

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OPERATING PROCEDURES FOR A PORTABLE CO DETECTION SYSTEM

1. Scope

1.1 This procedure is intended to screen indoor air environments for carbon monoxide. Screening is accomplished by monitoring CO within an area onsite using a portable detection system (Portable Air Sampling System (PASS), R. Jay Equipment Co, Winston-Salem, NC, (919) 741-3582, or equivalent). This procedure is not intended to yield quantitative or definite qualitative information regarding the substance detected. Rather, it provides a profile of the occurrence and intensity of CO which assists in placement of fixed-site monitors and the selection of individuals for the use of personal exposure monitors.

1.2 The PASS is contained within an ordinary briefcase which allows environmental measurements to be made unobtrusively without affecting behavior of occupants (See Figure A-1). The CO monitoring system is comprised of a sampling pump and a detector utilizing an electrochemical measurement principle. During normal operation, the output of the detector feeds directly to a data logger. The PASS also monitors for nicotine and respirable suspended particulate (RSP) matter. The temperature and barometric pressure of the environment are also monitored. Data is stored on a microcomputer within the briefcase and can be transferred to a computer for data analysis at a later time. For the benefit of the user, this write-up describes only the PASS operations of the CO detection system. However, there is mention of other parts in the system (i.e., power supply) because they are interconnected in the current design.

2. Applicable Documents and References

2.1 Operator's Manual for Portable Air Sampling System (PASS), R. Jay Equipment Co., Winston-Salem, NC, (919) 741-3582, September, 1988.

2.2 Guy B. Oldaker III and Fred C. Conrad, Jr., "Estimation of Environmental Tobacco Smoke on Air Quality Within Passenger Cabins of Commercial Aircraft," Research and Development Dept., Boyman Gray Technical Center, R. J. Reynolds Tobacco Co., Winston-Salem, NC 27102, October, 1987.

2.3 United States Patent Abstract, Patent No. 4,786,472, November 22, 1988.

3. Summary of Method

3.1 Sample air is introduced into the system through an inlet port. Air from the inlet port is passed through Tygon tubing to a diaphragm pump. The pump then passes the sample air from the inlet port to an electrochemical sensor cell where CO is oxidized to CO_2. The oxidation of CO produces a voltage signal proportional to the CO concentration present in the air sample. Data generated from the CO oxidation are obtained and stored in a

microcomputer over discrete periods of time (e.g., at about one minute intervals). Figure A-1 provides a complete illustration of the PASS.

3.2 The PASS CO detection system employs an electrochemical sensor cell that provides an analog signal proportional to the level of CO being monitored. The analog signal is connected to the PASS data logger. The sensor head consists of durable glass reinforced polypropylene junction box that is coupled to the gas sensor and signal conditioning circuitry. The PASS CO sensor operates on the same principle (i.e., electrochemical oxidation) as the GE CO monitor described in Section 3.4 of Method IP-3C. In the PASS sensor, sample air combines with water in the following reaction: $CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$ (at the anode). The hydrogen ions and electrons combine to form the following reaction: $1/2\ O_2 + 2H^+ + 2e^- = H_2O$ (at the cathode). When both of the reactions are combined, the following reaction occurs, causing CO in the sample to be oxidized to CO_2: $CO + 1/2\ O_2 \rightarrow CO_2$. When CO is oxidized, electrons travel through a circuit which produces a current directly proportional to the CO concentration in the air sample. Table A-1 provides operating specifications for the CO sensor.

4. Significance

4.1 Recent interest towards studying the nature, characteristics and quality of indoor air has developed. Of particular interest is sampling and analysis of indoor air in a specific setting over a fairly long period of time. However, for a realistic and representative assessment of the indoor air, it is often necessary to measure several substances over a range of known conditions. Unfortunately, the sampling and collection of air samples often involve noisy, large, obtrusive equipment. Such equipment often does not provide realistic or representative assessments of a particular setting due to the fact that the obtrusive nature of the equipment can tend to affect human behavior during data collection periods.

4.2 The PASS provides a flexible system for sampling air in a wide variety of indoor environments. The portable device is self contained, is easily operated, and is unobtrusive. The device can measure more than one substance as well as relative conditions of the environment such as temperature, relative humidity and atmospheric pressure. The device can be operated over relatively long periods of time. Thus, it is possible to monitor environmental air for predetermined substances on a continuous basis while having the ability to identify short term changes in concentration of particular substances.

4.3 The PASS has been commercially available for three years and can be purchased from the reference provided in section 1 of this appendix. The CO monitoring device has been purchased from various foreign countries as well as industrial parties in the United States.

4.4 For purposes of the Compendium, the PASS is presented as a means to screen indoor environments in order to locate fixed-site monitors. The fixed-site monitors employ NDIR spectrometry based on federal reference methods. To meet the needs of the user, this Appendix provides information on the PASS to inform the user of its capabilities and to furnish the information necessary to construct a similar instrument.

5. Definitions

Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with applicable ASTM procedures. 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.

6. Interferences

6.1 When sample air passes through the monitoring system, the sensor cell may tend to become dry. Interferences may occur if the sensor cell is allowed to become dry.

6.2 Daily calibration of the CO monitoring system is recommended until the operator becomes familiar with and documents the drift typical of the individual PASS.

6.3 The PASS is powered by two battery packs (i.e., one for the data logger and one for the sampling pumps) and can be operated continuously for at least 20 hours. It is strongly recommended that operators check voltages of batteries before each use of the PASS for sampling. Voltages are deemed adequate if above 12 volts for the battery pack serving the data logger and above 5 volts for the battery pack serving the sampling pumps. These voltage limits were selected to guarantee the availability of sufficient power to collect one one-hour sample. In the event that either of these limits is not met, all cells are replaced. While conservative, this practice is supported by the fact that the cost of batteries is insignificant when compared to the cost of lost data and more important lost time.

7. Apparatus

7.1 Briefcase or portable container - appropriate housing which allows for easy movement of the sampling system and its components. An example of a suitable container is a hard sided leather briefcase (National Luggage, Montreal, Canada, or equivalent). The sampling components should be held in place with an appropriate material (i.e., a machined polymethylmetha-crylate sheet or polyurethane foam).

7.2 Carbon monoxide detector - a suitable means of detecting CO such as an electrochemical sensor cell where CO is oxidized to CO_2 producing an electrical current proportional to CO concentration in the air sample (Neotronics Ltd., Gainesville, GA, (800) 535-0606, Model Otox 2001 or equivalent).

7.3 Tygon tubing - used to connect sampling components, with an inner diameter of 1/4" (Tygon by Norton Co, Akron, OH).

7.4 Carbon monoxide pump - used to draw in sample air to detection system (Gillian Instrument Corporation, 8 Daives Highway, Wayne, NJ, (201) 831-0440, P/N 10037, or equivalent).

7.5 Data logger - data storage means that provides for collection and storage of data relating to the following sampling parameters: CO values, time periods over which known

quantities of sample air pass through pumps and amount of voltage used by the pumps (Campbell Scientific, Inc., Logan, UT, (801) 753-2342, 21x Micrologger, or equivalent).

7.6 Relative humidity probe - used to monitor relative humidity of the sampling environment (Rotronic Instrument Corp., Huntington, NY, (801) 753-2342, MP-100F Relative Humidity Probe, or equivalent).

7.7 Cassette recorder - used to record sampling data (Campbell Scientific, Inc., Logan, UT, (801) 753-2342, Model RC35, or equivalent).

7.8 Cassette interface cable - provides for sampling data input into a computer (Campbell Scientific, Inc., Logan, UT, (801) 753-2342, C-20 Cassette Interface, or equivalent).

7.9 Flowmeter - 500 mL/min capability used to calibrate CO sampling pump (SKC South, Inc., P. O. Box 2016, Appomattox, VA 24522, (804) 352-7149, Film flowmeter, Cat. No. 307-2000, or equivalent).

7.10 Brass sampling port - sample air is introduced into the detector through the sampling port, suitable ports are Swagelok brass bulk head reducer tube fittings. The other portion of the fittings are machined and polished to a square or circular shape for aesthetic purposes (Crawford Fitting Co., 29500 Solon Rd, Solon, OH 28213, Part # B-400-R1-4, or equivalent)

7.11 Power source - the PASS is powered by two battery packs. One battery pack (i.e., four D cells each rated 1.5 V) powers the CO monitoring system pump. The second battery pack (i.e., eight AA cells pack rated at 1.5 V) powers the data logger and CO monitoring system detector. Experience has shown that Duracell™, non-rechargeable alkaline cells are used in the batteries for reasons of cost, availability, reliability, and power capacity. Other cells having comparable power capacity should be acceptable.
Note: All cells must be alkaline.

8. Reagents and Materials

8.1 Gas cylinder containing 0.5 ppm CO in air, working standard, certified, cylinder size AL (Scott Specialty Gases, Rt. 611, Plum-steadville, PA, 18949, (215) 766-8861, or equivalent).

8.2 Gas cylinder containing 50 ppm CO in air, working standard, certified, cylinder size AL (Scott Specialty Gases, Rt. 611, Plumsteadville, PA, 18949, (215) 766-8861, or equivalent).

8.3 Two-stage regulator for CO cylinder - two (2) required, one for each cylinder, used with non-corrosive, high purity gases (Scott Specialty Gases, Plumsteadville, PA 18949, (215) 766-8861, Model 18, or equivalent).

8.4 Gas sampling bag - 22 L, 16" X 29" with on 1 off valve (Calibrated Instruments, 731 Saw Mill River Rd, Ardsley, NY 10502, (914) 693-9232, or equivalent).

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8.5 Twp piece tubing connectors, that are different sizes, used to connect flowmeter to sampling port for pump calibration (Cole-Palmer Instrument Co., 7425 N. Oak Parks Ave, Chicago, Il 60648, (312) 647-7600, Cat. No. J-6289-10 (12/Pkg), or equivalent).

8.6 Port connector for CO port - brass port connector (Charlotte Valve and Fitting Co., 7838 North Tryon St., Charlotte, NC 28213, (704) 598-7040, Part #B-401-PC, or equivalent).

9. PASS Preparation

9.1 Calibration of the CO monitoring system should be done just before the PASS is used for sampling. The operator should allow sufficient time because calibration can take up to 1.5 hours if both zero and span potentiometer require significant adjustment. The operator should check that sufficient battery voltage is available to power both the data logger and the pump within the PASS.

9.2 During sampling, measurements are recorded by the data logger at 60 second intervals. To facilitate calibration of the CO system the interval is changed to 1 second. (Note that this change in the program causes loss of the PASS identification number. The operator must re-enter the PASS identification number at the completion of calibration.) The interval change is accomplished with the following procedure. First, key in the sequence: * 1 A. The programmed sampling interval is displayed (usually 60). The operator should then key in the sequence: * 1 A, and return to recording mode by keying in the sequence: * 0.

9.3 Pump Calibration

9.3.1 The CO sampling pump should next be calibrated to a flow rate of 500 mL/min at standard conditions of temperature and pressure. The flowmeter is connected directly to the CO sampling port with the appropriate size tubing connector. Alternately, the flowmeter can be connected to the tubing leading to the CO pump by carefully disconnecting the CO pump tubing from the CO port fitting inside the briefcase.

9.3.2 The CO pump is a non-compensating, voltage regulated pump. It is very sensitive to the pressure drop of the calibration device. A soap-film flowmeter or similar device is highly recommended. Operators should use consistently the same tubing and fitting for all calibrations. The tubing and fitting should be sized to minimize the pressure drop.

9.3.3 After activating the CO pump with the slide switch under the handle, the pump flow rate is adjusted at the potentiometer labeled "PUMP" just below the label "CARBON MONOXIDE DETECTOR." The voltage supplied to the CO pump is next displayed by keying in the sequence: * 6 7 A. This voltage should be carefully recorded, as in the future, CO pump calibration can be accomplished without a flowmeter by simply adjusting the CO pump voltage to this value.

9.3.4 Once set, the CO pump voltage should not change unless the "PUMP" potentiometer is inadvertently adjusted. No change in the CO pump voltage or flow rate is noted over a two-month testing period. Set the data logger to display the CO concentration (ppm) by keying in the sequence: * 6 3 A.

9.4 Calibration Materials

9.4.1 Two gas sampling bags and two calibration gases are required for calibration. Concentrations of 0.5 ppm and 50 ppm carbon monoxide in air (Working Standard Certified) should be used. Purchase of 0.5 ppm CO rather than 0 ppm CO is recommended so that the detector response to CO is measured on the low end of the calibration range. Preparation of calibration gases takes the supplier a minimum of two weeks; delivery can add another week. Therefore, gases should be ordered as far in advance as possible. The exact concentration of each cylinder of gas is provided by the supplier and that concentration should be used by the operator during calibration.

9.4.2 For the supplier, 0.5 and 50 ppm are target concentrations. Blended and analyzed calibration gases may end up with concentrations, for example, of 0.491 and 49.98 ppm CO. For ease of reference, 0.5 and 50 ppm will be used within these instructions to denote the low and high concentrations of CO used for calibration.

9.5 Calibration Procedure

9.5.1 Fill the two gas sampling bags 1/2 to 2/3 full of CO. Do note overfill bags, as a sudden burst of gas may cause a fluctuation in the flow rate and the CO detector response. Turn "ON" the PASS with the handle switch. Open the valve of the 0.5 ppm gas bag and quickly connect the bag to the CO pump inlet. Place the gas bag in a fixed position on a surface; do not allow either the bag or tubing to develop crimps during calibration as these may cause fluctuations in the flow rate which in turn influence the CO detector response.

9.5.2 Operators should ensure that bags remain as stationary as possible to prevent pressure (and therefore, flow rate) fluctuations during calibration. Wait ten minutes. If necessary, adjust the "ZERO" potentiometer until the CO concentration of the 0.5 ppm gas provided by the supplier is displayed on the data logger. After adjustment of the potentiometer, continue to observe the display concentration to be sure a stable reading is obtained. Remove the gas bag and quickly close the valve on the bag to prevent contamination by indoor air.

9.5.3 Operators may wish to note that within the program provided with the PASS that the last entry on the line labeled "READ CO ANALYZER" is "-2." The CO monitoring system is incapable of producing negative readings. To avoid difficulty in setting the "ZERO", the system is electronically offset by 2 ppm. With the exception of the program line mentioned above, no indication is given by the PASS that adjustments of CO concentration data are made. Again the exact concentration of each cylinder of gas as provided by the supplier is the value used during calibration.

9.5.4 The 50 ppm CO can be introduced immediately after the bag containing the 0.5 ppm CO has been removed. It is important that the operator wait the full 10 minutes before setting the "SPAN" potentiometer to the nominal value of the high concentration.

9.5.5 Operators are encouraged not to be tempted into short-cutting the calibration procedure by introducing gases for periods less than 10 minutes. When 0.5 ppm CO gas is introduced, a stable reading may be obtained before the entire ten minute period elapses. When the 50 ppm gas is introduced, on the other hand, the CO monitoring system initially responds rapidly; however, this rate slows substantially as the final, stable reading is

approached. Adjustments made to calibration before 10 minutes have elapsed and therefore before a final, stable reading has been obtained can lead to inaccurate CO measurements or to extra time being spent in calibration. Consequently, calibration is completed most quickly and accurately if the full ten minutes elapse before the "SPAN" potentiometer is adjusted. The 22 liter gas sampling bag filled to 1/2 to 2/3 full contains enough gas for ten minutes of sampling.

9.5.6 Following adjustment of the "SPAN" potentiometer, allow the PASS to sample indoor air for approximately 5 minutes to allow the detector to return to low levels without expending the calibration gas. If any adjustments to either potentiometer are made, then the entire process beginning with the introduction of the 0.5 ppm CO gas followed by the 50 ppm gas and then indoor air must be repeated until neither potentiometer requires adjustment. Last, turn "OFF" the PASS and reset the sampling interval to 60 seconds (or the desired time interval) by keying in the sequence: * 1 A 60 A. Return the PASS to the recording mode by entering: * 0.

9.6 Transporting the PASS

9.6.1 The PASS is a fairly rugged piece of equipment; however, it is intended for use in indoor environments. Consequently, operators should ensure that PASS is not exposed to extreme environmental conditions including precipitation, and temperatures below 40°F (4°C) and above 100°F (40°C).

9.6.2 The PASS is designed to be unobtrusive. There are occasions when this aspect can be a disadvantage. Operators should be aware that the technology may disturb people sensitive to suspicious activities. However, experiences to date indicate that questions seldom arise when PASS's are checked through security at airports located in the United States. When questions have arisen, the PASS documentation (for example, the operator's manual) has proven to be invaluable in demonstrating the true nature and purpose of the system.

9.6.3 Operators in the United States should note that because the PASS includes the 21X Micrologger, U.S. laws require an export license be obtained in order to carry or to ship the PASS to certain foreign nations. An application for an export license may be obtained from the U.S. Department of Commerce. Failure to comply with the law may result in fines and permanent confiscation of the entire PASS. It is therefore highly recommended that operators seek legal counsel in considering export of the PASS.

9.7 Locating the PASS

The selection of sampling location is governed by the objective of obtaining a sample that represents exposure to CO. Unfortunately, ideal locations seldom exist; instead, users typically must compromise in selecting locations. Guidelines relative to the selection of sampling location are as follow:

- PASS's should be positioned at least two feet from walls and as far from corners as practical.
- PASS's should be placed from two to seven feet above the floor, for example, on tabletops, unoccupied seats, desktops, filing cabinets, ledges, etc.

- PASS's should be positioned such that the air being sampled has an unobstructed path to the inlet ports. The narrow side of the briefcase containing the inlet ports should be flush with or extend beyond the surface the PASS is placed on. The exhaust ports should be unobstructed. Obstruction of ports may cause variable pump flow and/or pump failure.
- PASS's should be placed as far as practical from the direct influence of ventilation sources such as ducts, open doors or windows, or fans.
- PASS's should not be exposed to the direct influence of sidestream or mainstream smoke, or other sources of CO.
- Sampling operations should be as unobtrusive as possible in order not to influence the behavior of occupants.
- Technicians should have as clear a view of the indoor environment as practical to facilitate observations.
- PASS's should not be moved once positioned, and
- Technicians should not smoke during sampling operations in order to avoid inconsistent results.

10. PASS Operating Procedures

10.1 The PASS remains closed for sampling. PASS operation involves simply moving the exterior switch to the "on" position. In performing this operation, it is important that the switch be fully engaged, because it is often very difficult to determine unobtrusively whether the PASS is indeed operating. The "on" direction of the switch is indicated by a green label affixed beneath the switch plate; this label is uncovered when the switch is moved toward the "on" position.

10.2 As a fail safe measure, it is strongly recommended that operators record the start and stop times for all sampling periods. By doing this, operators ensure that volumetric results for the nicotine and particulate matter samples may still be obtained in the event of loss of power to the data logger in the interim between sampling and data retrieval.

11. Observations and Recordkeeping

11.1 Clearly, observation and recordkeeping practices will depend on the nature of the monitoring survey. For the purpose of this document, PASS is employed for characterizing environments with respect to exposure to CO. Presented in the following paragraphs are guidelines which PASS operators may consider in implementing such investigations.

11.2 The following subject areas may be considered in connection with observation and recordkeeping practices. These include: PASS location in the environment sampled; sources of CO other than cigarettes; characteristics of the heating, ventilating, and air conditioning (HVAC) system; and substantial deviations from the guidelines listed in Section 9.7.

11.3 The HVAC system can have a profound effect on results; therefore, it is important to obtain as thorough a characterization of the HVAC system as practical. Of prime importance is estimating the volume of the environment served by the HVAC system. Additionally, operators should attempt to identify locations of air supplies and returns, fans,

and other factors affecting ventilation, such as doors and windows. Often, the degree of air mixing can be assessed based upon the manner in which cigarette smoke disperses. The inclusion of detailed guidelines regarding the characterization of HVAC systems is, unfortunately, beyond the scope of this document. A sampling data sheet is provided in Figure A-2.

12. Data Retrieval and Interpretation

Several methods exist for transferring data from the data logger. This document addresses only data transfer operations involving use of a cassette recorder. This method was incorporated in the PASS approach because it allows information to be recovered easily from the field.

12.1 Voltage Checks

12.1.1 The data logger consumes power in controlling operation of the cassette recorder during data transfer. If the battery pack serving the data logger has gone through periods of extended use, insufficient power may be available to transfer data successfully. In addition, it is also possible that the data logger, if in this condition, may lose stored data in the process of attempting transfer. Because of the above concerns, it is recommended that PASS's be placed in the alternate power mode, if possible, before transfer operations are initiated. A cable and associated transformer (charger) with plug is provided with each PASS for this purpose. The transformer having the plug goes to any convenient wall socket with 120V 60Hz rating; and the other plug goes to the jack located on the PASS's front panel and below the data logger's keyboard. In the alternate power mode, battery power is not used by the data logger and is only used by the CO detector.

12.1.2 If the batteries serving the data logger have been used extensively, and additionally, if alternate power is unavailable, operators should check the battery pack voltage before attempting transfer. Checking entails keying the sequence: *6 5 A. Power for data transfer is not recommended.

12.1.3 The operator may find the data logger's display to be clear before checks can be made. This condition does not necessarily indicate that data are lost and therefore transfer is no longer worthwhile. As the last portion of available battery power is consumed, the display is affected before the data logger's memory. If the "LOG 1" signal can be returned to the display after connection is made to the alternate power supply, then it is highly likely that the data and the program have been retained.

12.2 Data Transfer From Logger

Data stored in the data logger are transferred to a cassette tape, which may then be taken to another location where transfer to computer may be performed. The data transfer procedures are described below.

12.2.1 Cassette Recorder Preparation - A data tape (as distinguished from a program tape) is inserted into the cassette recorder and the tape is then rewound. When rewound, most of the tape will appear on the left spool as viewed from the front of the cassette recorder. Operators should ensure that recording is started beyond the header on the tape.

With the tape rewound, disconnect the plug labeled "ear" from the jack on the cassette recorder. Next, engage the key labeled "Record" and allow the tape to advance several seconds before stopping. In addition to ensuring that the header will not interfere with recording of data, this operation also erases any information which may have existed on the tape from earlier uses, thereby preventing interference with data transfer which otherwise could result. The volume control on the cassette is then set to the "5" position.

12.2.2 Logger and Cassette Recorder Connection - The data logger and the cassette recorder are connected with a cable having at one end one large plug and at the other end three small plugs. The small plug labeled "EAR" is inserted into the jack labeled "EAR" on the cassette recorder. The remaining two plugs are inserted into the jacks labeled "DC 6V" and "MIC"; these connections can be made in only one manner. The large plug is then connected to the data logger at the socket labeled "SERIAL I/O" located above the keyboard.

12.2.3 Sampling Data Transfer With Cassette Tapes - The following steps detail the data transfer procedure:

12.2.3.1 On the data logger's keyboard, key in the sequence: * 8 A. Record the number displayed by the logger. This number is important because it allows the data transfer operation to be easily repeated in the event that the first attempt at transfer is unsuccessful. The number refers to the memory location of the first data point.

12.2.3.2 Continue the process by keying an "A" and recording the number displayed by the data logger. This number is important for the same reason described above and corresponds to the memory location of the final data point. Next, key in the sequence: A 1.

12.2.3.3 On the cassette recorder, simultaneously engage the keys labeled "RECORD" and "PLAY". Therefore enter "A" on the logger's keyboard. Data transfer should then occur.

12.2.3.4 The progress of data transfer may be observed from the data logger's display. (Data transfer is also indicated by blocks of noise produced by the cassette recorder.) Transfer, which involves blocks of data, is complete when the displayed number no longer changes and is equal to the second number recorded earlier, namely, the location of the final data point. The cable is then disconnected from the cassette recorder and data logger. The cassette recorder must be disconnected from the cable in order to check that data transfer was successful.

12.2.3.5 Rewind the cassette tape, engage the "PLAY" key on the cassette recorder, and listen for blocks of noise signifying the successful transfer of blocks of data. If no noise occurs, repeat the data transfer procedure with the following modifications.

12.2.3.6 On the logger's front panel, key in the sequence: * 8 A and enter the number recorded in step 12.2.3.1.

12.2.3.7 Next, key in "A" and enter the number recorded in step 12.2.3.2. Proceed as described in 12.2.3.3.

12.2.4 Data Storage on Cassettes - Two considerations relating to bookkeeping should be observed if cassette tapes are to be used to store multiple sets of data. First, operators

should record the cassette recorder's tape counter readings corresponding to data sets. For obvious reasons, numbering should start from the totally rewound position with the counter reset to "000". Second, operators should provide spacers (that is, periods of no data) between adjacent sets of data. Spacers are added to the recording at the conclusion of transferring a set of data from the data logger to the cassette recorder. Accordingly, after transfer is completed, disconnect the plug labeled "ear" from the corresponding jack on the cassette recorder and allow the tape to run at least 5 seconds before replacement. (Used tapes may be cleaned by the same process.)

12.2.5 Sampling Data Transfer with Computers - Data transfer from the cassette to computer file requires either a Campbell Scientific, Inc. C20 Cassette Interface or a PC201 "Clock-SI0 Tape Read Card & Software for IBM-PC," or equivalent. Descriptions relating to the use of these devices are beyond the scope of this document. Operators are referred to the appropriate literature from the software manufacturer. It is the PASS operator's responsibility to implement the transfer operations to computer systems.

13. Sample Calculations

13.1 The following paragraphs presume that the data have been transferred to a computer. Figure A-3 illustrates the appearance of transferred PASS data and identifies the data entries. This table was obtained through use of a PC201 board and a Compaq portable PC and includes data from nicotine and RSP sampling. LOTUS 1-2-3® software was used to label the columns.

13.2 The data record provides valuable information regarding the quality of the data and samples. Operators are encouraged to scan visually data records before initiating calculations in order to obtain a general assessment of the quality of the overall sample. The temperature, barometric pressure, and CO concentration entries represent one set of data deserving attention. With experience, operators can scan the record in a matter of seconds and assure that unusual data are absent.

13.3 The voltage to the sampling pump of the CO monitoring system should be checked for consistancy 1) throughout the sampling period and 2) relative to its value for the last calibration. If the voltage has changed since the last calibration, operators should assume that the calibration of the CO monitoring system has changed as well. Operators may have to quantify the change in calibration in order to ensure the acceptable quality of the recorded CO concentration data. Experience has shown that voltages to CO sampling pumps are constant and generally change as a result of unintentional adjustment of the associated potentiometer on the PASS's control panel.

13.4 Sampling Times - Sampling times are calculated from the data record by summing the number of minute entries for each block of data. Data blocks are readily distinguished by their accompanying clock times or dates. For the example in Figure A-3, sampling time was 10 minutes.

13.5 Carbon Monoxide Concentration Data - Carbon monoxide data are readily manipulated with Lotus 1-2-3 software. Statistics often computed include maximum,

minimum, and mean concentrations. Graphics software allow for strip chart type records to be produced.

Table A-1. CO Sensor Operating Specifications

Range: 0-50 ppm, 0-100 ppm, 0-500 ppm

Signal Outputs Available: 2 to 4 mA, 4 to 20 mA, 0-1 Volt

Input Voltage: 8-30 Volts DC (at head)

Power Consumption: < 1 Watt

Operating Temperature: -15°C to +50°C

Humidity: 0-99 %RH, non-condensing

Sensor Life: 12 months guaranteed, 24-36 months typical

Housing: Industrial Junction

Size (Mounting): 120 mm/120 mm/70 mm

Cable Entry Size: 20 mm

Outputs: 2-10 mA loop, 4-20 mA loop, 0-1 Volt

Connections: 2 wire (current outputs), 4 wire (voltage outputs)

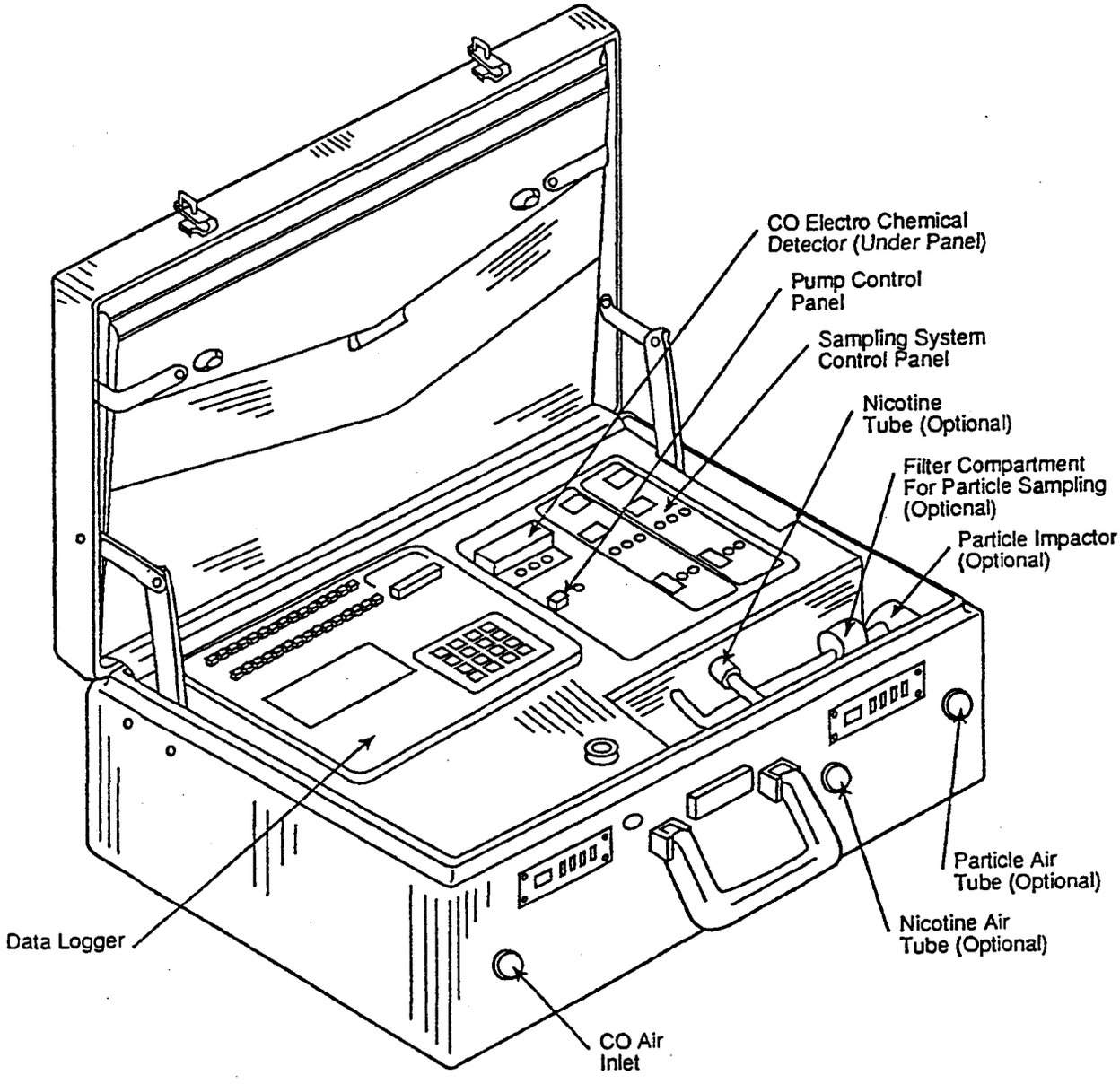

Figure A-1. Portable Air Sampling System

General Information:

Date: _____ Operator(s): _____ PASS ID: _____
Time: _____ Start: _____ Stop: _____

Location: (Address)

_____
_____

Description : _____
_____
_____
_____
_____

Heating, Ventilating, and Air Conditioning (HVAC) System, Information:

No. of Supply Vents: _____ No. of Return (intake): _____
Size of Supply Vents: _____ Size of Return (intake): _____

Air Conditioning Information:

1. Air Cooling System
   Is A/C on? _____ If yes, how long during sampling? _____
   Is A/C Central ____ Window ____ Other ____

2. Fans
   Ceiling Fans on? _____ If yes, how long during sampling? _____
   Window Fans on? _____ If yes, how long during sampling? _____
   Exhaust, Stove on? _____ If yes, how long during sampling? _____

3. Entrances and Exits
   Doors Open _____ Closed _____
   Windows Open _____ Closed _____
   Curtains and Blinds Open _____ Closed _____

4. Combustion Sources
   Heaters _____ Cigarette Smoking _____
   Stoves _____ Parking or Traffic _____
   Fireplace _____

Figure A-2. PASS Field Data Sheet

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OUTPUT ID	PASS NO	J DATE	TIME	TEMP	BAR PRESS	CO	21X VOLT	SKC VOLT	CO VOLT	NIC FLT	TMP FLT
109	11	187	930	24.95	743	1.280	11.18	5.449	1.878	0.003	0.004
109	11	187	931	24.99	743	1.645	11.17	5.389	1.878	0.004	0.004
109	11	187	932	25.04	743	1.976	11.16	5.404	1.878	0.004	0.004
109	11	187	933	25.06	743	2.208	11.15	5.531	1.878	0.003	0.004
109	11	187	934	25.11	743	2.274	11.15	5.378	1.877	0.005	0.005
109	11	187	935	25.13	743	2.241	11.14	5.359	1.878	0.004	0.005
109	11	187	936	25.15	743	2.208	11.13	5.354	1.878	0.003	0.004
109	11	187	937	25.18	743	2.207	11.13	5.334	1.878	0.003	0.004
109	11	187	938	25.20	743	2.241	11.12	5.317	1.878	0.004	0.004
109	11	187	939	25.23	743	2.207	11.11	5.298	1.878	0.004	0.005

OUTPUT ID	=	User program number 1 plus program line number 09, hence 109.
PASS NO	=	PASS identification number
J DATE	=	Julain Date for each row of data
TIME	=	Time, on a 24-hour clock, for each row of data
TEMP	=	Temperature, ^{0}C
BAR PRESS	=	Barometric pressure, torr.
CO	=	Carbon monoxide, ppm.
21X VOLT	=	Voltage, v, to batteries serving 21x data logger.
SKC VOLT	=	Voltage, v, to batteries serving nicotine and particulate matter pumps.
CO VOLT	=	Voltage, v, to batteries serving CO pump.
NIC FLT	=	Fault status of nicotine pump.
TPM FLT	=	Fault status of particulate matter pump.

Figure A-3. Example Data Table

Chapter IP-4

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR

- **Method IP-4A - Perfluorocarbon Tracer (PFT)**
- **Method IP-4B - Tracer Gas**

1. Scope

1.1 Method IP-4A is a description of the sampling and analytical protocol for air exchange rate (AER) using perfluorocarbon tubes (PFT) and passive samplers (i.e., capillary adsorption tubes - CATS). This methodology was developed by Brookhaven National Laboratory as an inexpensive way of measuring AER in large-scale field studies. The PFT emitters are utilized indoors to measure the rate of air exchange which occurs over time. This method may be used with multiple PFT source types to allow inter-compartmental flows as well as whole-house AERs to be calculated. The emitters are placed in the dwelling of interest a day in advance of the passive samplers. The source emissions are collected on the passive samplers which are analyzed by a gas chromatograph coupled with an electron capture detector (GC-ECD) for the air exchange rate. If more than one source/sampler is used in a single dwelling, the average of all the calculated AERs is computed.

1.2 Method IP-4B describes the determination of the air exchange rate by the release of sulfur hexafluoride (SF_6) tracer gas. The ambient air is subsequently sampled by commercially available automated syringe samples and analyzed for trace amounts of SF_6 by gas chromatography with electron capture detection or monitored on-site by tracer gas monitors. This concentration-decay technique (also called tracer-gas dilution) has been designated as a standard practice by the American Society for Testing and Materials. In this technique, a small amount of tracer gas is injected into the indoor airspace and thoroughly mixed. Indoor concentrations "decay" with time as the exfiltrating air removes the tracer. The general procedure involves releasing tracer gas at one or more points at sufficient quantities to produce useful initial concentrations. The method of release and quantities involved depend on the internal volume of the structure, the configuration of the air-handling system, estimates of allowable versus useful concentrations, and the sensitivity of the detection system.

2. Applicability

2.1 For some time, it has been a primary focus of the U.S. EPA to compile the missing exposure data needed to complete the risk equation. The data from exposure measurements help to evaluate progress in the efforts to control environmental pollution and provide guidance for modifying approaches to make them more effective. Ultimately, the effectiveness of the regulatory process on reducing pollutant levels may be judged by exposure measurements.

2.2 In addition to measuring mass and elements, total exposure assessment studies should be organized to provide background information on indoor and outdoor air pollutant concentrations. Emphasis should be placed on collecting information on indoor air

pollutant concentrations or the relationship between indoor and outdoor air levels. Air infiltration rates are a critical component in the process of determining the influence of outdoor pollution on indoor concentrations.

2.3 Air infiltration represents an important part of the heating and cooling load of residential, commercial and industrial buildings. The heat loss associated with air leakage through the enclosure of a typical house may be as much as 40% of the total heat load. Considerable energy savings can be realized by reducing the air infiltration in a structure.

2.4 Air leakage is also an important parameter in indoor-outdoor air pollution relationships.

Method IP-4A

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR USING PERFLUOROCARBON TRACER (PFT)

Method IP-4A

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR USING PERFLUOROCARBON TRACER (PFT)

1. Scope

1.1 This document describes the protocol for the measurement of an integrated air exchange rate (AER) between the outside and inside of detached dwellings over periods ranging from approximately 10 hours to several weeks. Perfluorocarbon tracer (PFT) emitters are utilized indoors to measure the rate of air exchange which occurs over time. This method may be used with multiple PFT source types to allow calculation of both inter-compartmental flows within houses and whole-house AERs.

1.2 The methodology was developed by Brookhaven National Laboratory as an inexpensive way of measuring AER in large-scale field studies. It is currently employed in the Particle Total Exposure Assessment Methodology (P-TEAM) program conducted by the U.S. Environmental Protection Agency (U.S. EPA) and in a 5000 building home measurements study. The Danish Building Research Institute and the Helsinki University of Technology have established analytical labs which offer full AER services. In addition, there are several groups in England who are in the process of establishing AER service facilities.

1.3 The equipment described herein can be utilized to measure air exchange on neighborhood or urban to regional scales. Neighborhood scale monitoring requires measurements to identify the contributions of specific sources. Urban/regional scale measurements would identify important reactant areas.

2. Applicable Documents

2.1 ASTM Standards

D 1356 Definitions of Terms Related to Atmospheric Sampling and Analysis
E 355 Recommended Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

Ambient Air Studies (1,2)
U.S. EPA Technical Assistance Document (3)

3. Summary of Method

3.1 Air exchange rate (AER) is measured by using the perfluorocarbon tracer (PFT) system. It is designed to measure the integrated rate of exchange of air between the outside and inside of detached dwellings, as well as the exchange between zones in multizone structures. The system is capable of measuring average air exchange rates over periods ranging from about 8 hours to several weeks (4-7).

3.2 Each dwelling can be treated as a single box with AER calculated as if interior partitions are nonexistent or it can be compartmentalized. Perfluorocarbon tracer (PFT) gas is released from one to several locations inside each dwelling chosen to provide uniform PFT dispersion throughout the structure. The tracer gas is allowed to equilibrate in the

dwellings and is then collected inside capillary adsorption tubes (CAT) by diffusion onto activated charcoal spherules. The diffusion rate, and hence the sampling rate, is set by controlling the geometric dimensions of the CAT. The impact of temperature on diffusion rates is generally ignored. Sampling rates are calculated for 25°C. The CAT samplers are located around each dwelling and their PFT burdens are averaged for the calculations. The AER for each home is calculated using laboratory measurements of the collected PFT, field measurements of the structure volumes, and the sampling duration.

3.3 The laboratory analysis (4-7) of PFT collected in the CATs is performed on a gas chromatograph system equipped with an electron-capture detector (GC-ECD). The GC-ECD is first calibrated with PFT standards then a calibration curve is constructed and used to determine the type(s) and amount(s) of PFTs present in the sample.

3.4 For analysis, the samples are thermally desorbed into a 95% nitrogen-5% hydrogen carrier gas stream through a Nafion column to remove water vapor, which can produce an interfering ECD response as well as degrade the ECD performance. The sample then passes through a special catalytic column to oxidize potentially interfering fluorochlorocarbon compounds; it then flows to a precolumn to effect a coarse separation. Sample compounds continue to flow to a Porapak QS adsorbent column trap where earlier eluting compounds pass through; PFTs are retained, and later eluting compounds are vented via a time-programmed switching valve before they reach the QS trap.

3.5 After all PFTs have been trapped, the flow is reversed by a time-programmed switching valve, and heat is electrically applied to the trapping column to release the adsorbed PFTs. The PFTs now flow to a second catalytic column which mimics the first catalytic column, and finally to a main chromatographic column which separates the compounds prior to detection by the ECD. When a compound reaches the ECD, it induces a voltage signal which is sent to a data acquisition/reduction system.

3.6 The detection system consists of a dedicated integrator which receives the signal, transforms it for graphical presentation, and finally calculates concentrations of the unknown PFTs using the stored calibration curve.

3.7 The limit of detection (LOD) for AERs depends on the LOD of the GC-ECD, the sampling rate of the CAT tubes, the sample duration, the emission rates of the PFT sources, the house volume and the true integrated air exchange rate. Most GC-ECD systems can detect PFT quantities as low as 1 picoliter (pL) with 30% precision. The minimum PFT air concentration LOD is controlled by this and the sample exposure time, and the effective sampling rate (4-7).

3.8 The PFT source is inexpensive and reusable. It is small, ready for use as received, and always emitting tracers. The passive sampler (CAT) is also very small and can be located inconspicuously throughout a dwelling. The CATS are reusable providing an analytical check of the remaining PFT background is negligible. The PFT/CATs operate for the desired time without supervision. Additionally, the PFT source has a high affinity for

reaction with electrons and a low atmospheric background which allows analysis by GC-ECD to be carried out with little interference and very low detection limits.

4. Significance

4.1 The measurement of exposure serves as a critical parameter in environmental protection. The data from exposure measurements help to evaluate progress in the efforts to control environmental pollution and provide guidance for modifying approaches to make them more effective. Ultimately, the effectiveness of the regulatory process on reducing pollutant levels may be judged by exposure measurements.

4.2 In the early 1980's the U.S. EPA began to undertake programs to find the missing exposure data needed to complete the risk equation. The application of personal monitors became an effective means to measure the exposures of individuals throughout their daily activities. Besides measuring the individual's exposure to pollutants, the idea to estimate the exposures of entire populations was formulated. Since the measurement of exposures of everyone in a large metropolitan area is expensive, a simpler approach was to combine probability sampling with environmental monitoring. In this manner, the exposures of a representative probability sample of the population could be used to make inferences about exposures of the entire population.

4.3 This initial concept was applied in exposure studies involving volatile organic chemicals (VOC). A number of these studies have now been completed including carbon monoxide personal exposure monitoring. The VOC and carbon monoxide exposure field studies were the beginning of a newly emerging field of total human exposure assessment. However, the need to consider size characteristics and chemical composition in the control of airborne aerosols has been a matter of continuing concern to the U.S. EPA since the establishment of the total suspended particle ambient air quality standards in 1971. More recently, the Science Advisory Board of the U.S. EPA has made a recommendation that calls for exposure assessment studies to assess man's exposure to environmental pollutants, including the determination of sources and their relative contribution to personal exposure.

4.4 In addition to measuring mass and elements, total exposure assessment studies should be organized to provide background information on indoor and outdoor air pollutant concentrations. Emphasis should be placed on collecting information on indoor air pollutant concentrations or the relationship between indoor and outdoor air levels, especially since there has been very little attention given to indoor pollutant concentrations. Air infiltration rates are a critical component in the process of determining the influence of outdoor pollutant concentrations on indoor concentrations.

4.5 The PFT method is less intrusive than alternative methods. The PFT uses a passive sampler which requires no pumps (8-23).

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. Additional definitions, abbreviations, and symbols are provided in Appendices A-1 and B-2 of this compendium.

6. Interferences

6.1 The PFT sources are temperature sensitive. Therefore, careful placement of the sources within a dwelling is necessary. Best results are obtained when the sources are deployed in different areas of a dwelling according to the permeation rates. Haphazard placement will lead to inaccurate measurement (See Section 10).

6.2 The PFT sources and passive samplers measure minute concentrations (ppt), therefore it is very important to keep the PFT containers and the samplers well separated. The samplers are not temperature sensitive, but extreme, abrupt changes in temperature exposure should be avoided. Sampling periods are restricted to a two hour minimum and several months maximum.

6.3 Electron capture detectors are sensitive to halogenated organic compounds. The most important potential interferents in the home are freon-type refrigerants. The GC system is designed to remove these compounds by control of their travel times through the system.

7. Apparatus

7.1 Perfluorocarbon Tracer (PFT) Source - PFT sources as seen in Figure 1 consist of a 6.6 mm inside diameter by 32 mm long cylindrical aluminum shell filled with 0.4 mL of a single PFT liquid and is slightly flared at both ends to facilitate the insertion of an oversized silicone rubber plugs. The PFT liquid takes about two hours to reach equilibrium. A code number is engraved onto the aluminum shell for identification of the PFT source, silicone rubber plug type, and the number of the source (Russell Dietz or ISC Chemicals Ltd., England).

7.2 Capillary Adsorption Tubes (CATs) - CATs are constructed of glass tubes which contain a measured amount of an adsorbent as illustrated in Figure 2. The outside diameter (OD) of the tube is 6.4 mm and it is 6.4 cm long with a 45° taper ground at the ends to about 1/3 the wall thickness (to prevent cutting of "0"-rings in the desorption apparatus). The adsorbent, a granular (small beads) Ambersorb material (usually activated charcoal), is held in place by stainless steel screens (9.5 mm OD; 150 mesh) which are friction-fitted into place. A special PFT impermeable polyurethane cap is used to seal each end of the CAT before and after sampling. An identification number is either hand-engraved using a diamond-tipped vibrator or fired into the glass using powdered lead glass black numbered decals (manufactured by Russell Dietz).

7.3 Gas Chromatograph/Electron Capture Detector (GC-ECD) - Equipped with a Nafion column, two catalytic columns, a pre-column, a QS adsorbent column trap, and a main chromatographic column.

7.4 Computer Integrator - Programmed to receive standard data and produce a calibration curve based on retention times, time windows, minimum areas, type of curves, etc.

8. Reagents

The GC-ECD carrier gas is of the highest quality reagent grade 95% nitrogen - 5% hydrogen carrier gas.

9. PFT Sources Available Commercially

9.1 There are four PFT sources in use today. These are listed below along with the properties which make them appealing for use as a gaseous tracer.

Conservative gaseous tracers

Properties

- Non-depositing
- Low atmospheric background
- Non-scavenged
- Limited industrial use
- Non-reactive
- Sensitively detectable

Perfluorocarbon tracers (PFTs)	Emission Type	Rate	Permeation Rate @ 25°C nL/min	Lifetime,yrs.
PDCB (P [a]- dimethylcyclobutane	1	Highest	36-50	2.9-2.1
PMCP (P - methylcyclopentane)	8	Next to highest	40-55	2.6-1.9
PMCH (P - methylcyclohexane)	2	Next to lowest	24-35	4.0-2.7
PDCH (P - dimethylcyclohexane)	3	Lowest	12-20	7.2-4.3

[a]P as in PDCB means "perfluoro".
[b]nL/min represents nanoliters/minute (10^{-9}/min).

9.2 PFT sources are advantageous over other methods in that they are used as received; they are always emitting tracer and they may be placed in any orientation. They are inexpensive and reusable. The PFT makes use of a passive sampler instead of an active one. Additionally, the PFTs high affinity for reaction with electron and low atmospheric background makes them some of the most sensitive compounds for detection on the ECD.

9.3 Although PFTs are ready for use when purchased, it is important to present how PFTs are made. There are two basic processes that have been used commercially for the production of PFTs, here restricted to the family perfluoroalkylcycloalkanes because they have the maximum response to the ECD. Other perfluoroalkanes and other perfluorocarbons are two or more orders-of-magnitude poorer in detection capability.

9.3.1 One process, cobalt trifluoride catalyzed fluorination, is available from ISC Chemicals Limited in England. The purity of their tracers has been from 85 to 99%, with a limited amount of the other existing and identified PFTs as impurities, generally less than 1%.

9.3.2 The other process for making PFTs is the dimerization of perfluoroalkenes at high pressures (up to 3000 atmospheres) and moderate temperatures (400°C). Originally patented by E.I. DuPont in Wilmington, Delaware, more than 19 years ago, the technique was used at one time to make the PDCB. They abandoned the technology more than five years ago and other small companies can now produce a number of the dimerization products, generally perfluorodialkylcyclobutanes, but at costs up to ten times or more those of the PFTs from ISC. However, the PDCB is a potential continental scale tracer because it has the highest ECD response of any of the PFTs and has a low ambient concentration. Recently, the Flora Corporation in North Carolina has indicated an interest in supplying tracers made by this process.

10. Placement of PFT Sources and Passive Samplers

10.1 Choosing PFT Sources

10.1.1 The choice of PFT source types with zone location is important in multizone structures. Because of the stack effect in all houses, a source placed on the second floor will have a very low concentration in the basement. To improve the precision of its measurement in the basement, the second floor-tracer selected should be one with the highest emission rate and the highest detectability, i.e., the earliest eluting tracer on the gas chromatograph (GC) column.

10.1.2 Thus, the choice for the second floor tracer in a 3-zone study is either Type 1 or Type 8 (see Section 9). The same reasoning extended to the other floors dictates that Type 2 be used on the first floor and Type 3 in the basement, as illustrated in Figure 3. The use of Type 1 in one zone and Type 8 in another zone in a 3-zone building should be avoided because those two tracers elute very close to each other and are therefore difficult to quantify without using special GC conditions. In stacked 4-zone structures, when both Types 1 and 8 must be used, the correct choice for the uppermost zone is Type 1, followed by Type 8 in the next lower zone, Type 2 in the next, and Type 3 in the lowest zone.

10.2 Placement of PFT Sources

Described herein is the placement of sources in family-type dwellings. The AER method can be used for other dwelling types (i.e., industrial, laboratories, offices, etc.).

10.2.1 The PFT sources should be shipped separately from the samplers. Each source shell is engraved with a code, the first number of which identifies it as one of the 4 available PFT types, i.e., type 1, 2, 3 (or TC), or 8.

10.2.2 The sources should be deployed one per every 500 ft^2 (46.5 m^2) of living area. Typically, in a single story ranch-type home, two sources are placed in the living room, dining room, kitchen area and one in each of the bedrooms. The same type of source should be used if the floor is to be treated as a single zone, as shown in Figure 3.

10.2.3 If the house has a basement, a different PFT type should be used since it is a separate but attached zone. For an open (unfinished) basement, one or two sources may be used; if it is divided into rooms, 2 sources should be used. Ignoring the basement by not

including any sources and samplers or using sources of the same type as the main floor, can result in errors in the determination of the living space ventilation rate.

10.2.4 Generally, a PFT source is placed within 0.5 to 1.5 meters of the floor and no closer than 1 meter to an outside wall. For example, it can be taped onto the leg of a table or end table or even on a lower portion of a hanging chandelier.

10.2.5 The emitters are placed in the building at least 8 hours in advance of the samples.

10.2.6 Since the source is sensitive to temperature, it should not be placed within a meter of a heating or cooling source, in direct sunlight or other drafty location such as a window, nor at a location where air would carry the PFT vapors outside or to another zone before they had mixed uniformly within the zone where they were placed.

Note: Since heated air rises and cooled air sinks, the PFT location should be at a vertical location not too far above or below the temperature measurement/control elevation and not be placed above a warm air source (e.g., a lamp or the top of a refrigerator) nor below a cooled air source (e.g., an air conditioner vent or a window sill).

10.2.7 Record the average temperature of the source on the Field Data Sheet illustrated in Figure 4. The daily average room temperature is usually adequate for this purpose, even in the case of one or more daily temperature set-back cycles.

10.2.8 It should be mentioned that the directions included in this method are for a typical dwelling (ACH = 0-2) Table 3 gives the number of sources needed if the building to be monitored is expected to have a higher air change per hour than a normal dwelling, i.e., an office building with higher ventilation.

10.3 Placement of Passive Samplers (CATs)

Note: DO NOT STORE THE SOURCES AND THE SAMPLERS IN THE SAME LOCATION. The sources and samplers should definitely not be shipped in the same container and, ideally, not even shipped on the same day. For example, if transported in the same car or truck, there is a possibility of contamination. During field deployment, the samplers can be placed in the engine compartment or roof rack of a vehicle (effectively outside) while the sources are maintained within the vehicle passenger compartment or trunk. To this end it is generally wise for 1 or 2 passive samplers to remain as controls, that is, to remain unopened, for each series of home infiltration measurements.

10.3.1 One or two samplers are usually deployed in each zone of the home with the same location restriction as the sources and at least 1 to 2 meters from any PFT source or source of air not representative of the room air (e.g., air from the outside or another zone). Thus, the samplers are usually placed near another inside wall location, but at least 2 cm from any wall, and not in a flowing air stream without a shelter such as an envelope or box.

10.3.2 In the bedroom zone of a ranch house or 2-story house, it is prudent to sample in the master bedroom plus one other bedroom; this provides a better average for that zone.

10.3.3 In the family zone, two samplers located as per the two-story diagram, as shown in Figure 3, give an average concentration which is better than just placing one sampler as per the one story diagram.

10.3.4 The samplers are not temperature sensitive, but extremes should be avoided. They can be placed on a table or taped to the leg of a chair or table in any orientation. The samplers have a rubber cap on each end.

10.4 Sampling Start-Up and Shut-Down

10.4.1 To initiate sampling, only one cap must be removed, the one near the numbered end, as seen in Figure 2. The sampler number, location, and time and date sampling commenced must be recorded on the Field Data Sheet shown in Figure 4.

10.4.2 At the end of the designated sampling period (e.g., one day, one week, one month, etc.), cap the sampler and record the time and date sampling ceased on the Field Data Sheet. Verify each CAT ID number upon removal from its sample location. CATs are stored in sealed ziplock bags for transport to the lab.

10.4.3 Record other information as called for on the Field Data Sheet. The volume of each zone of the house should be obtained from inside dimension measurements or estimated from outside lengths and widths, subtracting 1 foot (0.3 m) from each, but using inside ceiling heights. A separate sheet should be used for each home. House floor plan should be drawn to show location of each source and CAT for each sampling event. House Volume should be recorded on house floor plan. These data are needed in conjunction with other information (e.g., from questionnaires) about open windows, presence of fireplaces, window fans, window air conditioners, etc. to assist in interpreting the data.

11. Gas Chromatography with an Electron Capture Detection

11.1 The determination of PFTs collected via either the passive or programmable samplers is accomplished with a gas chromatograph system (Varian Instrument Corp., Floral Park, New Jersey, Model 3700 GC with a Model CDS-111 integrator-controller). The analysis includes thermal desorption, chemical and physical processing, chromatographic separation, and ECD determination of the tracer gas as illustrated in Figure 5.

11.2 Calibration of GC-ECD

11.2.1 Gas standards for calibrating the GC are prepared in the concentration range of 1 to 10,000 pL/L by first preparing 1000 ppm primary standards of PFT in helium (He) either gravimetrically or volumetrically and verifying on a thermal conductivity GC that has been calibrated with pure PFT vapors. These primary standards are then further successively diluted with ultra pure air (Scientific Gas Products, Plainfield, New Jersey) in Spectra-Seal aluminum cylinders (Airco Industrial Gases, Riverton, New Jersey).
Note: Regular steel cylinders have been found to adsorb significant amounts of the higher boiling point tracers (PMCH and PDCH), especially at concentrations of 1 and 10 pL/L, but the Spectra-Seal cylinders showed no adsorption loss (7).

11.2.2 Calibration of the GC is performed by setting flow rates of 5 and 50 mL/min on the gas cylinder standards and passing the flow through consecutive CATS tubes for different durations.

11.2.3 Quantities of from 0.05 to 5000 pL (pL = 10^{-12}) of tracer then are analyzed to calibrate the GC response for each tracer.

11.2.4 The limit of detection (LOD) for AER depends on the LOD of the GC-ECD, the sampling rate of the CAT tubes, the sample duration, the emission rates of the PFT sources, the house volume and the true integrated air exchange rate. It is recommended that GC-ECD systems which can detect PFT quantities at least as low as 1 picoliter with 30% precision be employed. The minimum PFT concentration LOD is controlled by this and the sample exposure time, and the effective sampling rate. For this instrument, the minimum detectable air concentration calculated by:

$$\text{(PFT LOD, pL/L)} = \frac{\text{(Minimum Measurable PFT Amount, pL)}}{\text{(Hours Exposed) x (Sampling Rate, L/hr)}}$$

$$= \frac{1 \text{ pL}}{24 \text{ hr x } 0.00892 \text{ L/hr}}$$

$$= 5 \text{ pL/L}$$

The maximum measurable PFT concentration can be calculated by:

$$\text{(PFT Concentration Maximum,pL/L)} = \frac{\text{(Maximum Measurable PFT Amount, pL)}}{\text{(Hours Exposed) x (Sampling Rate, L/hr)}}$$

$$= \frac{270 \text{ pL}}{24 \text{ hr x } 0.00892 \text{ L/hr}}$$

$$= 1260 \text{ pL/L}$$

Note: The highest PFT concentrations expected in normal dwellings are about 200 pL/L, so the upper limit should be of no consequence. The lowest PFT concentrations may be on the order of 1 pL/L for houses with open windows and fans in use.

11.2.5 The concentration of PFT produced by sources in a home is dependent on the number of PFT sources, their emission rates, the house volume, and the air exchange rate, as outlined by the following equation:

$$C = \frac{n \text{ x } S/V}{[n \text{ x } S/V)/R]}$$

where:
S ~ 1800 nL/hr, PMCH source @ 25°C
n = number of sources
V = house volume, m^3
R = air changes per hour (ACH)
The lowest PFT values are expected to be found in large houses with high AER rates. As an example, for a house with the following dimensions:

3.6

V = 500 m^3
R = 12 ACH
n = 6 PMCH sources,
the average PFT level is expected to be about 1.8 nL/m^3. This is about equal to the system LOD. The highest PFT levels will be found in small homes with low AER. As an example, for a house with the following dimensions:
V = 150 m^3
R = 0.5 ACH
n = 6 PMCH sources,
the expected PFT level is 144 nL/m^3 which is well below the system PFT capacity.

11.3 GC-ECD Analysis Protocol

11.3.1 Whether for initial bakeout or for thermal desorption and recovery of sampled PFTs, a special rack with 23 positions should be constructed as illustrated in Figure 4. The resistance heating wire element consists of about 10 turns of 0.8 mm OD (20 gage) nichrome wire (approximately 23 cm in length) such that 4.2 Vac (≈8.5 A or 36 W) heats the CATS tube to 450°C in 0.5 min and 1.9 Vac (≈3.8 A or 7 W) holds that temperature for another 0.5 min to effect the sample recovery; power is supplied from a transformer with a secondary rated at 6.3 Vac and 10 A (Essex/Stancor No. P-6308).

11.3.2 The tubes are placed into the rack by slipping through the heating coil (with one rack end removed) until they contact the spring-loaded "0"-ring seal pistons; the removal end, a 25-mm (1-in.) aluminum square stock, is replaced and the eccentric cam compresses the tube ends against the spring-loaded seals. The open 1.59 mm (1/16 in.) tubing ends are connected to a 24-position Scanivalve rotary valve assembly (Gilian Instrument Corp., Wayne, New Jersey) which has an electrical rotary switch to bring the desorption power to the proper tube.

11.3.2.1 Before the sample is thermally desorbed, the sampler tube is purged with carrier gas (5% H_2 in N_2) for a short period of time to remove any traces of oxygen which otherwise would react with the PFTs during the 400°C desorption recovery. The sample is purged through the precut catalyst as seen in Table 1, the dryer to remove water vapor, and the two precut columns before entering an adsorbent trap. The 10 cm long catalyst bed in the presence of the hydrogen in the carrier gas reduces any chlorofluorocarbon compounds, as well as any remaining oxygen, to their hydrogenated forms, thus rendering these interfering compounds nonelectron-capturing.

11.3.2.2 After the surviving PFTs elute from the precut column, heavier molecular weight constituents still within the column are purged to the atmosphere by reversing the direction of flow. Meanwhile, the eluted PFTs are reconcentrated within a 10 cm long Porapak QS adsorbent trap.
Note: The purpose of the QS trap on the gas chromatograph (GC) is two-fold. First, by not opening the trap until the first PFT eluting from the precut column arrives, some lighter constituents are discarded. Second, after the precut column is backflushed, the trap remains open for 1 min to further purge away light-interfering gases and then is closed.

11.3.2.3 When the Porapak QS trap has been heated to 200°C and opened, the PFTs are flushed through the main catalyst as seen in Table 1 for final cleanup before entering the main column for separation of the PFTs prior to detection in the ECD.

11.3.2.4 While this is occurring, the next sample tube can be thermally desorbed and loaded onto the QS trap once it has sufficiently cooled (about 50°C), thus almost halving the overall PFT sample recovery and analysis time by overlapping the stages.

Note: Automation of the sequential analysis of all 23 tubes in either a CATS desorption rack or a BATS lid is accomplished by using the BATS base timing capability to initiate the GC timing sequence as each new tube steps in place. Each analysis, including reporting of the peak areas, takes 10 minutes; 23 tubes are analyzed in just under 4 hours.

11.3.2.5 Figure 5 illustrates the detailed plumbing and valving used to effect the automated chemical and physical processing during the analysis of the PFT samples. Automation occurs through the use of eight external events contained within the integrator-controller. As illustrated in Table 2, one event starts and stops the recorder paper, four events operate the four valves, and three events control the heating of the sampler tube and the Porapak QS trap. Three 6-port (Valco Instrument Co., Houston, Texas, SSAC6T Shaft Seal) and one 4-port (Valco SSAC4UT Shaft Seal) valves with air operators are used. Vespel cone seals are preferred to the Teflon®-filled ceramic type because the latter have been found to bleed contaminants at temperatures above 100°C. With the exception of the sample valve, they are mounted within the GC oven.

11.3.2.6 When the recorder shuts off at 8.01 min, the analysis is complete and the report of the peak areas, which is proportional to the quantity of each tracer, is printed as well as transmitted to a magnetic tape, which can then be processed on a Tektronix 4052 desk top computer. The GC is ready for the repeat of the cycle on a 10 minute frequency. Figure 7 is a typical chromatogram.

12. Calculations

Numerous researchers have proposed models and methods for using tracer gases in the solution of those models for determining the air infiltration rate into a home or building considered as a single, well-mixed chamber or zone. Recently, however, it has been recognized that many larger, more complex buildings, especially those with multiple-zoned HVAC systems and even one- and two-story homes with basements, realistically can only best be represented by models which recognize the building as multiple-connected zones, each of which is well-mixed.

12.1 One-Zone Case

For a building considered as a single, well-mixed zone of known volume, V, containing one type of tracer of known emission rate, $R_s(t)$, such that a tracer concentration, C(t), is measured throughout the house which has an air exfiltration rate of $R_E(t)$, a simple material balance gives:

$$V \frac{dC(t)}{dt} = R_s(t) - R_E(t)C(t) \qquad (1)$$

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where:
V = volume of the building (constant), m^3
$R_s(t)$ = total tracer source rate (variable), nL/h
$C(t)$ = average tracer concentration in the building (variable),nL/m^3 ≡ pL/L
$R_E(t)$ = air exfiltration rate (variable), m^3/h
Equation 1 is a general solution in which it is assumed that the tracer source rate, the tracer concentration, and the exfiltration rate can vary with time; it also was assumed that the tracer concentration is the ambient air, that is, the infiltrating air is negligible, which is always the case for PFT's. Equation 1 then can be solved for various modes of tracer experiments, including tracer decay, constant concentration, and constant emission rate. The PFT sources are designed to provide a constant emission rate source in the building. About 5 to 10 h after deployment, the tracer concentration will become more or less constant, dependent only on slow changes in the exfiltration rate due either to mechanical ventilation or weather changes. For these steady state assumptions [that is, $dC(t)/dt \approx 0$], Equation 1 becomes:

$$\frac{1}{n}\sum_{t=1}^{n}\frac{R_s(t)}{C(t)} = \frac{1}{n}\sum_{t=1}^{n}R_E(t) = R_s\frac{1}{n}\sum_{t=1}^{n}\frac{1}{C(t)} \qquad (2)$$

assuming that the source rate is constant, that is $R_s(t) = R_s$, over n periods of concentration. But:

$$\frac{1}{n}\sum_{t=1}^{n}\frac{1}{C(t)} = \frac{1}{n}\left(\frac{1}{C(1)} + \frac{1}{C(2)} + \ldots + \frac{1}{C(n)}\right)$$

$$= \frac{1}{n}\left(\frac{C(2)C(3)\ldots C(n) + C(1)C(3)\ldots C(n) + \ldots + C(1)C(2)\ldots C(n-1)}{C(1)C(2)\ldots C(n)}\right)$$

$$\approx \frac{1}{n}\left(\frac{n\bar{C}^{\,n-1}}{\bar{C}^{\,n}}\right) \approx \frac{1}{\bar{C}}$$

The second term in Equation 2 is the average infiltration rate, $\bar{R}_E$. Thus:

$$\bar{R}_E \approx \frac{R_s}{\bar{C}} \qquad (3)$$

The approximation in Equation 3 is because it was shown that the reciprocal of an average concentration, $\bar{C}$, which is the quantity that the passive sampler determines, is close to but not identical to the average of reciprocal concentrations.

12.2 Two-Zone Case

Examples of two-zone cases are a two-story house on a slab, a one-story (for example, ranch) with a basement or a crawl space, and any building which is ventilated with two separate HVAC systems. Figure 8 depicts the model for a one-story house (Zone 1) with a basement (Zone 2). Air can infiltrate from outside the house into each zone (R_{11} and R_{12}) and exfiltrate each zone to the outside (R_{E1} and R_{E2}). In addition, air can exchange between the zones in both directions (R_{E12} and R_{E21}). Assuming that a different tracer type is used in each zone (Tracer 1 in Zone 1, etc.), tracer material balances, assuming that steady state pertains and that there is negligible tracer in the outside air, give the following:

Zone 1

$$R_{21}C_{12} - R_{12}C_{11} - R_{E1}C_{11} = -R_{s1} \quad (4)$$

$$R_{21}C_{22} - R_{12}C_{21} - R_{E1}C_{21} = 0 \quad (5)$$

Zone 2

$$R_{12}C_{11} - R_{21}C_{12} - R_{E2}C_{12} = 0 \quad (6)$$

$$R_{12}C_{21} - R_{21}C_{22} - R_{E2}C_{22} = -Rs2 \quad (7)$$

where:

R_{12}, R_{21} = air exchange rates from Zone 1 to Zone 2 and Zone 2 to Zone 1, m^3/h,

R_{E1}, R_{E2} = air exfiltration rates from Zones 1 and 2, m^3/h,

R_{s1}, R_{s2} = rates of tracer sources in each respective zone, nL/h, and

C_{11}, C_{21}, C_{12}, C_{22} = concentration of Tracer 1 in Zone 1, etc., $nL/m^3 (\equiv pL/L)$.

The concentrations are measured with the passive samplers, and the tracer source rates are known. Thus, the four unknowns, two air exchange rates and two exfiltration rates, can be solved from the four simultaneous equations. The rate of infiltration for each zone then can be calculated from air mass balances:

$$R_{11} = R_{E1} + R_{12} - R_{21} \quad (8)$$

$$R_{12} = R_{E2} + R_{21} - R_{12} \quad (9)$$

The solutions to Equations 4 to 7 can be obtained by solving as two sets of simultaneous equations, noting that R_{21} can be solved from Equations 4 and 5 and R_{12} from Equations 6 and 7. Then R_{E1} and R_{E2} can be obtained from Equations 5 and 7, respectively. The solutions, which are given in the Appendix, also can be obtained, by any standard matrix inversion routine for use on a desktop computer. This is especially useful when the number of zones increases to three or four. Once all the flow rates have been determined, simple

material balances then can be performed for pollutants in the same building. The following equations

$$R_{21}C_{p2} + R_{11}C_{pa} - 2R_{12}C_{p1} - R_{E1}C_{p1} = -R_{p1} + k_1V_1Cp1 \quad (10)$$

$$R_{12}C_{p1} + R_{12}C_{pa} - R_{21}C_{p2} - R_{E2}C_{p2} = -R_{p2} + k_2V_2C_{p2} \quad (11)$$

where:

C_{p1}, C_{p2}, C_{pa} = concentration of pollutant in Zone 1, Zone 2, and the ambient outside air, respectively,

R_{p1}, R_{p2} = rate of the pollutant source in zone.

k_1, k_2 = rate of pollutant scavenging in each zone, and

V_1, V_2 = volume of each zone.

would then give the pollutant net source strength in each zone of the building. The solutions to the tracer and air material balance equations are:

Two-Zone Case

$$R_{21} = (R_{s1}C_{21})/(C_{11}C_{22} - C_{12}C_{21})$$

$$R_{12} = (R_{s2}C_{12})/(C_{11}C_{22} - C_{12}C_{21})$$

$$R_{E1} = R_{21}(C_{11/C21}) - R_{12}$$

$$R_{E2} = R12(C11/C12) - R_{21}$$

R_{11} and R_{12} are calculated from Equations 8 and 9 in the text.

12.3 Three-Zone Case

A typical example of a three-zone building is a two-story house with a basement. Again, assuming that a different tracer source is used in each zone and that the steady state assumption applies, a set of nine tracer material balance equations can be developed to solve for nine unknown flow terms (three exfiltration flow rates, one from each zone, and six air exchange rate terms, two leaving each zone). A set of three air mass balance equations would provide the three unknown infiltration rates. It is apparent that as the number of zones increases, the matrix solution approach with computer assistance is the only manageable way.

Three-Zone Case

Let:

$$[\ ] = [C_{11}(C_{22}C_{33}-C_{23}C_{32}) + C_{12}(C_{23}C_{31} - C_{21}C_{33}) + C_{13}(C_{21}C_{32} - C_{22}C_{31})]$$

Then:

$$R_{21} = R_{s1}(C_{21}C_{33} - C_{23}C_{31})/[\ ]$$

$$R_{31} = R_{s1}(C_{22}C_{31} - C_{21}C_{32})/[\ ]$$

$$R_{32} = R_{s2}(C_{11}C_{32} - C_{12}C_{31})/[\ ]$$

$$R_{12} = R_{s2}(C_{12}C_{33} - C_{13}C_{32})/[\ ]$$

$$R_{13} = R_{s3}(C_{13}C_{22} - C_{12}C_{23})/[\ ]$$
$$R_{23} = R_{s3}(C_{23}C_{11} - C_{13}C_{21})/[\ ]$$
$$R_{E1} = R_{31}(C_{23}/C_{21}) + R_{21}(C_{22}/C_{21}) - R_{13} - R_{12}$$
$$R_{E2} = R_{32}(C_{13/C12}) + R_{12(C11}/C_{12}) - R_{23} - R_{21}$$
$$R_{E3} = R_{13}(C_{11/C13)} + R_{23}(C_{12}/C_{13}) - R_{31} - R_{32}$$
$$R_{11} = R_{E1} + R_{12} + R_{13} - R_{21} - R_{31}$$
$$R_{12} = R_{E2} + R_{21} + R_{23} - R_{12} - R_{32}$$
$$R_{13} = R_{E3} + R_{31} + R_{32} - R_{13} - R_{23}$$

The total ACH in a house is given simply by the sum of the exfiltration rates of all zones divided by the sum of the volume of all zones. (See Section 12.2 entitled "Two-Zone Case" of the text for definition of the terms.)

12.4 N-Zone Case

It is apparent, then, that for N zones, a set of N trace material balance equations can be written to solve for N^2 unknown flow terms (N exfiltration flow rates, one from each zone, and N(N - 1) air exchange rates, that is, N - 1 leaving each zone to flow to another zone). Also, a set of N air mass balance equations would provide the N unknown infiltration rates.

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Table 1. Gas Chromatography Specification and Conditions

Main Column	1.2 m (4 ft) long packed with 0.1% SP-1000 on Carbopack C (Supelco, Inc., Bellefonte, PA)
Precut Columns	1.2 m (4 ft) long Porasil F followed by 0.3 m (1 ft) long of 0.1% SP-1000 on Carbopack C
Column Oven	140°C
Precut Catalyst	10.1 cm (4 in) long packed with palladium (Pd) (1%) on polyethylenimine/SiO_2-Royer Pd catalyst (Strem Chemicals, Inc., Newburyport, Mass.); 200°C
Main Catalyst	3.2 cm (1.24 in) long packed similarly; 200°C
Carrier Gas	5% H_2 in N_2 at 25 and 20 mL/min, respectively, through the precut and main columns
Porapack QS Trap	10.1 cm (4 in) long packed with Porapack QS
Permeation Dryer	1.2 m (4 ft) long Nafion dryer (Permapure Products Inc., Oceanport, N.J., Model MD-125-48S) located in the top of GC (~35°C)
ECD	180°C

Note: All columns (including catalyst beds and adsorbent trap) are made with 3.2 mm (0.125 in) OD stainless steel tubing.

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Table 2. Gas Chromatograph[a] Sequence of Events

Event Time, min	Event Code	Event	Event Status
0.00	---	System steps to next sample tube; starts event clock	---
0.01	0.01	Recorder starts	Off
0.01	0.14	QS/sampler heating relay switches to QS trap	On
0.02	0.10	Desorption Power turned on	On
0.02	0.12	High power position	On
0.35	0.13	Low power position	Off
0.50	0.08	Sample in QS trap injected (that is, V4 on)	On
1.60	0.09	V_4 is off	Off
1.60	0.11	Desorption power turned off	Off
1.62	0.15	QS/sampler relay switches to sampler	Off
2.30	0.06	V_3 is on	On
4.95	0.04	V_2 is on	On
5.00	0.02	V_1 is on	On
5.00	0.10	Desorption power turned on	On
5.00	0.12	High power position	On
5.40	0.13	Low power position (not used for BATS tubes)	Off
5.70	0.08	V_4 is on	On
7.30	0.11	Desorption power turned off	Off
7.60	0.09	V_4 is off	Off
7.70	0.07	V_3 is off	Off
7.75	0.03	V_1 is off	Off
7.80	0.05	V_2 is off	Off
8.01	0.00	Recorder off	On

Table 3.
Number of PFT Sources Needed Per Zone to Achieve the
Lower Limit of Detection When the Exposure Time Varies*

	Hours Exposed				
Source Type	8	12	24	48	168 (7 days)
PDCB	13	9	4	2	1
PMCP	11	8	4	2	1
PMCH	18	12	6	3	1
PDCH	37	25	13	6	2

*Assuming:

ACH	≤ 6
Vol. per zone	$\approx 314\ m^3$ (500 ft^2 floor space with 8 foot ceilings)
GC-ECD	Limit of Detection ≤ 1 pL
PFT	minimal emission rate

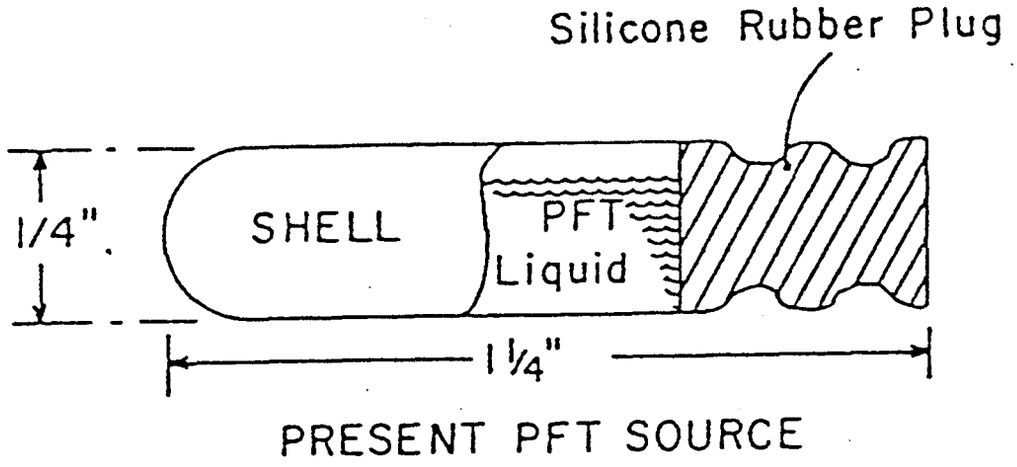


Figure 1. Diagram of the PFT Source Configuration

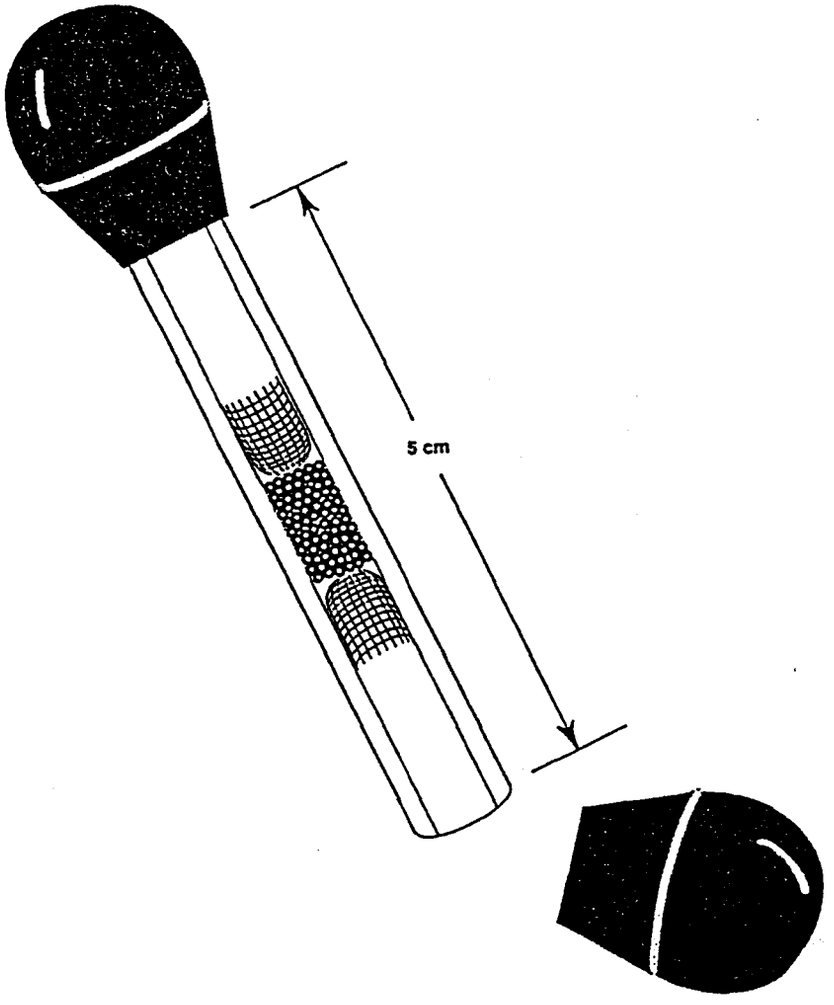
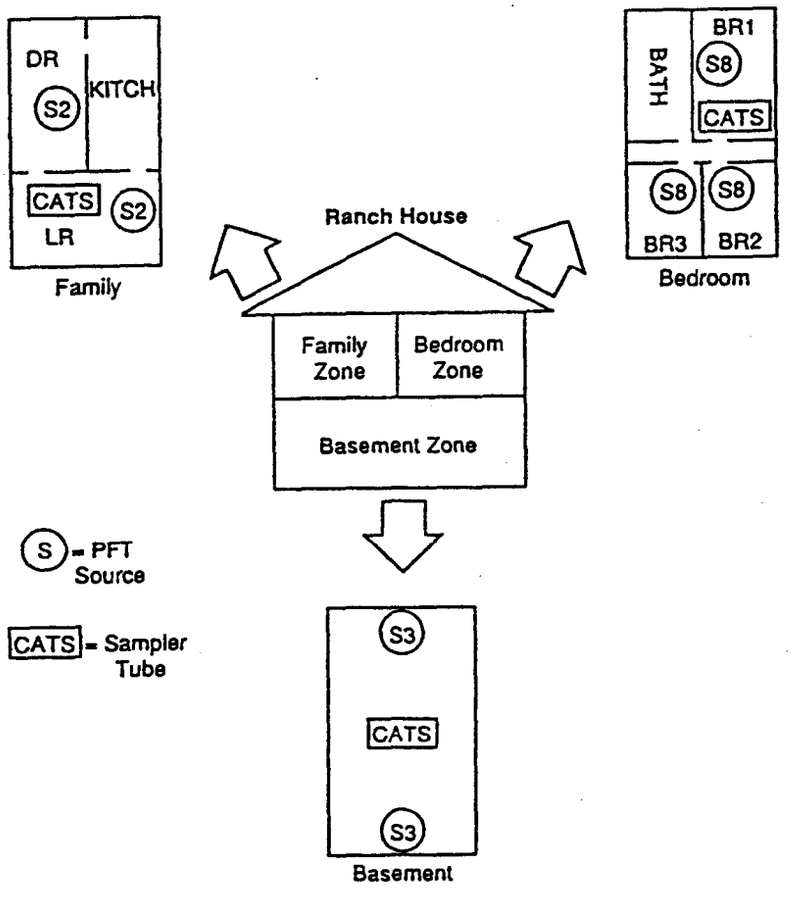


Figure 2. Diagram of a Typical capillary Adsorbent Tube (CAT)

One-Story, Ranch Style House with a Basement



Basement Zone
Sources- Place two PTF type 3 sources on opposite ends of the basement. If an obstruction exists, place a source on either side of the obstruction.
Sampler- Place the CATS in the center of the basement or within the largest open area.

Family Zone
Sources- Place two PFT type 2 sources within the two largest rooms.
Sampler- Place a CATS in the largest room.

Bedroom Zone
Sources- Place one PFT type 8 source in each bedroom.
Sampler- Place a CATS in the largest bedroom in the zone.

Figure 3A. Placement of PFT Sources

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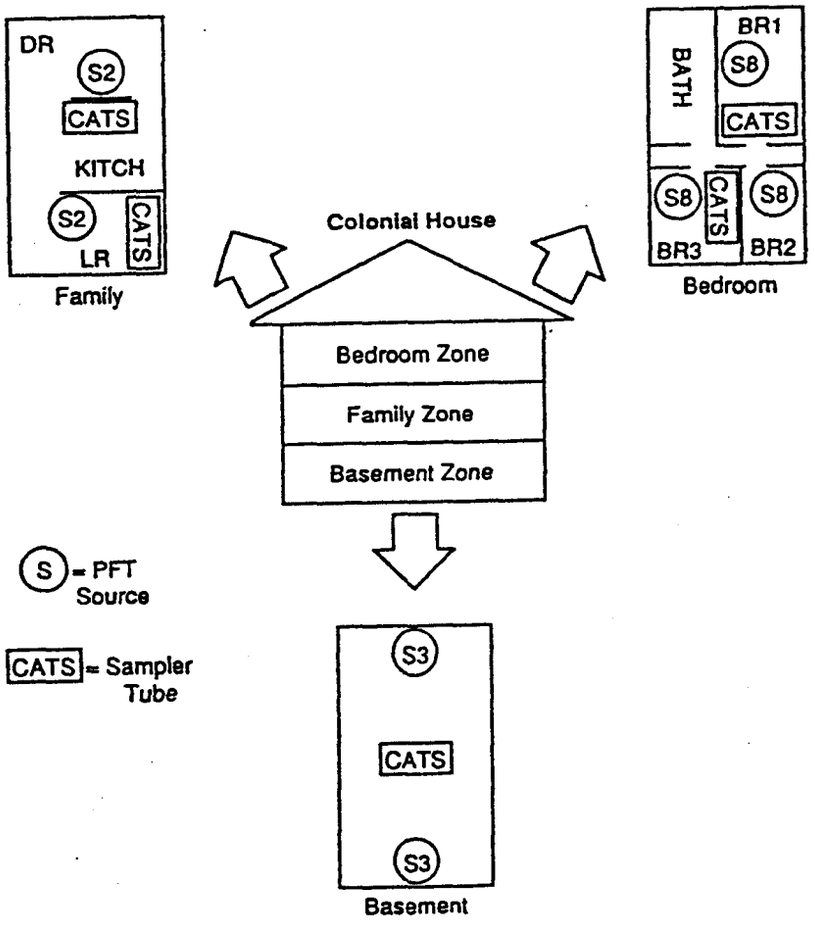
Two- Story, Colonial Style House with a Basement



Basement Zone
Sources- Place two PTF type 3 sources on opposite ends of the basement. If an obstruction exists, place a source on either side of the obstruction.
Sampler- Place the CATS in the center of the basement or within the largest open area.

Family Zone
Sources- Place two PFT type 2 sources in the rooms at opposite ends of the zone.
Sampler- Place two CATS in the largest rooms in this zone, twords the center, but away from each other and the sources.

Bedroom Zone
Sources- Place one PFT type 8 source in each bedroom.
Sampler- Place two CATS in the largest bedrooms within this zone.

Figure 3B. Placement of PFT Sources

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Project Title____________________

House Description
____1 story
____2 story
____w/basement
____split level
____w/fireplace
____w/woodstove

House ID:____________ # of Zones:_____

Circle one

Start Date: / / Start Time: : am pm

Stop Date: / / Stop Time: : am pm

Zone #:_____ Zone ID:______# of Sources:______ Source Code:______

Avg. Temp. (°F):______ Volume (ft^3):______ # of CATS:______
(°C):______ (m^3):______

CATS ID	Room	Item Placed On	Source Location Room	Source Location Item Placed On

Zone #:_____ Zone ID:______# of Sources:______ Source Code:______

Avg. Temp. (°F):______ Volume (ft^3):______ # of CATS:______
(°C):______ (m^3):______

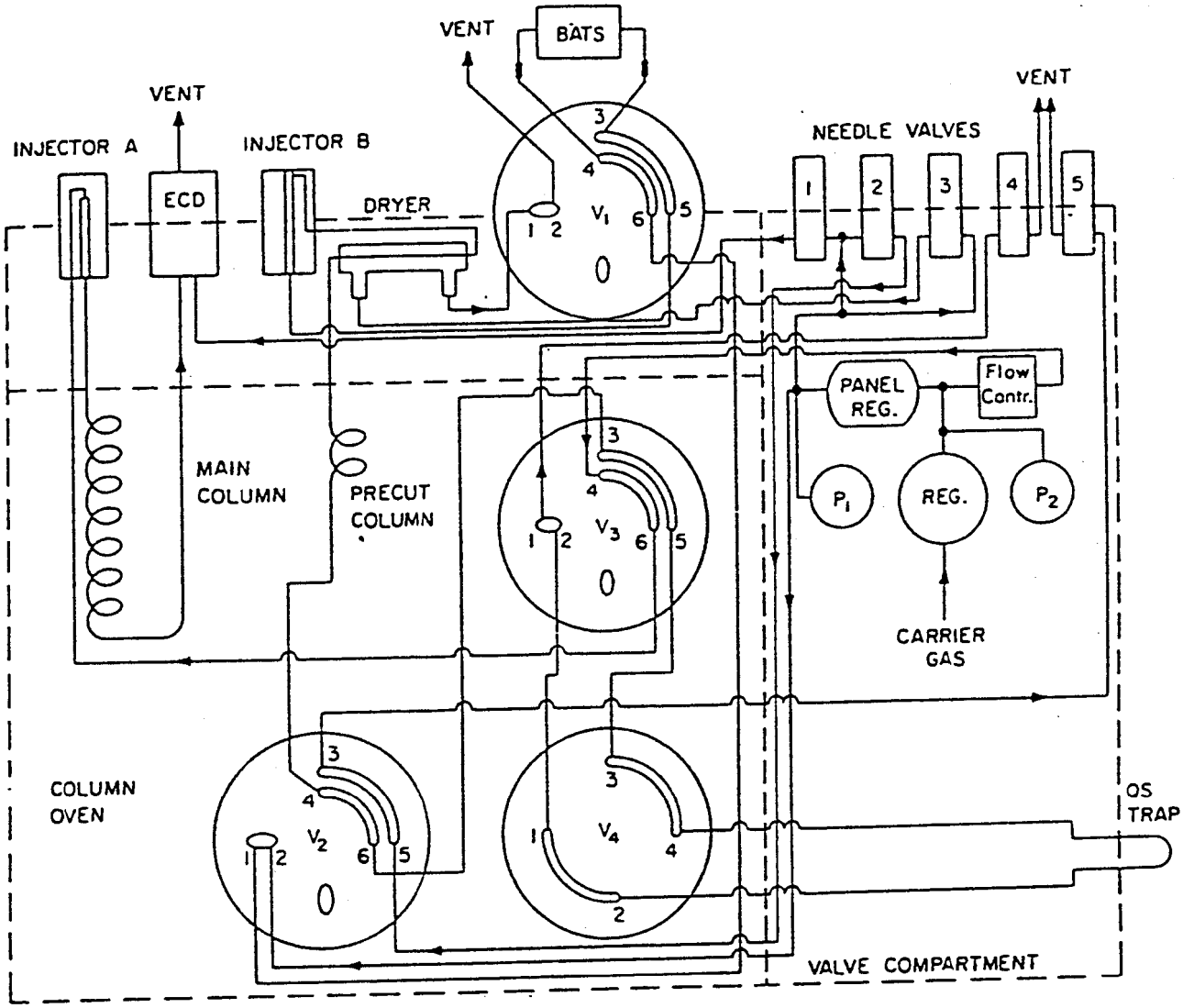
CATS ID	Room	Item Placed On	Source Location Room	Source Location Item Placed On

Zone #:_____ Zone ID:______# of Sources:______ Source Code:______

Avg. Temp. (°F):______ Volume (ft^3):______ # of CATS:______
(°C):______ (m^3):______

CATS ID	Room	Item Placed On	Source Location Room	Source Location Item Placed On

Figure 4. Data Sheet



V_1 = The sampler valve.
V_2 = The precut valve.
V_3 = The flow direction valve.
V_4 = The Porapak QS valve.

Each is shown in its "ON" position; in the "OFF" position, the valve slots are rotated 90° counterclockwise.

Figure 5. Schematic of Laboratory GC Analyzer

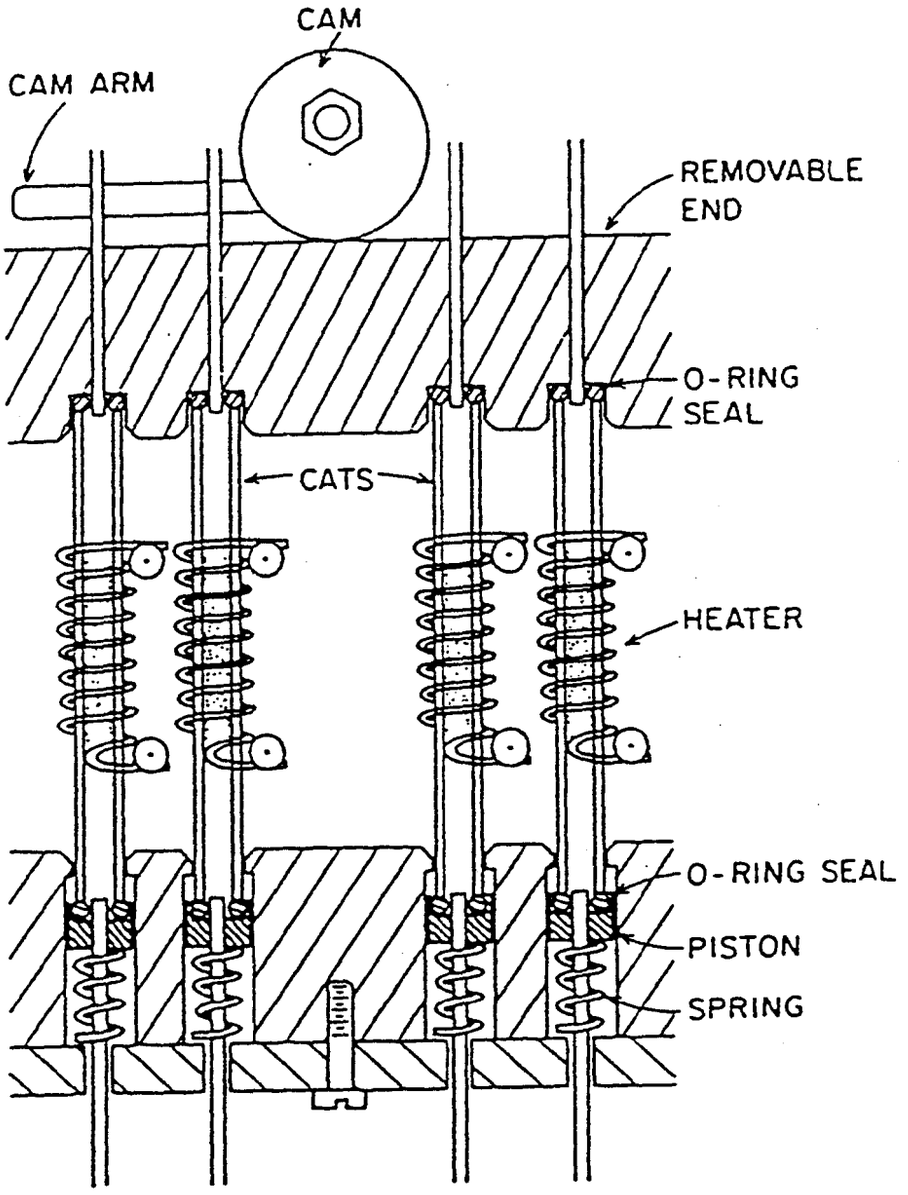


Figure 6. Passive Sampler Thermal Desorption Rack

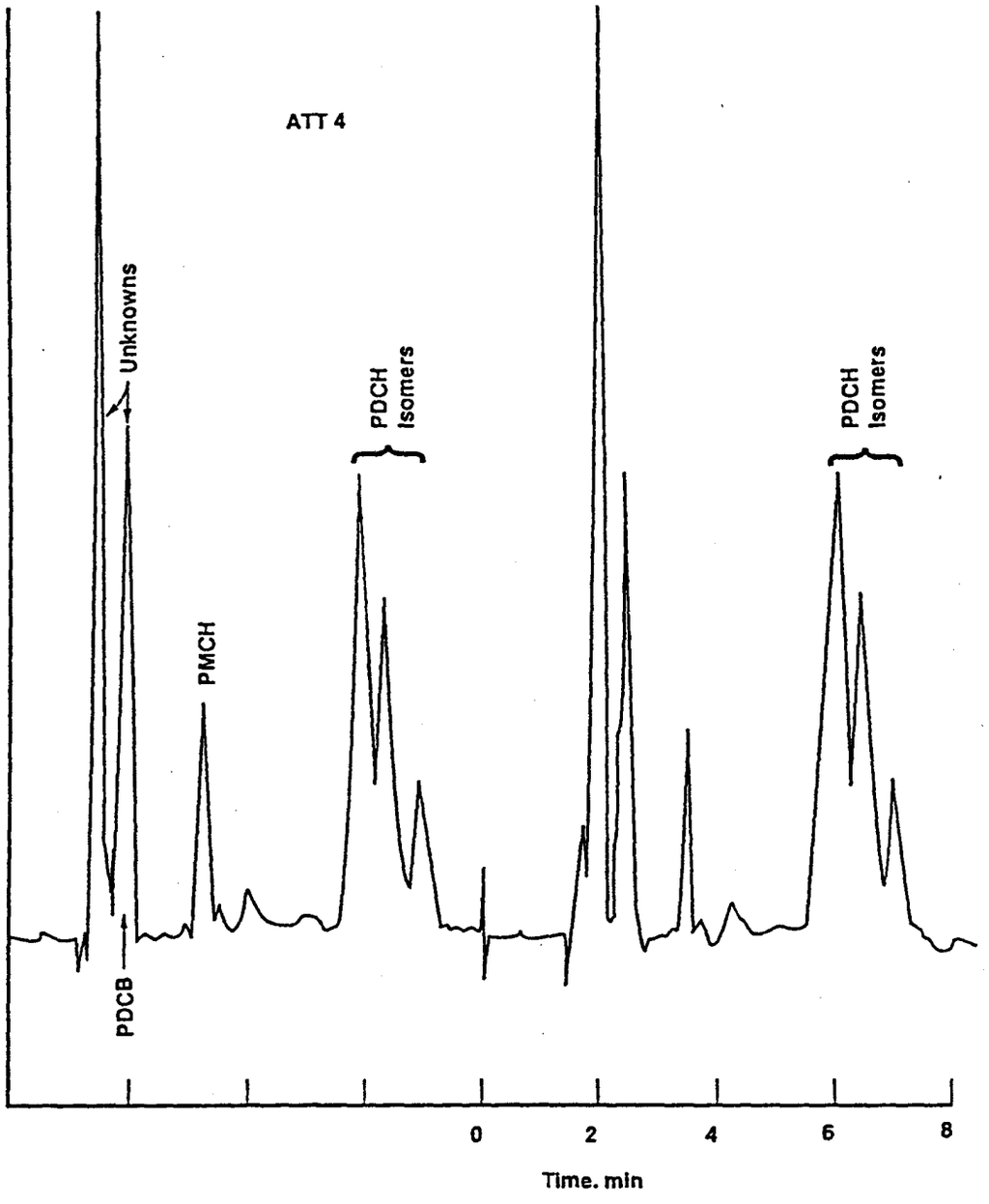
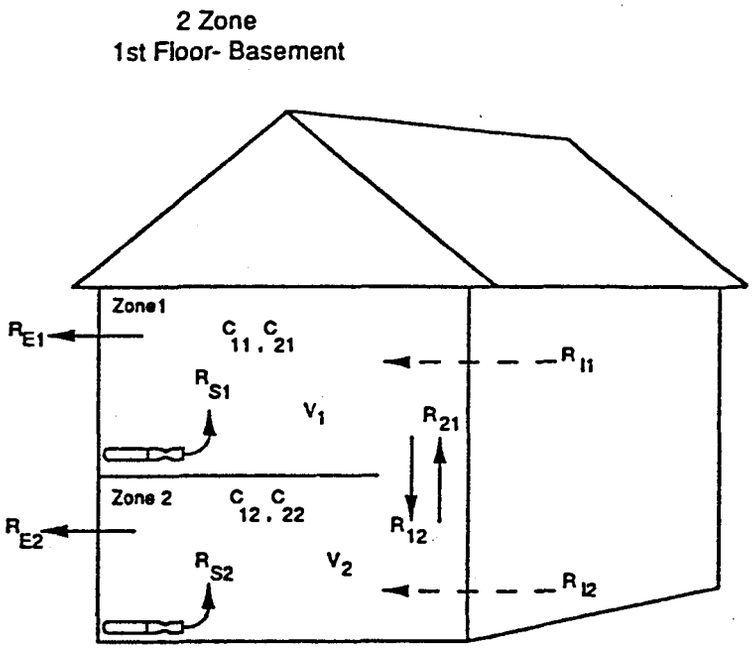


Figure 7. Chromatograms of Two 25-L Ambient Air Samples with the GC Specifications Shown in Table 1. The Unknown Peak after PDCB is PMCP.



R_{I1}, R_{I2} = Air Infilttration

R_{E1}, R_{E2} = Air Leakage

R_{12}, R_{21} =Air Exchange Between Zones

R_{S1}, R_{S2} =PFT Sources

V_1, V_2 =Zone Volumes

C_{11}, C_{21} = Connection of Tracer 1 in Zone 1

C_{12}, C_{22} = Connection of Tracer 2 in Zone 2

Figure 8. Model Considered for a Two-Zone House

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Method IP-4B

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR USING TRACER GAS

Method IP-4B

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR USING TRACER GAS

1. Scope

1.1 This document describes the protocol for the measurement for an air exchange rate (AER) between the outside and inside of buildings under natural meteorological conditions by trace gas dilution.

1.2 The tracer gas suggested for this method is sulfur hexafluoride (SF_6). Other tracer gases are available. This document lists other tracers and discusses the advantage of using SF_6. Occasionally more than one tracer gas may be desired in an application. Situations where it may be advantageous to utilize more than one tracer gas will be discussed.

1.3 To facilitate ease of operation, convenience and accuracy, this method suggests the use of commercially available automated syringe samplers and tracer gas monitors.

1.4 This test method describes a standardized technique for determining air change rate in buildings under natural meteorological conditions by trace gas dilution.

1.5 This test method shall not be used to determine the individual contribution of various building components to the air change rates of a building.

1.6 Use of this test method requires a knowledge of the principles of gas analysis and instrumentation.

1.7 The current state of the art does not possess analytical techniques to extrapolate precisely measured air change rates to meteorological conditions different from those prevailing during measurement.

1.8 This standard may involve hazardous materials, operations, and equipment. This standard 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 limitations prior to use.

2. Applicable Documents

2.1 ASTM Standards

E741 Determining Air Leakage Rate by Tracer Dilution (1)
E779 Test Method for Determining Air Leakage Rate by Fan Pressurization
D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis
E355 Recommended Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

Scientific Publications (2-7)
U.S. EPA Technical Assistant Documents (8)

3. Summary of Method

3.1 This test method entails introducing a small amount of tracer gas into a structure, thoroughly mixing it, and measuring the rate of change (decay) in tracer concentration. The air change rate can be estimated from the decay rate of tracer concentration with respect to time. On-site meteorological conditions are measured concurrently. In the on-site monitor variant, after the tracer gas has thoroughly mixed, an initial air sample container is filled. The air change rate can be determined from the decay in tracer concentrations.

3.2 A quantity of tracer is released at one or more points in the test building. The amount of tracer released should be sufficient to produce an easily discernible response in the gas measuring instrument. Under no circumstances should the initial tracer gas concentration exceed the Occupational Safety and Health Administration's (OSHA) time weighted average for substances included in the latest OSHA standards.

3.3 Fans or the central air system should be used to circulate the air within the room or structure in order to mix the gas thoroughly. Connecting doors, closet doors, and the like should be opened to allow unobstructed internal air flow. Several minutes should be allowed for mixing.

3.4 Air samples from one central location or several strategic points are collected at timed intervals.

3.5 The tracer concentration of each sample is determined by a gas chromatograph equipped with an electron capture detector.

3.6 The decay in tracer gas concentration as a function of time can be related to the air exchange rate of the building at the place of collection under the current meteorological conditions.

3.7 By repeating this procedure a number of times, it is possible to characterize the effects of climatological (temperature and wind) on structural (wall, windows, floors, ceilings, doors, etc.) factors on infiltration rate.

4. Significance

4.1 Air leakage accounts for a significant portion of the thermal space conditioning load; it can introduce outdoor air contaminants in conditioned indoor air, and it can dilute indoor-generated contaminants, therefore detracting from or providing for occupant comfort.

4.2 Air leakage rates are difficult to predict analytically because they are functions of building tightness and configuration, inside-outside temperature differences, wind speed and direction, quality of workmanship in construction, and numerous other factors.

4.3 This test method describes measurements of air leakage rates. In applying the results of this test method to the design of buildings, consider that the air leakage

characteristics of a structure are affected by building operation, maintenance, and the resistance of the building components to deterioration.

4.4 The tracer dilution method has been proven to be an effective way of measuring the air leakage rate of a structure under field conditions. The measurement of air infiltration using the tracer gas dilution method and on-site gas monitor equipment requires field deployment of equipment and the use of trained technicians. It is possible to take tracer gas samples on site and analyze them at a laboratory facility. The practice of taking container samples can be performed by persons not trained in the operation of the gas monitor equipment.

4.5 As an alternative to the tracer gas method, the fan pressurization method (ASTM Test Method E779) provides an indirect way to relate the air leakage rate or air tightness to the leakage area of a structure. This test method has several differences from the tracer dilution method. It can be used to compare the relative air tightness of several buildings, to identify the leakage source and rate of leakage from different components of the same building envelope, and to determine the air leakage reduction for individual retrofit measures applied incrementally to an existing building.

4.6 When the absolute air leakage rate is needed, the tracer dilution method should be used over a wide range of wind velocities and indoor and outdoor temperature differences. It is best to use the fan pressurization method for diagnostic purposes and resolve the absolute air leakage rate with the tracer dilution method. However, the measuring equipment and techniques are relatively complicated for the tracer dilution method, and the data analysis and correlation are more involved.

4.7 In contrast with the tracer gas dilution method, two other tracer gas techniques are employed:

4.7.1 One is the constant concentration approach in which the tracer gas concentration is maintained essentially constant (order of ±10%) in a given volume. The air infiltration rate is determined from how much tracer gas must be injected to maintain the constant concentration. The constant concentration feature is particularly desirable in multi-chamber buildings, since leakage from chamber-to-chamber does not disturb the air infiltration measurement.

4.7.2 The second method is the constant injection method where, as the name implies, tracer gas injection is maintained constant over time.

4.7.3 The governing equations for both constant concentration and constant injection are different from the tracer gas dilution method.

5. Definitions

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

5.1 Air change rate - the ratio of hourly indoor air change and indoor space volume measured in identical volume units (normally expressed in air changes per hour, ACH or ACPH).

5.2 Air leakage rate - the volume of air movement per unit time across the building envelope. This movement includes flow through joints, cracks, and porous surfaces, or combinations thereof. The driving force for such air leakage in service can be either mechanical pressurization and evacuation, natural wind pressures, or air temperature differentials between the building interior and the outdoors, or combinations thereof.

5.3 Building envelope - the exterior shell enclosing the indoor space.

5.4 Exfiltration - air leakage from a building space.

5.5 Indoor space - the volume of a building that exchanges air with outside ambient air. In most cases, this volume is the deliberately conditioned space within a building, generally not including the attic space, basement space, interstitial spaces (such as a double envelope), and attached structures, unless such spaces are connected to the heating and air conditioning system.

5.6 Infiltration - air leakage into a building.

5.7 Natural ventilation - unpowered airflow through intentional building openings such as open windows and vents.

5.8 Tracer gas - a gas that can be mixed with air and measured in very small concentrations, making it possible to detect air movements and measure air changes.

5.9 Ventilation - intentional outdoor air intake through a ventilation system, with mechanical ventilation being that ventilation induced by a mechanical system.

6. Interferences

6.1 SF_6 has a low natural background concentration (typically 0.1 to 0.5 ppt.). One exception to its low natural background, however, can be in the vicinity of electrical power switching equipment which may use SF_6 as an insulating material.

6.2 Tennis balls can contain SF_6 which may pose another possible source of background interference.

7. Apparatus

7.1 This description of apparatus is general in nature, and any equipment capable of performing the test measurements within the allowable tolerances is permitted (see Tables 1 and 2).

7.2 Tracer gas monitor - a device to measure tracer gas used in the study, capable of measuring the tracer gas to within ±5% at any concentration. In this case, a gas chromatograph specifically designed for tracer gas monitoring is described.

7.3 Sampling network - consisting of tubing, tubing junctions, a pump, and possibly an aspirator. This network is used to draw samples from remote locations within a structure, blend them, and bring the blended sample to a convenient place for analysis. In general, it is best to avoid plasticized tubing, such as vinyl, and use copper, stainless steel, or possibly polypropylene or nylon. The technician should be aware that surface absorption within the sampling network can be a major source of confusion in any concentration decay measurement.

7.4 Sample containers - non-absorbent, inert, low-permeability containers (such as sample bags, syringes with needle caps, of plastic bottles) used to collect and store air samples from buildings under test. With this method syringes are utilized because of air volume accuracy and ease of injection into the chromatograph.

7.5 Pump - non-contaminating air sample pump, either manual or powered, used to fill sample containers. Plastic bottles can be filled by hand squeezing. With this method a commercially available automatic syringe sampler is utilized.

7.6 Syringes - disposable syringes may be used as sample containers if sealed or to inject gas samples when the gas monitor is a gas chromatograph. A plastic bottle containing tracer gas or tracer gas/air mix can also be used.

7.7 Circulating fans - used to circulate air within a structure, capable of circulating air over 360°. Oscillating or hassock fans are preferred. Such fans are normally unnecessary in buildings with ducted forced air systems.

7.8 Meteorology stations - portable, that records wind speed and direction, outside temperature, and (if available) relative humidity, is used to obtain on-site meteorological data.

7.9 Barometer - a device to measure local barometric pressure is useful. If one is not available, barometric pressure from the nearest weather station is obtained for the time during which measurements are performed. These data are corrected for any elevation difference between the weather station and the test structure.

7.10 Tracer gas - a cylinder or container of gas chosen from those listed in Tables 1 and 2 is necessary as a source of the tracer used in the test. On this method SF_6 is used.

7.11 Timing device - a clock, watch, chronometer, or similar device suitable for measuring elapsed time and time intervals.

8. Reagents and Materials

8.1 Tracer gas - pure form SF_6.

8.2 Nitrogen gas - high purity reagent gas as the electron capture detector carrier gas.

9. Safety Precaution

The maximum allowable concentration in air for each of the tracer gases that have been used for tracer dilution air leakage measurements is provided in Tables 1 and 2. Do not

exceed this concentration under any circumstances. Good experimental practice is to ensure that the maximum allowable concentration of the particular tracer is less than this maximum by at least a factor of four. The initial tracer gas concentration must not exceed under any circumstances the OSHA time-weighted average for substances included in the latest OSHA-controlled gases list.

10. Tracer Gas Technology

10.1 General

The implementation of tracer gas technology provides quantitative information concerning air mass or pollutant transport and dispersion which cannot be readily obtained in any other manner. Applications that have used this technology include:

- Meteorological tracing and atmospheric diffusion studies.
- Isolation of the contribution of a specific emitting source from other local sources.
- Large distance plume tracking and impact assessment.
- Determination of the transport and dispersion characteristics of a locale prior to new facility construction to assess potential new source impact on air quality.
- Examination of pollutant species dispersion, depletion or conversion.
- Characterization and assessment of gaseous effluents from nuclear generating stations.
- Evaluation of highway air pollutant emission factors in the vicinity of a major highway in an urban area.
- Studying of air movement within or around an enclosed volume for ventilation studies.
- Validation and correlation of ambient air quality advection and dispersion models.
- Infiltration measurements in structures to quantify convective energy losses.
- Assessment of mine ventilation and air flow characteristics.
- Prediction of smoke movement in building fires.
- Characterization of air transport/communication and earth media permeability assessment in underground structures.

10.2 SF_6 Tracer Gas

10.2.1 Sulfur hexafluoride is a colorless, tasteless, incombustible gas, with an inertness resembling nitrogen, unchanged even at the softening temperature of hard glass and unaffected by water or caustic potash. This gas possesses excellent properties for use as a voltage insulation.

10.2.2 SF_6 is considered to be one of the most desirable tracers. It possesses one of the highest electron capture responses (it can be detected down to 10^{-12} parts SF_6 per part air - 1 ppt); and it has a low natural background concentration (typically 0.1 to 0.5 ppt). Other factors which make SF_6 the ideal tracer gas are:

- Non-toxic, non-allergenic, non-radioactive, colorless and odorless.
- Gaseous at ambient temperatures.
- Chemically inert and thermally stable for atmospheric applications.
- Capable of rapid and controlled atmospheric release from a point or area source.

- Amenable to conventional sample collection techniques.
- Commercially available.

10.2.3 One exception to its low natural background, however, can be in the vicinity of electrical power switching equipment which may use SF^6 (or Freon C-318) as an insulating material. Tennis balls contain SF_6. Thus, in any tracer release/monitoring study, care must be taken to determine whether there are background concentrations, potential tracer gas interferences or contamination prior to performing the tracer release.

11. Release of Tracer Gas

11.1 On Site Monitor Method

11.1.1 The assumption underlying the tracer gas measurement of air change rate is that for perfect mixing with steady air flow, the loss rate of tracer gas concentration conforms to the exponential dilution law; that is, the loss rate or dilution of an escaping gas is proportional to its concentration. Mathematically, this assumption leads to Equation 1.

$$C = C_0 \exp(-It) \quad (1)$$

where:
C = tracer gas concentration at time, t
C_0 = tracer gas concentration at time = 0
I = air change rate
t = time

11.1.2 Injection and Mixing of Tracer Gas - At one or more points in the test structure, release an amount of tracer gas sufficient to produce an easily discernible response in the gas-measuring instrument. The location of release is governed by the location of air handling system(s) or mixing fans in a structure with no air-handling system. This release can be done with a gas-tight syringe or a plastic bottle filled with tracer gas.

11.1.3 In a building with ducted forced air system(s), operate the main fan(s) continuously. Introduce tracer gas into the main supply or return duct(s), preferably in the vicinity of the main fan(s).

11.1.4 Leaks in the ductwork system may produce an incremental increase in the air leakage rate. Two methods to assess this leakage are:

11.1.4.1 After beginning a test, as in 10.3.3, operate the main fan(s) only for initial mixing and shortly before sampling.

11.1.4.2 Use portable fans for mixing after initiating a test as in 10.3.3. Perform the remainder of the test as in 10.3.5.

11.1.5 In a building without central heating and air conditioning system(s), release the tracer gas at one or more points within the structure. Use fans to circulate the air and mix the gas. Take care not to affect the pressure distribution within the structure. Open all doors connecting contiguous living spaces.

11.2 Container Method

11.2.1 Injection of Tracer Gas - A predetermined quantity of the tracer gas is initially injected into the building so that the initial concentration of the tracer gas is below the safety limits listed in Tables 1 and 2 and within the optimum detection range of the gas monitor used. Graduated syringes can be used for this injection. These can be prepared before the test or filled from a bottle of compressed tracer gas at the site. The injection is accomplished by slowly walking around inside the structure, injecting gas into each room in a quantity approximately proportional to the volume of the room. The graduation on the syringe greatly aids in this process. A sample container with tracer gas/air can be used in a similar manner.

11.2.2 Mixing Tracer Gas in Dwelling - A waiting period of approximately ½ to 1 h should then be allowed for proper mixing of the tracer gas. For a building with a forced air heating system, the fan on the furnace can be turned on to assist in the mixing. Experience in dwellings without an air system suggests that natural convection currents will mix the tracer gas well. This is also true for each floor of the building (if the doors between rooms are open). In multi-story structures there seems to be higher on the upper floors. This is probably due to natural convection currents caused by rising warm air. Circulating fans can be used to assist mixing of the tracer gas.

12. Sampling

12.1 General Procedures

Collecting of SF_6 samples during periods of gaseous release may be performed by several techniques. The current state-of-the-art in this topical area encompasses:

- Grab samples (syringes)
- Sequential instantaneous samples
- Portable bagged samples (time-averaged)
- Sequential bagged samples at fixed sites (time-averaged)
- Spatially-averaged bagged samples from mobile platforms (automobiles, vans, aircraft)
- Limited semicontinuous sampling (frontal chromatography)
- Continuous detector sampling
- Time-averaged samples - evacuated containers

12.2 Sampling for On Site Monitor Method

12.2.1 Before taking gas samples, allow at least 30 minutes for mixing.

12.2.2 To test for homogeneity in tracer gas concentration, take samples from a number of building spaces. When concentrations differ by less than 5% of the average concentration measured within the structure, begin monitoring the decay of tracer concentration. In a residential structure, two or more samples from widely separated locations are required. In multi-story structures, two widely separated samples per floor are required.

12.2.3 Tracer samples may be measured at a single location by taking individual samples (grab samples) at a number of distinct locations, or by drawing samples from a number of locations through a common network (multi-point sampling).

12.2.4 When multi-point sampling is used, place sensors at strategic points within the test structure and feed to a central measuring terminal. For methods that analyze air with a single measurement device, use a sampling network to bring blended air to the analyzer. A diagram of a sampling network and a sampling junction are shown in Figures 1 and 2. Note that if the dilution rate in different rooms or floors is different, samples drawn by this method yield air leakage rates slightly less than the true average rate. For example, if one of the rooms or floors is leaking air at twice the rate of the other (1 ACPH and 0.5 ACPH), analysis of the blended samples of the two will lead to an air leakage rate estimate about 4% lower than the true average rate.

12.3 Sampling for Container Method

12.3.1 Filling Initial Sample Containers - After adequate mixing of the tracer gas, an initial air sample container is filled for each floor of living space. If it is suspected that certain volumes of the building are not in perfect communication with each other, then separate air sample containers should be filled for each volume. This is accomplished by walking around the floor, filling the sample container by means of a small pump, or hand squeezing a plastic sample bottle or syringe. This will provide an integrated sample. The important criterion is that the air sample container must be filled slowly, thus ensuring that an integrated sample is obtained.

12.3.2 Label each air sample container as follows: Identification of the building (address), time of injection, time of sample, section of building from which sample was taken (first floor, basement, etc.), meteorological conditions, and indoor temperature. A suitable alternative procedure is to record these data on a log sheet and identify the samples by numbers corresponding to log entries.

12.3.3 Decay of Tracer Gas - Wait 1 hour for the tracer gas concentration to decay. Note the activities of occupants and the operating mode of mechanical equipment during this period.

12.3.4 Fill Sample Containers - Repeat the procedure in 11.3.3 at known intervals to obtain two or more additional samples of air for each floor of the building.

12.3.5 The procedures 12.3.1 through 12.3.4 are graphically shown in Figure 3.

12.4 Sampling for the Container Method with Automatic Syringe Samplers

12.4.1 A brief overview of the latest techniques used in the collection of air samples during tracer gas experiments indicates an evolution from simple, manual sampling to programmable, automated sample collection using advanced, multi-station samplers. The design and operation of microcomputer controlled sequential syringe samplers provides reliability, efficiency, and portability at a moderate cost.

12.4.2 In order to meaningfully interpret data from pollution monitoring programs, the accuracy, reliability, and reproducibility of sampling and measuring techniques become major areas of concern. Additional demands placed on sampling programs include

minimizing personnel and equipment requirements to meet specific measurement tasks, and low maintenance and replacement costs. Typical areas of interest are indoor residential and work atmospheres (Small, 1983; Spengler and Sexton, 1983; Berglund and Johansson, 1982), industrial environments, and studies concerned with transport and fate of air pollutants.

12.4.3 An automatic sampler commercially available from Scientific Instrumentation Specialists (Moscow, Idaho 208-882-3860) contains an advanced timing system which allows automatic collection of twelve sequential, time-averaged gas samples. Rack and pinion gears driven by a stepper motor mechanically actuate each syringe. In operation, the syringe plunger remains stationary while the rack and pinion drive gradually extends the syringe body. At the end of travel, the syringe needle drives into a silicone septum, and power transfers to the next syringe. A digital clock, controlled by a quartz crystal oscillator governs the operation of the sampler. The overall time accuracy is better than + 0.001% and the station-to-station sampling time reproducibility is about + 0.01%. The time base interval (2-8 minutes) is internally selectable. An operator can pre-program the unit up to 15 days ahead of the actual operation, locate it on a suitable site, and leave it unattended. The sampler will start collecting sequential, time-averaged samples (each ranging from 2 minutes to several hours) at the pre-selected time, and upon collection of each sample, seal the syringe needle to prevent diffusion or sample contamination. The unit can be very quickly turned around for another sampling cycle. A rechargeable battery, which allows up to 50 hours of continuous operation, assures portability. An optional 115/230V A/C power supply kit is available. The unit is enclosed in a sturdy aluminum case, secured with two key locks, and easily portable by one person as the overall weight is approximately 13.5 kg, as illustrated in Figure 4.

12.4.4 For collection of SF_6 air samples, polyethylene, glass, or stainless steel syringes are recommended.

12.5 Sampling Method for Large Buildings

12.5.1 Residential infiltration measurements utilizing tracer gas are relatively straightforward to accomplish. Generally, a small amount of tracer gas is released in the structure and either the central heating system or a few optimally placed fans are used to assure a homogeneous tracer gas concentration in the structure. After this, the decay in tracer gas concentration as a function of time is monitored. In the case of electronegative gases such as SF_6 and the halocarbons, the monitoring instrument of choice is a gas chromatograph equipped with an electron capture detector. By repeating this procedure a number of times, it is possible to characterize the effects of climatological (temperature and wind) and structural (walls, windows, floors, ceilings, doors, etc.) factors on the infiltration rate.

12.5.2 Approaches are not so straightforward for large buildings. The sheer volume of the building indicates that a simple tracer release/sampling operation may not provide data which are valid for the structure as a whole. Two general approaches, however, can be undertaken. If one is more concerned about the relative contribution of a given floor to total structure infiltration (as would be the case in deciding on a retrofitting program), it

is generally sufficient to perform measurements in a manner similar to that for residential structures for each floor. An anomalously high ACPH for a given floor would imply that retrofitting should concentrate on this floor.

12.5.3 A useful improvement of this established technique is the use of multiple tracer gases to characterize air exchange between the floor immediately above and below the floor being studied. By releasing three different tracer gases on three consecutive floors and monitoring their relative concentration decays with time on all three floors, one can completely characterize infiltration across the floor ceiling and external envelope of the middle floor. This technique is identified as the "sandwich approach" and depicted in Figure 5.

12.5.4 On the other hand, to characterize the total infiltration of a large structure, it is necessary to provide a tracer supply and sampling network. In this technique (identified as the "simultaneous approach"), each floor is provided with the same tracer gas and sampled independently of all other floors. As shown in Figure 6, flexible tubing is run to each floor generally through the heating/ventilating of air-conditioning ducting or the service channel in a particular building. Sampling and gas injection are performed at one central location within the structure. Actual installation details are strongly dependent on the physical characteristics of each individual building.

12.5.5 The "simultaneous approach" allows one to obtain individual decay rates for each floor at approximately the same time. Suitable averaging then provides the average infiltration rate for the structure, thereby allowing one to study systemic variations in infiltration rate due to temperature, wind, or other factors.

13. Analytical System

13.1 Samples analyzed for SF_6 during tracer release projects use gas chromatographs with an electron capture detector. In practice these instruments should be measurement-specific units optimized for SF_6 or other selected gaseous tracers.

13.2 The SF_6 concentration can be determined by on-site monitors or in the laboratory by transporting the air sample in a suitable container.

13.3 If the automatic syringe samples (Section 11) are utilized, the samples can be injected directly into the gas chromatograph.

13.4 Any gas chromatograph with an electron capture detector can be utilized, however, tracer gas monitors specifically optimized for sulfur hexafluoride are commercially available from Systems, Science and Software (S-Cubed, La Jolla, CA; Telephone: 619/453-0060).

13.4.1 Tracer gas monitors designed and manufactured by Systems, Science and Software (S-Cubed) are capable of providing measurements of unusual sensitivity (few ppt for SF_6). Parts per trillion identification allows remote detection with a minimum of tracer gas discharge. A unique feature of the S-Cubed tracer gas monitors is the use of a gated LED display which outputs values characteristic only of the tracer gas being monitored. Spurious, anomalous, or additional chromatographic peaks are not outputted; hence, confusion over the identity of a given peak cannot occur.

13.4.2 Functionally, the monitor is a measurement specific gas chromatograph with an electron capture detector. This type of detector utilizes the high electron affinity of gases with halogen group elements to provide a measurable signal. Sulfur hexafluoride is such a gas and is an ideal tracer because it is transported and dispersed exactly as other atmospheric gases.

13.4.3 The heart of the instrument, as discussed previously, is the GC column. It separates the various gaseous components of a sample by selectively slowing down some gases relative to others. The column can be thought of as a device to elute the distinct components in a gas sample in a definite order. In the case of monitoring for SF_6 only, the column material is 5A Molecular Sieve (synthetic zeolite). Columns constructed with this material possess the unique property that SF_6 is eluted prior to oxygen. In making low level tracer determinations, this property allows easy identification of a small SF_6 peak due to the absence of an uncertain baseline disturbed by the relatively high amplitude signal corresponding to an oxygen peak.

13.4.4 For field tracer gas projects, the S-Cubed Model 215AUP Environmeter has been repeatedly selected to serve as the primary instrument. The reasons for this choice in preference to other units are:

- Instrument is designed and built for field atmospheric tracing applications (Unit is not a converted or modified laboratory bench GC).
- Monitor is portable and self-contained (power supply, carrier gas and signal output display are on-board).
- Unit has range selectable capability; peak-holding digital display of signal output is directly related to SF_6 concentration.
- Rotary shear valve with a constant volume sample loop insures consistent and reproducible sample loadings with syringe injection (grab samples) or use of a remote sampling wand.
- Monitor contains printed circuit electrometer and pulse drive circuitry for low noise electronic functions, reliability and ruggedness.
- Unit is optimized for detection of SF_6 over the range 10^{-9} to 10^{-12} parts SF_6 per part air.
- Detector cell design (concentric foil and collector geometry), ionization source (tritiated-titanium foil) and pulse drive circuitry provide three decade linear dynamic range. (Unit does not require pulse counting or other output signal conditioning).
- Unit is easily operated by non-professional personnel; it does not require operation by or supervision of an analytical chemist.
- Individual calibration curves for each operating range are provided with the unit.
- Unit complies with U.S. Nuclear Regulatory Commission or Agreement States health safety requirements for sealed radioactive sources; no film badges required.
- Transfer, possession and use of unit authorized under a general distribution radiation license. (Eliminates customer filing for a specific radiation license).

14. Calibration

14.1 State the method of calibration of the gas analyzer. If the analyzer is not provided with a manufacturer's calibration, perform an actual calibration. Use standard mixtures of at least two different concentrations in the range anticipated in an actual test, unless manufacturer's specifications allow single point calibration.

14.2 Instrument calibration should be performed on a regular basis, i.e., monthly, weekly or when in the field on a daily basis (pre- and post-test measurements). This activity uses calibration gases (SF_6 in dry nitrogen or pre-purified air). Six calibration standards are used at the analyzer manufacturing site when the initial calibration curve is generated. For field use, one, or at most two, calibration concentrations are all that are required. A mid-range standard, or two standards spanning the measurement range of interest is sufficient in most cases. However, if six point calibration is desired, gases could be maintained in the following SF_6 concentrations: 5×10^{-9}, 1×10^{-9}, 5×10^{-10}, 5×10^{-11}, 1×10^{-11}, and 5×10^{-12}. Supplementing this activity, daily pre- and post-test ambient background measurements should be made in the release area to ascertain the magnitude of this condition on the specific tracer gas being released.

15. Calculations

15.1 Calculations for On Site Method

15.1.1 Rearrange Equation 1 (Section 11.1.1) as follows:

$$I = (1/t)\ln(C_0/C) \tag{2}$$

where:
C = measured time-dependent concentration
C_0 = concentration at $t = 0$
I = air change rate
t = time

Equation 2 is the starting point for several means of calculating air change rate from concentration and time measurements.

15.1.2 Graphical Method - Plot the natural logarithm of concentration on a linear scale against time in hours on a linear scale. The measurements should fall on a straight line with time, provided the air change rate remains constant. Scatter of points is expected and a straight line may have to be faired in the "best fit" sense. A minimum of three points over 1 hour should be used to determine this straight line.

15.1.2.1 On the straight line determined in 14.1.2, choose two points with coordinates (C_1, t_1) and (C_2, t_2) where C_1 is the concentration at time i. Calculate I, the air change rate, as follows:

$$I = (\ln C_2 - \ln C_1)/(t_2 - t_1) \tag{3}$$

This technique is shown in Figure 7.

15.1.2.2 This graphical method lends itself well to field study of the data, since it is easy to plot the log of concentration as a function of time. It is less sensitive to errors in concentration than other methods. It has the further advantage that a graph provides a visual display of any departures in the exponential decay law. So long as the data fall on a reasonably straight line, one has confidence that the data obtained are valid within the assumptions necessary for the validity of the tracer dilution method. One caveat that should be observed during any measurement interval is that the data points used in determining an air leakage rate should encompass the mean winds observed during the course of the measurement.

15.1.2.3 When many data points are obtained, a least-square computer program is used to calculate a "best fit" to the straight line.

15.1.3 Finite Difference Method - Calculate the air change rate after each sampling using the finite difference form of Equation 2 as follows:

$$I = L/V = 1/(t_{i+1} - t_1) \ln C_1/C_{i+1} \quad (4)$$

where:
L = leakage rate
V = room volume
t_1 = time at "i"th interval
C_1 = tracer concentration at "i"th sample interval

For measurement over N sampling intervals, form a mean and standard deviation as follows:

$$\text{Mean } I = T = (1/N)I$$

$$\text{Standard Deviation} = S_1 = [I^2 - (I)^2/N]/[N - 1]$$

The air change rate, $I = L/V$, is "best fit" to the sample values of this parameter. The best fit for I is the mean, and is determined from the test data in accordance with Equation 5. This finite difference method has the advantage of simplicity, but it is very sensitive to errors in concentration or to the effects of poor mixing, especially when short sampling intervals are used.

15.1.4 Decay Time Method - Concentration decay usually occurs quickly; this allows for a rapid means of estimating I. For example, with time measured in minutes, the time for one half the initial concentration to decay is noted as $t_{\frac{1}{2}}$ and the I estimate is given by $41.59/t_{\frac{1}{2}}$. Similar ratios are given for other decay fractions and are shown in Table 3. These ratios are simply computed for C/C_0 ratios of 3/4, 2/3, 1/2, etc. The measurer has to record the time that a desired ratio is encountered.

15.2 Calculations for the Container Method

Determination of Tracer Gas Concentration - Tracer gas concentrations are determined in an off-site laboratory using gas monitor equipment. The air leakage rate I is then

determined from Equation 2. For periods from 1 to 2 hours, Equation 2 is an accurate relation for determining the air exchange.

16. Records and Reports

The report should include the following information. Include as much of this information as possible to facilitate comparison with other data at a later time.

16.1 Measurement Characterization

- Air Mixing - method of initial mixing and method of maintaining mixing during the measurement if one is used
- Air Sampling - location of sampling site, sample interval, initial sample time, and method of sampling
- Tracer Gas - type, initial concentration, method of introduction
- Detector - type and method of calibration
- Type of Calculation - finite difference, decay time, graphical, least square.

16.2 Meteorological Conditions

- Location and height of meteorological measurement
- Wind speed and direction (both maximum and average)
- Temperature and measurement technique
- Barometric pressure and measurement technique
- Relative humidity or wet bulb temperature

16.3 Test Space Characterization

- Structure Type - residential, commercial, industrial, other
- Location of structure relative to other structures (give type) and roadways
- Location of structure relative to surrounding terrain (give type, that is, gullies, mountain, mounds, cliffs, etc.)
- Structure orientation and elevation relative to other structures, roadways and surrounding terrain
- Windows - type, dimensions, number, and location in test space
- Walls - interior and exterior
- Leakage - noticeable areas
- Location of chimneys, vents, and other such specified opening
- Type and capacity of heating, ventilation, and air-conditioning systems

16.4 Test Space Operating Characteristics

- Doors - open or closed
- Windows - open or closed
- HVAC System - on or off
- Vent Fans - on or off
- Special Circumstances or Characteristics During Test - occupied, unoccupied, ingress, egress

- Indoor temperature and measurement technique
- Relative humidity and measurement technique

17. Performance Criteria and Quality Assurance

17.1 General

17.1.1 At present, insufficient data exist for purposes of precision and accuracy determination. A reasonable estimate of the uncertainty in a given air change rate determination is about 10% or less.

17.1.2 Note that the air change rate is a strong function of indoor-outdoor temperature difference and wind speed and direction. When interpreting or comparing air change rate data, the fact that a pressure and temperature dependence does exist should be considered. It can have a strong effect on the results.

17.1.3 Integral to all SF_6 tracer gas acquisition, release, field sample acquisition and tracer gas analyses, established quality control methods should be applied. This activity reflects: use of SF_6 and carrier gases which conform to manufacturers' specification; use of components and materials that are compatible with SF_6; use of standardized field operating procedures; and, the comprehensive documenting of test data.

17.2 Instrumentation

17.2.1 Automatic syringe sampler - The sequential tracer gas samplers have proven extremely effective and reliable in a variety of atmospheric tracer field studies. The samplers have been used to collect fifteen minute, thirty minute, sixty minute, or longer average air samples in a number of different environments. Data return rates of 92%, 95%, and 97% have been reported. These results and investigations are good indicators of the usefulness, flexibility, and reliability of the samplers. In particular, the high degree of success (>90% in all documented cases) points to the reliability of the sequential syringe samplers.

17.2.2 Tracer Gas Monitors

17.2.2.1 To complement the comprehensiveness of the gas chromatographic measurements, instrument calibration runs should be performed on a regular basis, i.e., monthly, weekly, or when in the field on a daily basis (pre- and post-test measurements). This activity uses calibration gases (SF_6 in dry nitrogen or pre-purified air). Section 14 discusses calibration. Supplementing this activity, daily pre- and post-test ambient background measurements should be made in the release area to ascertain the magnitude of this condition on the specific tracer gas being released.

17.2.2.2 In practice, the SF_6 analyses from the 1-hour time-averaged sequential samplers are tabulated. The results of analysis for the instantaneous grab samples are recorded on the field test sheets, i.e., aligned to site, location, and time listings. In addition, all gas chromatographic analyses (sample measurements, background concentration tests and calibration runs) are generally recorded on strip charts (chromatograms).

18. Acknowledgements

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8. Riggin, R. M., *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

Table 1. Gases and Techniques for Tracer Dilution Method (1)

Tracer	Measuring Apparatus	Maximum Allowable Concentration in Air (vol/vol)	Maximum Detectable Concentration, ppm	Toxicology
Hydrogen	Katharometer	4% (lower explosive limit)	200	nontoxic
Helium	Katharometer		300	nontoxic
Carbon monoxide	infrared absorption	50 ppm	5	combines with hemoglobin to produce asphyxia
	gas chromatograph with gas flame ion detector		0.4	
Carbon	infrared absorption	5000 ppm	1	nontoxic
	thermal conductivity detector		70	
Sulfur hexafluoride	electron capture gas chromatograph	1000 ppm	0.000002	nontoxic
Nitrous oxide	infrared absorption	25 ppm	1	nontoxic
Ethane	flame ionization detector	3% (lower explosive limit)	5	nontoxic
Methane	infrared absorption	5% (lower explosive limit)	5	nontoxic

Table 2. Atmospheric Constituents (1)

Compound	Average Tropospheric Background Concentrations, ppm	Typical Indoor and Urban Ambient Concentrations, ppm	Anthropogenic Sources
H_2	0.5	0.5	---
He	5.2	5.2	---
CO	0.1	5-50	combustion
CO_2	320	30-5000	combustion
N_2O	0.3	0.3-several ppm	combustion
Ethane	1.5×10^{-3}	0.1	incomplete combustion
Methane	1.5	2-5	incomplete combustion
SF_6	10^{-3}	10^{-5}	telephone switching stations

Table 3. Decay Ratios to Compute ACPH

Concentration Ratio	Decay Time, min.	I, ACPH
3/4	$t_{3/4}$	$17.26/t_{3/4}$
2/3	$t_{2/3}$	$24.33/t_{2/3}$
1/2	$t_{1/2}$	$41.59/t_{1/2}$
1/3	$t_{1/3}$	$65.92/t_{1/3}$
1/4	$t_{1/4}$	$83.18/t_{1/4}$
1/8	$t_{1/8}$	$124.77/t_{1/8}$

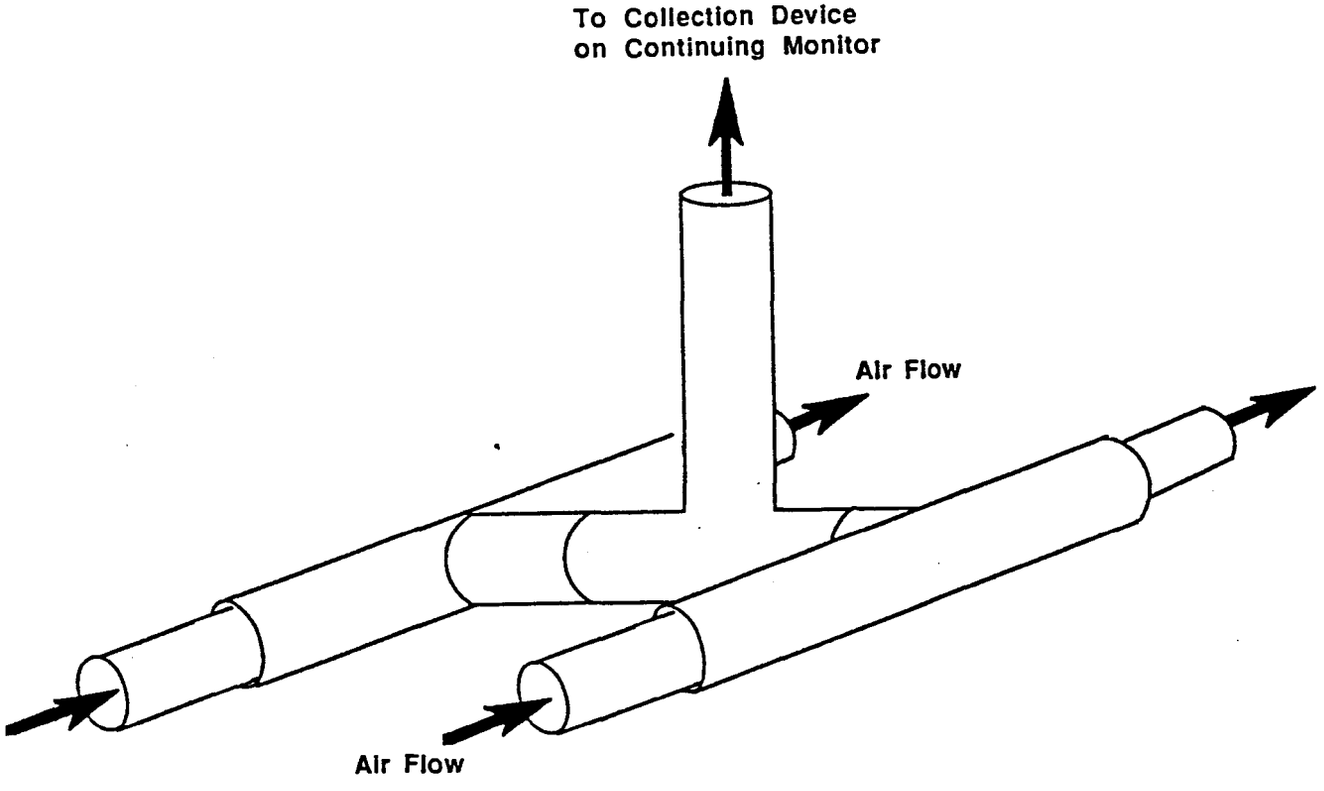

Figure 1. Four-Point Sampling Junction

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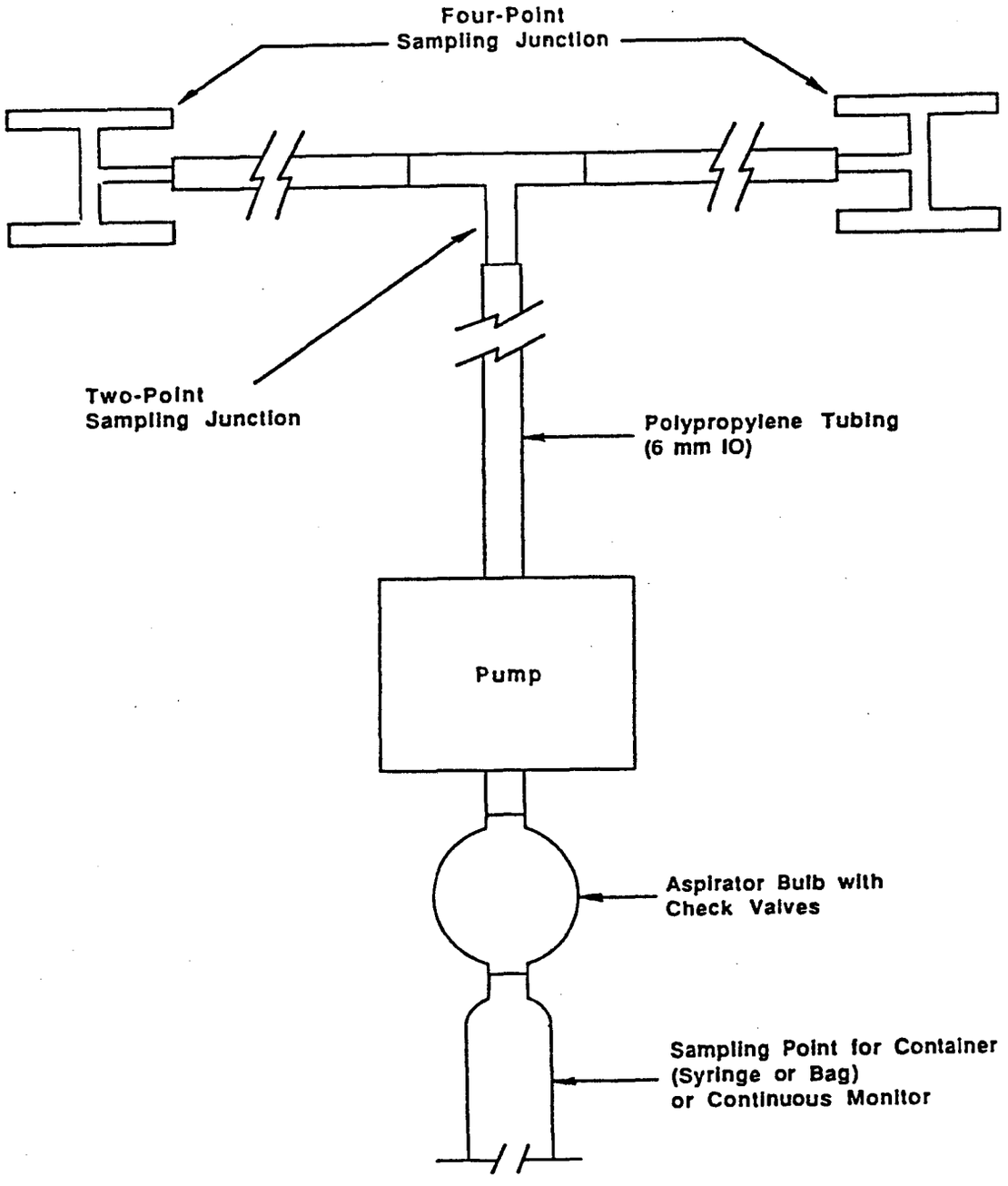

Figure 2. Symmetrical Light-Point Sampling System

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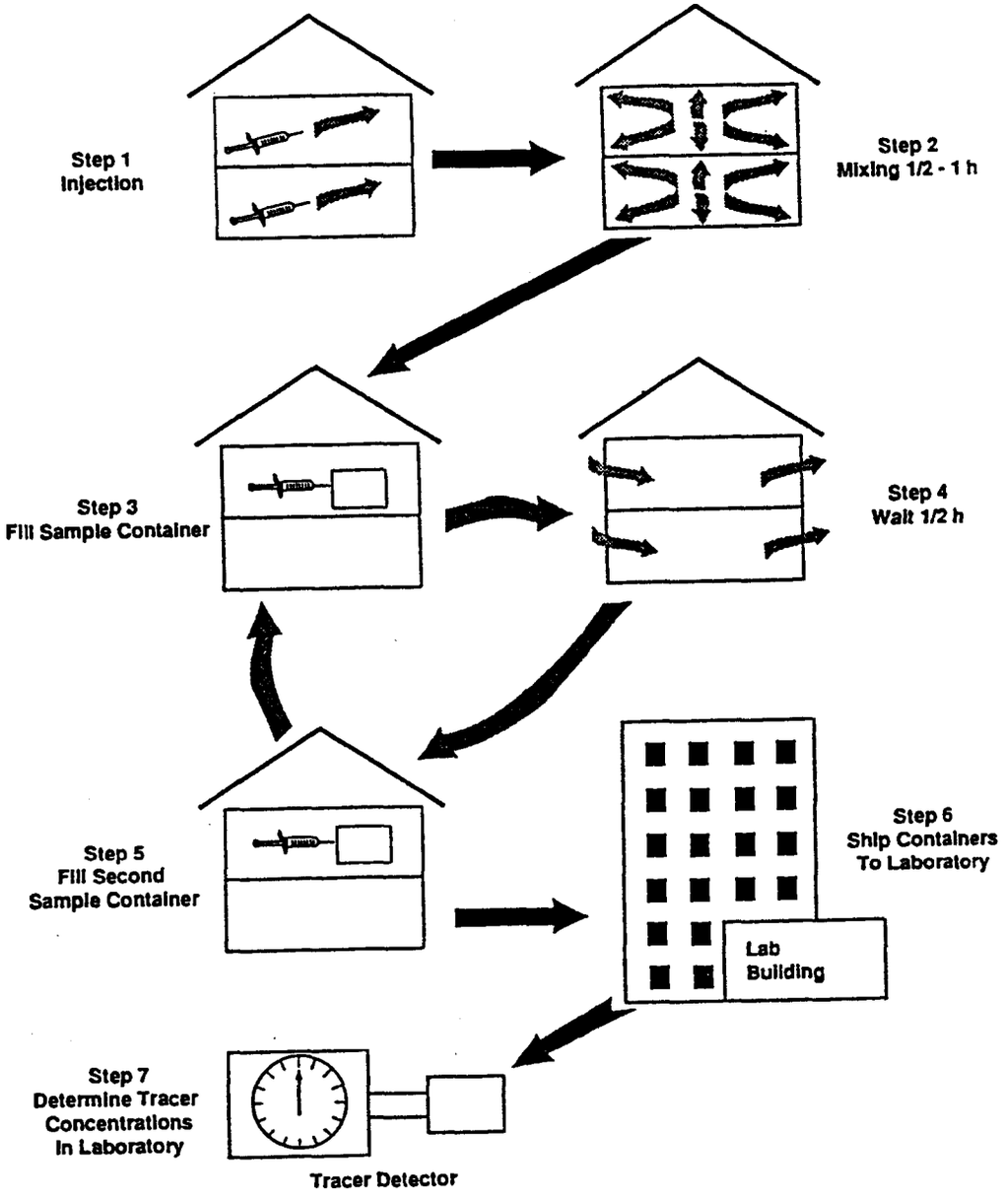


Figure 3. Procedure for Measuring Air Leakage Rate Using Sample Containers

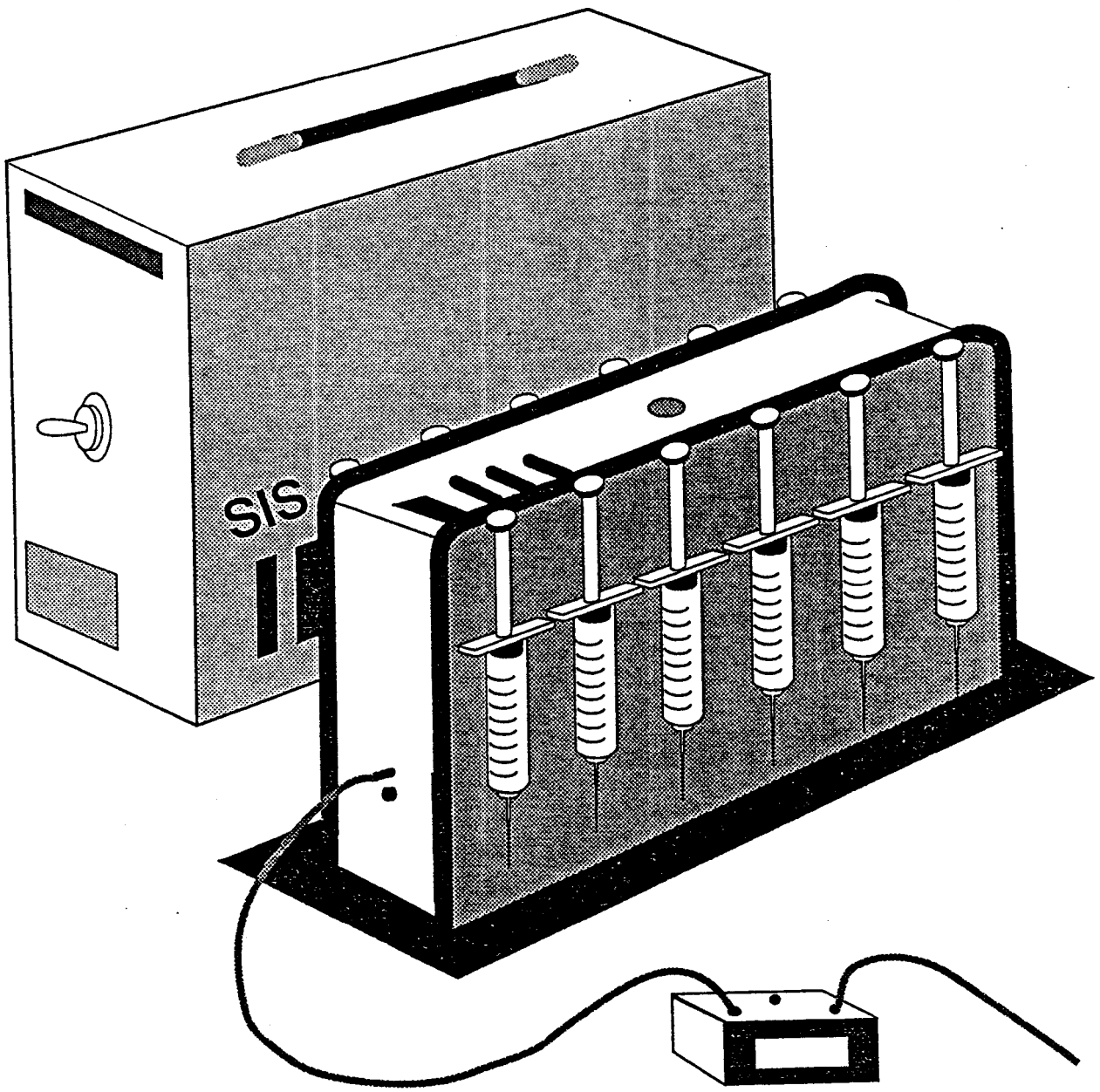


Figure 4. SIS Series 12A Multi-Station Sequential Environmental Gas Sampler

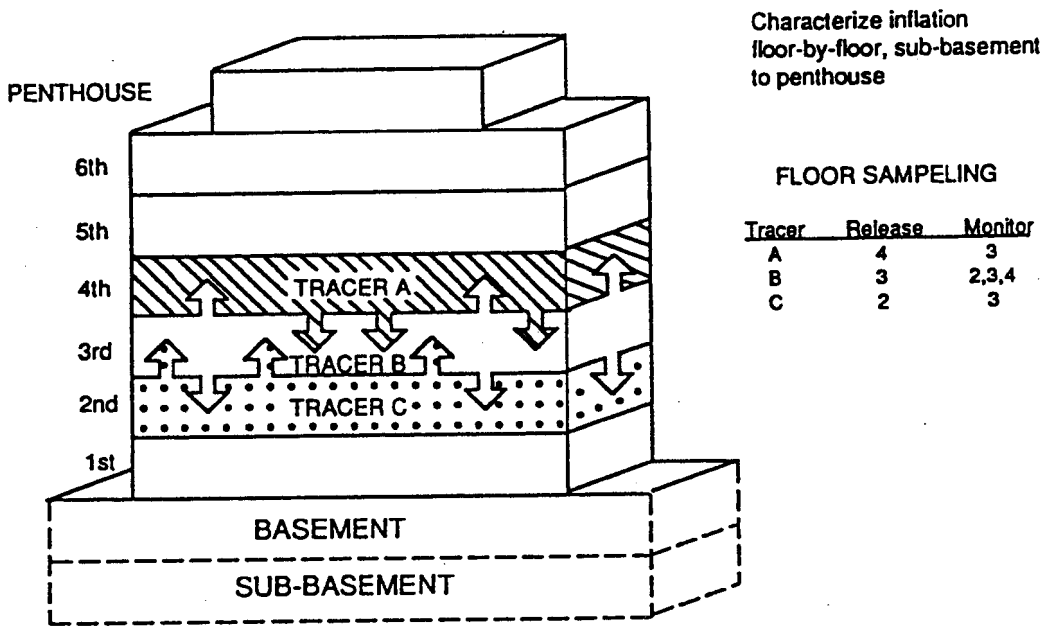


Figure 5. Multiple Tracer "Sandwich Approach" for Characterizing Air Infiltration in High-Rise Buildings

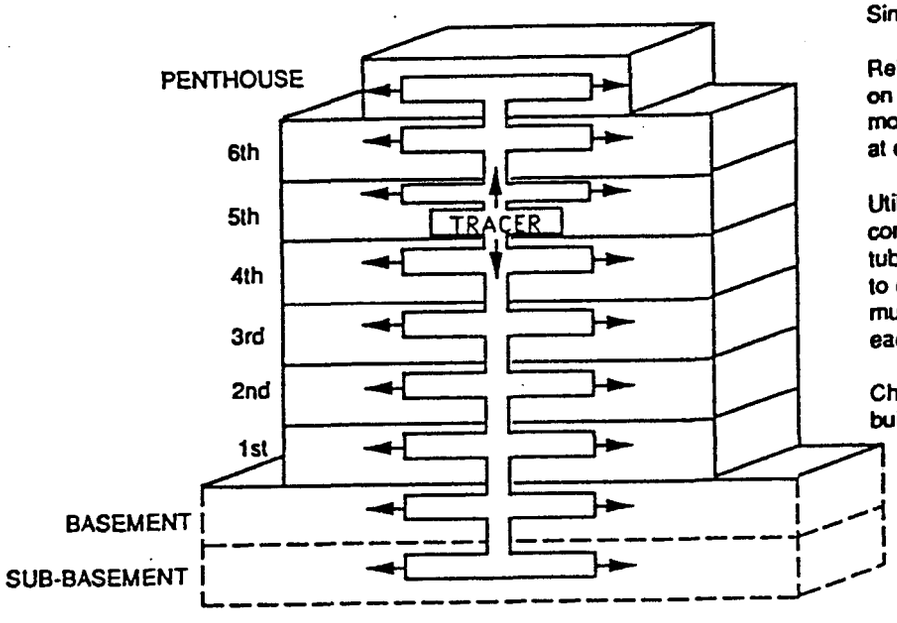
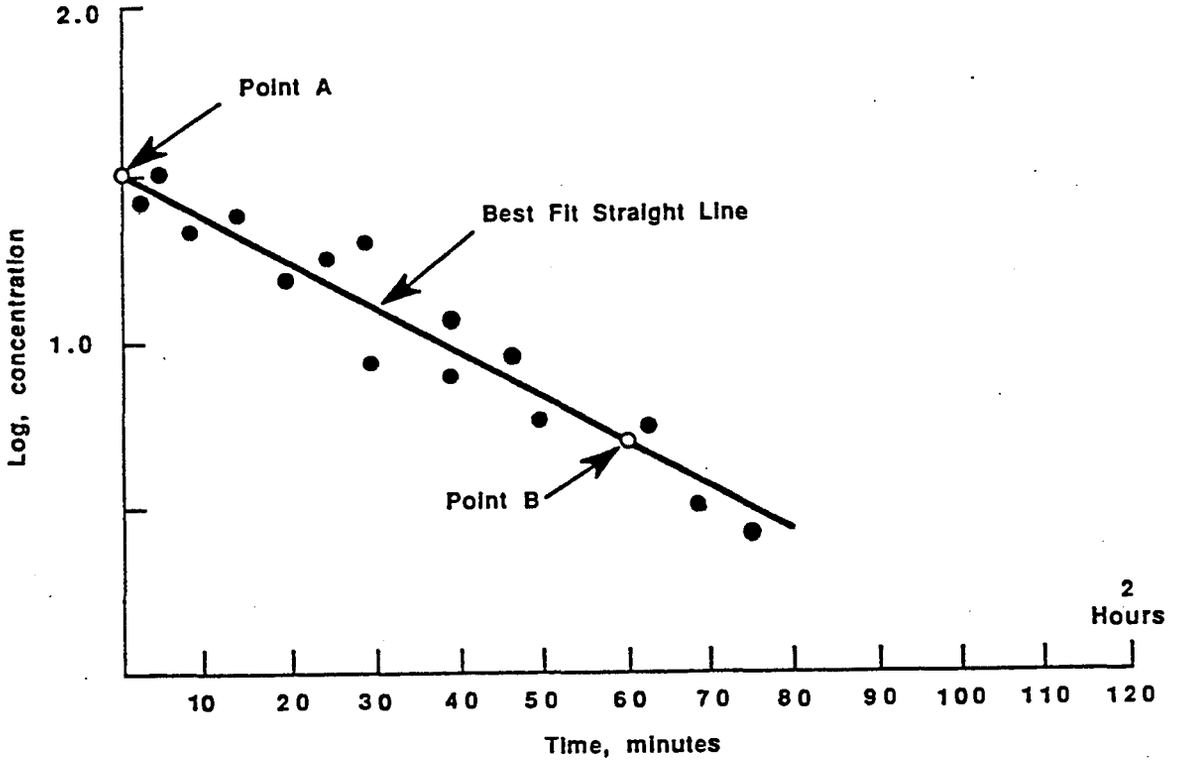


Figure 6. Single Tracer "Simultaneous Approach" for Characterizing Air Infiltration in High-Rise Buildings



● Data Points (Natural Logarithm of Concentration Values)

○ Concentration Points 60 Minutes Apart

For $C_A = 5$ and $C_B = 2$; the exact ACH = 0.916

Graphically

$ACH = \ln C_A - \ln C_B$

$= 1.6 - 0.7$

$= \underline{0.9}$

Point A = Start
Point B = 60 Minutes

Figure 7. Graphical Determination of Air Change Rate

Chapter IP-5

DETERMINATION OF NITROGEN DIOXIDE (NO_2) IN INDOOR AIR

- **Method IP-5A - Continuous Luminox Monitor**
- **Method IP-5B - Palmes Diffusion Tube**
- **Method IP-5C - Passive Sampling Device**

1. Scope

This document describes three methods for determination of NO_2 in indoor air. An active sampling device and two passive sampling devices are discussed. The monitoring of nitrogen dioxide (NO_2) at sub-ppm and low-ppb levels is of primary concern in indoor, nonindustrial locations such as the home. The trend toward much more airtight homes which began during the energy crisis of the early 1970s has caused concern among health experts about increased levels of NO_2 in indoors. 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.

2. Applicability

2.1 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 to detect the presence of 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). 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.

2.2 In recent years, interest has been increasing in the use of diffusion-base passive sampling devices (PSDs) for the collection of NO_2 in indoor air. PSDs are more attractive for indoor air because of their characteristics of small size, quiet operation (no pump), and low unit costs.

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

2.4 Since the PSDs are 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 concentration.

2.5 Compendium Method IP-5B and Method IP-5C use the diffusion principle for monitoring NO_2 in indoor air. Method IP-5B uses the Palmes tube, while Method IP-5C utilizes the passive sampling device (PSD).

Method IP-5A

DETERMINATION OF NITROGEN DIOXIDE (NO_2) IN INDOOR AIR USING A CONTINUOUS LUMINOX MONITOR

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Method IP-5A

DETERMINATION OF NITROGEN DIOXIDE (NO_2) IN INDOOR AIR USING A CONTINUOUS LUMINOX MONITOR

1. Scope

1.1 Nitrogen dioxide (NO_2) 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.

1.2 Described herein as a method by which nitrogen dioxide can be sampled and analyzed in the air. The detection of NO_2 by chemiluminescence takes place between gas and liquid phases whereby the contact of NO_2 gas with a solution of Luminol causes direct oxidation of the solution.

1.3 The following method describes an instrument using chemiluminescence detection for the determination of NO_2.

2. Applicable Documents

2.1 ATSM Standards

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

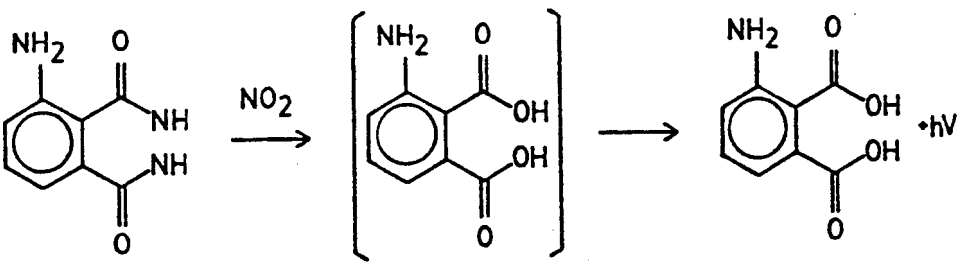
2.2 Other Documents

U.S. Environmental Protection Agency Technical Assistance Document (1)
Laboratory and Indoor/Ambient Air Studies (2-10)
Other Documents (11-12)

3. Summary Of Method

3.1 The instrument monitors NO_2 gas concentrations by the real-time, direct measurement of the fluorescent energy emitted from the reaction of NO_2 with Luminol solution (5-Amino-2,3 dihydro-1,4 phthalazine dione).

3.2 The LMA-3 NO_2 analyzer operates by detecting the fluorescent energy produced when NO_2 reacts with a solution of Luminol. In operation, sampled air is drawn through the instrument and across a fabric wick wetted with the Luminol solution. The solution is continuously replenished at the top of the wick and removed at the bottom by a small peristaltic pump. If the sampled air contains NO_2, the Luminol solution is oxidized, producing fluorescent energy according to the reaction shown on the next page.



Luminol Solution

Luminescence Emission

3.3 To detect the release of energy (hv) from the reaction, a photomultiplier tube (PMT) is positioned to view the central portion of the wick. The signal from the PMT is directly proportional to the NO_2 concentration in the sampled air. Unlike other chemiluminescent NOx detectors, the Luminox monitor measures NO_2 directly without prior conversion of NO_2 to NO. The operational block diagram for the LMA-3 NO_2 analyzer is illustrated in Figure 1.

3.4 A 500-mL polypropylene bottle serves as a reservoir to supply fresh Luminol solution continuously through the instrument. The solution is moved from the reservoir to the reaction chamber by a peristaltic pump operating at about 0.05 mL/min. The wick material is kept saturated while 1.5 L/min of sample air is drawn over the surface where reaction takes place. The emitted light from the reaction of NO_2 and Luminol is measured by a photomultiplier tube situated in front of the chamber. After leaving the wick material, Luminol is transported via the peristaltic pump into a reservoir for spent solution. Sample air drawn from the chamber and exhausted to the rear of the instrument by a small air pump.

4. Significance

4.1 Nitrogen dioxide is a reactive gas product of combustion. Household combustion sources include gas stoves, gas heating, wood burning stoves, furnaces and fireplaces. NO_2 levels in indoor air are usually equal to or lower than outdoor levels. But if combustion sources are present, then NO_2 levels can exceed outdoor concentrations. The National Ambient Air Quality Standard (NAAQS) for NO_2 for a 24-hour average is 100 $\mu g/m^3$ (~53 ppb).

4.2 Numerous investigations have documented that NO_2 concentrations may be substantially greater indoor in homes that have unvented combustion sources. Specifically, increase levels of NO_2 may be encountered in homes with gas heating, gas stoves with pilot lights and cigarette smoke.

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4.3 NO_2 has been known to cause acute lung damage at high concentrations. Concentrations at five parts per million (ppm) can cause respiratory distress. However, data on health effects of NO_2 at concentrations commonly encountered in the residential environment (500 ppb to 1 ppb) is unknown. In experimental models at these NO_2 levels, reduced efficiencies of lung defense mechanism, effects on mucociliary clearance, alveolar macrophages and the immune system have all been documented (13-14).

4.4 Consequently, the need exists for a continuous, extrasensitive NO_2 analyzer which is reliable, accurate, portable and suitable for indoor air measurements.

4.5 Historically NO_2 has been determined by colorimetric methods, and chemiluminescence methods using catalytic oxidation whereby the catalytic converter converted NO_2 to NO. In turn, NO would react with ozone and cause measurable chemiluminescence. Consequently NO would interfere with NO_2 analysis.

4.6 By using Luminol in an alkaline solution, gaseous NO_2 at atmospheric pressure reacts with the Luminol to also produce chemiluminescence. This reaction has little NO interference.

4.7 Consequently, Scintrex Ltd. applied this technology to a continuous NO_2 analyzer capable of monitoring down to the low ppb range. Recently, the monitor was extensively evaluated (10). Table 1 outlines the results of the laboratory evaluation.

5. Definitions

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

5.1 Chemiluminescence - the emission of radiation from a molecule which, after being in a vibrationally excited state, returns to its ground state.

5.2 Fluorescence - the process by which electromagnetic radiation of one spectral region is absorbed and radiated as nonthermal radiation at other wavelengths, usually longer.

5.3 Luminol - a modified solution of Luminol (5-amino-2, 3-dihydro-1,4 pthalamine dione), NaOH, NA_2SO_3 and alcohol dissolved in deionized water.

5.4 Precision - the ability of an analyzer to produce a uniform response with repeated measurements under identical conditions. The analyzer's precision is estimated by the standard deviation of a set of measurements at a uniform pollutant concentration.

5.5 Interferents - Any chemical compound which produces a response in or change of response in the analyzer is an interferent. Widely occurring compounds which may interfere include water vapor (H_2O), CO_2, oxygen (O_2), ozone (O_3) and peroxyacetyl nitrate (PAN). These compounds are known to quench various fluorescent and photochemical processes.

5.6 Limit of detection (LOD) - a limit of detection is defined as the minimum signal that may be distinguished from the background signal with a given confidence level. An LOD equal to three standard deviations of the signal for clear air (6) has been accepted.

5.7 Noise - noise (7) is the standard deviation of twenty-five consecutive measurements of zero air taken at two-minute intervals.

5.8 Lower detection limit (LDL) - lower detection limit (7) is specified as "the minimum pollutant concentration which produces a signal of twice the noise level."

5.9 Drift - drift (7) is specified as the difference between two measurements taken at the beginning and end of a specific test period (12-hour or 24-hour period).

6. Interferences

6.1 Historically, ozone has been reported in the literature (7,8) as an interference as a quenching agent to the ultraviolet light given off from the chemical reaction. An O_3 trap has been added to the analyzer to eliminate this interference.

6.2 PAN has been documented (7,9) as an interference in instruments employing the Luminol reaction. Reported relative response of the LMA-3 analyzer has been both qualitative and less than quantitative. A recent laboratory evaluation (10) indicated an average relative interference response of 0.62.

6.3 In a recent laboratory test (10), the LMA-3 analyzers illustrated measurable interference from CO_2 of 1 to 2 ppb at an NO_2 concentration level of 25 ppb (or a 5 to 7% error).

6.4 Oxygen is an effective quencher of fluorescent and photochemical reactions. Although the O_2 concentration in indoor air is largely constant and no O_2-dependent effect should be seen in the measurements, possible problems could exist during calibration. Laboratory evaluation (10) has indicated an analyzer response variation of approximately ± 0.6 ppb at an NO_2 concentration of 26.5 ppb (or 2% of the total response of the LMA-3 analyzer). Consequently, indoor air levels of O_2 should be contained as part of the calibration gas mixtures.

6.5 Water is a common interference for many fluorescent analyzers. In a recent study (10), results indicated an analyzer response variation of approximately -7 ppb at a concentration of 25 ppb of NO_2 (or a 29% error). However, since indoor air normally has a constant relative humidity, this should not affect monitor response during sampling. However, if calibration gases contain no moisture, then an error can be introduced into the analytical system. Each calibration point generated should contain approximate levels of water representing the indoor air parcel being sampled.

7. Apparatus

7.1 Sampling and Analysis

7.1.1 Chemiluminescent NO_2 monitor - Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, LMA-3 Part No. 856 000 or equivalent.

7.1.2 Rechargeable battery - back-up one 12 volt 1.5 amp-hr. gel cell. or 115 or 220 volt AC battery, best source.

7.1.3 Tubing - tubing for the liquid pump, 9.8 cm long for the waste line, 8.9 cm long for the feed line, Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 856 019 or equivalent.

7.1.4 Wick - wick for the monitor, Scintrex, Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 856 020 or equivalent.

7.1.5 Air line trap - trap protects the air pump from liquid infiltration, best source.

7.1.6 Filter cartridge - Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 200 213 or equivalent.

7.1.7 2 liter external reservoir kit - to reduce replenishing Luminol solution (optional), Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 856 018 or equivalent.

7.1.8 Carrying case - for portable operation, Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 856 014 or equivalent.

7.1.9 Calibrator - portable calibrator for LMA-3 monitor (optional). Provides a continuous supply of purge gas and a stable constant temperature environment for permeation device(s), Scintrex, Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, LC5-3 Luminox Calibration Source or equivalent.

7.1.10 Data logger - portable calibration controller (optional). Provides accurate dilutions of a gas standard using mass flow controllers and mixing chambers, Scintrex, Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, LCC-3 Luminox Calibration Controller or equivalent.

7.2 Calibration

7.2.1 Flowmeters and controllers - In order to obtain an accurate dilution ratio, in the dilution method used for calibration, the flow rates must be regulated to 1% and be measured to an accuracy of at least 2%. The meter and controller can be two separate devices, or combined in one device. The user's manual for the meter should be consulted for calibration information. Additional information on the calibration of flow devices can be found in the Quality Assurance Handbook (15). If the calibration system uses the same type of flow meter (e.g. bubble flow meter, rotameter, mass flow meter, etc.), then no correction to standard temperature and pressure (STP) need to be made.

7.2.2 Mixing chambers - A chamber constructed of glass, Teflon®, or other nonreactive material, and designed to provide thorough mixing of NO_2 and diluent air for the dilution method.

7.2.3 Output manifold - The output manifold should be constructed of glass, Teflon®, or other nonreactive material, and should be of sufficient diameter to insure an insignificant

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pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent indoor air from entering the manifold.

8. Reagents and Material

8.1 Luminol Solution

8.1.1 The Luminol solutions used by the LMA-3 NO_2 analyzer contains additives which enhance the response to NO_2, and reduce interferences from other gases such as ozone. Note: The Luminol solutions are weakly basic and should be handled accordingly. Avoid contact with the eyes or prolonged contact with the skin. Wash with water after contact with the skin.

8.1.2 A variety of Luminol solutions have been formulated to give linear responses over different concentration ranges.
Note: The information supplied with each bottle will outline the range of linearity, rejection ratio for the ozone response as well as the PAN (peroxyacetyl nitrate) response for all of the available formulations at that time.

8.2 Calibration Gas

Note: In a recent laboratory test (10) O_2, CO_2 and water vapor were determined to cause interference to the monitor output; therefore, it is important to calibrate the LMA-3 analyzer with calibration mixtures containing indoor levels of these species.

8.2.1 Zero-air source - A source of dry zero-air that is verified to be free of contaminants that could cause detectable responses from the NO_2 analyzer will be needed. The zero-air must contain <0.1 ppb NO_2.

8.2.2 Calibration standard - NO_2 standards must be traceable (16) to a National Institute of Standards and Technology - Standard Reference Material (NIST-SRM) or a NIST/EPA approved commercially available Certified Reference Material (CRM). The NO_2 standards must be in air unless the dilution method is used. For dilution, NO_2 in nitrogen may be used if the zero-air contains O_2, CO_2 and H_2O similar to indoor air. An acceptable protocol for demonstrating the traceability of commercial cylinder gas to an NITS-SRM or CRM cylinder gas is provided in Section 14, reference 17. In order to establish a calibration curve and determine linearity of the LMA-3 analyzer, the calibration gas cylinder should correspond to 10, 20, 40, 60, and 80% of monitor full scale.

8.2.3 Span gas - pressurized cylinder containing NO_2 concentration corresponding to 80% of full scale, best source.

8.2.4 Flow control valves - used to regulate gas cylinder flow rate to analytical system, best source.

8.2.5 Multistage pressure regulators - standard two-stage, stainless steel diaphragm regulators with pressure gauges for gas cylinders.

8.2.6 Tubing - Polypropylene tubing to connect analyzer to gas cylinders when calibrating, zeroing, and spanning the instrument.

8.2.7 Thermometer - used to measure monitoring area temperature.

8.2.8 Barometer - capable of measuring barometric pressure of monitoring area.

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9. Sampling System

9.1 Description

The LMA-3 NO_2 analyzer is contained in an instrument housing approximately 15" x 8" x 8" (20 x 22 x 38 cm). The instrument can be operated continuously on 110 VAC or for 2 to 3 hours with the assistance of an onboard battery. The monitor can operate at a range of either 0 to 20 or 0 to 200 ppbv, and can be connected to a strip-chart recorder or data acquisition system for permanent record of the NO_2 measurements.

9.1.1 Front Panel Controls (see Figure 2)

9.1.1.1 The power switch turns on the power to the electric and the liquid pump motor. When it is ON (upper position) the yellow LED above it will be illuminated.

9.1.1.2 The air pump switch turns on the air pump if the power is ON. A yellow LED indicates that the air pump is ON.

9.1.1.3 The backflush momentary push button initiates the backflush cycle. During the backflush, waste Luminol is pumped into the wick area to rinse out any residue, then it is pumped away. The cycle takes about 5 minutes. During this time the red LED above the backflush switch will light up. No readings may be taken during this period.

9.1.1.4 The battery charger is active any time the unit is plugged into line current. The yellow "battery charge" LED should be illuminated under this condition.

9.1.1.5 The battery low red LED indicates two warning conditions. If the unit is operating from the battery and the voltage drops below 11.6 volts, the LED will be illuminated. Secondly, if the unit is plugged in and the current acceptance of the battery exceeds 100 mA, the LED will come ON. The LED may be illuminated for a few minutes each time the unit is plugged into line current. This does not indicate a fault. It will stay ON for an extended period if the battery has been substantially discharged. If the unit is put into battery service before the light goes out, a full three hours of use should not be expected.

9.1.1.6 The three-position time constant switch is used to select 0.3, 1.0 or 3.0 seconds as the time constant for the last amplifier. The setting of 0.3 seconds provides the least amount of signal damping and is suitable for most applications. The slower settings may be selected if it is desirable to damp out noise in the signal originating from fluctuations in the NO_2 concentration, or from the instrument when measuring very low NO_2 mixing ratios.

9.1.1.7 The zero control is used to bring the displayed or output signal to zero when there is no NO_2 present.

9.1.1.8 The span control sets the photomultiplier tube high voltage (PMT HV) and hence the gain of the light detection system. It is used to change the displayed value or output voltage when a calibration source of known mixing ratio is introduced to the instrument.

9.1.1.9 The BNC type output connector provides an output voltage for use with a chart recorder or other data acquisition system. Each volt at this output corresponds to

100.00 in the display range 200, or to 10.000 in the display range 20. The output voltage extends to 5 volts even though the display shuts down above values of 2 volts.

9.1.1.10 This is a two-position toggle switch for selection of either 0 to 20 ppbv or 0 to 200 NO_2 range. This display is 4.5 digits so that the last decimal place represents 1 pptv when the instrument is in the 20 range. This display shows a single "+" sign at the left hand side when the input to the digital panel meter is above its acceptable range.

9.1.1.11 This is a three-position momentary toggle switch by which the input to the digital panel meter is chosen. If the unit is properly calibrated in the normal center position (signal), the NO_2 mixing ratio is continuously displayed. When the toggle is lifted up, the battery voltage is displayed. In order to give a true voltage reading, the battery charger is off line while this switch is held in the upper position. If the battery low light was ON due to high current acceptance, it will go out when the battery voltage is checked. When the toggle is held down, the photomultiplier high voltage will be displayed. The normal operating range for the photomultiplier is -400 to -800 volts.

9.1.1.12 The signal overload red LED indicates two fault conditions. If the light is ON steadily, then the first amplifier is overloaded. The second fault indication occurs when there is severe overloading at the first amplifier. The signal overload light will flash. This will usually be the result of the light leaking into the system from improper assembly after servicing.

9.1.2 Rear Panel Controls (see Figure 3)

9.1.2.1 These fittings are provided so that the user may attach larger fluid reservoirs for longer unattended use. They are not connected when the instrument leaves the factory.

9.1.2.2 Fittings are provided on the back panel for connecting tubing to and from the instrument. They are compression type fittings constructed on stainless steel with teflon ferrules. Suitable tubing sizes are 0.25 inch or 6 mm outside diameter.

9.1.2.3 Two access hole through the back panel are provided just below the Air Out connector. They are provided to make servicing of the wick area easier. These are normally closed with press-in chrome plated hole plugs.

9.1.2.4 This connector permits the external control of two of the LMA-3's functions: 1) operation of the air pump and 2) initialization of the backflush sequence. In addition, the circuit to the air pump indicator may also be controlled through this connector. The pin assignments are as follows:

Air pump live (A)
Air pump return (B)
Air pump LED live (C)
Air pump LED return (D)
LMA-3 supply (9.2 Volts) (E)
LMA-3 ground (F)
Ground for backflush trigger (H)
Input for backflush trigger (J)

When external control is not desired, the "shorting plug" must always be installed. The shorting plug connects pins A to B, C to D and H to J. For external control of functions

within the LMA-3 it is recommended that optical isolators or relays be used in order to avoid having to tie the grounds of the LMA-3 and the driving electronics together.

The following external functions are possible:

- Air pump control - Opening and closing the contact between pins A and B will turn the air pump OFF an ON, provided the air pump switch that is located on the front panel is turned ON.
- Air pump indicator control - Opening and closing the contact between pins C and D will turn the air pump LED OFF and ON provided the air pump switch that is located on the front panel is turned ON.
- External backflush control - For control of the backflush trigger, wire the switching device as follows: 1) pin E through a 100 k ohm resistor to normally open, 2) pin F through a 100 k ohm resistor to common, 3) pin H to common, and 4) pin J to normally closed. The switch may be held high between 20 microseconds and 10 seconds before going low again. This will put 4.6 Volts down pin H to trigger the backflush cycle. The front panel backflush control will still be usable if this wiring is used.

9.1.2.5 The BNC type output connector is provided for the convenience of the operator. It carries exactly the same signal as the Output connector on the front panel.

9.1.2.6 The power cord receptacle also carries the instrument's main fuse and a supply voltage selection card. Locate the power receptacle on the rear of the instrument. Slide the plastic window to the left to expose the fuse and voltage selector. Observe the number showing on the small circuit board which is now visible. This number should indicate the nominal value of the power supply to be used (i.e. 120 or 240 volts). If it does not indicate the proper voltage, pull it out and re-orient it so that the desired figure shows when the board is re-installed. There are also positions which indicate 100 or 220 volts. These are not used on this instrument. If they are selected, the power circuits will be supplied as if 120 had been selected (for 100) or if 240 had been selected (for 220). The instrument is shipped with the voltage selector in the 120 position and a 0.2 amp slo-blow fuse installed. To inspect or change the main fuse, pull the small lever marked "Pull Fuse".
Note: If 240 volt service is required the main fuse must be changed to 0.1 amp slo-blow. Four spare fuses are supplied with the instrument, two of each value. Once the proper voltage selection and fusing have been verified, the plastic window may be slid to the right and the power cord inserted in the receptacle.

9.1.2.7 The LMA-3 may be operated from lead-acid type batteries of larger capacity than the rechargeable batteries built-in to the instrument. The nominal voltage of the external battery should be 12 volts. When the plug is pushed into the jack, the internal battery is disconnected from the power circuit and the external battery takes its place. If the external battery is of much higher capacity, then the built-in battery charger will not provide enough current to recharge the battery in a reasonable amount of time. For this reason, large external batteries should be recharged separately.

Note: When connecting an external battery, make sure the LMA-3 is turned OFF and is not plugged in to line current. First, clamp the jaws onto the external battery (red to positive and black to negative) and then plug the cable into the back of the LMA-3.

9.1.3 Inside display area - The inside display area contains several distinct functional areas. They are:

- Detection assembly
- Liquid/air handling components
- Power supplies/signal processing

9.1.3.1 The detection assembly contains the photomultiplier tube (PMT), the air passage and wick plates and the liquid and air fittings.

9.1.3.2 Air passage plate - The function of this plate is to direct the sample air onto the wick. The air passage plate incorporates a window which admits light to the PMT detector. The air pathway in the plate is convoluted in order to stop ambient light from reaching the PMT detector.

9.1.3.3 Wick plate - The wick plate is fastened directly to the air passage plates. The wick itself consists of a strip of absorbent material held to the plate by bars at the top and bottom. The liquid fittings project from the left side of the detector assembly. The upper fitting carries a slow continuous feed of the Luminol solution to the top of the wick and the lower fitting carries away the expended solutions to a waste bottle. The air fittings face the rear of the instrument. The upper AIR IN fitting is oriented upwards to facilitate the attachment of the PFA Teflon® air tubing by means of a teflon compression fitting. The lower AIR OUT fitting is a simple nipple over which the tygon outlet tubing is pressed.

9.1.3.4 Liquid/air handling components - The miniature air pump is attached to the top right side of the instrument frame. The pump draws air through the air passage circuit and then exhausts the sampled air through the AIR OUT fitting located in the rear panel. A trap is provided in the air line to protect the air pump from liquid that may escape from the detector assembly as well as from particulates in the sample air. The trap is located between the detector assembly and the air pump and consists of two stages, a liquid trap and a particulate trap. The liquid trap is a round chamber, mounted high on the inside wall of the LMA-3, which captures by means of gravity any large amounts of liquid in the air line. The second trap is a disposable cartridge air filter, located beneath the liquid trap, which captures any particulates in the air being sampled. The liquid pump is a two-channel peristaltic pump, mounted on the left portion of the center bulkhead. When the power is turned ON, the roller assembly can be seen to rotate at approximately 3 rpm. The direction of the rotation coincides with the direction of the liquid flowing through the tubing. The liquid lines can be traced quite easily. It can be observed that the liquid lines run from the Luminol supply bottle, through one side of the pump, to the top fitting on the wick plate, then from the bottom fitting on the wick plate to the other side of the pump, and finally to the waste bottle.

9.1.3.5 Power supplies/signal processing - The main power supplies are controlled from the sealed power supply section that can be seen in the left rear corner of the case. Housed inside are two printed circuit boards. The power circuit board provides voltages

for logic circuits, power for running the motors, charging the battery, and supplying the photomultiplier high voltage circuitry. The second board carries the main power transformer with its secondary fuse and the timer circuit for controlling the air and liquid pump motors during the backflush operation. The backup battery is located underneath the rear chassis and cannot be seen from above. Any time the unit is plugged in to line current, the battery is automatically charged.

9.1.3.6 Signal processing - The remainder of the electronics lie forward of the center bulkhead. One printed circuit board is devoted to the high voltage power supply for the photomultiplier while the other carries the signal generation and temperature compensation circuits. The normal switches, potentiometers and indicator lights are found in this area as well as the self-contained liquid crystal digital voltmeter attached to the front panel.

9.2 Operating Procedures

9.2.1 Installation

9.2.1.1 Install the instrument in an upright position.

Note: The instrument can be operated continuously on an angle of up to 30 degrees from vertical in any direction. It can also tolerate momentary tipping in any direction of up to 60 degrees from vertical.

9.2.1.2 Before operating, ensure that the air INLET and OUTLET parts on the back panel, are not obstructed.

9.2.2 Internal Reservoir (see Figure 4)

9.2.2.1 Confirm that the instrument is turned OFF and unplugged.

9.2.2.2 Remove the top cover of the instrument.

9.2.2.3 Working with one bottle at a time, pull the tubing from the top of the bottle and remove the bottle from the instrument.

9.2.2.4 The Luminol fluid may then be emptied or replenished as appropriate by removing the lid from the bottle.

Note: The "feed" bottle sits in the well closest to the front and the "waste" bottle sits to the rear.

9.2.2.5 Replace the bottle and push the tubing back onto the fitting.

9.2.2.6 Proceed with the second bottle as described above.

9.2.2.7 Replace the instrument cover and tighten the cover fastener located on the rear panel.

9.2.3 External Reservoirs

Note: An external reservoir kit is commercially available. To install the external reservoirs, the following sequence of steps are outlined below.

9.2.3.1 Confirm that the instrument is turned OFF and unplugged.

9.2.3.2 Loosen the instrument cover fastener located on the rear panel and slide the cover off.

9.2.3.3 Loosen the fittings on top of the standard liquid bottles so that the black plastic fitting may be pulled out.

9.2.3.4 Remove the standard bottles from the instrument.

9.2.3.5 Plug the black tubes into the bulkhead fittings on the rear panel and finger tighten the fitting caps.

9.2.3.6 Tubes from the external reservoirs are attached to the LIQUID IN and LIQUID OUT fittings on the rear panel.

Note: The liquid lines should be kept as short as possible and very small inner diameter so that fresh solution will reach the wick quickly after liquid changes and so that the backflush cycle will operate correctly.

9.2.3.7 Replace the instrument cover and tighten the cover fastener located on the rear panel.

9.2.4 Powering the Unit and Sampling

9.2.4.1 If line current is available, plug the LMA-3 into the power source. The yellow battery charge light emitting diode (LED) should be illuminated.

Note: Because the battery is charged with a "float" voltage, the unit may be safely left plugged into the power source without damaging the battery.

9.2.4.2 Turn the power switch ON. The yellow LED above the switch should be illuminated. The digital panel meter will also be activated and will show a four digit number approximately equal to zero.

9.2.4.3 Insure that the liquid pump motor is operating. In operation, the loading on the pump is uneven as a result of the work involved in compressing the pump tubing with each successive roller.

Note: The motor will sound alternately as if it is straining then running free. This is normal as long as the rotation does not significantly slow during the high load periods. The rotation speed of the pump should be approximately 3 rpm. After the liquid pump has been operating for about 10 minutes, you should be able to see plugs of liquid traveling down the waste tubing to the waste bottle.

9.2.4.4 Turn ON the air pump switch.

Note: You should now hear a fairly loud buzzing noise. This noise may be muffled by attaching a short length of one-quarter inch plastic tubing to the AIR OUT port. Tubing (preferably 0.030" wall x 0.25" OD teflon) may also be attached to the AIR IN port to deliver sample gas from a remote location or to muffle the air pump noise. Figure 5 illustrates the air flow through the LMA-3 NO_2 analyzer.

9.2.4.5 Check the battery voltage and photomultiplier tube high voltage (PMT HV) using the momentary DISPLAY SELECT switch. The battery voltage should be between 11.6 and 13.5 volts depending upon its state of charge. The PMT HV will normally be in the -400 to -800 volt range.

9.2.4.6 Select the appropriate DISPLAY RANGE and TIME CONSTANT. Where the NO_2 levels are very low, or if fast fluctuations in the signal are undesirable, choose a longer time constant setting.

9.2.4.7 Operate the instrument for 30 minutes in order to insure stable operation, then commence sampling at designated location.

9.2.5 Backflushing

9.2.5.1 As the LMA-3 operates, a certain amount of evaporation takes place in the reaction cell. Eventually this action leaves a solid residue which can block the detector window and reduce the readings. Recent field studies (10) have demonstrated that the LMA-3, when operated continuously for several days, will provide erratic responses. To eradicate the residue and erratic responses, a backflush cycle has been incorporated into the LMA-3 to dissolve and flush the residue into the waste bottle. The backflush cycle should be performed on a daily basis.

9.2.5.2 When the BACKFLUSH switch is pressed the backflush cycle will commence, shutting down the air pump and reversing the liquid pump at a higher than normal rate. This action draws liquid from the waste bottle and pumps it into the air passages. After about 2 1/2 minutes, the liquid pump returns to the normal direction of rotation at high speed. This quickly empties the air passages of liquid. After another 2 1/2 minutes, the liquid pump returns to its normal speed and the air pump restarts.

9.2.5.3 Backflush the system each time the reservoir is refilled (about every three days during continuous operation, or if a decrease in sensitivity is observed). Backflushing is recommended every 24 hours if the instrument is to be operated without daily calibration.

9.2.5.4 Ensure there is at least one-half inch of liquid in the waste bottle.

9.2.5.5 Place the three-way switch in the BACKFLUSH mode for about two minutes. The red LED above the BACKFLUSH button will remain lit during the cycle.

Note: If for any reason the instrument power is turned OFF during a backflush cycle, make sure that the AIR PUMP switch is in the OFF position before turning the power back ON. Run the instrument in this mode (normal liquid flow, air pump OFF) for at least 6 minutes before putting the air pump back ON or initiating another backflush.

9.2.5.6 When the fluid lines are full and the reaction chamber flooded, place the three-way switch in the PRIME position for approximately 2 minutes to clear sampling lines of fluid.

9.2.5.7 Return the three-way switch to the NORMAL position.

9.2.5.8 The LMA-3 signal will take 10 to 30 minutes to return to normal after a backflush operation.

Note: The backflush cycle should be initiated, whenever any of the conditions listed below are met:

- Each time the reservoir is refilled, or
- If a decrease in sensitivity is observed, or
- Daily if the analyzer is operated continuously.

10. Analytical Systems

10.1 System Description

10.1.1 The analytical system consists of a reducing agent, Luminol solution, with NO_2 gas acting as an oxidizing agent. A microphotometer measures the relative transmittance of the fluorescent energy emitted from the oxidation reaction of the Luminol.

10.1.2 A photomultiplier tube serves as the microphotometer by viewing the reaction site which is a cloth wick saturated in Luminol solution upon which the gas liquid reaction occurs.

10.1.3 The signal from the wick provides a measure of the NO_2 mixing ratio.

10.1.4 The signal is inputted to an analog to digital converter, a liquid crystal digital (LCD) voltmeter, and onto an LCD screen.

10.1.5 The analog can also be inputted to a strip recorder or to data acquisition instrumentation.

10.2 Systems Performance Criteria

10.2.1 Calibration - Calibrate the NO_2 air monitor every time the Luminol solution is changed or if the monitor has not been used for twelve or more hours.

10.2.2 Manual Zero and Span Calibration

10.2.2.1 Prior to operating the analyzer, an initial calibration must be performed. The following provides procedures to measure NO_2 concentrations in indoor air using the NO_2 LMA-3 continuous monitor.

Note: Follow the manufacturer's detailed instructions when calibrating a specific analyzer.

10.2.2.2 Assemble the analyzer as discussed in Section 9.2.4.

10.2.2.3 Connect zero gas to the analyzer at the AIR IN port.

10.2.2.4 Open the gas cylinder pressure valve.

10.2.2.5 Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired delivery pressure.

Note: If the air flow is pressurizing the unit, a "T" connection can be used to direct excess air to the atmosphere. Connect one end of the "T" to the AIR IN port and leave the other end open to the atmosphere.

10.2.2.6 Set the sample flow rate as read by the rotameter (read the widest part of the float) to the value that is to be used during sampling (2 Lpm is recommended).

10.2.2.7 Let the zero gas flow long enough to establish a stable trace. Allow at least 5 minutes for the analyzer to stabilize.

10.2.2.8 Adjust the zero control knob until the trace corresponds to the line representing 5% of the strip chart width above the chart zero or baseline. The above is to allow for possible negative zero drift. If the strip chart already has an elevated baseline, use it as the zero setting.

10.2.2.9 Let the zero gas flow long enough to establish a stable trace. Allow at least 5 minutes. Mark the strip chart trace as adjusted zero.

10.2.2.10 Disconnect the zero gas.

10.2.2.11 Connect the span gas with a concentration corresponding to approximately 80% of full scale, depending upon the Luminox solution, to the "T" connection.

Note: The calibration gas should contain O_2, CO_2 and H_2O in concentrations expected in indoor air.

10.2.2.12 Open the gas cylinder pressure valve. Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired pressure.

10.2.2.13 Set the sample flow rate, as read by the rotameter, to the value that is to be used during sampling, which should be approximately 2 Lpm.

10.2.2.14 Let the span gas flow until the analyzer stabilizes.

10.2.2.15 Adjust the span control until the deflection corresponds to the correct percentage of chart, as computed by:

$$\text{Correct percentage of chart} = [C_s(\text{ppb})]/[C_f(\text{ppb})] \times 100 + 5\ \%\ \text{zero offset}$$

where:
C_s = concentration of NO_2 span gas, ppb
C_f = full scale reading of analyzer, ppb

As an example where the % zero offset is 5 and the correct percentage of chart for the span gas of 40 ppb would be:

$$40\ \text{ppb}/50\ \text{ppb} \times 100 + 5 = 85$$

10.2.2.16 Allow the span gas to flow until a stable trace is observed. Allow at least 5 minutes. Mark the strip chart trace as adjusted span.

10.2.2.17 Disconnect the span gas.

10.2.2.18 Repeat Section 10.2.2.8 through Section 10.2.2.17 and if no readjustment is required, go to Section 10.2.3. If a readjustment greater than 1 ppb is required, repeat Section 10.2.2.8 through Section 10.2.2.9.

10.2.2.19 Lock the zero and span controls.

10.2.2.20 Record final zero and span potentiometer setting.

10.2.3 Multipoint Calibration

10.2.3.1 A multipoint calibration is required when the analyzer is first purchased, the analyzer has had maintenance which could affect its response characteristics, or when results from the auditing process show that the desired performance standards are not being met.

10.2.3.2 A multipoint calibration required calibration gases with concentrations corresponding to approximately 10, 20, 40, 60, and 80% of full scale. The calibration gases should be certified to be within ±2% of the stated value and purchased in high pressure cylinders with inside surfaces of a chromium-molybdenum alloy of low iron content or other appropriate linings. The cylinders should be stored in areas not subject to extreme temperature changes nor exposed to direct sunlight.

Note: Each span gas cylinder should contain O_2, CO_2 and H_2O in concentrations expected in indoor air.

There are two acceptable methods for dynamic multipoint calibration of the LMA-3 analyzer. They are:

- the use of individual certified standard cylinders of NO_2 for each concentration needed, and
- the use of one certified standard high concentration cylinder of NO_2, diluted as necessary with zero-air, to obtain the various calibration concentrations needed.

The equipment needed for calibration can be purchased commercially, or can be assembled by the user as illustrated in Figure 6. When a calibrator or its components are being purchased, certain factors must be considered:

- traceability of the certified calibration gases to an NIST-SRM (16,17) or a NIST/EPA-approved commercially available Certified Reference Manual (see Section 8.2),
- accuracy of the flow-measuring device or devices (rotameter, mass flow meter, bubble meter),
- maximum and minimum flows of dilution air and calibration gases, and
- ease of transporting the calibration equipment from site to site.

10.2.3.3 For an individual cylinder multipoint calibration, assemble the monitor and calibration system as illustrated in Figure 6.

10.2.3.4 Perform a manual zero and span calibration as in Section 10.2.2 and record the adjusted zero and span concentrations and their respective chart values.

10.2.3.5 Connect the span gas with a concentration value corresponding to 80% of full scale to the analyzer system.

10.2.3.6 Open the gas cylinder pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired pressure.

10.2.3.7 Set the sample flow rate as read by the rotameter (read the widest part of the float) to the value to be used when sampling, normally 2 Lpm.

10.2.3.8 Let the span gas flow long enough to establish a stable trace on the strip chart recorder; allow a least 5 minutes. Mark the chart trace as an unadjusted span.
Note: No adjustments are made at this point.

10.2.3.9 Disconnect the span gas.

10.2.3.10 Connect zero gas to the analyzer.

10.2.3.11 Open the gas cylinder pressure valve and adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired pressure.

10.2.3.12 Set the sample flow rate as read by the rotameter to the value that is used when sampling, usually 2 Lpm.

10.2.3.13 Let the zero gas flow long enough to establish a stable zero trace on the strip chart recorder; allow at least 5 minutes. Mark the chart trace as an unadjusted zero.

10.2.3.14 Repeat Section 10.2.3.5 through Section 10.2.3.13 for each of the calibration gases with concentrations corresponding to approximately 60, 40, 20 and 10% of full scale in that order.

10.2.3.15 Fill in the information required and construct a calibration curve of analyzer response as percent of chart versus concentration in ppb. Draw a best fit, smooth curve passing through the zero and minimizing the deviation of the remaining upscale points from the curve. The calibration curve should have no inflection points, i.e., it should either be a straight line or bowed in one direction only. Curve fitting techniques may be used in constructing the calibration curve by applying appropriate constraints to force the curve through the zero. This procedure becomes quite involved; however, the most frequently used technique is to graph the curve (see Section 10.2.3.28 through Section 10.2.3.30).

10.2.3.16 Recheck any calibration point deviating more than ±1.0 ppb NO_2 from the smooth calibration curve. If the recheck gives the same results, have the calibration gas reanalyzed. Use the best fit curve as the calibration curve.

10.2.3.17 For a dynamic dilution multipoint calibration, assemble the analyzer and dynamic dilution system as illustrated in Figure 6.

10.2.3.18 Adjust the zero air flow from the dilution system to the analyzer. The flow must exceed the total demand of the analyzer connected to the output manifold to ensure that no ambient air is pulled into the manifold vent.

Note: Zero and calibration gases should contain O_2, CO_2 and H_2O in concentrations expected in indoor air.

Note: In lieu of connecting analyzer to manifold, one may fill Tedlar® bags with generated standards to be sampled by the LMA-3 NO_2 analyzer.

10.2.3.19 Allow the analyzer to sample the zero air until a stable response is obtained; adjust the analyzer zero control to within ±0.5 ppb of zero base line.

Note: Offsetting the analyzer zero adjustment to +5% of scale is recommended to facilitate observing negative zero drift. On most analyzers this should be done by offsetting the recorder zero.

10.2.3.20 Determine the 80% of monitor full scale. Example: For an analyzer with an operating range of 0 to 50 ppb, the 80% value would be:

$$0.80 \times 50 = 40 \text{ ppb}$$

10.2.3.21 Adjust the NO_2 flow from the standard NO_2 cylinder to generate a NO_2 concentration of approximately 80% of the monitor full scale. Measure the NO_2 flow and record.

10.2.3.22 Measure the dilution air flow and record.

10.2.3.23 Calculate the generated NO_2 standard by the following equation:

$$(NO_2)_{gen} = [(NO_2)_{std}(Q_{NO_2})]/[Q_{dil} + Q_{NO_2}]$$

where:

$(NO_2)_{gen}$ = concentration of NO_2 generated, by dilution, ppb
$(NO_2)_{std}$ = concentration of NITS-SRM or CRM NO_2 gas standard, ppb
Q_{NO_2} = flow rate of NO_2 standard, L/min
Q_{dil} = flow rate of dilution air flow, L/min

Note: If wet test meter or bubble meter is used for flow measurement, the vapor pressure of water at the temperature of the meter must be subtracted from the barometric pressure.

Note: If both the NO_2 and the zero-air flow rates are measured with the same type of flow meter (e.g. bubble flow meter, rotameter, mass flow meter, wet test meter, etc.) correction to standard temperature and pressure (STP) is not necessary. However, if this is not the case, then the flow of NO_2 gas and dilution gas must be corrected to STP by the following equation:

$$Q_{NO_2} = (Q_1)\,[(P_{bar}/760)(298/T + 273)]$$

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where:
Q_{NO_2} = flow rate of NO_2 standard corrected to STP, L/min
Q_1 = uncorrected flow rate of NO_2 standard, L/min
P_{bar} = barometric pressure, mm Hg
T = temperature of gas being measured, °C

10.2.3.24 Allow the analyzer to sample until the response is stable; adjust the analyzer span until the required response is obtained, and record the NO_2 recorder response. After the zero and 80% points have been set, without further adjusting the instrument, generate four approximately evenly spaced points between zero and 80% by increasing the dilution flow (Q_{dil}) or by decreasing the NO_2 flow (Q_{NO_2}). For each concentration generated, calculate the NO_2 concentrations and record the results for each point.
Note: If substantial adjustments of the span control are necessary, recheck the zero and span adjustments by repeating Section 10.2.2.

10.2.3.25 Construct a calibration curve of monitor response as percent of chart versus concentration in ppb. Draw a best fit, smooth curve passing through the zero and minimizing the deviation of the remaining upscale points from the curve. The calibration curve should have no inflection points, i.e., it should either be a straight line or bowed in one direction only. Curve fitting techniques may be used in constructing the calibration curve by applying appropriate constraints to force the curve through the zero. This procedure becomes quite involved; however, the most frequently used technique is to graph the curve.

10.2.3.26 Recheck any calibration point deviating more than $\pm 1.0 + 0.02\ C_c$ ppb from the smooth calibration curve. If the recheck gives the same results, have that calibration gas reanalyzed. Use the best fit curve as the calibration curve.

10.3 Analytical Procedure

The analytical procedure is concurrent with the operating procedures. Therefore, it is recommended to follow procedures outlined in Section 9.2 and Section 10.2 for analysis.

11. Systems Maintenance

11.1 Periodic Maintenance

Proper maintenance is necessary for successful monitor performance. Periodic maintenance should be performed to reduce equipment failure and maintain calibration integrity of the instrument. Instrument calibration should be checked on a schedule established after the analyzer has operated for a period of time. The sensitivity and linearity should also be checked. These instrument checks should be done at least on an annual basis. However, when any component (i.e., detector or pump) is changed, the linearity and selectivity of the instrument should be confirmed. The settings of the zero and span controls of instruments which operate continuously should be checked as often as required. A log of these settings and a service and repair log should be kept to assist in evaluating maintenance difficulties.

11.2 Routine Maintenance

Regular checks of the instrument and its operation are mandatory. Even though a system may provide excellent quality data initially, without routine maintenance and system checks the quality of the data will degenerate with time. Follow all routine maintenance procedures specified in the manufacturer's instruction manual.

11.2.1 Sampling system - The sampling system to which the analyzer is connected must be checked at regular intervals according to a maintenance schedule based on the components used in the specific application. Sampling system maintenance normally includes the following steps:

- checking the entire system for leaks and proper flow rates,
- cleaning and/or renewing sample system components,
- ensuring that calibration cylinders are shut off when not in use,
- ordering filled and assayed cylinders at intervals which include ample lead time to ensure continuous supply of calibration gas,
- checking operation of pumps, recorders, motors, timers and other commercial components by referring to manufacturer's instructions,
- checking and/or cleaning the entire sampling system, including the sample cell in the analyzer, when abnormal sample conditions occur, such as when slugs of water, dirt or oil are introduced.

11.2.2 Daily servicing - Automatic 80% full scale span (40 ppb) and zero precision checks should be performed utilizing the instrument's automatic zero/span standardization feature (if so equipped) and individual secondary standard gases of NO_2 in air with the above concentrations. In addition, backflushing should be performed daily, immediately before daily zero/span precision check.

11.2.3 Each visit servicing - Verify that the zero and span potentiometer settings are at the proper position. Likewise, verify that the sample flow is correct. Plot the daily zero, precision check, and span values on their respective days. If any of the zero and span values exceed 5% of stated value, perform a manual zero and span check and adjust the analyzer to the correct zero and span values using the front panel zero and span potentiometer, respectively. If there is insufficient range in the span potentiometer, a multipoint calibration must be performed.

11.2.4 Weekly servicing - Perform a leak check weekly and whenever the loosening or tightening of a fitting is involved in maintenance procedures. Using an individual cylinder, introduce a 20% of full scale (10 ppb) intermediate span gas at ambient pressure upstream of the sample pump as a precision check. Maintain the same excess flow each time the manual precision check is performed. The manual precision check should be within 10% of value. If not, investigate the cause and initiate repairs.

11.2.5 Biweekly servicing - Field evaluation (10) of the LMA-3 illustrated erratic results when the pump tubing was not changed at approximately two-week intervals. Therefore, changing of pump tubing biweekly will eliminate this source of analytical error.

11.2.6 Cleaning - Clean the upper chamber when there is an accumulation of liquid in the chamber or if large amounts of residue plug the cartridge filter.

Note: Usually minute amounts of liquid can evaporate, but if liquid stays in the chamber it may leak into and ruin the air pump.
Disassemble the trap as follows:

11.2.6.1 Confirm that the instrument is turned OFF and unplugged.

11.2.6.2 Loosen the instrument cover fastener, located on the rear panel, and slide the cover off.

11.2.6.3 Remove the "feed" and "waste" bottles from the instrument.

11.2.6.4 Remove the two phillips head retaining screws from the outside of the case and pull away the panel. The upper side trim panel on the air pump side of the instrument must be removed.

11.2.6.5 Pull the air tubes off of the trap. Separate the filter cartridge from the upper chamber.

11.2.6.6 Remove the two flat head screws which hold the chamber to the side of the instrument case. Lift the chamber out of the instrument.

11.2.6.7 Observe and note the relative positions of the air tubes and the mounting holes before disassembling the chamber.

11.2.6.8 Unscrew the two black end pieces from each other.

Note: It may be necessary to soak the unit in water to loosen the chemical residues that can bind the pieces to the center tube.

11.2.6.9 After cleaning the chamber, re-assemble it. The ends should be screwed together firmly by hand. Check the relative positions of the tubes. As mounted in the instrument, the longer black tube should point straight upwards and the short tube should point towards the front of the instrument. Adjust end pieces or switch them accordingly.

11.2.6.10 Reassemble in the reverse order of disassembly.

Note: Pass tygon tubing through the clamp on the side panel, and make sure the tubing rises sharply from the detector assembly.

12. Standard Operating Procedures (SOPs), Quality Assurance (QA) and Performance Criteria

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

12.1 Standard Operating Procedures

12.1.1 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.

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

12.2 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 and operation procedures in Section 9.2, and maintenance procedures in Section 11 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 should be provided by the manufacturer.

12.2.1 Precision Check

12.2.1.1 A periodic precision check is used to assess the data. A one-point check on the analyzer is carried out at least once every 2 weeks at a NO_2 concentration between 8 and 10 ppb.

12.2.1.2 The analyzer must be operated in its normal sampling mode, and the precision test gas must pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling. The standards from which the precision check test concentrations are obtained must be traceable to a NITS-SRM or a commercially available CRM; the standards used for calibration may be used for the precision check. They must conform to specifications outlined in Section 8.2.

Note: All gas standards should contain O_2, CO_2 and H_2O in concentrations expected in indoor air.

12.2.1.3 Connect the analyzer's sample inlet line to a precision gas source that has a concentration between 8 and 10 ppb NO_2 and that is traceable to a NITS-SRM or a CRM as illustrated in Section 9.2.3. If a precision check is made in conjunction with a zero/span check, it must be made prior to any zero and span adjustments.

12.2.1.4 Allow the analyzer to sample the precision gas for a least 5 min or until a stable recorder trace is obtained.

12.2.1.5 Record this value and mark the chart as "unadjusted" precision check.

12.2.1.6 The expected response of the LMA-3 analyzer should be within 10% of the precision calibration gas standard.

12.2.2 Performance Audit

12.2.2.1 An audit is an independent assessment of the accuracy of data generated by an analyzer.

12.2.2.2 Independence is achieved by having the audit performed by an operator other than the one conducting the routine field measurements and by using audit standards, reference materials, and equipment different from those routinely used in monitoring.

12.2.2.3 The audit should be an assessment of the measurement process under normal operations, that is, without any special preparation or adjustment of the system. Routine quality assurance checks conducted by the operator are necessary for obtaining and reporting good quality data, but they are not to be considered part of the auditing procedure.

12.2.2.4 Proper implementation of an auditing program will ensure the integrity of the data and assess the accuracy of the data.

12.2.2.5 A performance audit consists of challenging the continuous analyzer with known concentrations of NO_2, containing O_2, CO_2 and H_2O in concentrations expected in indoor air, within the measurement range of the analyzer. Known concentrations of NO_2 can be generated by using individual cylinders for each concentration (see Section 10.2.3) or by using one cylinder of a high NO_2 concentration and diluting it to the desired levels with zero-air (see Section 10.2.3.17). In either case, the gases used must by traceable to a NITS-SRM or a commercially available CRM.

12.2.2.6 A dynamic dilution system must be capable of measuring and controlling flow rates to within ±2% of the required flow. Flow meters must be calibrated under the conditions of use against a reliable standard such as a soap bubble meter or a wet test meter; all volumetric flow rates should be corrected to STP at 25°C (77°F) and 760 mm Hg (29.92 in Hg); but if both the NO_2 and the zero air flow rates are measured with the same type device at the same temperature and pressure, the STP correction factor in the audit equations can be disregarded.

12.2.2.7 The analyzer should be challenged with at least one audit gas of known concentration from each of the following concentrations within the measurement range of the analyzer being audited:

Audit Point	NO_2 Concentration Range, ppb
1	3 to 7
2	8 to 12
3	18 to 22
4	28 to 32
5	38 to 42

The difference in NO_2 concentration (ppb) between the audit value and the measured value is used to calculate the accuracy of the analyzer.

12.2.2.8 All measurement of audit concentrations should fall within ±10% of the audit value as a precision check.

12.3 Performance Criteria

12.3.1 Specific performance criteria have been discussed and are outlined in Table 1.

12.3.2 The lower detection limit of the method is 5 ppt_v.

12.3.3 The sensitivity of the method is 1 second for a 20% change in NO_2 mixing ratio.

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12.3.4 The precision of the method is linear up to about 5 ppm_v, provided that a flow rate of 0.1 mL/min is maintained through the system.

13. 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.

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Table 1. Laboratory Performance Parameter Results of the LMA-3 NO_2 Extrasensitive Monitor Evaluation

Performance Parameter	Results
Mean Noise	0.003 ppb
Mean Precision (0% FS)	0.003 ppb
Mean Precision (20% FS)	0.040 ppb
Mean Precision (50% FS)	0.065 ppb
Mean Precision (80% FS)	0.105 ppb
Limit of Detection	0.009 ppb
Lower Detection Limit	0.005 ppb
Mean Daily Zero Drift	-0.00 ppb
Mean Daily Span Drift (20% FS)	-1.3%
Mean Rise Time	1.8 min
Mean Fall Time	0.2 min

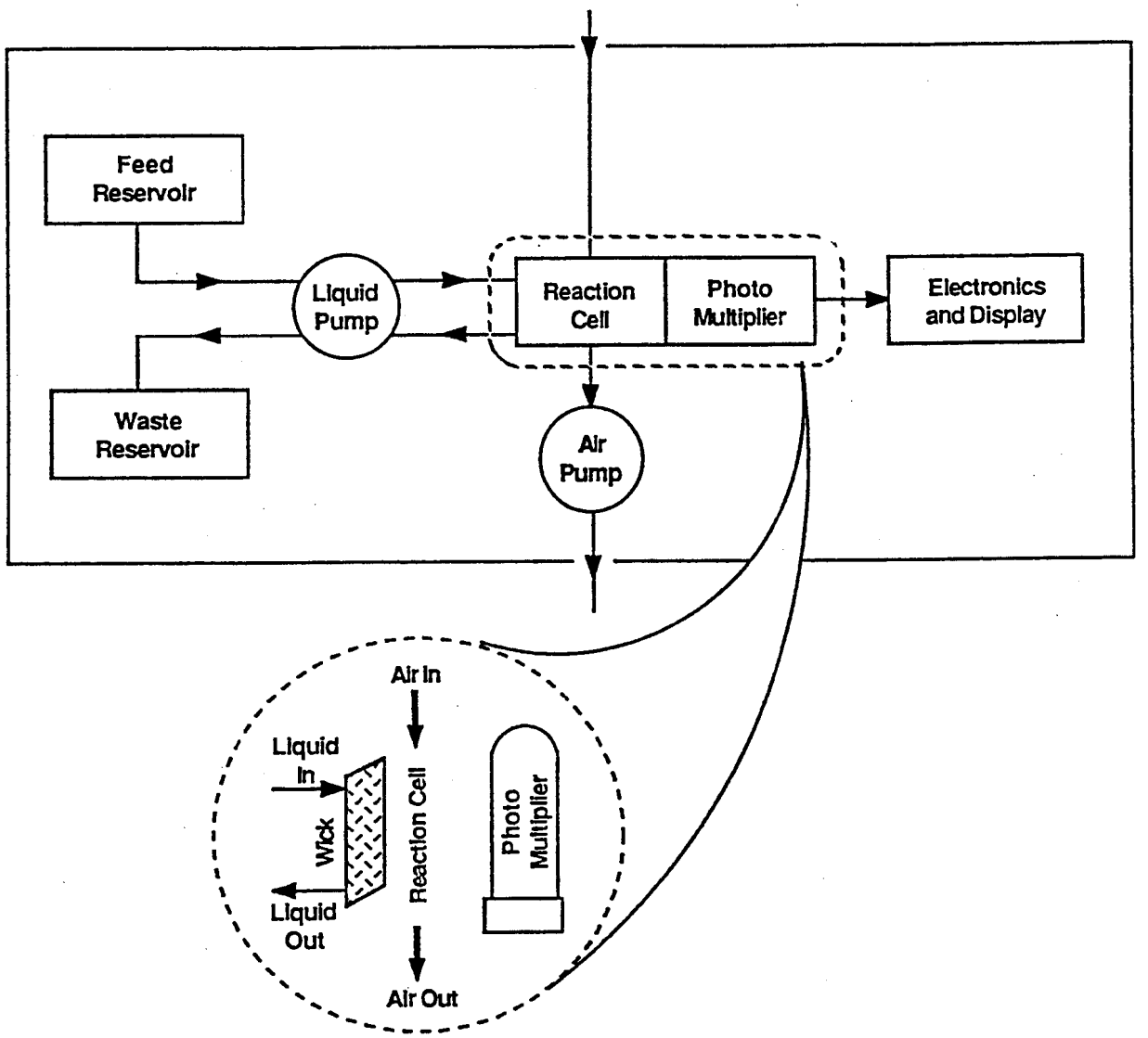

Figure 1. Operational Block Diagram of the LMA-3 NO_2 Analyzer

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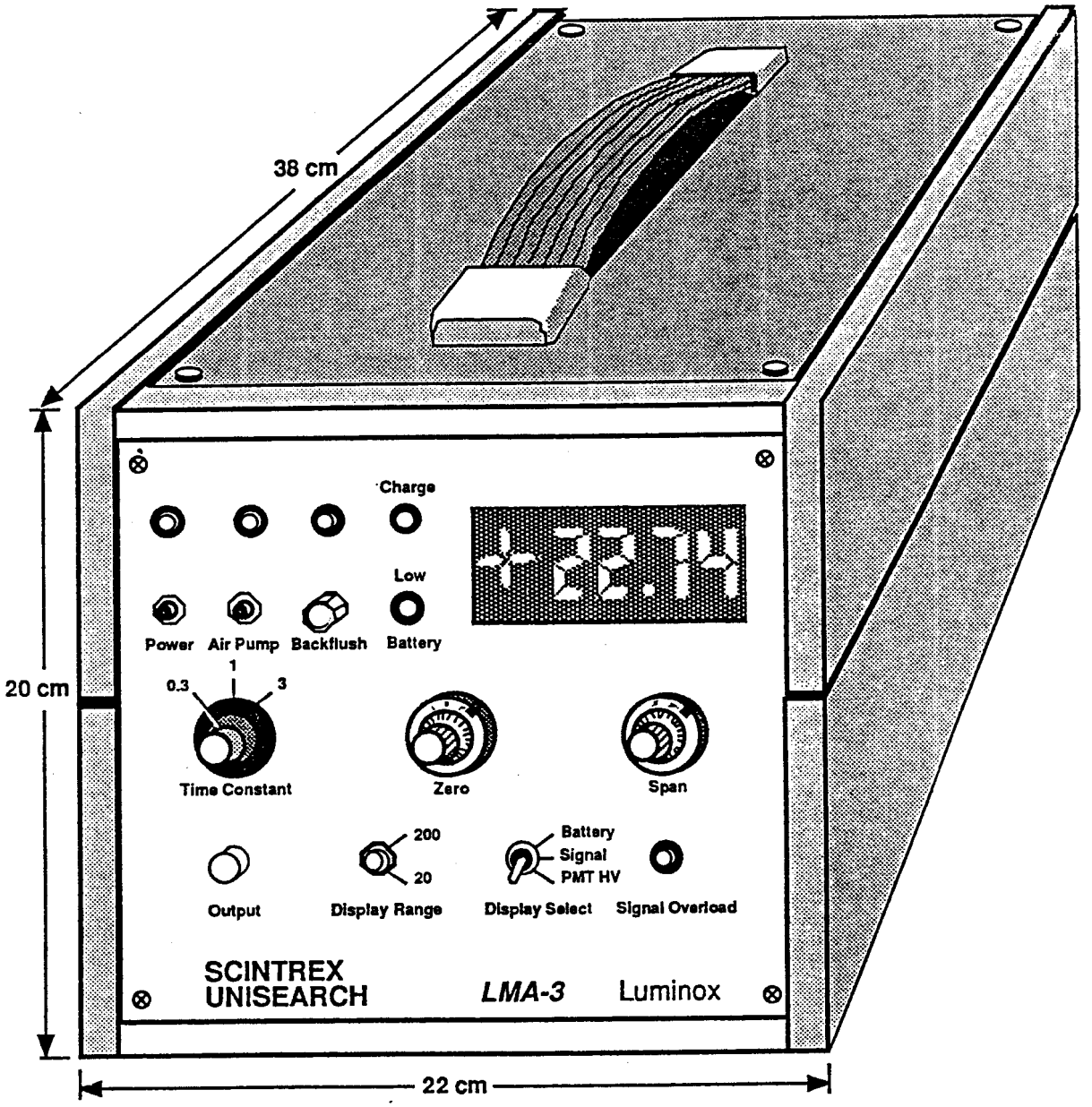

Figure 2. Front View LMA-3 NO_2 Analyzer

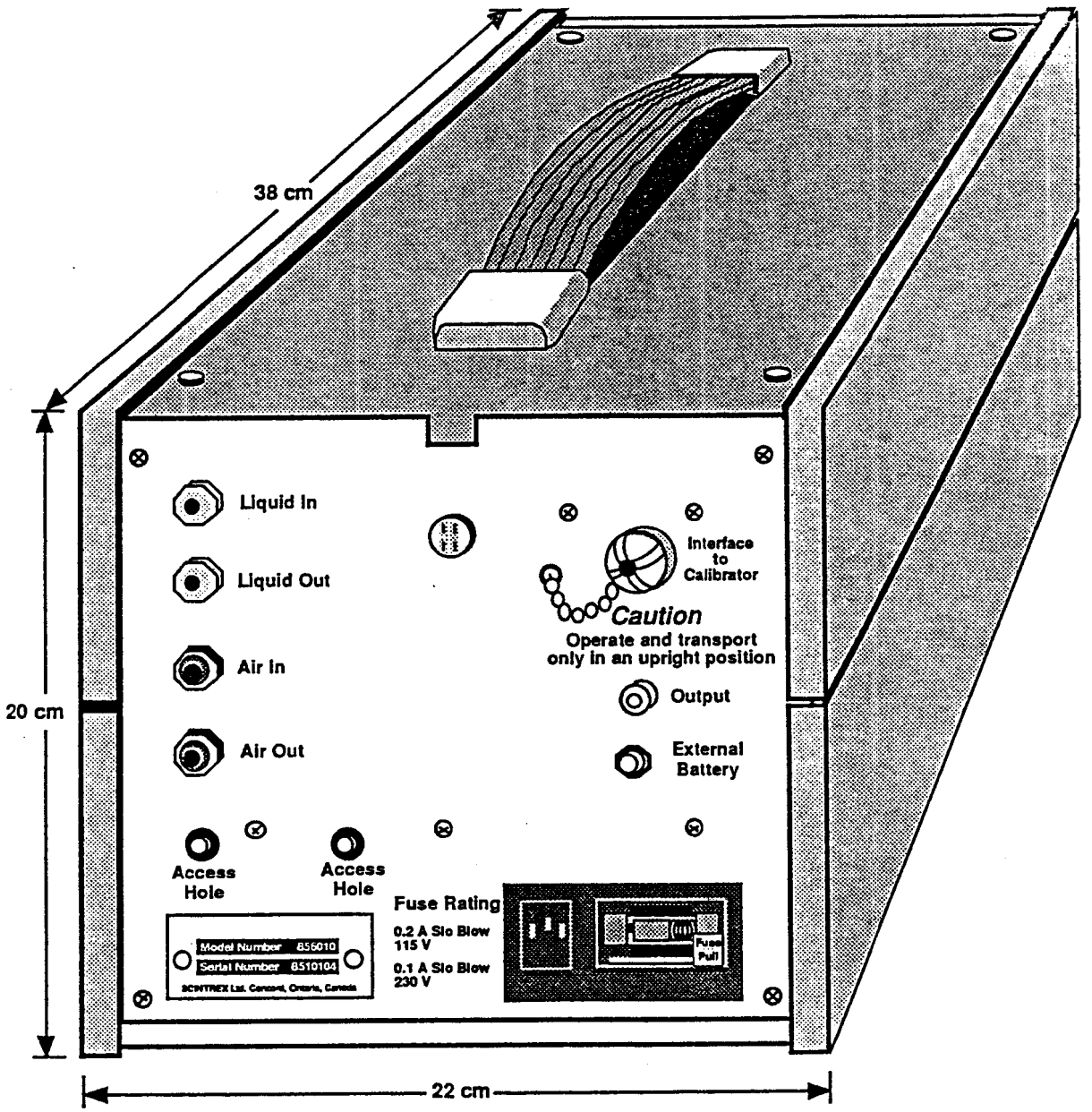

Figure 3. Back View LMA-3 NO_2 Analyzer

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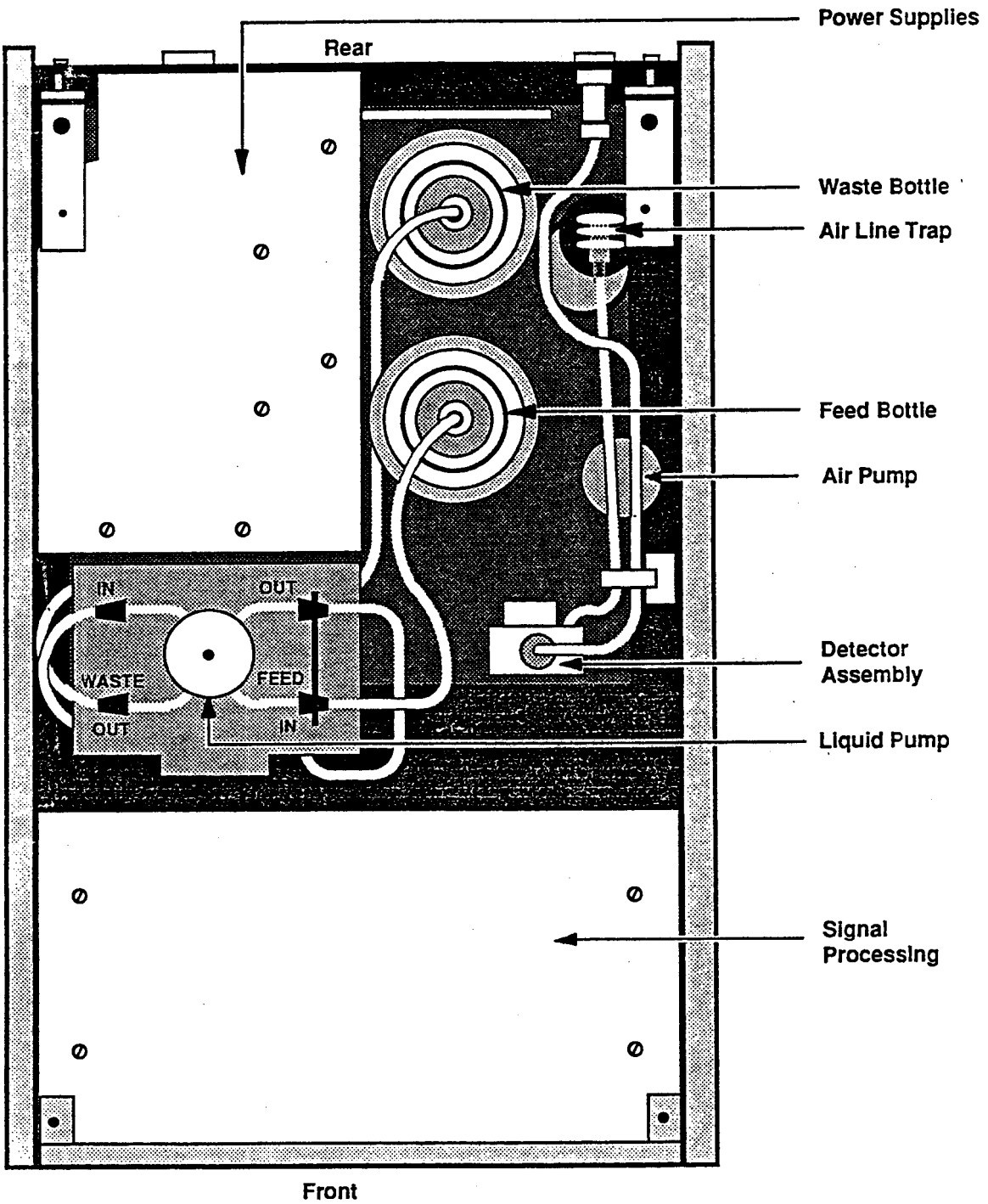

Figure 4. Top View LMA-3 NO_2 Analyzer

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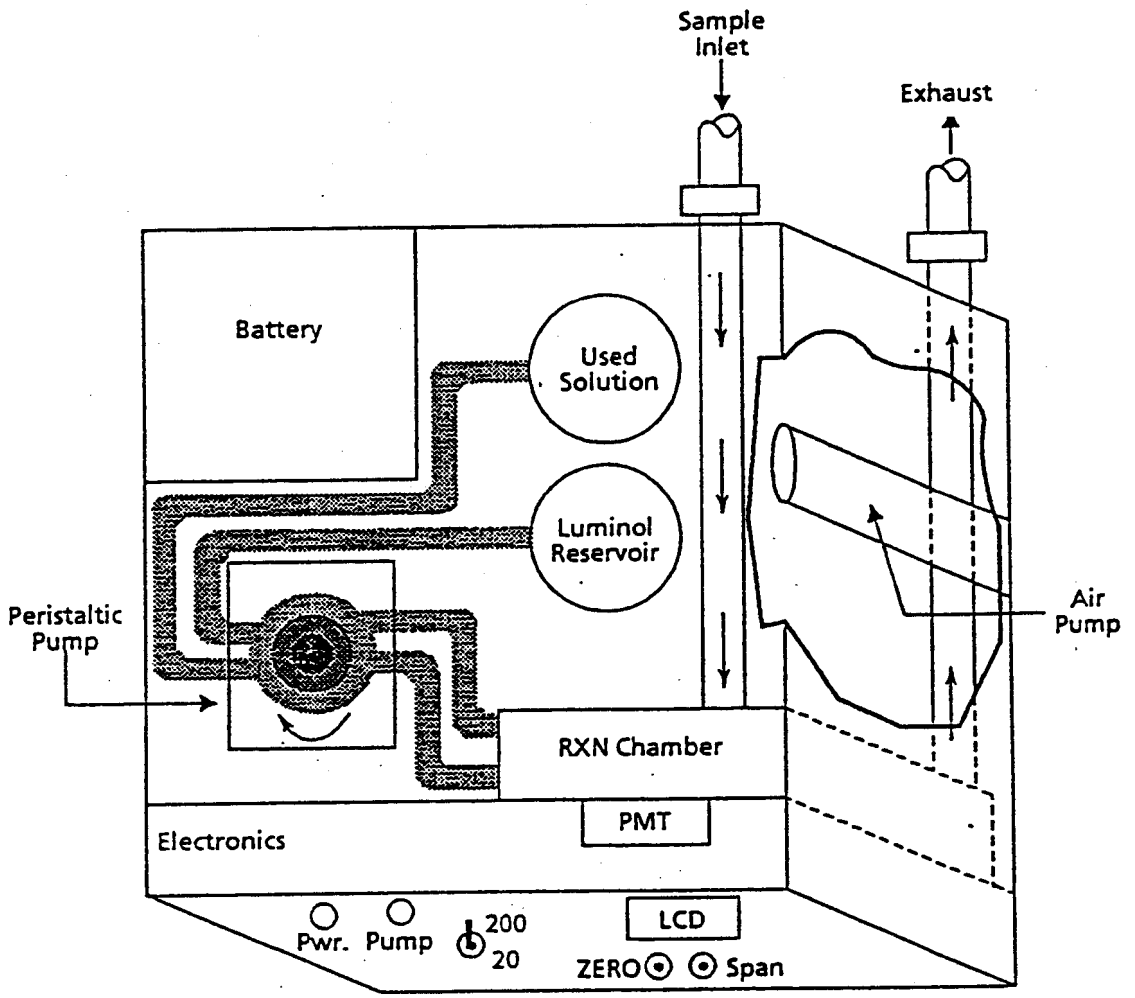

Figure 5. Sample Air through the LMA-3 NO_2 Analyzer

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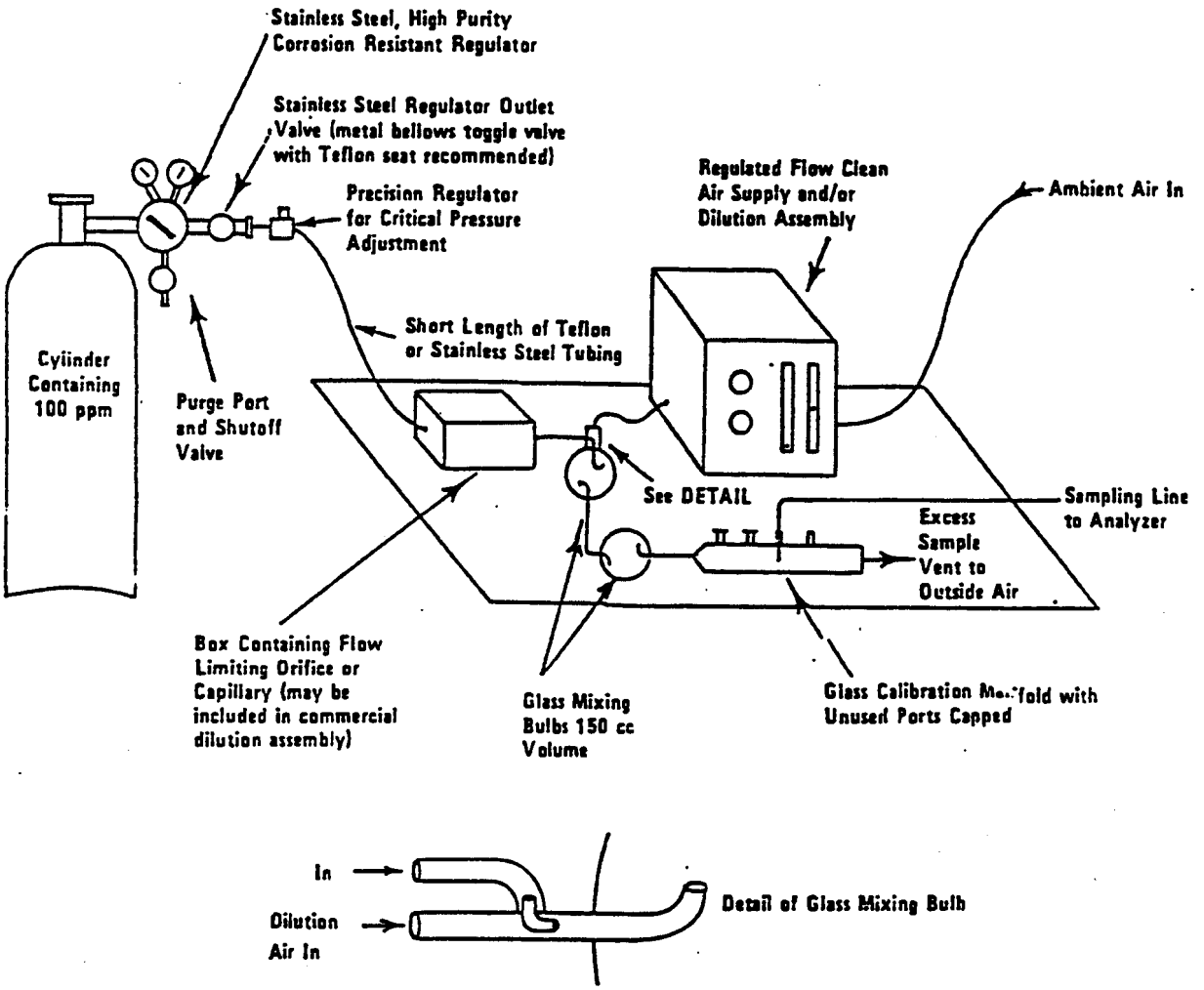

Figure 6. Assembly for Dilution of NO_2 from Cylinder for Use in Calibration or Span Check

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