

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 $\mu\text{g}/\text{m}^3$ 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

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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 $0.17 \mu\text{g}/\text{m}^3$ for a

one hour sample and $0.02 \mu\text{g}/\text{m}^3$ 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 $1.8\text{-}83.0 \mu\text{g}/\text{m}^3$ 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 μ m 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 μ m 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 μ L 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:

$$\mu\text{g nicotine} = [\text{Area ratio} - (\text{y-intercept})]/\text{slope}$$

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:

$$\text{desorption efficiency (DE)} = [\text{Avg. wt. } (\mu\text{g}) \text{ recovered/wt. } (\mu\text{g}) \text{ added}] \times 100$$

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:

$$\mu\text{g nicotine} = (\mu\text{g sample}) - (\text{avg. } \mu\text{g blank})$$

where:

$\mu\text{g sample}$ = nicotine found in front section of sample tube or on filter, μg

avg. $\mu\text{g blank}$ = 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):

$$\text{corrected } \mu\text{g/sample} = [\text{total nicotine weight}]/[\text{desorption efficiency (DE)}] \times 100$$

12.2.5 Convert the amount of nicotine found to micrograms per cubic meter of air by the equation:

$$\mu\text{g/m}^3 = [\text{corrected } \mu\text{g} \times 1000 (\text{L/m}^3)]/[\text{air volume sampled (L)}]$$

12.2.6 If desired, adjust the nicotine concentration found in the sampled air to standard conditions of temperature and pressure by the equation:

$$\text{corrected } \mu\text{g/m}^3 = \mu\text{g/m}^3 \times 760/P \times (T + 273)/298$$

where:

- P = barometric pressure of air sampled, torr
T = temperature of air sampled, °C
760 = standard pressure, torr
298 = standard temperature, °K

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 $\mu\text{g}/\text{m}^3$ 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/m³) 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.

<u>Topic</u>	<u>Contact</u>	<u>Address/Phone No.</u>
XAD-4 Adsorbent	Dr. Michael W. Ogden Dr. Guy B. Oldaker Dr. Charles W. Nystrom	R.J. Reynolds Tobacco Co. Bowman Gray Technical Center Winston-Salem, N.C., 27102 (919) 741-5000
	Dr. Roger A. Jenkins Mr. Michael R. Guerin	Oak Ridge National Laboratory Building 4500 South P. O. Box X Oak Ridge, TN 37851-6120 (615) 576-8594
General Method- ology	Dr. John D. Spengler	Harvard School of Public Health Department of Environmental Science and Physiology 665 Huntington Avenue Boston, MA 02115 (617) 732-1255
	Dr. James E. Woods	Honeywell Corporation 1985 Douglas Drive North Golden Valley, MN 55422-3992 (615) 542-6773

Dr. Nancy Wilson

U.S. Environmental Protection Agency
Environmental Monitoring Systems
Laboratory
MD-44
Research Triangle Park, NC 27711
(919) 541-4723

16. References

1. Ogden, M. W., "Procedure for Determination of Nicotine Collected in Indoor Environments (1987)," R. J. Reynolds Tobacco Co., Bowman Gray Technical Center, Winston-Salem, NC, 27102.
2. Hammond, S. K., Leaderer, B. P., Roche, A. C., and Schenker, M., "Collection and Analysis of Nicotine as a Marker for Environmental Tobacco Smoke," *Atmospheric Environment*, 21(2):457-462, 1987.
3. *Manual of Analytical Methods*, National Institute for Occupational Safety and Health, Cincinnati, OH, 1977, Part II, Vol. 3, Method No. S293.
4. Eatough, D. J., Benner, C. L., Mooney, R. L., Lewis, L., Lamb, J. D., and Eatough, N. L., "Gas and Particle Phase Nicotine in Environmental Tobacco Smoke," *Proceedings, 79th Annual APCA Meeting*, Paper 86-68.5, 22-27 June, Minneapolis, MN, 1986.
5. Eudy, L. W., Thome, F. A., Heavner, D. L., Green, C. R., and Ingbrethsen, B. J., "Studies on the Vapor-Particulate Phase Distribution of Environmental Nicotine by Selective Trapping and Detection Methods," *Proceedings, 79th Annual APCA Meeting*, Paper 86-38.7, 22-27 June, Minneapolis, MN, 1986.
6. Riggin, R. M., *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, EPA-600/483-027, U.S. Environmental Protection Agency, Research Triangle Park, NC, April, 1980.
7. Oldaker III, G. B., and Conrad Jr., F. W. "Estimation of Effect of Environmental Tobacco Smoke (ETS) on Air Quality Within Aircraft Cabins," *Environmental Science & Technology*, 21:994-999, 1987.
8. Eatough, D. J., and Benner, C. L., "Sampling for Gas Phase Nicotine in Environmental Tobacco Smoke with Diffusion Denuder and a Passive Sampler," *Proceedings of the 1987 EPA/APCA Symposium on Measurements of Toxic and Related Air Pollutants*, Pittsburgh, PA, 1987.
9. Hammond, S. K., "Protocol and Quality Assurance Plan for Nicotine Analysis," University of Massachusetts, Family and Community Medicine, Worcester, MA, 1987.
10. Hammond, S. K., Coghlin, J., and Leaderer, B. P., "Field Study of Passive Smoking Exposure With Passive Sampler," *Indoor Air '87, Proceedings of the 4th International Conference on Indoor Air Quality and Climate*, Berlin (West), 17-21 August 1987 Vol. 2:

Environmental Tobacco Smoke, Multicomponent Studies, Radon, Sick Buildings, Odors and Irritants, Hyperreactivities and Allergies, pp. 131-136 (1987).

11. Steiner, E. H., and Youden, W. J., "Statistical Manual of the Association of Official Analytical Chemists," Association of Official Analytical Chemists, Washington 1975.
12. Ogden, M. W., Eudy, L. W., Heavner, D. L., Conrad Jr., F. W., and Green, C. R., "Improved Gas Chromatographic Determination of Nicotine in Environmental Tobacco Smoke," *Analyst*, In Press, 1989.
13. Ogden, M. W., "Gas Chromatographic Determination of Nicotine in Environmental Tobacco Smoke: Collaborative Study," *J. Assoc. Off. Anal. Chem.*, In Press, 1989.
14. Nagda, N. L., and Harper, J. P. (Editors), *Design and Protocol for Monitoring Indoor Air Quality*, (STP;1002), American Society for Testing and Materials, Philadelphia, PA, 1988.
15. Nagda, N. L., Rector, H. E., and Koontz, M. D., *Guidelines for Monitoring Indoor Air Quality*, Hemisphere Publishing Corp., New York, NY, 1987.
16. Eatough, D. J., Benner, C. L., Bayona, J. M., Caka, F. M., Mooney, R. L., Lamb, J. D., Lee, M. L., Lewis, E. A., Hansen, L. D., and Eatough, N. L., "Identification of Conservative Tracers of Environmental Tobacco Smoke," *Proceedings of the 4th International Conference on Indoor Air Quality and Climate*, Berlin (West), 17-21 August, 1987.
17. Muramatsu, M., Umemura, S., Okada, T., and Tomita, H., "Estimation of Personal Exposure to Tobacco Smoke with a Newly Developed Nicotine Personal Monitor," *Environmental Research*, 35:218-227, 1984.
18. Ogden, M. W., "Environmental Tobacco Smoke Analysis Collaborative Study Program," R. J. Reynolds Tobacco Co., Bowman Gray Technical Center, Winston-Salem, NC, 1987.

Table 1. GC/NSD Settings

<u>Column</u>	*(1) 30 m x 0.53 mm I.D., fused silica capillary 1.50 μ m film DB-5 (2) 30 m x 0.32 mm I.D., fused silica capillary 1.00 μ m, film DB-5
<u>Temps</u>	
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 μ g/mL Standard)
<u>Gas Flows</u>	
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
<u>Auto Sampler</u>	
Prewashes	5 with sample
Rinses	5 with sample
Postwashes	10 with solvent
Injection	2 μ L
Settings	"Default"
Calibration	5 point check at beginning, middle and end of tray
Standards	
<u>Integration Parameters</u>	
Threshold	0
Peak width	0.04
<u>Retention Time</u>	(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.

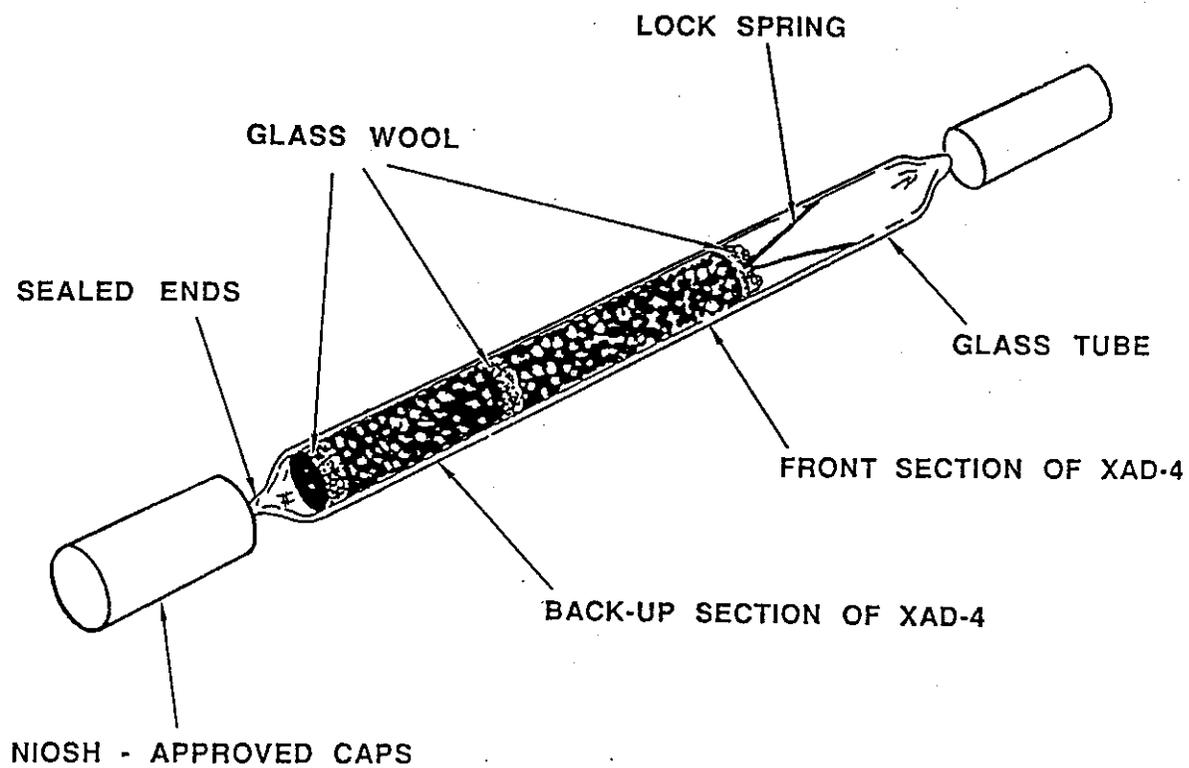


Figure 1. XAD-4 Sorbent Tube

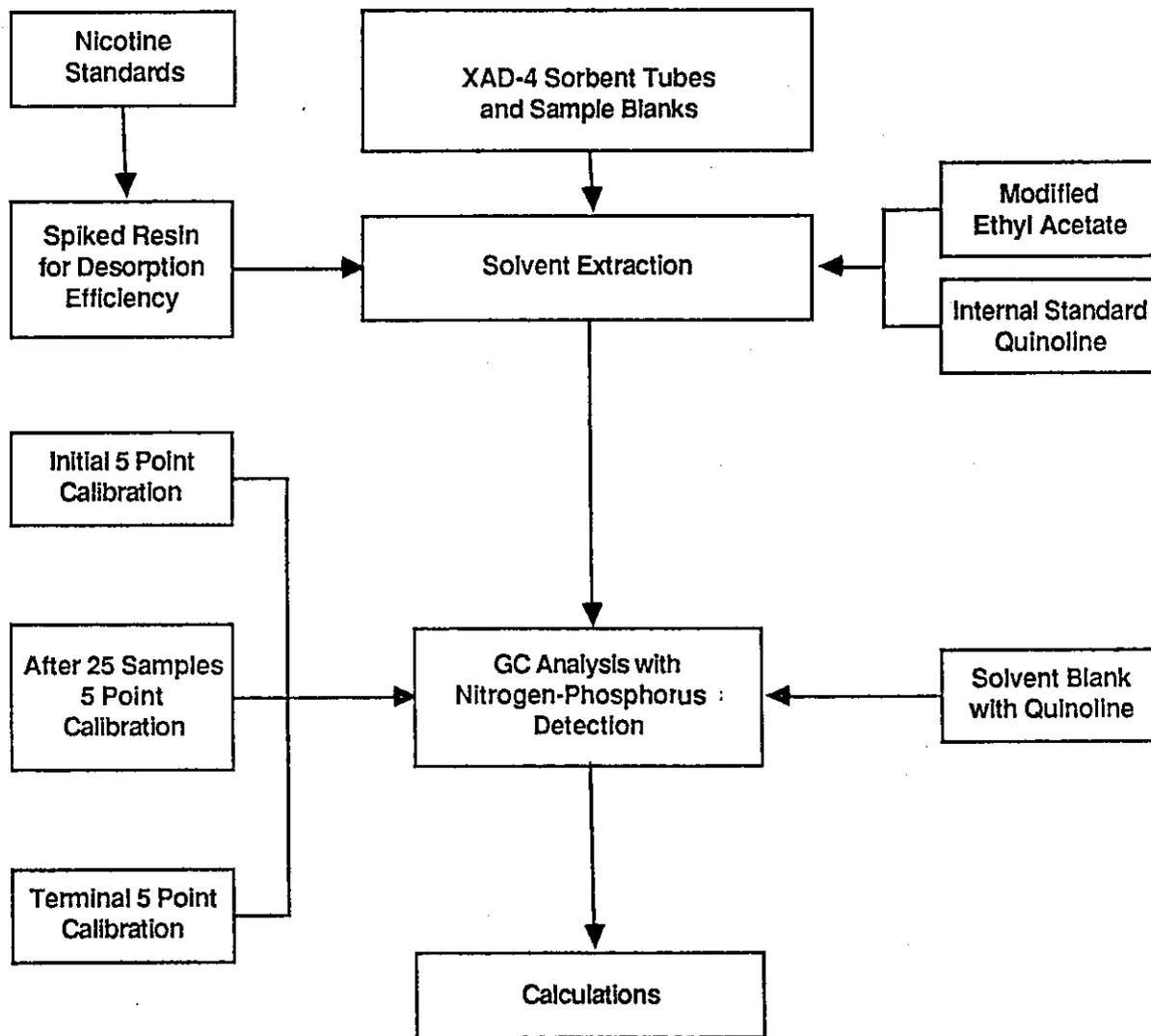


Figure 2. Sampling/Analysis Using XAD-4 Sorbent Tubes

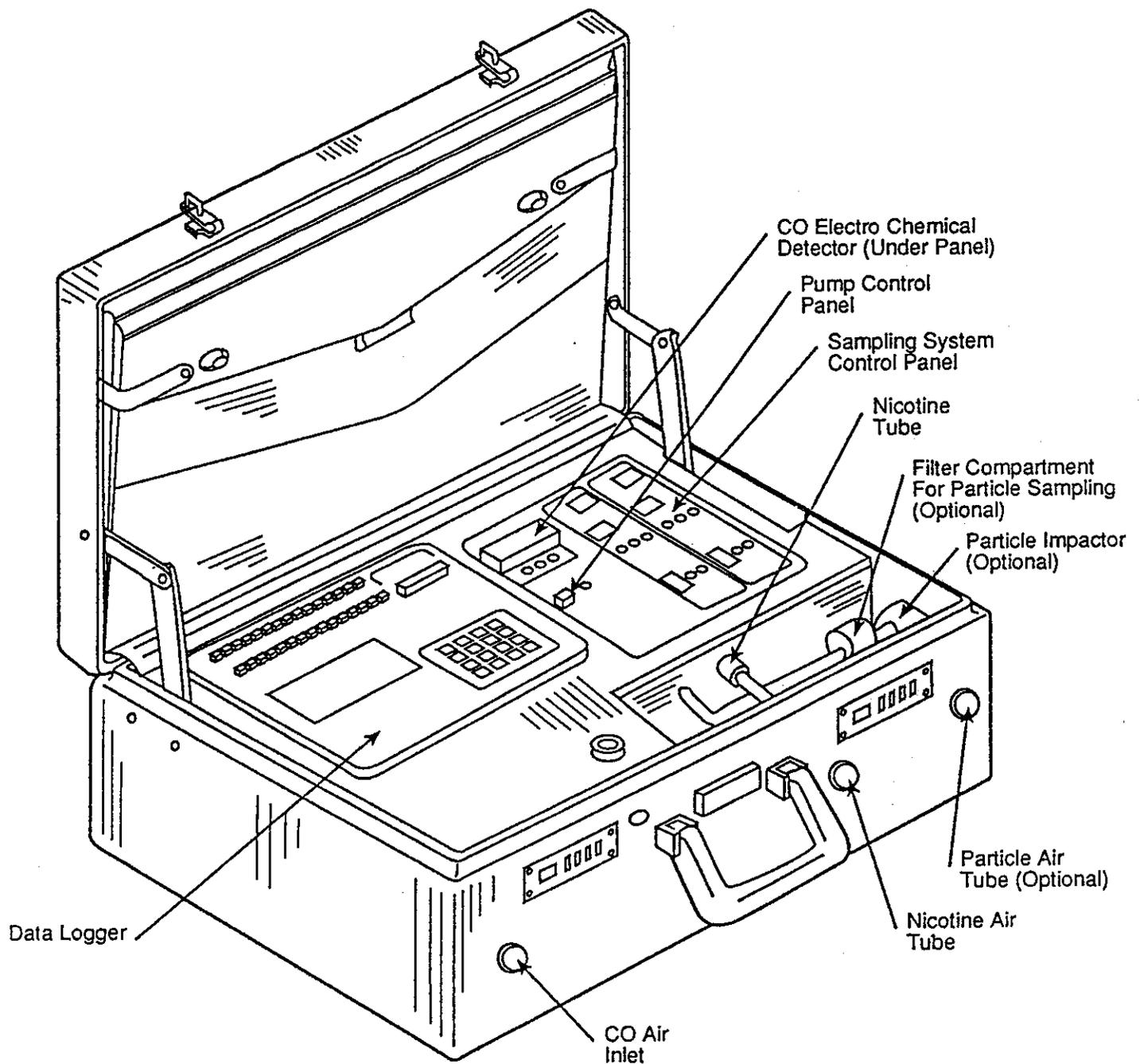
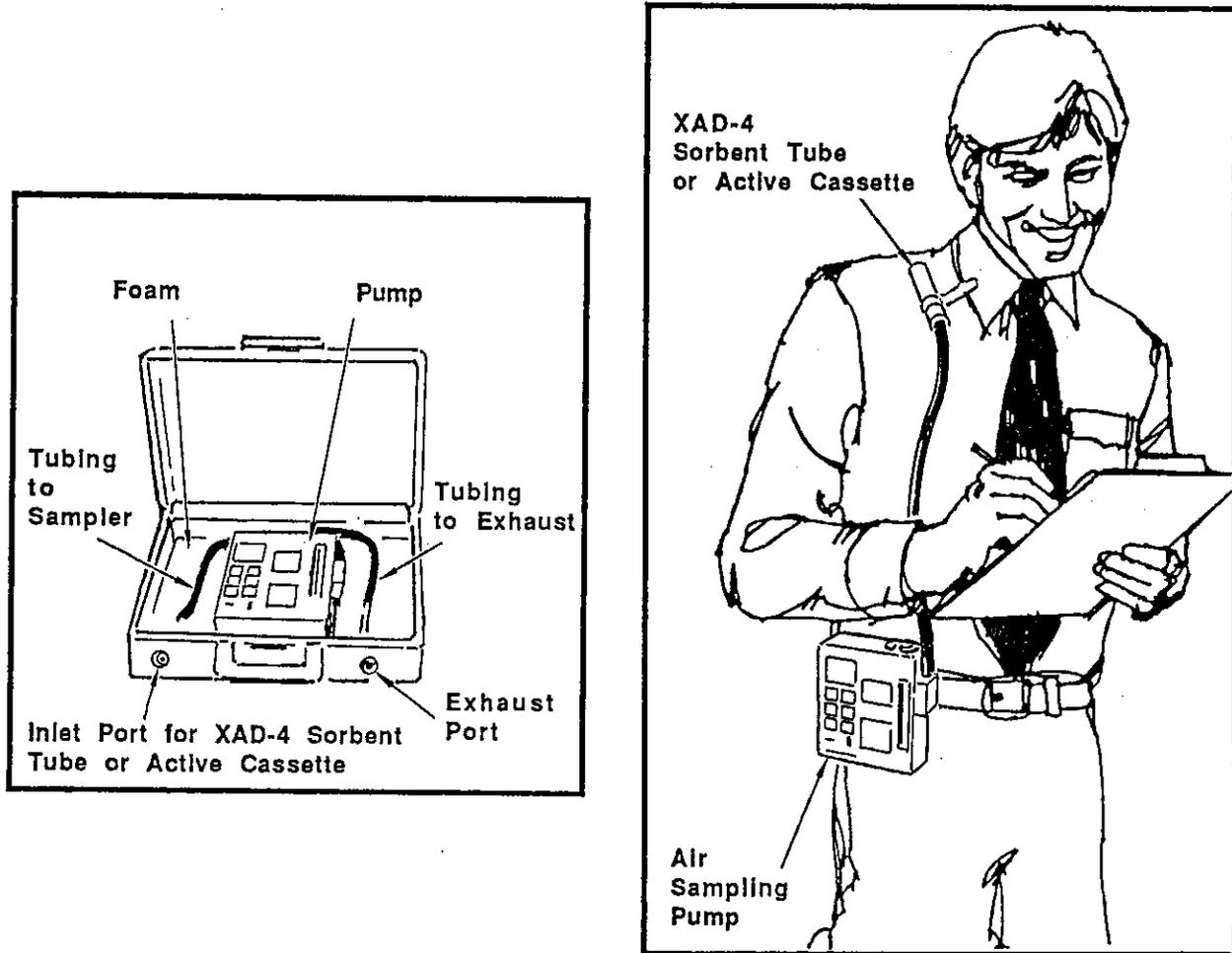


Figure 3. Briefcase Sampling System Containing Nicotine Adsorbent Tube Sampler with Optional Particulate and CO Capabilities



(a) Briefcase Sampling

(b) Personal Monitoring

Figure 4. Sampling Setup

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

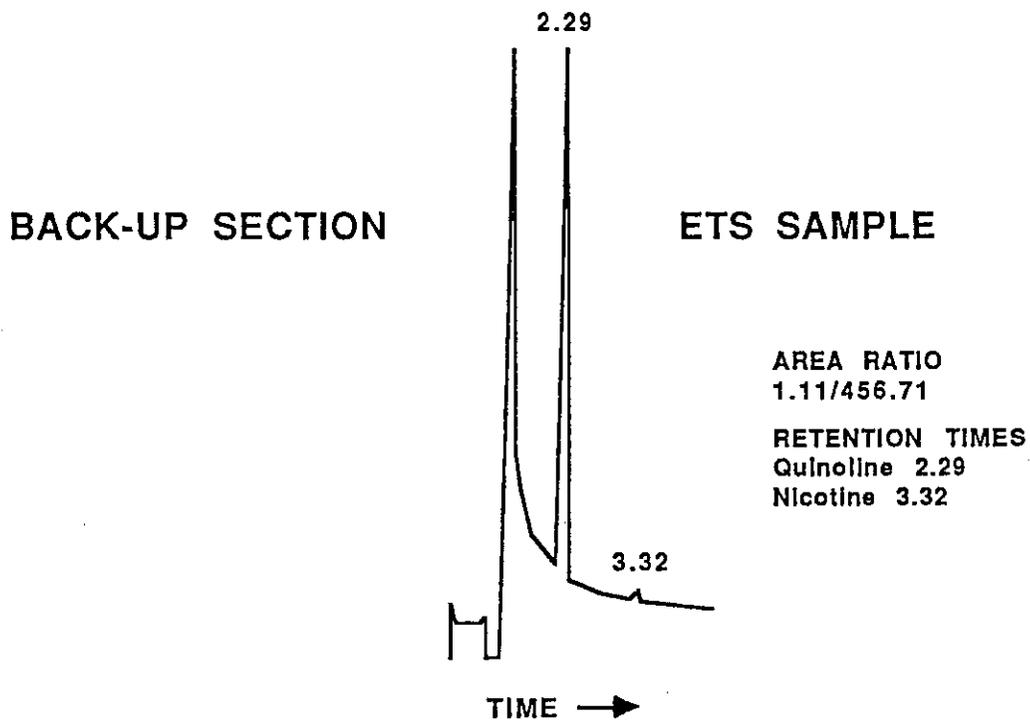
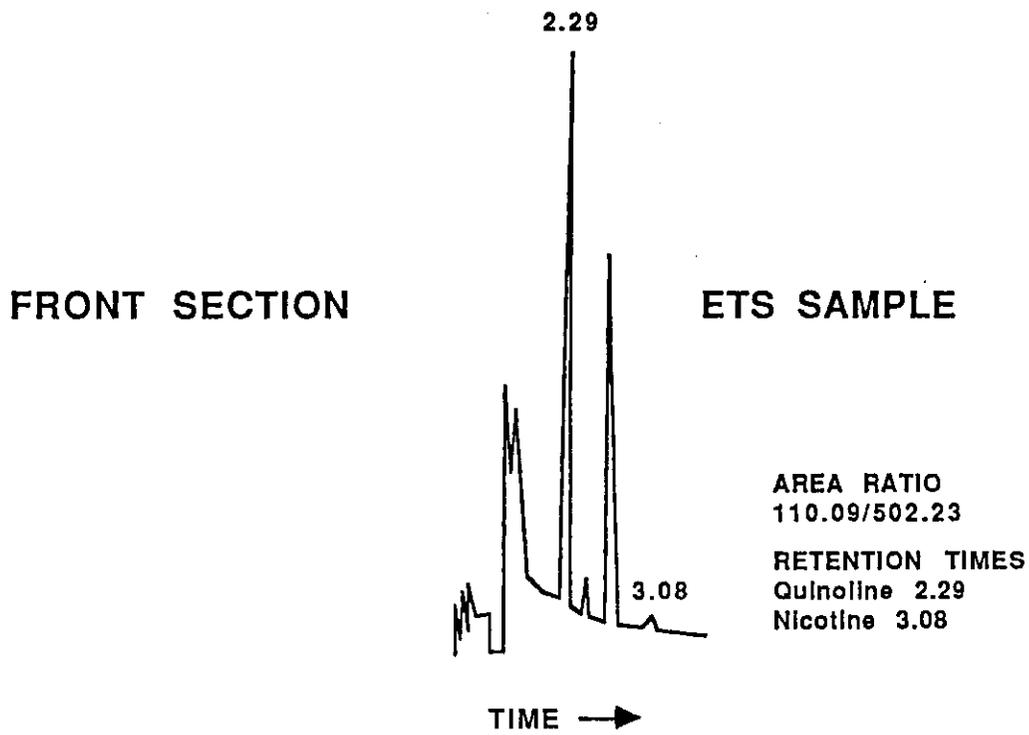
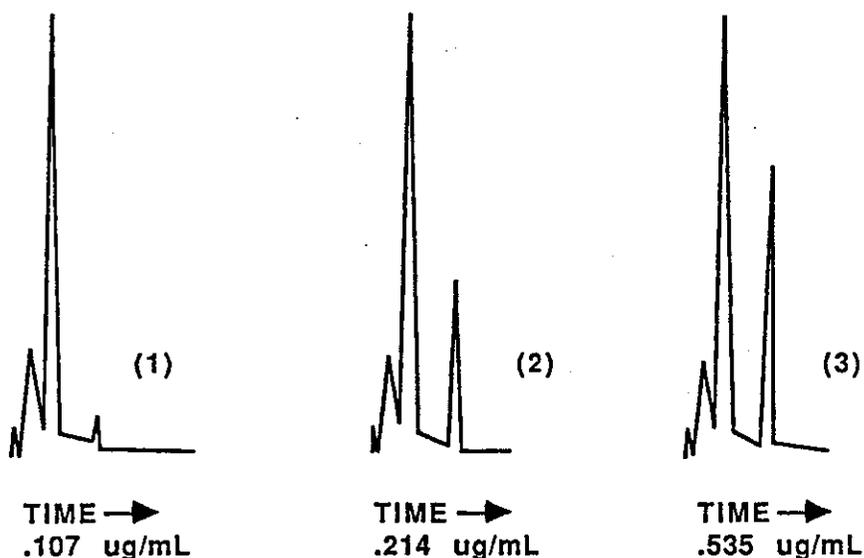
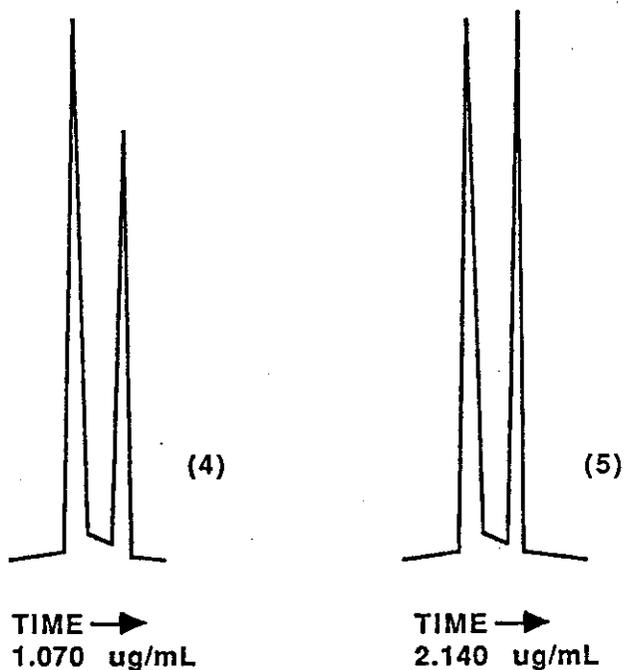


Figure 6. Chromatograms of an ETS Sample



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

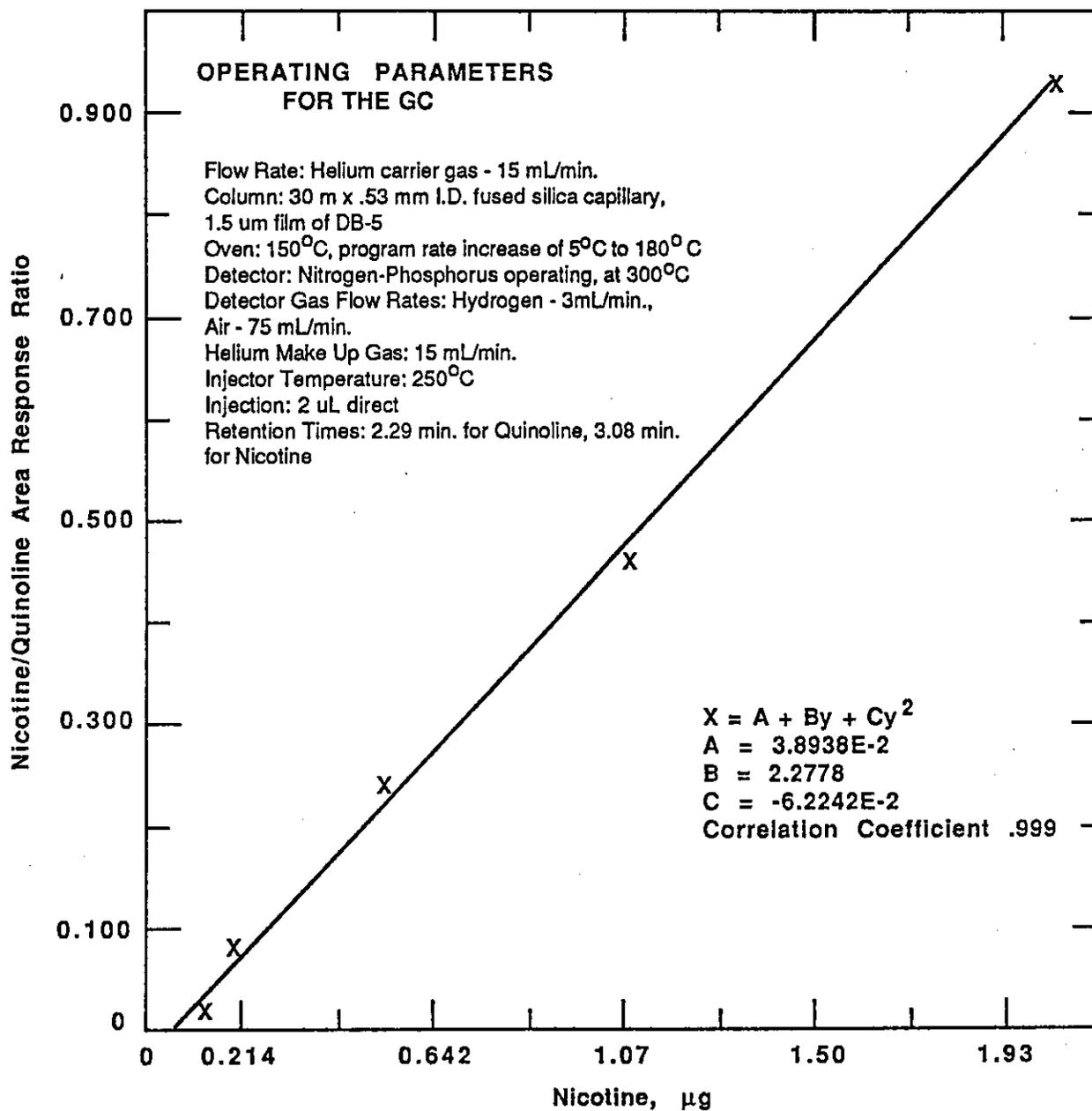


Figure 8. Nicotine Calibration Curve

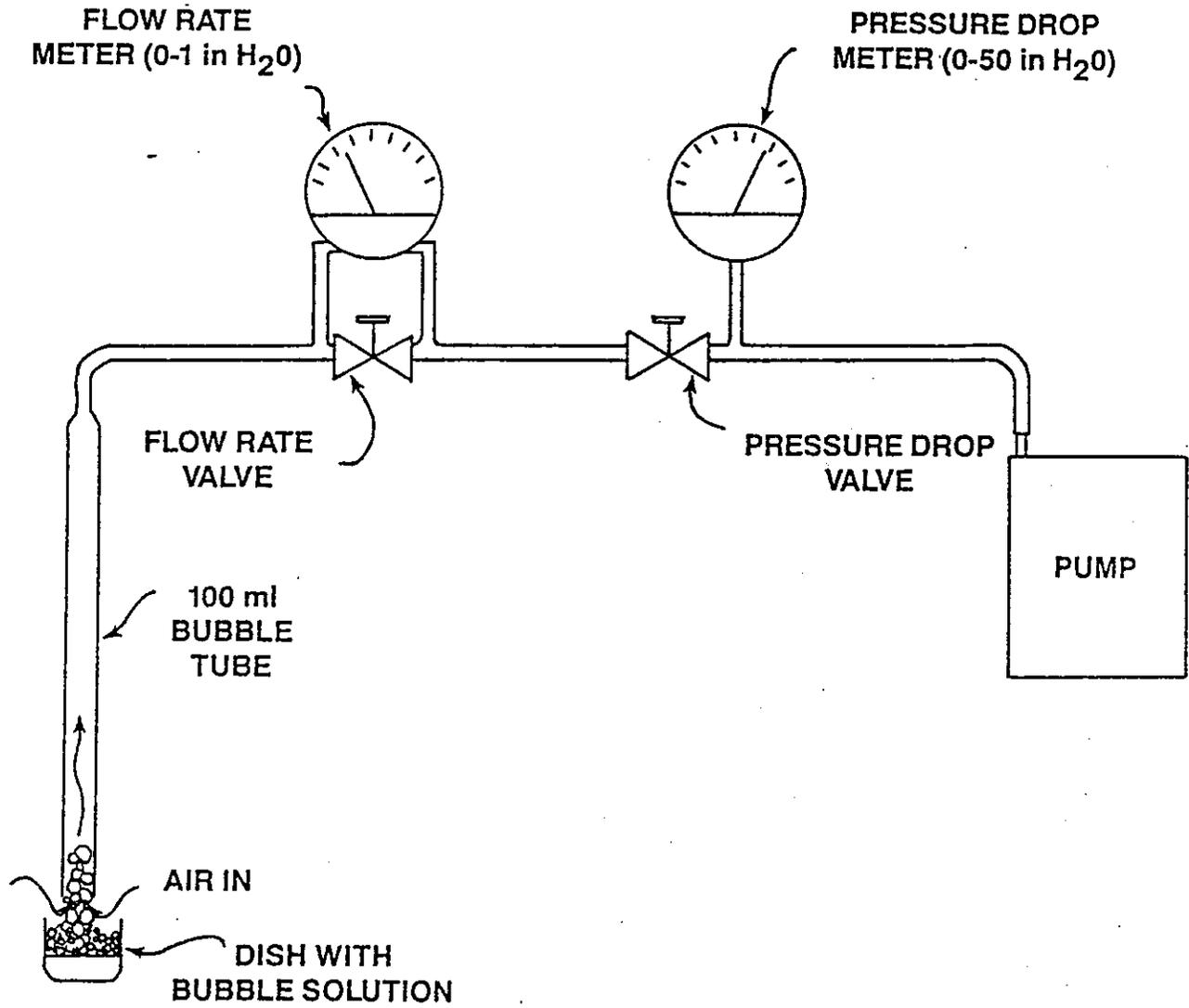


Figure 9. Calibration Assembly for Personal Sampling Pump

Method IP-2B

DETERMINATION OF NICOTINE IN INDOOR AIR USING TREATED FILTER CASSETTES

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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 $\mu\text{g}/\text{m}^3$ and at a rate

of 3 L/min with a limit of detection of $0.03 \mu\text{g}/\text{m}^3$ (1). It has also shown a limit of detection of $0.5 \mu\text{g}/\text{m}^3$ 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 $16 \mu\text{g}/\text{m}^3$ and for a one-week sampling period with a limit of detection of $0.2 \mu\text{g}/\text{m}^3$ (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 $1.8\text{--}83.0 \mu\text{g}/\text{m}^3$ 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 undecivated 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 adsorbed 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^o Carbowax 20M held at a constant temperature of 140°C.

10.1.3 A 3- μ L 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% \pm 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 μ L 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 ($100\ \mu\text{g}/\text{mL}$) 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 $5\ \mu\text{g}/\text{mL}$ to $50\ \mu\text{g}/\text{mL}$. For low concentration samples and passive sampling, prepare standards from $0.05\ \mu\text{g}/\text{mL}$ to $5\ \mu\text{g}/\text{mL}$.

10.3.3.2 Prepare all standards daily as follows: For a $50\ \mu\text{g}/\text{mL}$ standard, measure 1 mL of $100\ \mu\text{g}/\text{mL}$ 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 $\mu\text{g}/\text{mL}$:	1 mL of $100\ \mu\text{g}/\text{mL}$ diluted to 10 mL
5.0 $\mu\text{g}/\text{mL}$:	1 mL of $10\ \mu\text{g}/\text{mL}$ diluted to 2 mL
1.0 $\mu\text{g}/\text{mL}$:	1 mL of $10\ \mu\text{g}/\text{mL}$ diluted to 10 mL
0.5 $\mu\text{g}/\text{mL}$:	1 mL of $1\ \mu\text{g}/\text{mL}$ diluted to 2 mL
0.1 $\mu\text{g}/\text{mL}$:	1 mL of $1\ \mu\text{g}/\text{mL}$ diluted to 10 mL
0.05 $\mu\text{g}/\text{mL}$:	1 mL of $1\ \mu\text{g}/\text{mL}$ 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 μ L 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 μ L 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 μ g of nicotine. For passive samples, spike with 0.1 to 5 μ g 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:

$$\mu\text{g nicotine} = [\text{Area ratio} - (\text{y-intercept})]/\text{slope}$$

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:

$$\mu\text{g nicotine} = (\mu\text{g sample}) - (\text{avg. } \mu\text{g blank})$$

where:

$\mu\text{g sample}$ = $\mu\text{g nicotine}$ found on filters

avg. $\mu\text{g blank}$ = average $\mu\text{g nicotine}$ 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):

$$\text{corrected } \mu\text{g/sample} = [\text{total nicotine weight/desorption efficiency (DE)}] \times 100$$

11.5.5 Convert the amount of nicotine found to micrograms per cubic meter of air by the equation:

$$\mu\text{g/m}^3 = [\text{corrected } \mu\text{g} \times 1000 (\text{L/m}^3)] / [\text{air volume sampled (L)}]$$

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 cm², L = 1.17 cm, and D = 0.063 cm²/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:

$$\text{corrected } \mu\text{g/m}^3 = \mu\text{g/m}^3 \times 760/P \times [(T + 273)/298]$$

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 $0.1 \mu\text{g}/\text{m}^3$ over an eight hour period and $0.5 \mu\text{g}/\text{m}^3$ 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 $16 \mu\text{g}/\text{m}^3$ over a five hour period and $0.2 \mu\text{g}/\text{m}^3$ 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.

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/m³) 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.

<u>Topic</u>	<u>Contact</u>	<u>Address/Phone No.</u>
Treated Filter Cassette (Active/ Passive)	Dr. Katherine Hammond	University of Massachusetts Medical Center Family and Community Medicine 55 Lake Avenue North Worcester, MA 01655 (508) 856-5636
	Mr. Brian Leaderer	The Pierce Foundation Lab Yale University School of Medicine 200 Congress Avenue New Haven, CT 06519 (203) 562-9901
	Mr. Ron Williams	Environmental Health Research and Testing, Inc. P.O. Box 12199 Research Triangle Park, NC 27709 (919) 541-7631
	Dr. Delbert J. Eatough Ms. Cindy L. Benner	Brigham Young University Chemistry Department 226 Eyring Science Ctr. Provo, UT 84602 (801) 378-6040

	Ms. Linda Forehand	Engineering-Science One Harrison Park, Ste. 305 401 Harrison Oaks Blvd. Cary, NY 27513 (919) 467-8999
General Methodology	Dr. John D. Spengler	Harvard School of Public Health Department of Environmental Science and Physiology 665 Huntington Avenue Boston, MA 02115 (617) 732-1255
	Dr. James E. Woods	Honeywell Corporation 1985 Douglas Drive North Golden Valley, MN 55422-3992 (615) 542-6773
	Dr. Nancy Wilson	U.S. Environmental Protection Agency Environmental Monitoring Systems Lab MD-44 Research Triangle Park, NC 27711 (919) 541-4723

14. References

1. Hammond, S. K., Leaderer, B. P., Roche, A. C., and Schenker, M., "Collection and Analysis of Nicotine as a Marker for Environmental Tobacco Smoke," *Atmospheric Environment*, 21(2):457-462, 1987.
2. Hammond, S. K., and Leaderer, B. P., "A Diffusion Monitor to Measure Exposure to Passive Smoking," *Environmental Science Technology*, 21(5):494-497, 1987.
3. Eatough, D. J., Benner, C. L., Mooney, R. L., Lewis, L., Lamb, J. D., and Eatough, N. L., "Gas and Particle Phase Nicotine in Environmental Tobacco Smoke," *Proceedings, 79th Annual APCA Meeting*, Paper 86-68.5, 22-27 June, Minneapolis, MN, 1986.
4. Eudy, L. W., Thome, F. A., Heavner, D. L., Green, C. R., and Ingbrethsen, B. J., "Studies on the Vapor-Particulate Phase Distribution of Environmental Nicotine by Selective Trapping and Detection Methods," *Proceedings, 79th Annual APCA Meeting*, Paper 86-38.7, 22-27 June, Minneapolis, MN, 1986.
5. Riggin, R. M., *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, EPA-600/483-027, U.S. Environmental Protection Agency, Research Triangle Park, NC, April, 1980.

6. Oldaker III, G. B., and Conrad Jr., F. W. "Estimation of Effect of Environmental Tobacco Smoke (ETS) on Air Quality Within Aircraft Cabins," *Environmental Science & Technology*, 21:994-999, 1987.
7. Eatough, D. J., and Benner, C. L., "Sampling for Gas Phase Nicotine in Environmental Tobacco Smoke with Diffusion Denuder and a Passive Sampler," *Proceedings of the 1987 EPA/APCA Symposium on Measurements of Toxic and Related Air Pollutants*, Pittsburgh, PA, 1987.
8. Hammond, S. K., "Protocol and Quality Assurance Plan for Nicotine Analysis," University of Massachusetts, Family and Community Medicine, Worcester, MA, 1987.
9. Hammond, S. K., Coghlin, J., and Leaderer, B. P., "Field Study of Passive Smoking Exposure With Passive Sampler," *Indoor Air '87, Proceedings of the 4th International Conference on Indoor Air Quality and Climate*, Berlin (West), 17-21 August 1987, Vol. 2: Environmental Tobacco Smoke, Multicomponent Studies, Radon, Sick Buildings, Odors and Irritants, Hyperreactivities and Allergies, pp. 131-136 (1987).
10. Steiner, E. H., and Youden, W. J., "Statistical Manual of the Association of Official Analytical Chemists," Association of Official Analytical Chemists, Washington 1975.
11. Ogden, M. W., Eudy, L. W., Heavner, D. L., Conrad Jr., F. W., and Green, C. R., "Improved Gas Chromatographic Determination of Nicotine in Environmental Tobacco Smoke," *Analyst*, In Press, 1989.
12. Ogden, M. W., "Gas Chromatographic Determination of Nicotine in Environmental Tobacco Smoke: Collaborative Study," *J. Assoc. Off. Anal. Chem.*, In Press, 1989.
13. Nagda, N. L., and Harper, J. P. (Editors), *Design and Protocol for Monitoring Indoor Air Quality*, (STP;1002), American Society for Testing and Materials, Philadelphia, PA, 1988.
14. Nagda, N. L., Rector, H. E., and Koontz, M. D., *Guidelines for Monitoring Indoor Air Quality*, Hemisphere Publishing Corp., New York, NY, 1987.
15. Eatough, D. J., Benner, C. L., Bayona, J. M., Caka, F. M., Mooney, R. L., Lamb, J. D., Lee, M. L., Lewis, E. A., Hansen, L. D., and Eatough, N. L., "Identification of Conservative Tracers of Environmental Tobacco Smoke," *Proceedings of the 4th International Conference on Indoor Air Quality and Climate*, Berlin (West), 17-21 August, 1987.
16. Muramatsu, M., Umemura, S., Okada, T., and Tomita, H., "Estimation of Personal Exposure to Tobacco Smoke with a Newly Developed Nicotine Personal Monitor," *Environmental Research*, 35:218-227, 1984.
17. Ogden, M. W., "Environmental Tobacco Smoke Analysis Collaborative Study Program," R. J. Reynolds Tobacco Co., Bowman Gray Technical Center, Winston-Salem, NC, 1987.

Table 1. GC/NPD Settings

<u>Treated Filter Cassette</u>	
<u>Column</u>	2% KOH on 10% Carbowax 20M 6 ft. glass (2 mmid)
<u>Temps</u>	
Injector	225°C
Oven	140°C (isothermal)
Detector NPD Bead	250°C
<u>Gas Flows</u>	
He, carrier	15 mL/min
H ₂ , detector	1 mL/min
Air, detector	115 mL/min
<u>Injection</u>	3 µl

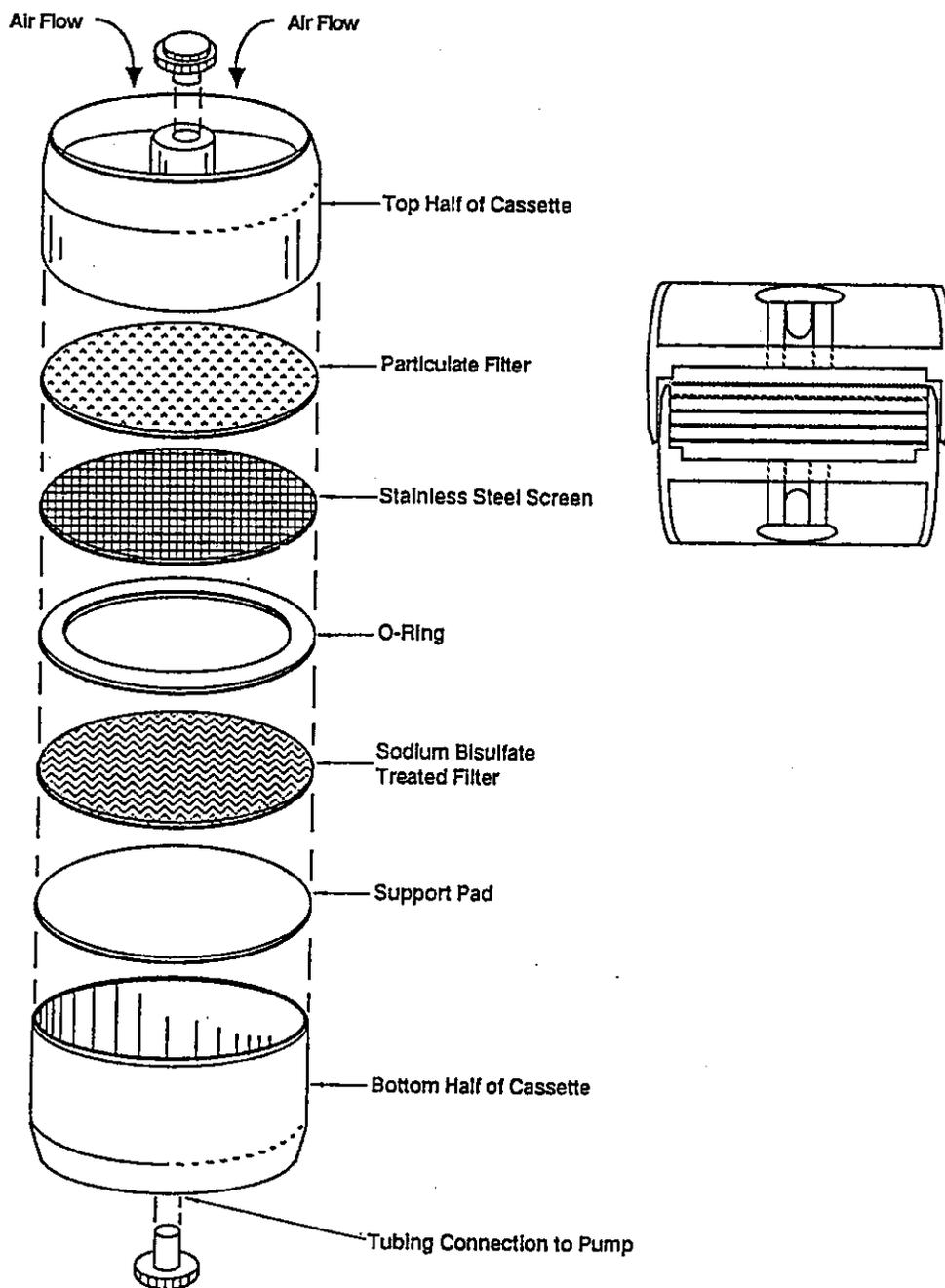


Figure 1. Filter Cassette Used for Active Sampling

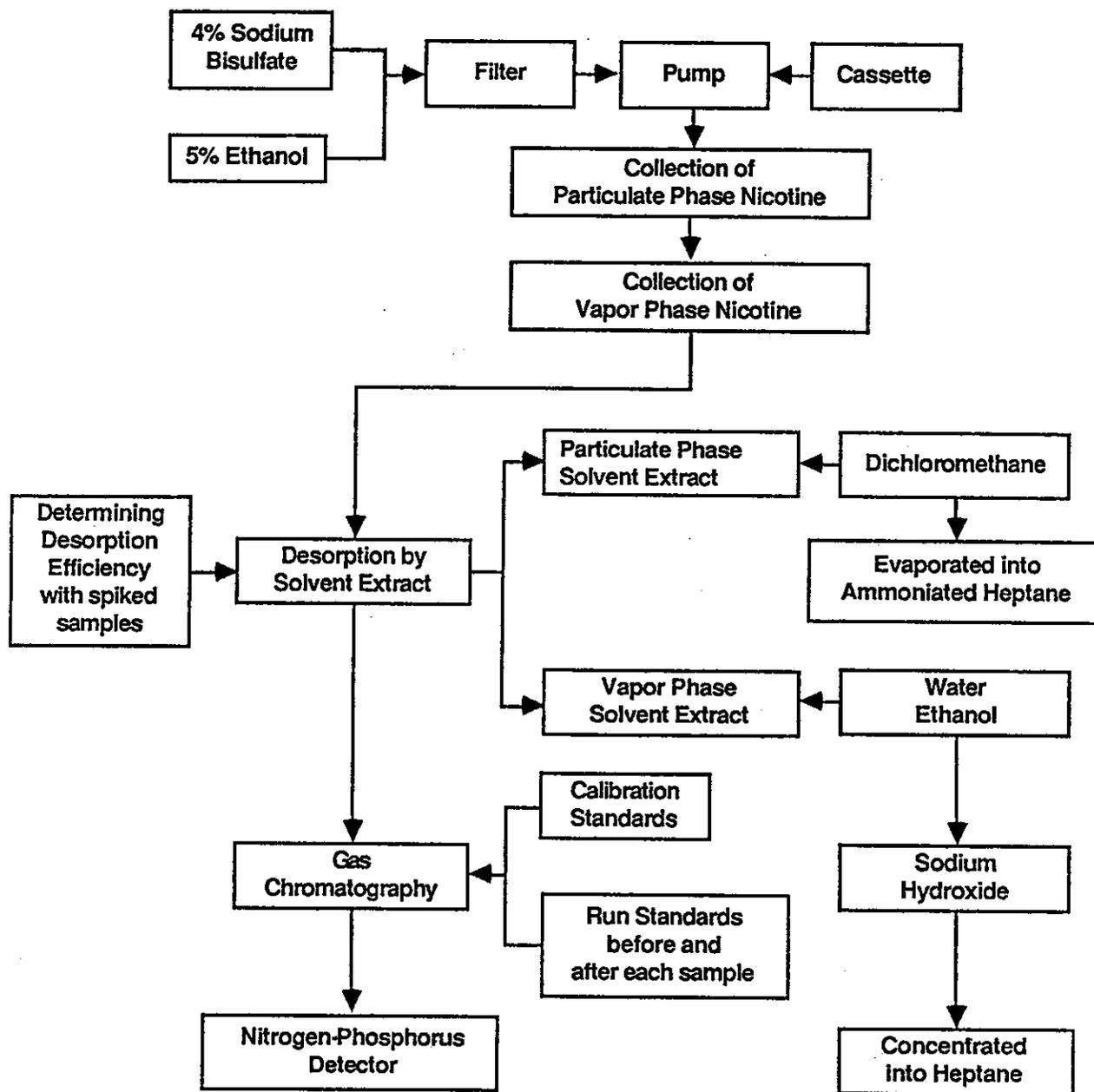


Figure 2. Sampling/Analysis for Active Sampling Using a Filter Cassette

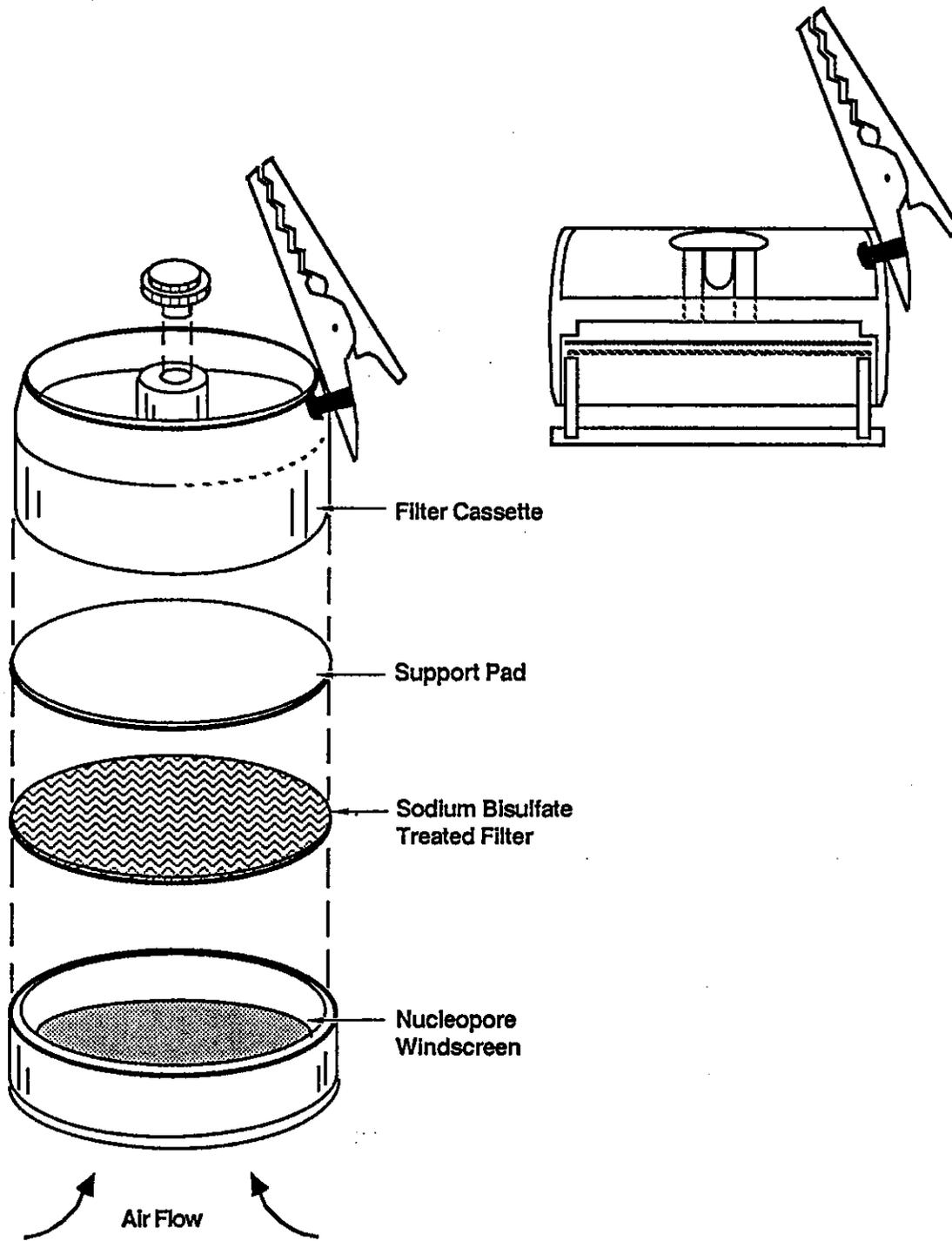


Figure 3. Filter Cassette Used for Passive Sampling

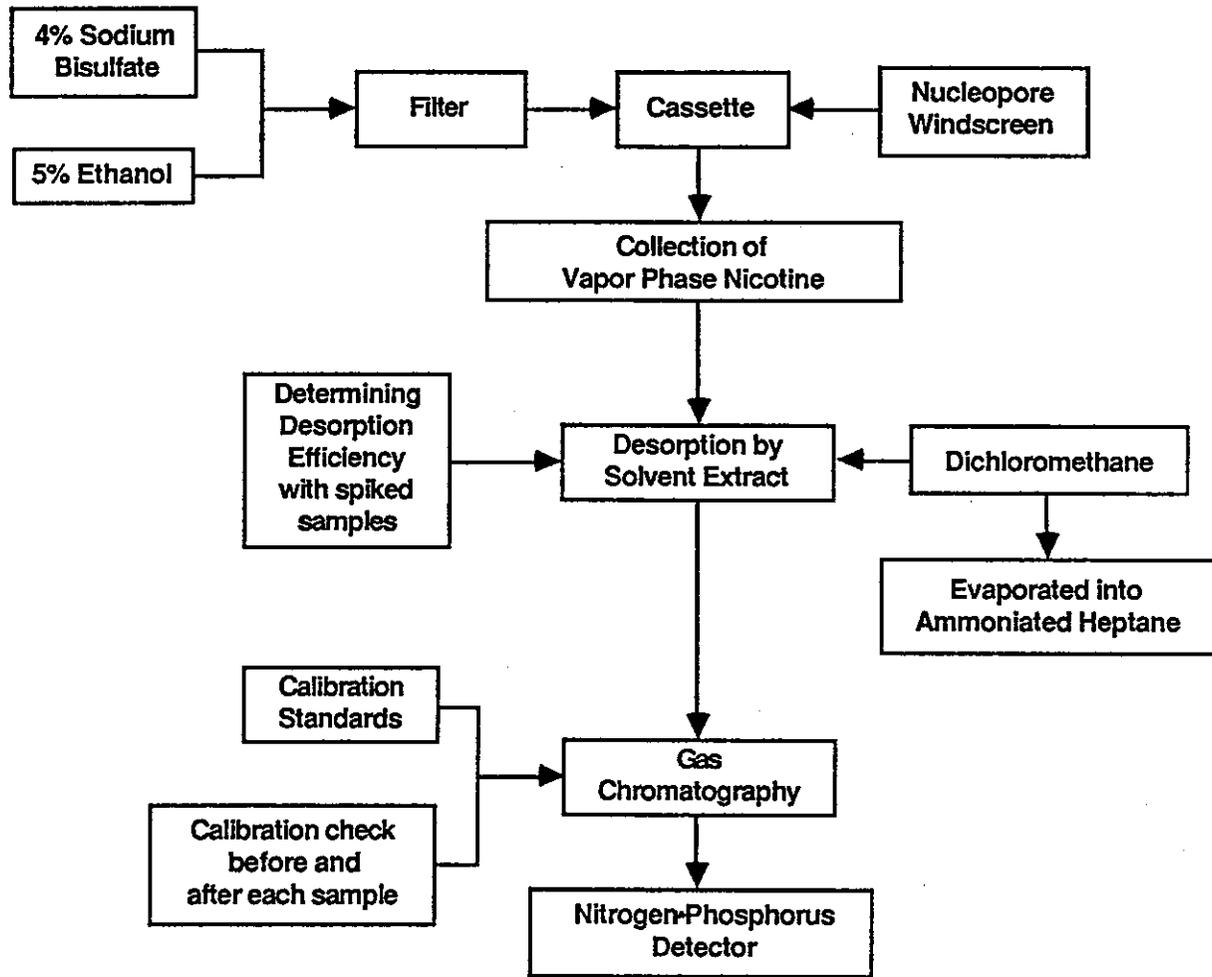


Figure 4. Sampling/Analysis for Passive Sampling Using a Filter Cassette

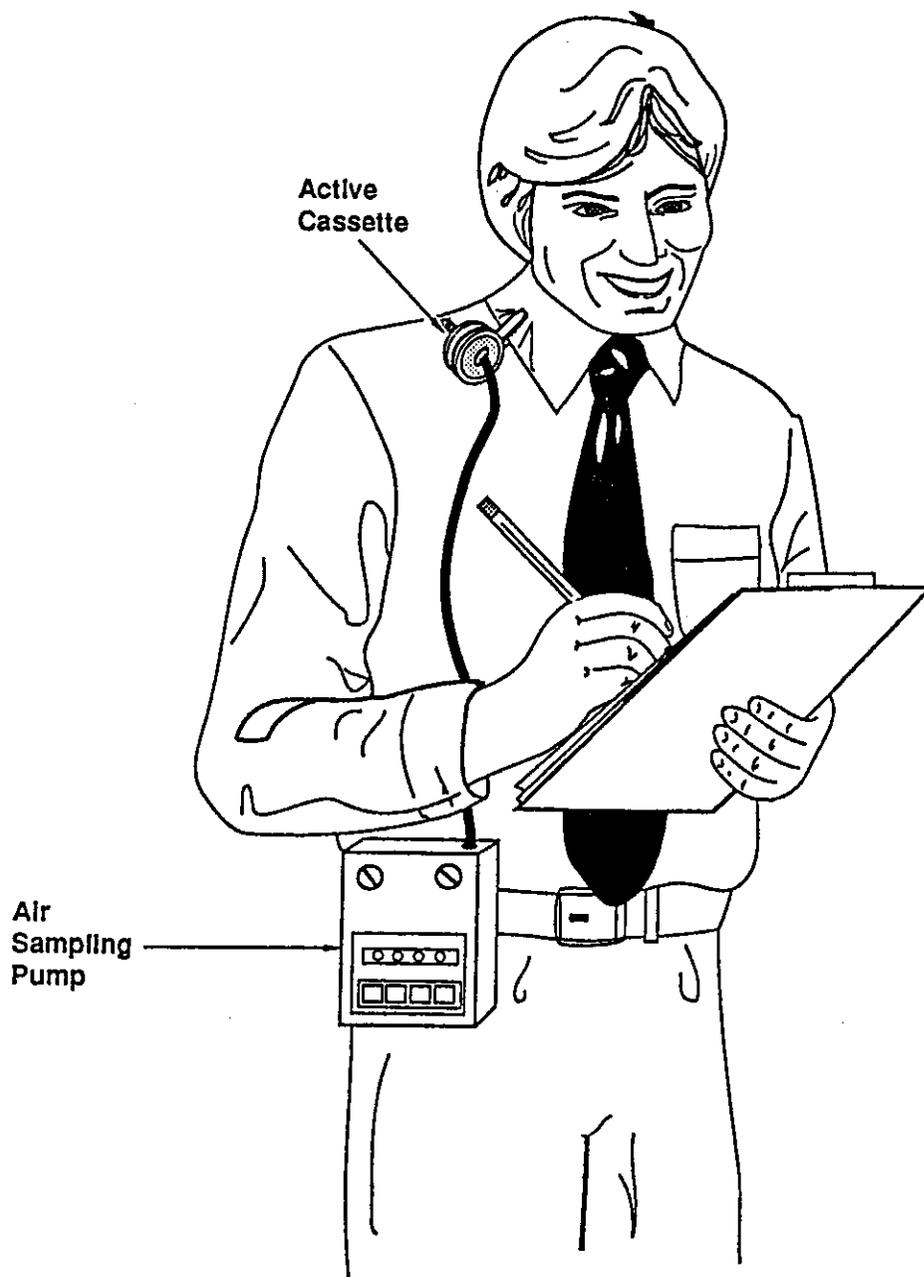


Figure 5. Sampling Setup for Personal Monitoring

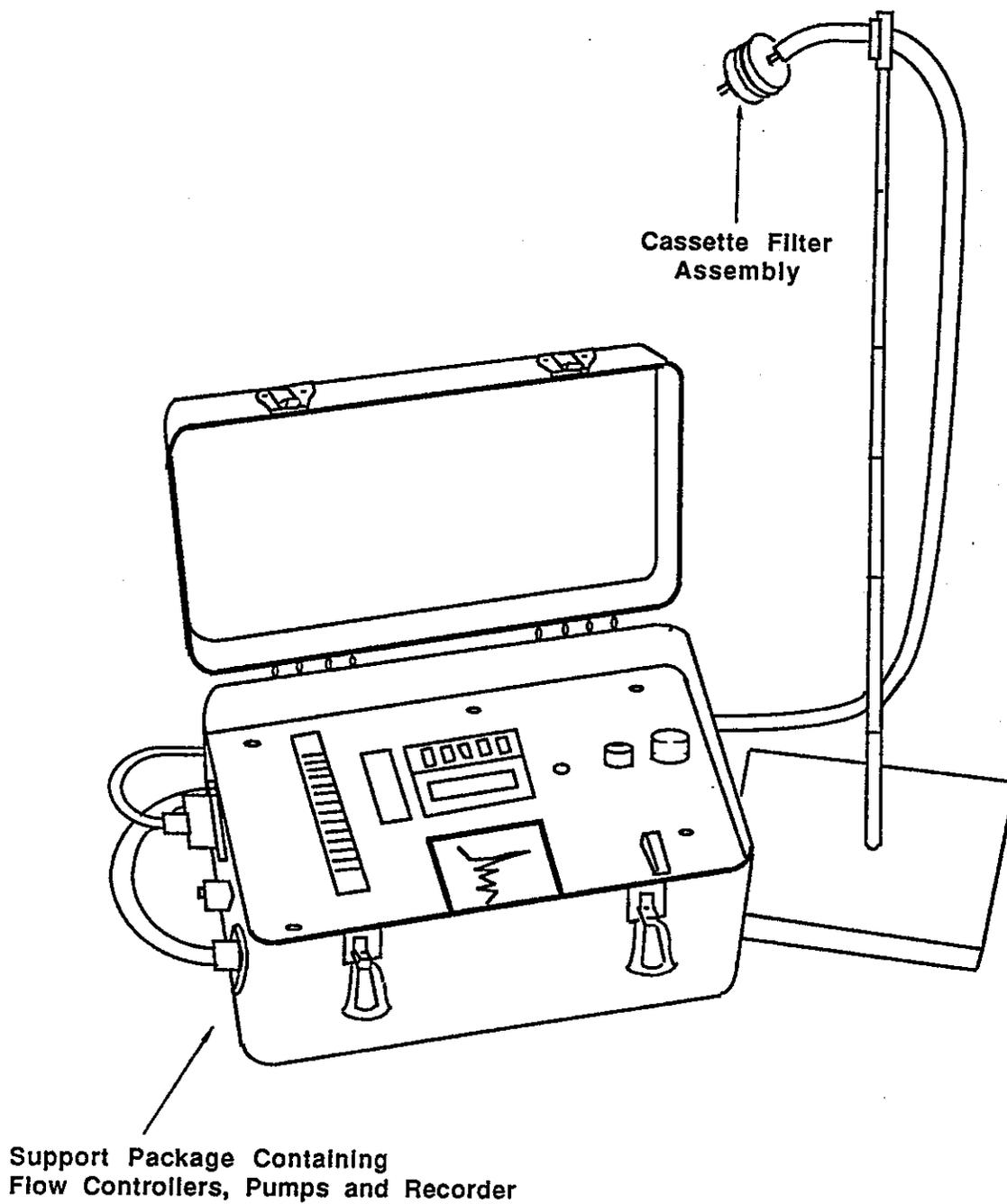


Figure 6. Sampling Setup for Stationary Sampling

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:

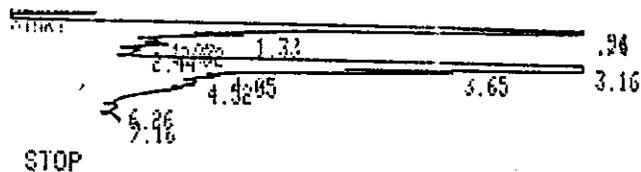
Type of Samplers Active, or Passive	Sampling Location	Temp. F°	Pressure in Hg	Flow Rate (Q) mL/min.	Sampling Period		Total Sampling Time, min.	Total Sample Volume, Liters
					Start	Stop		

Checked by _____

Date _____

* Flow rate from soap bubble calibrator

Figure 7. Nicotine Field Sampling Data Sheet



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

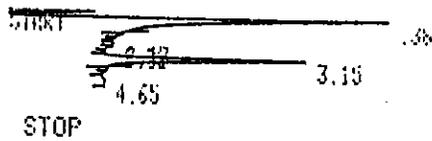
RUN # 47

AREA#

RT	AREA	TYPE	AMOUNT	AREA#
0.96	2771700	PH	0.128	2.265
0.74	2.1823E+07	SHH	0.213	17.836
1.33	213810	DTBP	0.136	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	0.292	78.661
3.65	809480	TBP	0.195	0.662
4.05	39248	DTPV	0.177	0.032
4.52	108820	TPV	0.264	0.039
6.26	32536	TBP	0.288	0.027
7.16	15755	TPB	0.245	0.013

TOTAL AREA= 1.2235E+08
MUL FACTOR= 1.0000E+00

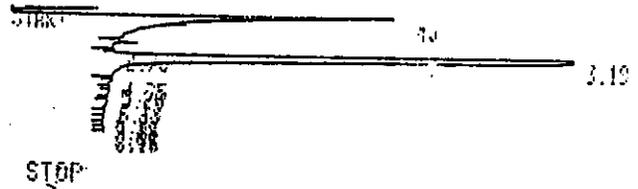
Figure 8. Chromatograms from an ETS Sample



RUN # 6

RT	AREA	TYPE	HEIGHT	AREA%
0.38	4639600	PB	0.374	76.321
2.13	19440	PV	0.139	0.320
2.32	18262	VP	0.127	0.300
3.15	1370600	PB	0.338	22.547
4.65	31098	PV	0.413	0.512

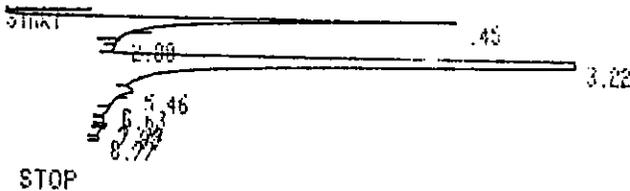
TOTAL AREA= 6079100
MUL FACTOR= 1.0000E+00



RUN # 8

RT	AREA	TYPE	HEIGHT	AREA%
0.45	3433200	PB	0.293	19.085
2.73	4444	PP	0.096	0.025
3.19	1.4425E+07	PB	0.228	80.192
4.75	13831	VP	0.170	0.077
5.20	15217	PV	0.169	0.085
6.19	41916	VP	0.406	0.233
6.82	19103	PV	0.219	0.106
7.19	15959	VP	0.279	0.089
7.64	5992	PV	0.133	0.033
7.92	12210	VP	0.133	0.068
8.15	1317	PP	0.349	0.007

TOTAL AREA= 1.7989E+07
MUL FACTOR= 1.0000E+00



RUN # 10

RT	AREA	TYPE	HEIGHT	AREA%
0.45	5857400	PB	0.407	4.016
2.00	8661	BP	0.148	0.006
3.22	1.3977E+08	SPB	0.269	95.824
5.46	130970	TBB	0.429	0.030
6.63	20151	BP	0.309	0.019
7.79	30109	VP	0.145	0.021
7.99	31492	VP	0.139	0.022
8.77	3925	PP	0.143	0.003

TOTAL AREA= 1.4586E+08
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

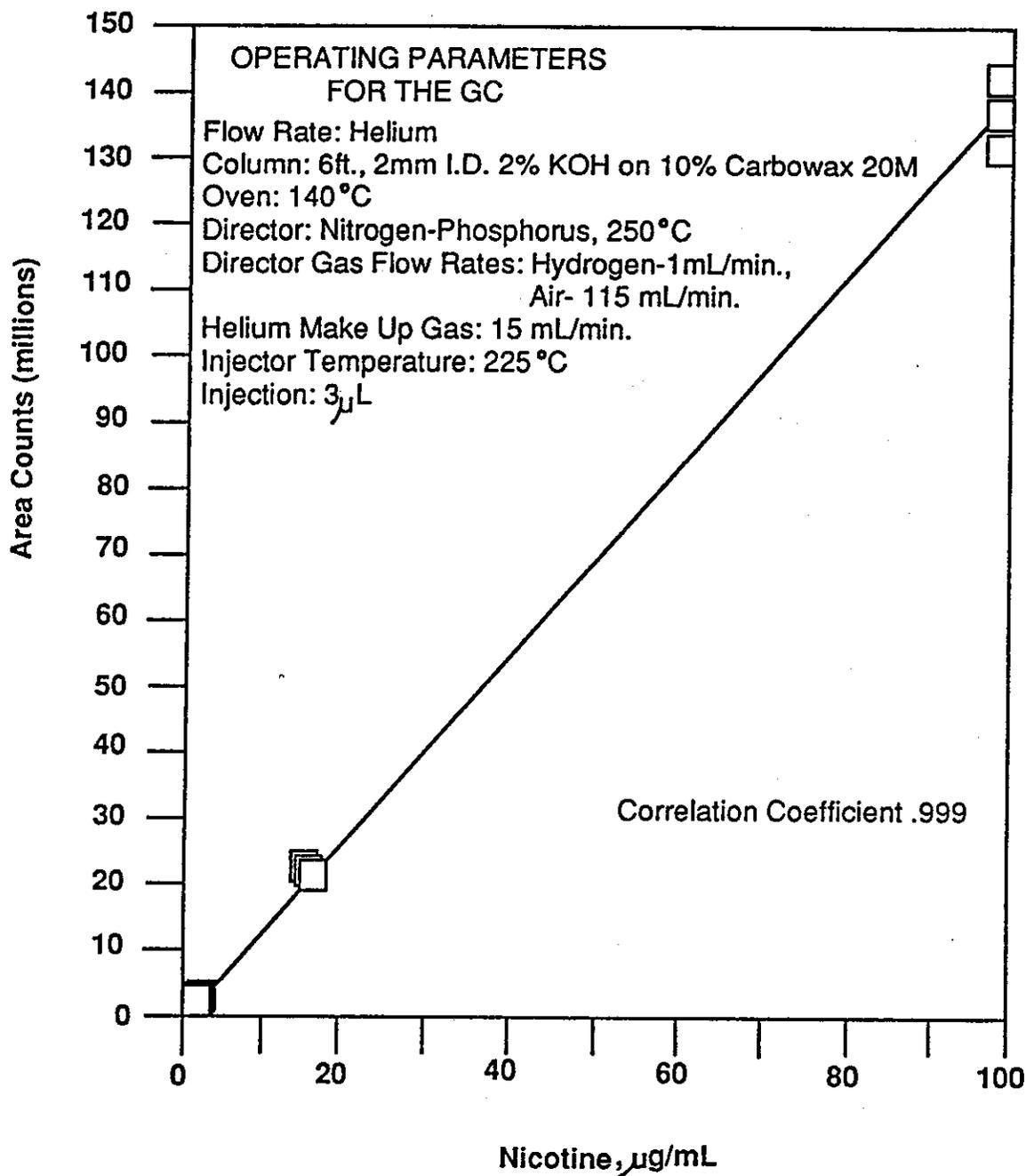


Figure 10. Nicotine Calibration Curve

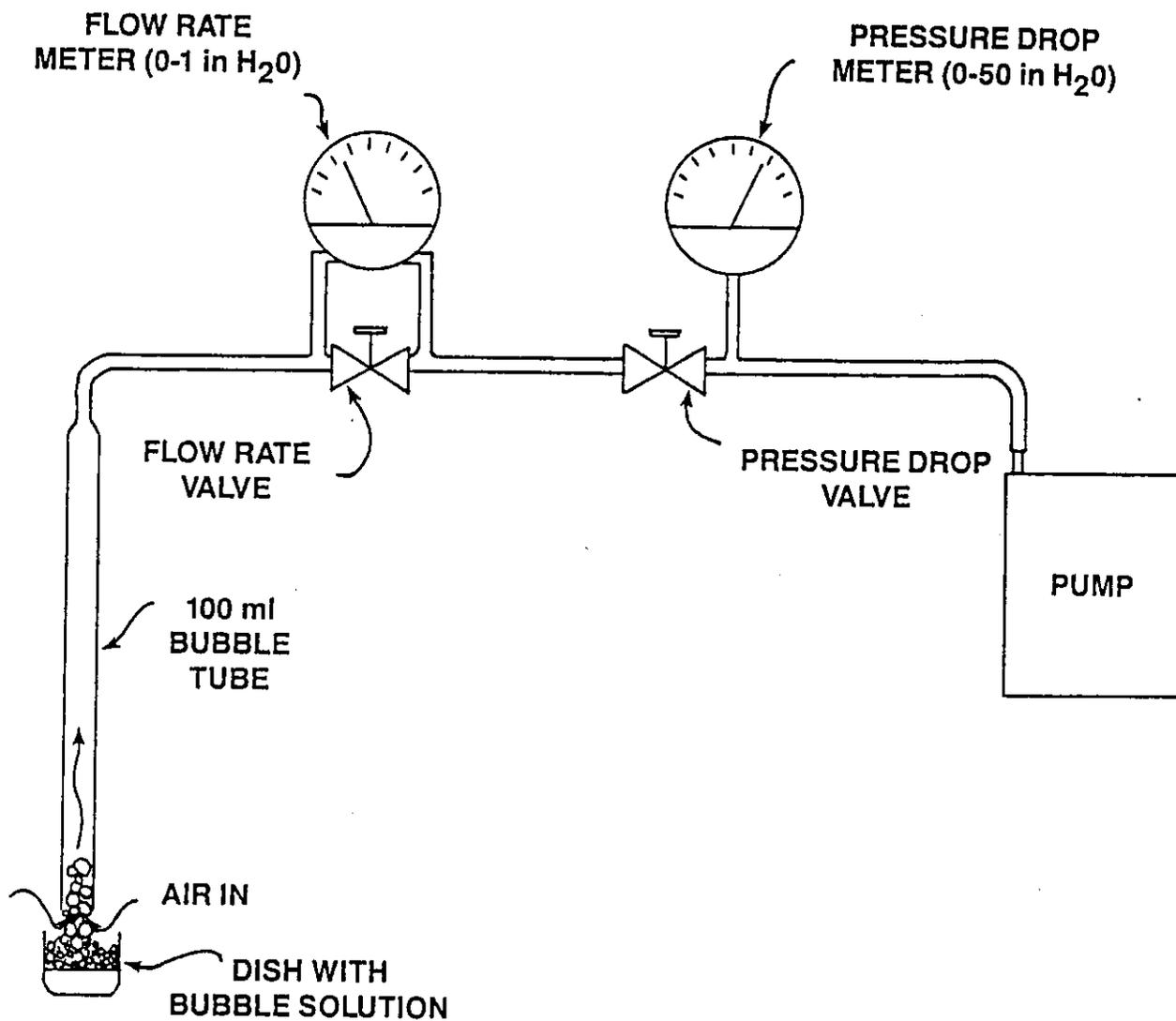


Figure 11. Calibration Assembly for Personal Sampling Pump

Chapter IP-3

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO₂) 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 CO₂ 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 CO₂ 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/CO₂ 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/m³) for an 8 hour period and 35 ppm (40 mg/m³) for a 1 hour period.

2.3 Carbon dioxide is a colorless, odorless, and tasteless gas that 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. CO₂ is produced by human metabolic activity and exhaled through the lungs. The amount of CO₂ produced is a function of an individual's activity level and composition of food consumed. The average amount of CO₂ 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, CO₂ 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% CO₂ for prolonged periods of time experience mild metabolic stress, while exposure to 7-10% CO₂ results in unconsciousness within a few minutes. Ventilation standards have historically been set to maintain CO₂ 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, CO₂ indoor concentrations should be maintained below 0.08%.

Method IP-3A

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO₂) IN INDOOR AIR USING NONDISPERSIVE INFRARED (NDIR)

1. Scope
2. Applicable Documents
 - 2.1 ASTM Standards
 - 2.2 Other Document
3. Summary of Detection
4. Significance
5. Definitions
6. Interferences
7. Apparatus
8. Reagents and Materials
9. NDIR Analyzer Operation
 - 9.1 Installation
 - 9.2 Operation
 - 9.2.1 Turn-on Procedure and Initial Inspection
 - 9.2.2 Manual Zero and Span Calibration
 - 9.2.3 Multipoint Calibration
10. System Maintenance
 - 10.1 Periodic Maintenance
 - 10.2 Routine Maintenance
 - 10.3 Preventive Maintenance
 - 10.4 Troubleshooting the Analyzer
11. Performance Criteria and Quality Assurance (QA)
 - 11.1 Standard Operating Procedures
 - 11.2 Quality Assurance Program
 - 11.2.1 Precision Check
 - 11.2.2 Performance Audit
12. Method Safety
13. References

Method IP-3A

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO₂) IN INDOOR AIR USING NONDISPERSIVE INFRARED (NDIR)

1. Scope

1.1 This document describes a combined method for determination of CO or CO₂ 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 CO₂ 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/m³) 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 (I₂O₅). 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/m³), 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 (CH₄), 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/m³) may be determined, and instrument output over this range is linear for both CO and CH₄.

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 CO₂ 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 CO₂, but also SO₂, 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 gratings are used in the monitor to disperse the infrared energy source into component wavelengths. Rather the measurement gas itself (i.e. CO or CO₂) 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 CO₂) 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 CO₂ 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 CO₂, 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% CO₂) and a flow-through design for the reference cell. In this design, a CO-CO₂ converter consisting of a temperature-controlled cartridge containing platinum-coated aluminum trioxide beads converts the sample gas CO to CO₂ on the reference cell side. At the same time, sample gas containing CO, but not converted to CO₂, flows through the sample cell. the CO-CO₂ 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 CO₂ 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 CO₂ wavelength energy has been absorbed in the distribution cell, there can be no further absorption from the increased CO₂ concentration in the "reference" cell. All other interferences, 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 interferences, 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 CO₂ 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 CO₂ in an air sample. The law states that the transmittance of light through a medium that absorbs light is decreased exponentially by the product $\alpha c l$. The Beer-Lambert Law is defined by the following equation:

$$T = I/I_0 = e^{-\alpha c l}$$

where:

T = transmittance of light through sample gas

I₀ = 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_0 , of the light beam. I_0 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 CO₂. 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 transducer.

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 CO₂ in the detector compartments absorb infrared radiation, they absorb the energy of that radiation. This increase in energy results in the CO or CO₂ molecule becoming more active (it begins to vibrate and move more rapidly). This increase in molecular activity causes the CO or CO₂ 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 CO₂ gas within the cell. The compartment receiving the reference signal receives more infrared energy and subsequently more energy is absorbed by the CO or CO₂ 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 CO₂ 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 (O₂Hb). 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/m³) 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 CO₂. Use of portable NDIRs may not yield defensible quantitative information regarding CO or CO₂ concentrations. Rather, they can be used to provide a "profile" of intensity of CO or CO₂ 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 \pm 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 CO₂) 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 CO₂ 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 CO₂. However, in air grossly contaminated with combustion products, CO₂ (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/m³) 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 CO₂ and water vapor (as well as other interferents) is designing the detector to contain a front and rear measuring chamber, each containing CO or CO₂, 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 CO₂ monitoring system - NDIR CO or CO₂ 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 CO₂ 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 $\pm 1\%$.

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 $\pm 2\%$.

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 CO₂ to simulate normal ambient concentrations. If synthetic air is used, CO₂ 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 CO₂ 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 CO₂ 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 CO₂ concentrations in indoor air using the CO or CO₂ 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 CO₂ to simulate normal ambient concentrations. If synthetic air is used, CO₂ may have to be added.

The calibration gases should be certified to be within $\pm 2\%$ 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:

$$(\text{CO})_{\text{gen}} = [(\text{CO})_{\text{std}}(Q_{\text{co}})]/[Q_{\text{dil}} + Q_{\text{co}}]$$

where:

$(\text{CO})_{\text{gen}}$ = concentration of CO generated, by dilution, ppm

$(\text{CO})_{\text{std}}$ = 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:

$$Q_{\text{co}} = (Q_1) [(P_{\text{bar}}/760)(298/T + 273)]$$

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., troubleshooting) 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 CO₂ 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 be traceable to a NITS-SRM or a commercially available CRM and contain about 350 ppm CO₂ to simulate normal ambient concentrations.

11.2.2.6 A dynamic dilution system must be capable of measuring and controlling flow rates to within $\pm 2\%$ 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:

<u>Audit Point</u>	<u>CO Concentration Range, ppm</u>
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 $\pm 10\%$ 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.

13. References

1. 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*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, 27711, EPA-600/4-87-006, May, 1986.
2. Nagda, N. L., et al., *Guidelines for Monitoring Indoor Air Quality*, ISBN: 0-89116-385-9, Hemisphere Publishing Co., New York, NY, 1987.
3. Wilson, M. L., Durham, O. G., Jr., and Elias, D. F., "Draft: APTI Course 435 Atmospheric Sampling," U.S. Environmental Protection Agency, Air Pollution Training Institute, Research Triangle Park, NC, 27711, March, 1979.
4. 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.

5. Riggin, R. M., *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, 27711, EPA-600/4-84-041, May, 1986.
6. Riggin, R. M., *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, 27711, EPA-600/4-83-027, May, 1983.
7. *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II - Ambient Air Specific Methods, Test Method Section 2.6*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, 27711, EPA-600/4-72-027a, January, 1983.
8. Kirby, D. L., and Joerger, K. C., *APT I Course 464 - Analytical Methods for Air Quality Standards*, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Air Pollution Training Institute, Research Triangle Park, NC, 27711, Draft, 1981.
9. *Air Quality Criteria for Carbon Monoxide*, U.S. Department of Health, Education and Welfare, Public Health Service, Washington, DC, March, 1970.
10. ACGIH, *TLV's Threshold Limit Values for Chemical Substances in Workroom Air Adopted by ACGIH for 1980*, American Conference of Government Industrial Hygienists, Cincinnati, OH, 1980.
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 Reference Methods and Other Commercially Available CO and CO₂ Analyzers

<u>Identification</u>	<u>Manufacturer</u>	<u>Fed. Register Notice</u>		
		<u>Vol.</u>	<u>Page</u>	<u>Date</u>
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 Reference Methods and Other Commercially Available CO and CO₂ Analyzers (Cont'd)

<u>Identification</u>	<u>Manufacturer</u>	<u>Fed. Register Notice</u>		
		<u>Vol.</u>	<u>Page</u>	<u>Date</u>
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

<u>Model #</u>	<u>Manufacturer</u>	<u>Portability</u>
Gas Analyzer Model RI-550A	CEA Instruments Box 303 Emerson, NJ 07630 (201)967-5660	Portable

Commercially Available NDIR CO₂ Analyzers

<u>Model #</u>	<u>Manufacturer</u>	<u>Portability</u>
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 Reference Methods and Other Commercially Available CO and CO₂ Analyzers (Cont'd)

Commercially Available NDIR CO₂ Analyzers (Cont'd)

<u>Model #</u>	<u>Manufacturer</u>	<u>Portability</u>
LIRA 3200	MSA Instrument Div. Box 427 Pittsburgh, PA 15230 (800)672-4678	Stationary

Table 2. Suggested Performance Specifications for NDIR CO Analyzers

<u>Analyzer Parameter</u>	<u>Specification</u>
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

<u>Service</u>	<u>Frequency</u>
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 ₂ O interference	Annually

Table 4. Typical NDIR Monitor Problems

<u>Observation</u>	<u>Possible Cause</u>	<u>Diagnostic Check</u>
CO level too low	Reference infrared 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
CO level too high	Amplifier failing	Completely check-out electronics system
	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
Abnormal positive zero drift	Amplifier failing	Completely check-out electronics system
	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

Table 5. QA/QC Operational Parameters

<u>QA/QC Parameters</u>	<u>Actions</u>
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.

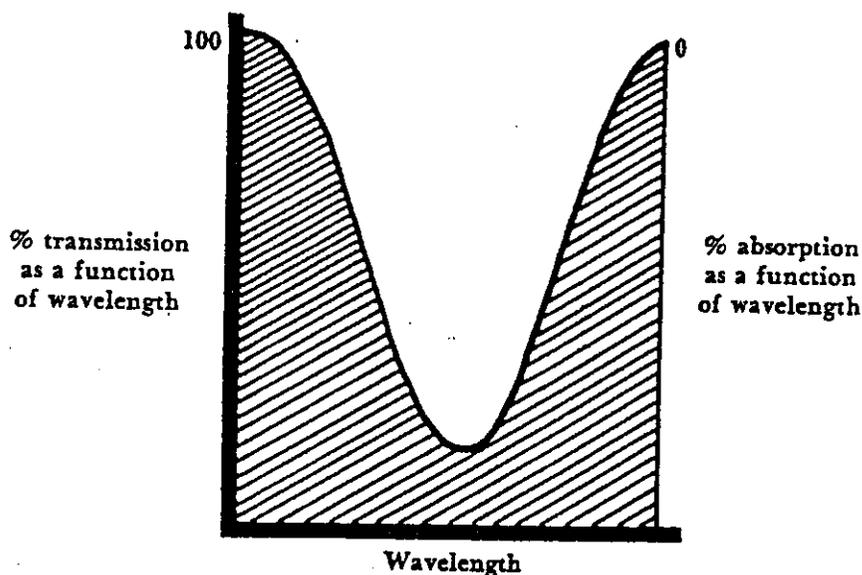


Figure 1A. Typical Absorption Curve in the IR

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 ₂ O	3.1	1000-1400
	5.0-5.5	1800-2000
	7.1-10	3200
CO	2.3	2200
	4.6	4300
CO ₂	2.7	850-1250
	5.2	1900
	8-12	3700
NH ₃	10.5	950
CH ₄	3.3	1300
	7.7	3000
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

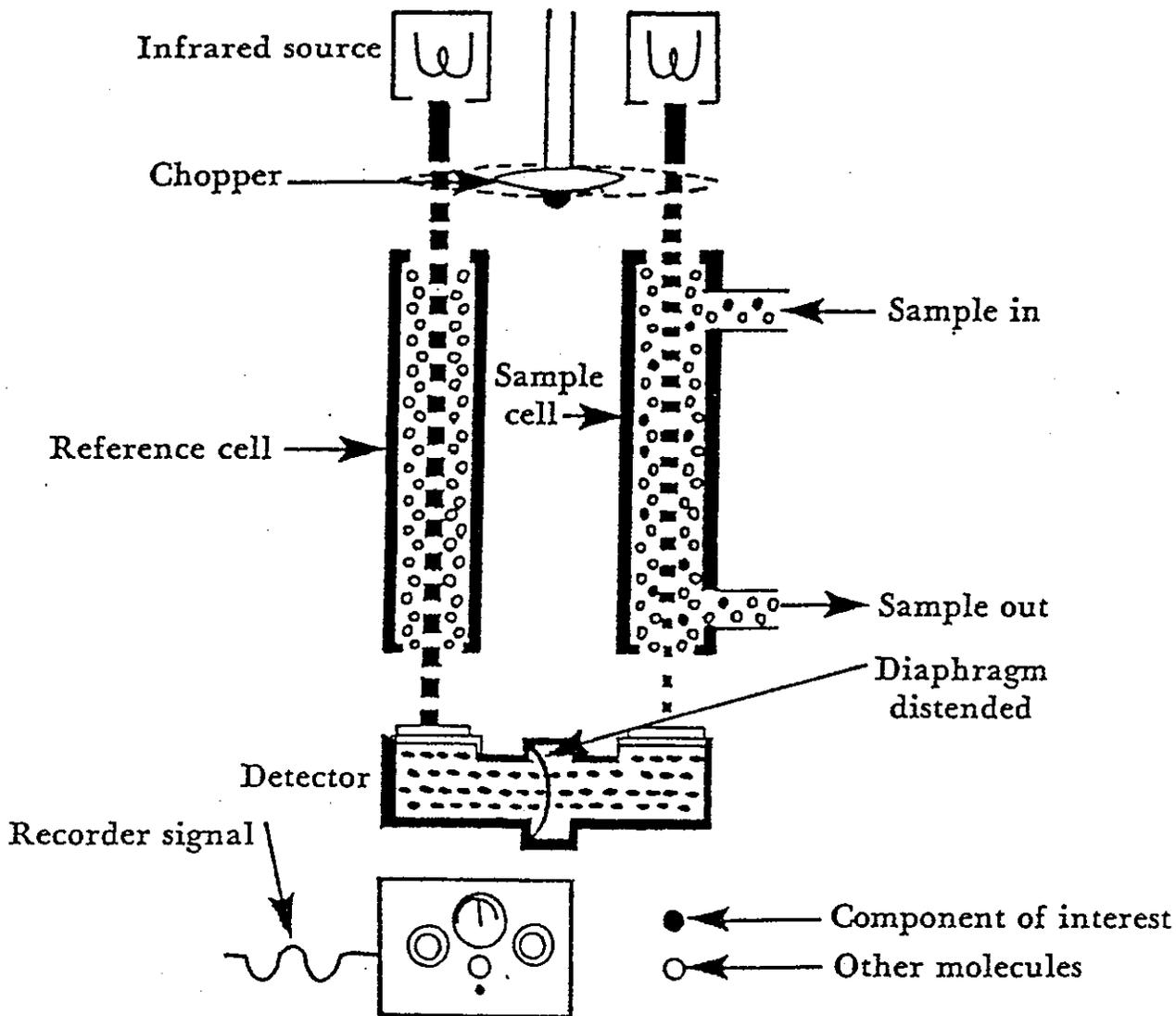


Figure 2. Major Components of a Commercially Available NDIR Instrument

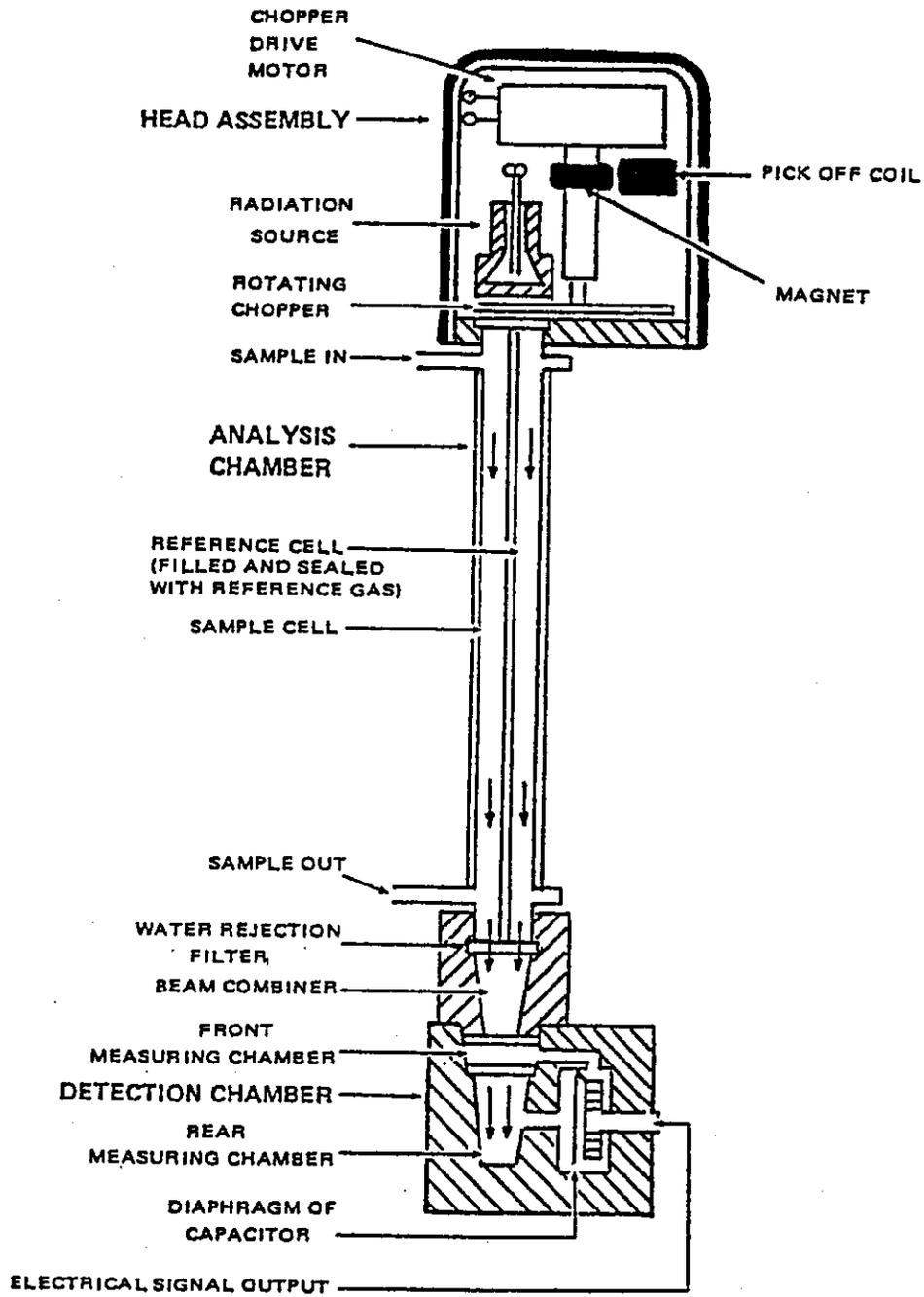


Figure 3. Front/Rear Chamber Detector Design

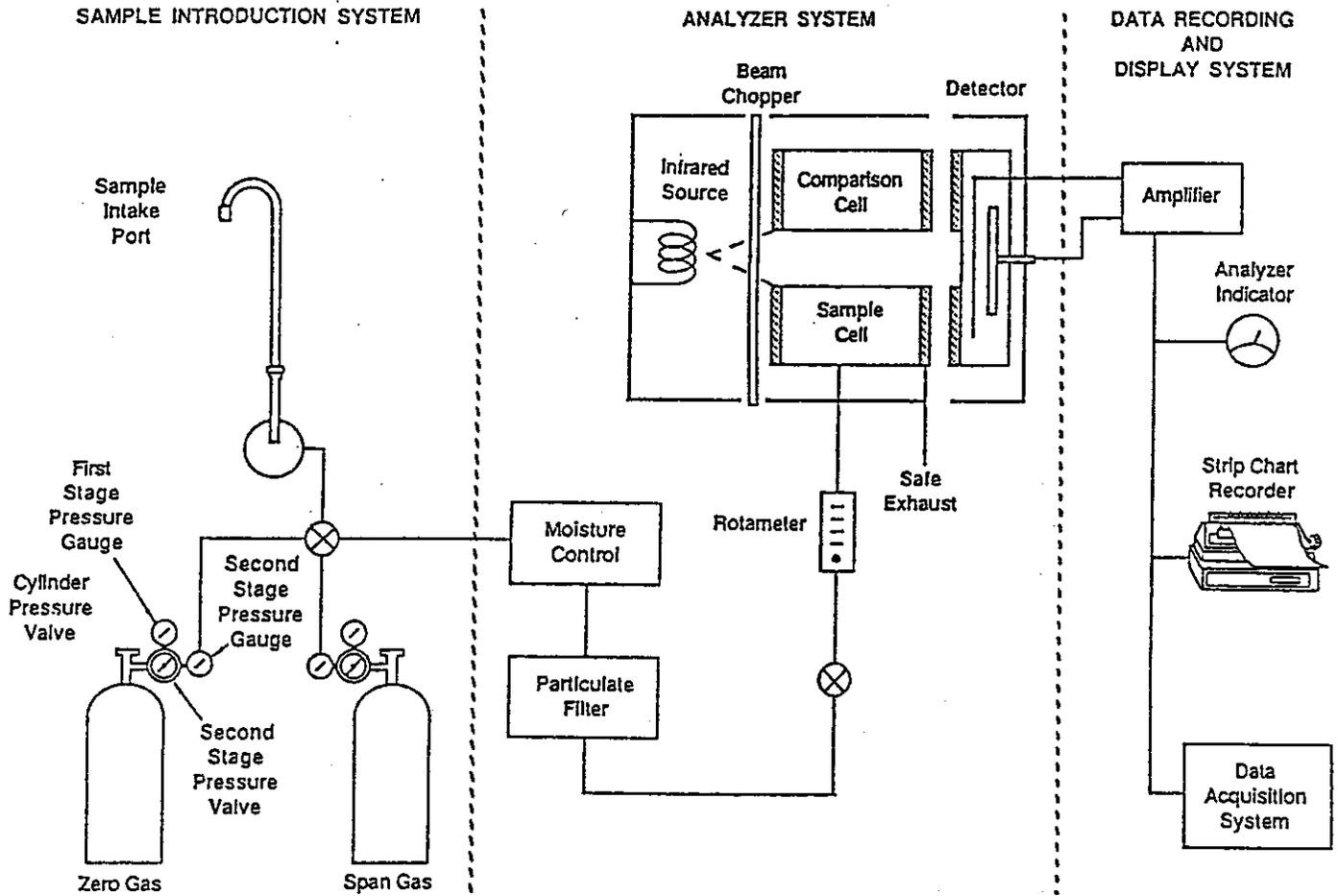


Figure 4. NDIR Calibration and Detector System

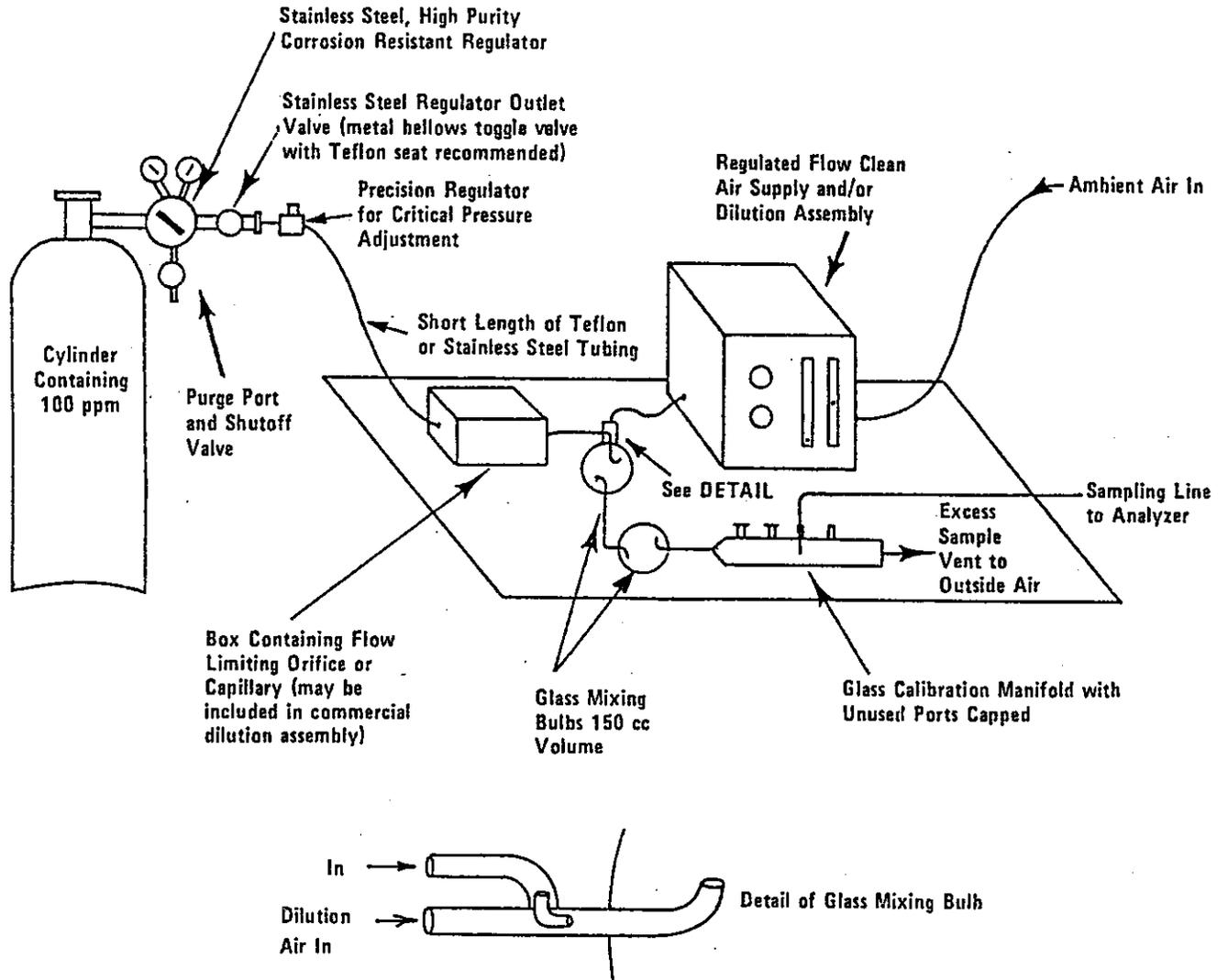


Figure 6. Assembly for Dilution of CO from Cylinder for Use in Calibration or Span Check

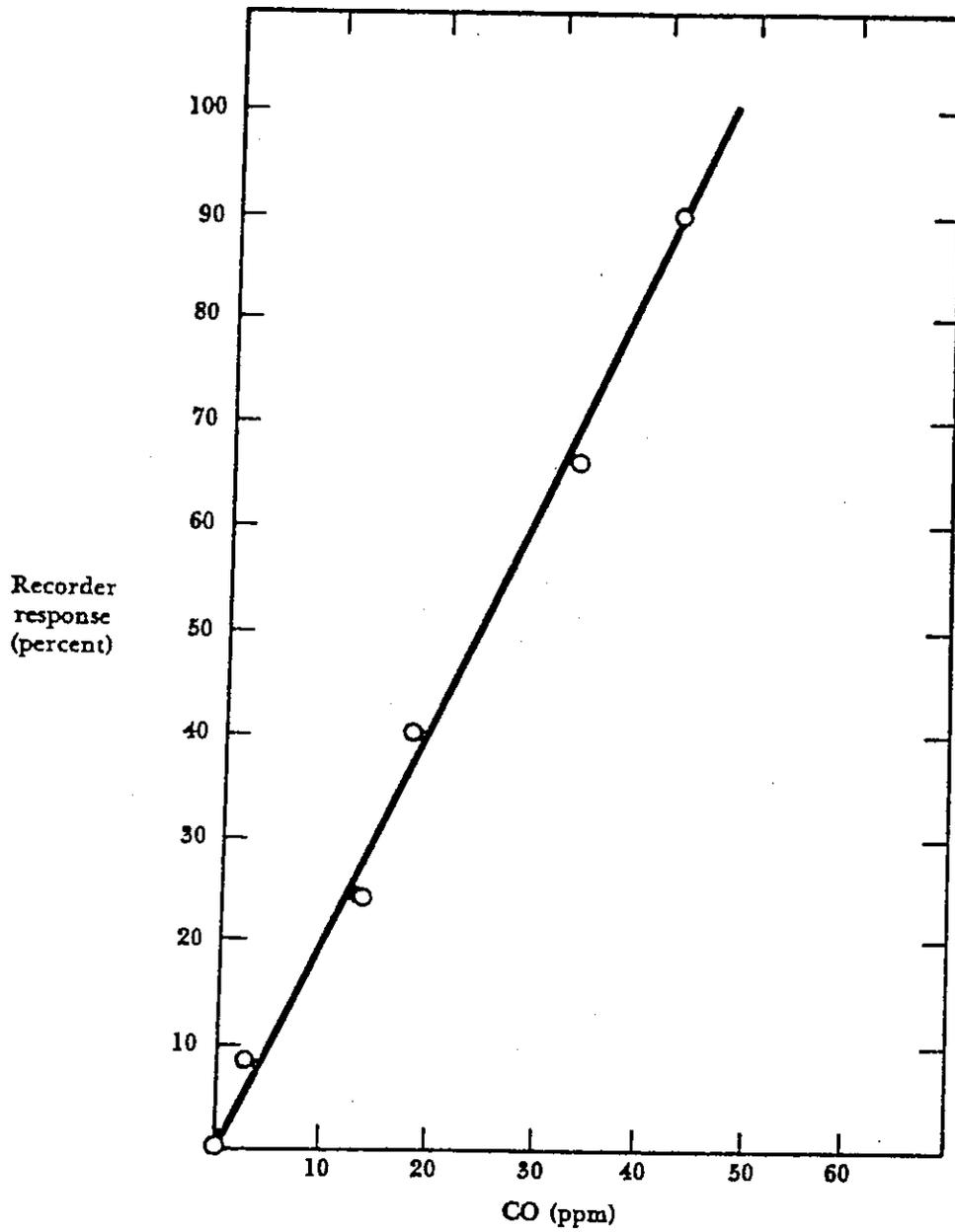


Figure 7. NDIR Calibration Curve

Method IP-3B

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO₂) IN INDOOR AIR USING GAS FILTER CORRELATION (GFC)

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Method IP-3B

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO₂) IN INDOOR AIR USING GAS FILTER CORRELATION

1. Scope

This document describes a procedure for determination of CO and CO₂ concentrations in indoor air using gas filter correlation (GFC). This procedure provides automatic and continuous measurement of CO and CO₂ in indoor atmospheres. Analyzers employing the GFC measurement principle rely on the properties of CO and CO₂ 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 CO₂, as a filter for the infrared radiation transmitted through the analyzer, hence the term GFC.

3.2 The basic components of the GFC CO/CO₂ spectrometer are shown in Figure 1. Radiation from an IR source is chopped and then passed through a gas filter alternating between CO and N₂ 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/CO₂ gas filter acts to produce a reference beam which cannot be further attenuated by CO and CO₂ in the sample cell. The N₂ side of the filter wheel is transparent to the IR radiation and therefore produces a measure beam which can be

absorbed by CO and CO₂ 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 CO₂ 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 CO₂.

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/CO₂ 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 CO₂. 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 CO₂ analyzer - Analyzer should provide a continuous CO₂ 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 CO₂ 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 CO₂ 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 CO₂ concentration standard - Cylinder of CO or CO₂ (depending on monitoring needs) in air containing an appropriate concentration of CO or CO₂ 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 CO₂ 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 CO₂ gas cylinders against a CO or CO₂ 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 CO₂ analyzers. The zero air should contain <0.1 ppm CO/CO₂ (best source). Since the analyzer is virtually interference free, it is only necessary to insure that CO/CO₂ has been removed. It should be noted that zero air as supplied in cylinders from commercial suppliers typically contains CO/CO₂ concentrations in the 0.1 - 0.3 ppm range. Thus, cylinder air should be scrubbed of the residual CO/CO₂ prior to its use in the analyzer as a dilution gas or a zero standard. Room air which has been scrubbed of CO/CO₂ can be used as the zero air source. It is not necessary to remove SO₂, NO, NO₂, CO₂, 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/CO₂ reference. (A platinum on alumina catalyst, operated at 250°C, has been found to be a convenient oxidizer to convert CO to CO₂. If it is desired to remove water vapor, SO₂, etc., a photolytic ozone generator can be used to convert NO to NO₂. This can be followed by a heatless air drier to remove water vapor, NO₂, SO₂, 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/CO₂ 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

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 resistor 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 value 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 $\pm .2^{\circ}\text{C}$, 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 $\pm 5\%$ 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/CO₂ 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 CO₂ using the Thermo Environmental CO₂ 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:

$$[\text{CO}]_{\text{out}} = ([\text{CO}]_{\text{std}} \times F_{\text{co}}) / (F_{\text{d}} + F_{\text{co}})$$

where:

[CO]_{out} = diluted CO concentration at the output manifold ppm.

[CO]_{std} = concentration of the undiluted CO standard ppm.

F_{co} = flow rate of the CO standard corrected to 25°C and 760 mm Hg, liters per minute.

F_d = 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:

$$\text{Recorder Response (percent scale)} = (([\text{CO}]_{\text{out}} \times 100) / \text{URL}) + Z_{\text{co}}$$

where:

URL = nominal upper range limit of the analyzer's operating range.

Z_{co} = 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 F_{co} or increasing F_d. 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 A_0 . Compute the zero drift from the following equation:

$$\text{Zero Drift } \% = A_0 - Z$$

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 A_{80} . Compute the span error from the following equation:

$$\text{Span Error, } \% = ([A_{80} - Z)URL/100] - [CO] \times 100/[CO]$$

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 CO₂ when using the Model 41/41H analyzer) and the other with N₂. 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 N₂ 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/CO₂ free air is discussed in Section 8.2.

11.2.2.3 Connect a source of CO span gas (i.e., use CO₂ span gas for CO₂ 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 0 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:

<u>Switch Setting</u>	<u>Full Scale Range (PPM)</u>
0	1
1	2
2	5
3	10
4	20

<u>Switch Setting</u>	<u>Full Scale Range (PPM) (cont.)</u>
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:

<u>Setting</u>	<u>Time Response (60 Hz)</u>	<u>Time Response (50 Hz)</u>
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 or 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., troubleshooting) 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

1. *Quality Assurance Handbook for Air Pollution Measurement Systems*, Volume II - Ambient Air Specific Methods, EPA 600/4-77-027a, May 1977.
2. 40 CFR Part 58, Appendix A, B.
3. "Guideline for Continuous Monitoring of Carbon Monoxide at Hazardous Waste Incinerators," Draft, Pacific Environmental Services, Reston, VA, January, 1987.
4. Instruction Manual, Model 48, GFC Ambient CO Analyzer, Thermo Environmental Corp., Instruments Div., Franklin, MA, January, 1989.
5. 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.
6. Nagda, N. L., et al., *Guidelines for Monitoring Indoor Air Quality*, ISBN: 0-89116-385-9, Hemisphere Publishing Co., New York, NY, 1987.
7. 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.
8. 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.
9. Riggan, 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.
10. 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.
11. Riggan, 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. 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

<u>Identification</u>	<u>Manufacturer</u>	<u>Fed. Vol.</u>	<u>Reg. Pg.</u>	<u>Notice Date</u>
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

<u>Detection Device I.D.</u>	<u>Manufacturer</u>	<u>Portability</u>
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

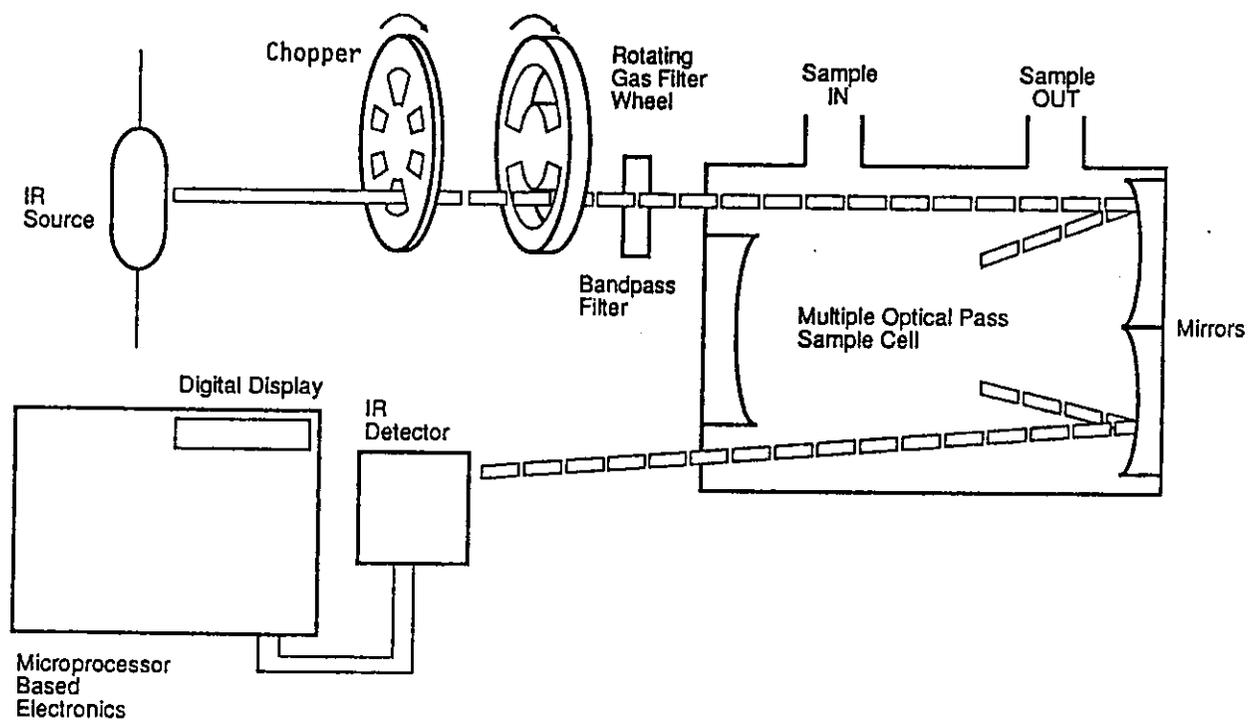


Figure 1. Gas Filter Correlation Basic Components

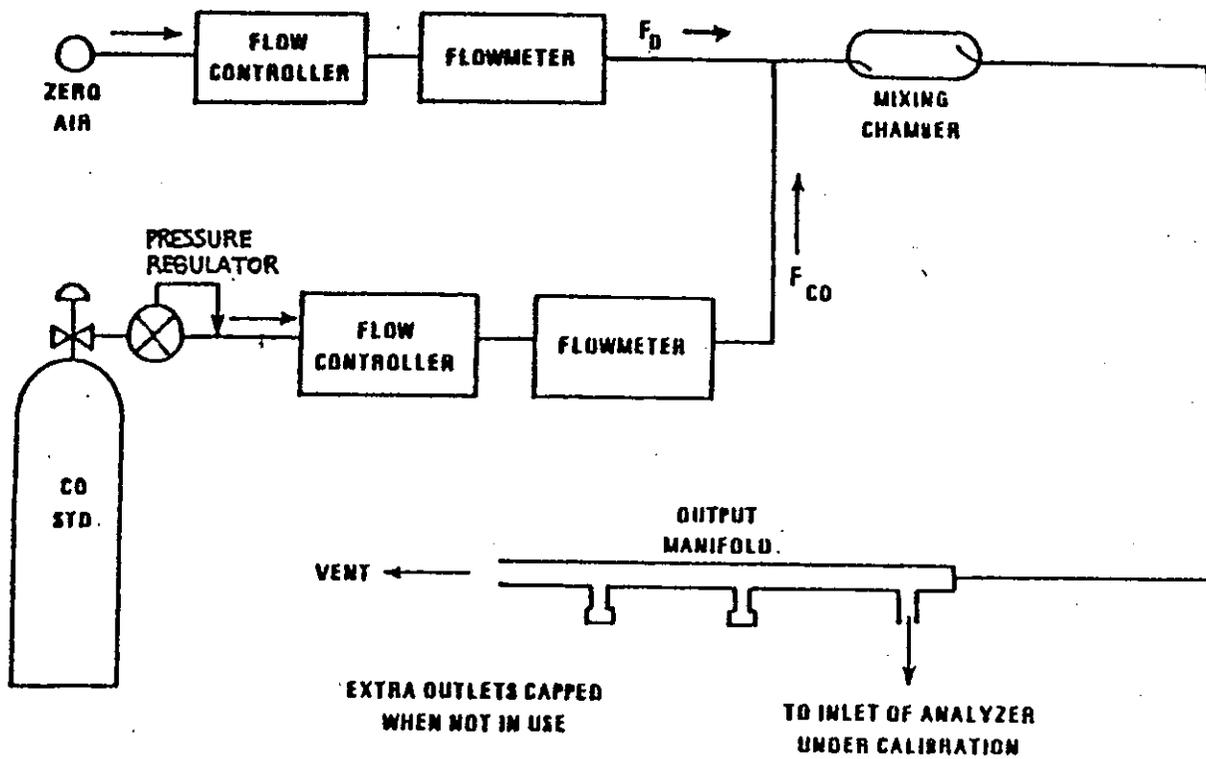


Figure 2. Flow Schematic of Calibration System

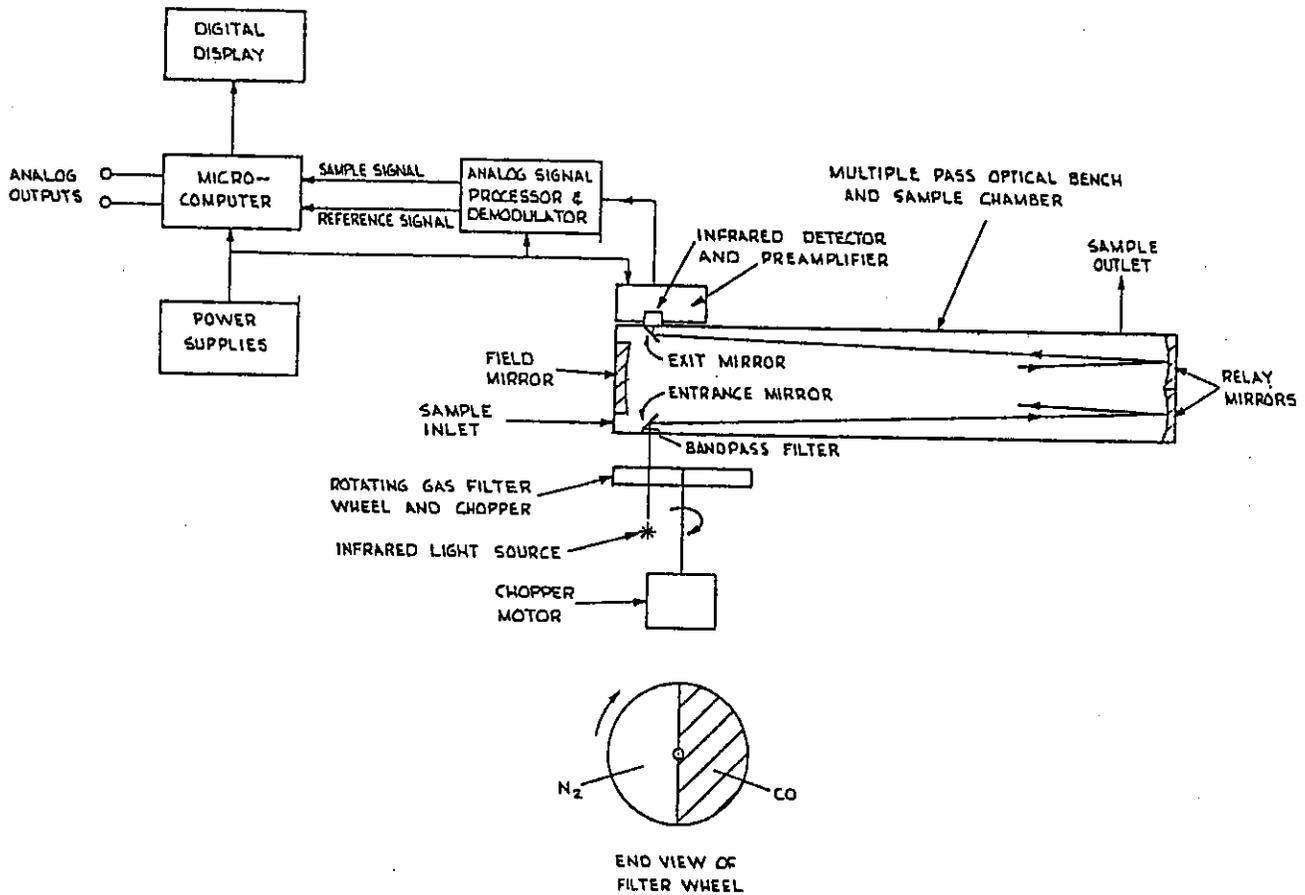


Figure 3. Block Diagram of a Gas Filter Correlation Spectrometer

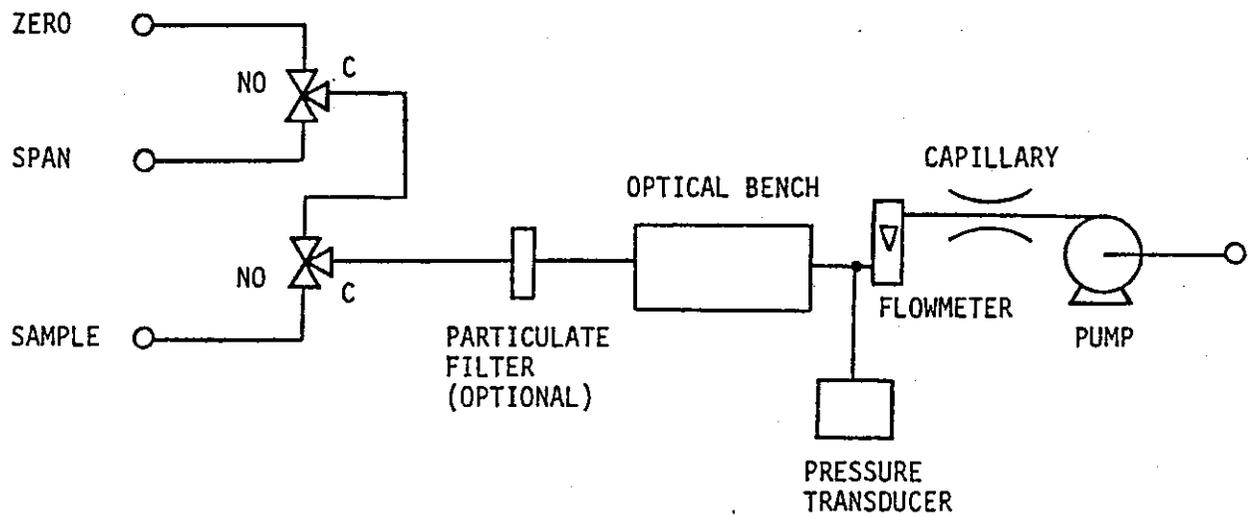


Figure 4. Flow Schematic for Calibration of GFC Analyzer

Method IP-3C

DETERMINATION OF CARBON MONOXIDE (CO) IN INDOOR AIR USING ELECTROCHEMICAL OXIDATION

1. Scope
2. Applicable Documents
 - 2.1 ASTM Standards
 - 2.2 Other Documents
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4. Significance
5. Definitions
6. Interferences
7. Apparatus
8. Reagents and Materials
9. Systems Maintenance
10. CO Monitor Calibration
 - 10.1 CO Monitor Zero Calibration
 - 10.2 CO Monitor Span Calibration
 - 10.3 CO Monitor Multipoint Calibration
11. CO Monitor Operation
12. Method Safety
13. Performance Criteria and Quality Assurance (QA)
14. References

Appendix - Operating Procedures for a Portable CO Detection System

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 CO₂ 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 CO₂ 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 CO₂. 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.

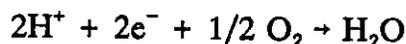
3.3 Signal integrators and data loggers can be used to record data from the personal exposure monitors. The monitors generally operate over a range of 0-1000 ppm.

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.

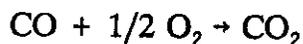
3.4.1 The GE monitor employed solid polymer electrolyte (SPE) technology (formerly patented by GE) using a membrane with deionized water stored on one side. Figure 2 provides a complete illustration of the GE CO monitor. The deionized water was stored in a plastic reservoir cell. The sample containing 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:



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:



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 :



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 interferences (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 CO₂. 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.

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 Electrochemical oxidation - Sample air is passed into an electrochemical cell where CO is oxidized to CO₂ producing a signal related to CO concentration present in the sample air.

5.2 Output - Electrical signal that is proportional to the pollutant concentration measurement, intended for connection to readout or data processing devices; usually expressed as millivolts or milliamps.

5.3 Operating temperature range - The range of indoor temperatures over which the instrument will meet all performance specifications.

5.4 Operating humidity range - The range of indoor relative humidity over which the instrument will meet all performance specifications.

6. Interferences

Hydrogen, ethylene, and acetylene are potential interferences. The interferences can be eliminated by using a filter (i.e., Purafil) that provides selectivity of the monitor to CO by absorbing these gases.

7. Apparatus

7.1 CO personal exposure monitor - gas monitor capable of measuring and recording CO concentrations to which personnel are exposed. The monitor should be equipped with a sensor cell assembly that would provide for electrochemical oxidation of CO to CO₂. Additionally, the PEM should include adequate power supply (i.e., battery pack) and recording system.

7.2 Sample air pump - required on some models to draw sample air into the monitor.

7.3 Air filter - optional, used to remove interfering gases (i.e., hydrogen, ethylene, and acetylene) and particulates.

7.4 Flowmeter - capable of measuring sample flow through the system.

7.5 Tubing - Teflon® tubing to connect monitor and gas cylinders when calibrating, zeroing, and spanning the instrument.

8. Reagents and Materials

8.1 Zero gas - nitrogen or helium containing less than 1 ppm CO, ultrahigh purity grade, best source.

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 polypropylene 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 Federal 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, 15ECS1C01 and 15ECS1C01A," 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 \pm 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 \pm 10% (1 week)

Zero drift: less than \pm 2 ppm (10 hours)

Table 2. Commercially Available Electrochemical CO Monitors

<u>Identification</u>	<u>Manufacturer</u>	<u>Data Logger</u>
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

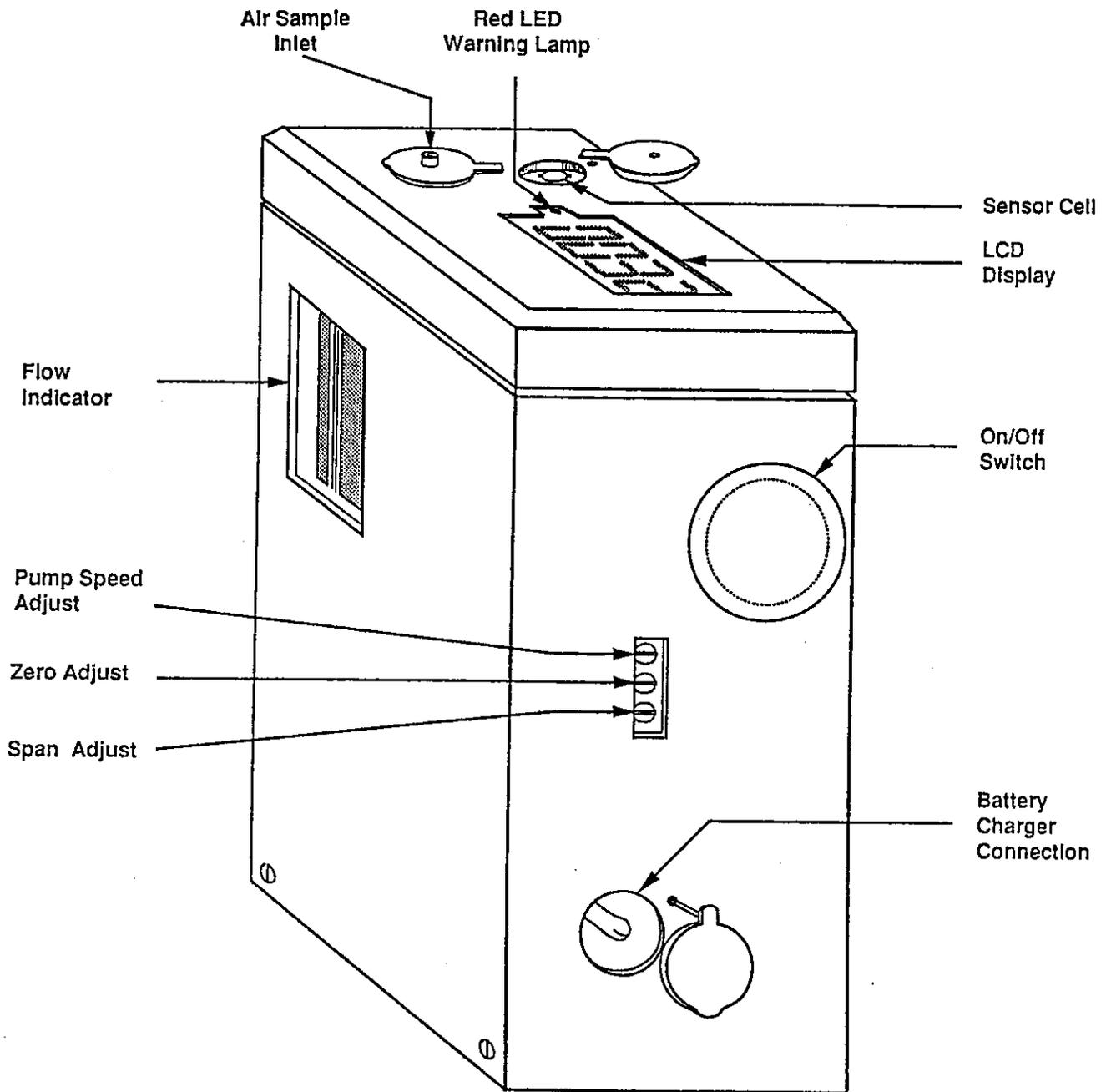


Figure 1. CO Personal Exposure Monitor

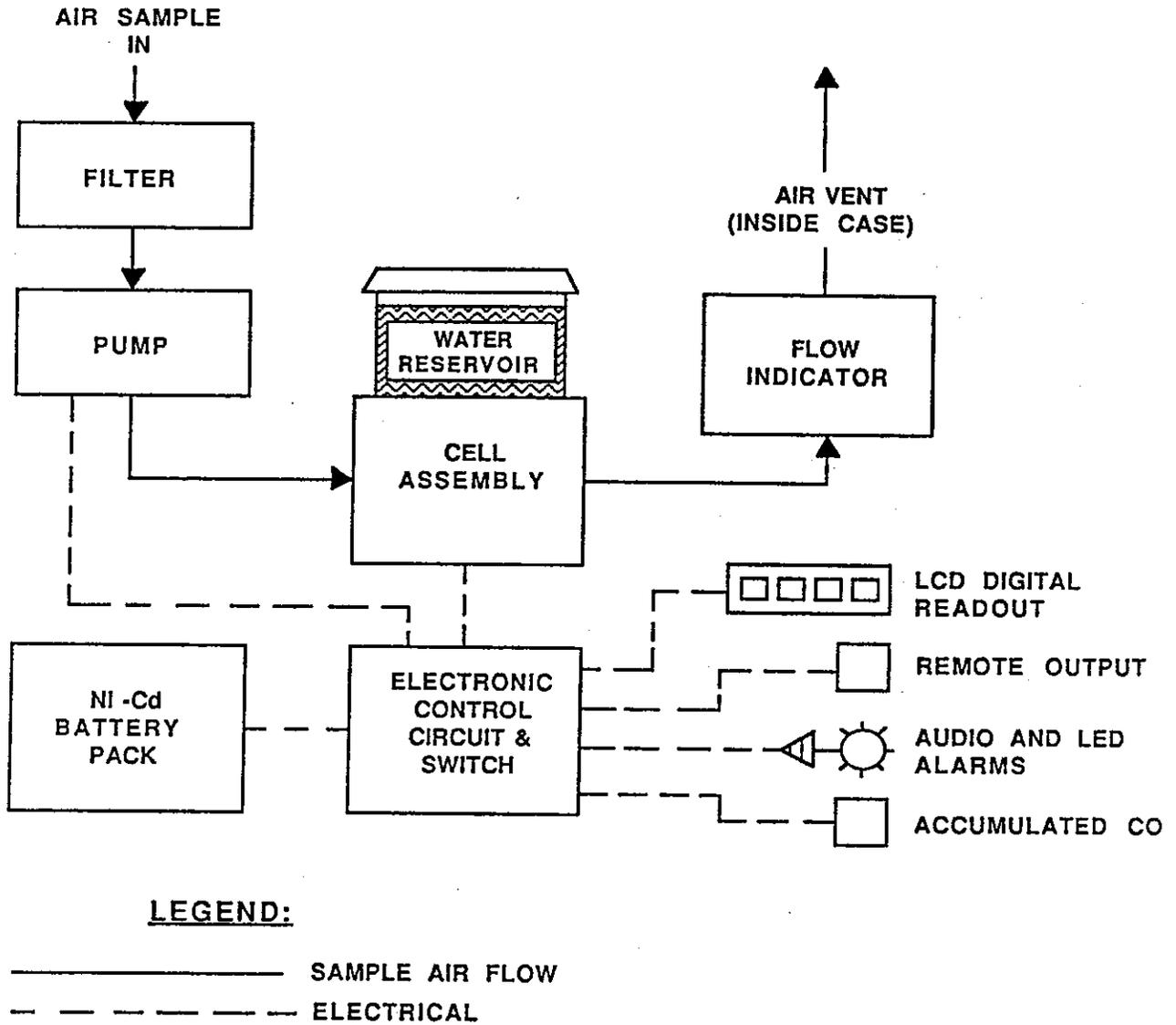


Figure 2. CO Monitor Functional Schematic

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 CO₂. 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: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$ (at the anode). The hydrogen ions and electrons combine to form the following reaction: $1/2 \text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}$ (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 : $\text{CO} + 1/2 \text{O}_2 \rightarrow \text{CO}_2$. 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 polymethylmethacrylate 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 CO₂ 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, Plumsteadville, 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).

8.5 Two 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 not 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-SIO 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 consistency 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)

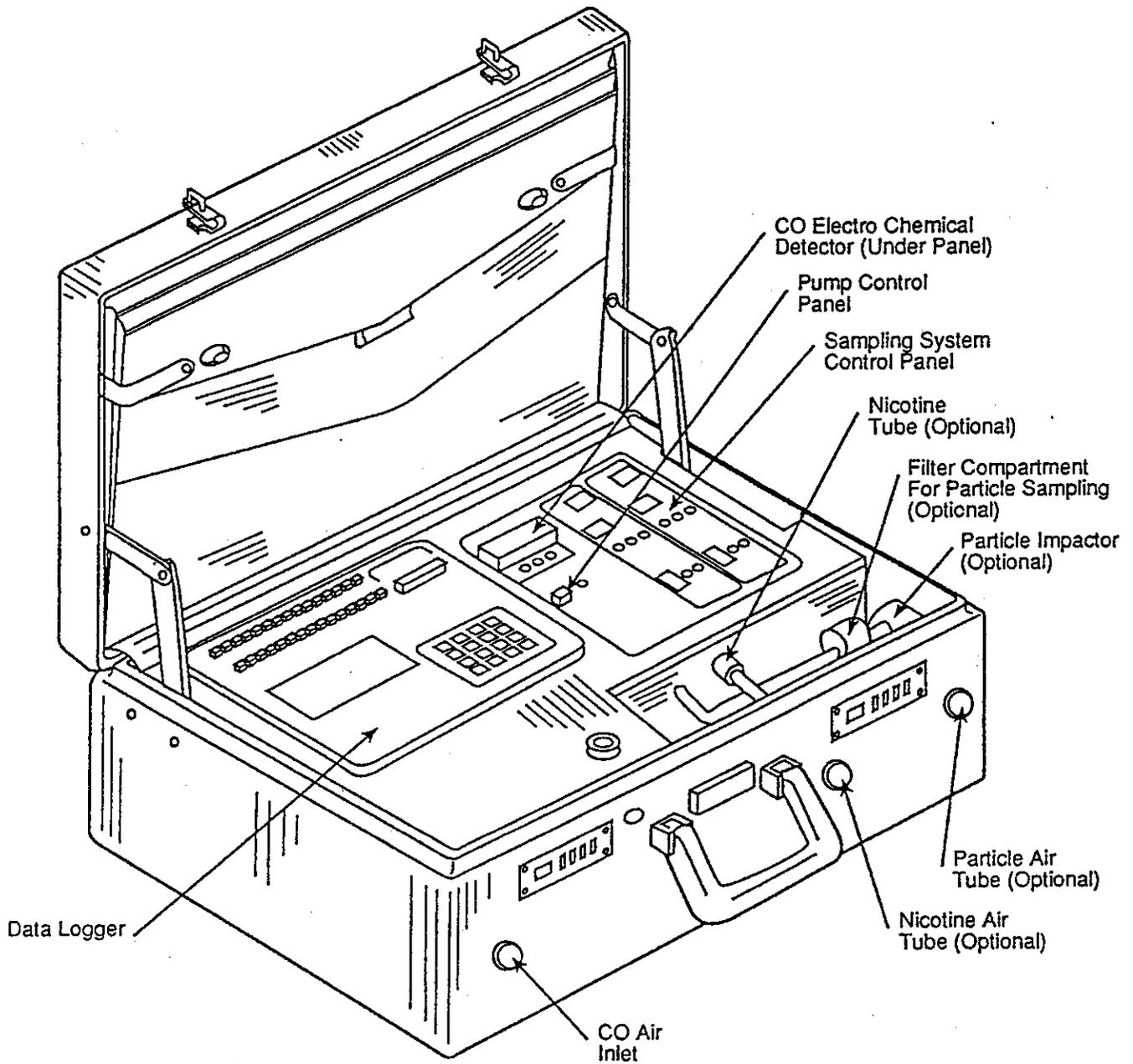


Figure A-1. Portable Air Sampling System

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

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, °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