EPA/600/4-90/010
April 1990

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

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Contract No. 68-04-4467 (W.A. #13)
and
Contract No. 68-02-4398 (W.A. #9 and #32)

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TECHNICAL REPORT DATA *(Please read Instructions on the reverse before completing)*	
1. REPORT NO. EPA/600/4-90/010	3. RECIPIENT'S ACCESSION NO. PB 90 200288/AS
4. TITLE AND SUBTITLE Compendium of Methods for the Determination of Air Pollutants in Indoor Air	5. REPORT DATE April 1990 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) W. T. Winberry, Jr., Linda Forehand, N. T. Murphy, Angela Ceroli, Barbara Phinney, and Ann Evans	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Engineering-Science One Harrison Park, Suite 305 401 Harrison Oaks Boulevard Cary, NC 27513	10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-04-4467 (WA 13) 68-02-4398 (WA 9, 32)
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Research and Exposure Assessment Laboratory, Office of Research and Development U. S. Environmental Protection Agency Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

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

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Indoor air quality Indoor air pollutants Monitoring methods		
18. DISTRIBUTION STATEMENT Release unlimited	19. SECURITY CLASS *(This Report)* Unclassified 20. SECURITY CLASS *(This page)* Unclassified	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

Disclaimer

The information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency under contract numbers 68-04-4467 and 68-02-4398. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Acknowledgement

This project is supported through the USEPA Indoor Air Program at Research Triangle Park, NC. Comments or recommendations for improvements may be directed to Frank McElroy (MD-77), Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC 27711.

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FOREWORD

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

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

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

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INTRODUCTION

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

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

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

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

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

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

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

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

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

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

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

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

Table 1. List of Methods in the Compendium

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

Table 2. List of Compounds of Primary Interest

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

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

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

Pesticides
(Method IP-8)

Organochlorine

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

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

Carbamates
Propuxur
Carbofuran
Bendicarb
Mexacarbate
Carbaryl

Triazine
Simazine
Atrazine
Propazine

Organochlorine

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

Ureas
Monuron
Diuron
Liuron
Terbuthiuron
Fluometuron
Chlortoluron

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

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

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

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

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

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

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

Nicotine (particle and gaseous)

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

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

Chapter IP-1

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN INDOOR AIR

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

1. Scope

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

2. Significance

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

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

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

Method IP-1A

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

Method IP-1A

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

1. Scope

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

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

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

2. Applicable Documents

2.1 ASTM Standards

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

2.2 Other Documents

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

3. Summary of Method

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

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

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

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

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

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

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

Non-Specific Multidetector Analytical System

Advantages

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

Disadvantages

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

Specific Detector Analytical System

GC-MS-SIM

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

GC-MS-SCAN

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

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

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

4. Significance

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

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

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

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

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

5. Definitions

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

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

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

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

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

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

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

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

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

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

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

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

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

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

6. Interferences and Limitations

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

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

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

7. Apparatus

7.1 Sample Collection

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

7.2 Sample Analysis

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

7.2.3.9 Chromatographic column - to provide compound separation such as shown in Table 7. (Hewlett Packard, Rt. 41, Avondale, PA 19311, OV-I capillary column, 0.32 mm x 50 m with 0.88 μm crosslinked methyl silicone coating, or equivalent).
Note: Other columns (e.g., DB-624) can be used as long as the system meets user needs. The wider Megabore® column (i.e., 0.53 mm I.D.) is less susceptible to plugging as a result of trapped water, thus eliminating the need for a Nafion® dryer in the analytical system. The Megabore® column has sample capacity approaching that of a packed column, while retaining much of the peak resolution traits of narrower columns (i.e., 0.32 mm I.D.).

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

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

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

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

7.3 Canister Cleaning System (see Figure 7)

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

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

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

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

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

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

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

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

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

7.4 Calibration System and Manifold (See Figure 8)

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

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

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

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

8. Reagents and Materials

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

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

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

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

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

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

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

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

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

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

9. Sampling System

9.1 System Description

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

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

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

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

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

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

9.1.3 All Samplers

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

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

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

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

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

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

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

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

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

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

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

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

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

9.2 Sampling Procedure

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

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

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

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

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

Note: The following discussion is related to Figure 2.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

10.1 System Description

10.1.1 GC-MS-SCAN System

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

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

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

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

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

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

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

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

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

10.1.2 GC-MS-SIM System

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

10.1.2.2 SIM analysis is based on a combination of retention times and relative abundances of selected ions (see Table 2). These qualifiers are stored on the hard disk of the GC-MS computer and are applied for identification of each chromatographic peak. The retention time qualifier is determined to be ± 0.10 minute of the library retention time of the compound. The acceptance level for relative abundance is determined to be ± 15% of the expected abundance, except for vinyl chloride and methylene chloride, which is determined to be ± 25%. Three ions are measured for most of the forty compounds. When compound identification is made by the computer, any peak that fails any of the qualifying tests is flagged (e.g., with an *). All the data should be manually examined by the analyst to determine the reason for the flag and whether the compound should be

reported as found. While this adds some subjective judgment to the analysis, computer-generated identification problems can be clarified by an experienced operator. Manual inspection of the quantitative results should also be performed to verify concentrations outside the expected range. A typical chromatogram of VOCs determined by GC-MS-SIM mode is illustrated in Figure 11(b).

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

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

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

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

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

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

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

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

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

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

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

10.2 GC-MS-SCAN-SIM System Performance Criteria

10.2.1 GC-MS System Operation

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

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

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

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

10.2.2 Daily GC-MS Tuning (see Figure 13)

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

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

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

10.2.2.3 The GC-MS tuning standard could also be used to assess GC column performance (chromatographic check) and as an internal standard. Obtain a background correction mass spectra of 4-bromofluorobenzene and check that all key ions criteria are met. If the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved.

10.2.2.4 The performance criteria must be achieved before any samples, blanks or standards are analyzed. If any key ion abundance observed for the daily 4-bromofluorobenzene mass tuning check differs by more than 10% absolute abundance from that observed during the previous daily tuning, the instrument must be retuned or the sample and/or calibration gases reanalyzed until the above condition is met.

10.2.3 GC-MS Calibration (see Figure 13)

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

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

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

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

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

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

10.3.1 Humid Zero Air Certification

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

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

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

10.3.2 GC Retention Time Windows Determination (see Table 7)

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

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

10.3.2.3 Make three injections of the standard containing all compounds for retention time window determination.

Note: The retention time window must be established for each analyte every 72 hours during continuous operation.

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

10.3.2.5 The laboratory must calculate retention time windows for each standard (see Table 7) on each GC column, whenever a new GC column is installed or when major components of the GC are changed. The data must be noted and retained in a notebook by the laboratory as part of the user SOP and as a quality assurance check of the analytical system.

10.3.3 GC Calibration

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

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

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

10.3.4 GC-FID-ECD-PID System Performance Criteria

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

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

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

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

10.4 Analytical Procedures

10.4.1 Canister Receipt

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

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

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

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

$$DF = Y_a/X_a$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

10.4.4.6 The electronic integrator is started.

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

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

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

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

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

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

11. Cleaning and Certification Program

11.1 Canister Cleaning and Certification

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

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

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

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

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

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

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

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

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

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

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

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

11.2 Sampling System Cleaning and Certification

11.2.1 Cleaning Sampling System Components

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

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

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

11.2.2 Humid Zero Air Certification

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

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

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

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

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

11.2.3 Sampler System Certification with Humid Calibration Gas Standards

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

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

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

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

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

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

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

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

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

12. Performance Criteria and Quality Assurance

12.1 Standard Operating Procedures (SOPs)

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

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

12.2 Method Relative Accuracy and Linearity

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

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

where:

Y = Concentration of the targeted compound recovered from sampler

X = Concentration of VOC targeted compound in the NBS-SRM or EPA-CRM audit cylinders

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

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

12.3 Method Modification

12.3.1 Sampling

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

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

12.3.2 Analysis

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

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

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

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

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

12.4 Method Safety

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

12.5 Quality Assurance (See Figure 21)

12.5.1 Sampling System

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

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

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

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

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

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

12.5.2 GC-MS-SCAN-SIM System Performance Criteria

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

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

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

12.5.3 GC-Multidetector System Performance Criteria

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

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

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

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

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

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

13. Acknowledgements

The determination of volatile and some semi-volatile organic compounds in indoor air is a complex task, primarily because of the wide variety of compounds of interest and the lack of standardized sampling and analytical procedures. While there are numerous procedures for sampling and analyzing VOCs/SVOCs in indoor air, this method draws upon the best aspects of each one and combines them into a standardized methodology. To that end, the following individuals contributed to the research, documentation and peer review of this manuscript:

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Table 1. Volatile Organic Compound Data Sheet

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

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

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

Table 2. (cont.)

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

Table 2. (cont.)

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

Table 3. General GC and MS Operating Conditions

Chromatography	
Column	Hewlett-Packard OV-1 crosslinked methyl silicone (50 m x 0.31-mm I.D., 17 μm film thickness), or equivalent
Carrier Gas	Helium (2.0 cm^3/min at 250°C)
Injection Volume	Constant (1-3 μL)
Injection Mode	Splitless
Temperature Program	
Initial Column Temperature	-50°C
Initial Hold Time	2 min
Program	8°C/min to 150°C
Final Hold Time	15 min
Mass Spectrometer	
Mass Range	18 to 250 amu
Scan Time	1 sec/scan
EI Condition	70 eV
Mass Scan	Follow manufacturer's instruction for selecting mass selective (MS) detector and selected ion monitoring (SIM) mode
Detector Mode	Multiple ion detection
FID System (Optional)	
Hydrogen Flow	30 cm^3/minute
Carrier Flow	30 cm^3/minute
Burner Air	400 cm^3/minute

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

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

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

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

Table 5. (cont.)

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

Table 6. GC-MS-SIM Calibration Table

*** External Standard . ***

8 Jan 87 10:02 am

Operator: JDF
Sample Info : SYR 1
Misc Info:
Integration File Name : DATA:SYR2A02A.I
Sequence Inde:: 1 Bottle Number : 2

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

Peak Num	Type	Int Type	Ret Time	Signal Description			Compound Name	Area	Amount	
1		1 PP	5.020	Mass	85.00	amu	FREON 12	12893	4011 pptv	
2		1 PP	5.654	Mass	50.00	amu	METHYLCHLORI	4445	2586 pptv	
3		1 BP	6.525	Mass	85.00	amu	FREON 114	7067	1215 pptv	
4		1 PB	6.650	Mass	62.00	amu	VINYLCHLORID	2892	1929 pptv	*
5		1 BP	7.818	Mass	94.00	amu	METHYLBROMID	2401	1729 pptv	
6		1 BB	8.421	Mass	64.00	amu	ETHYLCHLORID	2134	2769 pptv	*
7		1 BV	9.940	Mass	101.00	amu	FREON 11	25069	6460 pptv	
8		1 BP	10.869	Mass	61.00	amu	VINDENECHLOR	5034	1700 pptv	
9		1 BP	11.187	Mass	49.00	amu	DICHLOROMETH	4803	2348 pptv	
10		1 PP	11.225	Mass	41.00	amu	ALLYLCHLORID	761	8247 pptv	*
11		1 BP	11.578	Mass	151.00	amu	3CHL3FLUETHA	5477	1672 pptv	
12		1 BP	12.492	Mass	63.00	amu	1,1DICHLOETH	5052	1738 pptv	#
13		1 VP	13.394	Mass	61.00	amu	c-1,2DICHLET	4761	1970 pptv	
14		1 PH	13.713	Mass	83.00	amu	CHLOROFORM	5327	1678 pptv	
15		1 BP	14.378	Mass	62.00	amu	1,2DICHLETHA	5009	2263 pptv	
16		1 PB	14.594	Mass	97.00	amu	METHCHLOROFO	6656	2334 pptv	
17		1 VP	15.009	Mass	78.00	amu	BENZENE	8352	2167 pptv	
18		1 VP	15.154	Mass	117.00	amu	CARBONTETRAC	5868	1915 pptv	
19		1 BB	15.821	Mass	63.00	amu	1,2DICHLPROP	3283	1799 pptv	+
20		1 BB	16.067	Mass	130.00	amu	TRICHLETHENE	4386	2109 pptv	
21		1 PB	16.941	Mass	75.00	amu	c-1,3DICHLPR	2228	987.3 pptv	
22		1 BP	17.475	Mass	75.00	amu	t-1,3DICHLPR	1626	689.2 pptv	
23		1 BB	17.594	Mass	97.00	amu	1,1,2CHLETHA	2721	1772 pptv	
24		1 BV	17.844	Mass	91.00	amu	TOLUENE	14417	2733 pptv	
25		1 PB	18.463	Mass	107.00	amu	EDB	4070	1365 pptv	+
26		1 PH	18.989	Mass	166.00	amu	TETRACHLETHE	6874	2065 pptv	
27		1 PB	19.705	Mass	112.00	amu	CHLOROBENZEN	5648	1524 pptv	
28		1 BP	20.168	Mass	91.00	amu	ETHYLBENZENE	11084	1842 pptv	
29		1 PB	20.372	Mass	91.00	amu	m,p-XYLENE	17989	3790 pptv	
30		1 BV	20.778	Mass	104.00	amu	STYRENE	3145	1695 pptv	
31		1 BH	20.887	Mass	83.00	amu	TETRACHLETHA	4531	1376 pptv	
32		1 BP	20.892	Mass	91.00	amu	o-XYLENE	9798	2010 pptv	
33		1 VV	22.488	Mass	105.00	amu	4-ETHYLTOLUE	7694	1481 pptv	
34		1 VB	22.609	Mass	105.00	amu	1,3,5METHBEN	6781	1705 pptv	
35		1 BB	23.144	Mass	105.00	amu	1,2,4METHBEN	7892	2095 pptv	
36		1 BV	23.273	Mass	146.00	amu	m-DICHLBENZE	3046	1119 pptv	
37		1 VV	23.279	Mass	91.00	amu	BENZYLCHLORI	3880	1006 pptv	
38		1 VB	23.378	Mass	146.00	amu	p-DICHLBENZE	6090	2164 pptv	
39		1 BP	23.850	Mass	146.00	amu	o-DICHLBENZE	2896	1249 pptv	
40		1 BB	26.673	Mass	180.00	amu	1,2,4CHLBENZ	562	767.1 pptv	
41		1 BB	27.637	Mass	225.00	amu	HEXACHLBUTAD	6309	1789 pptv	

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

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

Table 7. (cont.)

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

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

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

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

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

Table 9. GC-MS-SIM Calibration Table

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

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

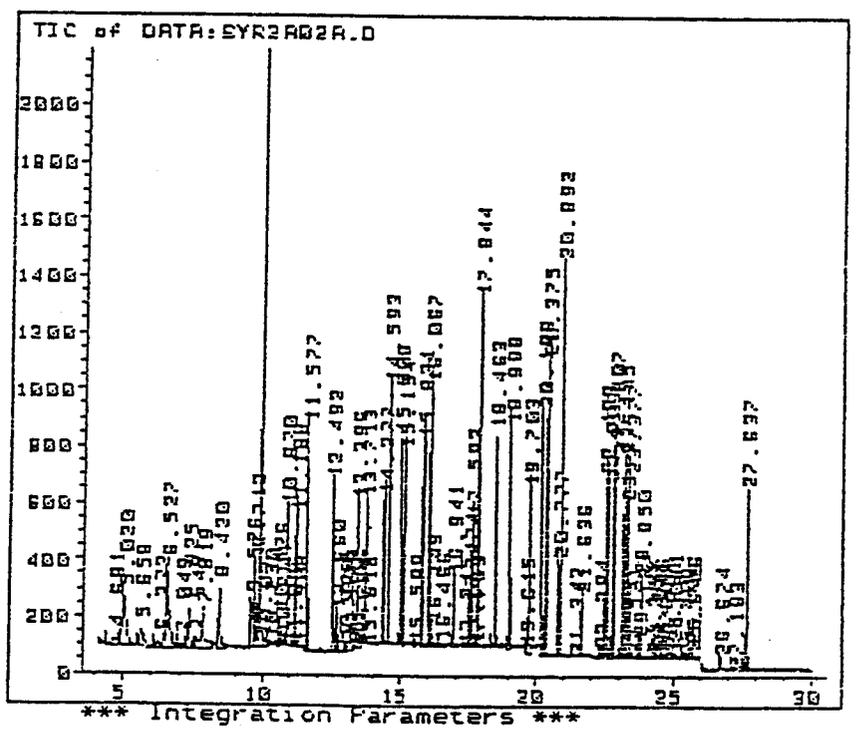
Table 10. Example of Hard-Copy of GC-MS-SIM Analysis

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

Name Info: SYR 1
Misc Info:
Operator : JDP

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

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




```
*** Integration Parameters ***

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

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

Table 10. (cont.)

8 Jan 87 10:02 am

Operator: JDP
Sample Info : SYR 1
Misc Info:
Integration File Name : DATA:SYR2A02A.I
Sequence Index: 1 Bottle Number : 2

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

Peak Num	Type	Int Type	Ret Time	Signal Description		Compound Name	Area	Amount	
1		1 PP	5.020	Mass	85.00 amu	FREON 12	12893	4011 pptv	
2		1 PP	5.654	Mass	50.00 amu	METHYLCHLORI	4445	2586 pptv	
3		1 BP	6.525	Mass	85.00 amu	FREON 114	7067	1215 pptv	
4		1 PB	6.650	Mass	62.00 amu	VINYLCHLORID	2892	1929 pptv	*
5		1 BP	7.818	Mass	94.00 amu	METHYLBROMID	2401	1729 pptv	
6		1 BB	8.421	Mass	64.00 amu	ETHYLCHLORID	2134	2769 pptv	+
7		1 BV	9.940	Mass	101.00 amu	FREON 11	25069	6460 pptv	
8		1 BP	10.869	Mass	61.00 amu	VINDENECHLOR	5034	1700 pptv	
9		1 BP	11.187	Mass	49.00 amu	DICHLOROMETH	4803	2348 pptv	
10		1 PP	11.225	Mass	41.00 amu	ALLYLCHLORID	761	8247 pptv	*
11		1 BP	11.578	Mass	151.00 amu	3CHL3FLUETHA	5477	1672 pptv	
12		1 BP	12.492	Mass	63.00 amu	1,1DICHLOETH	5052	1738 pptv	#
13		1 VP	13.394	Mass	61.00 amu	c-1,2DICHLET	4761	1970 pptv	
14		1 PH	13.713	Mass	83.00 amu	CHLOROFORM	5327	1678 pptv	
15		1 BP	14.378	Mass	62.00 amu	1,2DICHLETHA	5009	2263 pptv	
16		1 PB	14.594	Mass	97.00 amu	METHCHLOROFO	6656	2334 pptv	
17		1 VP	15.009	Mass	78.00 amu	BENZENE	8352	2167 pptv	
18		1 VP	15.154	Mass	117.00 amu	CARBONTETRAC	5888	1915 pptv	
19		1 BB	15.821	Mass	63.00 amu	1,2DICHLPROP	3283	1799 pptv	+
20		1 BB	16.067	Mass	130.00 amu	TRICHLETHENE	4386	2109 pptv	
21		1 PB	16.941	Mass	75.00 amu	c-1,3DICHLPR	2228	987.3 pptv	
22		1 BP	17.475	Mass	75.00 amu	t-1,3DICHLPR	1626	689.2 pptv	
23		1 BB	17.594	Mass	97.00 amu	1,1,2CHLETHA	2721	1772 pptv	
24		1 BV	17.844	Mass	91.00 amu	TOLUENE	14417	2733 pptv	
25		1 PB	18.463	Mass	107.00 amu	EDB	4070	1365 pptv	+
26		1 PH	18.989	Mass	166.00 amu	TETRACHLETHE	6674	2065 pptv	
27		1 PB	19.705	Mass	112.00 amu	CHLOROBENZEN	5648	1524 pptv	
28		1 BP	20.168	Mass	91.00 amu	ETHYLBENZENE	11084	1842 pptv	
29		1 PB	20.372	Mass	91.00 amu	m,p-XYLENE	17989	3790 pptv	
30		1 BV	20.778	Mass	104.00 amu	STYRENE	3145	1695 pptv	
31		1 BH	20.887	Mass	83.00 amu	TETRACHLETHA	4531	1376 pptv	
32		1 BP	20.892	Mass	91.00 amu	o-XYLENE	9798	2010 pptv	
33		1 VV	22.488	Mass	105.00 amu	4-ETHYLTOLUE	7694	1481 pptv	
34		1 VB	22.609	Mass	105.00 amu	1,3,5METHBEN	6781	1705 pptv	
35		1 BB	23.144	Mass	105.00 amu	1,2,4METHBEN	7892	2095 pptv	
36		1 BV	23.273	Mass	146.00 amu	m-DICHLBENZE	3046	1119 pptv	
37		1 VV	23.279	Mass	91.00 amu	BENZYLCHLORI	3880	1006 pptv	
38		1 VB	23.378	Mass	146.00 amu	p-DICHLBENZE	6090	2164 pptv	
39		1 BP	23.850	Mass	146.00 amu	o-DICHLBENZE	2896	1249 pptv	
40		1 BB	26.673	Mass	180.00 amu	1,2,4CHLBENZ	562	767.1 pptv	
41		1 BB	27.637	Mass	225.00 amu	HEXACHLBUTAD	6309	1789 pptv	

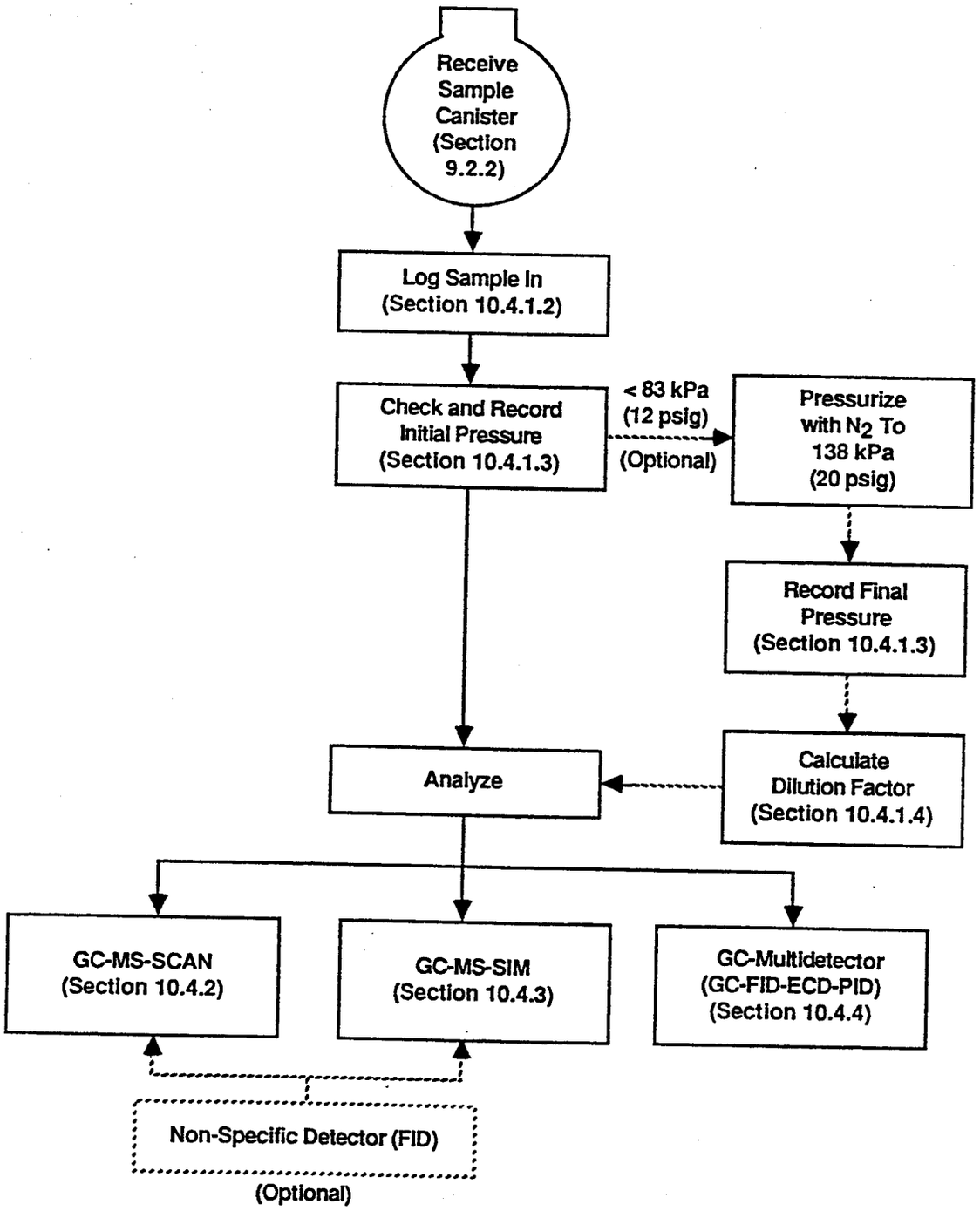


Figure 1. Analytical Systems Available for Canister VOC Identification and Quantitation

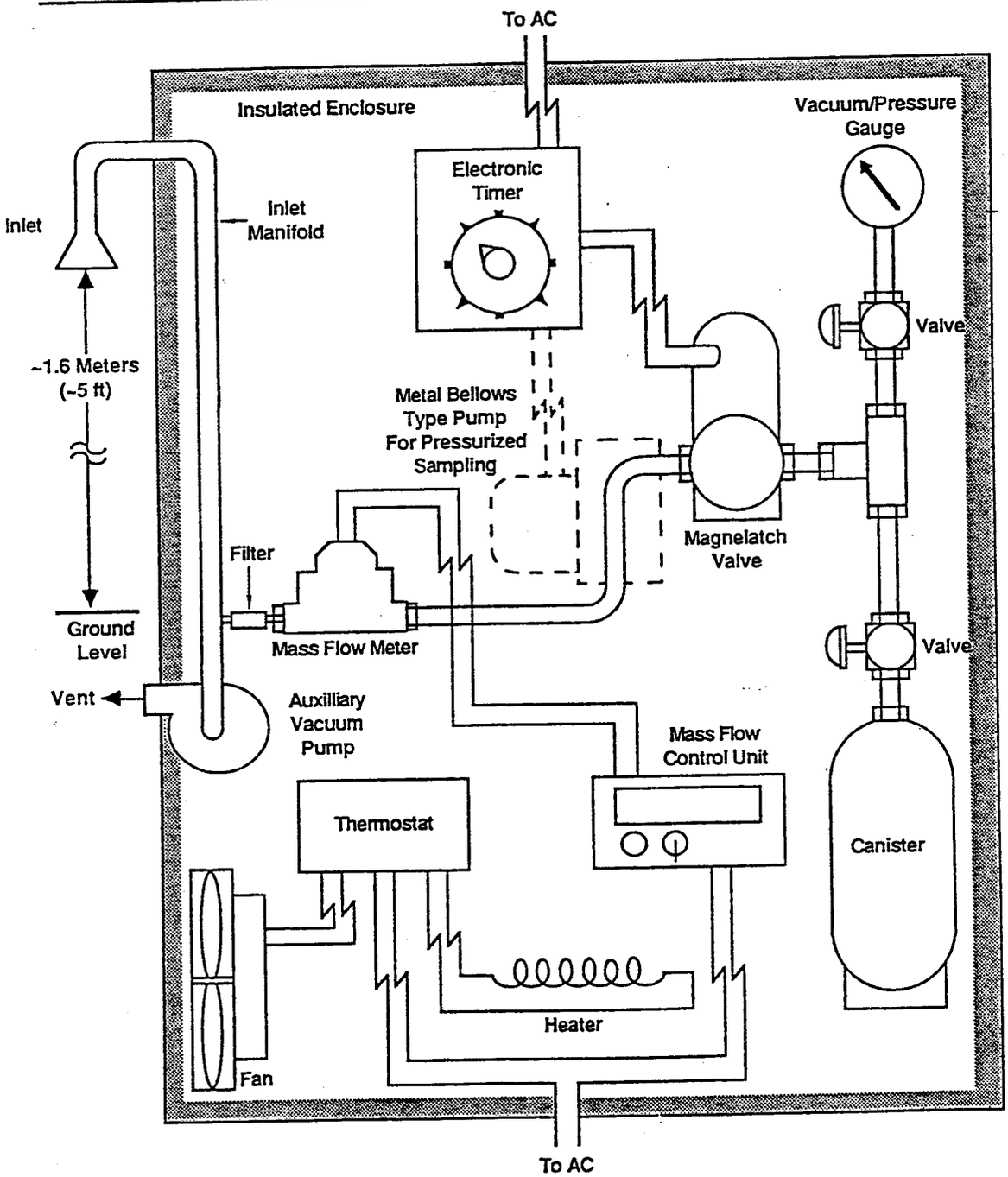


Figure 2. Sampler Configuration for Subatomic Pressure or Pressurized Canister Sampling

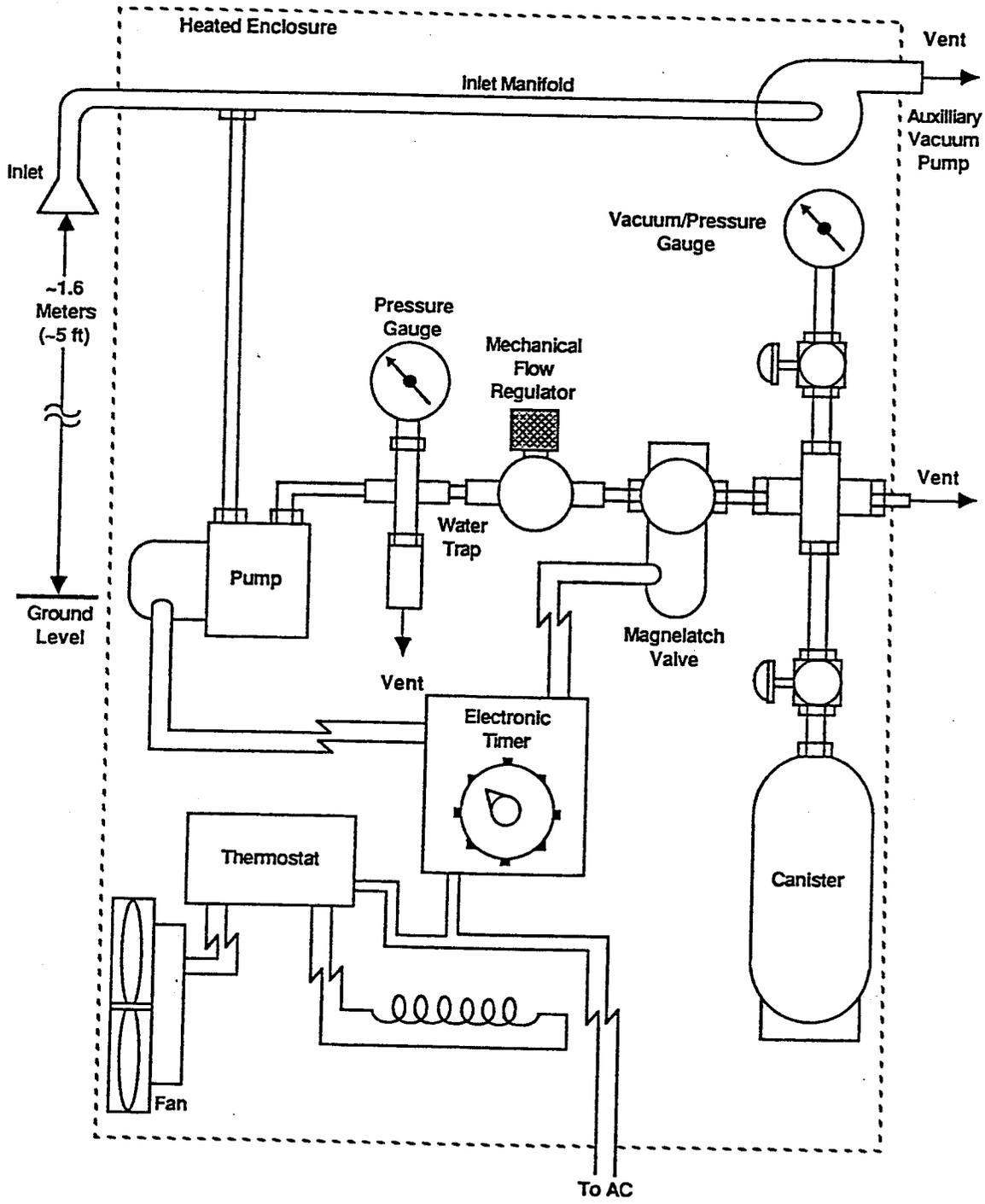


Figure 3. Alternative Sampler Configuration for Pressurized Canister Sampling

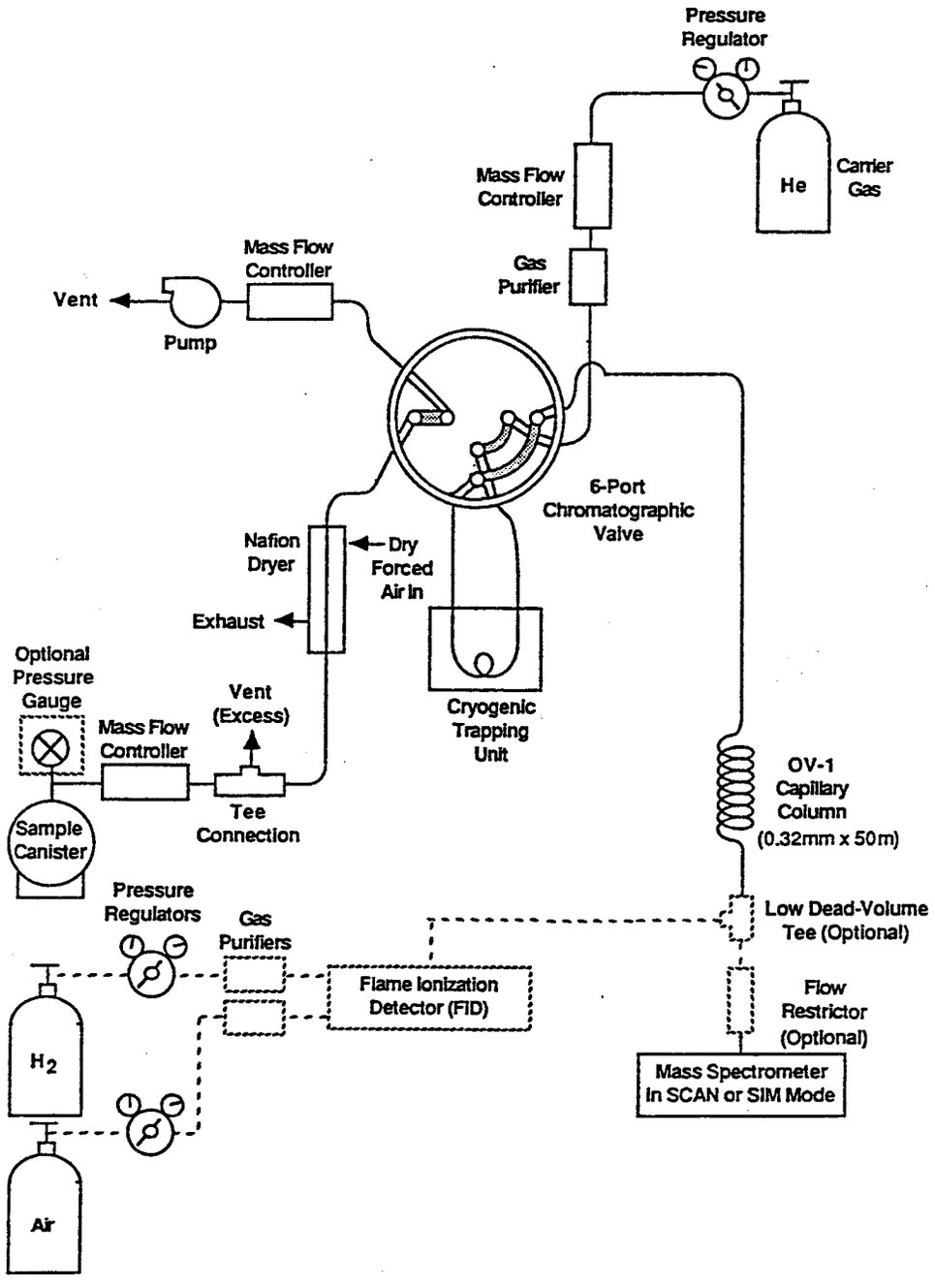


Figure 4. Canister Analysis Utilizing GC-MS-SCAN-SIM Analytical System with Optional Flame Ionization Detector with the 6-Port Chromatographic Valve in the Sample Desorption Mode

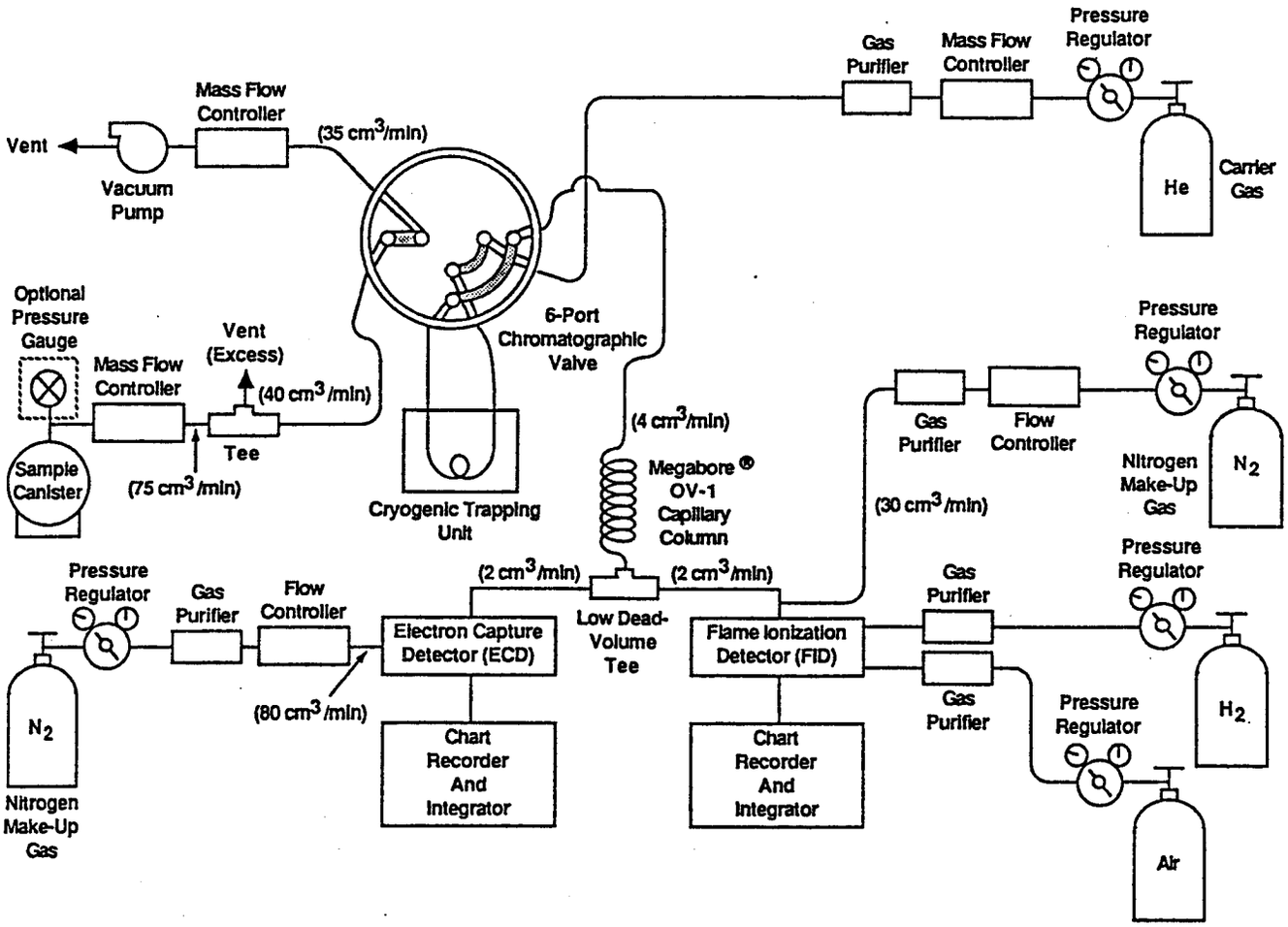


Figure 5. GC-FID-ECD Analytical System with the 6-Port Chromatographic Valve in the Sample Desorption Mode

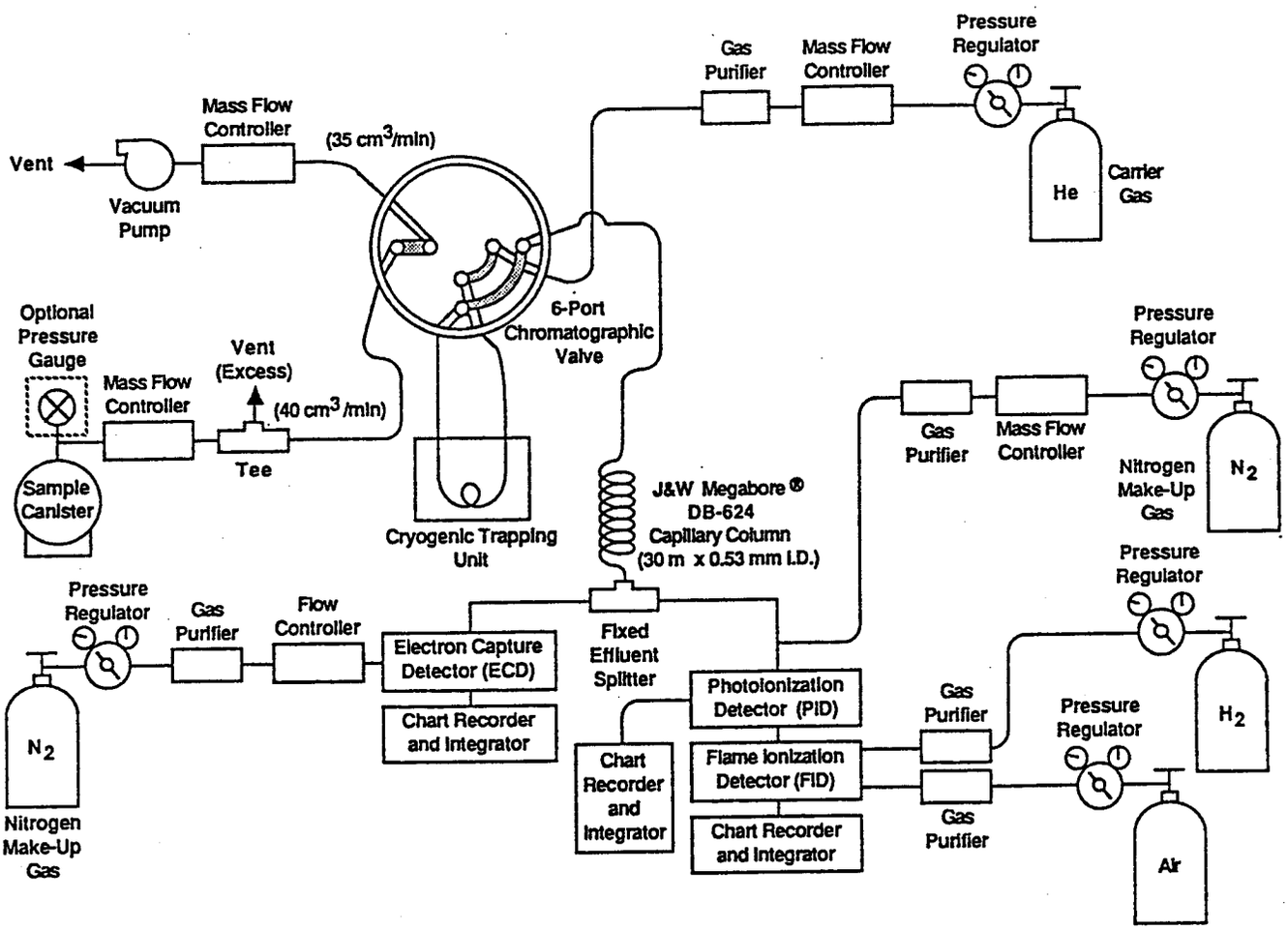


Figure 6. System Configuration Associated with the GC-FID-ECD-PID Analytical System with the 6-Port Chromatographic Valve in the Sample Desorption Mode

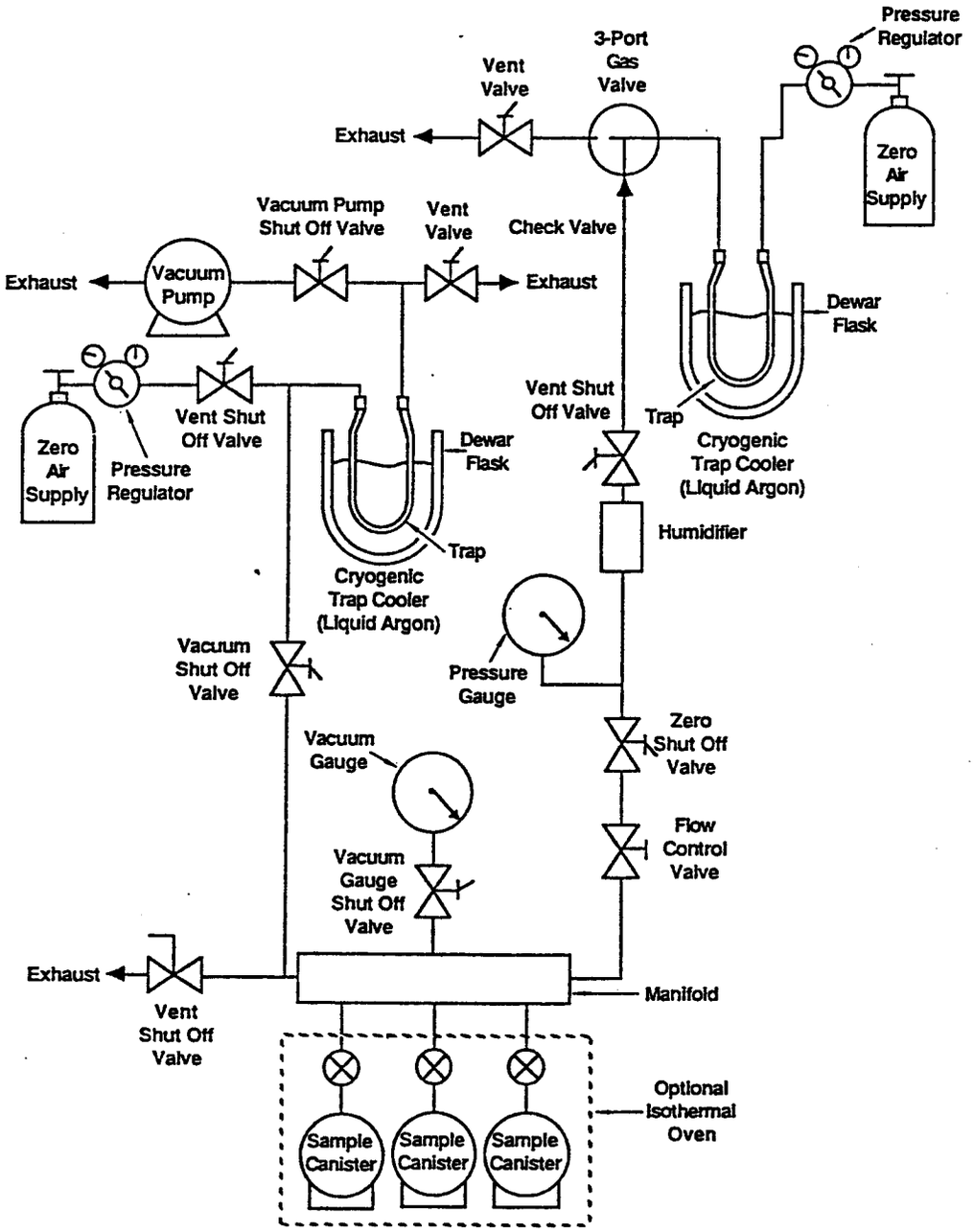


Figure 7. Canister Cleaning System

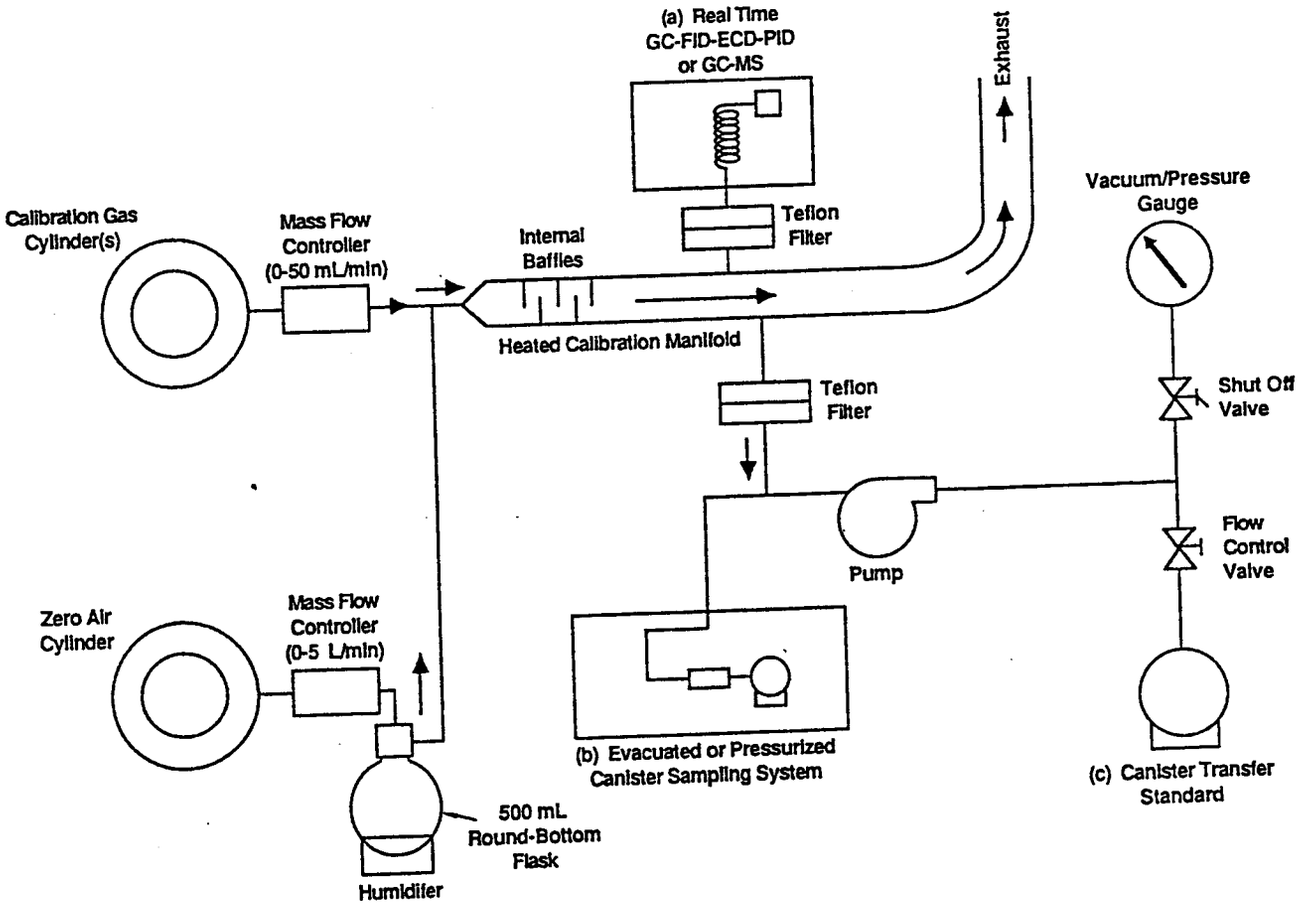
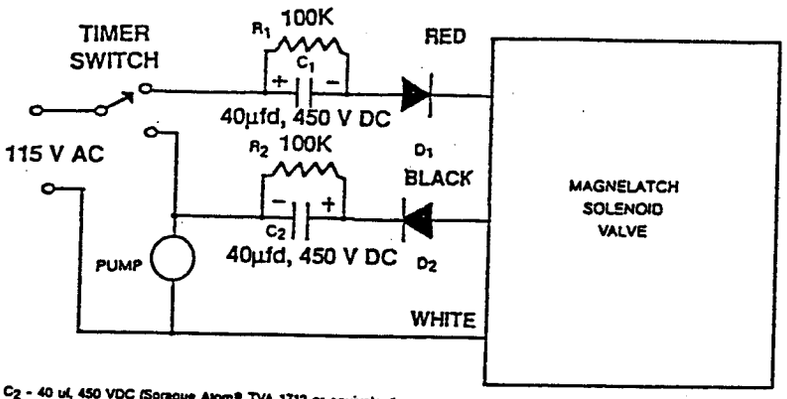


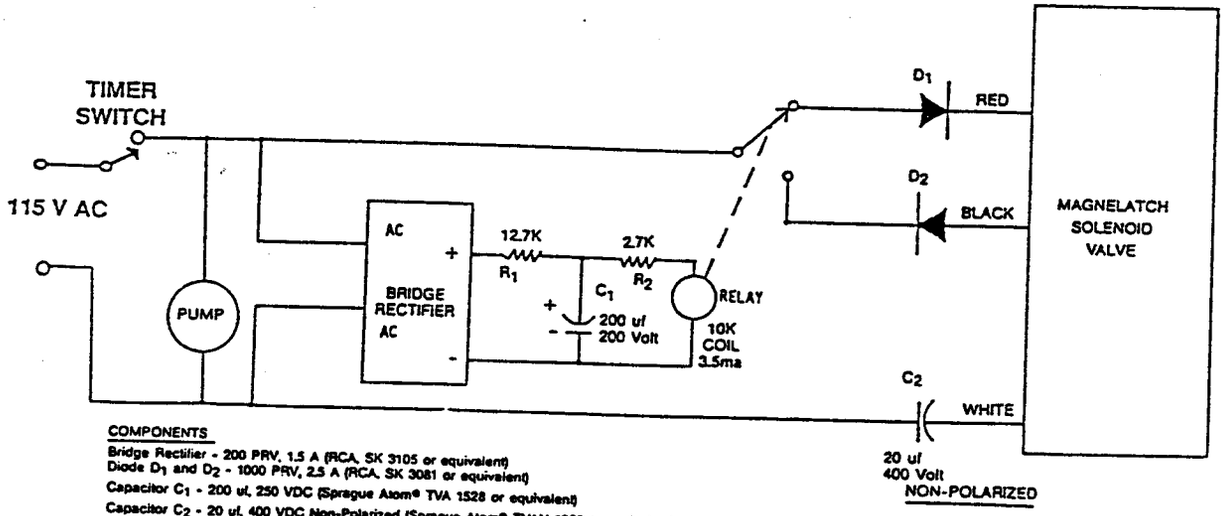
Figure 8. Schematic of Calibration System and Manifold for a) Analytical System Calibration, b) Testing Canister Sampling System and c) Preparing Canister Transfer Standards



COMPONENTS

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

(a). Simple Circuit For Operating Magnelatch Valve



COMPONENTS

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

(b). Improved Circuit Designed To Handle Power Interruptions

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

CANISTER SAMPLING FIELD DATA SHEET

A. GENERAL INFORMATION

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

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

B. SAMPLING INFORMATION

TEMPERATURE

	INTERIOR	AMBIENT	MAXIMUM	MINIMUM
START				
STOP				

PRESSURE

CANISTER PRESSURE	

SAMPLING TIMES

	LOCAL TIME	ELAPSED TIME METER READING
START		
STOP		

FLOW RATES

MANIFOLD FLOW RATE	CANISTER FLOW RATE	FLOW CONTROLLER READOUT

SAMPLING SYSTEM CERTIFICATION DATE: _____
QUARTERLY RECERTIFICATION DATE: _____

C. LABORATORY INFORMATION

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

_____
SIGNATURE/TITLE

* ATTACH DATA SHEETS

Figure 10. Canister Sampling Field Data Sheet

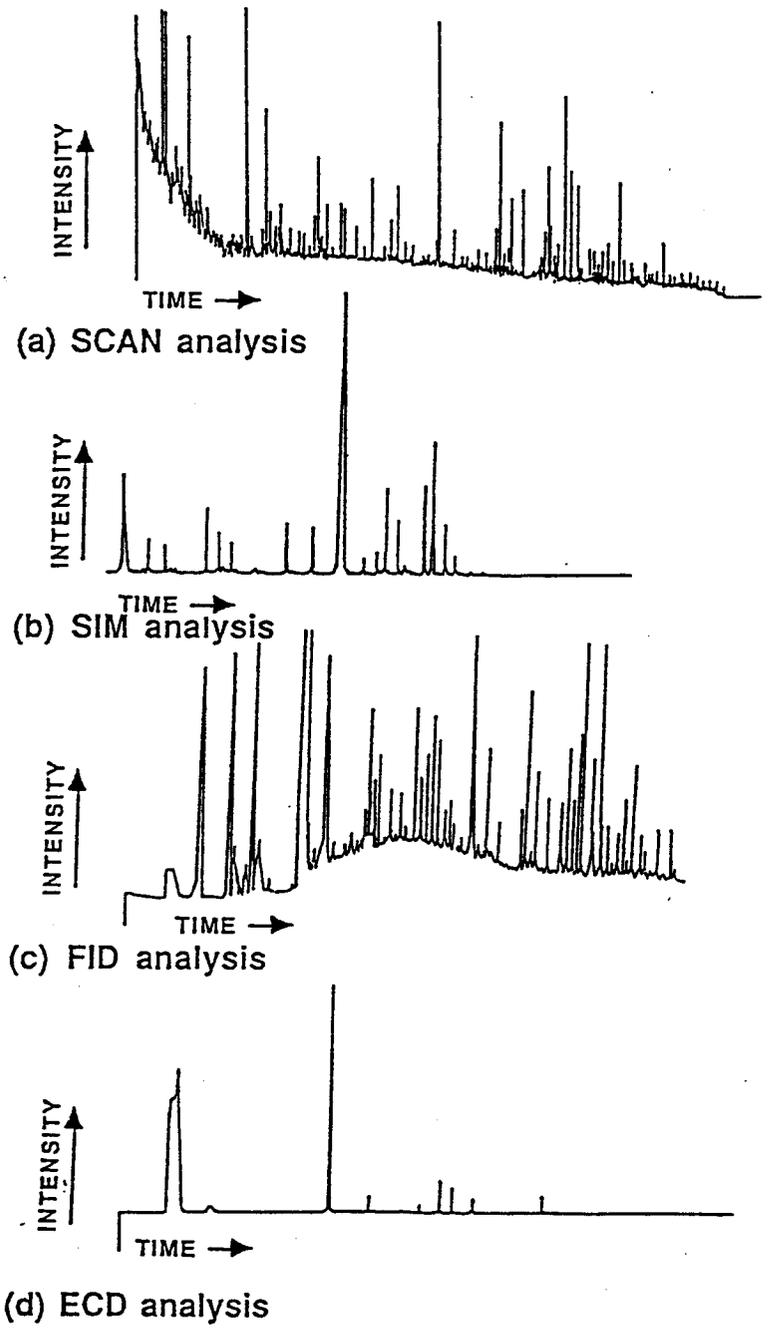


Figure 11. Typical Chromatograms of a VOC Sample Analyzed by GC-MS-SCAN-SIM Mode and GC-Multidetector Mode

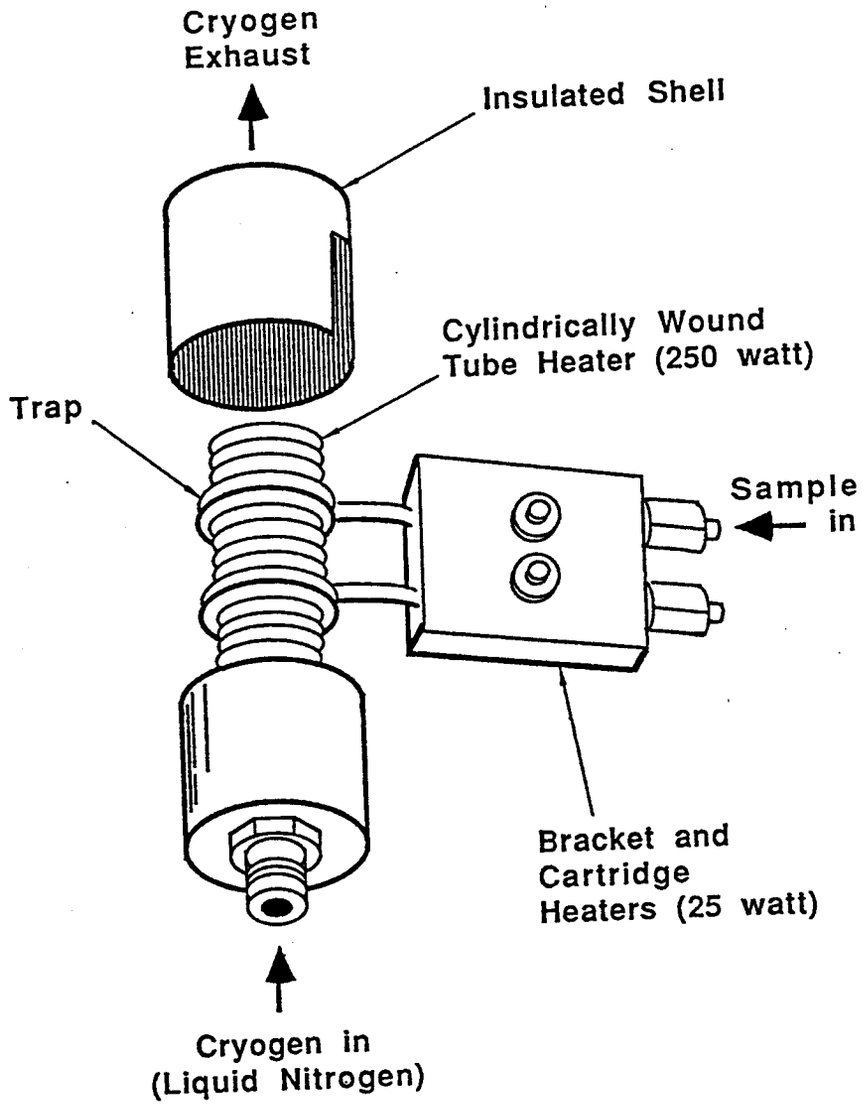


Figure 12. Cryogenic Trapping Unit

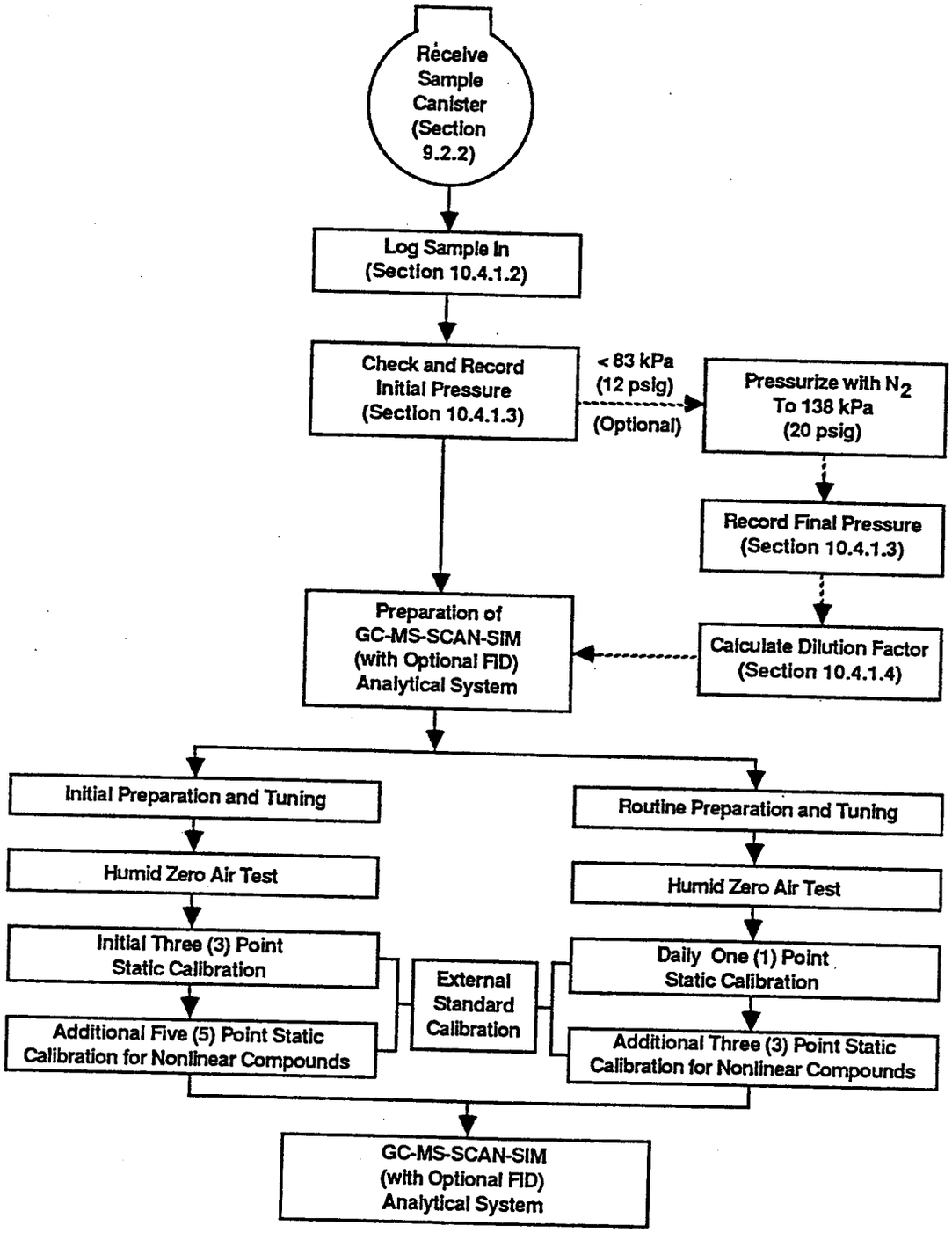


Figure 13. Flowchart of GC-MS-SCAN-SIM Analytical System Preparation (with Optional FID System)

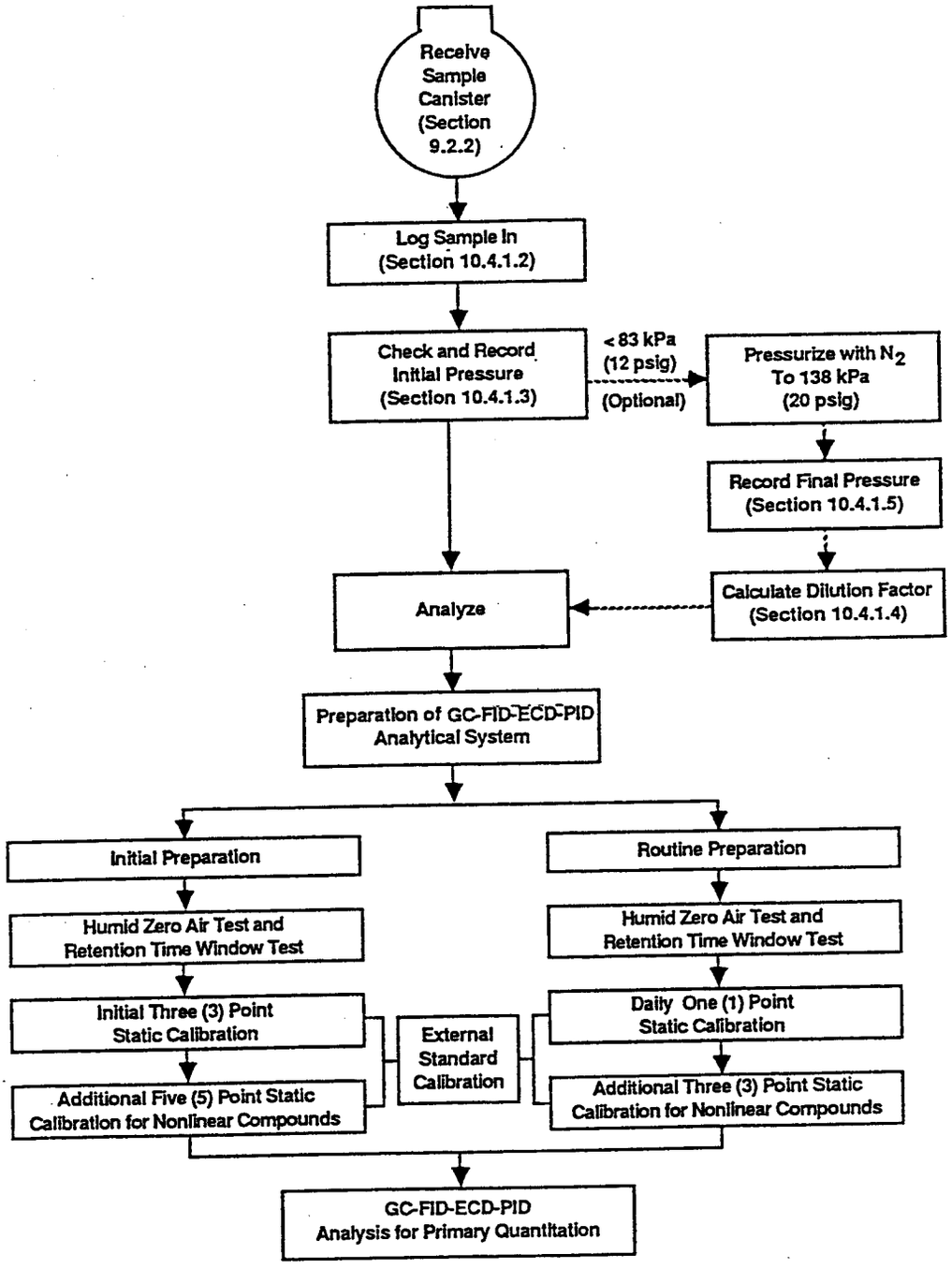


Figure 14. Flowchart of GC-FID-ECD-PID Analytical System Preparation

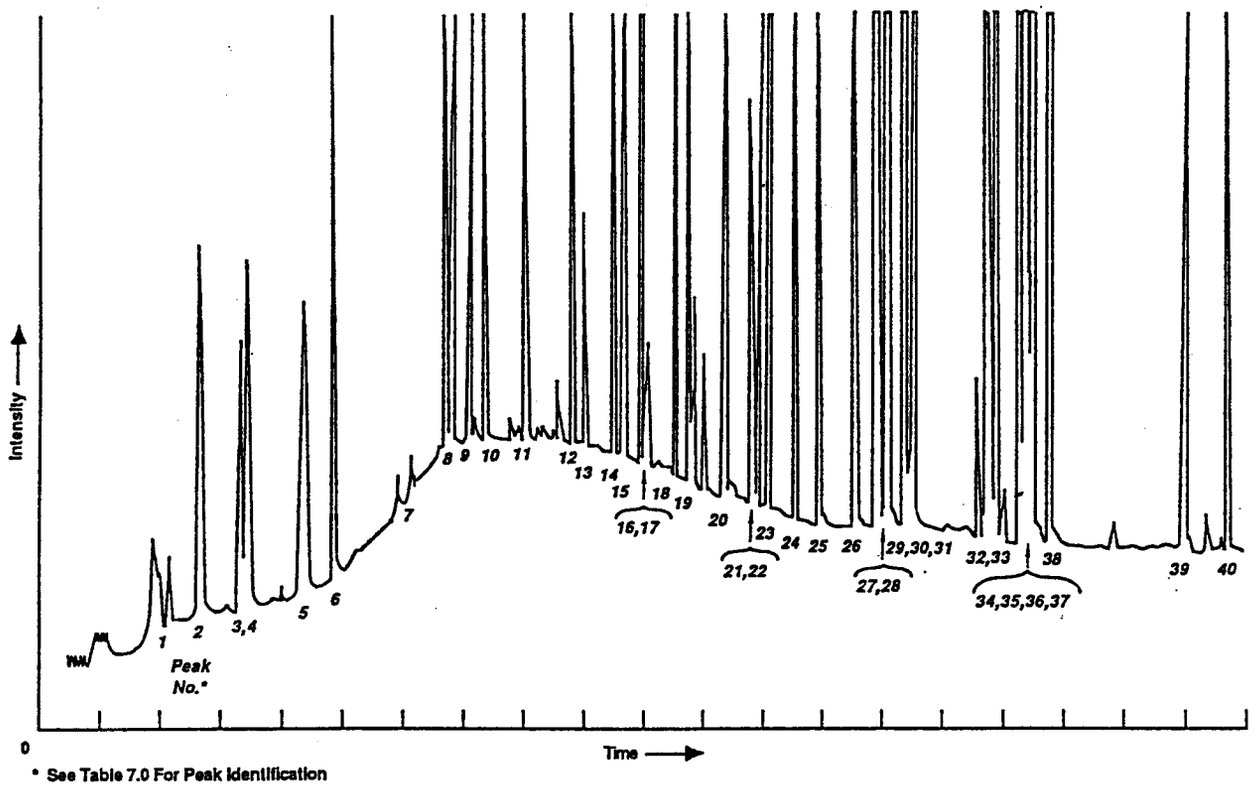
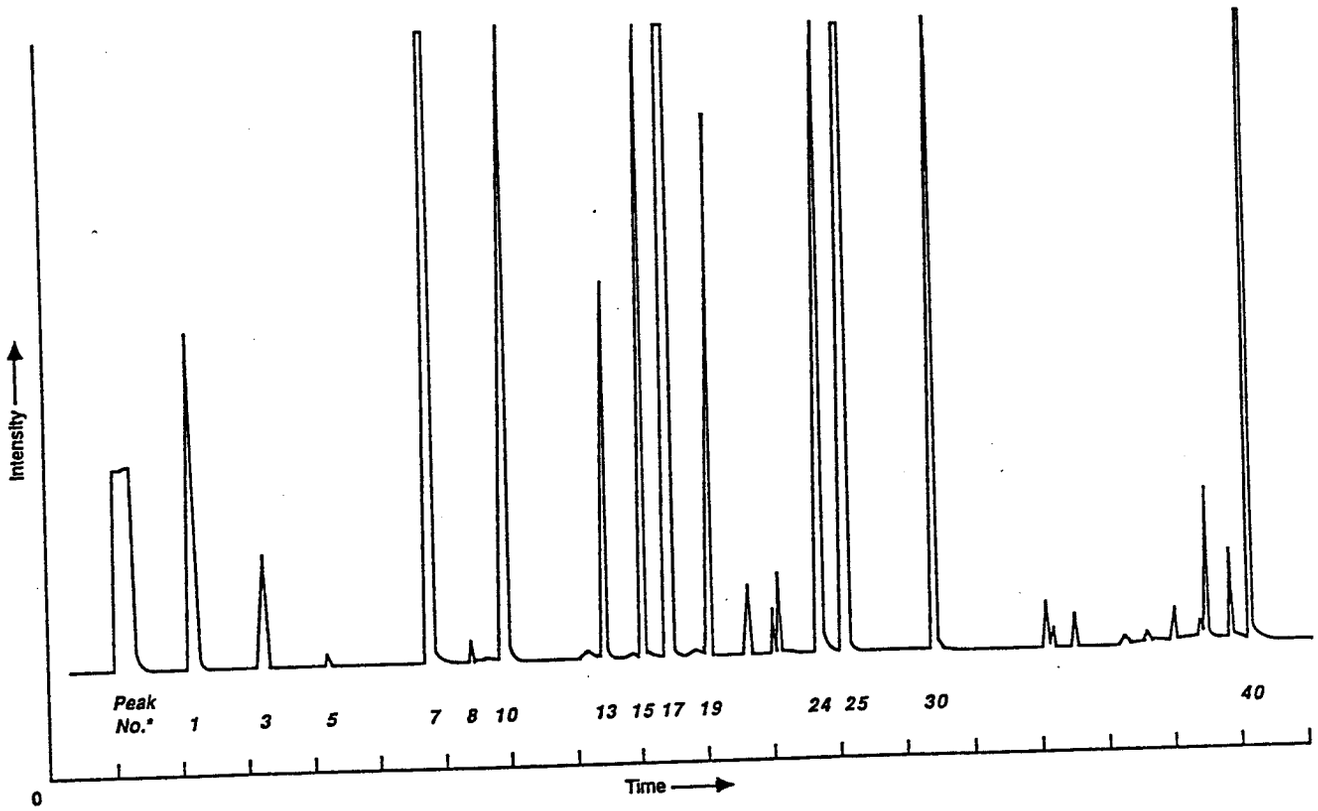
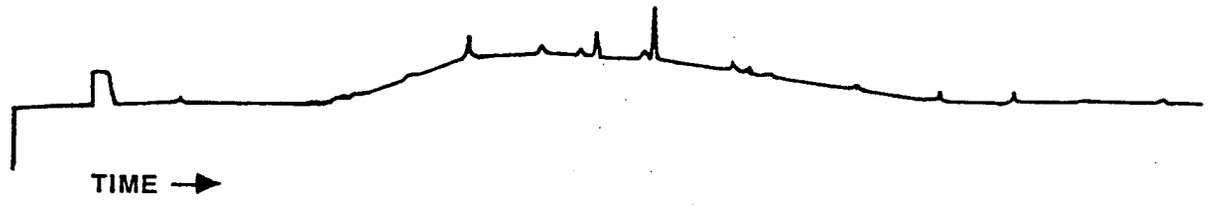


Figure 15. Typical FID Response to Selective VOCs

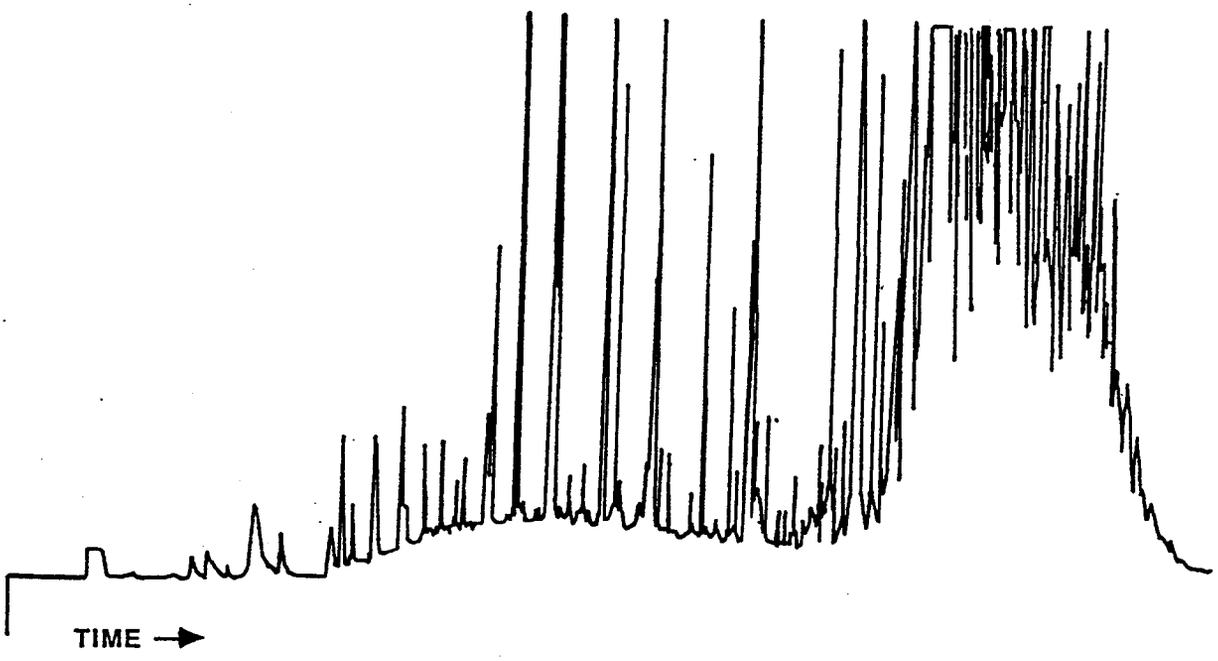


* See Table 7.0 For Peak Identification

Figure 16. Typical ECD Response to Selective VOCs



(a). Certified Sampler



(b). Contaminated Sampler

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

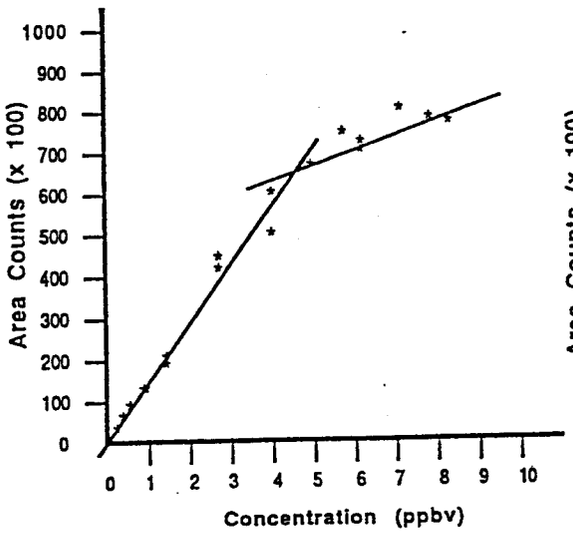


FIGURE 18(a). NONLINEAR RESPONSE OF TETRACHLOROETHYLENE ON THE ECD

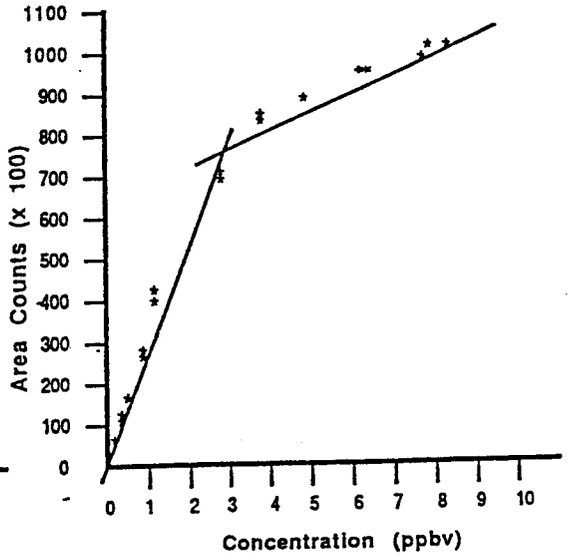


FIGURE 18(b). NONLINEAR RESPONSE OF CARBON TETRACHLORIDE ON THE ECD

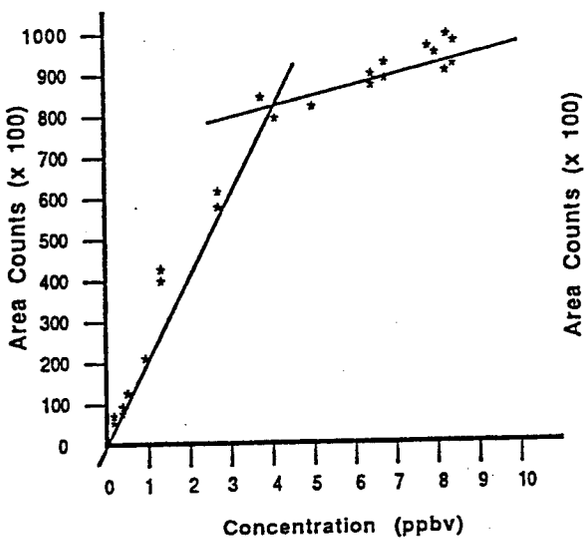


FIGURE 18(c). NONLINEAR RESPONSE OF HEXACHLOROBUTADIENE ON THE ECD

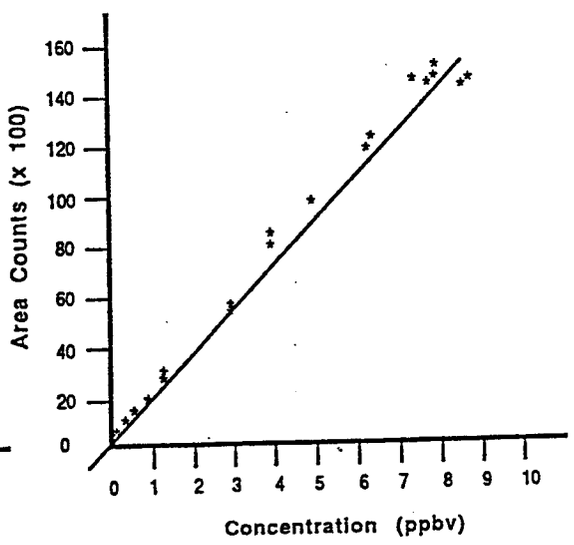


FIGURE 18(d). LINEAR RESPONSE OF CHLOROFORM ON THE ECD

Figure 18. Response of ECD to Various VOCs

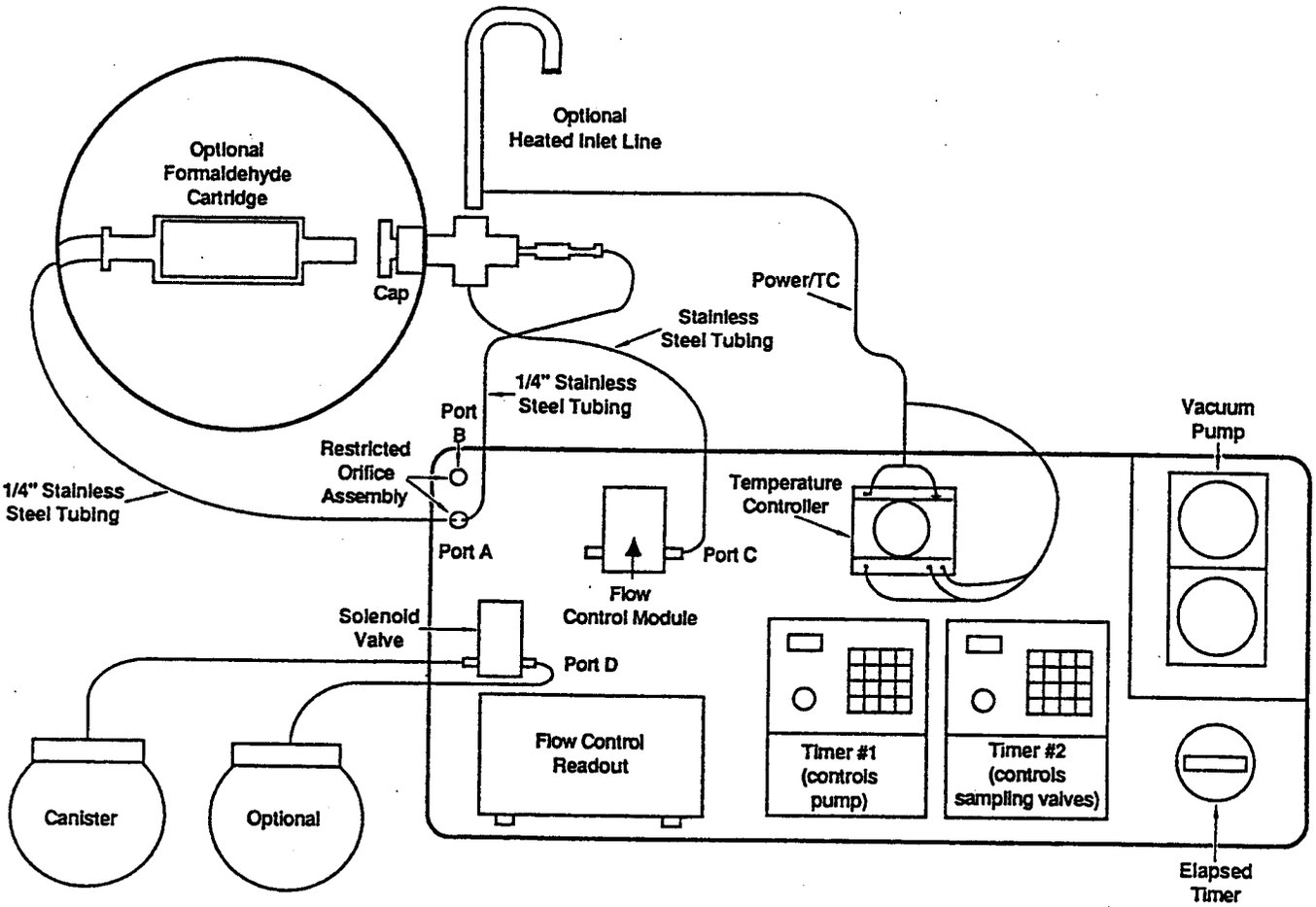


Figure 19. U.S. Environmental Protection Agency UTAP, Schematic of Sample Inlet Connections Sampler

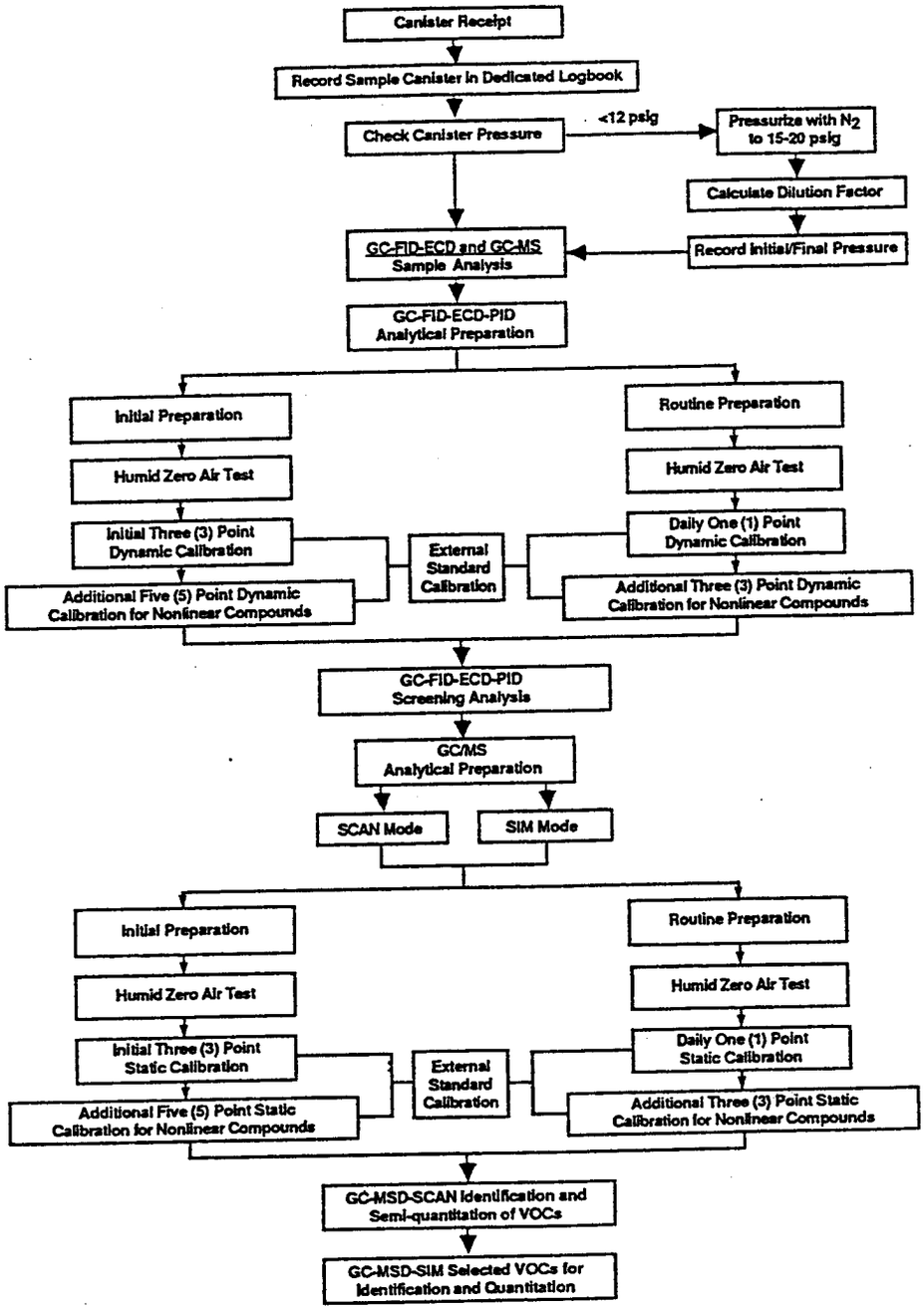


Figure 20. Flowchart of Analytical Systems Preparation

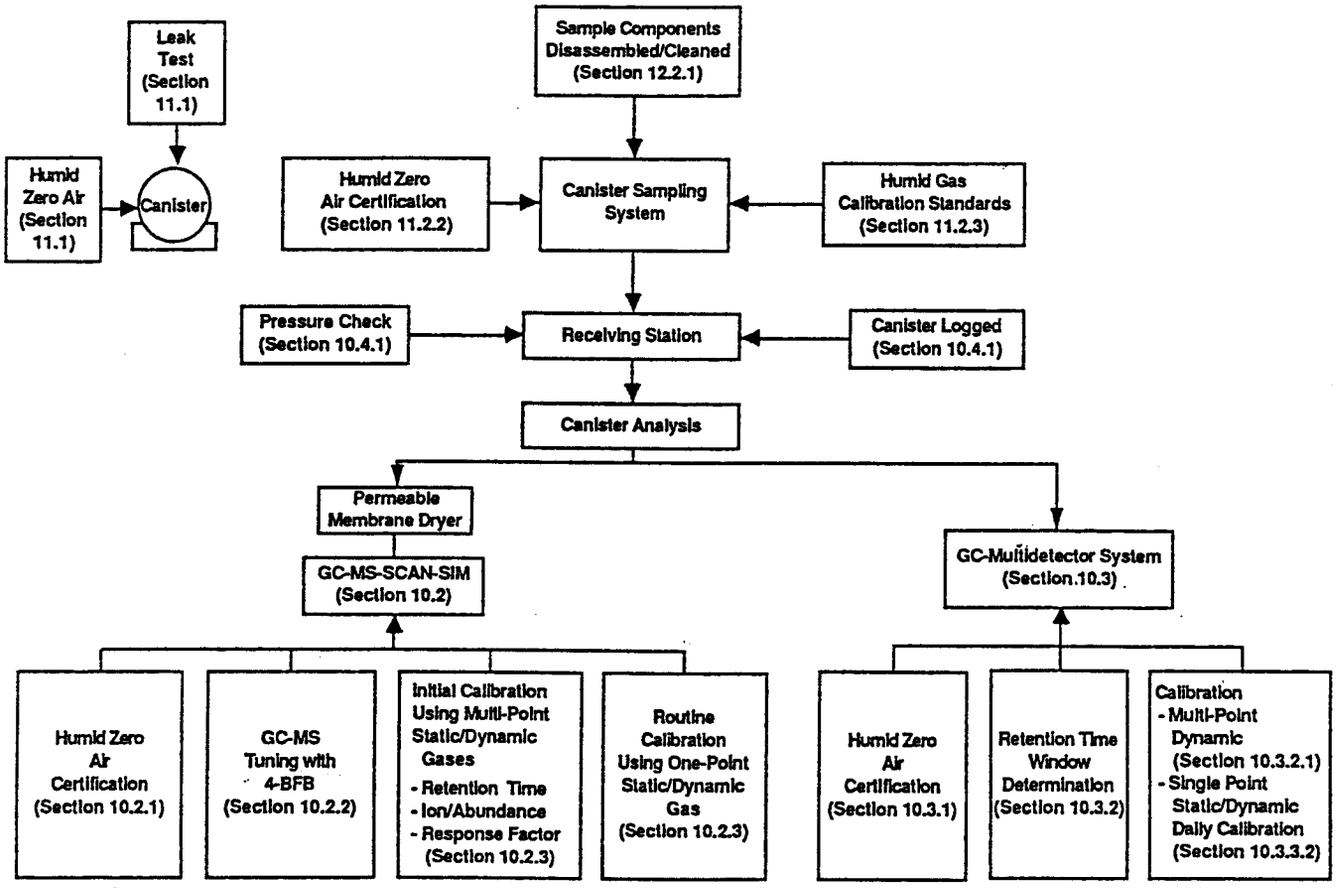


Figure 21. System Quality Assurance/Quality Control (QA/QC) Activities Associated with Various Analytical Systems

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

1. Availability of Audit Cylinders

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

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

2. Audit Cylinder Certification

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

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

3. Audit Cylinder Acquisition

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

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

3.2 The audit cylinders may be acquired by contacting:

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

Table A-1. Available USEPA Performance Audit Cylinders

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

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

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

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

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

1. Scope

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

2. Applicable Documents

2.1 ASTM Standards

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

2.2 Other Documents

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

3. Summary of Method

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

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

4. Significance

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

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

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

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

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

5. Definitions

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

6. Interferences

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

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

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

7. Apparatus

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

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

8. Reagents and Materials

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

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

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

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

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

9. Procedure

9.1 Instrument Setup

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

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

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

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

9.2 Sample Collection

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

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

9.2.3 Indoor air samples are injected onto the 3% SP2100 column. The chromatogram is developed for 15 minutes. Samples which produce particularly complex chromatograms, especially for early eluting components, are reinjected on the 5% SE-30 column.

Note: In no instance should a syringe which has been used for the injection of the calibrant/system performance mixture be used for the acquisition and collection of samples, or vice versa.

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

9.3 Sample Analysis

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

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

10. Performance Criteria and Quality Assurance

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

10.1 Standard Operating Procedures

10.1.1 SOPs should be generated by the users to describe and document the following activities in their laboratory: 1) assembly, calibration, leak check, and operation of the specific portable GC sampling system and equipment used; 2) preparation, storage, shipment, and handling of the portable GC sampler; 3) purchase, certification, and transport of standard reference materials; and 4) all aspects of data recording and processing, including lists of computer hardware and software used.

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

10.2 Quality Assurance Program

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

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

10.2.3 Blanks, Duplicates, and System Performance Samples

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

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

10.3 Method Precision and Accuracy

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

10.4 Range and Limits of Detection

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

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

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

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

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

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

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

Table B-2. Commercially Available Portable VOC Detection Instruments

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

Table B-3. Portable Gas Chromatograph Sampling Data Sheet

DATE: LOCATION: TIME:

CHROMATOGRAPHIC CONDITIONS:

COLUMN 1: COLUMN TYPE:

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

COLUMN 2: COLUMN TYPE:

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

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

SITE PLAN (indicate sampling locations):

_____ _____

DATE SIGNATURE

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

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

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

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

Peak Assignments For Standard Mixture

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

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

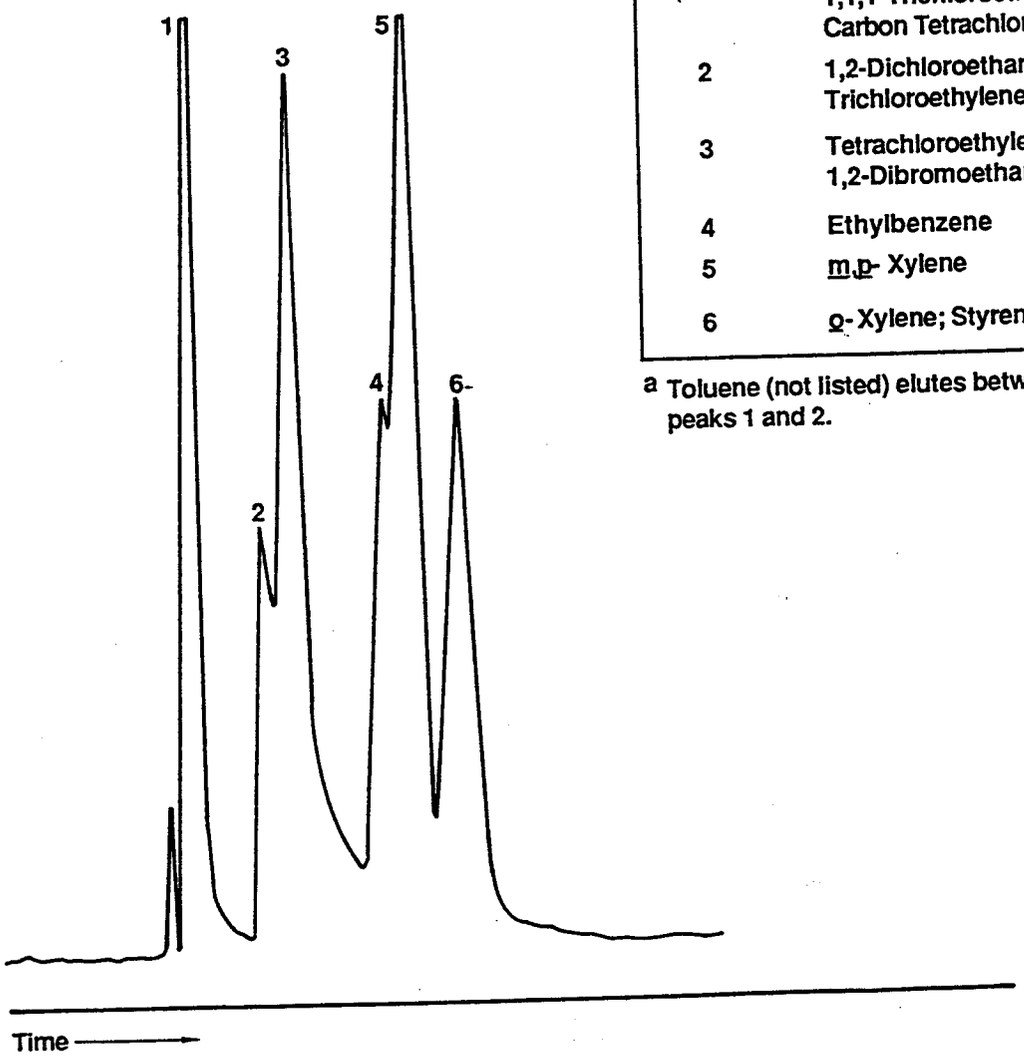


Figure B-1. Typical Chromatogram of VOCs Determined by a Portable GC

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

1. Scope

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

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

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

2. Summary of Method

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

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

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

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

3. Sampler Installation

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

3.2 Electrical Connections (Figure C-1)

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

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

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

3.3 Pneumatic Connections

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

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

4. Sampler Preparation

4.1 Canister

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

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

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

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

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

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

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

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

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

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

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

4.1.11 The canister valve(s) are fully opened.

4.2 Timers

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

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

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

4.2.3 The elapsed time meter is set to 0.

4.3 Sampler Check

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

4.3.1.1 Canister(s) is (are) connected properly and the unused connection is capped if only one canister is used.
4.3.1.2 Canister valve(s) is (are) opened.
4.3.1.3 Both timers are programmed correctly for the scheduled sample period.
4.3.1.4 Both timers are set to "AUTO".
4.3.1.5 Both timers are initially OFF.
4.3.1.6 Both timers are set to the correct current time of day and day number.
4.3.1.7 Elapsed time meter is set to 0.

4.4 Sampler Recovery (Post Sampling)

4.4.1 The valve on the canister is closed.
4.4.2 The canister is disconnected from the sampler, the sample data sheet is completed, and the canister is prepared for shipment to the analytical laboratory.
4.4.3 If two canisters were sampled, step 2.4.2 is repeated for the other canister.

5. Timer Setting

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

5.1.1 Pressing the reset button,
5.1.2 Entering the correct day number and time of day,
5.1.3 Entering the ON and OFF times for the sample period, and
5.1.4 Verifying that the ON and OFF time settings are correct.

5.2 Timer Reset

The timer reset button is pressed, which is recessed in a small hole located just above the LED (light emitting diode) indicator light. A small object that will fit through the hole, such as a pencil, match, or pen is used to press the timer. After reset, the timer display should show |1| |10:00|.
Note: The timers may operate erratically when the batteries are discharged, which happens when the sampler is unplugged or without power for several hours. When the sampler is again powered up, several hours may be required to recharge the batteries. To avoid

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

5.3 Date and Time Entry

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

5.4 ON and OFF Entry

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

5.5 ON and OFF Verification

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

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

Table C-1. Net Flow Controller Setting

DATE	1 CANISTER	2 CANISTERS

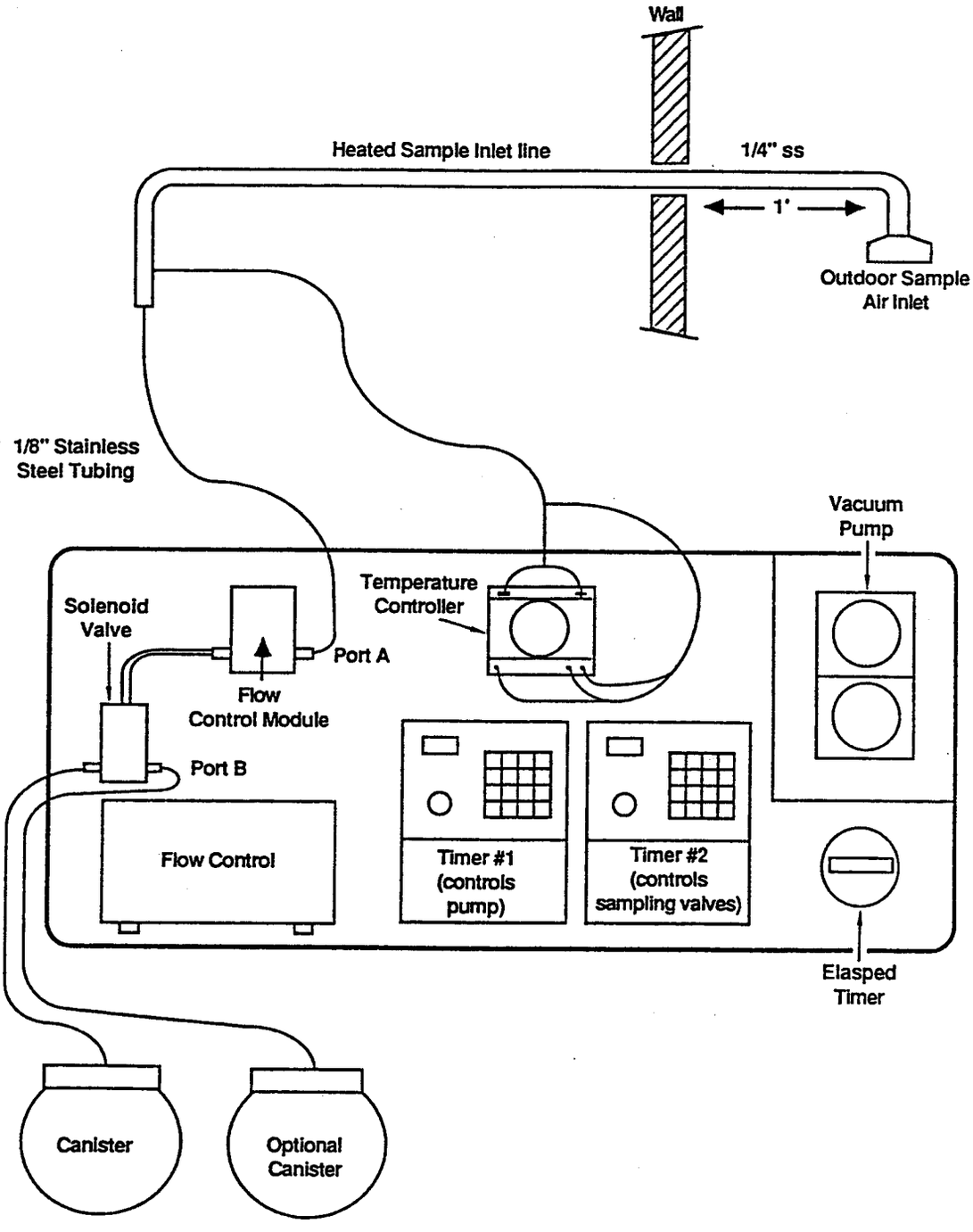


Figure C-1. Alternative 24-Hour Air Toxic Sampling System

Method IP-1B

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

97

Method IP-1B

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

1. Scope

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

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

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

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

2. Referenced Documents

2.1 ASTM Standards

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

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

2.2 Other Documents

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

3. Summary of Protocol

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

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

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

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

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

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

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

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

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

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

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

4. Significance and Use

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

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

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

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

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

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

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

<u>Charcoal</u>

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

Silica Gel

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

XAD-2

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

Tenax®

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

Carbon Molecular Sieve

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

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

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

5. Definitions

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

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

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

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

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

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

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

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

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

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

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

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

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

6. Interferences and Limitations

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

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

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

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

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

7. Range/Limits of Detection and Reproducibility

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

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

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

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

8. Apparatus

8.1 Sample Collection

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

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

8.1.3 Bubble flow meter - 25mL, best source.

8.1.4 Stopwatch/calculator, best source.

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

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

8.1.7 Forceps, best source.

8.1.8 Kimwipes®, best source.

8.1.9 Sampling vests (optional) - user prepared.

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

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

8.1.12 Barometer, best source.

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

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

8.2 Sample Analysis

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

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

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

8.3 Tenax® Cleaning

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

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

8.3.3 Condenser, best source.

8.3.4 Tweezers, best source.

8.3.5 Beaker - 100 mL, best source.

8.3.6 Variable transformer, best source.

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

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

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

8.4 Drying the Tenax®

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

8.4.2 Jar, wide mouth amber, best source.

8.4.3 Crystallizing dish, Kimax®, best source.

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

8.4.5 Aluminum foil, best source.

8.4.6 Funnel, best source.

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

8.5 Sieving of Tenax®

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

8.6 Packing of Tenax® Tubes

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

8.7 Desorption

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

8.8 Calibration of DuPont Pump

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

8.9 Standard Preparation

8.9.1 Static Dilution Bottle

8.9.1.1 Two-liter round-bottom flask containing 30 3-mm diameter glass beads and a 1-in. Teflon®-coated magnetic stirring bar - the flask is modified to accept a screw-on Mininert septum cap, TEKMAR Co., P.O. Box 371856, Cincinnati, OH 45222, 800-543-4461.

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

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

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

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

8.9.1.6 Vacuum syringe cleaner, best source.

8.9.1.7 Magnetic stirrer, best source.

8.9.1.8 Heat gun, best source.

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

8.9.2 Flash Vaporization

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

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

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

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

8.9.2.5 Soap bubble, flow meter, best source.

8.9.2.6 Thermal conductivity detector, best source.

8.9.2.7 Vacuum syringe cleaner, best source.

8.9.3 Permeation Tube System

8.9.3.1 Permeation system

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

8.9.3.3 Nylon gloves, best source.

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

8.9.3.5 Permeation tubes, best source.

8.9.3.6 Kimwipes®, best source.

8.9.3.7 Stopwatch, best source.

9. Reagents and Materials

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

9.2 Tenax® Cleaning

9.2.1 Acetone - pesticide quality or equivalent, best source.

9.2.2 Methanol - distilled in glass, best source.

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

9.2.4 Glass wool, silanized, best source.

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

9.3 Standard Preparation

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

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

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

10. Cartridge Construction and Preparation

10.1 Cartridge Design

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

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

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

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

10.2 Adsorbent Purification

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

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

10.2.1 Tenax® Selection

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

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

10.2.2 Tenax® Cleaning Procedure

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

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

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

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

10.2.2.4 Place the thimble in the Soxhlet.

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

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

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

10.2.2.7 Turn on the water to the condenser.

10.2.2.8 Turn on the Variac controlled heating mantle.

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

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

10.2.2.11 Continue the extraction for 48 hours.

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

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

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

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

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

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

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

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

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

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

10.2.2.20 Continue the extraction for 48 hours.

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

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

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

10.2.2.24 Discard the pentane.

10.2.3 Drying Tenax®

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

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

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

10.2.3.4 Cover the dish loosely with aluminum foil.

10.2.3.5 Set the dish in the vacuum oven.

10.2.3.6 Place dry ice/isopropanol in the vacuum trap.

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

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

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

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

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

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

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

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

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

10.2.3.13 Remove the Tenax® from the vacuum oven.

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

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

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

10.2.4 Sieving of Tenax®

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

10.3 Cartridge Preparation

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

10.4 Cartridge Packing

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

10.5 Cartridge Pretreatment

10.5.1 Place adsorbent cartridges into conditioning unit.

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

10.5.3 Place liquid nitrogen in the cryogenic trap.

10.5.4 Open the helium line to the desorption chambers.

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

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

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

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

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

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

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

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

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

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

10.5.12 Seal the tube.

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

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

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

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

10.6 Cartridge Spiking

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

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

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

11. Sample Collection

11.1 Description of Sampling Apparatus

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

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

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

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

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

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

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

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

11.2 Breakthrough Volume Determination

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

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

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

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

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

where:
V_{MAX} = the calculated maximum total volume (safe sample volume), L
V_b = the breakthrough volume for the least retained compound of interest, L/g of Tenax®
W = the weight of Tenax® in the cartridge, g

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

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

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

where:
Q_{MAX} = calculated maximum flow rate, mL/min
t = desired sampling time, min. Times greater than 24 hours (1440 minutes) generally are unsuitable because the flow rate required is too low to be accurately maintained

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

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

where:
B = linear flow velocity, cm/min
r = internal radius of the cartridge, centimeters

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

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

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

11.3 Collection of Samples

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

11.3.13 Install the Tenax cartridge in the sampling train.

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

11.3.14 Using forceps replace the glass wool pad.

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

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

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

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

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

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

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

where:

Q_A = average flow rate, mL/min

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

N = number of points averaged

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

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

where:

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

T_2 = stop time

T_1 = start time

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

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

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

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

12. GC-MS-DS Analysis

12.1 Description of Analytical Apparatus

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

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

The negative aspects of operating in the SIM mode are:

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

The mass spectrometer operated in the SIM mode should be used in a clearly defined monitoring program that provides a clearly defined chemical. For an unknown atmosphere, it is suggested that the mass spectrometer be operated in the scan mode to acquire as much spectral data about the sample as possible.

Note: Considerable variation from one laboratory to another is expected in terms of instrument configuration. Therefore, each laboratory must be responsible for verifying that their particular system yields satisfactory results. Section 17 discusses specific performance criteria which should be met.

12.1.2 GC-MS-DS is based on a combination of retention times and relative abundances of target ions. These qualifiers are stored on the hard disk of the GC-MS-DS computer and are applied for identification of each chromatographic peak. The retention time qualifier is determined to be ± 0.10 minute of the library retention time of the compound. The acceptance level for relative abundance is determined to be ± 15% of the expected abundance. Three ions are measured for each compound. When compound identification is made by the computer, any peak that fails any of the qualifying tests is flagged (e.g., with an *). All the data is manually examined by the analyst to determine the reason for the flag and whether the compound should be reported as found. While this adds some subjective judgment to the analysis, computer generated identification problems can be clarified by an experienced operator. Manual inspection of the quantitative results is also performed to verify concentrations outside the expected range.

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

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

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

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

12.2 Initial Start-Up

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

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

12.2.3 The MS and data system are set according to the manufacturer's instructions. Electron impact ionization (70 eV) and an electron multiplier gain of approximately 5×10^4 should be employed. The mass range should be from 35 to 320 amu, the scan timer should be at least five scans per peak and not to exceed one second per scan. Table 4 outlines general operating conditions for the GC-MS-DS system.

12.2.4 Once the entire GC-MS system has been setup, the user should prepare a detailed standard operating procedure describing the operation of the specific instrument being used.

12.2.5 Turn on the power to the Tylan mass-flow controllers.

12.2.6 Turn on the following gases and set line pressures:

- Helium 60 psig
- Compressed Air 40 psig
- Nitrogen 30 psig

12.2.7 Typical flow rates for the thermal desorption and GC system are:

- Carrier flow through thermal desorption unit 1.2 mL/min

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- Carrier through injector 1.2 mL/min
- Injector septum purge 2.6 mL/min
- Thermal desorption unit purge 10.0 mL/min

12.2.8 Turn on the master power switch to the chromatograph.

12.2.9 Set manifold temperature to 105 ± 5°C.

12.2.10 Set ionization temperature to 260°C.

12.2.11 Turn on the power to the thermal desorption unit. Set the following temperatures for the valve, trap, and transfer line on the vernier dials on the control box of the thermal desorption unit:

- Valves 275°C
- Trap 190°C
- Line 210°C

12.2.12 Tune the radio frequency of the mass spectrometer using the manufacturer's procedures.

12.2.13 Set the zero of the mass spectrometer according to manufacturer's instructions.

12.3 Tuning the Mass Spectrometer with p-Bromofluorobenzene (BFB)

12.3.1 Tuning and mass standardization of the MS system is performed according to manufacturer's instructions and relevant information from the user-prepared SOP.

12.3.2 It is necessary to establish that a given GC-MS meets the standard mass spectral abundance criteria prior to initiating any on-going data collection. This is accomplished through the analysis of p-bromofluorobenzene (BFB).

12.3.3 Each GC-MS used for analysis must be hardware tuned daily or once per each twelve hour time period of operation, whichever is most frequent, to meet the technical acceptance criteria for BFB. Also, whenever corrective action which could change or affect the tuning for BFB (e.g., ion source cleaning or repair, column replacement, etc.), the tune must be verified immediately irrespective of the twelve-hour daily tuning requirement.

12.3.4 Prepare a 25 ng/μL solution of BFB in methanol. Prepare fresh BFB solution every six months or sooner if the solution has degraded or evaporated.

Note: The 25 ng/μL concentration is used with a 2 μL injection volume. The laboratory may prepare a 50 ng/μL solution of BFB if a 1 μL injection volume is used.

12.3.5 Inject 50 ng/μL BFB sample into the GC-MS.

12.3.6 Set time and parameters for the acquisition of the data and initiate data acquisition by following instructions in the operator's manual.

12.3.7 The instrumental parameters (e.g., lens voltages, resolution) should be adjusted to give the relative ion abundances shown in Table 5 as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria. These alternate values, however, must be repeatable on a day-to-day basis.

12.3.8 Typical criteria for an acceptable standardization as specified by manufacturer procedures and recommendation are:

- Base Peak Fit ≤15
- Mass Range ≤50 to ≥414
- Projection Error (MMU) < +75 to > -75
- Fit Error (MMU) ≤1.5%

Note: If the standardization is rejected because of total ion intensity, it can probably be corrected by slight adjustment of the "calibration" gas metering valve, followed by restandardization. If standardization is rejected because of the diagnostics, the percent relative abundances, or the ion intensities, the instrument must be returned and restandardized.

12.3.9 The abundance criteria listed in Table 5 must be met for a 50 ng injection of BFB.

12.4 Performance Specifications of the GC-MS with Perfluorotoluene (PFT)

Note: The initial tuning of the mass spectrometer to the manufacturer's criteria for an acceptable tune using BFB does not guarantee that an acceptable mass spectrum for perfluorotoluene (PFT) will be obtained.

12.4.1 Control of the percent relative abundances of ions of perfluorotoluene, the compound selected as the tuning standard for the analysis of volatile organic compounds from Tenax® cartridges, is essential for obtaining data of the desired quality. The relative abundances (RA) of the ions of perfluorotoluene should be reproducible within a specific range established by an historical data base from day-to-day.

12.4.2 Check the appearance of the mass spectrum of PFT by injecting a 50 ng/μL sample into the GC-MS.

12.4.3 When PFT is present in the ion source, set the oscilloscope in SINGLE mode and set the first Mass Control for mass 50 and the Last Mass for mass 250.

12.4.4 Observe all the major ions of the PFT mass spectrum on the oscilloscope.

12.4.5 Set up data acquisition and acquire several scans of the PFT mass spectrum.

12.4.6 Select one scan to check the % RA.

Note: The spectrum of PFT obtained by introduction of PFT into the GC-MS using the syringe inlet will differ slightly from the PFT mass spectrum obtained by thermal desorption of the PFT from a Tenax® cartridge and introduction to the mass spectrometer through the GC column, but the appearance of the mass spectrum should be a very good indication of whether the tune will meet the criteria for acceptable analysis.

12.4.7 Tuning criteria set for the major ions of the mass spectrum of PFT are as follows:

Ion	% RA of Base Peak
69	29
79	7
93	15
117	39
167	12
186	59
217	100
236	75

Ideally, the % RA should not vary by more than 10%.

12.4.8 If the mass spectrum of PFT does not meet the criteria for instrument operation, retune the instrument to meet these criteria.

12.5 Calibration of the GC-MS-DS System

12.5.1 External Standard Calibration Procedure

12.5.1.1 After the mass standardization and tuning process has been completed and the appropriate values entered into the data system, the user must calibrate the entire system daily by introducing known quantities of the standard components of interest into the system. Two suggested procedures may be employed for the external calibration process. They are: 1) direct syringe injection of dilute vapor phase standards, prepared in a dilution bottle, onto the GC column and 2) spiking of dilute vapor phase standards onto a Tenax® cartridge, then analysis by thermal desorption to the GC-MS-DS. The standards preparation procedures for each of these approaches are described in Section 15.3. The following paragraphs describe the instrument calibration process for each of these approaches.

12.5.1.2 If the instrument is to be calibrated by the external standard calibration mixture approach by direct injection of a 50 µL gaseous standards (see Table 1 asterisk compounds), the standards are prepared in a dilution bottle as described in Section 15.3. The GC column is cooled to -70°C (or, alternately, a portion of the column inlet is manually cooled with liquid nitrogen). The MS and data system is set up for acquisition as described in the relevant user SOP. The ionization filament should be turned off during the initial 2-3 minutes of the run to allow oxygen and other highly volatile components to elute. An appropriate volume (less than 1 mL) of the gaseous standard is injected onto the GC system using an accurately calibrated gas tight syringe. The system clock is started and the column is maintained at -70°C (or liquid nitrogen inlet cooling) for 2 minutes. The column temperature is rapidly increased to the desired initial temperature (e.g., 30°C). The temperature program is started at a consistent time (e.g., four minutes) after injection. Simultaneously the ionization filament is turned on and data acquisition is initiated. After the last component of interest has eluted, data acquisition is terminated and a calibration curve for each compound can be generated or RF evaluated according to Section 12.7.1.8.

12.5.1.3 If the system is to be calibrated by analysis of spiked Tenax® cartridges, a set of spiked cartridges are prepared as described in Sections 15.2 or 15.4. Prior to analysis the cartridges are stored as described in Section 10.5. If glass cartridges [Figure 1(a)] are employed care must be taken to avoid direct contact, as described earlier. The GC column is cooled to -70°C, the collection loop is immersed in liquid nitrogen and the desorption module is maintained at 250°C. The inlet valve is placed in the desorb mode and the standard spiked cartridge is placed in the desorption module, making certain that no leakage of purge gas occurs. The cartridge is purged for 10 minutes and then the inlet valve is placed in the inject mode and the liquid nitrogen source removed from the collection trap. The GC column is maintained at -70°C for two minutes and subsequent steps are taken as described in Section 12.7.1.2. After the process is complete the cartridge

is removed from the desorption module and stored for subsequent use as described in Section 10.5.

12.5.1.4 Data processing for instrument calibration involves determining retention times, and integrated characteristic ion intensities for each of the compounds of interest. A calibration curve for each compound can be generated or RF evaluated according to Section 12.7.1.8. In addition, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectra to ensure proper instrumental performance. Since the steps involved in data processing are highly instrument specific, the user should prepare a SOP describing the process for individual use. Overall performance criteria for instrument calibration are provided in Section 17. If these criteria are not achieved the user should refine the instrumental parameters and/or operating procedures to meet these criteria.

12.5.1.5 Calibration and quantitation of volatile organic compounds by GC-MS-DS can be performed by the Response Factor (RF) technique.

12.5.1.6 A RF is determined for each compound of interest.

12.5.1.7 To establish a RF data base for the target compounds prior to analysis of field sample cartridges, analyze a series of at least three cartridges by thermal desorption with the GC-MS-DS containing the target compounds applied to them by flash vaporization (see Section 15.2) technique. Table 6 outlines typical target compounds and number of nanograms/cartridge used in the RF determination.

12.5.1.8 Calculate three sets of RFs for each ion of interest for each target compound by the following equation:

$$\text{Response Factor (RF)} = A_i/C_i$$

where:
A_i = area counts for most intense ion, and
C_i = nanograms of standard deposited on cartridge

12.5.1.9 Tabulate these RFs.

12.5.1.10 If several RFs in a particular assay can be identified as outliers by their lack of correspondence to the other values obtained, discard that set of RFs.

12.5.1.11 If the ratio of response to concentration is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio of RF can be used in place of a calibration curve.

12.5.1.12 If the set of three RFs does not appear to be consistent, immediately check the desorption unit, gas chromatograph, and mass spectrometer for the presence of an air leak or some other problem, rectify the problem, and repeat the series of three cartridges. Note: If substantial nonlinearity is present in the calibration curve a nonlinear least squares fit (e.g., quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where:
Y = peak, area counts

X = quantity of component, ng
A, B, and C are coefficients in the equation

12.5.1.13 Initiate quantitation of the calculated RFs for target compounds and creation of the library in the data system to obtain ion peak areas and scan numbers automatically for each ion of each compound.

Note: The data system should include information about compound ions, the scan number at which the compound should be sought, and the Method file. The Method file contains information needed to designate a mass range in which to search for ions of the target compounds and establishes parameters required for peak area quantitation.

12.5.1.14 Create a library file for the target compounds within the data system.

12.5.1.15 Verify the correctness of all information entered (RFs, amount added to cartridge, etc.) for the ion of a compound by inspecting the terminal display.

12.5.1.16 When both a Quantitation List and a Library have been created, obtain calculated Response Factors by making a correlation between the ion of the compound and a library entry number.

12.5.1.17 Correlate all ions to a library entry.

12.5.1.18 Store RFs in a Response list of the computer.

Note: The computer, using a QUAN program, will automatically calculate ng/cartridge for targeted compounds.

12.5.1.19 Transfer all data acquired to a nine-track magnetic tape for archiving and possible further reference.

12.5.2 Internal Standard Technique Using Relative Response Factors (RRFs)

12.5.2.1 To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standards can be suggested that is applicable to all samples. The compounds recommended for use as surrogate spikes have been also used successfully as internal standards, because of their generally unique retention times.

12.5.2.2 Prepare five calibration standards, containing all the target compounds, spiked on clean Tenax® tubes as outlined in Section 15.3.

12.5.2.3 To each of these tubes, add a known concentration of an internal standard, as outlined in Section 10.6.2.

12.5.2.4 Analyze each tube according to Section 12.5.

12.5.2.5 Tabulate peak height or area responses against concentration for each compound and internal standard. Calculate relative response factors (RRF) for each target compound and the internal standard using the following equation.

Note: Table 1 contains primary quantitation ions to be used for each target compound and internal standard.

$$RRF = (A_x/A_{is})(C_{is}/C_x)$$

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where:
A_x = area response for the compound to be measured
A_{is} = area response ion for the internal standard
C_{is} = concentration of the internal standard, ng
C_x = concentration of the compound to be measured, ng

12.5.2.6 Initiate quantitation of the RRFs for the target compounds and creation of the library in the data system.

12.5.2.7 If the RRF value over the working range is constant (<10% RSD), the RRF can be assumed to be invariant and the average RRF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RRF.

13. Receipt of Samples

13.1 Receive all Tenax® cartridge tubes in a sealed can with the appropriate Chain-of-Custody sheet after standards have been loaded on them.

13.2 Match the Chain-of-Custody Sheet with the corresponding sample to ensure no mixup has occurred.

13.3 Check each Chain-of-Custody Sheet carefully for the following items: 1) a signature of a person relinquishing custody, 2) the amounts of standards loaded on the cartridge, 3) the temperature and volume collected amounts, and 4) the Tenax® batch number.

13.4 Do not analyze any sample that has no Chain-of-Custody sheet or is missing any of the above information.

13.5 Put all cans of samples in the cartridge freezer when received.

13.6 Log each sample in the appropriate notebook as received.

13.7 Place each Chain-of-Custody sheet in the project notebook (with all other information regarding that particular sample) after signing and dating it.

13.8 Store any used cartridges in sealed cans so they can be recycled, cleaned, and used again.

14. GC-MS-DS Analysis of Tenax® Adsorbent Tubes by Thermal Desorption

14.1 Description of Analytical Process

14.1.1 The instrumental conditions for the analysis of volatile organics on Tenax® sampling cartridge are outlined in Table 4. The thermal desorption chamber and the six port Valco valve are maintained at 275°C during analysis. The mass spectrometer is set to scan the mass range from approximately 35-350. The helium purge gas through the desorption chamber should be 10 mL/min. The nickel capillary trap on the inlet manifold should be cooled with liquid nitrogen.

14.1.2 Initially, the thermal desorption unit is cold while the Tenax® traps are placed inside while flowing helium through them. This allows oxygen to be purged from the trap, reducing oxidative degradation of Tenax®.

14.1.3 Then, during the thermal desorption cycle, helium gas continues to flow through the cartridge to purge the organic vapors on the Tenax® into the liquid nitrogen capillary trap.

14.1.4 After the desorption has been completed, the six-port valve is rotated and the temperature on the capillary loop is rapidly raised (greater than 100°C/min); the carrier gas then introduces the vapors onto the high resolution GC column. The bonded phase fused silica capillary column is temperature programmed from 40°C (5 min hold) to 240°C at 4°C/min and held at the upper limit for a minimum of 15 min.

14.1.5 The column is programmed to a temperature to allow the elution of all of the organic compounds while the mass spectrometer is scanning. Data are recorded by the computer for subsequent processing. Quantitation is performed by the method of response factors (see Section 12.5), where the proportionate system responses for analyte and standard are determined prior to the analysis of the sample and this relative system response is used to determine the quantity of compound present on the sample cartridge.

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

14.2 Desorption Process

Note: The following outlines typical steps associated with thermal desorption using the NuTech device. They are presented as a guideline to follow when using general equipment.

14.2.1 Remove the sealed paint can containing the desired cartridge from the freezer. Note: Use the freezer in the laboratory designated for cartridge storage ONLY for this purpose. Inadvertent storage of containers of solvent in this freezer will result in contamination of all cartridges stored in the freezer and will compromise the analysis, since organic solvents are frequently target compounds for quantitative analysis. Verify that the laboratory personnel are not involved in any process which requires the presence of open containers of organic solvents as the fumes of organic solvents will hopelessly contaminate a Tenax® cartridge exposed to this atmosphere for only a few seconds, thus compromising the quantitative and/or qualitative assay.

14.2.2 Open the sealed lid of the paint can, using a flat-bladed screwdriver, beverage can opener, or other convenient tool for this purpose.

Note: The cartridge will be in a stainless steel culture tube with a Teflon-lined screw cap.

14.2.3 Remove a single culture tube from the paint can and place in the wooden cartridge holder in front of the gas chromatograph.

14.2.4 Seal the paint can and replace in the freezer.

14.2.5 Release the Teflon cap of the desorption chamber.

14.2.6 Remove the cartridge from the culture tube using forceps.

Note: DO NOT TOUCH THE CARTRIDGE WITH YOUR HANDS! The slightest trace of organic compounds present on the fingertips can be sufficient to compromise the analysis. If the cartridge is inadvertently touched, make careful note of the circumstances in both the instrument log and the project notebook.

14.2.7 Insert the cartridge immediately into the desorption chamber.

14.2.8 Close the Teflon cap of the desorption chamber.

14.2.9 Initiate the timing of the eight-minute desorption cycle.

14.3 Injection Procedure

14.3.1 At the end of the eight-minute desorption cycle, turn the desorption unit valve to the INJECT mode (down).

Note: The following sets are automatic on some commercially available instruments.

14.3.2 Initiate heating of the nickel trap.

14.3.3 Begin acquisition of data system.

14.3.4 Turn off the trap after it has heated to 240°C.

14.3.5 Press the "start run" key on the GC microprocessor simultaneously with the <CR> key on the data-system terminal. This starts the GC temperature program and the data acquisition program.

14.3.6 Turn the thermal desorption unit valve back to desorb and remove the Tenax® cartridge.

14.3.7 At the end of the run, the GC will recycle and cool to 30°C, and the data acquisition will stop automatically after 4500 scans have been acquired.

14.3.8 The analysis may be stopped before 4500 scans by pressing the "stop run" key on the GC microprocessor. The data acquisition may then be stopped by typing [<CTRL>D] on the data system terminal and then typing [E<CR>STOP<CR>].

14.3.9 Repeat this procedure for each Tenax® cartridge to be analyzed.

14.4 Data Tabulation and Storage

14.4.1 Data from GC-MS runs are normally processed by the data system in an automated program which locates the compounds of interest in the data set, quantifies those compounds for which calibration data are available, and prints a report. A typical report will present the quantification parameters and result for those compounds present and quantifiable. The report will typically list those compounds which were searched for in the sample, indicate which ones were not found, print the identifying characteristics and quantification results for those which were found, and present comments for the operator's benefit, such as the criteria which caused a peak to be rejected or the center scan for any search which failed. The information in the report can also be saved in a DS file for archival storage and DS transfer purposes.

14.4.2 The library in the data system should contain a file composed of one entry for each compound of interest. For each entry, the library contains the compound name, its mass spectrum from the Mass Spectral Data Base, its absolute retention time, and its

retention time relative to perfluorotoluene, the retention time marker, as determined from authentic standards. Response lists (RL) are compound specific DS files containing the quantitative calibration data for each of the target compounds.

14.4.3 The automated procedure attempts to locate chromatographic peaks corresponding to target compounds by a reverse library search using the following criteria for scan window:

- for internal standards: ± 100 scans from library scan number
- for single compounds: ± 20 scans from the calculated scan
- for isomer groups: -20 and +20 scans from the calculated scans for the earliest and latest eluting members of the group, respectively
- Peak identification: peak 1/2-width ≥ 5 scans, purity ≥200, fit ≥700
- Peak selection: the scan list is partitioned in order of increasing distance from the center of the scan window, except for isomer groups

14.4.4 The automated procedure begins by attempting to locate the two retention time markers (PFT and 1,2-dichlorobenzene) and the internal standards ($toluene_{d8}$). If the early eluting standard, PFT, is not located a warning message is printed and the procedure is terminated. If only the late eluting internal standard is not found, the procedure uses the scan number calculated from the library retention time for this standard as a default value. Note: Alternatively, the operator may specify scan numbers for the internal standards and then initiate the remainder of the automated procedure. The procedure cycles through the compounds in the library list attempting to locate each compound in turn.

14.4.5 If one or more peaks are identified in the search for a target compound, the resulting scan list is partitioned to order the scans in increasing distance from the center of the search window. The mass spectra in the partitioned list are sequentially compared to the library entry for the target compound in order to the mass weighted purity, fit and rfit. The following ratio ranges are tested:

- Fit/purity: >0.99, <1.30
- Rfit/purity: >0.99, <1.05

If rfit/purity passes but fit/purity exceeds 1.29 the spectrum is enhanced, reprocessed through the library comparison, and tested against the above criteria.

14.4.6 If the mass spectrum at the peak maximum passes either of the above tests, the procedure attempts to quantify the peak. If the target is a single compound, only the first peak to pass the qualitative criteria is processed further. If the target is an isomer group, all peaks detected by the search are processed through the qualitative filters and all that pass these filters are quantified. If no peaks are found by the search or pass through the qualitative filters, a "not found" entry is placed in the report.

Note: The failure of a peak to satisfy these criteria does not necessarily prove the absence of the compound in the sample. Interfering compounds or low levels of the compound of interest may cause the test values to fall outside of the acceptance range. It is also possible to obtain acceptable values for fit/purity and rfit/purity, but have a questionable identification. If the absence of a particular compound is of crucial importance and the DS procedure fails to locate the compound, or for any compound which has a fit, purity, or rfit

less than 700, manual inspection of the data by a person skilled in the interpretation of GC-MS data is necessary for confirmation.

14.5 Qualitative Peak Identification

14.5.1 Relative intensities of major ions in the reference spectrum (ions greater than 25% of the most abundant ion) should be present in the sample spectrum.

14.5.2 The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% of the standard spectra, the corresponding sample ion abundance must be between 30 and 70%).

14.5.3 Molecular ions present in reference spectrum should be present in sample spectrum.

14.5.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

14.5.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

14.5.6 If in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (e.g., unknown aromatic, unknown hydrocarbon, unknown chlorinated compound). If a probable molecular weight can be distinguished, include it.

14.6 Peak Quantification

The procedure attempts to quantify peaks which have been qualitatively identified. Quantification is based on integration of the extracted ion current profile (EICP) of a quantitation mass or ion for the compound. This mass has been previously selected for each compound based on its spectral uniqueness, intensity, and lack of potential interferences from known coeluting compounds. Currently used masses are listed in Table 1.

14.7 Sample Quantitation

14.7.1 Sample quantitation is performed by the data processing system for all desired ions of all target compounds.

14.7.2 Utilizing the QUAN package of the data system involving compound identification and response factor to obtain quantitation data of the target compounds by the following equation:

$$X_A = [(A_A)(\mu g_{STD})]/[A_{STD})(RRF)]$$

where:
X_A = amount of target compound, μg
A_A = area of ion of analyte, counts
μg_{STD} = mass of standard applied to tube, μg

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A_{STD} = area of standard, counts
RRF = relative response factor (see Section 12.5.2)

14.7.3 The computer, upon request, will print out peak number, m/e, scan, time, relative retention time, area and amount.

14.7.4 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = [(X_A - B_A)(1000\ L)]/[(m^3)(V_S)(R_A)]$$

where:
C_A = calculated concentration of target compound, ng/L
X_A = defined in Section 14.7.2
B_A = amount of target compound on blank, μg
V_S = calculated in Section 11.3.21
R_A = recovery factor, if applicable

15. Generation of Known Concentrations Procedures

15.1 Three procedures are discussed for generating known concentrations of targeted VOCs to be used for direct injection into the GC-MS-DS for calibration or depositing upon Tenax® tubes to be used in calibration of the entire GC-MS-DS analytical system. They are: 1) preparation of known concentrations utilizing static dilution bottles, 2) use of flash vaporization technique for loading targeted VOC standards upon Tenax® tubes and 3) use of permeation tube system for generating known concentrations of VOC standards upon Tenax® tubes. The standards preparation procedures are based on U.S. Environmental Protection Agency SOPs (41,45).

15.2 Flash Vaporization (see Figure 5)

15.2.1 Principle

15.2.1.1 A dilute solution of one or more organic compounds in methanol is injected into a heated zone in a helium stream. The methanol and the solute compounds are rapidly vaporized and then swept onto a sorbent cartridge. Methanol has little affinity for Tenax® sorbent and is rapidly eluted from the cartridge.

15.2.1.2 The solute compounds remain in the sorbent bed when the cartridge is removed from the flow system, and may subsequently be desorbed from the cartridge and delivered to an analytical instrument for analysis.

15.2.1.3 Since the quantity of each compound in the cartridge can be determined from its concentration in the solution and the volume of solution injected, this method may be used to spike quantitative standards on sorbent cartridges.

15.2.2 Interferences

15.2.2.1 Contamination of the methanol solvent with compounds to be calibrated, or with compounds producing similar instrumental responses, will result in false high or false positive responses.

15.2.2.2 Contamination of a compound used as a standard will result in a decreased response. Contamination of one compound with another one to be used in the same solution will result in incorrect responses for both compounds.

15.2.2.3 Chemical reaction between two compounds in a standard mixture will result in low responses for both. Absorption of a compound into the matrix of sorbent particles will probably result in part of it being retained in the cartridge during desorption, with consequent decreased response.

15.2.3 Flash Vaporization Assembly

15.2.3.1 Assemble the flash vaporization unit, as illustrated in Figure 5.

15.2.3.2 Adjust the helium flow to 30 mL/min and the heating mantle to 310 ± 10°C.

15.2.3.3 Allow the helium to flow for approximately 30 minutes to equilibrate the system.

15.2.4 Syringe Cleaning

15.2.4.1 Rinse individual syringe with methanol and acetone.

15.2.4.2 Dry in a vacuum syringe cleaner for ~30 seconds. (A heat gun is used to heat the barrel of the syringe during vacuum drying).

Note: Syringes must be rigorously cleaned after each injection to remove traces of sample. Even if more than one injection is needed from any given source a freshly cleaned syringe must be used for each injection. Failure to do so will probably result in erratic responses.

15.2.5 Helium Volume Required

15.2.5.1 The volume of helium required to elute methanol from a sorbent cartridge is determined by using a thermal conductivity detector.

15.2.5.2 Several different flow rates are tried to find one which results in as sharp a methanol peak as possible without sweeping volatile solutes out of the cartridge before it can be removed from the system.

15.2.6 Preparation of Standard Gas Concentration

15.2.6.1 Set the helium flow to 30 mL/min and the heater to 310° ± 10°C.

15.2.6.2 Place a clean (see Section 10.2) Tenax® cartridge in line.

15.2.6.3 Pass helium through the cartridge for a period of 5 minutes.

15.2.6.4 Using a heated syringe retrieve from the individual standard flask an aliquot by the following procedure:

15.2.6.4.1 Pull a 1 µL sample of methanol into the syringe.

15.2.6.4.2 Next draw a 1 µL plug of air.

15.2.6.4.3 Then pull the calculated quantity of standard solution into the syringe.

15.2.6.4.4 Finally, continue to pull another 1 µL plug of air.

Note: This insures that the sample solution is flushed completely out of the needle by the methanol plug during injection.

15.2.6.5 With the aliquot of the standard in the syringe, inject smoothly, at the standard injection point, the syringe contents over a period of about 5 seconds.

15.2.6.6 Allow the helium containing the injection standard to pass through the cartridge for 50 minutes or until 1500 mL of helium has passed.

15.2.6.7 Remove the cartridge from the system, cap and store at 5°C.

15.2.7 Calculation of Deliverable Concentration

15.2.7.1 The approximate volume of solution to be injected is calculated by working backward from the size of the spike to be placed in the sorbent cartridge.

15.2.7.2 For example, if a 500 ng spike is needed, it could be done by injecting 10 µL of methanol containing 50 ng/µL of solute. Therefore, 10 µL x 50 ng/µL solution = 500 ng.

15.2.7.3 A solution containing 50 ng/µL of solute is prepared by dissolving 5 mg of neat compound in a 100 mL volumetric flask and diluting to mark with methanol.

15.2.7.4 If the density of the neat compound is 0.9726 g/mL (0.9726 mg/µL), then the measured neat compound would be

$$5 \text{ mg}/(0.9726 \text{ mg}/\mu\text{L}) = 5.14 \ \mu\text{L}$$

15.2.7.5 Therefore, 5.14 µL of solute measured with a syringe would produce 50 ng/µL solution when diluted to 100 mL with methanol.

15.2.7.6 It is not practical to measure fractions of microliters, so usual practice would be to dissolve 5 µL of sample in 100 mL of methanol to produce a concentration of

$$(0.9726 \text{ mg}/\mu\text{L} \times 5 \ \mu\text{L})/100 \text{ mL} = 0.0486 \text{ mg/mL} = 48.63 \text{ ng}/\mu\text{L}$$

A 10 µL aliquot of this solution would contain 486.3 ng.

15.2.7.7 No correction for impurities in the neat sample is needed if manufacturer's determined purity is 98% or better.

15.2.7.8 As an example, a typical column evaluation mixture can be prepared as follows:

Standard	Density, g/mL	Volume, µL	Weight, mg	Deliverable Volume, µl	Spiked on Cartridges, ng
Ethylbenzene	0.867	11.0	9.54	3	286
p-Xylene	0.861	12.0	10.33	3	310
Acetophenone	1.028	10.0	10.28	3	308
2-Nonanone	0.821	12.0	9.85	3	296

These compounds should be 98% pure or better, and purity should be checked by capillary GC. Each compound is measured into a 100 mL volumetric flask using a microsyringe. The flasks are filled to the mark with spectrographic grade methanol and the contents mixed thoroughly. The solution must be used within half a day. Three microliters of those solutions, when injected into the flash vaporization unit in the manner specified above, will

deposit approximately 300 ng of each compound on a sorbent cartridge as shown in the table above.

15.3 Static Dilution Bottle

15.3.1 Principle

15.3.1.1 A quantity of liquid organic compound is injected into a two-liter round bottom helium-filled flask through a septum cap. After injections are completed, the flask is agitated and heated to achieve complete vaporization.

15.3.1.2 Aliquots of the resulting vapor are then delivered to sorbent cartridges or analytical instruments. The weight of each compound delivered is calculated from 1) the density of the liquid, 2) the volume of liquid injected into the known volume of the bottle, and 3) the volume of the vapor aliquot removed.

Note: The quantity of any compound injected into the dilution flask must be substantially less than that which would result in a partial pressure equal to its vapor pressure at ambient temperature. Vaporization of liquid aliquots injected into the bottle must not result in a large positive pressure, and removal of vapor aliquots from the flask must not result in a substantial vacuum. If these precautions are not taken erratic responses will occur.

15.3.2 Interferences

15.3.2.1 Contamination of a compound used as a standard will result in decreased response. Contamination of one compound with another one used in the same vapor mixture will result in an incorrect response for both compounds.

15.3.2.2 Adsorption of vapor molecules on the walls of the bottle or on the septum will result in loss of material, with a consequent decrease in response. This is especially likely when new, freshly annealed bottles are used. Contamination of apparatus can result in adsorption loss or provide unexpected sources of compounds in a mixture.

15.3.2.3 Chemical reactions between compounds can deplete them from the mixture and might also result in unexpected reaction products. Use of a syringe for consecutive injections from the same bottle without cleaning after each injection will probably result in erratic responses due to buildup of sample residues in the syringe.

15.3.3 Applicability

15.3.3.1 The static dilution bottle technique for preparing standards has been validated for the following 22 substances:

Acetophenone
Benzonitrile
1,1,1,2-Tetrachloroethane
1,4-Dioxane
1-Chloro-2,3-epoxypropane
1,3-Dichlorobutane
1,4-Dichlorobenzene
cis-1,4-Dichloro-2-butene
3,4-Dichloro-1-butene
Perfluorotoluene
Fluoroiodobenzene
1-Ethenyl-4-chlorobenzene
3-Chloro-1-propene
1,4-Dichlorobutane
1,2,3-Trichloropropane
1,1-Dichloroethane

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2-Chlorobutane	1-Methyl-4-(1-Methyl-ethyl)-benzene
2-Chloroethoxyethene	Butylbenzene
1-Methylethylbenzene	1,3,5-Trimethylbenzene

15.3.3.2 Amounts used have ranged between 0.3 and 4 μL of liquid samples. Repeatability of daily injections of a mixture of the 22 compounds into the GC-MS is about ± 10% relative standard deviation. Precision depends on the substance introduced, the skill of the individual producing the flask standard, and the skill of the operator of the instrument used to analyze the flask contents. Accuracy has not been established.

15.3.4 Flask Cleaning

15.3.4.1 Wash the two-liter flask with detergent and water.
15.3.4.2 Rinse several times with deionized water.
15.3.4.3 Dry in an oven at 300°C for 4 hours.

15.3.5 Syringe Cleaning

15.3.5.1 Rinse individual syringes with methanol and acetone.
15.3.5.2 Dry in a vacuum syringe cleaner for ~30 seconds. (A heat gun is used to heat the barrel of the syringe during vacuum drying.)
Note: Syringes must be rigorously cleaned after each injection to remove traces of sample. Even if more than one injection is needed from any given source a freshly cleaned syringe must be used for each injection. Failure to do so will probably result in erratic responses.

15.3.6 Flask Calibration

15.3.6.1 Place 30 3-mm glass beads inside the flask and weigh on an analytical balance to an accuracy of 0.01 g.
15.3.6.2 Fill the flask with deionized water to the level of the septum cap.
15.3.6.3 Weigh the flask containing the glass beads and water on an analytical balance to an accuracy of 0.01 g.
15.3.6.4 The weight of the water required to fill the bottle is the difference between the two weights, as calculated below:

$$V_f = (Wt_f - Wt_i)$$

where:
V_f = volume of flask, mL
Wt_f = final weight of flask with beads and water, g
Wt_i = initial weight of flask with beads, g

15.3.7 Preparation of a Standard Gas Solution in a Flask

15.3.7.1 Two methods have been used to load the dilution flask with organic components for standards: 1) direct injection of each compound separately into the flask and 2) a single direct injection of a previously prepared mixture of compounds.

Note: These methods have been shown to produce indistinguishable results.

15.3.7.2 The first method involves injecting each compound (one at a time) into the flask. The flask is inverted after each injection with the syringe in place through the septum, in order for the beads to remove any liquid remaining on the syringe needle. The second method involves preparing a master solution by injecting 1 mL of each component into a culture vial fitted with a septum cap. After all the compounds have been added, the vial is agitated to produce a homogeneous liquid mixture. The vial is then recapped with a new septum. Aliquots of this master solution are removed and injected into the dilution flask as needed in the same manner as indicated above.

15.3.7.3 Retrieve a clean, dry two liter flask containing 70 3 mm glass beads.

15.3.7.4 Flush the flask with helium for a period of five minutes.

15.3.7.5 At the end of the flushing process, immediately cap with a Mininert septum cap.

15.3.7.6 Place the two liter flask on a magnetic stirring apparatus and set at the maximum speed.

15.3.7.7 Using the syringes, inject the calculated volume of each compound (one at a time) or from the mixture solution into the flask while the glass beads are agitated by the stirring bar at the maximum setting of the magnetic stirrer.

15.3.7.8 Invert the flask after each injection with the syringe in place through the septum, in order for the beads to remove any liquid remaining on the syringe needle.

15.3.7.9 After all substances have been introduced, place the flask in the oven at 60°C for 30 minutes to equilibrate.

15.3.7.10 Store the flask in the oven at 60°C until needed. Bottles are stable for one week after preparation.

Note: The technique of injecting a solution of targeted compounds rather than individual injection of specific compounds is preferred if many substances are involved, because it is more rapid, and the master solution can be used over a long period if it is refrigerated at 0°C. Before use, the refrigerated solution is allowed to sit at room temperature for about an hour. It is recommended that a total less than 90 µL of liquid be injected and a total less than 20,000 µL of gas be removed.

15.3.8 Withdrawal of an Aliquot

15.3.8.1 Remove the flask from the oven and place on the magnetic stirrer for approximately 15 seconds.

15.3.8.2 Place the syringe to be used in the extraction procedure in the oven at 60°C to prevent condensation in the syringe during delivery.

15.3.8.3 Using the heated syringe, insert its needle through the septum and pump three times slowly.

15.3.8.4 After the third pump, fill the syringe to approximately 25% greater volume than needed.

15.3.8.5 After a 5-second pause, withdraw the needle from the Mininert septum valve.

15.3.8.6 Flush the excess sample from the syringe, then draw a small quantity of air into the syringe to retard diffusion of sample through the syringe tip.

15.3.8.7 The aliquot sample must be used immediately.

15.3.9 Delivery of an Aliquot

15.3.9.1 If the sample is to be injected into a clean sorbent cartridge, the tip of the needle is inserted to the center of the sorbent bed. Then the plunger is depressed over a 10 second period while the needle tip is being withdrawn about half the distance to the end of the bed.

15.3.9.2 If the sample is injected directly into the analytical instrument, injection is made in the normal manner unless column-head freeze-trapping (cryofocusing) is being employed, in which case the plunger is depressed over about a 10 second period.

15.3.9.3 If a sample is too large to be injected in one step, two or more injections may be made. This causes no complication for injection into a sorbent cartridge, but cryofocusing must be employed when multiple injections are made directly into a gas chromatograph.

15.3.10 Calculation of Deliverable Concentration

15.3.10.1 Volumes to be introduced into the 2 liter flask are calculated by working backwards from the quantity of material to be delivered.

15.3.10.2 For example, if a 500 ng delivery is needed, it could conveniently be accomplished by using a 50 µL syringe containing 10 ng/µL of compound. Therefore,

$$50\ \mu L \text{ syringe} \times 10\ ng/\mu L \text{ solution} = 500\ ng$$

15.3.10.3 If the typical volume of the flask is 2.065 L, then to get that concentration (10 ng/µL) in the flask, one would have to add 20.65 mg of liquid compound to the flask. The calculation would therefore involve:

$$10\ ng/\mu L \times 2.065\ L = \text{quantity of liquid needed to develop a flask concentration of } 10\ ng/\mu L.$$

$$10\ ng/\mu L \times 2.065\ L = 20.65\ mg$$

15.3.10.4 If the density of the solution was 0.9726 g/mL (or 0.9726 mg/µL), then the volume of solution needed to add to the flask to maintain a concentration of 10 ng/µL or a deliverable of 500 ng would be 21.23 µL, as calculated:

$$20.65\ mg/(0.9726\ mg/\mu L) = 21.23\ \mu L$$

15.3.10.5 It is not practical to deliver and measure fractions of a microliter, so, in practice, 21 µL would be used. Therefore, the deliverable would be calculated:

$$(21\ \mu L \times 0.9726\ mg/\mu L)/2065\ mL = 0.00989\ mg/mL = 0.00989\ \mu g/\mu L$$

15.3.10.6 This is equivalent to 9.89 ng/µL, so a 50-µL injection of the vapor compound from the static dilution flask would contain:

$$9.89\ ng/\mu L \times 50\ \mu L = 494.5\ ng \text{ of compound delivered}$$

15.3.10.7 No correction for impurities in the neat sample is needed if manufacturer's determined purity is ≥98% or better.

15.4 Permeation Calibration Generator (see Figure 18)

15.4.1 Principle

15.4.1.1 A permeation calibration generator is designed to allow the permeation of gas through Teflon® or other plastic material at a constant rate in a water bath at constant temperature to generate test atmospheres.

15.4.1.2 The permeation tube is made by sealing a liquid chemical in a tube made of some permeable material. It is essential that the chemical be in the liquid state for the permeation tube to operate properly. In many cases the chemical is a gas at atmospheric pressure, but is maintained in the liquid state under its own saturation vapor pressure in the permeation tube. The tube is sealed at both ends with a non-permeable plug.

15.4.1.3 Permeation of the pollutant vapor within the tube occurs through the exposed sidewalls because of the concentration gradient that exists between the inner and outer tube walls. By passing different flows of diluent gas over the tube, gases of varying concentration can be generated. If the tube is held at a constant temperature, the permeation rate will remain constant. By measuring the weight loss at this constant temperature over a given period of time, the permeation rate may be determined. The output rate of the tube will remain essentially constant until nearly all of the liquid in the tube has permeated through the walls. In general, permeation tubes can be used to generate known pollutant concentration between 0.7 to 200 ppbv.

15.4.1.4 Before a permeation device can be used in the laboratory or in the field, its permeation rate must be determined. The permeation rate, R, is determined gravimetrically. In essence, the tube is weighed, then placed in a temperature bath (±1°C) for a period of time. The tube is removed and reweighed. This process is repeated over several days to calculate a permeation rate at that specific temperature. The difference between initial and recorded weight (ng), divided by time (min) determines the permeation rate at that specific temperature.

$$R = W/T$$

where:
R = permeation rate, ng/min
W = weight change, ng
T = time, minutes

The permeation rate can be calculated either manually, as shown in the above equation, or recorded automatically. At different temperatures, different permeation rates can be calculated.

15.4.1.5 Permeation tubes should be kept at the temperature specified by the manufacturer and at a constant temperature (±0.05°C) during calibration procedures. Changes in temperature as small as 0.1°C can significantly affect the permeation rate.

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Tubes should initially be allowed to equilibrate for 24 hours. After small changes in temperature (1 to 5°C), the tube should be allowed to equilibrate for at least half an hour.

15.4.2 Applicability

15.4.2.1 A permeation tube system has been developed for application of loading known standards onto Tenax® cartridges for use in determining the relative response factor and the column performance evaluation (CPMX) of the GC-MS-COMP system in conjunction with the flash vaporization system.

15.4.2.2 In addition, the permeation tube system is used for generating external standards [perfluorobenzene (PFB) and perfluorotoluene (PFT)] to be loaded by syringe onto the Tenax® tube to determine relative retention times, relative response factors and stability of the GC-MS-DS system and for generating deuterated standards used in the evaluation of breakthrough volumes associated with Tenax®.

15.4.3 Permeation Generator Assembly

15.4.3.1 A permeation system consists of four main parts (see Figure 18): 1) a temperature-controlled chamber containing permeation tubes, 2) a mixing chamber, and 3) permeation tube storage chamber. A stream of nitrogen flows through the system. The amounts of compounds transported downstream remain constant once the system has become equilibrated with the compounds to be loaded. The amount of compounds can be determined by measuring the time and the gas flow through the cartridge.

15.4.3.2 The permeation system may be used to load any volatile compound that will permeate at a constant rate under controlled conditions, and to inject a calibration standard onto a sorbent via syringe.

15.4.4 Preparation of Standard Gas Concentration

Note: The following routine should be followed when Tenax® cartridges are loaded with deuterated standards via a permeation system: 1) determine the number of cartridges to be loaded, 2) select the permeation tubes, 3) determine the loading conditions to be used, 4) equilibrate the system, 5) load the cartridges, 6) calculate the amounts of compounds loaded, 7) ensure the integrity of the loading procedure, and 8) pack and store the cartridges.

15.4.4.1 Determination of the Number of Cartridges to be Loaded

15.4.4.1.1 Obtain a copy of the field sampling schedule from the Monitoring Coordinator or Program Manager.

15.4.4.1.2 Determine the number of deuterated standards and external standards required to satisfy the sampling objectives.

15.4.4.2 Selection of the Permeation Tubes

15.4.4.2.1 Check the permeation notebooks (located in the laboratory) to see which permeation tubes are available for the needed standards.

15.4.4.2.2 Select only the permeation tubes whose permeation rates are stable.

Note: A permeation rate is considered stable when the mean permeation rate has a coefficient of variation (CV) of less than 10%. The mean permeation rate is calculated using the last five individual permeation rates. Do not use permeation tubes with permeation rates below 100 ng/min or above 1 x 10^5 ng/min.

15.4.4.2.3 In a bound notebook assigned for the specific project, prepare a table including: 1) the numbers of the tubes to be used, 2) the names of the compounds, and 3) the corresponding mean permeation rates.

15.4.4.3 Determination of the Permeation System Conditions

15.4.4.3.1 For any compound, calculate the amounts needed to be loaded onto a Tenax® cartridge using the following formula:

$$G = (P)(t)[F_1/(F_1 + F_2)]$$

where:
G = amount loaded of compound onto Tenax® tube, ng
P = permeation rate of specific compound, ng/min
t = total time of loading of compound onto Tenax® tube, minutes
F_1 = flow rate through the Tenax® cartridge, mL/min
F_2 = exhaust flow rate, mL/min
Note: The four variables G, t, F_1, and F_2 determine the loading conditions. Any three may be fixed and the fourth one calculated from the equation.

15.4.4.3.2 The following restrictions must be followed to minimize error: 1) do not load for less than two minutes, 2) do not load with a cartridge flow below 50 mL/min or above 150 mL/min, 3) do not operate the system with a total flow below 250 mL/min.

15.4.4.3.3 If the GC-MS-DS system needs to operate in the range of 200-500 ng per analyte, then the analyst must generate standards concurrent with that range. Fixing three of the four variables of the above equation will enable calculation of the needed loading onto the Tenax® tube.

15.4.4.3.4 As an example, the following calculations are provided to assist the user in determining operating parameters of the permeation tube system in generating standards on QA/QC checks.

OBJECTIVE: To load chlorobenzene and chloroform onto a cartridge in the range of 200-500 per analyte.

GIVEN: G = 200 ng per analyte
F_1 = 80 mL/min
t = 4 min
P = 270 ng/min for chlorobenzene
= 520 ng/min for chloroform

Chlorobenzene

$$G = (P)(t)[F_1/(F_1+F_2)]$$

$$200 \text{ ng} = (270 \text{ ng/min})(4 \text{ min})[(80 \text{ mL/min})/(80 \text{ mL/min} + F_2)]$$

$$F_2 = \{[(270 \text{ ng/min})(4 \text{ min})(80 \text{ mL/min})]/200 \text{ ng}\} - 80 \text{ mL/min}$$

$$F_2 = 352 \text{ mL/min}$$

Now, since all tubes are in the permeation device together, the flow (F_2) for chloroform will be 352 mL/min. Therefore, the loading on the Tenax® tube for chloroform must be calculated to verify that it falls within the 200-500 ng per tube loading.

Chloroform

$$G = (P)(t)[F_1/(F_1 + F_2)]$$

$$G = (520 \text{ ng/min})(4 \text{ min})[(80 \text{ mL/min})/(80 \text{ mL/min} + 352 \text{ mL/min})]$$

$$G = 385 \text{ ng}$$

All values obtained are within the acceptable range.

15.4.4.4 Equilibration of the Permeation System

15.4.4.4.1 Locate the chambers in which the selected permeation tubes are stored.

15.4.4.4.2 With a long glass hook, remove the selected permeation tubes from the storage chamber and transfer immediately to the loading chamber of the permeation system.

Note: Failure to wear nylon gloves when handling permeation tubes may result in skin damage and/or contamination of the permeation tubes.

Note: Perform this operation as quickly as possible. The tubes contain toxic materials, some of which are cancer suspect agents.

15.4.4.4.3 Direct nitrogen flow to the side where the Tenax® cartridge will be loaded.

Note: When a cartridge is not being loaded, a dummy cartridge is placed in the loading position.

15.4.4.4.4 Allow the system to equilibrate for 90 minutes before loading cartridges with the generated test atmospheres.

15.4.4.5 Loading of the Tenax® Cartridges

Note: Be sure the background of the Tenax® cartridges is acceptable before loading them.

15.4.4.5.1 Divert the nitrogen flow to the side that will not be used for loading cartridges.

15.4.4.5.2 Insert the Tenax® cartridge into the chamber.

15.4.4.5.3 Direct the test atmospheres gas flow through the cartridge.

15.4.4.5.4 Concurrently, start the stopwatch.

15.4.4.5.5 Calculate the time needed to load the amounts desired as follows:

$$t = (G/P) \times [(F_1 + F_2)/F_1]$$

Do the calculation based only on the compound whose permeation tube has the highest or lowest permeation rate.

15.4.4.5.6 At the calculated time rotate the two stopcocks to direct gas flow away from the cartridge being loaded.

15.4.4.5.7 Handling the cartridge with a Kimwipe®, remove the cartridge and return it to its culture tube. Seal the tube.

15.4.4.5.8 Label the tube. Include the following information: 1) project number, 2) deuterated standard mixture followed by a number indicating the order of loading, and 3) the date.

15.4.4.5.9 Prepare a Chain-of-Custody sheet with the information concerning amount loaded on the tube.

15.4.4.6 Storage of the Deuterated Standard Cartridges

15.4.4.6.1 Secure the cartridge inside the Kimax® tube with a glass wool plug to avoid breakage during transport.

15.4.4.6.2 Label the top of the screw cap with the following symbol: D*.

Note: * The star indicates that deuterated standards have been loaded onto the cartridge. This symbol will also be added to the participant's code.

15.4.4.6.3 Store the cartridges in a sealed paint can in the freezer until they are ready to be sent to the field.

15.4.4.7 Calculations of the Amounts Loaded

15.4.4.7.1 For every compound, calculate the amount loaded onto a cartridge using the general formula:

$$G = (P)(t)[F_1/(F_1 + F_2)]$$

15.4.4.7.2 Deliver the loaded permeation tubes to the GC-MS-DS for use in the quality assurance program.

16. Calibration of Personal Sampling Pump

16.1 The pump is calibrated so the flow controller is set at the desired sampling rate at standard conditions for the Tenax® sorbent sampling tube.

16.2 Sampling pumps are calibrated at the beginning and at the conclusion of each sampling period. To ensure quality volumetric results, pump calibration is recommended at random points throughout each study.

16.3 Assemble the personal sampling pump calibration system (see Figure 19). Connect a soap-film flowmeter of suitable volume (typically 1 liter) with Tygon tubing to the back-end of the active sampler, as illustrated in Figure 19.

Note: With higher sampling rates, a considerable pressure drop through the tube can result. To minimize this effect, a larger capacity pump would be necessary for higher sampling rates (i.e., >5 L/min).

16.4 Record the barometric pressure and ambient temperature on the sampling data sheet.

16.5 Thoroughly wet the surface of the flowmeter before any measurements are recorded. Measure the time for a soap-film bubble to travel a known volume with a stopwatch. Perform five replicate measurements and compute the average time. Calculate the standard volume (V_S) in liters from the equation:

$$V_S = (V_a \times P_b \times 298)/[(T + 273) \times 760]$$

where:
V_S = volume corrected to standard conditions of 298°K and 760 torr, L
V_a = actual volume measured with the soap-film flowmeter, L
T = temperature at calibration, °C
P_b = barometric pressure at calibration, torr
760 = standard pressure, torr
298 = standard temperature, °K

16.6 The standard flow rate (Q_S) is then calculated with the equation:

$$Q_S = V_S/R$$

where:
Q_S = standard flow rate, L/min
V_S = volume corrected to standard conditions, L
R = average time obtained from soap-film measurement, minutes

16.7 Once the flow has been set, record calibration date in laboratory logbook.
Note: Set flow rate of pump and indicate flow rate on a sticker attached to the pump.

17. Performance Criteria and Quality Assurance

17.1 This section summarizes quality assurance (QA) measure and provides guidance concerning performance criteria which should be achieved within each laboratory. In many cases the specific QA procedures have been described within the appropriate sections of this protocol. Figure 20 summarizes these performance criteria discussed in this protocol.

17.2 Standard Operating Procedures (SOPs)

17.2.1 Each user should generate SOPs describing the following activities as they are performed in their laboratory: 1) assembly, calibration, and operation of the sampling system, 2) preparation, handling and storage of Tenax® cartridges, 3) assembly and operation of GC-MS system including the thermal desorption apparatus and data system, and 4) all aspects of data recording and processing.

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

17.3 Tenax® Cartridge Preparation

17.3.1 Each batch of Tenax® cartridges prepared should be checked for contamination by analyzing one cartridge immediately after preparation. While analysis can be

accomplished by GC-MS, many laboratories may choose to use GC-FID due to logistical and cost considerations.

17.3.2 Analysis by GC-FID is accomplished as described for GC-MS except for use of FID detection.

17.3.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria the entire lot should be rejected.

17.4 Sample Collection

17.4.1 During each sampling event at least 10% of all field samples should accompany the samples to the field and back to the laboratory, without being used for sampling, to serve as a field blank. The average amount of material found on the field blank cartridge may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data for that component must be identified as suspect.

17.4.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) will be collected, preferably at different flow rates. If agreement between parallel samples is not generally within ± 25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples one should consider using a reduced flow rate and longer sampling interval if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest may be required.

17.4.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 20% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater. The frequency of use of backup cartridges should be increased if increased flow rate is shown to yield reduced component levels for parallel sampling. This practice will help to identify problems arising from breakthrough of the component of interest during sampling.

17.5 GC-MS Analysis

17.5.1 Performance criteria for MS tuning and mass calibration have been discussed. Additional criteria may be used by the laboratory if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC-MS system.

17.5.2 Chromatographic efficiency should be evaluated using spiked Tenax® cartridges since this practice tests the entire system. In general, a reference compound such as perfluorotoluene should be spiked onto a cartridge at the 100 nanogram level. The cartridge is then analyzed by GC-MS. The perfluorotoluene (or other reference compound)

peak is then plotted on an expanded time scale so that its width at 10% of the peak can be calculated. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The asymmetry factor should be between 0.8 and 2.0. The asymmetry factor for any polar or reactive compound should be determined using the process described above. If peaks are observed that exceed the peak width or asymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings and is necessary. Some laboratories may choose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature. Such schemes cannot be conducted by placing the substances onto Tenax® because many of the compounds (e.g., acids, bases, alcohols) contained in the test mix are not retained, or degrade, on Tenax®.

17.5.3 The system detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where:

DL = calculated detection limit injected, ng
A = the intercept of the slope
S = the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required)

In general, the detection limit should be 20 nanograms or less and for many applications detection limits of 1-5 nanograms may be required. The lowest level standard should yield a signal to noise ratio, from the total ion current response, of approximately 5.

17.5.4 The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation should be 25% or less.

17.5.5 A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present in ambient air (e.g., perfluorotoluene). The integrated ion intensity for this compound helps to identify problems with a specific sample. In general the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any sample giving a value greater than ±2 standard deviations from the mean (calculated excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

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Table 1. Compounds Identified and Quantified by Automated GC-MS-DS Procedure with Typical Detection Limits in Full Scan Mode

Compound	Quantitation Mass (m/z)	Detection Limits (ng)
perfluorotoluene (internal standard)*	217	0.3
benzene*	78	2.6
methylbenzene*	91	2.0
1,2-dimethylbenzene*	106	0.5
1,3,5-trimethylbenzene	120	2.5
ethylbenzene*	91	1.6
ethylbenzene*	104	1.7
(1-methylethyl) benzene	105	1.1
butylbenzene	91	0.7
1-methyl-4-(1-methylethyl) benzene	119	4.0
chlorobenzene*	112	1.7
bromobenzene	156	14.1
1,2-dichlorobenzene*	146	12.4
1-ethenyl-4-chlorobenzene	138	2.0
trichloromethane	83	2.7
tetrachloromethane*	82	2.1
bromochloromethane*	130	2.1
bromotrichloromethane*	163	1.6
dibromomethane*	174	4.5
tribromomethane*	171	8.5
1,1-dichloroethane*	63	5.7
1,2-dichloroethane	62	3.8
1,1,1-trichloroethane*	99	1.7
1,1,2-trichloroethane*	85	2.1
1,1,1,2-tetrachloroethane	31	0.9
1,1,2,2-tetrachloroethane	83	6.5
pentachloroethane*	167	1.8
1,1-dichloroethane*	961	6.9
trichloroethene*	132	0.8
tetrachloroethene	166	2.6
bromoethane*	108	7.8
1,2-dibromoethane*	107	3.3
1-chloropropane*	42	1.7
2-chloropropane*	43	3.4
1,2-dichloropropane	63	4.0
1,3-dichloropropane	76	9.6
1,2,3-trichloropropane	753	4.7
1-bromo-3-chloropropane	158	1.6
3-chloro-1-propene	41	1.6

Table 1 (cont'd)

Compound	Quantitation Mass (m/z)	Detection Limits (ng)
1,2-dibromopropane*	121	14.4
2-chlorobutane	57	3.5
1,3-dichlorobutane	55	0.5
1,4-dichlorobutane	55	8.2
2-3-dichlorobutane*	90	5.1
1,4-dichloro-2-butane (cis)	752	1.9
3,4-dichloro-1-butane	75	6.5
tetrahydrofuran	72	1.2
1,4-dioxane	88	3.9
1-chloro-2,3-epoxypropane	71	8.1
2-chloroethoxyethene	631	8.2
benzaldehyde*	77	5.9
acetophenone	105	2.9
benzonitrile	103	1.3
ISOMER GROUPS		
1,3- & OR 1,4-dimethylbenzene	106	0.5
1,2- & OR 1,3-dichlorobenzene*	146	1.3
2- & OR 3- & OR 4-chloro-1-methylbenzene*	126	0.5
SURROGATE GROUPS AND INTERNAL STANDARDS		
4-bromofluorobenzene (BFB)	95	
chlorobenzene-d_5	117	
1,4-dichlorobenzene	150	
1,4-difluorobenzene	114	

* Compounds used to calibrate GC-MS-DS on a daily basis either by direct injection or on spiked adsorbent tubes.

Table[a] 2. Breakthrough Volumes[b] and Safe Sampling Volumes[b] for Tenax-GC and Tenax-TA

	Tenax-GC breakthrough volume[b]	Tenax-TA breakthrough volume[b]		Tenax-GC safe sampling volume[c]	Tenax-TA safe sampling volume[c]	
	38°C	20°C	35°C	38°C	20°C	35°C
Acetaldehyde	0.6	0.6	0	0.3	<1	<1
Acrolein	4	5	2	1.7	2	<1
Acrylonitrile	-	8	3	-	3	1
Allyl chloride	-	8	3	-	3	1
Benzene	19	36	15	8.2	14	6
Benzyl chloride	300	440	200	130	175	80
Bromobenzene	300			130		
Carbon tetrachloride	8	27	13	3.5	11	5
Chlorobenzene	150	184	75	6.5	5	2
Chloroform	8	13	5	4	5	2
Chloroprene	-	26	12	-	10	5
Cresol	440	570	240	191	230	95
p-Dichlorobenzene	510	820	330	221	290	130
1,4-Dioxane	-	58	24	87	23	10
Ethylene dibromide	60	77	35	26	30	14
Ethylene dichloride	-	29	12	-	12	5
Ethylene oxide	-	0.5	0.3	-	<1	<1
Formaldehyde	-	0.6	0.2	-	<1	<1
Hexachlorocyclo-pentadiene	-	2000	900	-	800	360
Methyl bromide	0.8	0.8	0.4	0.4	<1	<1
Methyl chloroform	-	9	4	-	3	2
Methylene chloride	3	5	2	1.5	2	<1
Nitrobenzene	-	520	240	-	200	95
Perchloroethylene	-	100	45	-	40	18
Phenol	-	300	140	-	120	55
Propylene oxide	3	3	1	1.5	1	<1
Trichloroethylene	21	45	17	8.5	18	7
Vinyl chloride	0.6	.06	.03	.03	<1	<1
Vinylidene chloride	-	4	2	-	2	<1
Xylene	200	177	79	89	70	32

[a]See Section 18, reference 58.
[b]Breakthrough volumes expressed as liters/gram of sorbent.
[c]Safe sampling volume = {[Breakthrough volume (L/g)]/1.5} x 0.65 grams of sorbent.
[d]Breakthrough volumes for other chemicals can be extrapolated on the basis of boiling points for chemicals in the same chemical class.

Table 3. Commercially Available Thermal Desorption Units

Company	Address	Number	Model Comments
Tekmar Co.	PO Box 371856 Cincinnati, OH 45222-1856 (800) 543-4461	5010GT	1. 1/4 or 5/8 in. tubes 3 to 7-inches long, glass or metal. 2. Desorption temperatures to 420°C.
Nutech Corp.	2806 Cheek Rd. Durham, NC 27704 (919 682-0402	320	1. Uses glass sorbent tubes.
Chrompack	1130 Rt. 202 South Raritan, NJ 08869 (800) 526-3687	TCT	1. Desorption temperatures to 300°C. 2. 1/4-in. OD x 3.0 in.
Chemical Data Sys., Inc.	7000 Limestone Rd. Oxford, PA 19363 (215) 932-3636	330	1. Desorption temperature to 350°C. 2. 1/4-in. OD x 3-in. long or 1/2 in.
Perkin-Elmer	2772 N. Garey Ave. Pomona, CA 91767 (714) 593-3581	ATD-50	1. Desorption temperatures to 250°C. 2. 1/4-in. OD x 3-in. long tubes. 3. Up to 50 samples processed automatically.
Envirochem, Inc.	Box 180 Kemblesville, PA 19347 (212) 255-4474		1. Desorption temperatures to 300°C. 2. 6-mm OD x 11.5-cm long tubes.

Table 4. Typical Operating Conditions for a GC-MS-DS

Thermal Desorption Unit - NuTech Model 320 or Tekman Model 5000 or equivalent

Purge Gas	Helium @ 1.2 mL/min
Desorption Cycle	8 Minutes
Initial Desorption Temperature	25°C
Final Desorption Temperature	190°C
Thermal Desorption Unit Purge	10 mL/min

Gas Chromatography

Injection/Detector Temperature	200°C
Initial Column Temperature	30°C
Initial Hold Time	0.1 minutes
Program	4°C/min to 240°C
Final Hold Temperature	240°C
Final Hold Time	0.1 minutes
Maximum Over Temperature	245°C
Carrier Gas	Helium velocity 20 cm^3/sec at 250°C
GC-MS Interface	Direct coupling or glass jet
Sample Injection to MS	Direct Probe
Column	Hewlett-Packard OV-1 glass capillary crosslinked methyl silicone (50 m x 0.3 mm, 0.17 μm film thickness) Scientific Glass Engineering SE-30 glass capillary crosslinked methyl silicone (50 m x 0.5 mm, 0.80 μm film thickness)

Mass Spectrometer - Quadrupole Spectrometer, Electron Impact (EI)

Mass Range	35 to 320 amu
Scan Time	1 sec-10 min over entire range
EI Condition	70 eV
Mass Scan and Detector Mode	Follow manufacturer instruction for select mass selective detector (MS) and selected ion monitoring (SIM) mode
Routine Tuning	p-bromofluorobenzene
Preamp Sensitivity	10^{-7}
Emission Current	-0.45
Electron Multiplier Voltage	1000 to 1500
Mass Filter	10 amu/sec
Filter	x 100
Total Ion Current Sensitivity	1
Resolution	Normal
Display	TIC
Response	Fast

Table 5. Suggested BFB Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	15-40% of the base peak
75	30-60% of the base peak
95	base peak, 100% relative abundance
96	5-9% of the base peak
173	<2% of mass 174
174	>50% of the base peak
175	5-9% of mass 174
176	>95% but <101% of mass 174
177	5-9% of mass 176

Table 6. Target Compound List Used in Response Factor (RF) Determination with Specific Mass Loading onto Spiked Cartridge

Compound	ng Loaded
Benzene	304
Chloroform	114
1,1,1-Trichloroethane	174
Carbon Tetrachloride	201
1,2-Dichloroethane	329
Trichloroethylene	403
1,1,2,2-Tetrachloroethane	409
Chlorobenzene	140
Tetrachloroethylene	323
Ethylbenzene	346
p-Xylene	344
o-Xylene	352
Styrene	362
o-Dichlorobenzene	260
p-Dichlorobenzene	260
n-Octane	288
n-Decane	292
5-Nonanone*	328
Acetophenone*	411
2,6-Dimethylphenol*	294
2,6-Dimethylaniline*	391
1-Octanol*	330
Perfluorobenzene	125
Perfluorotoluene	130

*Used in the calculation of column performance parameters; not a target compound.

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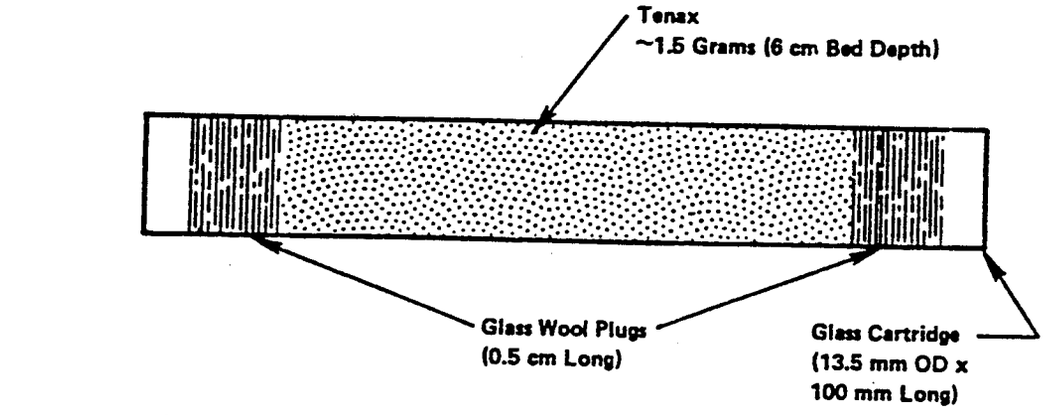
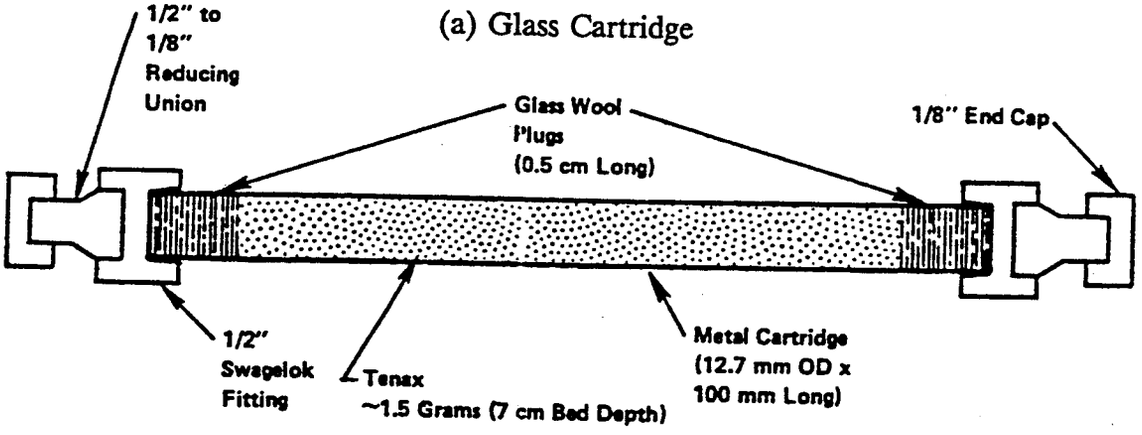
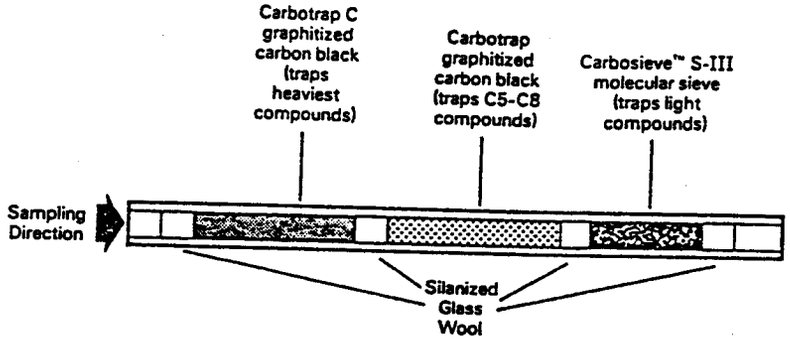


(a) Glass Cartridge

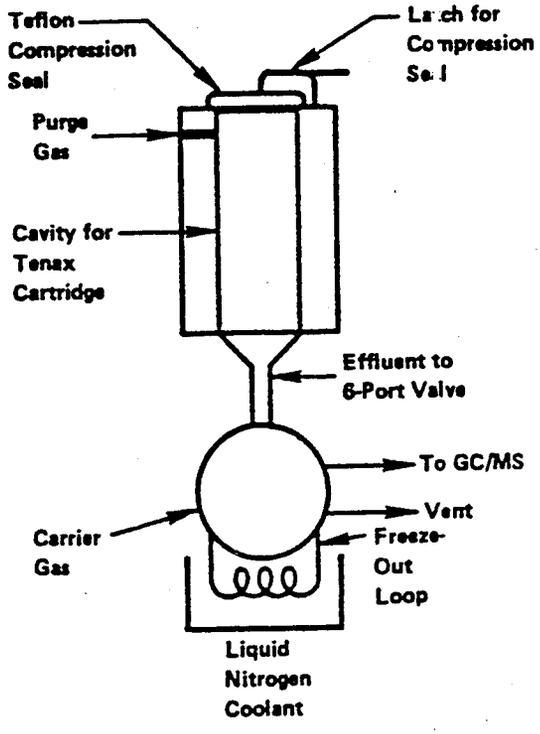


(b) Metal Cartridge

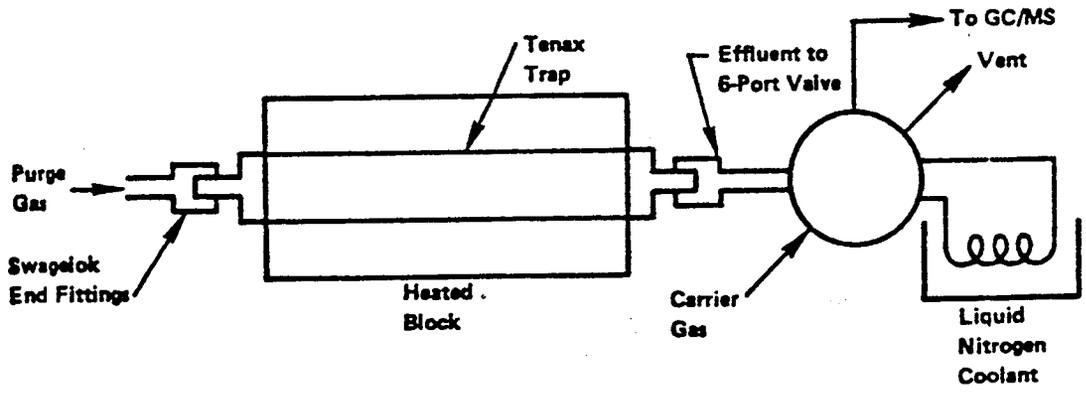


(c) Multibed Adsorbent Tube

Figure 1. Common Designs of Adsorbent Cartridges



(a) Glass Cartridges (Compression Fit)



(b) Metal Cartridges (Swagelok Fittings)

Figure 2. Tenax® Cartridge Desorption Modules

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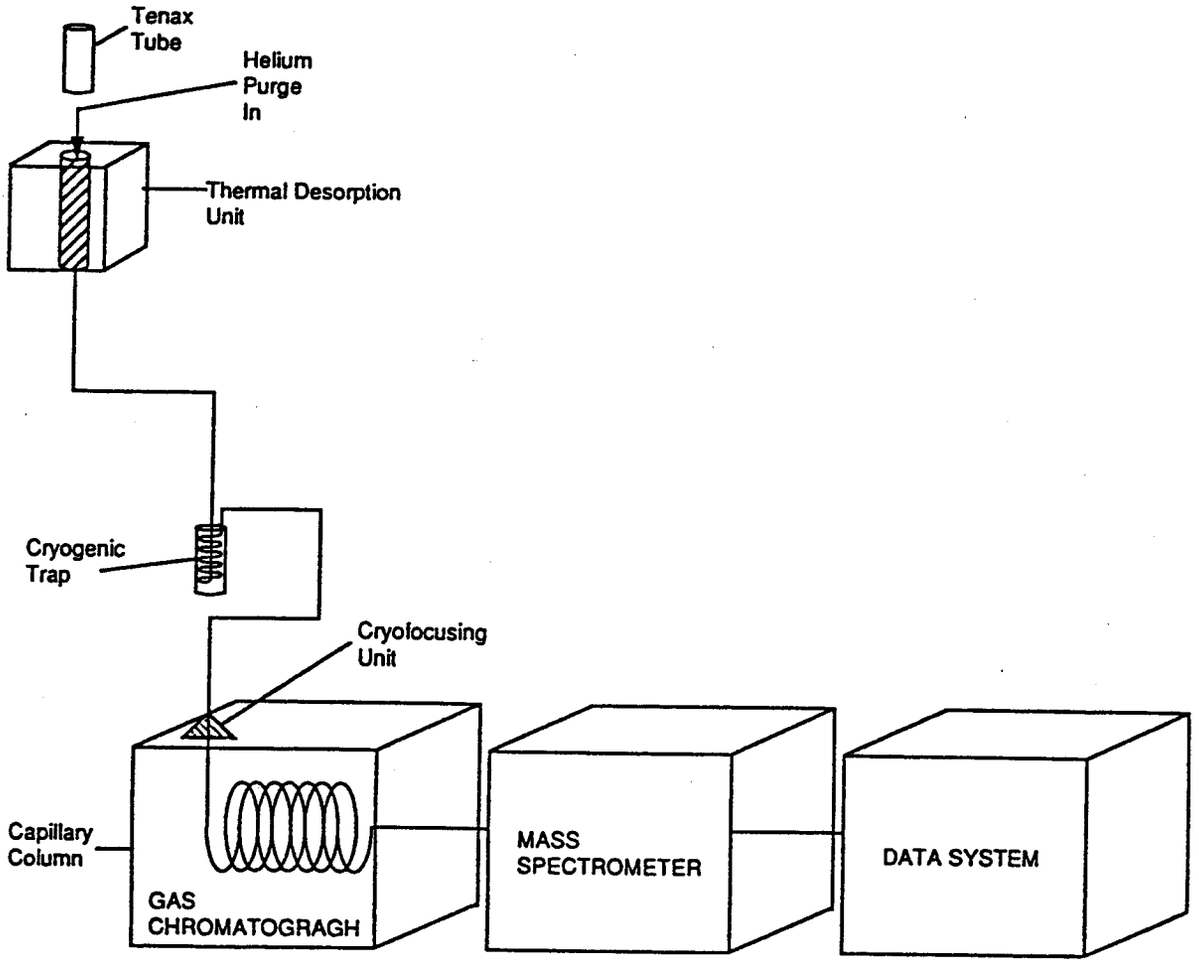

Figure 3. Typical Desorption GC-MS-DS Configuration

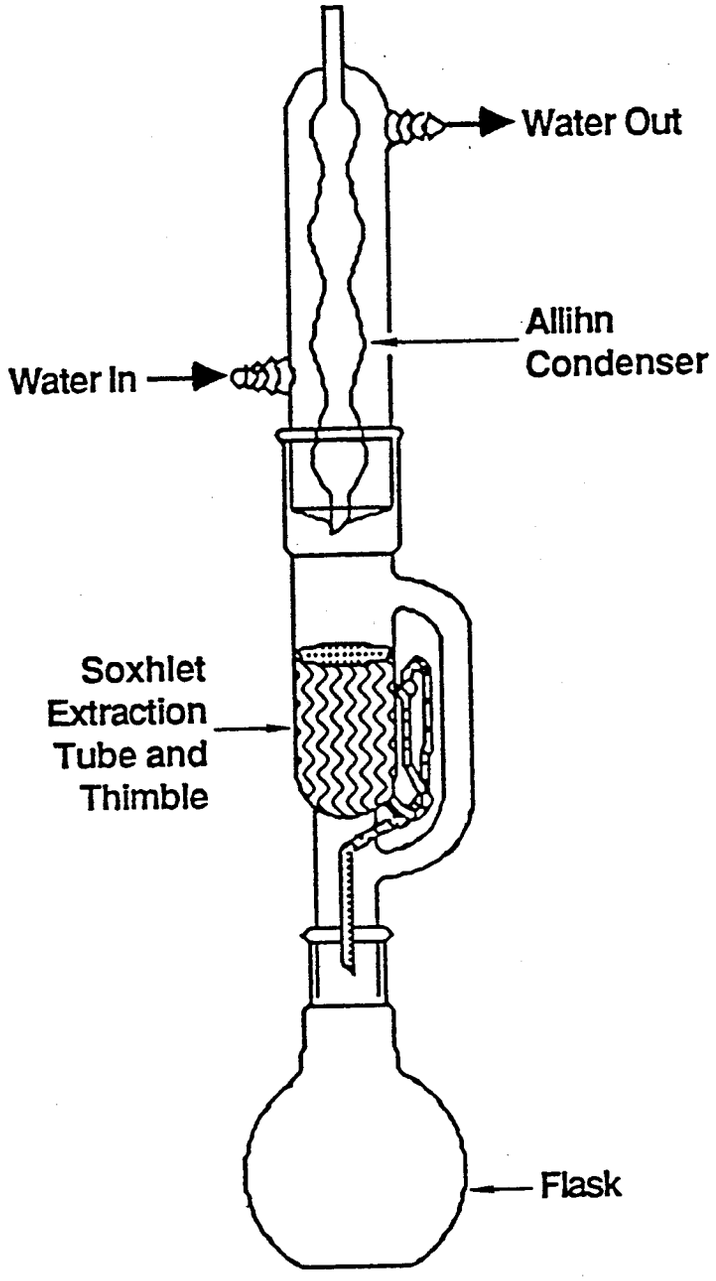

Figure 4. Soxhlet Extraction Apparatus with Allihn Condenser

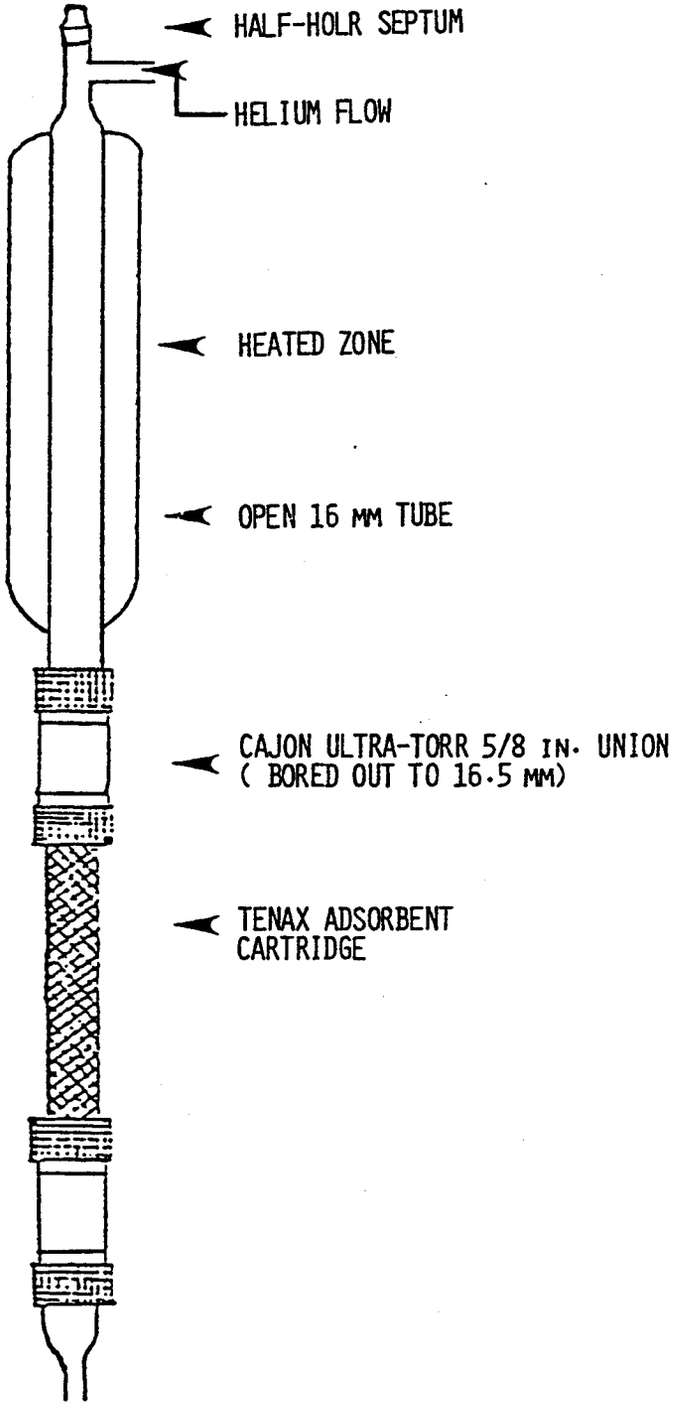

Figure 5. Flash Evaporation Unit

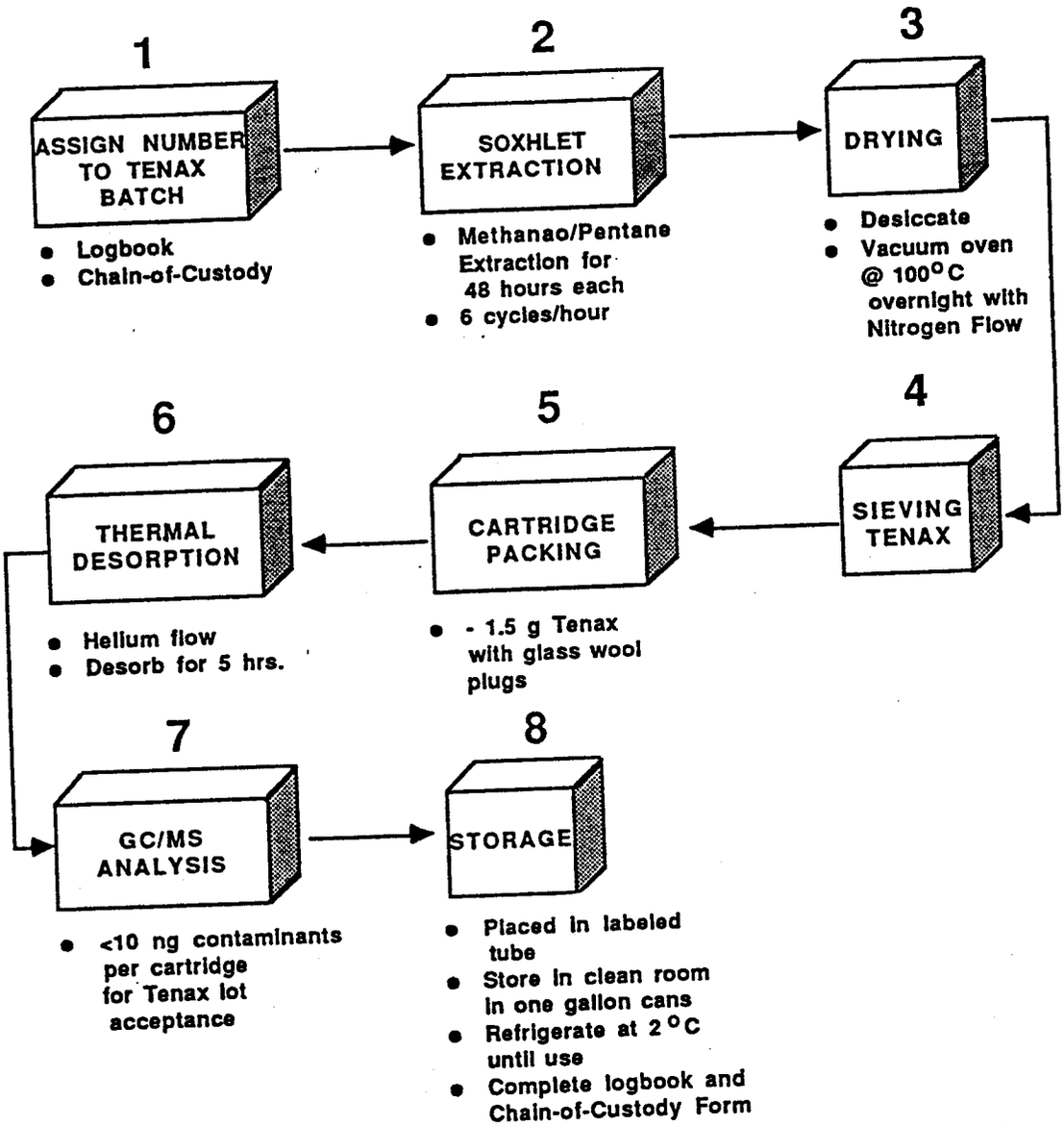

Figure 6. Tenax® Clean-Up Scheme

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TENAX CLEANUP WORKSHEET

Tenax Batch No. _____ Projected Use _____
Virgin/Recycled. Recycled Source _____ No. of Cartridges _____

Extraction

Number of Soxhlet Units (circle one): 1 2 3 4 5

Methanol Extraction: Date (Hours)

Siphon Rate

Pentane Extraction:

Date (Hours)

Siphon Rate

Drying

Nitrogen Chamber:

Date (Hours)

Approx. Flowrate

Vacuum Oven:

Date (Hours)

Pump Trap

Cooldown (Hours)

N_2 Vent Thru Act. C

Sieving/Packing

Sieve (40/60) Date:

Packing Date(s):

Cleanup

Teflon Septum; Date:

Teflon Liner; Date:

Figure 7. Tenax® Clean-Up Worksheet

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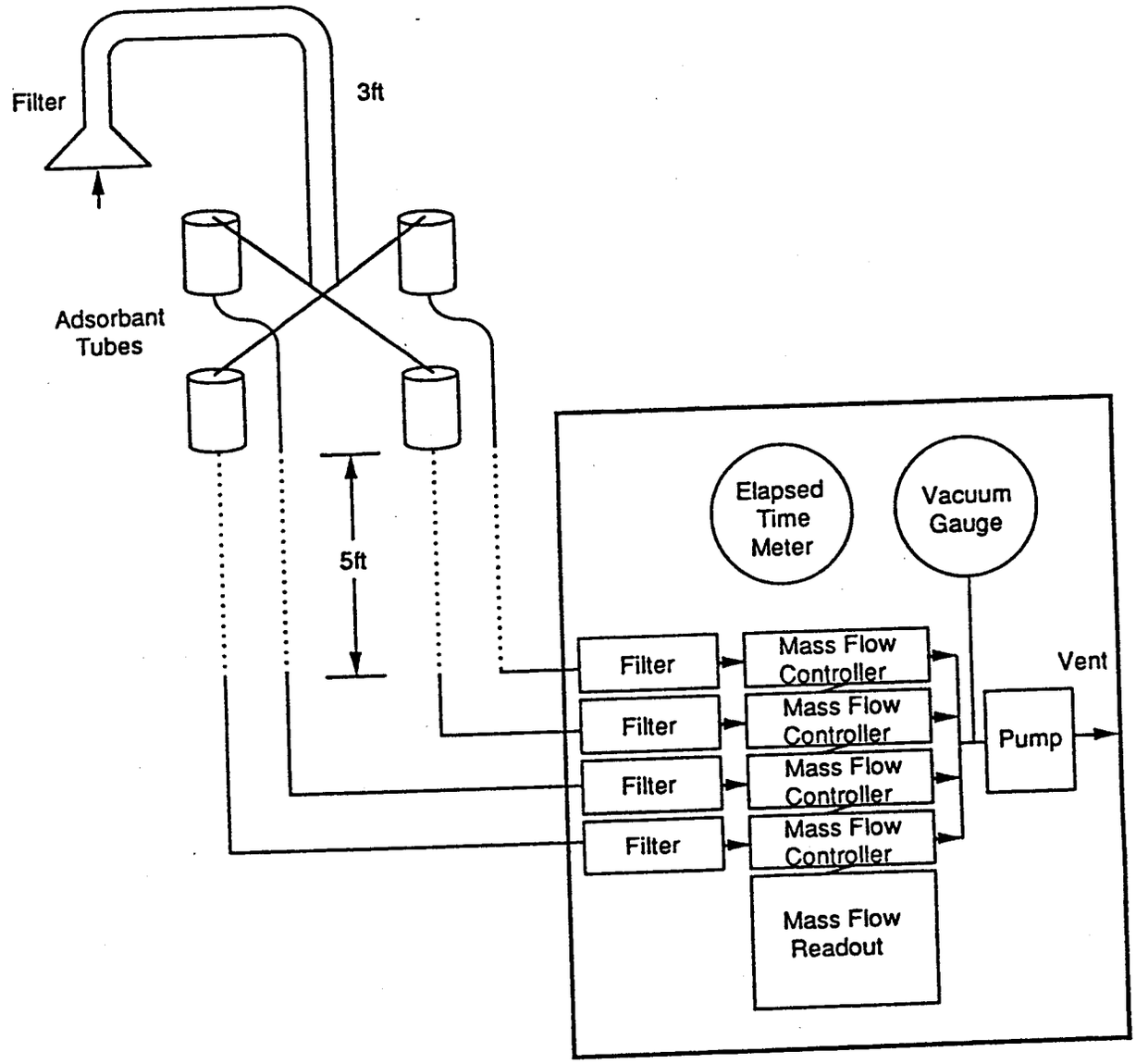


Figure 8. Flow Diagram for TAMS Toxic Air Sampler

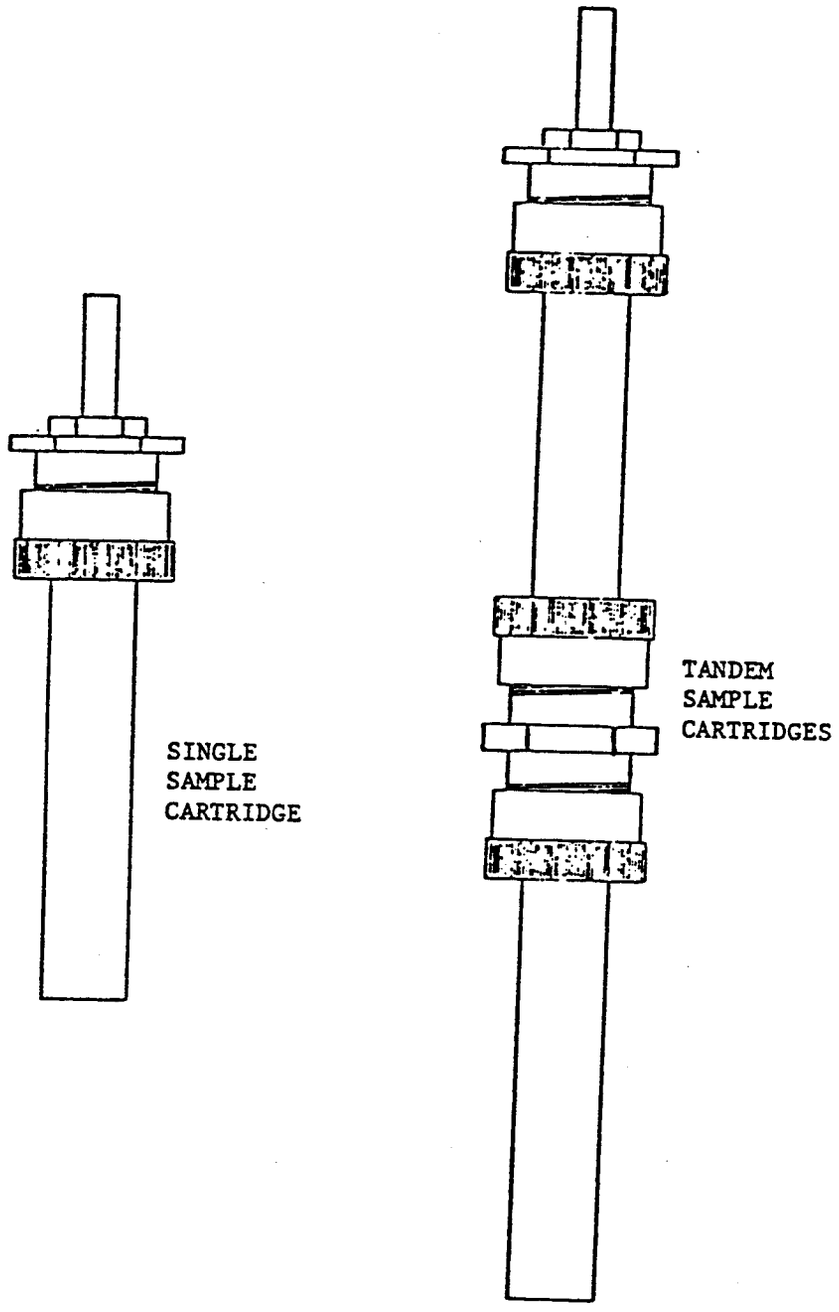
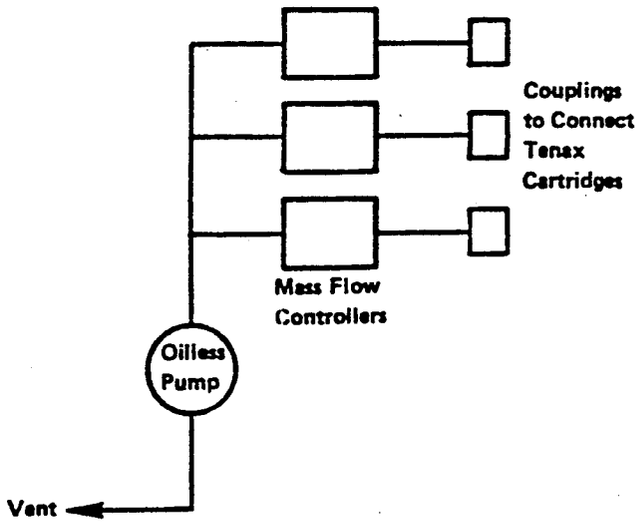
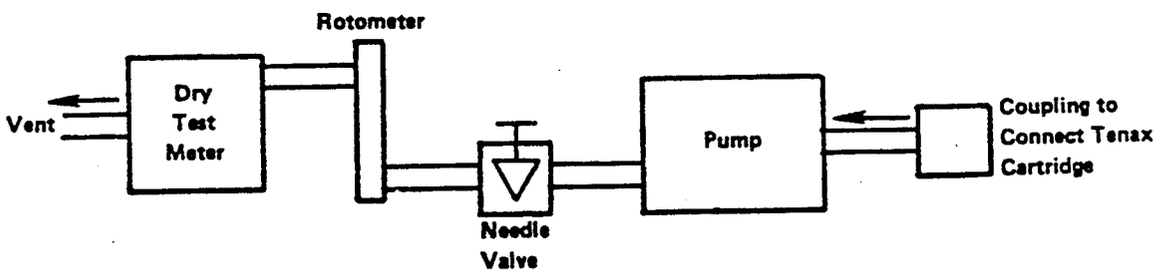


Figure 9. Single and Tandem Sample Cartridges



(a) Mass Flow Control



(b) Needle Valve Control

Figure 10. Typical Sampling System Configurations

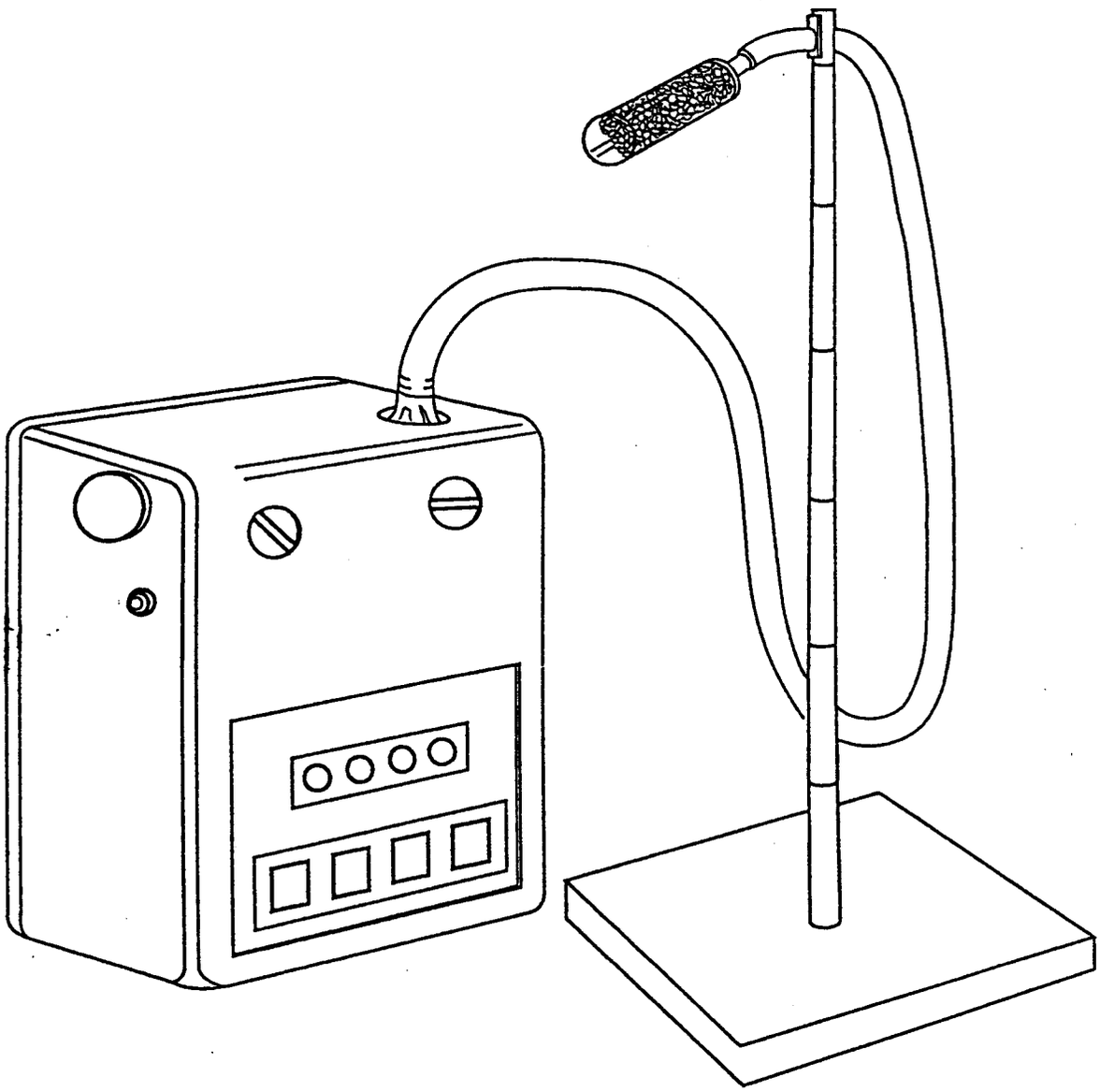


Figure 11. Adsorbent Cartridge Attached to Personal Pump

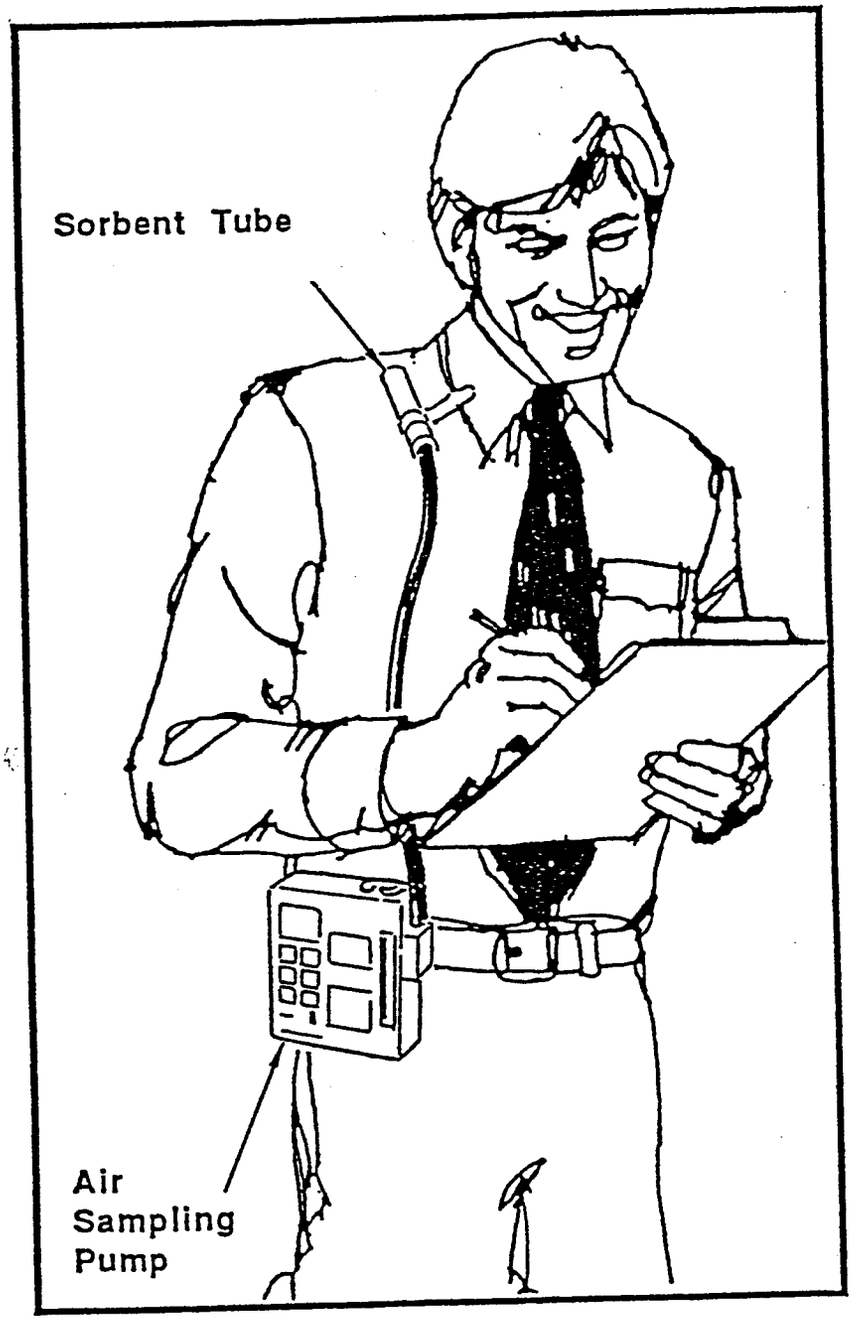


Figure 12. Personal Monitoring

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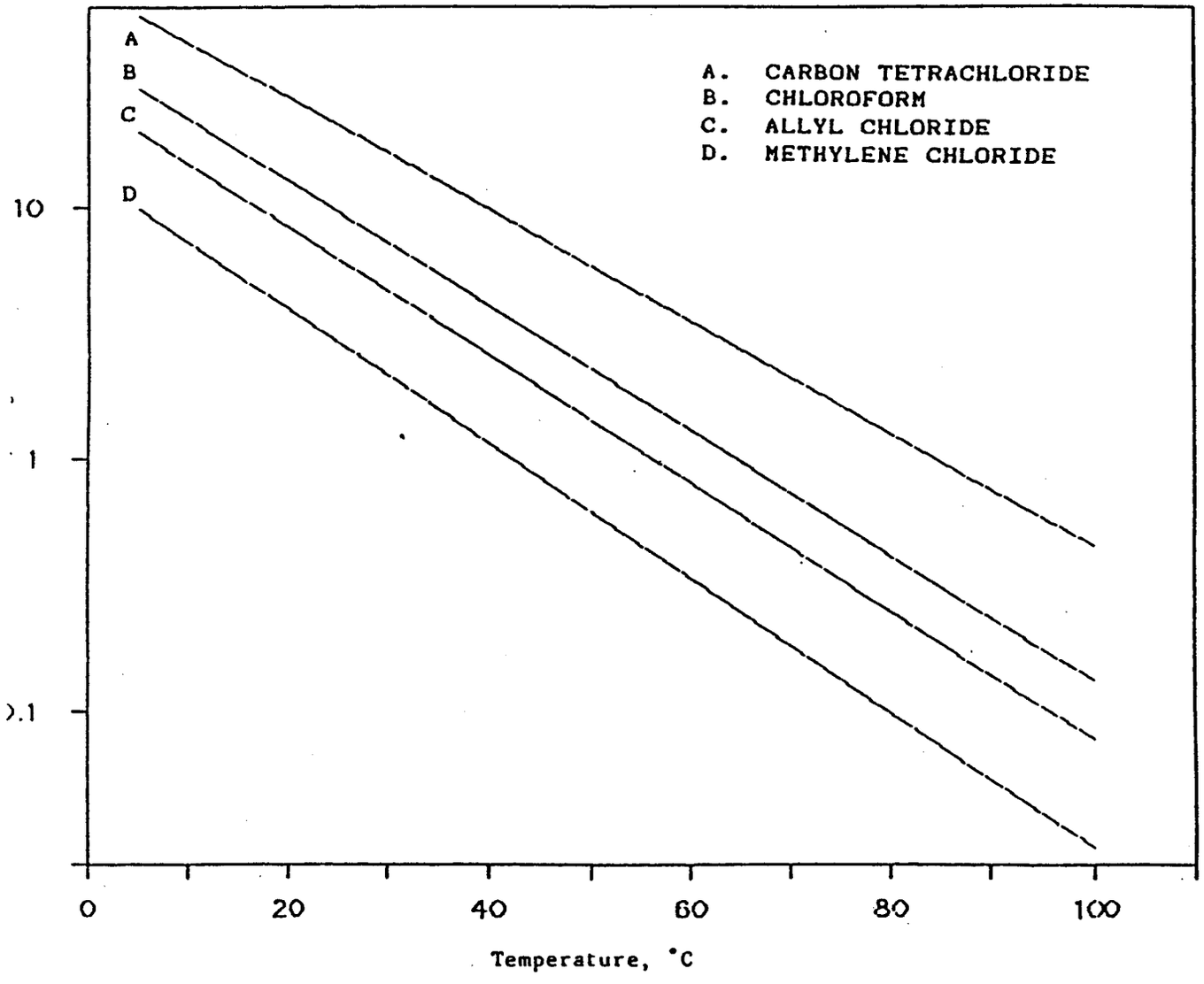

Figure 13. Breakthrough Curves for Carbon Tetrachloride, Chloroform, Allyl Chloride, and Methylene Chloride on Tenax®

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CHAIN-OF-CUSTODY FORM
(One Sample per Custody Sheet)

GENERAL:
Project: _____
Site: _____
Location: _____
Instrument Model #: _____
Pump Serial #: _____
Pump Calibration Date: _____
Sample Code: _____
Sample Type: _____

Date(s) Sampled: _____
Time Period Sampled: _____
Operator: _____
Calibrated by: _____
Breakthrough volume for most volatile compound: _____
Safe-sample volume for most volatile compound: _____

TENAX® DATA:
Tube #: _____
Batch #: _____
Certification Clean Date: _____

SAMPLING DATA:
Volume Collected: _____

TUBE HISTORY:

RELIN-QUISHED BY	REC'D BY	TIME	DATE	OPERATION PERFORMED

Figure 14. Chain-of-Custody Form

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FIELD SAMPLING DATA SHEET
(One Sample Per Data Sheet)

GENERAL:

PROJECT: _____
SITE: _____
LOCATION: _____
INSTRUMENT MODEL NO: _____
PUMP SERIAL NO: _____

PUMP CALIBRATION DATE: _____

DATE(S) SAMPLED: _____
TIME PERIOD SAMPLED: _____
OPERATOR: _____
CALIBRATED BY: _____
BREAKTHROUGH VOLUME FOR MOST VOLATILE COMPOUND: _____
SAFE-SAMPLE VOLUME FOR MOST VOLATILE COMPOUND: _____

TENAX® DATA:

TUBE NUMBER: _____
BATCH NUMBER: _____
CERTIFICATION CLEAN DATE: _____

SAMPLING DATA:

START TIME: _____ STOP TIME: _____

TIME	ROTAMETER READ	FLOW RATE (Q) mL/min	AMBIENT TEMPERATURE °C	BAROMETRIC PRESSURE mm Hg	RELATIVE HUMIDITY %	COMMENTS
1)						
2)						
3)						
4)						
5)						

TOTAL VOLUME DATA

$$V_m = \frac{Q_1 + Q_2 + Q_3 \ldots . Q_N}{N} \times \frac{1}{1000 \times (\text{sampling time in minutes})} = \_\_\_\_\_ \text{ L}$$

Flow rate from rotameter or soap bubble calibrator (specify which).

Figure 15. Field Sampling Data Sheet

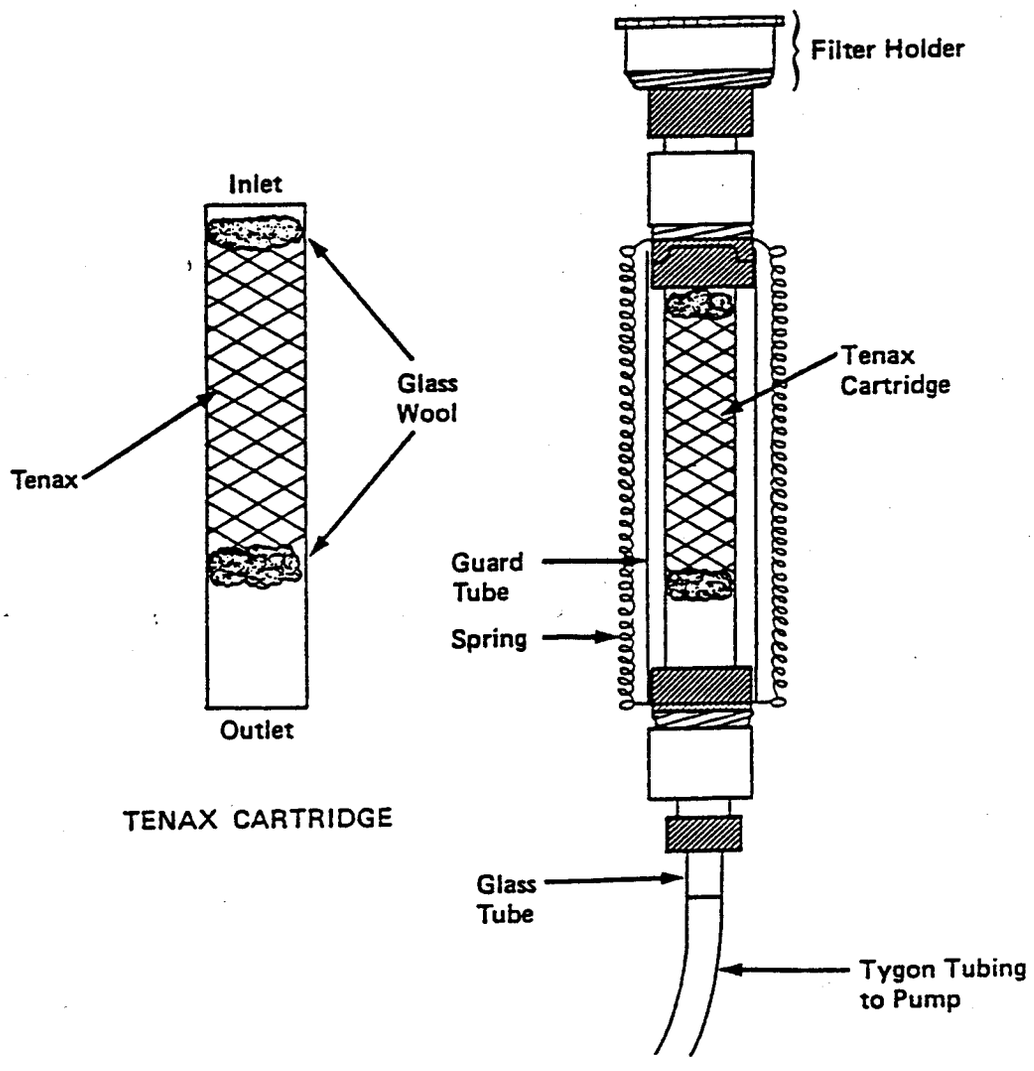

Figure 16. Optional Particulate Filter Assembly Attached to Adsorbent Cartridge

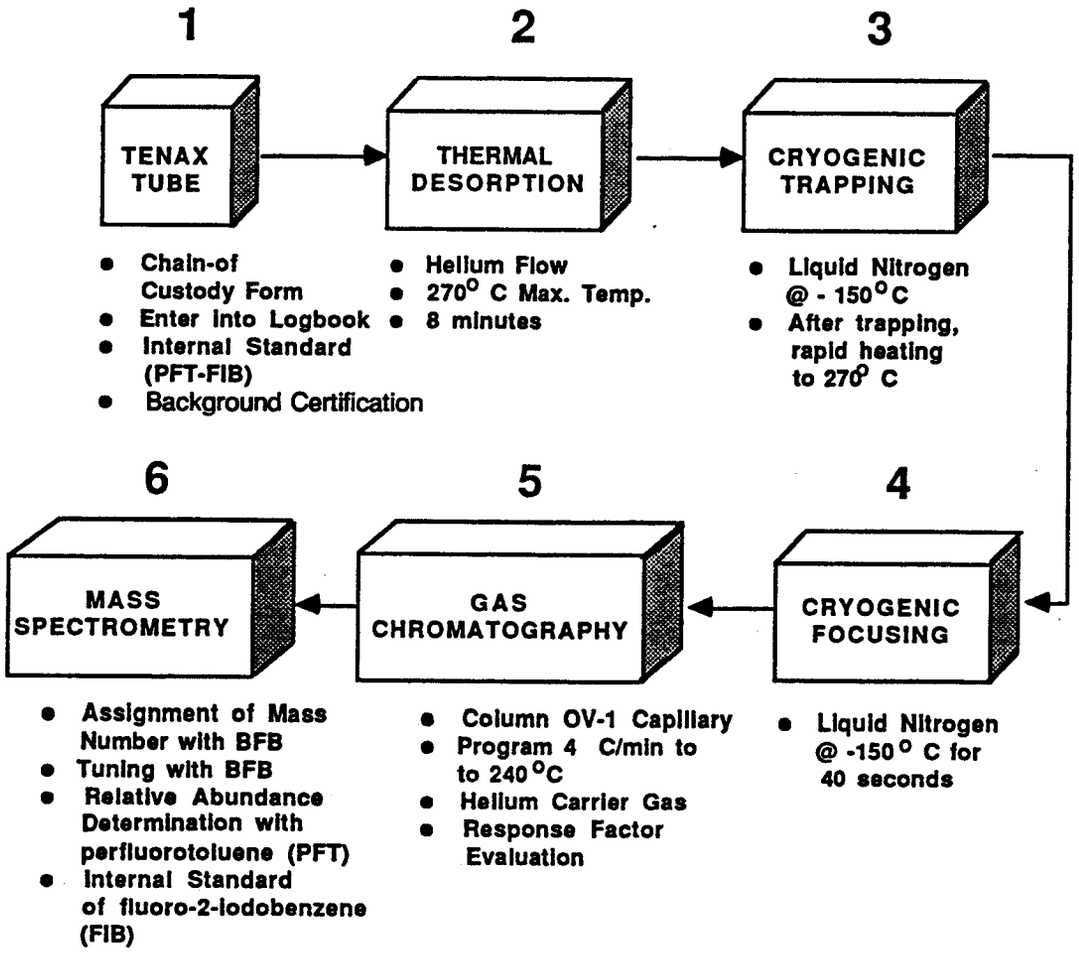

Figure 17. Specific Activities Associated with the GC-MS-DS

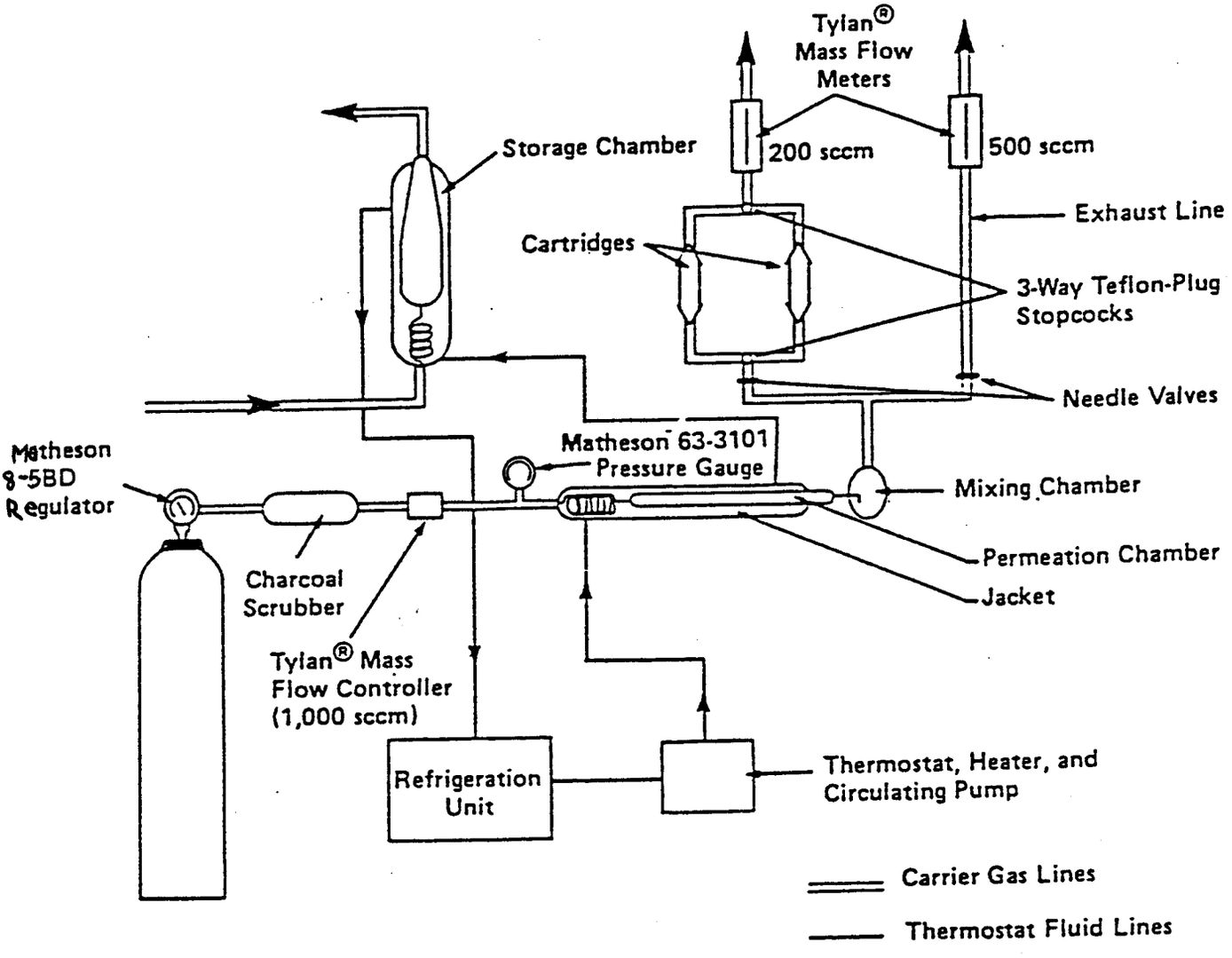

Figure 18. Permeation Tube System for Generating Standard Gas Atmospheres

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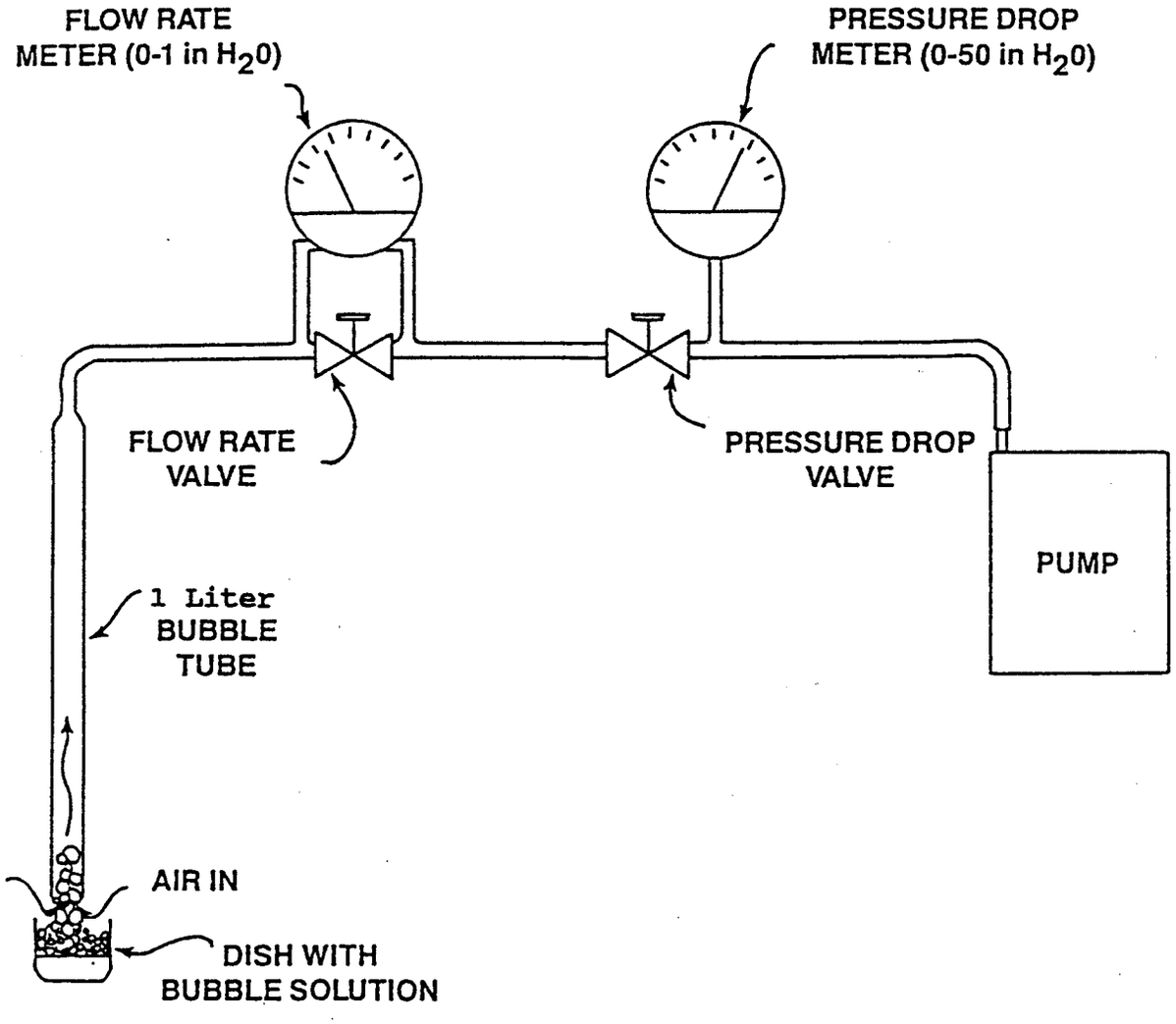

Figure 19. Calibration Assembly for Personal Sampling Pump

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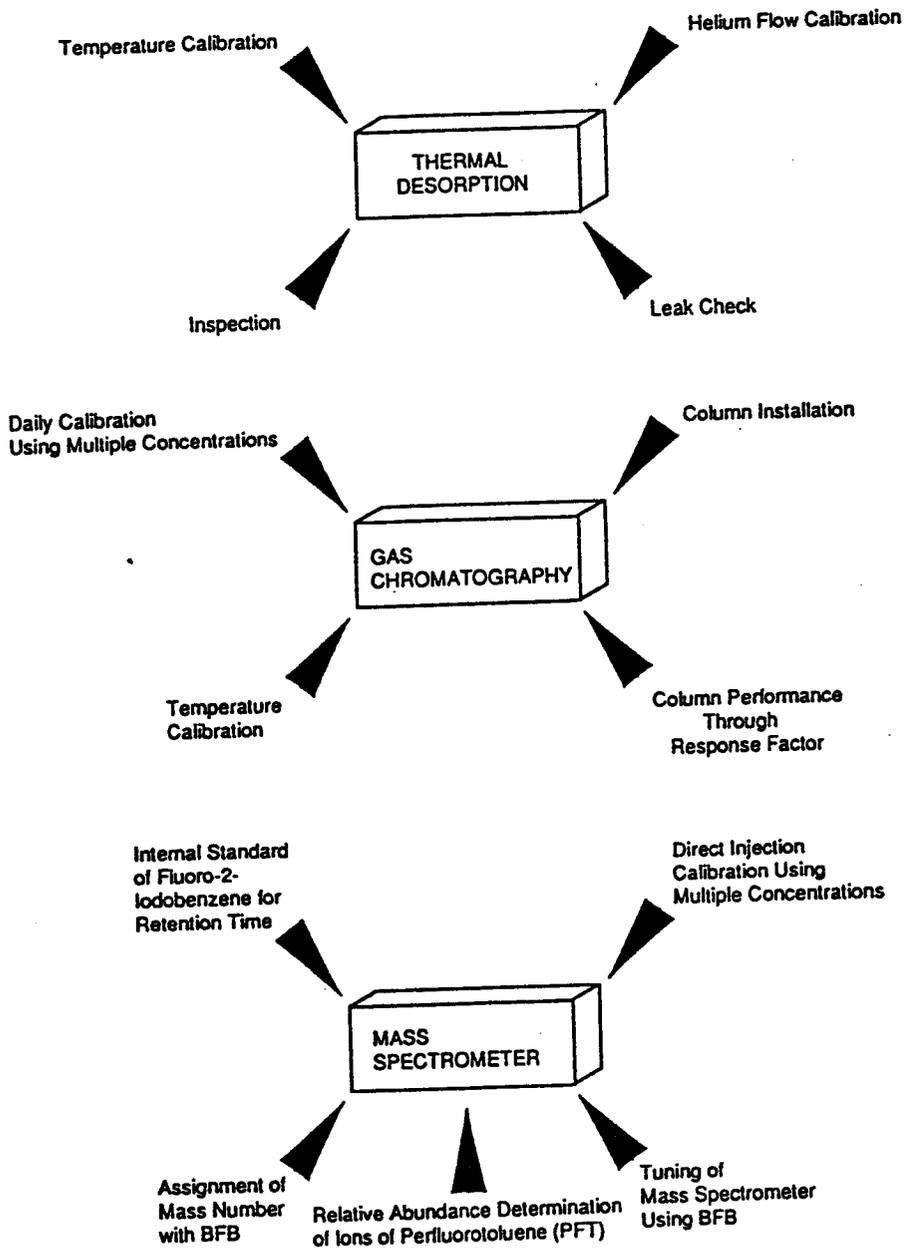

Figure 20. Performance Criteria Associated with the GC-MS-DS

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

1. Availability of Audit Cylinders

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

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

2. Audit Cylinder Certification

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

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

3. Audit Cylinder Acquisition

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

- RCRA Hazardous Waste Trial Burns For PHOC's; and
- Ambient/Indoor Air Measurement of Toxic Organics.

3.2 The audit cylinders may be acquired by contacting:

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

AVAILABLE USEPA PERFORMANCE AUDIT CYLINDERS

Group I Compounds

Carbon tetrachloride
Chloroform
Perchloroethylene
Vinyl chloride
Benzene

Group II Compounds

Trichloroethylene
1,2-dichloroethane
1,2-dibromoethane
Acetonitrile
Trichlorofluoromethane (Freon-11)
Dichlorodifluoromethane (Freon-12)
Bromomethane
Methyl ethyl ketone
1,1,1-trichloroethane

Group III Compounds

Pyridine (Pyridine in Group III cylinders but certified analysis not available)
Vinylidene chloride
1,1,2-trichloro-1,2,2 trifluoroethane (Freon-113)
1,2-dichloro-1,1,2,2 tetrafluoroethane (Freon-114)
Acetone
1-4 Dioxane
Toluene
Chlorobenzene

Group I Ranges

7 to 90 ppb
90 to 430 ppb
430 to 10,000 ppb

Group II Ranges

7 to 90 ppb
90 to 430 ppb

Group III Ranges

7 to 90 ppb
90 to 430 ppb

Group IV

Acrylonitrile
1,3-butadiene
Ethylene oxide
Methylene chloride
Propylene oxide
o-xylene

Group V

Carbon tetrachloride
Chloroform
Perchloroethylene
Vinyl chloride
Benzene
Trichloroethylene
1,2-dichloroethane
1,2-dibromoethane
1,1,1-trichloroethane

Methylene chloride
Trichlorofluoromethane (Freon-11)
Bromomethane
Toluene
Chlorobenzene
1,3-Butadiene
o-xylene
Ethyl benzene 1,2-dichloropropane

Group IV Ranges

7 to 90 ppb
430 to 10,000 ppb

Group V Ranges

1 to 40 ppb

Chapter IP-2

DETERMINATION OF NICOTINE IN INDOOR AIR

- **Method IP-2A - XAD-4 Sorbent Tubes**
- **Method IP-2B - Treated Filter Cassette**

1. Scope

This document describes two methods for sampling and analysis of nicotine in indoor air. The methods are based upon collection of nicotine by adsorption on a sorbent resin or acidic surface. Gas chromatographic separation with nitrogen-selective detection (NSD) is employed for analysis. Two active samplers and one passive sampler are described. The active samplers consist of an XAD-4 sorbent tube or a treated filter cassette attached to a personal sampling pump. The XAD-4 sorbent tube method is a modification of the NIOSH Method S293. The passive sampler consists of a modified treated filter cassette used in active sampling.

2. Applicability

2.1 Nicotine is the major alkaloid in tobacco. During cigarette smoking, burned tobacco emits nicotine to the atmosphere. In indoor environments, nicotine is found as a main constituent of environmental tobacco smoke (ETS). ETS is a mixture of exhaled cigarette smoke, smoke from the burning tip of a cigarette and smoke that diffuses to the air through the paper of a cigarette. Because nicotine is characteristic of ETS, it is frequently used as a marker for ETS.

2.2 Studies show that more than 90% of nicotine in indoor air is found in the vapor phase. However, the following methods quantify total nicotine from indoor air samples. The methods are not able to sample and analyze for the distinct phases of nicotine because particulate phase nicotine has the ability to volatilize after initial impact on a filter or other collection surface.

2.3 Concentrations of 1.8-83.0 $\mu g/m^3$ nicotine have been found in various indoor environments. Because such low concentrations of nicotine are encountered, sophisticated analytical procedures and equipment are used for determining nicotine in indoor air.

2.4 These methods are still under development, but have been tested in several field studies and laboratories. The active methods employ a personal sampling pump with a sorbent sampling tube or a treated filter cassette. The passive method employs a treated filter cassette. Analysis employs solvent extraction and GC/NSD determination. XAD-4 sorbent tubes are commercially available, enabling ease and uniformity in the sampling procedure. In addition, older model GCs (equipped with packed or Megabore® columns) can be adapted with a split/splitless injector to use with capillary columns.

Method IP-2A

DETERMINATION OF NICOTINE IN INDOOR AIR USING XAD-4 SORBENT TUBES

Method IP-2A

DETERMINATION OF NICOTINE IN INDOOR AIR USING XAD-4 SORBENT TUBES

1. Scope

1.1 This method describes a procedure for sampling and determination of nicotine in indoor air. The method is based upon collection of nicotine by adsorption on a sorbent resin. Gas chromatographic separation with nitrogen-selective detection is employed for analysis.

1.2 The active sampler consists of an XAD-4 sorbent tube (1-2) attached to a personal sampling pump. The XAD-4 sorbent tube method is a modification of the NIOSH Method S293 (3).

1.3 Nicotine is the major alkaloid in tobacco. During cigarette smoking, burned tobacco emits nicotine to the atmosphere. In indoor environments, nicotine is found as a main constituent of environmental tobacco smoke (ETS). ETS is a mixture of exhaled cigarette smoke, smoke from the burning tip of a cigarette and smoke that diffuses to the air through the paper of a cigarette. Because nicotine is characteristic of ETS, it is frequently used as a marker for ETS.

1.4 Studies show that more than 90% of nicotine in indoor air is found in the vapor phase (4,5). However, the following method quantifies total nicotine from indoor air samples. The method is not able to sample and analyze for the distinct phases of nicotine because particulate phase nicotine has the ability to volatilize after initial impact on a filter or other collection surface.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis
E260 Recommended Practice for General Gas Chromatography Procedures
E355 Practice for Gas Chromatography Terms and Relationships D4185 - Annex Procedure to Calibrate Small Volume Air Pumps

2.2 Other Documents

U.S. EPA Technical Assistance Document (6)
Laboratory and Ambient/Indoor Air Studies (7-12)
General Guidelines for Indoor Air Studies (13-15)

3. Summary of Method

3.1 An indoor air sample is collected using a personal sampling pump. The pump draws air at a rate of 1.0 L/min through a 7 cm long, 6 mm O.D., 4 mm I.D. glass tube containing XAD-4 sorbent as seen in Figure 1. The method has been evaluated for sampling periods from one to eight hours with a limit of detection of 0.17 $\mu g/m^3$ for a

one hour sample and 0.02 $\mu g/m^3$ for an eight hour sample (1). During sampling, vapor phase nicotine is adsorbed onto the sorbent.

3.2 For sample recovery, the XAD-4 is transferred to a sample vial where it is desorbed with ethyl acetate. The ethyl acetate is modified with 0.01% triethylamine to prevent adsorption of nicotine onto the glass walls of the sample vial.

3.3 Analysis employs a gas chromatograph (GC) equipped with a fused silica capillary column and a nitrogen-selective detector (NSD). The internal standard method of quantitation is used with quinoline serving as the internal standard. Figure 2 outlines the steps associated with the sampling/analysis of nicotine utilizing XAD-4 sorbent tubes.

4. Significance

4.1 Nicotine emissions result primarily from the combustion of tobacco, e.g., cigarette smoking. Nicotine is toxic when inhaled causing excessive stress to the circulatory and nervous systems and has been linked to increased susceptibility for developing cancer (16). Because smokers and nonsmokers are both exposed to ETS, accurate measurements of nicotine in indoor environments are important in assessing human health impacts as a marker for ETS (which contains other toxic compounds) and controlling indoor air pollution.

4.2 Concentrations of 1.8-83.0 $\mu g/m^3$ nicotine have been found in various indoor environments (17). Because such low concentrations of nicotine are encountered, sophisticated analytical procedures and equipment are used for determining nicotine in indoor air.

4.3 Method IP-2A is still under development, but has been tested in several field studies and laboratories (2,10,18). XAD-4 sorbent tubes are commercially available, enabling ease and uniformity in the sampling procedure. In addition, older model GCs (equipped with packed or column injectors) can be adapted for use with Megabore® columns or a GC equipped with a split/splitless injector to use with capillary columns.

4.4 The XAD-4 sorbent tube method described here is the approved Interim First Action Method of the Association of Official Analytical Chemists (AOAC).

5. Definitions

Note: Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D1356, E620, E355 and D4185. All pertinent abbreviations and symbols are defined within this document at point of use. Additional definitions, abbreviations, and symbols are located in Appendix A-1 and B-2 of this Compendium.

5.1 Autosampler - an automatic injection device whereby a mechanical syringe withdraws an aliquot of sample and injects the sample into the instrument for analysis.

5.2 Capillary column - small diameter open tube (typically fused silica) that is specially coated on the inner wall to enable separation of compounds in a GC. A polymer

coating allows the column to be coiled inside the GC oven, hence capillary columns can be of unlimited length (typically 15-60 m).

5.3 Coefficient of variation - a measure of precision calculated as the standard deviation of a series of values divided by their average. It is usually multiplied by 100 and expressed as a percentage.

5.4 Environmental tobacco smoke (ETS) - a composite of exhaled cigarette smoke, smoke from the tip of a burning cigarette and smoke which diffuses through the paper of the cigarette.

5.5 GC terminal - data system and strip chart recorder integrated with a GC. These components are available as a whole package with some GCs.

5.6 Nitrogen-selective detector (NSD) - a highly sensitive detector selective for detection of nitrogen and phosphorus, whereby the detector gas propagates surface ionization on an alkali-salt bead.

5.7 Personal sampling pump - pump with a capacity of 1-5 L/min sampling rate used in personal monitoring.

5.8 Split/splitless injector - a type of injector on a GC to enable sample to enter a capillary column.

6. Interferences

Using packed columns in GCs may result in readings lower than expected because nicotine can adsorb onto undeactivated glass, metal, and solid support particles. Using a fused silica capillary column and modified solvent prescribed here can circumvent this problem. The following describes potential problems that may occur with sample collection and analysis:

- calibration curves defined with a correlation coefficient below 0.990.
- sampling at levels below the sensitivity of the method.
- using glass columns (such as packed columns) in GCs may result in readings lower than expected because nicotine can adsorb onto glass. Using a fused silica capillary column and modified solvent prescribed here can circumvent this problem.
- spiking XAD-4 sorbent tubes with large volumes of nicotine solution when preparing blind samples can result in abnormally low nicotine concentrations because nicotine can adhere to the glass walls of the tube.
- incorrect identification and recording of retention times, nicotine peaks, and associated peak areas.
- neglecting to use consistent significant figures when constructing calibration curves and calculating nicotine content in samples.

7. Apparatus

7.1 Sampling System

7.1.1 XAD-4 sorbent tube sampler - glass tube with both ends flame-sealed, approximately 7 cm long with 6 mm outside diameter (O.D.) and 4 mm inside diameter (I.D.), containing two sections of 20/40 mesh XAD-4 resin (SKC, Inc., 334 Valley View Rd., Eighty Four, PA 15330-9614, Cat. No. 226-30-11-04, or equivalent; buyer should specify glass wool spacers instead of foam for nicotine sampling). The front section contains 80 mg of resin and the back-up section contains 40 mg of resin. A glass wool plug is located at each end of the tube and in between the front and back-up sections. The front plug is held in place with a metal lockspring as illustrated in Figure 1.

7.1.2 Tube holder with clip attachment - for attaching tube to clothing or objects (SKC, Inc., Cat. No. 224-28A, or equivalent).

7.1.3 Tube breaker/capper - to break sealed ends off sample tubes (SKC, Inc., Cat. No. 222-3-50, or equivalent).

7.1.4 NIOSH-approved plastic caps - for capping tubes after sampling.

7.1.5 Barometer, thermometer and stopwatch - for calibrating sampling pumps and taking pressure and temperature readings during sampling.

7.1.6 Personal sampling pump - calibrated for a flow rate of 1 L/min at standard conditions (SKC, Inc., Model No. 224, or equivalent).

7.1.7 Tubing - Tygon 1/4 inch I.D. to connect sampler to pump (SKC, Inc., Cat. No. 225-13-4, or equivalent).

7.2 Analytical System

7.2.1 Tool - for breaking open tubes (SKC, Inc. Cat. No. 222-3-50, or equivalent).

7.2.2 Glass cutter - for opening tubes, optional.

7.2.3 Vial-rack SKC, Inc., Cat. No. 226-04, or equivalent.

7.2.4 Vibrator - for solvent extraction (SKC, Inc., Cat. No. 226D-03, or equivalent).

7.2.5 Gas chromatograph with a nitrogen-selective detector and GC terminal with electronic peak integration and temperature programming capability (Hewlett-Packard, Rte. 41, Avondale, PA 19311, Model 5880A, or equivalent) and autosampler (Hewlett-Packard, Model 7673A, or equivalent).

7.2.6 GC column - either a 30 m x 0.53 mm I.D. fused silica capillary column, coated with a 1.5 um film of 5% phenyl methylpolysiloxane (DB-5) (J&W Scientific, Inc., 3781 Scientific Park Dr., Rancho Cordova, CA 95670, Cat. No. 125-5032) or a 30 m x 0.32 mm I.D. fused silica capillary column, coated with a 1.0 um film of DB-5 (J&W Scientific, Inc., 3781 Scientific Park Dr., Rancho Cordova, CA 95670, Cat. No. 1235033) or equivalent.

7.2.7 Sample containers - 2-mL autosampler vials with Teflon®-lined closures.

7.2.8 Dispensing pipets - 1.0 mL.

7.2.9 Volumetric flasks - 100 mL for making standard solutions.

7.2.10 Microliter syringes - 25, 50, 100 μL for making standard solutions.

7.2.11 Forceps - for transferring XAD-4 resin from tube to sample vial (SKC, Inc., 334 Valley View Road, Eighty Four, PA 15330, Cat. No. 225-15-1, or equivalent).

8. Reagents and Materials

8.1 Helium cylinders - for detector and/or carrier gas, 99.9995% grade.

8.2 Hydrogen cylinders - for detector gas, 99.9995% grade.

8.3 Air - for detector gas (<0.1 ppm hydrocarbon).

8.4 Volumetric flasks - 100 mL or convenient sizes for making internal standards.

8.5 Nicotine - reagent grade (Eastman Kodak Co., Dept. 412-L-236, 343 State St., Rochester, NY, Cat. No. 112 4973, or equivalent).

8.6 Quinoline (internal standard) >99% A.C.S. reagent, Gold Label (Aldrich Chemical Co., Inc., Dept. T, P.O. Box 355, Milwaukee, WI 53201, Cat. No. 25, 401-01, or equivalent).

8.7 Nicotine salicylate - reagent grade (Eastman Kodak Co., Dept. 412-L-236, 343 State St., Rochester, NY).

8.8 Ethyl acetate - chromatographic quality.

8.9 Triethylamine (solvent modifier) >99% Gold Label (Aldrich Chemical Co., Cat. No 23, 962-3, or equivalent).

8.10 Empty vials - to hold wastes from the wash-pump cycle on the GC autosampler or injection procedure.

9. System Description

9.1 Sampling System

9.1.1 The active sampling system consists of a sampler and personal sampling pump. In active sampling the pump draws a volume of air through either an XAD-4 sorbent tube or a treated filter cassette to adsorb any nicotine present.

9.1.2 The sampling systems are portable and can be used effectively in several setups. A sampling case resembling a briefcase is recommended for active sampling in public areas (7). A typical briefcase sampler is illustrated in Figure 3. Disguising the apparatus ensures unobtrusive sampling and reduces interferences caused by curious, smoking onlookers who may be encouraged to increase or decrease smoking upon seeing the sampling system.

9.1.3 Alternately, the active sampling systems can be attached to a person for personal monitoring. In this setup, the pump is attached to a belt and Tygon tubing connects the sampler to the pump. The sampler is then clipped onto clothing near the breathing zone. Figure 4(a) illustrates the briefcase sampler, while Figure 4(b) depicts the personal monitoring arrangement.

9.1.4 In a third setup, the active sampler may be located on a stationary surface for area monitoring in any indoor environment.

9.2 Analytical System

9.2.1 Analysis is performed using a GC equipped with an autosampler, a nitrogen-selective detector, and injectors equipped either for split/splitless injection (0.32 mm I.D.) or on-column/direct injection (0.53 mm I.D.). Recommended modes of injection are split (ratio 10:1) for 0.32 mm I.D. columns and direct for 0.53 mm I.D. columns.

9.2.2 The GC column is a fused silica capillary column (30 m x 0.53 mm or 0.32 mm I.D.) with a film of 1.5 or 1.0 μm DB-5, respectively.

9.2.3 Helium is the carrier gas.

9.2.4 Hydrogen and air are detector gases with helium as detector make-up gas.

9.2.5 The oven temperature is programmed from 150°C to 180°C at a rate of 5°C/min with a total run time of 6 minutes.

9.2.6 The autosampler uses default settings for the injection sequence. A 1 or 2 μL sample is injected for analysis.

9.2.7 Parameters concerning sample and injection integrity should include 5 prewashes with sample, 5 pumps with sample, and 10 postwashes with solvent.
Note: Settings for the GC analysis are summarized in Table 1.

10. Sampling Procedure

10.1 XAD-4 sampling tubes are prepared immediately before sampling. Both ends of the sealed sorbent tube are broken off using a tube breaker/capper tool. The opening should measure at least 2 mm in diameter.

10.2 The back-up section of the XAD-4 sorbent tube is positioned near the pump and connected to the pump with Tygon tubing. The inlet end of the tube is located in the sampler housing so the front section of the tube end is directly exposed to the atmosphere (i.e., the air being sampled is not passed through any hose or tubing before entering the XAD-4 sorbent tube). The tube is either put into a safety casing in the personal sampling setup as in Figure 4(b) and attached accordingly to clothing, or placed in the sampling port of the briefcase setup as in Figure 4(a).

10.3 After the XAD-4 sorbent tube is correctly inserted and positioned, the power switch for the pump is turned on and the sampling begins.
Note: Newer pumps have microprocessing capabilities for preset sampling periods. The elapsed-time meter is activated and the start time recorded. The pumps are checked during the sampling process and any abnormal conditions discovered are recorded on the Field Sampling Data Sheet as in Figure 5.

10.4 Record on the Field Sampling Data Sheet the temperature and pressure of the atmosphere being sampled.

10.5 At the end of the desired sampling period the pump is turned off.

10.6 Record the time elapsed during sampling.

10.7 Immediately after sampling, remove the XAD-4 sorbent tubes from their casing, detach from the pump, cap with plastic caps, and label.

10.8 Three tubes are handled in the same manner as the sample tubes (break, seal, and transport) except that no air is sampled through these tubes. These tubes are labeled and processed as "sample blanks".

10.9 Transport capped XAD-4 sorbent tubes to the laboratory for analysis.
Note: If the samples are not prepared and analyzed immediately, they should be stored at 0°C or lower until analysis. All XAD-4 samples should be analyzed within two weeks after arrival in the laboratory. However, no absolute time limit has been documented.

11. Analytical Procedure

The analytical procedure for nicotine is performed by extraction of the XAD-4 resin followed by GC/NSD analysis. Ethyl acetate extracts nicotine from the XAD-4 beads; however, the solvent is modified with 0.01% v/v triethylamine to prevent any adsorption of nicotine on the glass walls of the vials. To modify the ethyl acetate solvent, add 0.5 mL of neat triethylamine to a freshly opened 4 L bottle of ethyl acetate and agitate for several minutes. ("Solvent" henceforth will refer to this modified ethyl acetate solvent.)
Note: Because of the sensitivity of the nitrogen selective detector and the possibility of hour to hour variations in response to standard solutions, the use of an internal standard is prescribed as an integral part of the analysis. For this method, quinoline performs very well as an internal standard.

11.1 Propagation of Calibration Standards and Internal Standard

11.1.1 Preparation of standard solutions - clean all volumetric flasks used for preparation of standard samples with detergent, thoroughly rinse with tap water and distilled water, and allow to air dry. Prepare a primary standard (1 mg/mL) of nicotine each month by weighing 100 mg of nicotine directly into a 100 mL volumetric flask, diluting to the mark with solvent, and shaking for several minutes. Prepare a secondary standard (10 µg/mL) of nicotine daily by transferring 1.0 mL of the primary standard to another 100 mL volumetric flask, diluting to the mark with solvent, and shaking for several minutes. A primary standard of quinoline is prepared in exactly the same manner as for nicotine. For the quinoline secondary standard, transfer 10.0 mL of the primary quinoline standard to a 100 mL volumetric flask and dilute to the mark with solvent. Store all standards in a freezer when not in use. Fresh primary standards are prepared from neat nicotine and quinoline once each month. Fresh secondary standards are prepared from the primary standards once each week.

11.1.2 Preparation of calibration standards - sets of five calibration standards covering the expected range of nicotine concentrations in the samples are prepared fresh each day from the individual secondary standards in the following way. Add 50 µL of the secondary quinoline stock solution to each of the prepared five autosampler vials with a microliter syringe. Add various volumes of the secondary nicotine stock solution

to the same five autosampler vials to yield final nicotine concentrations which cover the expected range of the samples. Typical volumes used are 10, 20, 50, 100, and 200 µL (dispensed with appropriate volume syringes) which give nicotine standards of 0.1 µg, 0.2 µg, 0.5 µg, 1.0 µg, and 2.0 µg, respectively. Next, add 1 mL of solvent to each vial. Cap and tightly seal the vials. The vials containing standards will be analyzed along with the sample vials. All solutions stored in the freezer are allowed to warm to room temperature before use. A minimum equilibration time of 1 hour is observed.

11.2 Extraction, Desorption and Analysis of XAD-4 Sample Cartridges

11.2.1 In preparation for analysis, the analyst should thoroughly wash his/her hands with soap and water immediately prior to handling the samples and refrain from smoking or otherwise contacting a known nicotine-containing environment until all samples and standards have been prepared and loaded in the autosampler tray.

11.2.2 Extraction/desorption of the XAD-4 requires transferring the contents of each section of the tube to the autosampler vials for extraction.

11.2.3 Break open the tubes at the back end to empty the contents more easily. The front section and back-up section are transferred to separate vials.

11.2.4 Starting from the back end of the tube, use forceps to transfer the glass wool, resin, and center glass wool plug to a 2-mL vial. Transfer the front section of resin along with the inlet glass wool plug to a second 2-mL vial.

Note: If the resin beads cling to the glass walls of the tube, push them out using the glass wool. If this does not work, flush them out of the tube with a stream of air.

11.2.5 Label each vial. Add 50 µL of the secondary quinoline stock solution along with 1 mL solvent to each vial containing the XAD-4 sample.

11.2.6 Solvent blanks should be prepared in a similar way such that vials without nicotine can be analyzed along with samples. Cap the vials tightly and place them in a holding tray.

11.2.7 After all samples and standards have been prepared, transfer the trays to the vibrator. Turn on the vibrator and let the samples desorb under agitation for 30 minutes.

11.2.8 When loading the autosampler, load the solvent blank in position number one in the tray. Its purpose is to verify correct operation of the gas chromatograph in terms of peak location and detector sensitivity. Load the 5 nicotine standards conveniently in the tray following the solvent blank. These will be used to construct the calibration curve. Next, load all the samples in the autosampler tray in random order. Finish loading the tray with another set of 5 standards.

Note: In the event that more than 25 sample vials are loaded after the first 5 standards, additional sets of standards should be loaded within the tray, so that no more than 25 samples are analyzed between standards. Place the same number of samples before and after the middle set of calibration standards. Load the injection tray with wash and waste vials.

Note: In the HP 7673A model, this is a small rotating tray (housed in the bottom of the autosampler containing the injection syringe) which has positions for wash and waste

vials, and one position dedicated for a sample vial. Before each sample is injected, pre-wash the syringe 5 times with sample; and then pump 5 times with sample. Wash the syringe 10 times with solvent after injection.

11.2.9 The operating conditions for the GC are listed in Table 1. Typical retention times for quinoline and nicotine under these GC conditions are approximately:

RETENTION TIMES

Capillary Column I.D.	Quinoline	Nicotine
0.53 mm	1.9 min	2.6 min
0.32 mm	3.3 min	4.2 min

11.2.10 Begin analysis of the standards and sample. The areas of the peaks are measured electronically by the GC terminal or integrator. Figure 6 illustrates typical chromatograms of an ETS sample. The areas of the sample peaks are compared to calibration standards and concentrations of nicotine are calculated using the calibration curve. Figures 7 and 8 depict typical calibration standards and the associated calibration curve, respectively.

11.3 Constructing the Calibration Curve

11.3.1 For the internal standard method of quantitation, construct a plot of the ratio of nicotine peak area divided by quinoline peak area (y-axis) versus the weight of nicotine in the calibration standards (x-axis). Plot the area ratios of nicotine to quinoline by using the average of all calibration standards prepared and analyzed at a given level, as illustrated in Figure 8.

11.3.2 Fit the data to either a linear or a second-order polynomial regression model, whichever is deemed more appropriate. In most cases, a second-order regression model shows clearly superior results and should be used.

11.3.2.1 The linear regression analysis yields the A and B parameters (slope and y-intercept, respectively) of the function $y = Ax + B$. For the internal standard method, the area ratios of nicotine to quinoline are converted to micrograms of nicotine by the equation:

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

Note: When not using an internal standard, the absolute nicotine area is used rather than an area ratio.

11.3.2.2 When fitting data to a second-order polynomial regression model, the coefficients A, B, C of the polynomial $y = A + Bx + Cx^2$ are found. In this analysis, y represents the weight of nicotine. A typical calibration curve is depicted in Figure 8.

11.3.2.3 The correlation coefficient (R^2) of either fitted line is expected to be at least 0.990 for the XAD-4 method and 0.998 for the cassette methods. A significantly

lower value indicates unusual scattering in the data points defining the calibration curve and preparation and analysis of additional standards should be carried out.

11.4 System Performance Criteria

11.4.1 Retention times for quinoline and nicotine at conditions set forth in Table 1 are approximately:

RETENTION TIMES

Capillary Column I.D.	Quinoline	Nicotine
0.53 mm	1.9 min	2.6 min
0.32 mm	3.3 min	4.2 min

11.4.2 Desorption efficiency should be determined for each analysis and is expected to be at least 95% at all concentrations of nicotine to ensure accuracy of the test results. Failure to calculate the desorption efficiency and adjust results may impair the accuracy of the test.

11.4.3 Breakthrough (>5% of tube contents found in backup resin section) can occur after collecting approximately 300 μg of nicotine in a single XAD-4 tube. A shorter sampling time is necessary if sample concentration and duration of sampling suggests a breakthrough occurrence.

12. Calculations

12.1 Determination of Desorption Efficiency

Note: The decimal fraction of nicotine recovered in the desorption process should be determined for every batch of XAD-4 sorbent tubes that are received.

12.1.1 Break open twenty XAD-4 sorbent tubes and transfer the XAD-4 constituting the front section of each tube together with the glass wool plug to one of twenty 2-mL autosampler vials. Dope three sets of five vials with nicotine to correspond to the three low calibration standards prepared in Section 11.2. For the first set, add 10 μL of the secondary nicotine stock solution directly to the XAD-4 resin in each of five vials. For the second set, add 20 μL of the secondary nicotine stock solution to each of five vials. For the third set, add 50 μL of the secondary nicotine stock solution to each of five vials. The fourth set of five vials are not doped with nicotine and are treated as blanks.

12.1.2 Cap all vials and store in a manner resembling conditions actual samples will experience. This normally entails storage in a freezer overnight for samples collected locally or storage in a dark area at room temperature for 24-48 hours for samples requiring overnight transportation. Since the desorption efficiency may be dependent on the length of time the tubes are stored, the storage time of tubes used in determining desorption efficiency is chosen as the average time required to analyze field samples. If samples are stored longer than 48 hours, perform additional desorption efficiency determinations in the same manner with appropriate storage time before analysis.

12.1.3 Add equal amounts of internal standard to each spiked sample and calibration standard, then desorb and analyze as described in Section 11.2.8.

12.1.4 Prepare ten calibration standards from the secondary nicotine stock solution as described in Section 11.2.

12.1.5 The desorption efficiency (DE) is defined as the average weight of nicotine recovered from the tube divided by the weight of nicotine added to the tube:

desorption efficiency (DE) = [Avg. wt. (μg) recovered/wt. (μg) added] x 100

12.1.6 The desorption efficiency may be dependent on the amount of nicotine collected on the XAD-4 resin. If so, construct a plot of desorption efficiency versus weight of nicotine found experimentally (not the amount added).

12.1.7 For most cases the desorption efficiency is 100% over the range of 0.1 to 2.0 μg nicotine (12).

12.2 Calculating Nicotine Concentrations

12.2.1 Read the weight in μg corresponding to each peak area from the standard curve.

12.2.2 Make corrections for the sample blank for each sample with the equation:

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

where:
μg sample = nicotine found in front section of sample tube or on filter, μg
avg. μg blank = nicotine found in front section of sample blank tubes or on filter, μg
Note: Follow a similar procedure for the back-up section of the XAD-4 sample tube.

12.2.3 To determine the total weight of nicotine in the sample, add the quantities of nicotine present in the front and back-up sections of the same XAD-4 sorbent tube after correcting them for their respective blanks.

12.2.4 If the desorption efficiency is less than 100%, read the desorption efficiency from the curve generated in Section 12.1.1 or if no curve was generated, use the simple arithmetic mean (if less than 100%). Determine the total weight of nicotine by dividing the weight of nicotine by the desorption efficiency (DE):

corrected μg/sample = [total nicotine weight]/[desorption efficiency (DE)] x 100

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

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

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

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

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

13. Performance Criteria and Quality Assurance

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

13.1 Standard Operating Procedures

13.1.1 Users should generate SOPs describing and documenting the following activities in their laboratory:

- assembly, calibration, leak check, and operation of the specific sampling system and equipment used,
- preparation, storage, shipment, and handling of samples,
- assembly, leak-check, calibration, and operation of the analytical system, addressing the specific equipment used,
- sampler storage and transport, and
- all aspects of data recording and processing, including lists of computer hardware and software used.

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

13.2 Calibration of Personal Sampling Pump

13.2.1 The pump is calibrated so the flow controller is set at a sampling rate of 1 L/min at standard conditions for the XAD-4 sorbent sampling tube.

13.2.2 Sampling pumps are calibrated at the beginning and at the conclusion of each sample study. To ensure quality volumetric results, pump calibration is recommended at random points throughout each study.

13.2.3 Connect a soap-film flow meter of suitable volume with Tygon tubing to the front end of the active sampler, as illustrated in Figure 9.

Note: With higher sampling rates, a considerable pressure drop through the XAD-4 sampling tube can result. To minimize this effect, a larger capacity pump would be necessary for higher sampling rates (i.e., >5 L/min).

13.2.4 Record the barometric pressure and ambient temperature on the Field Sampling Data Sheet.

13.2.5 Thoroughly wet the surface of the flowmeter before any measurements are recorded. Measure the time for a soap-film bubble to travel a known volume with a stopwatch. Perform five replicate measurements and compute the average time. Correct the volume (liters) to standard conditions from the equation:

$$V_s = [V_a \times P_b \times 298]/[(T + 273) \times 760]$$

where:
V_s = volume corrected to standard conditions of 298°K and 760 torr, L
V_a = actual volume measured with the soap-film flowmeter, L
T = temperature at calibration, °C
P_b = barometric pressure at calibration, torr
760 = standard pressure, torr
298 = standard temperature,°K

13.2.6 The standard flow rate (Q_s) is then calculated with the equation:

$$Q_s = V_s/R$$

where:
Q_s = standard flow rate, L/min
V_s = volume corrected to standard conditions, L
R = average time obtained from soap-film measurement, min

13.3 Method Sensitivity, Precision and Linearity

13.3.1 The sensitivity of the method is specified by a limit of detection of 0.17 $\mu g/m^3$ for one hour sampling. The XAD-4 sorbent tube method described here is the approved Interim First Action Method of the AOAC (13).

13.3.2 Determining desorption efficiency (see Section 12.1), repeatability and reproducibility ensures method precision.

Note: Coefficients of variation of repeatability and reproducibility were calculated for the XAD-4 method in a collaborative study involving six labs (18).
The method uses a 0.53 mm wide-bore capillary column in the GC with the prescribed sampling analysis. Combining spiked sample and ETS sample results showed acceptable margins of a variation by a 2-way analysis of variance (ANOVA as described in "Statistical Manual of the Association of Official Analytical Chemists"). The coefficient of variation of repeatability was found in the range 4.2-13.2% and the coefficient of variation of reproducibility was found in the range 7.0-14.5%.

13.3.3 Non-linearity in the calibration curve or desorption efficiency curve may occur at concentrations near the limit of detection for the method or at high concentrations near the breakthrough limit of 300 μg nicotine per tube.

13.4 Method Modification

13.4.1 General

13.4.1.1 The sampling time described in the XAD-4 method (up to one hour) may be increased up to eight hour periods.

13.4.1.2 To perform eight hour sampling, modifications in the analysis might involve diluting the sample by using additional solvent in the analysis or adjusting the calibration standards and constructing a calibration curve with a higher range of nicotine concentrations.

13.4.1.3 Flow rate of air through the XAD-4 tube may be increased up to 1.5 L/min.

13.4.1.4 Capabilities of the method may be extended to determine other organic compounds. Semi-volatile and nonvolatile organics containing nitrogen with appreciable carbon content (six carbons or more) may be detected by the prescribed sampling and analysis with GC separation and NSD determination.

13.4.1.5 There is an alternate procedure for adding the internal standard to the autosampler vials. Instead of adding the quinoline after the addition of the resin beads and the extraction solvent, the quinoline could be added to a batch of the modified solvent and added with the solvent.

13.4.2 Standard Preparation with Nicotine Salicylate

Note: Because nicotine is extremely toxic and readily absorbed through the skin, direct contact with the reagent should be avoided. Using a solid reagent (subsequently dissolved in a solvent) reduces the amount of initial contact with nicotine already in a liquid form. The following provides a procedure for preparing primary nicotine standard solutions with nicotine salicylate, which is more easily handled and less hazardous if spilled.

13.4.2.1 Weigh 0.1851 g nicotine salicylate. Add to 100 mL volumetric flask partially filled with ultra high purity water. Bring to 100 mL mark. This is the stock 1000 ppm nicotine solution (aqueous).

13.4.2.2 Place a clean magnetic stirring bar into a clean 50 mL Erlenmeyer flask.

13.4.2.3 Accurately pipet 10 mL of 1000 ppm nicotine stock solution into this flask.

13.4.2.4 Add 10 mL of 10 N NaOH to flask. Stir gently for approximately two minutes.

13.4.2.5 Add 10 mL of ammoniated heptane to the flask and stir an additional five minutes.

13.4.2.6 Carefully transfer the supernatant (heptane) to a 100 mL volumetric flask using a pipet.

13.4.2.7 Add an additional 10 mL ammoniated heptane, stir 2 minutes, transfer to a 100 mL volumetric flask.

13.4.2.8 Repeat Section 13.4.2.7 two more times.

13.4.2.9 Dilute the 100 mL volumetric flask to volume with ammoniated heptane and label "100 ppm nicotine".

13.4.2.10 Pipet 0.5, 1.0, 2.0, 5.0, and 10.0 mL of the 100 ppm nicotine into labelled volumetric flasks and dilute to 100 mL with ammoniated heptane. Resulting concentrations are 0.5, 1.0, 2.0, 5.0, and 10.0 ppm nicotine respectively.

Note: Use freshly ammoniated heptane.

14. Safety

14.1 If spilling of nicotine reagent or solvent occurs, take quick and appropriate clean up action.

14.2 When preparing standards, as with handling any chemicals, protective gloves, lab coats and safety glasses should always be worn to avoid contact with skin and eyes. Particular caution should be taken with nicotine because it is quite toxic, (TLV = 0.5 mg/m^3) and easily absorbed through the skin.

14.3 Use an efficient tube breaking tool when breaking open sealed ends of the XAD-4 tube and when breaking tubes open to transfer contents for analysis. This should prevent injury from raw glass edges of the tube.

15. Acknowledgements

The determination of nicotine in indoor air is a complex task, primarily because of the lack of standardized sampling and analysis procedures. Compendium Method IP-2 is an effort to address these difficulties. While there are numerous procedures for sampling and analyzing nicotine in indoor air, this method draws upon the best aspects of each one and combines them into standardized methodology. To that end, the following individuals contributed to the research, documentation, and peer review of this manuscript.

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Table 1. GC/NSD Settings

Column	*(1) 30 m x 0.53 mm I.D., fused silica capillary 1.50 μm film DB-5 (2) 30 m x 0.32 mm I.D., fused silica capillary 1.00 μm, film DB-5
Temps	
Injector	250°C
Oven	Initial 150° Increase 5°C/min Final 180°C
Detector	300°C
NPD Bead Current	10-20 units to give 0 offset (S/N > 50 for 0.1 μg/mL Standard)
Gas Flows	
He, carrier	(1) 15 mL/min (12 psig) (2) 4 mL/min (15 psig)
H_2, detector	3 mL/min
Air, detector	75 mL/min
He, makeup	15 mL/min
Auto Sampler	
Prewashes	5 with sample
Rinses	5 with sample
Postwashes	10 with solvent
Injection	2 μL
Settings	"Default"
Calibration Standards	5 point check at beginning, middle and end of tray
Integration Parameters	
Threshold	0
Peak width	0.04
Retention Time	(1) 1.9 min for Quinoline 2.6 min for Nicotine (2) 3.3 min for Quinoline 4.2 min for Nicotine

*Note: (1) and (2) designate different settings according to column type. Where no number designation exists, setting accounts for both column types.

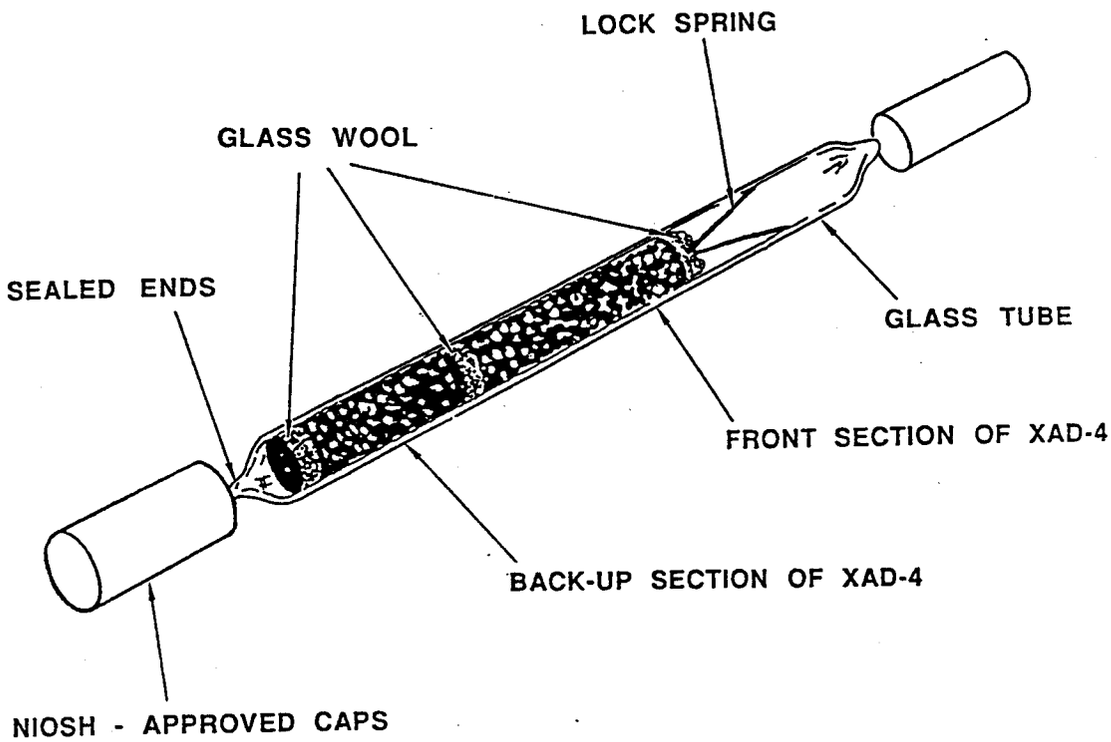


Figure 1. XAD-4 Sorbent Tube

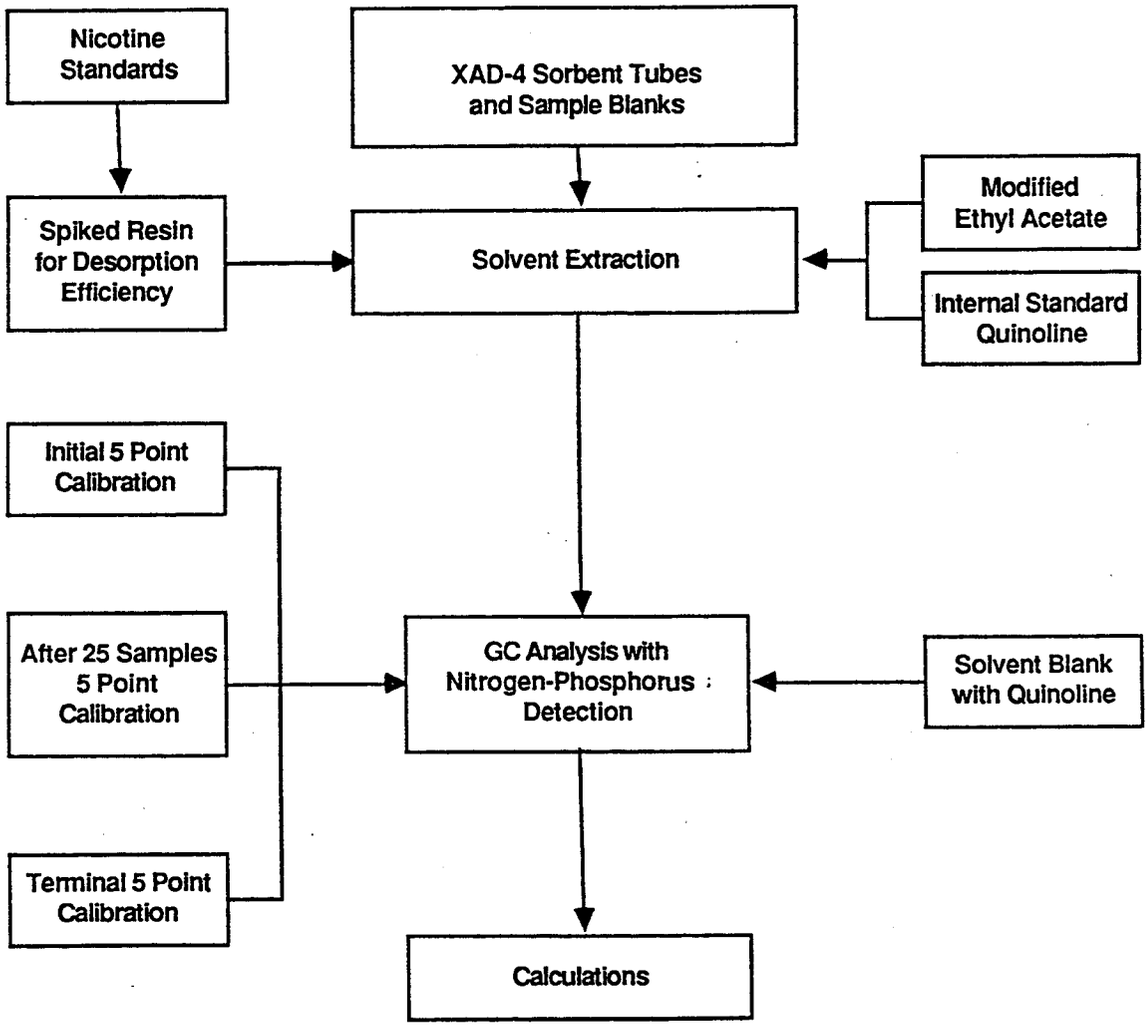


Figure 2. Sampling/Analysis Using XAD-4 Sorbent Tubes

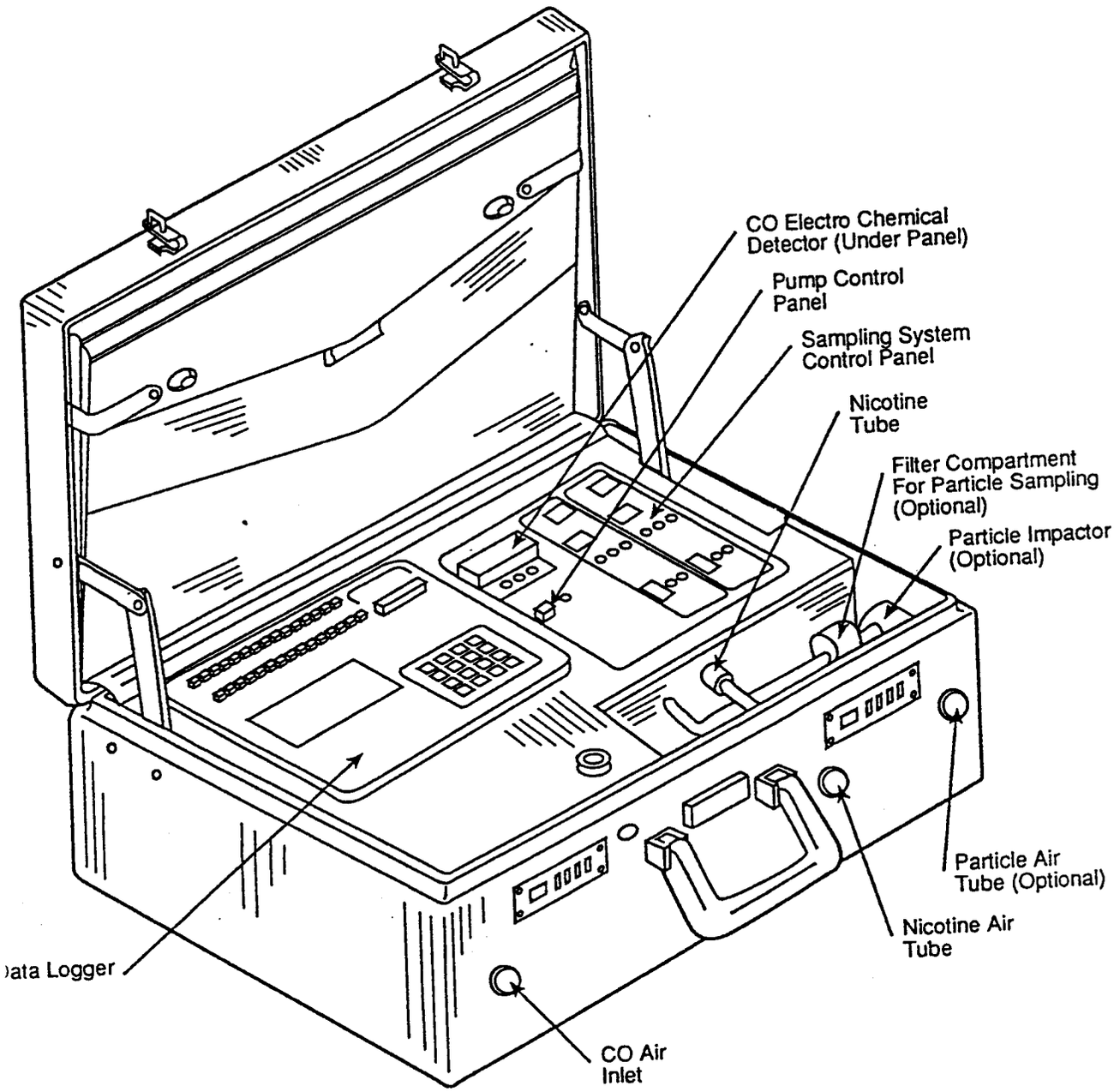
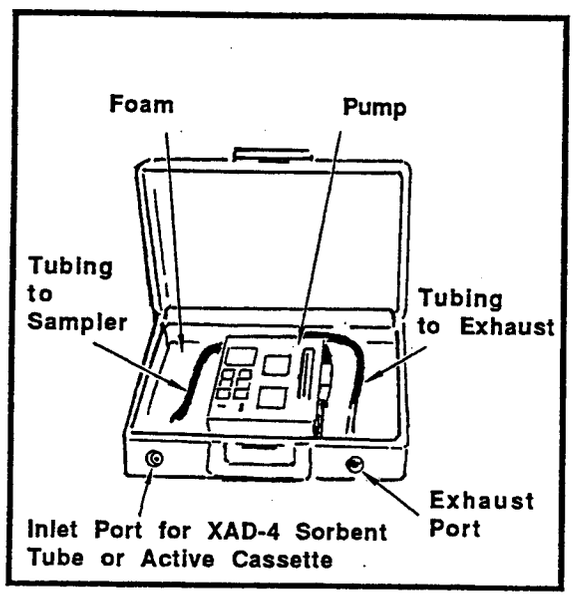
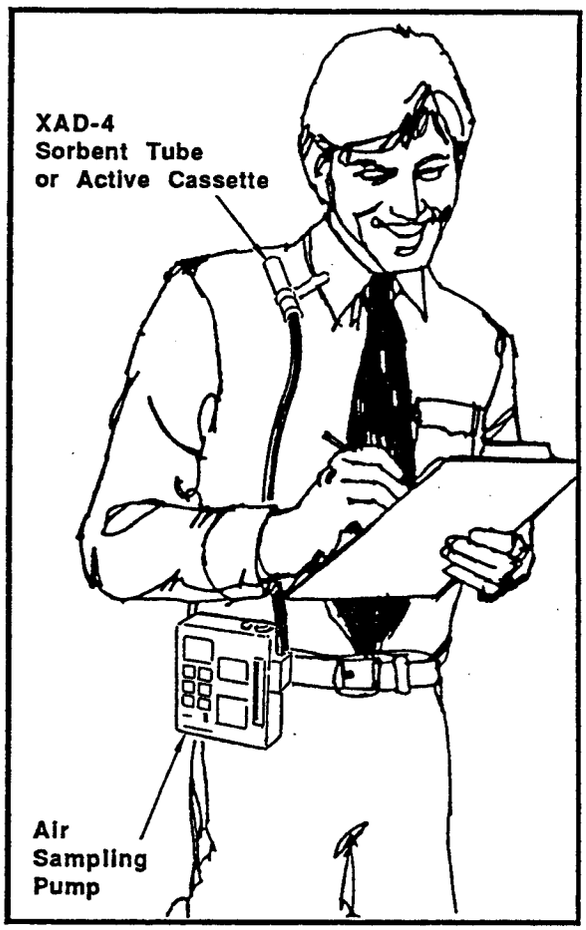


Figure 3. Briefcase Sampling System Containing Nicotine Adsorbent Tube Sampler with Optional Particulate and CO Capabilities





(a) Briefcase Sampling (b) Personal Monitoring

Figure 4. Sampling Setup

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SAMPLING DATA SHEET
(One Sample per Data Sheet)

PROJECT: _____
SITE: _____
LOCATION: _____
INSTRUMENT MODEL NO.: _____
PUMP SERIAL NO.: _____

DATE(S) SAMPLED: _____
TIME PERIOD SAMPLED: _____
OPERATOR: _____
CALIBRATED BY: _____

ADSORBENT CARTRIDGE INFORMATION:
Type: _____
Adsorbent: _____

Serial Number: _____
Sample Number: _____

SAMPLING DATA:

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

Checked by _____

Date _____

* Flow rate from soap bubble calibrator

Figure 5. Nicotine Field Sampling Data Sheet

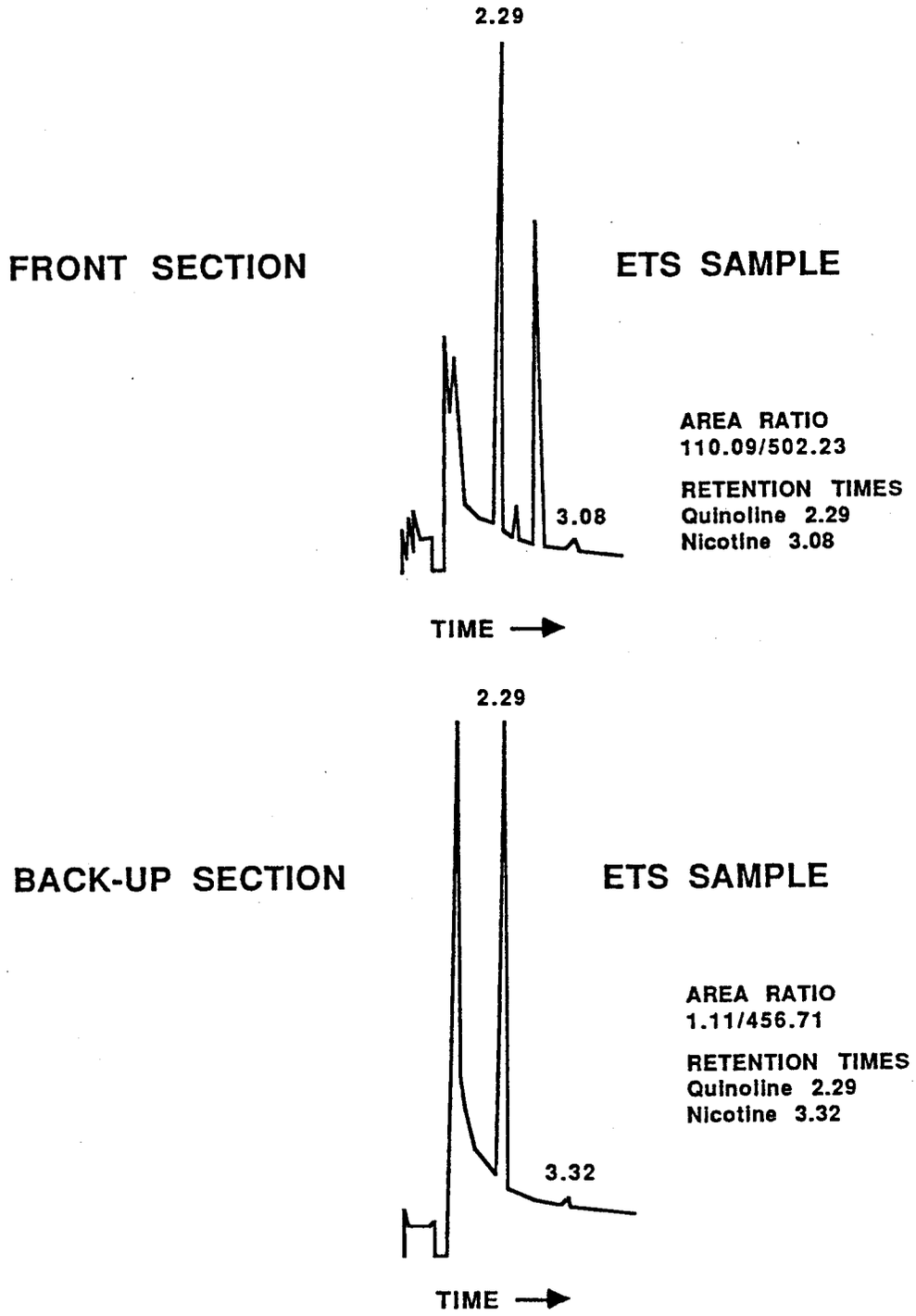
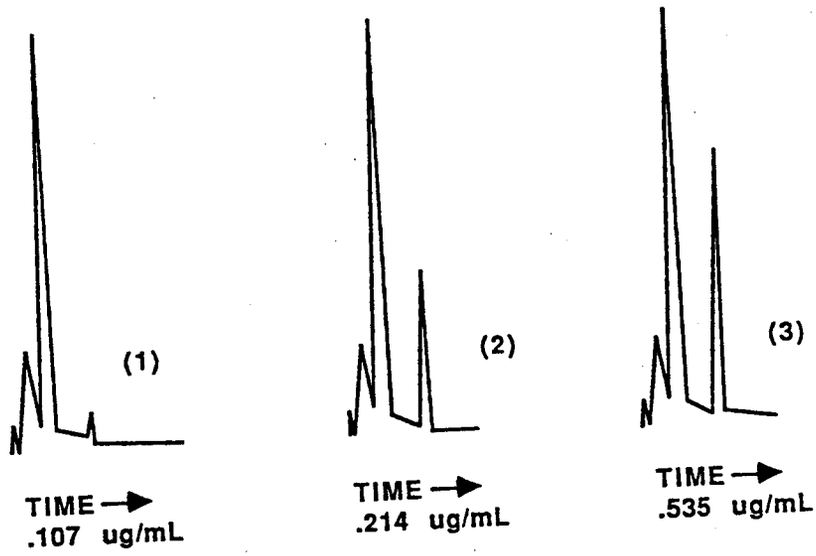
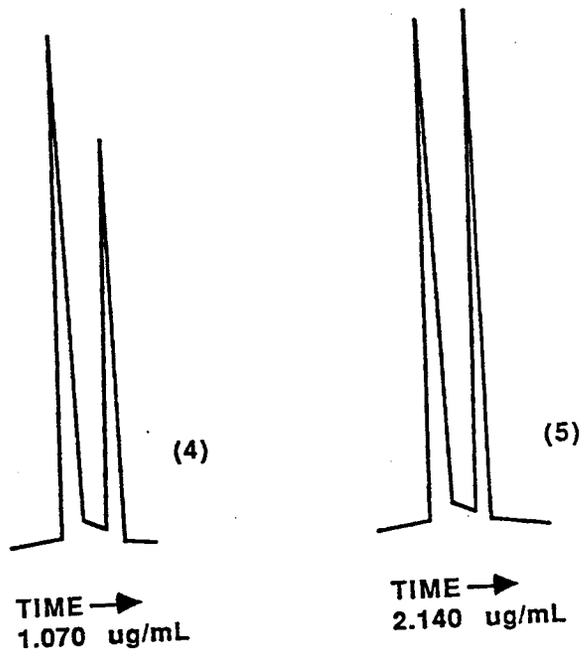


Figure 6. Chromatograms of an ETS Sample



OPERATING PARAMETERS FOR THE GC

Flow Rate: Helium carrier gas - 15 mL/min.
Column: 30 m x .53 mm I.D. fused silica capillary, 1.5 um film of DB-5
Oven: 150°C, program rate increase of 5°C to 180° C
Detector: Nitrogen-Phosphorus operating, at 300° C
Detector Gas Flow Rates: Hydrogen - 3mL/min., Air - 75 mL/min.
Helium Make Up Gas: 15 mL/min.
Injector Temperature: 250°C
Injection: 2 uL direct
Retention Times: 2.29 min. for Quinoline, 3.08 min. for Nicotine



CONC	RATIOS
.107 ug/mL	9.29/466.25
.214 ug/mL	36.91/437.42
.535 ug/mL	106.48/462.95
1.070 ug/mL	237.42/529.03
2.140 ug/mL	453.63/478.30

Figure 7. Chromatograms of Nicotine Calibration Standards

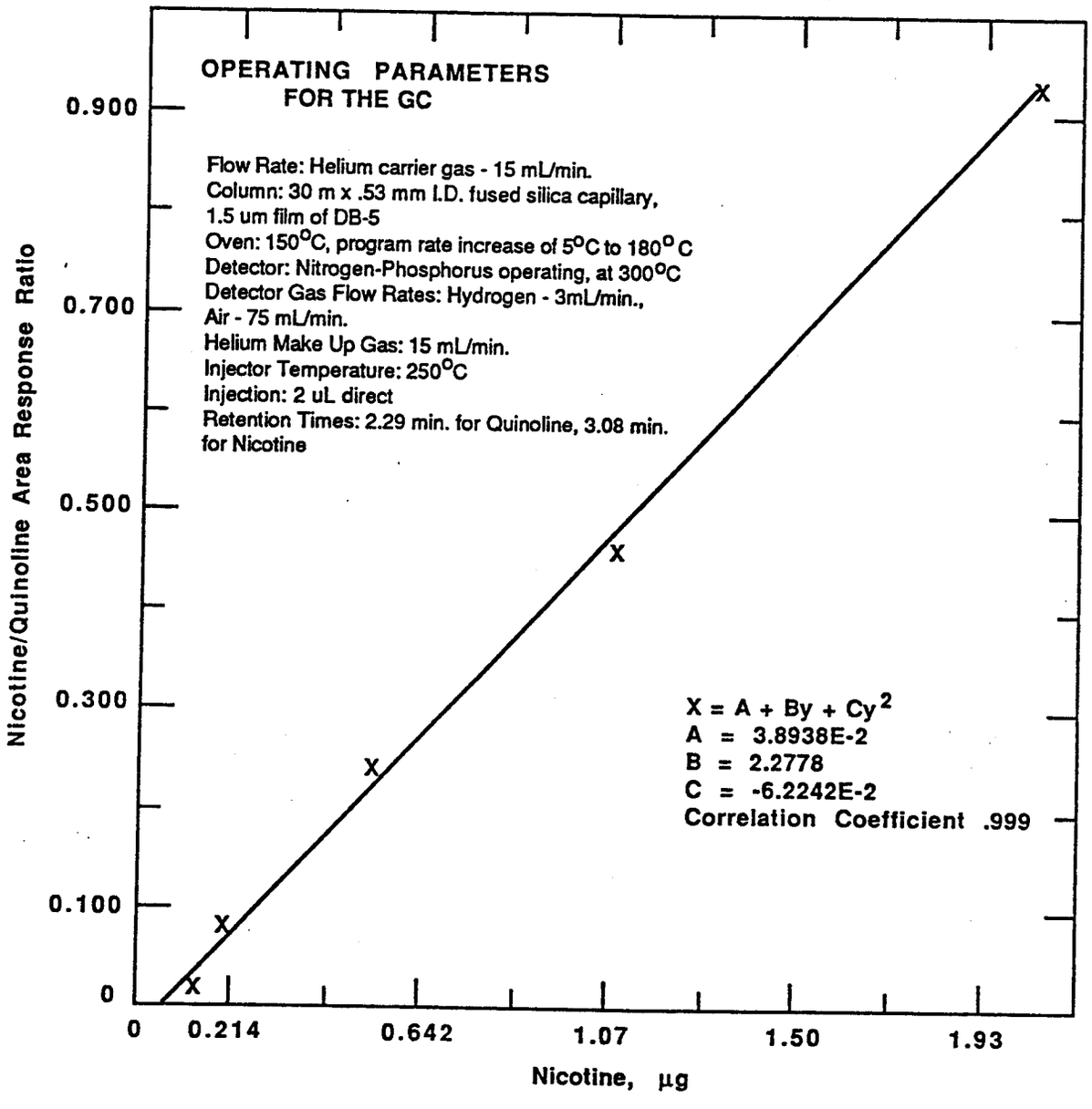


Figure 8. Nicotine Calibration Curve

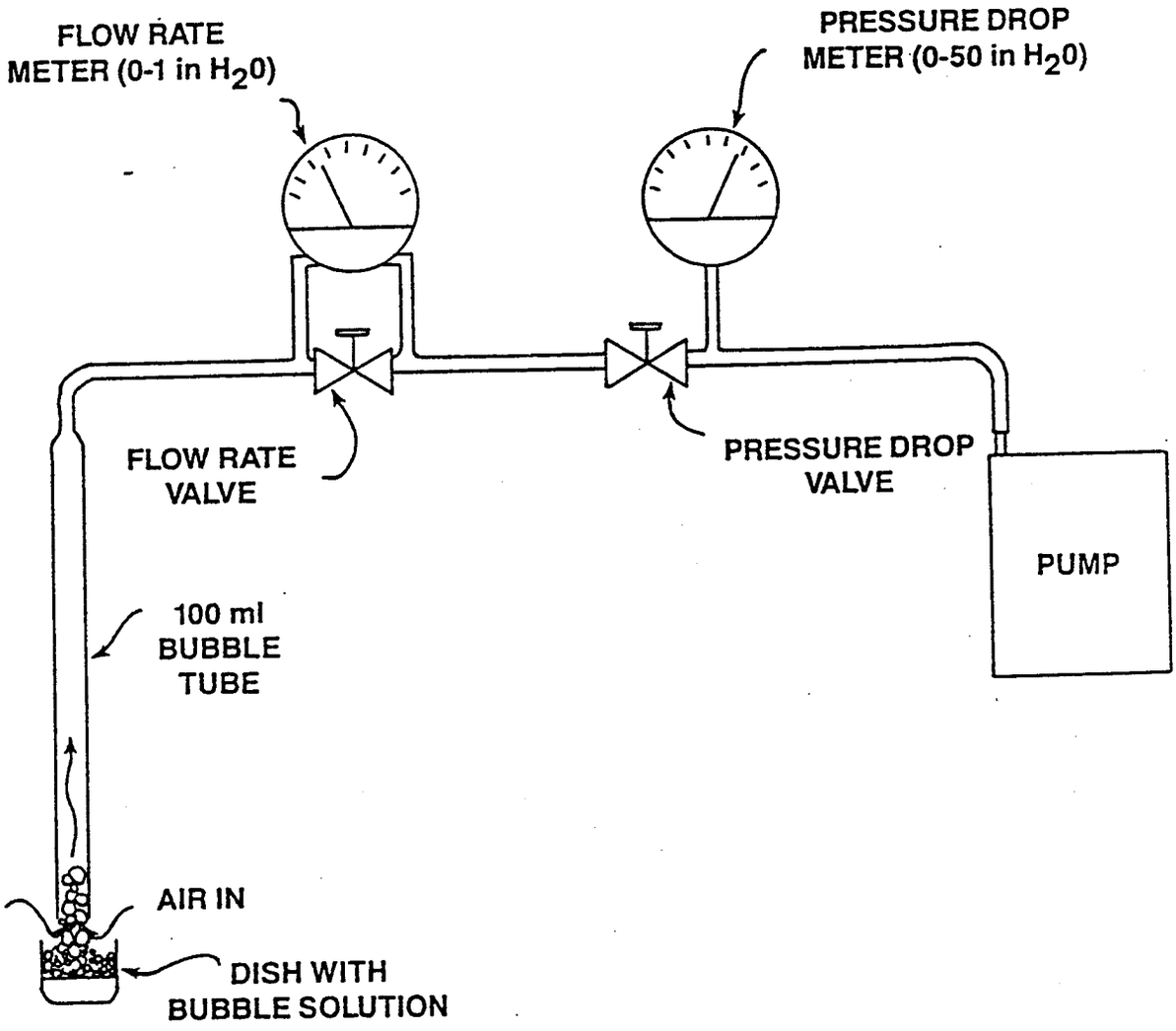


Figure 9. Calibration Assembly for Personal Sampling Pump

Method IP-2B

DETERMINATION OF NICOTINE IN INDOOR AIR USING TREATED FILTER CASSETTES

Method IP-2B

DETERMINATION OF NICOTINE IN INDOOR AIR USING TREATED FILTER CASSETTES

1. Scope

1.1 This method describes two variations for sampling and determination of nicotine in indoor air using treated filter cassettes. The method is based upon collection of nicotine by adsorption on an acidic surface. Gas chromatographic separation with nitrogen-selective detection is employed for analysis.

1.2 One active sampler and one passive sampler are described. The active samplers consist of a treated filter cassette (1) attached to a personal sampling pump. The passive sampler consists of a modification of the treated filter cassette used in active sampling (2).

1.3 Nicotine is the major alkaloid in tobacco. During cigarette smoking, burned tobacco emits nicotine to the atmosphere. In indoor environments, nicotine is found as a main constituent of environmental tobacco smoke (ETS). ETS is a mixture of exhaled cigarette smoke, smoke from the burning tip of a cigarette and smoke that diffuses to the air through the paper of a cigarette. Because nicotine is characteristic of ETS, it is frequently used as a marker for ETS.

1.4 Studies show that more than 90% of nicotine in indoor air is found in the vapor phase (3,4). The following method quantifies total nicotine from indoor air samples. They are not able to sample and analyze for the distinct phases of nicotine since particulate phase nicotine has the ability to volatilize after initial impact on a filter or other collection surface.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis
E260 Recommended Practice for General Gas Chromatography Procedures
E355 Practice for Gas Chromatography Terms and Relationships
D4185 Annex A1 Procedure to Calibrate Small Volume Air Pumps

2.2 Other Documents

U.S. EPA Technical Assistance Document (5)
Laboratory and Ambient/Indoor Air Studies (6-11)
General Guidelines for Indoor Air Studies (12-14)

3. Summary of Method

3.1 Active Sampling Using Treated Filter Cassettes

3.1.1 An indoor air sample is collected using a personal sampling pump. The pump draws air at a rate of 1.7 to 3 L/min through a cassette containing a particulate filter and a filter treated with sodium bisulfate. The method has been evaluated for an eight hour sampling period at a rate of 1.7 L/min with a limit of detection of 0.1 $\mu g/m^3$ and at a rate

of 3 L/min with a limit of detection of 0.03 $\mu g/m^3$ (1). It has also shown a limit of detection of 0.5 $\mu g/m^3$ for a one hour sampling period at a sampling rate of 1.7 L/min. Figure 1 illustrates the active cassette approach.

3.1.2 For analysis, the filters are transferred to test tubes and extracted. The particulate filter is extracted using dichloromethane and the nicotine is concentrated into ammoniated heptane. The dichloromethane is then evaporated from the sample. The treated filter is extracted with a 5% ethanol solution. Sodium hydroxide is added to deprotonate the nicotine and the solution is concentrated into ammoniated heptane for analysis. Ammoniated heptane prevents adsorption of nicotine to the glass walls of the test tubes and sample vials.

3.1.3 Analysis employs gas chromatographic separation with nitrogen-selective detection and a packed column rather than a capillary column. Figure 2 outlines the analytical sequence employing the active treated filter cassette technique.

3.2 Passive Sampling Using Treated Filter Cassettes

3.2.1 Passive sampling requires no pump, and functions on the basis of molecular diffusion. Ideally, the sampling rate follows Fick's First Law of Diffusion and was determined to be 25 mL/min. The passive cassette has been evaluated for a 4-5 hour sampling period with a limit of detection of 16 $\mu g/m^3$ and for a one-week sampling period with a limit of detection of 0.2 $\mu g/m^3$ (2). Figure 3 shows the passive cassette containing a filter treated with sodium bisulfate behind a windscreen which limits mass transport to diffusion.

3.2.2 Analysis of the treated filter is the same as the analysis of the treated filter used in the active cassette. Figure 4 outlines the steps associated with the sampling/analysis of nicotine utilizing the passive filter cassette technique.

4. Significance

4.1 Nicotine emissions result primarily from the combustion of tobacco, e.g., cigarette smoking. Nicotine is toxic when inhaled causing excessive stress to the circulatory and nervous systems and has been linked to increased susceptibility for developing cancer (15). Because smokers and nonsmokers are both exposed to ETS which contains other toxic compounds, accurate measurements of nicotine in indoor environments are important in assessing human health impacts and controlling indoor air pollution.

4.2 Concentrations of 1.8-83.0 $\mu g/m^3$ nicotine have been found in various indoor environments (16). Because such low concentrations of nicotine are encountered, sophisticated analytical procedures and equipment are used for determining nicotine in indoor air.

4.3 These methods are still under development, but have been tested in several field studies and laboratories (1,9,17). The active method employs a personal sampling pump with a treated filter cassette. The passive method employs a treated filter cassette and windscreen for sampling. Analysis employs solvent extraction and gas chromatography separation followed by nitrogen-selective detection.

5. Definitions

Note: Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D1356, E620, E355 and D4185. All pertinent abbreviations and symbols are defined within this document at point of use. Additional definitions, abbreviations, and symbols are located in Appendix A-1 and B-2 of this Compendium.

5.1 Autosampler - an automatic injection device whereby a mechanical syringe withdraws an aliquot of sample and injects the sample into the instrument for analysis.

5.2 Coefficient of variation - a measure of precision calculated as the standard deviation of a series of values divided by their average. It is usually multiplied by 100 and expressed as a percentage.

5.3 Environmental tobacco smoke (ETS) - a composite of exhaled cigarette smoke, smoke from the tip of a burning cigarette and smoke which diffuses through the paper of the cigarette.

5.4 GC terminal - data system and strip chart recorder integrated with a GC. These components are available as a whole package with some GCs.

5.5 Nitrogen-selective detector (NSD) - a highly sensitive detector selective for detection of nitrogen and phosphorus, whereby the detector gas propagates surface ionization on an alkali-salt bead.

5.6 Personal sampling pump - pump with a capacity of 1-5 L/min sampling rate used in personal monitoring.

6. Interferences

Using packed columns in GCs may result in readings lower than expected because nicotine can adsorb onto undeactivated glass, metal, and solid support particles. The following describes potential problems that may occur with sample collection and analysis:

- calibration curves defined with a correlation coefficient below 0.990.
- sampling at levels below the sensitivity of the method.
- using glass columns (such as packed columns) in GCs may result in readings lower than expected because nicotine can adsorb onto glass. Using a modified solvent prescribed here can circumvent this problem.
- incorrect identification and recording of retention times, nicotine peaks, and associated peak areas.
- neglecting to use consistent significant figures when constructing calibration curves and calculating nicotine content in samples.

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7. Apparatus

7.1 Sample Collection

7.1.1 Active Cassette Technique

7.1.1.1 37-mm Teflon®-coated glass fiber filters (Pallflex Products Co., Kennedy Dr., Putnam, CT 06260, Type TX40H120WW, or equivalent).

7.1.1.2 37-mm diameter polystyrene air sampling cassette (SKC, Inc., Cat. No. 225-3-03) or equivalent.

7.1.1.3 Support pad (Millipore Corp., 80 Ashby Rd., Bedford, MA 01730, Cat. No. AP10 03700, or equivalent).

7.1.1.4 O-ring - to separate filters in active samplers.

7.1.1.5 Stainless steel screen (Supelco, Inc., Supelco Park, Bellefonte, PA 16823-0048, or equivalent).

7.1.1.6 Sealing bands - to wrap around cassette connections (SKC, Inc., Cat. No. 225-25-01, or equivalent).

7.1.1.7 Tubing - Tygon 1/4 inch I.D. (SKC, Inc., Cat. No. 225-13-4, or equivalent).

7.1.2 Passive Cassette Technique

7.1.2.1 Windscreen (15-um pore) - 37-mm membrane filter (Schleicher and Schuell, Inc., Keene, NH 03431, Product #TE39, or equivalent).

7.1.2.2 37-mm Teflon®-coated glass fiber filters - refer to Section 7.1.1.1 for description and source.

7.1.2.3 37-mm polystyrene air sampling cassette-refer to Section 7.1.1.2 for description and source.

7.1.2.4 Support pad - refer to Section 7.1.1.3 for description and source.

7.2 Analytical System

7.2.1 Watch glasses.

7.2.2 13 x 100 mm borosilicate glass disposable test tubes.

7.2.3 Aluminum foil - used as surface for drying treated filters.

7.2.4 Gas chromatograph with nitrogen-selective detector (Hewlett-Packard, Rt. 41, Avondale, PA 19311, Model 5890A, or equivalent) and integrator (Hewlett-Packard, Model 3391A, or equivalent); sampler event-control module (Hewlett-Packard, Model 19405A, or equivalent); autosampler (Hewlett-Packard, Model HP 7673A, or equivalent); and precision sampling syringe with 10-uL reinforced plunger 23 gauge needle.

7.2.5 GC column - 2% KOH on Carbowax 20M, 2 mmid, 6 ft glass.

7.2.6 Vortex mixer - for extraction.

7.2.7 Sample containers - 2-mL and 300-mL autosampler vials with Teflon®-lined crimp-cap closures.

7.2.8 Crimp-cap sealer.

7.2.9 Dispensing pipets - 1.00 mL.

7.2.10 Volumetric flasks - 100 mL for making standard solutions.

7.2.11 Microliter pipets - 25, 50, 100 and 1000 µL, for making solutions.

7.2.12 Forceps - for handling treated filters and for assembling cassettes (SKC, Inc., 334 Valley View Road, Eighty Four, PA 15330 Cat. No. 225-15-1, or equivalent).

8. Reagents and Materials

8.1 General

8.1.1 Helium cylinders - for detector and/or carrier gas, 99.9995% grade.
8.1.2 Hydrogen cylinders - for detector gas, 99.9995% grade.
8.1.3 Air - for detector gas (<0.1 ppm hydrocarbon).
8.1.4 Volumetric flasks - 100 mL or convenient sizes for making internal standards.
8.1.5 Nicotine - reagent grade (Eastman Kodak Co., Dept. 412-L-236, 343 State St., Rochester, NY, Cat. No. 112 4973, or equivalent).
8.1.6 Quinoline (internal standard) >99% A.C.S. reagent, Gold Label (Aldrich Chemical Co., Inc., Dept. T, P.O. Box 355, Milwaukee, WI 53201, Cat. No. 25, 401-01, or equivalent).
8.1.7 Nicotine salicylate - reagent grade (Eastman Kodak Co., Dept. 412-L-236, 343 State St., Rochester, NY).

8.2 Active and Passive Cassettes

8.2.1 Absolute ethanol - USP or reagent grade used in treated filters extraction.
8.2.2 Sodium bisulfate - monohydrate, reagent grade.
8.2.3 Heptane - HPLC grade, ultra high purity (J. T. Baker Chemical Co., 222 Red School Lane, Phillipsburg, NJ, or equivalent).
8.2.4 High quality water - deionized, double-distilled.
8.2.5 Sodium hydroxide pellets - reagent grade, used in treated filters extraction.
8.2.6 Ammonia - anhydrous, bubbled through heptane and used in extraction.
8.2.7 Dichloromethane - reagent grade, used for extraction of particulate filter in active sampling only.

9. Sampling System

9.1 System Description

9.1.1 Active Cassette Sampling System

9.1.1.1 The active sampling system consists of a sampler and personal sampling pump. In active sampling the pump draws a volume of air through a treated filter cassette to adsorb any nicotine present.

9.1.1.2 The sampling systems are portable and can be used effectively in several setups.

9.1.1.3 The active sampling system can be attached to a person for personal monitoring. In this setup, the pump is attached to a belt and Tygon tubing connects the sampler to the pump. The sampler is then clipped onto clothing near the breathing zone as in Figure 5.

9.1.1.4 The active sampler may be located on a stationary surface for area monitoring in any indoor environment as in Figure 6.

9.1.2 Passive Cassette Sampling System

9.1.2.1 For passive sampling, the sampling system consists of a modified treated filter cassette without a pump. The cassette is simply attached to clothing, with the windscreen exposed to the atmosphere.

9.1.2.2 In passive sampling, nicotine diffuses to a modified treated filter inside a cassette.

9.2 Preparation of Filters for Active and Passive Cassettes

9.2.1 Filter Treatment

9.2.1.1 Fill a watchglass with an aqueous solution of 4% sodium bisulfate and 5% ethanol.

9.2.1.2 With forceps transfer a filter to the watchglass. Soak filter in the solution. Note: It will become saturated in a few seconds.

9.2.1.3 Remove filters to aluminum foil and allow them to dry. Caution should be taken during the drying process to ensure the absence of possible nicotine contamination. Note: The sodium bisulfate solution should coat 7-10 mg sodium bisulfate onto the filter surface.

9.2.2 Assembling Active Filter Cassette

Note: Active cassette sampling collects particulates on a Teflon®-coated glass fiber filter and vapor phase nicotine on a treated filter. Assembly must be performed in a nicotine-free environment. Gloves and clean lab coats should be worn. Place the components into the cassette in the same sequence as shown in Figure 1.

9.2.2.1 Place a support pad into the bottom half of the cassette.

9.2.2.2 Using forceps, place a treated filter on top of the support pad.

9.2.2.3 Place an o-ring (or spacer section of the cassette) on top of the treated filter, followed with a stainless steel screen and an untreated filter on top.

9.2.2.4 Push the top half of the cassette over the bottom as in Figure 1.

Note: A spacer section placed between the two halves can be substituted for the o-ring to hold the stainless steel screen and particulate filter in place.

9.2.2.5 Wrap connection with sealing bands so cassette is air tight.

9.2.2.6 Cap at both ends and label cassette for sampling.

9.2.3 Assembling Passive Filter Cassette

Note: Assembly must be performed in a nicotine-free environment. Gloves and clean lab coats should be worn. Prior to assembling the modified treated filter cassette for passive sampling, a windscreen must be made to distribute air over the entire face of the cassette, subsequently distributing the air being sampled over the entire surface area of the treated filter. In passive sampling, nicotine diffuses through the windscreen and is chemically adsorpted on the treated filter.

9.2.3.1 To prepare the windscreen, take a cassette spacer (see note below) and remove the outer rim from one side. This is usually done by a machine shop. This alteration should expose the inner diameter of the spacer and provide a flat surface for attachment of a membrane filter.

Note: A spacer is generally used in between the top and bottom halves of a cassette to separate a series of filters. In passive sampling, the spacer is converted to a top half of the cassette as in Figure 3. Swab a TE39 membrane filter with methylene chloride and stick the edges of the filter to the edges of the spacer.

9.2.3.2 Referring to Figure 3, place a support pad into the bottom of a cassette, then place a treated filter on top of the support pad. This assembly comprises the top half of the cassette.

9.2.3.3 Remove the small plastic cap from the bottom half of the cassette. Removing the cap prevents a vacuum from forming which can damage the windscreen. Push the top half of the cassette into the bottom half of the cassette.

9.2.3.4 Recap the bottom and immediately put sampler in a clean, airtight container until needed for sampling.

9.3 Sampling Procedure

9.3.1 Active Cassette Technique

9.3.1.1 The active sampling cassette is connected to the calibrated pump and arranged in either the stationary sampling setup or situated for personal monitoring (see Figures 5 or 6, respectively).

9.3.1.2 Record on the Field Sampling Data Sheet as in Figure 7, the temperature and pressure of the atmosphere being sampled.

9.3.1.3 After the cassette is correctly situated for sampling the power switch is turned on and sampling begins. Sample at a rate of 1.7 L/min for the duration of the sampling period.

9.3.1.4 At the end of the desired sampling period the pump is turned off.

9.3.1.5 Record the time elapsed during sampling.

9.3.1.6 Immediately after sampling, remove the cassette, detach from the pump, cap each half of the cassette with plastic caps, and label. Record pertinent information on the Field Sampling Data Sheet.

9.3.1.7 Two or three cassettes are handled in the same manner as the sample cassette except that no air is sampled through these cassettes. These cassettes are labeled and processed as "sample blanks".

9.3.1.8 Transport capped treated filter cassettes to the laboratory for analysis. Samples are stable at room temperature for at least six months after collection.

9.3.2 Passive Cassette Technique

9.3.2.1 The passive cassette should be transported to the sampling site in an air tight container made of glass or metal; plastic is not acceptable.

9.3.2.2 The cassettes should be located on a stationary surface or attached to a person for sampling.

Note: As soon as the cassette is removed from the air tight container, sampling begins.

9.3.3.3 Immediately record on the Field Sampling Data Sheet the start time.

9.3.3.4 At the end of the sampling period, record the stop time and transfer the passive cassette to a clean, airtight container until analysis is performed.

10. Analytical System

10.1 System Description

10.1.1 Analysis is performed using a GC with a nitrogen-selective detector. The analytical system also includes an autosampler, integrator, and system sampler-event-control module. A chromatogram from an ETS sample is shown in Figure 8. Figure 9 depicts chromatograms of varying nicotine concentrations and lists GC operating parameters.

Note: Settings for the GC analysis are summarized in Table 1.

10.1.2 The GC column is a 6 ft glass packed column (2 mmid): 2% KOH on 10° Carbowax 20M held at a constant temperature of 140°C.

10.1.3 A 3-μL sample is injected for analysis.

10.2 System Performance Criteria

10.2.1 To check reproducibility of the GC system, duplicate injections for all calibration standards should agree within 5%.

10.2.2 The calibration curve should have a correlation coefficient of at least 0.998.

10.2.3 Spiked samples should show a recovery of at least 90% ± 5% before proceeding with sample preparation.

10.3 Analytical Procedure

10.3.1 Preparation of Reagents

10.3.1.1 Prepare ammoniated heptane daily by bubbling ammonia through 100 mL heptane for 2 minutes to saturate.

10.3.1.2 When preparing standards, use ammoniated heptane for all dilutions. Prepare 5% ethanol in water daily by measuring 5 mL of ethanol into a 250-mL Erlenmeyer flask and diluting to 100 mL with water.

10.3.1.3 All water is deionized, double-distilled or equivalent. Prepare 10 N NaOH weekly by placing 40 grams NaOH pellets in a 250 mL Erlenmeyer flask and diluting to 100 mL with water or use reagent grade 10 N NaOH solution.

10.3.2 Preparation of Standard Solutions

10.3.2.1 Prepare a primary nicotine stock solution (1 mg/mL) every month by the following procedure: Add about 50 mL ammoniated heptane to a 100-mL volumetric flask. Measure 100 μL of nicotine with a syringe and add to the heptane. Dilute to the mark with heptane and mix well. Place aliquots into four crimp top vials and seal. Label each vial with concentration and date.

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10.3.2.2 Store in a freezer at -20°C or less. (One vial will be used each week to prepare calibration standards.)

10.3.2.3 Prepare a secondary nicotine stock solution (100 µg/mL) daily. Use a 1 mL positive displacement autopipet with fresh tip to measure 1 mL of the primary stock solution into a 10 mL volumetric flask. Dilute to the mark with ammoniated heptane.

Note: Due to nicotine's extreme toxicity, caution should be employed when handling the reagent. SOPs should be developed for using nicotine when preparing standard solutions.

Note: An alternative procedure for making the primary nicotine standard is provided in Section 12.4. The alternative procedure uses nicotine salicylate, which is a crystalline salt.

10.3.3 Preparation of Calibration Standards

10.3.3.1 Calibration standards should cover a tenfold range of concentration. For high concentration samples, prepare standards from 5 µg/mL to 50 µg/mL. For low concentration samples and passive sampling, prepare standards from 0.05 µg/mL to 5 µg/mL.

10.3.3.2 Prepare all standards daily as follows: For a 50 µg/mL standard, measure 1 mL of 100 µg/mL primary standard of nicotine into a 10 mL volumetric flask and dilute with ammoniated heptane to 2 mL. Similarly prepare the other standards using the following quantities of nicotine standards and ammoniated heptane:

10.0 µg/mL:	1 mL of 100 µg/mL diluted to 10 mL
5.0 µg/mL:	1 mL of 10 µg/mL diluted to 2 mL
1.0 µg/mL:	1 mL of 10 µg/mL diluted to 10 mL
0.5 µg/mL:	1 mL of 1 µg/mL diluted to 2 mL
0.1 µg/mL:	1 mL of 1 µg/mL diluted to 10 mL
0.05 µg/mL:	1 mL of 1 µg/mL diluted to 20 mL

Note: If an internal standard is desired, quinoline has been used in nicotine analysis using gas chromatography with nitrogen selective detection. (Refer to Method IP-2A of this Compendium, Determination of Nicotine in Indoor Air Using XAD-4 Sorbent Tubes.)

10.3.4 Extraction/Desorption for Active Cassette

Note: Analysis of the active cassette sample requires extraction of the treated filter and the particulate filter.

10.3.4.1 Extract the nicotine from the treated filter and the support pad by the following steps.

10.3.4.1.1 Transfer the treated filter and support pad to separate 13 x 100 mm test tubes.

10.3.4.1.2 Add 2 mL of 5% ethanol solution to the test tube containing the support pad and vortex 1 minute. Draw off liquid and add to the test tube containing the filter.

10.3.4.1.3 Add 1 mL of 5% ethanol solution to test tube support pad and vortex 15 seconds. Transfer liquid to the test tube containing the filter.

10.3.4.1.4 Vortex the test tube containing the filter one minute. Add 2 mL 10 N NaOH and vortex 1 minute. Add 250 µL ammoniated heptane (measured with positive displacement pipet) and vortex 1 minute.

10.3.4.1.5 Draw off top layer of prepared sample and transfer to sample vial. Cap with crimp top. Inject manually or load into autosampler.

10.3.4.2 Extract the nicotine from the particulate filter by the following steps.

10.3.4.2.1 Transfer the particulate filter to a 13 x 100 mm test tube. Add about 2 mL dichloromethane (or enough to cover the filter) to test tube and ultrasonically desorb.

10.3.4.2.2 Add 200 µL heptane to the test tube and evaporate the dichloromethane from the sample.

Note: This step is necessary because chlorinated solvents should not be used with nitrogen-selective detectors.

10.3.4.2.3 Transfer an aliquot from the test tube to a sample vial. Cap with crimp top. Inject manually or load into autosampler for injection into the GC and run samples according to settings listed in Table 1.

10.3.5 Extraction/Desorption for Passive Cassette

10.3.5.1 Transfer the treated filter to a 13 x 100 mm test tube. Add 2 mL 5% ethanol solution to test tube and vortex 1 minute.

10.3.5.2 Add 2 mL 10 N NaOH and vortex 1 minute.

10.3.5.3 Add 250 mL ammoniated heptane and vortex 1 minute.

10.3.5.4 Draw off top layer of prepared sample and transfer to sample vial. Cap with crimp top. Inject manually or load into autosampler.

10.3.6 Loading the Autosampler

10.3.6.1 Run a set of standards to establish linear response of the detector.

10.3.6.2 Intersperse the samples with blank heptane and standards so that there are no more than four samples between standards.

10.3.6.3 Run the samples at the conditions set forth in Table 1.

10.3.6.4 At the end of each day, replace the septum on the GC injector.

11. Calculations

11.1 Determination of Desorption Efficiency For Treated Filters

The decimal fraction of nicotine recovered in the desorption of nicotine from treated filters is determined as follows:

11.1.1 Prepare several treated filters in the manner described in Section 9.1.2.

11.1.2 Spike the filters with nicotine in dichloromethane creating a range of concentrations of nicotine. For active samples, spike with 1 to 50 µg of nicotine. For passive samples, spike with 0.1 to 5 µg of nicotine.

11.1.3 Let the filters dry for a time equivalent to sampling period (at least 24 hours).

11.1.4 Desorb the spiked treated filters as described in Section 10.3.1.

11.1.5 The desorption efficiency is defined as the weight of nicotine recovered from the filter divided by the weight of nicotine added to the filter.

11.1.6 The desorption efficiency may be dependent on the amount of nicotine collected on the filter. If so, construct a plot of desorption efficiency versus weight of nicotine found experimentally.

11.2 Determination of the Extraction Efficiency For Treated Filters

Note: The extraction efficiency for the liquid/liquid extraction from the aqueous solution to the heptane layer should be performed at the beginning of each study and should show no loss of nicotine.

11.2.1 Add a known amount of nicotine to 2 mL water containing 200 µL of 4% sodium bisulfate.

11.2.2 Extract as described in Section 10.3.4.1.

11.3 Determination of the Extraction Efficiency For Particulate Filters

Note: The extraction efficiency for the evaporation of dichloromethane from heptane should be performed at the beginning of each study and should show no loss of nicotine.

11.3.1 Measure 200 µL of heptane and 1 mL dichloromethane into a test tube.

11.3.2 Add a known amount of nicotine to the test tube.

11.3.3 Evaporate the dichloromethane from the heptane as described in Section 10.3.4.2.

Note: Heptane always refers to ammoniated heptane.

11.4 Constructing the Calibration Curve

11.4.1 The linear regression analysis yields the A and B parameters (slope and y-intercept, respectively) of the function $y = Ax + B$. For the internal standard method, the area ratios of nicotine to quinoline are converted to micrograms of nicotine by the equation:

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

Note: When not using an internal standard, the absolute nicotine area is used rather than an area ratio.

11.4.2 When fitting data to a second-order polynomial regression model, the coefficients A, B, C of the polynomial $y = A + Bx + Cx^2$ are found. In this analysis, y represents the weight of nicotine. A typical calibration curve is depicted in Figure 7.

11.4.3 The correlation coefficient (R^2) of either fitted line is expected to be at least 0.998 for the cassette methods. A significantly lower value indicates unusual scattering in the data points defining the calibration curve and preparation and analysis of additional standards should be carried out.

11.5 Calculating Nicotine Concentrations

11.5.1 Read the weight in µg corresponding to each peak area from the standard curve.

11.5.2 Make corrections for the sample blank for each sample with the equation:

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

where:
μg sample = μg nicotine found on filters
avg. μg blank = average μg nicotine found in front section of sample blank filter

11.5.3 To determine the total weight of nicotine in the sample, add the quantities of nicotine present in the front and back-up sections of the treated and particulate filters from the active cassette, after correcting them for their respective blanks. For passive sampling, the amount of nicotine from the treated filter is used.

11.5.4 If the desorption efficiency is less than 100%, read the desorption efficiency from the curve generated in Section 11.1, or if no curve was generated, use the simple arithmetic mean (if less than 100%). Determine the total weight of nicotine by dividing the weight of nicotine by the desorption efficiency (DE):

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

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

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

Note: In passive sampling the air volume sampled is calculated from:

$$\text{sampling rate} = \text{mass collected}/[(\text{conc.})(\text{time})] = DA/L$$

where:
D = diffusion coefficient
A = cross-sectional area of sampler
L = length of sampler (distance between windscreen and treated filter)
Note: For this sampler, A = 8.11 cm^2, L = 1.17 cm, and D = 0.063 cm^2/s, with a resulting theoretical sampling rate equal to 25 mL/min. This sampling rate has been confirmed experimentally (3).

11.5.6 Adjust the nicotine concentration found in the sampled air to standard conditions of temperature and pressure by the equation:

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

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

12. Performance Criteria and Quality Assurance

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

12.1 Standard Operating Procedures

12.1.1 Users should generate SOPs describing and documenting the following activities in their laboratory:

- assembly, calibration, leak check, and operation of the specific sampling system and equipment used
- preparation, storage, shipment, and handling of samples
- assembly, leak-check, calibration, and operation of the analytical system, addressing the specific equipment used
- sampler storage and transport
- all aspects of data recording and processing, including lists of computer hardware and software used

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

12.2 Calibration of Personal Sampling Pump

12.2.1 The pump is calibrated so the flow controller is set at a sampling rate of 1.7 L/min for the treated filter cassette.

12.2.2 Sampling pumps are calibrated at the beginning and at the conclusion of each sample study. To ensure quality volumetric results, pump calibration is recommended at random points throughout each study.

12.2.3 Connect a soap-film flow meter of suitable volume with Tygon tubing to the front end of the active sampler, as illustrated in Figure 11.

12.2.4 Record the barometric pressure and ambient temperature on the Field Sampling Data Sheet.

12.2.5 Thoroughly wet the surface of the flowmeter before any measurements are recorded. Measure the time for a soap-film bubble to travel a known volume with a stopwatch. Perform five replicate measurements and compute the average time. Correct

$$V_s = (V_a \times P_b \times 298)/[(T + 273) \times 760]$$

where:

V_s = volume corrected to standard conditions of 298°K and 760 torr, L
V_a = actual volume measured with the soap-film flowmeter, L
T = temperature at calibration, °C
P_b = barometric pressure at calibration, torr
760 = standard pressure, torr
298 = standard temperature,°K

12.2.6 The standard flow rate (Q_s) is then calculated with the equation:

$$Q_s = V_s/R$$

where:
Q_s = standard flow rate, L/min
V_s = volume corrected to standard conditions, L
R = average time obtained from soap-film measurement, min

12.3 Method Sensitivity, Precision and Linearity

12.3.1 The sensitivity of the active sampling technique has a limit of detection of 0.1 $\mu g/m^3$ over an eight hour period and 0.5 $\mu g/m^3$ over a one hour sampling period at a sampling rate of 1.7 L/min. The sensitivity of the passive sampling technique is specified by a limit of detection of 16 $\mu g/m^3$ over a five hour period and 0.2 $\mu g/m^3$ over a one week period at a sampling rate of 1.7 L/min.

12.3.2 Determining desorption efficiency (see Section 11.1), repeatability and reproducibility ensures method precision.

12.3.3 Non-linearity in the calibration curve or desorption efficiency curve may occur at concentrations near the limit of detection of the method or at high concentrations near the saturation limit of 100 μg nicotine per treated filter.

12.4 Method Modification

Note: Because nicotine is extremely toxic and readily absorbed through the skin, direct contact with the reagent should be avoided. Using a solid reagent (subsequently dissolved in a solvent) reduces the amount of initial contact with nicotine already in a liquid form. The following provides a procedure for preparing primary nicotine standard solutions with nicotine salicylate, which is more easily handled and less hazardous if spilled.

12.4.1 Weigh 0.1851 g nicotine salicylate. Add to 100 mL volumetric flask partially filled with ultra high purity water. Bring to 100 mL mark. This is the stock 1000 ppm nicotine solution (aqueous).

12.4.2 Place a clean magnetic stirring bar into a clean 50 mL Erlenmeyer flask.

12.4.3 Accurately pipet 10 mL of 1000 ppm nicotine stock solution into this flask.

12.4.4 Add 10 mL of 10 N NaOH to flask. Stir gently for approximately two minutes.

12.4.5 Add 10 mL of ammoniated heptane to the flask and stir an additional five minutes.

12.4.6 Carefully transfer the supernatant (heptane) to a 100 mL volumetric flask using a pipet.

12.4.7 Add an additional 10 mL ammoniated heptane, stir 2 minutes, transfer to a 100 mL volumetric flask.

12.4.8 Repeat Section 12.4.7 two more times.

12.4.9 Dilute the 100 mL volumetric flask to volume with ammoniated heptane and label "100 ppm nicotine".

12.4.10 Pipet 0.5, 1.0, 2.0, 5.0, and 10.0 mL of the 100 ppm nicotine into labelled volumetric flasks and dilute to 100 mL with ammoniated heptane. Resulting concentrations are 0.5, 1.0, 2.0, 5.0, and 10.0 ppm nicotine respectively.

Note: Use freshly ammoniated heptane.

12.5 Safety

12.5.1 If spilling of nicotine reagent or solvent occurs, take quick and appropriate clean up action.

12.5.2 When preparing standards, as with handling any chemicals, protective gloves, lab coats and safety glasses should always be worn to avoid contact with skin and eyes. Particular caution should be taken with nicotine because it is quite toxic, (TLV = 0.5 mg/m^3) and easily absorbed through the skin.

13. Acknowledgements

The determination of nicotine in indoor air is a complex task, primarily because of the lack of standardized sampling and analysis procedures. Compendium Method IP-2 is an effort to address these difficulties. While there are numerous procedures for sampling and analyzing nicotine in indoor air, this method draws upon the best aspects of each one and combines them into standardized methodology. To that end, the following individuals contributed to the research, documentation, and peer review of this manuscript.

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Table 1. GC/NPD Settings

	Treated Filter Cassette
Column	2% KOH on 10% Carbowax 20M 6 ft. glass (2 mmid)
Temps	
Injector	225°C
Oven	140°C (isothermal)
Detector NPD Bead	250°C
Gas Flows	
He, carrier	15 mL/min
H_2 , detector	1 mL/min
Air, detector	115 mL/min
Injection	3 µl

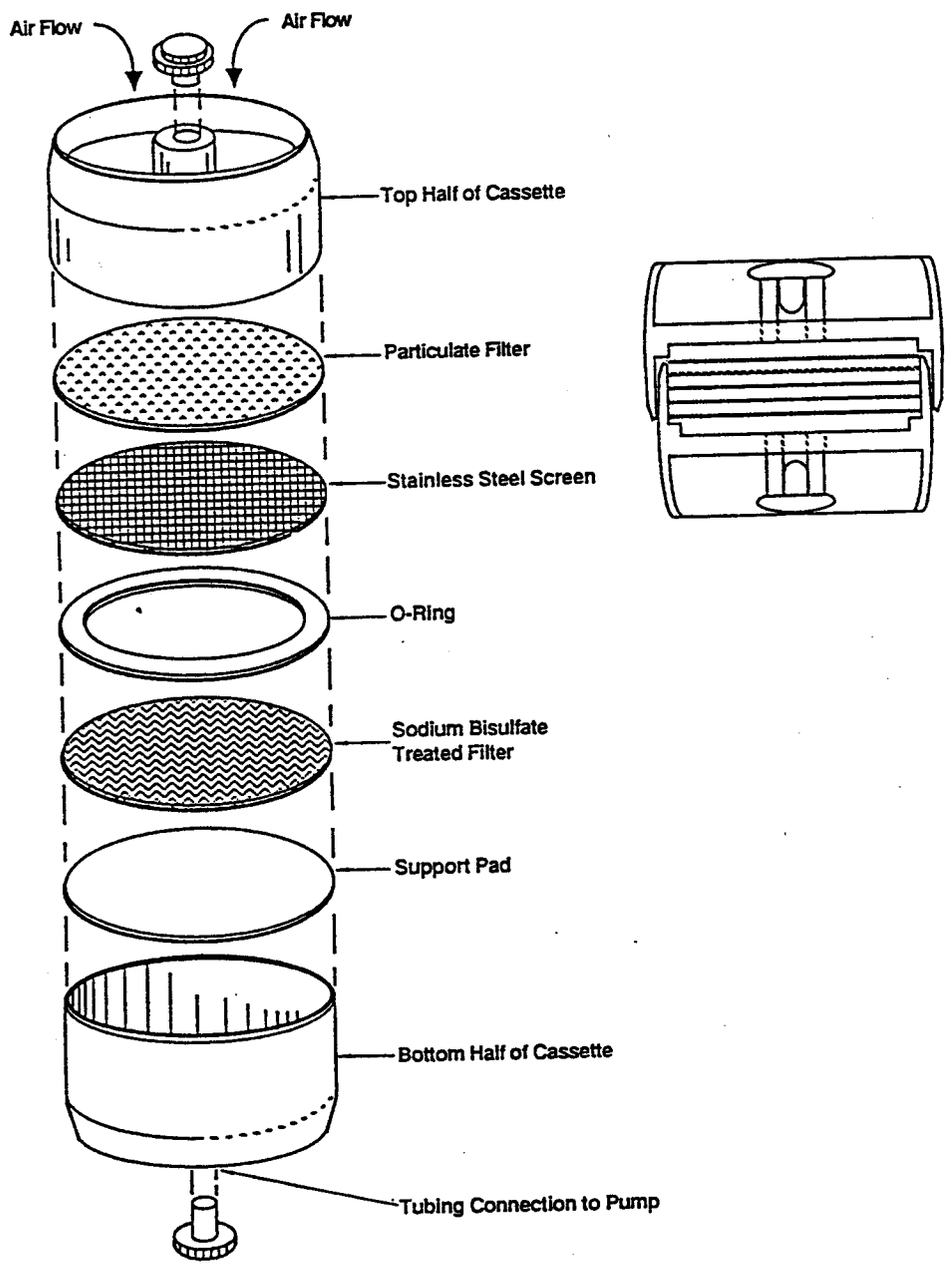

Figure 1. Filter Cassette Used for Active Sampling

231

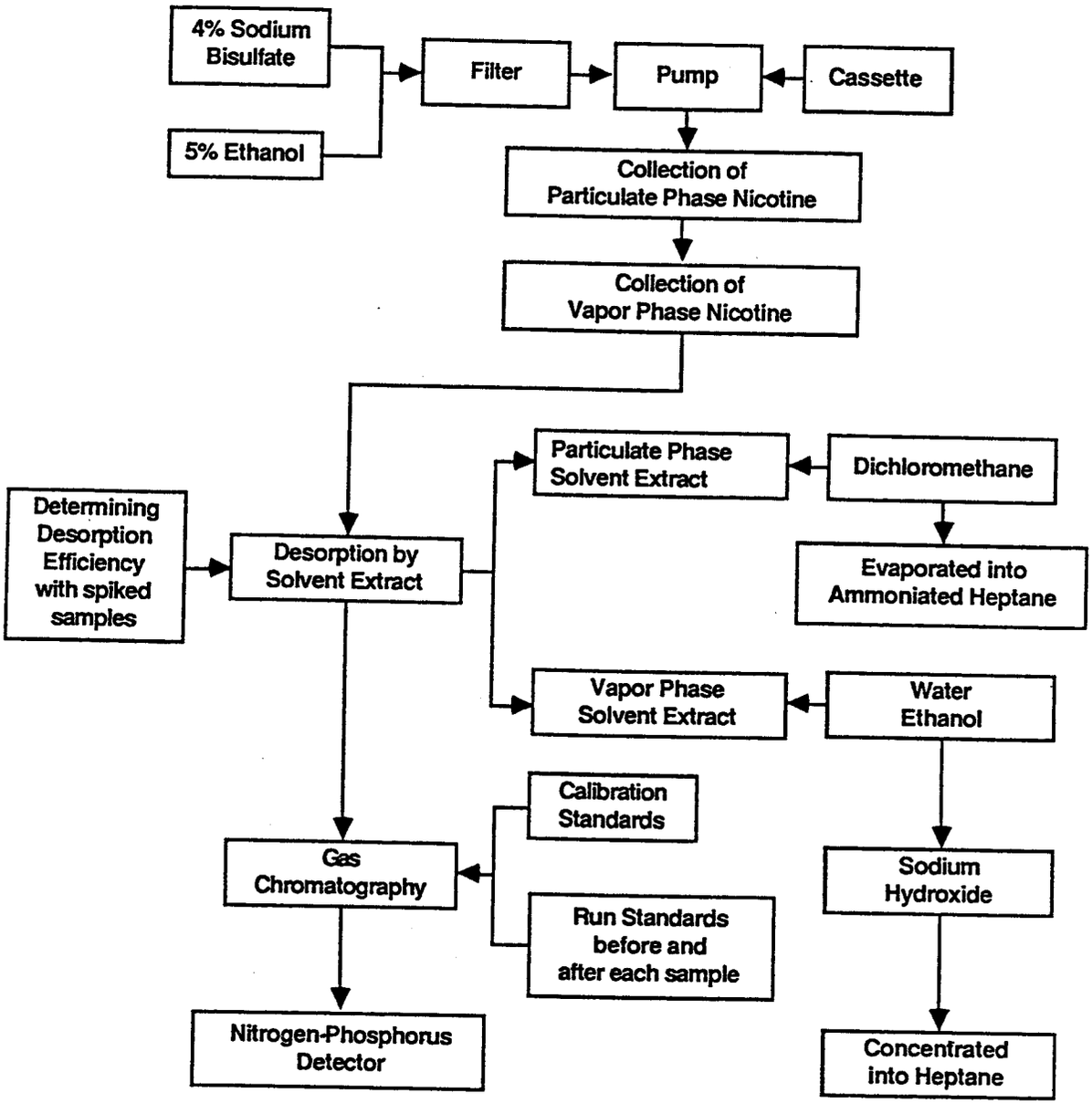

Figure 2. Sampling/Analysis for Active Sampling Using a Filter Cassette

232

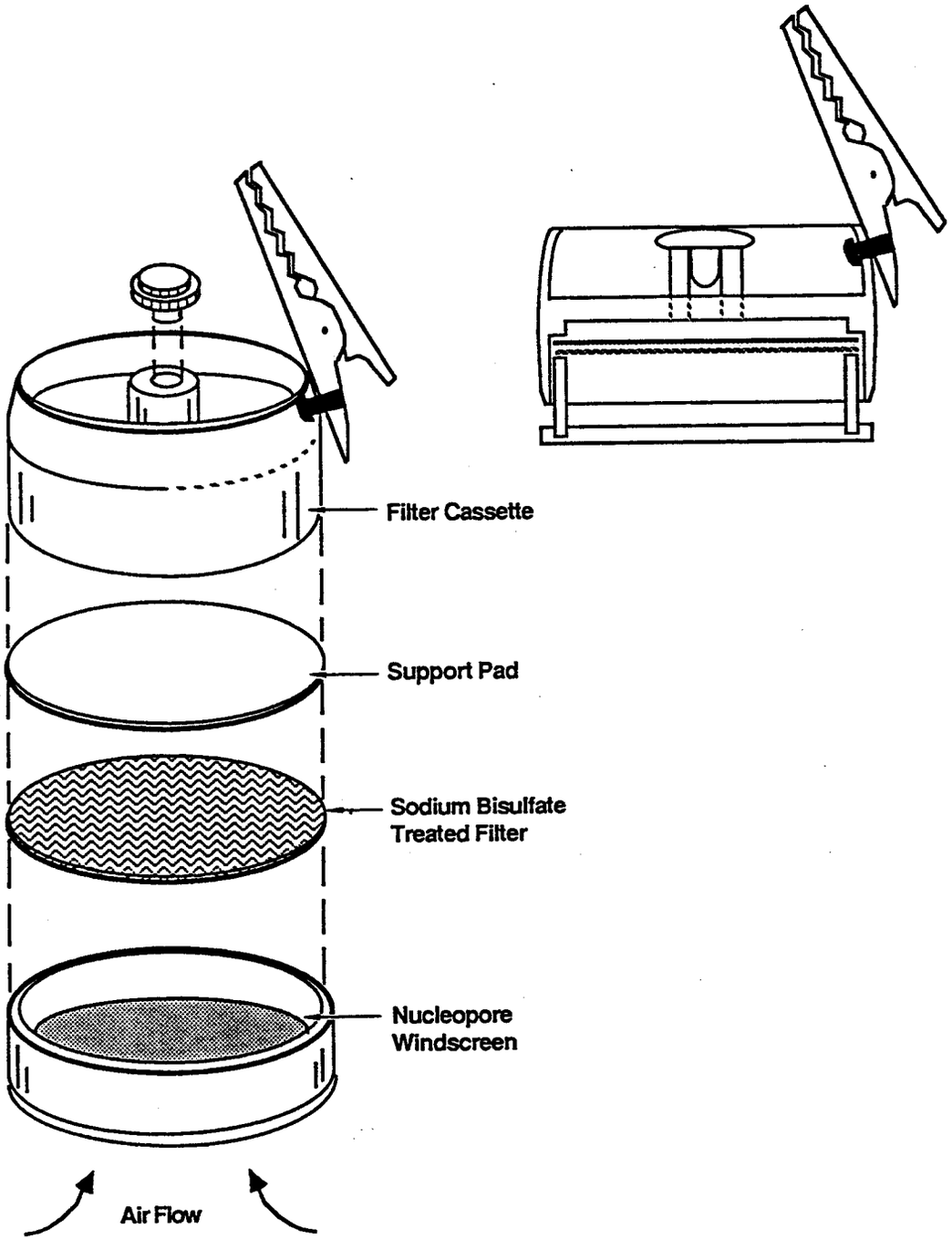

Figure 3. Filter Cassette Used for Passive Sampling

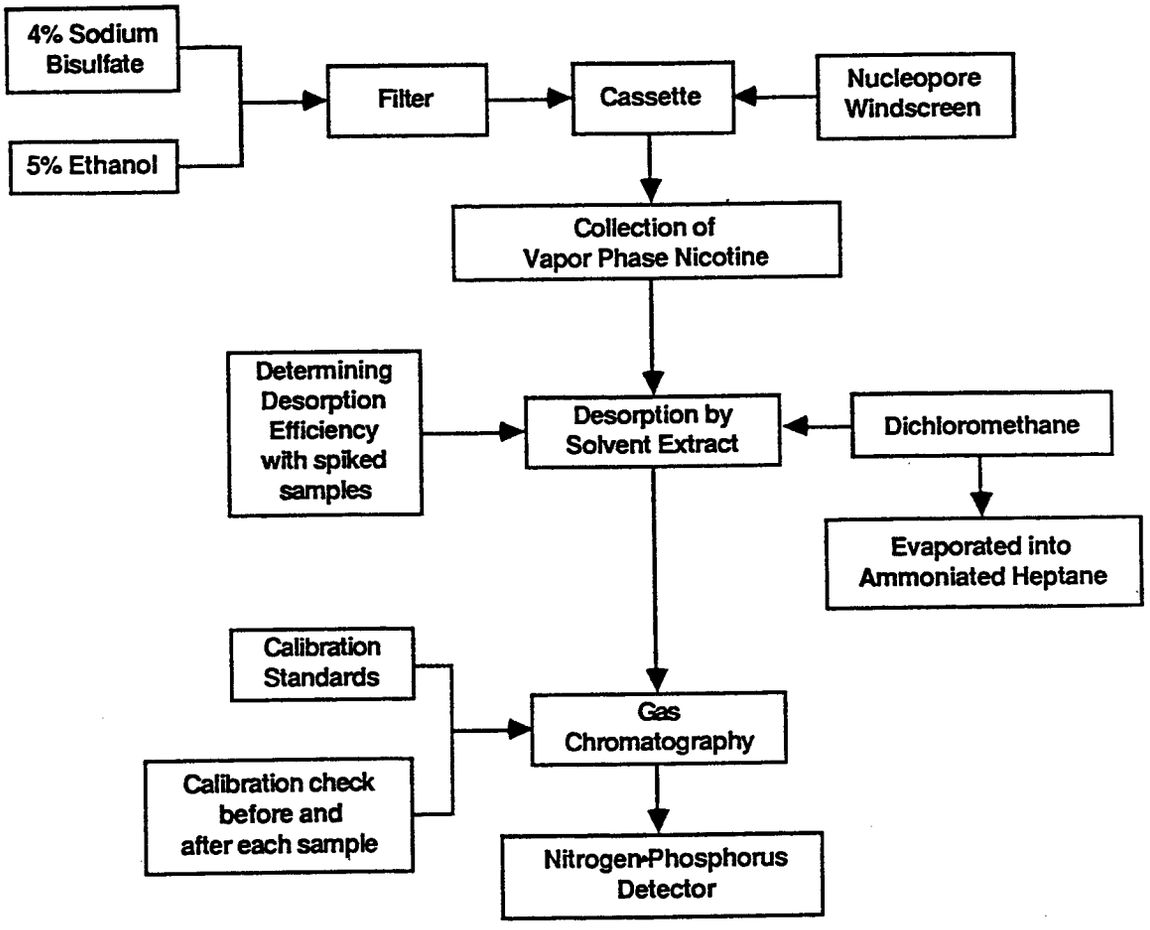

Figure 4. Sampling/Analysis for Passive Sampling Using a Filter Cassette

234

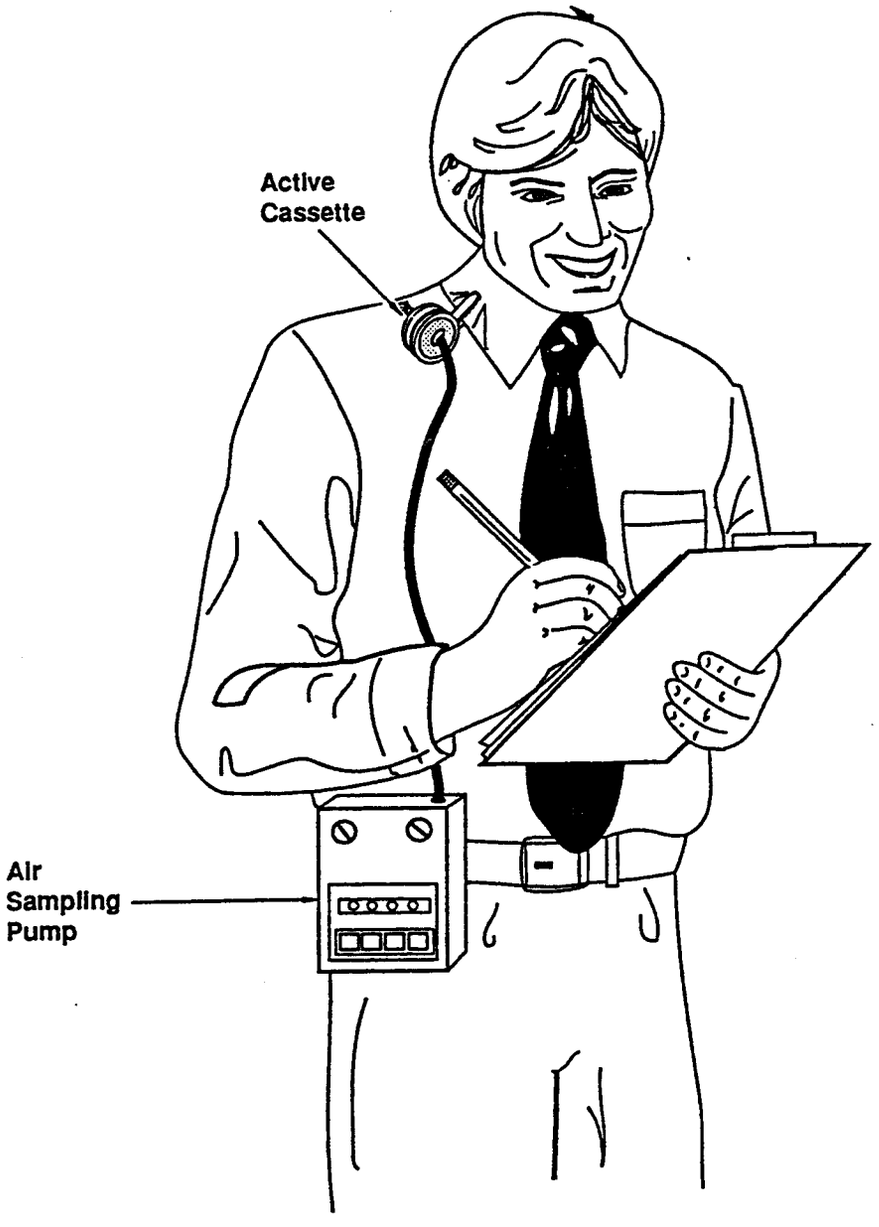

Figure 5. Sampling Setup for Personal Monitoring

235

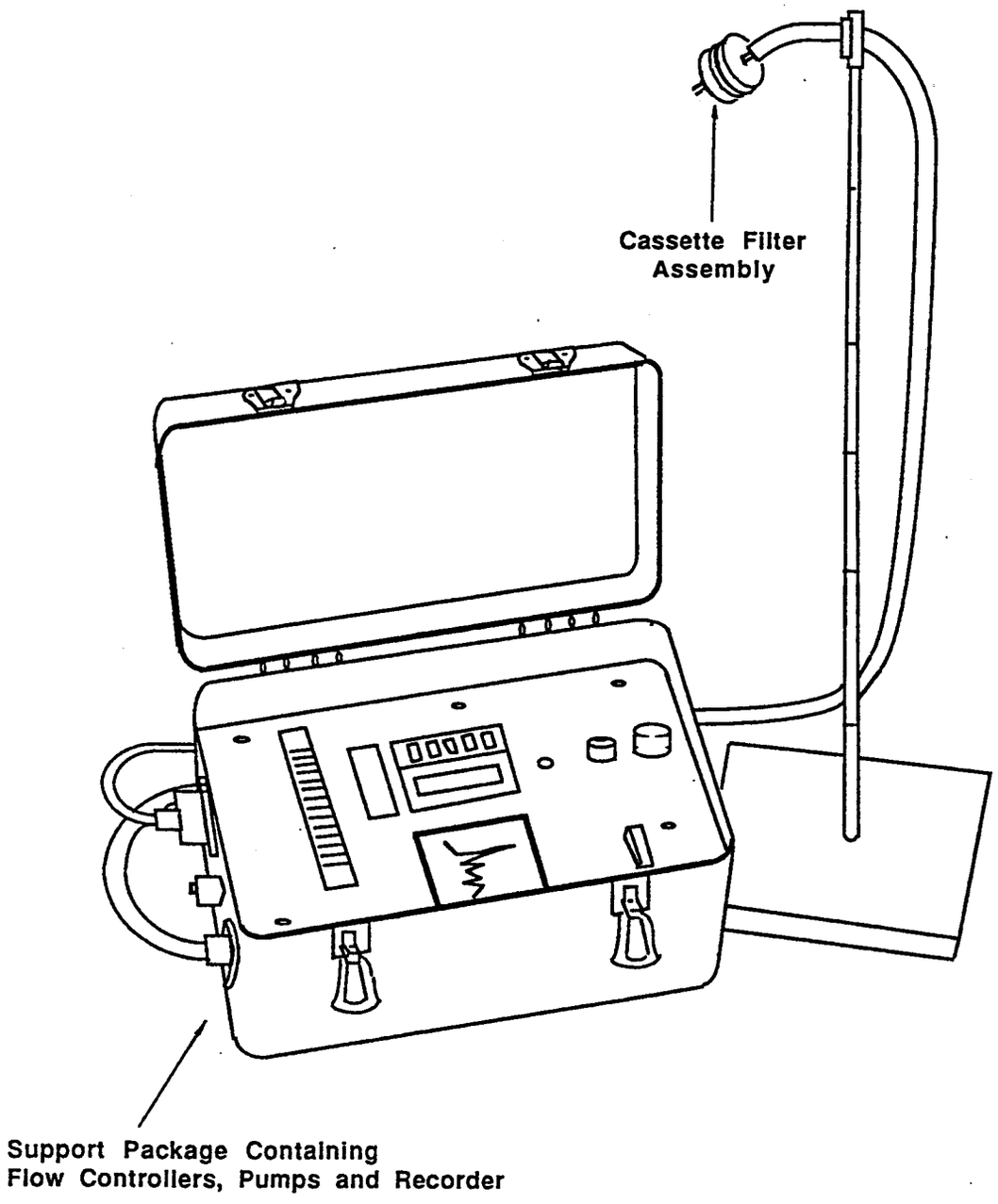

Figure 6. Sampling Setup for Stationary Sampling

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

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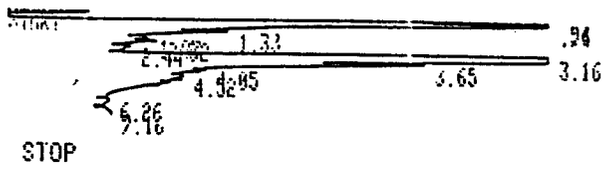


Operating Parameters for the GC

Flow Rate: Helium carrier, 15 ml/min
Column: 2 mm 6 foot 2% KOH on 10% Carbowax 20 M
Oven: 140°C
Detector: 250°C
Detector Gas Flow Rates: Hydrogen 1 mL/min; Air 115 mL/min
Injector: 225°C
Injection: 3 µl
Retention Time: ~3.16 min for Nicotine

RUN # 47

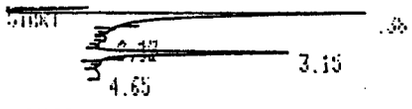
AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.56	277100	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	0.202	78.661
3.65	809480	TBP	0.195	0.662
4.05	39248	DTPV	0.177	0.032
4.52	108820	TPV	0.264	0.089
6.26	32536	TBP	0.268	0.027
7.16	15755	ITPB	0.245	0.013

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

Figure 8. Chromatograms from an ETS Sample

238

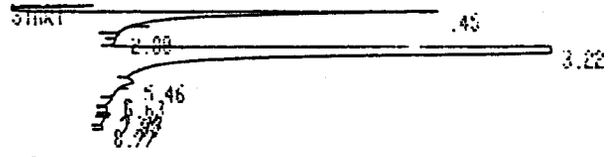


RUN # 6

AREA%

RT	AREA	TYPE	AREA%
0.38	4639600	PB	76.321
2.13	19440	PV	0.320
2.32	18262	D VP	0.300
3.15	1370600	PB	22.547
4.65	31098	PV	0.512

TOTAL AREA= 6079100
MUL FACTOR= 1.0000E+00

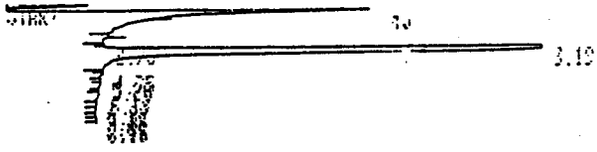


RUN # 10

AREA%

RT	AREA	TYPE	AREA%
0.45	5857400	PB	4.016
2.00	8661	D BP	0.006
3.22	1.3977E+08	↑SPB	95.824
5.46	130970	TBB	0.090
6.63	28151	BP	0.019
7.79	30109	D VV	0.021
7.99	31492	D VP	0.022
8.77	3925	PP	0.003

TOTAL AREA= 1.4586E+08
MUL FACTOR= 1.0000E+00



RUN # 8

AREA%

RT	AREA	TYPE	AREA%
0.45	3433200	PB	19.035
2.73	4444	PP	0.025
3.19	1.4425E+07	PB	80.192
4.75	13831	VP	0.077
5.20	15217	PV	0.085
6.19	41916	VP	0.233
6.82	19103	PV	0.106
7.19	15959	VP	0.089
7.64	5992	PV	0.033
7.92	12210	VP	0.068
8.15	1317	I PP	0.007

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

Operating Parameters for the GC

Flow Rate: Helium carrier, 15 mL/min
Column: 2 mm 6 foot 2% KOH on 10% Carbowax 20 M
Oven: 140°C
Detector: 250°C
Detector Gas Flow Rates: Hydrogen 1 mL/min; Air 115 mL/min
Injector: 225°C
Injection: 3 µL
Retention Time: ~3.16 min for Nicotine
Run #6 = 1 µg/mL
Run #8 = 10 µg/mL
Run #10 = 100 µg/mL

Figure 9. GC Chromatograms of Varying Nicotine Concentrations

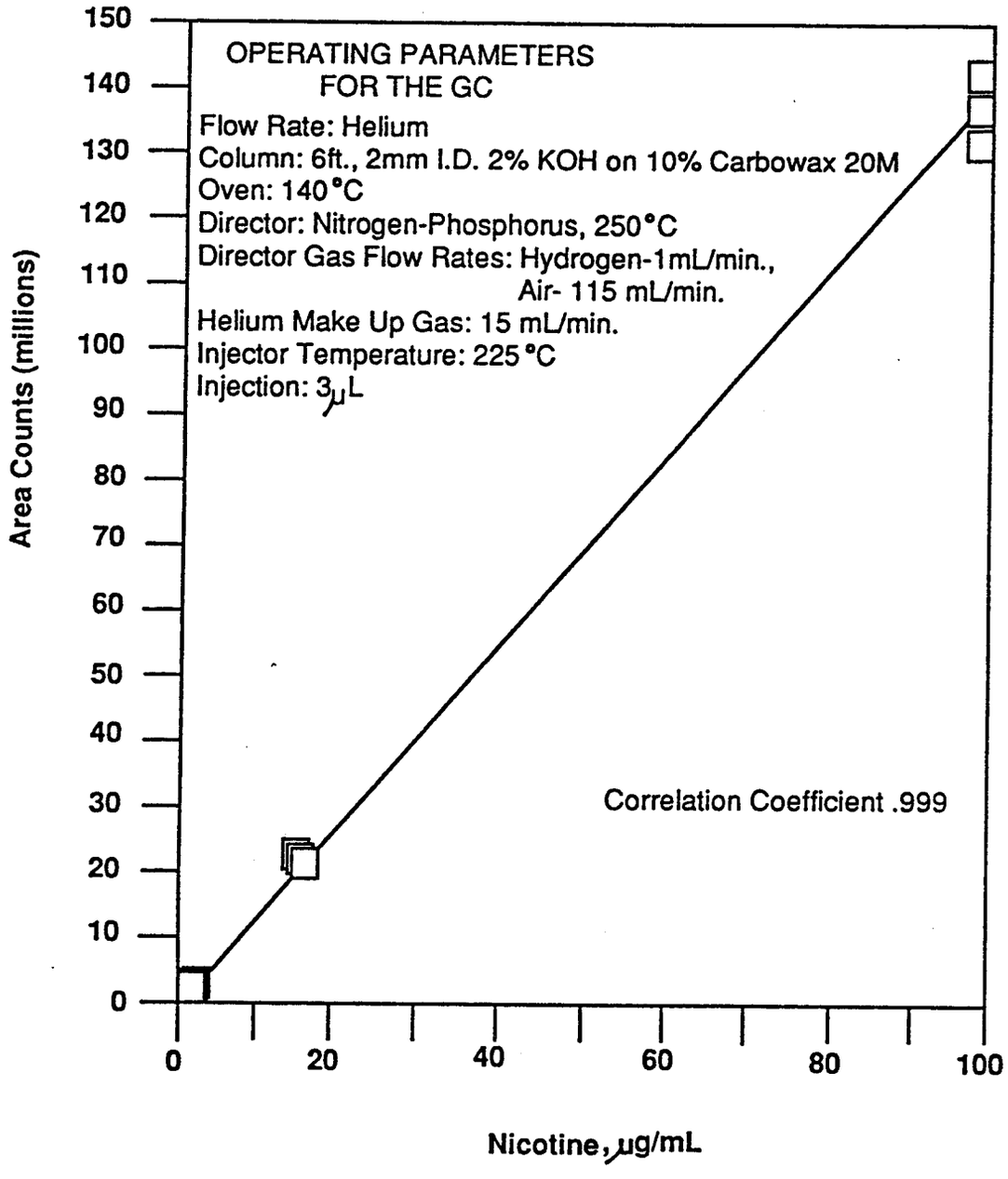


Figure 10. Nicotine Calibration Curve

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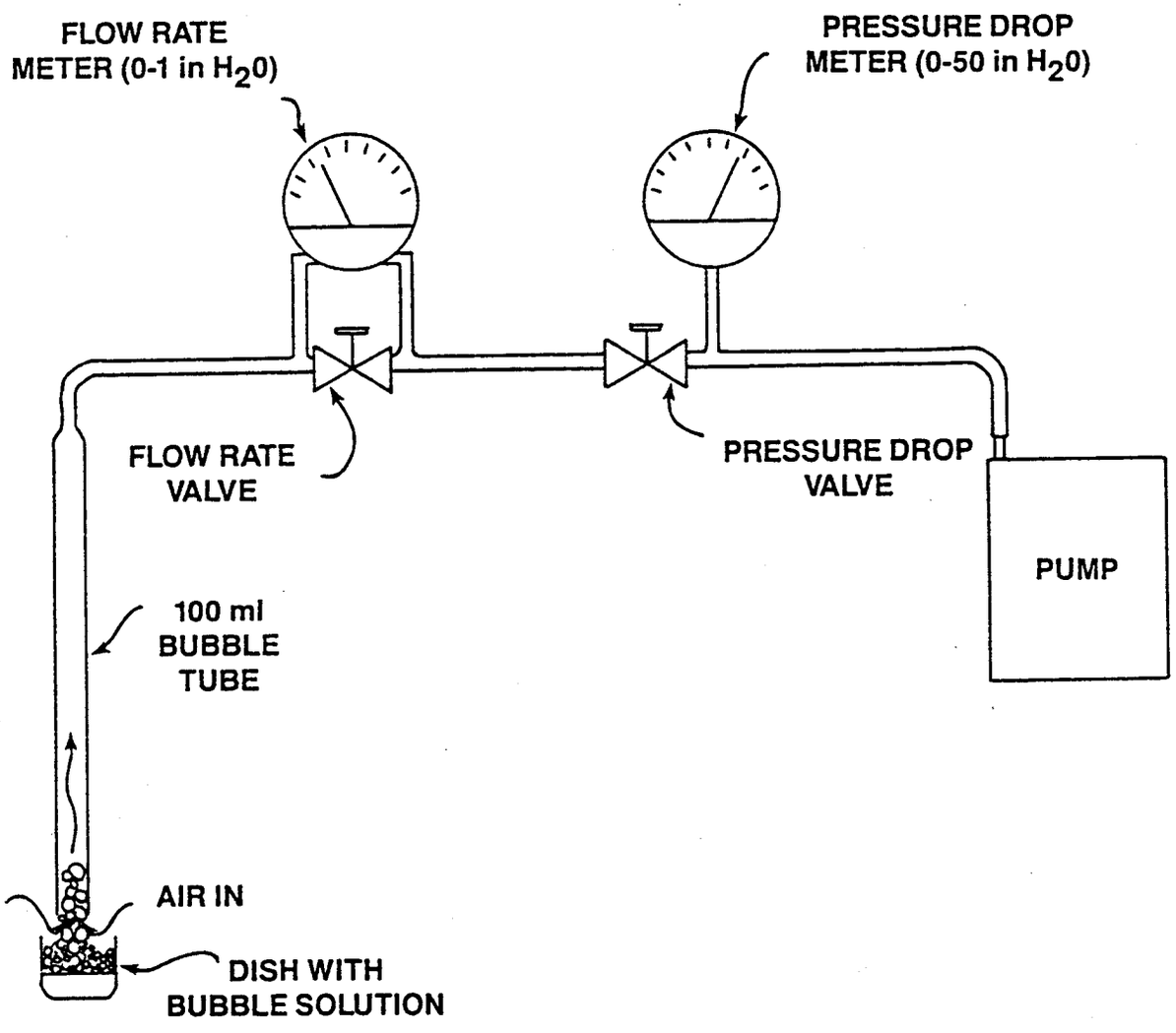

Figure 11. Calibration Assembly for Personal Sampling Pump

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Chapter IP-3

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO_2) IN INDOOR AIR

- **Method IP-3A - Nondispersive Infrared (NDIR)**
- **Method IP-3B - Gas Filter Correlation (GFC)**
- **Method IP-3C - Electrochemical Oxidation**

1. Scope

This document provides three methods for determination of CO or CO_2 in indoor air. The first method (IP-3A) employs nondispersive infrared (NDIR) spectrometry for fixed-site monitoring using a real-time continuous monitor. The second method (IP-3B) presents the use of the gas filter correlation (GFC) technique for determination of CO or CO_2 in indoor air. Method IP-3B utilizes GFC analyzers that are located at fixed sites within the monitoring area. The third method (IP-3C) utilizes electrochemical oxidation principles to determine CO in indoor air. An Appendix to Method IP-3C describes a specific portable air sampling system (PASS) using electrochemical techniques.

2. Applicability

2.1 Indoor air quality has become a significant environmental health issue because most people spend the majority of their time indoors. As with outdoor air quality and occupational exposure, monitoring pollutant concentrations indoors is essential to evaluate potential health threats and identify proper abatement approaches. Indoor CO/CO_2 emissions contribute to poor indoor air quality. With the presence of these pollutants in indoor air, there is a need to assess human exposure and at least meet ambient air and occupational standards.

2.2 Indoor CO emissions are mostly due to incomplete fuel combustion in unvented cooking and heating appliances and from consumption of tobacco products. Vehicular exhaust originating in attached or underground garages may also be a major contributor. CO is essentially nonreactive, and in the absence of indoor sources, average indoor CO concentrations are comparative to outdoor concentrations. However, when indoor sources are present, indoor levels can be much higher than those outdoors. Indoor levels can exceed the 8-hour ambient standard when indoor sources are substantial. The National Ambient Air Quality Standards (NAAQS) for CO are 9 ppm (10 mg/m^3) for an 8 hour period and 35 ppm (40 mg/m^3) for a 1 hour period.

2.3 Carbon dioxide is a colorless, odorless, and tasteless gas than can produce a debilitating effect on humans, including impaired breathing and unconsciousness. This gas is heavier than air and it seeks the lowest levels, displacing normal air. CO_2 is produced by human metabolic activity and exhaled through the lungs. The amount of CO_2 produced is a function of an individual's activity level and composition of food consumed. The average amount of CO_2 normally exhaled by an adult with an activity level equivalent to an office worker is approximately 200 mL/min.

2.4 In addition to being a product of human respiration, CO_2 is also an indicator of inadequately vented combustion processes such as gas or oil-fired space and hot water heaters. Individuals exposed to 1.5% CO_2 for prolonged periods of time experience mild metabolic stress, while exposure to 7-10% CO_2 results in unconsciousness within a few minutes. Ventilation standards have historically been set to maintain CO_2 indoor concentrations $\leq$ 0.5%, a level which appears not to adversely affect persons with normal health. Under standards newly adopted by the American Society of Heating, Refrigeration, and Air Conditioning Engineers (ASHRAE) utilizing a 20 cfm/person fresh air intake rate, CO_2 indoor concentrations should be maintained below 0.08%.

Method IP-3A

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO_2) IN INDOOR AIR USING NONDISPERSIVE INFRARED (NDIR)

Method IP-3A

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO_2) IN INDOOR AIR USING NONDISPERSIVE INFRARED (NDIR)

1. Scope

1.1 This document describes a combined method for determination of CO or CO_2 in indoor air using nondispersive infrared spectrometry. This method makes use of a commercially available nondispersive infrared (NDIR) analyzer that is located at a fixed site for continuous measurement of CO or CO_2 in indoor atmospheres.

1.2 The NDIR method described herein is based on ASTM Standard Procedure D3162-78 and 40 CFR Part 50, Appendix C. This procedure has a detection limit of approximately 0.5 ppm (0.6 mg/m^3) CO in air. NDIR analyzers are relatively insensitive to flow rate, require no wet chemicals, are sensitive over wide concentration ranges, and have short response times.

1.3 While nondispersive infrared analyzers are the most commonly used continuous, automated devices for measuring ambient level CO concentrations, other instruments have been developed and tested.

1.4 Galvanic and coulometric analyzers are two other instruments commercially available for continuously measuring CO concentrations. The function of both instruments depends on the oxidation of CO by iodine pentoxide (I_2O_5). These instruments are flow- and temperature-dependent and suffer from multiple interferences; consequently, they have not been widely used.

1.5 A mercury vapor analyzer, which depends on the liberation of mercury vapor when CO is passed over hot mercuric oxide, has been used as a portable, continuous-monitoring analyzer. Though especially adaptable for measuring low CO concentrations 0.25 ppm (0.29 mg/m^3), this instrument does not appear suitable for routine air monitoring because of numerous interferences and electronic instability.

1.6 A recently developed automated gas chromatographic system operates by quantitatively converting CO to methane (CH_4), which is subsequently semi-continuously measured by a flame ionization detector. This arrangement shows considerable promise as a monitoring device. Concentrations of from 0.1 to 1,000 ppm (0.1 to 1,150 mg/m^3) may be determined, and instrument output over this range is linear for both CO and CH_4.

1.7 The NDIR systems have several advantages over these monitoring techniques. They are:

- Insensitive to flow rates,
- Require no wet chemicals,
- Independent of room temperature change,
- Sensitive over a wide concentration range,
- Quick responding, and
- Operatable by non-technical personnel.

1.8 Consequently, this method is based upon the NDIR principle of detection of CO and CO_2 in indoor air.

2. Applicable Documents

2.1 ASTM Standards

D1356	Definition of Terms Relating to Atmospheric Sampling and Analysis
D1357	Recommended Practice for Planning the Sampling of the Atmosphere
D3195	Recommended Practice for Rotameter Calibration
D1914	Recommended Practice for Conversion Units and Factors Relating to Atmospheric Analysis
D3249	Recommended Practice for General Ambient Air Analyzer Procedures
E1	Specification for ASTM Thermometers
E180	Recommended Practice for Development of Precision Data for ASTM Methods for Analysis and Testing of Industrial Chemicals
D3162-78	Standard Test Method for Carbon Monoxide in the Atmosphere (Continuous Measurement by Nondispersive Infrared Spectrometry)

2.2 Other Documents

Laboratory and Indoor/Ambient Air Studies (1-5)
U.S. Environmental Protection Agency Technical Assistance Document (6)
U.S. Environmental Protection Agency Quality Assurance Handbook (7)

3. Summary of Detection

3.1 Nondispersive infrared analyzers have been developed to monitor not only CO or CO_2, but also SO_2, NO_x, hydrocarbons and other gases that absorb in the infrared region of the electromagnetic spectrum. The term "nondispersive" is used to describe the fact that no prisms or grating are used in the monitor to disperse the infrared energy source into component wavelengths. Rather the measurement gas itself (i.e. CO or CO_2) is used in the detector to detect wavelength, and hence species, specificity.

3.2 A broad wavelength band of infrared emission is used instead of employing monochromatic filters or diffraction gratings to isolate one particular wavelength (8). As illustrated in Figure 1A, a gas will have characteristic absorption peaks centered at specific wavelengths (λ_0) in the infrared spectrum when exposed to broad band infrared radiation (λ). The center of these absorption peaks are specific for individual compounds, as illustrated in Figure 1B.

3.3 An NDIR analyzer operates on the principle that CO (or CO_2) has a sufficiently characteristic infrared absorption spectrum such that the absorption of infrared radiation by the CO molecule can be used as a measure of CO concentration in the presence of other gases that may occur in indoor air. Although the size, shape, sensitivity, and range of these instruments vary with manufacturer, basic components and configurations are similar. Most commercially available instruments include a hot filament source of infrared radiation, a

rotating sector (chopper), a sample cell, a reference cell, and a detector, as illustrated in Figure 2.

3.4 In operation, broad band infrared radiation is emitted from the infrared source and passes through the chopper wheel into the compartments containing the reference and sample cells. The reference cell is filled with a non-absorbing inert gas such as nitrogen or argon. The sample cell is a flow-through design enabling the passing of the gas stream of interest. Equal amounts of infrared energy enter both the sample and reference cells. If no CO or CO_2 is present in the gas stream, then the amount of radiation exiting the sample cell compartment will be equal to that exiting the reference cell. If, however, the gas stream contains molecules of CO or CO_2, then the infrared energy exiting the sample cell will be less than that exiting the reference cell because of molecular absorption.
Note: Recent models have included a distribution cell (containing 100% CO_2) and a flow-through design for the reference cell. In this design, a CO-CO_2 converter consisting of a temperature-controlled cartridge containing platinum-coated aluminum trioxide beads converts the sample gas CO to CO_2 on the reference cell side. At the same time, sample gas containing CO, but not converted to CO_2, flows through the sample cell. the CO-CO_2 converter causes no other change to the sample gas, thus the only difference between the sample and reference gases is the CO content. Since only the CO has been removed from the reference gas, and due to the distribution cell, all the CO_2 wavelength IR energy has been removed from both beams, then the only difference between the IR energy emanating from the sample cell and reference cell is that caused by CO wavelength absorption in the sample cell. Because all the CO_2 wavelength energy has been absorbed in the distribution cell, there can be no further absorption from the increased CO_2 concentration in the "reference" cell. All other interferents, such as water, exist similarly in both cells and do not contribute to the difference. The distinct advantage of this system over systems using cylinder reference gas or static reference cells is that all interferents, known and unknown, are similarly present in the sample and reference cells and thus their effect is cancelled.

3.5 A mathematical relationship exists between the amount of CO or CO_2 in the sample and the amount of absorption or energy attenuation. The mathematical relationship is known as the Beer-Lambert Law and is used to determine the concentration of CO or CO_2 in an air sample. The law states that the transmittance of light through a medium that absorbs light is decreased exponentially by the product αcl. The Beer-Lambert Law is defined by the following equation:

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

where:
T = transmittance of light through sample gas
I_o = intensity of light entering the sample gas
I = intensity of light leaving the gas
c = concentration of the pollutant, mol/liter
l = distance light beam travels through sample gas, path length, cm
α = attenuation coefficient, liter/mol-cm

3.6 The attenuation coefficient, α, is dependent upon the wavelength of the radiation and also upon the properties of the molecule. The coefficient tells how much a gas species will absorb light energy at a given wavelength. If no absorption occurs, α will be zero, and the transmittance of IR energy would equal 100%. If an electronic or vibrational-rotational transition occurs in the gas at some wavelength, α will be some value, and the reduction of light energy across the path will depend upon the pollutant concentration and the original intensity, I_o, of the light beam. I_o is determined by taking a reading from the detector when no pollutant gas is in the sample cell. The concentration is obtained from the Beer-Lambert Law if α and ℓ are known. Generally, a calibration curve is generated with known gas concentrations rather than using a theoretical value for α.

3.7 The resultant IR energy exiting both the sample and reference cells now strike the detector compartment.

3.8 The uniqueness of commercially available NDIR monitors lies within the detection of the remaining IR radiation. More specifically, the detector consists of two compartments filled with equal concentrations (%) of the pollutant being monitored, i.e. CO or CO_2. Because the pollutant absorbs at discrete wavelengths, its specificity enables it to be an excellent detector for monitoring the change in IR energy entering the detector system caused by the same pollutant gas in the sample cell.

3.9 As illustrated in Figure 2, the detector compartments, containing similar concentrations of specific pollutant of interest, are separated by a thin diaphragm whose movement is detected by an induction tranceducer.

3.10 The resultant infrared signal from the reference cell strikes one compartment of the detector cell, while the resultant infrared energy from the sample cell strikes the other side of the detector cell (1). The detector functions in the following manner: when the molecules of CO or CO_2 in the detector compartments absorb infrared radiation, they absorb the energy of that radiation. This increase in energy results in the CO or CO_2 molecule becoming more active (it begins to vibrate and move more rapidly). This increase in molecular activity causes the CO or CO_2 gas to expand. However, because the gas is contained in a rigid compartment, expansion results in an increase in the pressure of the CO or CO_2 gas within the cell. The compartment receiving the reference signal receives more infrared energy and subsequently more energy is absorbed by the CO or CO_2 molecules contained within that cell. This results in a higher gaseous pressure on the reference side of the detector relative to the sample side of the detector. The thin metal diaphragm naturally bends toward the area of lower pressure (the sample side), and the amount of this deflection is measured by means of the induction transducer. This signal is then amplified and used to determine the concentration utilizing the Beer-Lambert Law. The use of CO or CO_2 in the detector compartments limits the measured absorption to one or more of the characteristic wavelengths at which CO strongly absorbs, thus providing specificity of the detector for that gas.

3.11 Because the diaphragm detector is sensitive to vibrations, the micro-flow® detector was developed. Similar to the diaphragm detector, it also contained two detector cells filled

with CO. However, the two cells are separated by a passage way which allows gas to flow between detector reference and sample cells. The flow of gas is monitored by a mini-flowmeter. In operation, the two detector cells filled with CO absorb the unequal infrared energy. This energy is absorbed in the CO-filled detector cell, raising the gas temperature and thus its pressure. The unequal pressure rise in the detector cells, due to the unequal IR energy striking the detector cells, causes a flow from the reference detector to the sample detector cell which is measured by the micro-flow® mini-flowmeter in the connecting passage. The detector cell gas flow continues from "reference" to "sample" until the chopper blade obscures the IR energy source. At that time the transmitted energy goes to zero, the reference detector cell temperature falls to approach the temperature of the sample cell and the detector cell flow reverses to re-equalize the detector cell pressures. At the chopping rate of 10 cycles per second (8.33 for a 50 Hz installation), the micro-flow® sensor generates an alternating signal whose amplitude is proportional to CO concentration in the sample cell. The alternating micro-flow® signals are fed to an AC differential amplifier and the output fed to a synchronous rectifier phased with the chopper. The DC output of the rectifier is then filtered and amplified, then linearized and presented to the output voltage terminals as % CO.

4. Significance

4.1 CO is absorbed by the lung and reacts primarily with hemoproteins and most notably with the hemoglobin of the circulating blood (9). The absorption of CO is associated with a reduction in the oxygen-carrying capacity of blood and in the readiness with which the blood gives up its available oxygen to the tissues. The affinity of hemoglobin for CO is over 200 times that for oxygen, indicating that carboxyhemoglobin (COHb) is a more stable compound than oxyhemoglobin (O_2Hb). About 20% of an absorbed dose of CO is found outside of the vascular system, presumably in combination with myoglobin and heme-containing enzymes.

4.2 The magnitude of absorption of CO increases with the concentration, the duration of exposure, and the ventilatory rate. With fixed concentrations and with exposures of sufficient duration, an equilibrium is reached; the equilibrium is reasonably predictable from partial-pressure ratios of oxygen to CO.

4.3 Long-term exposures to sufficiently high CO concentrations can produce structural changes in the heart and brain. It has not been shown that ordinary ambient exposures will produce this. The lowest exposure producing any such changes has been 50 ppm (58 mg/m^3) continuously for 6 weeks. The recommended American Conference of Government Industrial Hygienists (ACGIH) permissible exposure limit for CO is 35 ppm for a 10-hour time weighted average (TWA) with a 200 ppm ceiling (10).

4.4 Consequently, due to the reliability and accuracy needed, this method recommends NDIR analyzers that have performance specifications similar to those for EPA designated reference methods (11) as outlined in Table 1 and Table 2. For monitoring ambient CO to determine compliance with the National Ambient Air Quality Standards (NAAQS), analyzers designated as reference methods are required. Portable NDIRs can be used to

screen residential environments, workplace, etc. for the presence and intensity of CO or CO_2. Use of portable NDIRs may not yield defensible quantitative information regarding CO or CO_2 concentrations. Rather, they can be used to provide a "profile" of intensity of CO or CO_2 and to assist in the placement of indoor fixed site monitors. Rigorous sampling strategy using fixed site NDIR (EPA reference models as listed in Table 2) can subsequently be instituted at specific locations based on this screening. This method will not attempt to detail the operation of portable NDIRs, which can be found in specific models users manuals.

5. Definitions

Note: Definitions used in this document and any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, E260, and E355. All abbreviations and symbols are defined within this method at point of use. Additional definitions, abbreviations, and symbols are located in Appendices A-1 and B-2 of this Compendium.

5.1 Range - The minimum and maximum measurement limits of a monitor.

5.2 Output - Electrical signal which is proportional to the measurement; intended for connection to data recording or data processing devices. Usually expressed as millivolts or milliamps full scale.

5.3 Full scale - The maximum measuring limit for a given range of a monitor.

5.4 Minimum detectable sensitivity - The smallest amount of input concentration that can be detected as the concentration approaches zero.

5.5 Accuracy - The degree of agreement between a measured value and the true value; usually expressed as ± percent of full scale.

5.6 Lag time - The time interval from a step change in input concentration at the instrument inlet to the first corresponding change in the instrument output.

5.7 Time to 90% response - The time interval from a step change in the input concentration at the instrument inlet to a reading of 90% of the ultimate recorded concentration.

5.8 Rise time (90%) - The interval between initial response time and time to 90% of the final response after a step increase in the inlet concentration (90% response-lag time).

5.9 Fall time (90%) - The interval between initial response time and time to 90% of final response change after a step decrease in the inlet concentration to zero.

5.10 Zero drift - The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is zero; usually expressed as percent full scale.

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5.11 Span drift - The change instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is a stated upscale value; usually expressed as percent.

5.12 Precision - The degree of agreement between repeated measurements of the same concentration, expressed as the standard deviation.

5.13 Operational period - The period of time over which the instrument can be expected to operated unattended within specifications.

5.14 Noise - Spontaneous deviations in measured concentrations from the mean not caused by input concentration changes.

5.15 Interference - An undesired positive or negative response caused by a substance other than the one being measured.

5.16 Interference equivalent - Quantitative interference response, measured as equivalent concentration units of the gas being measured.

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

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

5.19 Linearity - The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between upper and lower calibration points.

5.20 NDIR - This measuring technique is based on absorption by a gaseous pollutant of radiation in the infrared region. This technique is termed nondispersive because no prism or grating is used to disperse the infrared radiation. Uniqueness of this approach is that compound specificity is achieved by using the pollutant being measured (CO or CO_2) in the detector compartments in a differential absorption application to discriminate the discrete wavelengths characteristic of that pollutant.

5.21 Discrimination ratio - Discrimination ratio equals the concentration of an interferent required to produce an instrument response equivalent to unit concentration of the gas being measured.

6. Interferences (8)

6.1 The degree of interference varies with individual NDIR analyzers. Manufacturer's specifications should be consulted to determine if possible interferences render the analyzer unsuitable for proposed use.

6.2 Interference may arise from gases that absorb infrared radiation in wave length bands that overlap that of carbon monoxide or carbon dioxide. Some of the possible interferents are organics, water vapor, methane, and ethane. Carbon dioxide (for CO monitors) and water vapor (for both CO and CO_2 monitors) pose the major interference problems due to

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their common occurrence in the atmosphere, and also due to their relatively much higher concentrations than typical CO concentrations.
Note: Concentrations of carbon dioxide found in ambient air (approximately 400 ppm) normally do not interfere with CO measurements, provided the calibration gas contains about the same concentration of CO_2. However, in air grossly contaminated with combustion products, CO_2 (in excess of 1,000 ppm) could result in positive interferences of 1 ppm or higher.

6.3 Water vapor absorbs infrared radiation to a varying degree throughout the infrared region. Its presence can be a primary positive interference in NDIR type instruments. With no correction, error from the moisture interference could be as great as 10 ppm (11 mg/m^3) CO.

6.4 Various measures may be taken to minimize moisture interference. The most obvious is a drying device in the sample inlet section of the analyzer. One device is a tube filled with silica gel or other suitable desiccant such as Drierite®. The sample air is passed over the desiccant before it enters the absorption cell. Another technique includes passing the sample air through a water saturator maintained at a constant temperature. The saturator maintains a constant humidity level in the sample gas stream. This constant humidity is also added to the calibration gases, thereby negating the moisture effects on concentration readings.

6.5 Refrigeration units in the sampling inlet systems are often used in commercial analyzers to maintain a constant, low humidity level. By cooling the sampled air, the moisture is condensed and subsequently removed from the air stream.
Note: Moisture-eliminating devices and constant humidity systems, when employed, should be used on all gases entering the analyzer - calibration, zero, and span gases as well as air samples.

6.6 Two other methods commonly employed to remove water vapor interference involve correcting the action of water vapor on the absorption phenomenon. Narrow band-pass optical filters can be used to remove those wavelengths most sensitive to water vapor from the irradiating beam. In a similar manner an "interference cell" containing water vapor and other principal interferents can be placed in line, between the infrared sources and the sample cell. The interference cell absorbs and reduces those wavelengths which overlap the CO absorption band. This reduces the interference effect of water vapor on the detector.

6.7 Another method of alleviating the interferences due to both CO_2 and water vapor (as well as other interferents) is designing the detector to contain a front and rear measuring chamber, each containing CO or CO_2, as illustrated in Figure 3. In this detector design, the infrared beams from both the reference and sample cells are geometrically combined into a single path into the detector, although the two beams are still separate due to the alternating action of the optical chopper. The front chamber is shorter than the longer rear chamber. The concentrations of pollutant gas in the two chambers are such that overall absorption, and hence the gas pressure, is equal in the two chambers (with no pollutant gas in the sample cell). Due to the peaked absorption characteristic of the detector gas,

absorption in the front chamber is substantially greater at the center wavelengths than at the side wavelengths. In the rear chamber, however, absorption is greater at the side wavelengths because the center wavelengths have been greatly attenuated by the front chamber. This differential absorption in the two chambers helps to compensate for interference from compounds whose absorption spectra overlap that of the detector gas.

6.8 Hydrocarbons at indoor levels should not cause interferences because of the specificity of the NDIR for the component of interest's spectrum. Effects of specific hydrocarbons on the analyzer are routinely provided by the manufacturer.

7. Apparatus

7.1 Analyzer

7.1.1 Continuous CO or CO_2 monitoring system - NDIR CO or CO_2 analyzer equipped with IR source, sample and reference gas cells, sample preconditioner (if needed), detector capable of sensing differences between infrared energy levels in the sample and reference cells, adequate power supply, amplifier/ control unit, meter, and recording system. The analyzer must meet or exceed manufacturer's specifications. Table 1 contains a listing of commercially available CO analyzers. The table lists reference method analyzers from U.S. EPA's List of Designated Reference and Equivalent Methods and also includes a sampling of portable CO or CO_2 analyzers available. Those monitors designated by U.S. EPA as reference methods generally meet or exceed the suggested performance specification listed in Table 2.

7.1.2 Pump - used to flow sample air into the analytical system, if required.

7.1.3 Flow control valve - used to control sample flow rate through the analytical system.

7.1.4 Flowmeter - used to measure sample flow rate through the analyzer.

7.1.5 Moisture control system - for analytical systems that require constant humidity control, refrigeration units are available with some commercial instruments. Drying tubes (with sufficient capacity to operate for 72 hours) containing silica gel (or equivalent drying agent) may be used for short-term sampling.

7.1.6 Particulate matter filter (inline) - used to remove particulate matter from sample flow and to keep sample cell clean. Filter porosity should be 2 to 10 microns.

7.2 Calibration

7.2.1 Pressure regulator(s) - Regulators must have a nonreactive diaphragm and suitable delivery pressure. A two-stage regulator with inlet and delivery pressure gauges is recommended.

7.2.2 Flow controller - The flow controller can be any device capable of adjusting and regulating the flow from the calibration standard. If the dilution method is to be used for calibration (see Section 9.2), a second flow controller will be required for the zero-air. For dilution, the controllers must be capable of regulating the flow to ± 1%.

7.2.3 Flow meter - A calibrated flow meter capable of measuring and monitoring the calibration standard flow rate will be required. If the dilution method is used, a second

flow meter will be required for the zero-air flow. For dilution, the flow meters must be capable of measuring the flow with an accuracy of ± 2%.

7.2.4 Mixing chamber - A mixing chamber is required only if the calibrator concentrations are generated by dynamic dilution of a CO standard. The chamber should be designed to provide thorough mixing of CO and zero-air.

7.2.5 Output manifold - The output manifold should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

7.2.6 Tubing - Polypropylene tubing to connect analyzer to gas cylinders when calibrating, zeroing, and spanning the instrument.

7.2.7 Thermometer - used to measure monitoring area temperature.

7.2.8 Barometer - capable of measuring barometric pressure of monitoring area.

8. Reagents and Materials

8.1 Zero-air source - A source of dry zero-air that is verified to be free of contaminants that could cause detectable responses from the CO analyzer will be needed. The zero-air must contain <0.1 ppm CO; some air cylinders sold as ultrapure may actually contain 1 to 2 ppm CO. The use of a catalytic oxidizing agent such as Hopcalite on any zero-air source would be prudent.

Note: Zero air and calibration gases for CO analyzers should contain about 350 ppm CO_2 to simulate normal ambient concentrations. If synthetic air is used, CO_2 may have to be added.

8.2 Calibration standard - CO standards must be traceable (12) to a National Institute of Standards and Technology - Standard Reference Material (NIST-SRM) or a NIST/EPA approved commercially available Certified Reference Material (CRM). The CO standards must be in air unless the dilution method is used. For dilution, CO in nitrogen may be used if the zero-air dilution ratio is not less than 100:1. An acceptable protocol for demonstrating the traceability of commercial cylinder gas to an NITS-SRM or CRM cylinder gas is provided in Section 12, reference 13. In order to establish a calibration curve and determine linearity of the NDIR analyzer, the calibration gases should correspond to approximately 10, 20, 40, 60, and 80% of full scale value.

8.3 Span gas - pressurized cylinder containing CO or CO_2 concentration corresponding to 80% of full scale, best source.

9. NDIR Analyzer Operation

9.1 Installation

9.1.1 Prior to locating the fixed site NDIR sampling system, the user may want to perform "screening analyses" using a portable CO detection system, such as the PASS as outlined in Method IP-3C, Appendix, or using a portable NDIR system, examples listed in Table 2, to determine presence of CO and variances in concentration. The information gathered from the portable screening analysis would be used in developing a monitoring

protocol, which includes the sampling system location based upon the screening analysis. After screening analysis is performed and sampling site(s) are determined, the fixed site NDIR sampling system is located.

9.1.2 Generally, CO or CO_2 fixed-site NDIR continuous monitors are designed for benchtop operation or installation into a rack. The instrument should be placed in an area that is relatively free of vibration. Appendix C-3 of this Compendium, Placement of Stationary Active Monitors, and Section 13, reference 4 gives further guidelines for monitor placement. If the analyzer is mounted on a rack, plumbing connections should be made on the rear of the cabinet for sample intake, span gas intake, zero gas intake, sample bypass and vent. Usually, on the table top analyzers, these intakes are connected to the front panel by quick-disconnect fittings. Additionally, for typical installation, primary power and recorder signal connections are also made. Portable NDIR monitors allow for much greater flexibility of employment. Some portable models are battery powered, allowing up to 8 hours of continuous operation or can be used continuously with an outside power source.

9.1.3 The manufacturer's operating instructions should include further instructions on the following: receiving inspection, typical/general installation, installation equipment required, and plumbing/electrical connections.

9.2 Operation

9.2.1 Turn-On Procedure and Initial Inspection

9.2.1.1 Turn on and inspect in accordance with specific model's user manual.

9.2.1.2 Ensure that indicators are illuminated, flow meters and pressure gauges are operational and flow meter is adjusted to obtain desired flow rate through the sample cell.

9.2.1.3 Allow the analyzer to stabilize as per user manual instructions (e.g., a minimum of two hours) prior to zeroing and spanning the instrument.

Note: Best performance can be expected if analyzer is left on continuously.

9.2.2 Manual Zero and Span Calibration

9.2.2.1 Prior to operating the analyzer, an initial calibration must be performed. The following provides procedures to measure CO or CO_2 concentrations in indoor air using the CO or CO_2 continuous monitor.

Note: Follow the manufacturer's detailed instructions when calibrating a specific analyzer.

9.2.2.2 Assemble the analyzer as illustrated in Figure 4.

9.2.2.3 Turn the power on and let the analyzer warm up. This usually requires several hours (2 hours minimum) depending on individual analyzers.

9.2.2.4 Connect zero gas to the analyzer.

9.2.2.5 Open the gas cylinder pressure valve (see Figure 4).

9.2.2.6 Adjust the secondary pressure valve until the secondary pressure gauge reads approximately (5 psi) more than the desired sample cell pressure.

Caution: Do not exceed the pressure limit of the sample cell.

9.2.2.7 Set the sample flow rate as read by the rotameter (read the widest part of the float) to the value that is to be used during sampling.

9.2.2.8 Let the zero gas flow long enough to establish a stable trace. Allow at least 5 minutes for the analyzer to stabilize.

9.2.2.9 Adjust the zero control knob until the trace corresponds to the line representing 5% of the strip chart width above the chart zero or baseline. The above is to allow for possible negative zero drift. If the strip chart already has an elevated baseline, use it as the zero setting.

9.2.2.10 Let the zero gas flow long enough to establish a stable trace. Allow at least 5 minutes for this. Mark the strip chart trace as adjusted zero and record on Multipoint Calibration Data Sheet, Figure 5.

9.2.2.11 Disconnect the zero gas.

9.2.2.12 Connect the span gas with a concentration corresponding to approximately 80% of full scale.

9.2.2.13 Open the gas cylinder pressure valve (see Figure 4). Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired sample cell pressure.

9.2.2.14 Set the sample flow rate, as read by the rotameter, to the value that is to be used during sampling.

9.2.2.15 Let the span gas flow until the analyzer stabilizes.

9.2.2.16 Adjust the span control until the deflection corresponds to the correct percentage of chart as computed by:

$$\text{Correct percentage of chart} = [C_s(\text{ppm})]/[C_f(\text{ppm})] \times 100 + 5\ \%\ \text{zero offset}$$

where:
C_s = concentration of span gas, ppm
C_f = full scale reading of analyzer, ppm

As an example where the percent zero offset is 5 and the correct percentage of chart for the span gas of 40 ppm would be:

$$40\ \text{ppm}/50\ \text{ppm} \times 100 + 5 = 85$$

9.2.2.17 Allow the span gas to flow until a stable trace is observed. Allow at least 5 minutes. Mark the strip chart trace as adjusted span and give concentration of span gas in ppm.

9.2.2.18 Disconnect the span gas.

9.2.2.19 Repeat Section 9.2.2.9 through Section 9.2.2.18 and if no readjustment is required, go to Section 9.2.3. If a readjustment greater than 1 ppm is required, repeat Section 9.2.2.9 through Section 9.2.2.10.

9.2.2.20 Lock the zero and span controls.

9.2.3 Multipoint Calibration

9.2.3.1 A multipoint calibration is required when the analyzer is first purchased, the analyzer has had maintenance which could affect its response characteristics, or when results from the auditing process show that the desired performance standards are not being met.

9.2.3.2 A multipoint calibration required calibration gases with concentrations corresponding to approximately 10, 20, 40, 60, and 80% of full scale and a zero gas containing less than 0.1 ppm CO (see Section 8).
Note: Zero air and calibration gases for CO analyzers should contain about 350 ppm CO_2 to simulate normal ambient concentrations. If synthetic air is used, CO_2 may have to be added.
The calibration gases should be certified to be within ± 2% of the stated value and purchased in high pressure cylinders with inside surfaces of a chromium-molybdenum alloy of low iron content or other appropriate linings. The cylinders should be stored in areas not subject to extreme temperature changes nor exposed to direct sunlight. There are two acceptable methods for obtaining multipoint calibration standard concentrations. They are:

- the use of individual certified standard cylinders of CO for each concentration needed, and
- the use of one certified standard cylinder of CO, diluted as necessary with zero-air, to obtain the various calibration concentrations needed.

The equipment needed for calibration can be purchased commercially, or can be assembled by the user as illustrated in Figure 6. When a calibrator or its components are being purchased, certain factors must be considered:

- traceability of the certified calibration gases to an NIST-SRM (12) or a NIST/EPA-approved commercially available Certified Reference Manual (see Section 8),
- accuracy of the flow-measuring device or devices (rotameter, mass flow meter, bubble meter),
- maximum and minimum flows of dilution air and calibration gases, and
- ease of transporting the calibration equipment from site to site.

9.2.3.3 For an individual cylinder multipoint calibration, assemble the monitor and calibration system as illustrated in Figure 4.

9.2.3.4 Perform a manual zero and span calibration as in Section 9.2.2 and record the adjusted zero and span concentrations and their respective chart values on the Multipoint Calibration Data Sheet, Figure 5.

9.2.3.5 Connect the span gas with a concentration value corresponding to 80% of full scale, to the analyzer system.

9.2.3.6 Open the gas cylinder pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired sample cell pressure.

9.2.3.7 Set the sample flow rate as read by the rotameter (read the widest part of the float) to the value to be used when sampling.

9.2.3.8 Let the span gas flow long enough to establish a stable trace on the strip chart recorder; allow a least 5 minutes. Mark the chart trace as an unadjusted span. Record unadjusted span reading in ppm on the Multipoint Calibration Data Sheet, Figure 5.
Note: No adjustments are made at this point.

9.2.3.9 Disconnect the span gas.

9.2.3.10 Connect zero gas to the analyzer.

9.2.3.11 Open the gas cylinder pressure valve and adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired sample cell pressure.

9.2.3.12 Set the sample flow rate as read by the rotameter to the value that is used when sampling.

9.2.3.13 Let the zero gas flow long enough to establish a stable zero trace on the strip chart recorder; allow at least 5 minutes. Mark the chart trace as an unadjusted zero. Record the unadjusted zero reading in ppm on the Multipoint Calibration Data Sheet, Figure 5.

9.2.3.14 Repeat Section 9.2.3.5 through Section 9.2.3.13 for each of the calibration gases with concentrations corresponding to approximately 60, 40, 20 and 10% of full scale in that order.

9.2.3.15 Fill in the information required on the Multipoint Calibration Data Sheet and construct a calibration curve of analyzer response as percent of chart versus concentration in ppm as illustrated in Figure 7. Draw a best fit, smooth curve passing through zero and minimizing the deviation of the four remaining upscale points from the curve. The calibration curve should have no inflection points, i.e., it should either be a straight line or bowed in one direction only. Curve fitting techniques may be used in constructing the calibration curve by applying appropriate constraints to force the curve through the zero. This procedure becomes quite involved; however, the most frequently used technique is to graph the curve (see Section 9.2.3.28 through Section 9.2.3.30).

9.2.3.16 Recheck any calibration point deviating more than ± 1.0 ppm CO from the smooth calibration curve. If the recheck gives the same results, have the calibration gas reanalyzed. Use the best fit curve as the calibration curve.

9.2.3.17 For a dynamic dilution multipoint calibration, assemble the analyzer and dynamic dilution system as illustrated in Figure 6.

9.2.3.18 Perform a manual zero and span calibration as in Section 9.2.2 and record the adjusted zero and span concentrations and their respective chart values on the Multipoint Calibration Data Sheet, Figure 5.

9.2.3.19 Now produce the zero air flow from the dilution system to the analyzer. The flow must exceed the total demand of the analyzer connected to the output manifold to ensure that no ambient air is pulled into the manifold vent.

Note: In lieu of connecting analyzer to manifold, one may fill Tedlar® bags with generated standards to be sampled by the NDIR.

9.2.3.20 Allow the analyzer to sample the zero air until a stable response is obtained; adjust the analyzer zero control to within ± 0.5 ppm of zero base line; and record the stable zero-air response (% scale) on the Multipoint Calibration Data Sheet.

Note: Offsetting the analyzer zero adjustment to +5% of scale is recommended to facilitate observing negative zero drift. On most analyzers this should be done by offsetting the recorder zero.

9.2.3.21 Determine the 80% of monitor full scale. Example: For an analyzer with an operating range of 0 to 50 ppm, the 80% value would be:

$$0.80 \times 50 = 40 \text{ ppm}$$

9.2.3.22 Adjust the CO flow from the standard CO cylinder to generate a CO concentration of approximately 80% of the monitor full scale. Measure the CO flow, and record on the Multipoint Calibration Data Sheet.

9.2.3.23 Calculate the generated CO standard by the following equation:

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

where:
$(CO)_{gen}$ = concentration of CO generated, by dilution, ppm
$(CO)_{std}$ = concentration of NITS-SRM or CRM CO gas standard, ppm
Q_{co} = flow rate of CO standard, L/min
Q_{dil} = flow rate of dilution air, L/min

Note: If wet test meter or bubble meter is used for flow measurement, the vapor pressure of water at the temperature of the meter must be subtracted from the barometric pressure.

Note: If both the CO and the zero-air flow rates are measured with the same type of flow meter (e.g. bubble flow meter, rotameter, mass flow meter, wet test meter, etc.), correction to standard temperature and pressure (STP) is not necessary. However, if this is not the case, then the flows of CO gas and dilution gas must be corrected to STP by the following equation:

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

where:
Q_{co} = flow rate of CO standard corrected to STP, L/min
Q_1 = uncorrected flow rate of CO standard, L/min
P_{bar} = barometric pressure, mm Hg
T = temperature of gas being measured, °C

9.2.3.24 Allow the analyzer to sample until the response is stable; adjust the analyzer span until the required response is obtained, and record the CO recorder response on the Multipoint Calibration Data Sheet. After the zero and 80% points have been set, without further adjusting the instrument, generate four approximately evenly spaced points between zero and 80% by increasing the dilution flow (Q_{dil}) or by decreasing the CO flow (Q_{co}). For each concentration generated, calculate the CO concentrations and record the results for each point under the appropriate column on the data sheet.

Note: If substantial adjustments of the span control are necessary, recheck the zero and span adjustments by repeating Section 9.2.2.

9.2.3.25 Fill in the information required on the Multipoint Calibration Data Sheet and construct a calibration curve of analyzer response as percent of chart versus concentration in ppm, as illustrated in Figure 7. Draw a best fit, smooth curve passing through the zero and minimizing the deviation of the remaining upscale points from the curve. The calibration curve should have no inflection points, i.e., it should either be a straight line or bowed in one direction only. Curve fitting techniques may be used in

constructing the calibration curve by applying appropriate constraints to force the curve through the zero. This procedure becomes quite involved; however, the most frequently used technique is to graph the curve.

9.2.3.26 Recheck any calibration point deviating more than $\pm$ 1.0 + 0.02 C_c ppm from the smooth calibration curve. If the recheck gives the same results, have that calibration gas reanalyzed. Use the best fit curve as the calibration curve.

10. Systems Maintenance

10.1 Periodic Maintenance

Proper maintenance is necessary for successful monitor performance. Periodic maintenance should be performed to reduce equipment failure and maintain calibration integrity of the instrument as illustrated in Table 3. Instrument calibration should be checked on a schedule established after the analyzer has operated for a period of time. The sensitivity and linearity should also be checked. These instrument checks should be done at least on an annual basis. However, when any optical component (i.e., detector, cell or source) is changed, the linearity and selectivity of the instrument should be confirmed. The settings of the zero and span controls of instruments which operate continuously should be checked as often as required. A log of these settings and a service and repair log should be kept to assist in evaluating maintenance difficulties. Figure 8 illustrates a monthly maintenance check sheet for a typical NDIR analyzer.

10.2 Routine Maintenance

Regular checks of the instrument and its operation are mandatory. Even though a system may provide excellent quality data initially, without routine maintenance and system checks the quality of the data will degenerate with time. Table 3 provides a routine servicing schedule for a typical NDIR analyzer. Follow all routine maintenance procedures specified in the manufacturer's instruction manual.

10.2.1 Sampling system - The sampling system to which the analyzer is connected must be checked at regular intervals according to a maintenance schedule based on the components used in the specific application. Sampling system maintenance normally includes the following steps:

- checking the entire system for leaks and proper flow rates,
- cleaning and/or renewing sample system components,
- ensuring that calibration cylinders are shut off when not in use,
- ordering filled and assayed cylinders at intervals which include ample lead time to ensure continuous supply of calibration gas,
- checking operation of pumps, recorders, motors, timers and other commercial components by referring to manufacturer's instructions,
- checking and/or cleaning the entire sampling system, including the sample cell in the analyzer, when abnormal sample conditions occur, such as when slugs of water, dirt or oil are introduced, or high temperature or pressure conditions arise.

10.2.2 Daily servicing - Automatic 80% full scale span (40 ppm) and zero precision checks should be performed utilizing the instrument's automatic zero/span standardization feature (if so equipped) and individual secondary standard gases of CO in air with the above concentrations.

10.2.3 Each visit servicing - Verify that the zero and span potentiometer settings are at the proper position. Likewise, verify that the sample cell flow is reading correctly and at the proper setting. Plot the daily zero, precision check, and span values on their respective days on the Maintenance Check Sheet. If any of the zero and span values exceed 5% of stated value, perform a manual zero and span check and adjust the analyzer to the correct zero and span values using the front panel zero and span potentiometer, respectively. If there is insufficient range in the span potentiometer, a multipoint calibration must be performed. Record the adjusted ppm values and zero and span potentiometer settings on the monthly Maintenance Check Sheet (see Figure 8).

10.2.4 Weekly servicing - At least once per week replace the Teflon® sample inlet particulate filter. Note the filter cleanliness and vary the replacement frequency accordingly. Change the filter even if only a slight particulate coating or discoloration is visible. Perform a leak check weekly and whenever the loosening or tightening of a fitting is involved in maintenance procedures. Using an individual cylinder, introduce a 20% of full scale (10 ppm) intermediate span gas at ambient pressure upstream of the sample pump as a precision check. Maintain the same excess flow each time the manual precision check is performed. The manual precision check should be within 10% of value. If not, investigate the cause and initiate repairs.

10.2.5 Monthly servicing - Inspect the water trap filter for particulate loading and replace if necessary. Note the filter cleanliness and adjust the replacement frequency accordingly. Check the span gas solenoid valve for leakage. Replace valve if necessary. Record the results and the date of the check on the Monthly Maintenance Check Sheet. An analyzer multipoint calibration should be performed monthly.

10.2.6 Quarterly servicing - Inspect and clean the filters downstream of the sample and reference flow meters. Note the filter cleanliness and adjust the cleaning frequency accordingly.

10.2.7 Semi-annual servicing - Perform an electronic bias adjustment utilizing the procedures outlined in the manufacturer's instruction manual. Perform a source balance adjustment utilizing the procedures outlined in the manufacturer's instruction manual.

10.2.8 Cell walls and windows - Inspect cell walls and windows for cleanliness and clean if necessary utilizing the procedures outlined in the manufacturer's instruction manual. Do not clean with cloth or paper towel; cleaning should be performed using distilled water followed by isopropyl alcohol and air drying.

10.3 Preventive Maintenance

The preventive maintenance section of the manufacturer's instruction manual of the NDIR monitoring system should contain a trouble shooting guide and diagnostic chart to assist operators in identifying and correcting instrument problems.

10.4 Troubleshooting the Analyzer

10.4.1 The manufacturer's instruction manual generally contains troubleshooting guidelines that cover most troubles which may occur. Table 4 illustrates typical NDIR monitor problems as outlined in a manufacturer's instruction manual.

10.4.2 The troubleshooting guidelines should be used only after the analyzer cannot be calibrated or aligned according to manufacturers' specifications or cannot be operated properly.

10.4.3 If the recording instrument indicates an incorrect value when a sample which contains a low concentration of the component of interest is measured, check the alignment and calibration of the analyzer for optical balance. If the meter does not deflect upscale when span gas is passed through the analyzer and the power indicator is on, check the output circuit. If the power indicator is off, check the power connections. If these or other problems cannot be located or corrected using the specified guidelines, contact the manufacturer for assistance.

11. Performance Criteria and Quality Assurance (QA)

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

11.1 Standard Operating Procedures (SOPs)

11.1.1 SOPs should be generated by the users to describe and document the following activities in their laboratory:

- assembly, calibration, leak check, and operation of the specific sampling system and equipment used,
- preparation, storage, shipment, and handling of the sampler system,
- purchase, certification, and transport of standard reference materials, and
- all aspects of data recording and processing, including lists of computer hardware and software used.

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

11.2 Quality Assurance Program

The user should develop, implement, and maintain a quality assurance program to ensure that the sampling system is operating properly and collecting accurate data. Established calibration, operation, and maintenance procedures should be conducted on a regularly scheduled basis and should be part of the quality assurance program. Calibration procedures and operation procedures in Section 9.2, and maintenance procedures in Section 10.3 of this method and the manufacturer's instruction manual should be followed and included in the QA program, as outlined in Table 5. Additional QA measures (e.g., trouble shooting) as well as further guidance in maintaining the sampling system should be provided by the manufacturer.

11.2.1 Precision Check

11.2.1.1 A periodic precision check is used to assess the quality of the data. A one-point check on the analyzer is carried out at least once every 2 weeks at a CO concentration between 8 and 10 ppm.

11.2.1.2 The analyzer must be operated in its normal sampling mode, and the precision test gas must pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling. The standards from which the precision check test concentrations are obtained must be traceable to a NITS-SRM or a commercially available CRM; the same standards used for calibration may be used for the precision check. They must conform to specifications outlined in Section 8.1 and Section 8.2.
Note: All gas standards used for precision or daily zero and span check should contain about 350 ppm CO_2 to simulate normal ambient concentrations.

11.2.1.3 Connect the analyzer's sample inlet line to a precision gas source that has a concentration between 8 and 10 ppm CO and that is traceable to a NITS-SRM or a CRM as illustrated in Section 9.2.3 and Figure 4. If a precision check is made in conjunction with a zero/span check, it must be made prior to any zero and span adjustments.

11.2.1.4 Allow the analyzer to sample the precision gas for a least 5 min or until a stable recorder trace is obtained.

11.2.1.5 Record this value on the Monthly Maintenance Check Sheet and mark the chart as "unadjusted" precision check.

11.2.1.6 The expected response of the NDIR analyzer should be within 10% of the precision calibration gas standard.

11.2.2 Performance Audit

11.2.2.1 An audit is an independent assessment of the accuracy of data generated by an analyzer.

11.2.2.2 Independence is achieved by having the audit performed by an operator other than the one conducting the routine field measurements and by using audit standards, reference materials, and equipment different from those routinely used in monitoring.

11.2.2.3 The audit should be an assessment of the measurement process under normal operations, that is, without any special preparation or adjustment of the system. Routine quality assurance checks conducted by the operator are necessary for obtaining and reporting good quality data, but they are not to be considered part of the auditing procedure.

11.2.2.4 Proper implementation of an auditing program will ensure the integrity of the data and assess the accuracy of the data.

11.2.2.5 A performance audit consists of challenging the continuous analyzer with known concentrations of CO within the measurement range of the analyzer. Known concentrations of CO can be generated by using individual cylinders for each concentration (see Section 9.2.3.3) or by using one cylinder of a high CO concentration and diluting it to the desired levels with zero-air (see Section 9.2.3.17). In either case, the gases used must by traceable to a NITS-SRM or a commercially available CRM and contain about 350 ppm CO_2 to simulate normal ambient concentrations.

11.2.2.6 A dynamic dilution system must be capable of measuring and controlling flow rates to within ± 2% of the required flow. Flow meters must be calibrated under the conditions of use against a reliable standard such as a soap bubble meter or a wet test meter; all volumetric flow rates should be corrected to STP at 25°C (77°F) and 760 mm Hg (29.92 in Hg); but if both the CO and the zero air flow rates are measured with the same type device at the same temperature and pressure, the STP correction factor in the audit equations can be disregarded.

11.2.2.7 The analyzer should be challenged with at least one audit gas of known concentration from each of the following concentrations within the measurement range of the analyzer being audited:

Audit Point	CO Concentration Range, ppm
1	3 to 7
2	8 to 12
3	18 to 22
4	28 to 32
5	33 to 42

The difference in CO concentration (ppm) between the audit value and the measured value is used to calculate the accuracy of the analyzer.

11.2.2.8 All measurements of audit concentrations should fall within ± 10% of the audit value.

12. Method Safety

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

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.

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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.

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12. National Institute of Standards and Technology (NIST) Catalog of Standard Reference Materials, NIST Special Publication, 1989 Edition, NIST, Gaithersburg, MD.

13. *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II - Ambient Air Specific Methods* - Section 2.0.7, U.S. Environmental Protection Agency, Quality Assurance Division, Research Triangle Park, NC, 27711, EPA-600/4-77-0272, May, 1987.

Table 1. Commercially Available NDIR CO Analyzers Designated by U.S. EPA as References Methods and Other Commercially Available CO and CO_2 Analyzers

Identification	Manufacturer	Fed. Register Notice Vol.	Page	Date
Bendix or Combustion Engineering Model 8501-5CA Infrared CO Analyzer, operated on the 0-50 ppm range and with a time constant setting between 5 and 16 seconds.	Combustion Engineering, Inc. Process Analytics P.O. Box 831 Lewisburg, WV 24901	41	7450	2/18/76
Beckman Model 866 Ambient CO Monitoring System, consisting of the following components: Pump/Sample-Handling Module, Gas Control Panel, Model 865-17 Analyzer Unit, Automatic Zero/Span Standardizer; operated with a 0-50 ppm range, a 13 second electronic response time.	Beckman Instruments, Inc. Process Instruments Div. 2500 Harbor Boulevard Fullerton, CA 92634	41	36245	8/27/76
LIRA Model 202A Air Quality Carbon Monoxide Analyzer System, consisting of a LIRA Model 202S optical bench (P/N 459839), a regenerative dryer (P/N 464084), and rack-mounted sampling system; operated on a 0-50 ppm range, with the slow response amplifier.	Mine Safety Appliances Co. 600 Penn Center Blvd. Pittsburgh, PA 15208	42	5748	1/31/77
Horiba Models AQM-10, AQM-11, and AQM-12 Ambient CO Monitoring Systems, operated on the 0-50 ppm range, with a response time setting of 15.5 seconds.	Horiba Instruments, Inc. 1021 Duryea Ave. Irvine Industrial Complex Irvine, CA 92714	43	58429	12/14/78
Monitor Labs Model 8310 CO Analyzer, operated on the 0-50 ppm range, with a sample inlet filter.	Monitor Labs, Inc. 10180 Scripps Ranch Blvd. San Diego, CA 92131	44 45	54545 2700	9/20/79 1/14/80

Table 1. Commercially Available NDIR CO Analyzers Designated by U.S. EPA as References Methods and Other Commerically Available CO and CO_2 Analyzers (Cont'd)

Identification	Manufacturer	Fed. Register Notice Vol.	Page	Date
Horiba Model APMA-300 Ambient Carbon Monoxide Monitoring System, operated on the 0-20/ 50/100 ppm range with a time constant switch setting of #5. The monitoring system may be operated at temperatures between 10-40°C.	Horiba Instruments, Inc. 1021 Duryea Ave. Irvine Industrial Complex Irvine, CA 92714	45	72774	11/03/80

Other Commercially Available NDIR CO Analyzers

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

Commercially Available NDIR CO_2 Analyzers

Model #	Manufacturer	Portability
Gas Analyzer Model 8000	Automated Custom Sys., Inc. 1238 West Grove Ave. Orange, CA 92665 (714)974-5560	Stationary
Gas Analyzer Model RI-411A	CEA Instruments Box 303 Emerson, NJ 07630 (201)967-5660	Portable
Closed Room Monitor Model 4776	Gastech, Inc. 8445 Central Ave. Newark, CA 94560 (415)794-6200	Portable
Gas Analyzer Model APBA-210	Horiba Instruments 1021 Duryea Ave. Irvine Industrial Complex Irvine, CA 92714 (800)556-7422	Portable

Table 1. Commercially Available NDIR CO Analyzers Designated by U.S. EPA as References Methods and Other Commerically Available CO and CO_2 Analyzers (Cont'd)

Commercially Available NDIR CO_2 Analyzers (Cont'd)

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

Table 2. Suggested Performance Specifications for NDIR CO Analyzers

Analyzer Parameter	Specification
Range (minimum)	0-50 ppm (0-58 mg/m^3)
Lower detection limit (LDL)	1.0 ppm (0.6 mg/m^3)
Lag time (maximum)	20 seconds
Rise time, (95% maximum)	15 minutes
Fall time, (95% maximum)	15 minutes
Zero drift (maximum)	± 1% per day and ± 2% per 3 days
Span drift (maximum)	± 1% per day and ± 2% per 3 days
Precision (maximum)	± 0.5%
Operational period (maximum)	3 days
Noise (maximum)	± 0.5%
Interference equivalent (maximum)	1% of full scale
Operating temperature range	5-40°C
Operating temperature fluctuation	± 5%
Linearity (maximum)	1%
Operating humidity range (maximum)	10-100%

Table 3. Typical NDIR Carbon Monoxide/Carbon Dioxide Analyzer Routine Servicing Schedule

Service	Frequency
Zero/span/precision checks	Daily
Zero/span/potentiometer settings	Daily
Range position checks	Each Visit
Sample & reference flow check	Each Visit
Replace sample inlet particulate filter	Weekly
Leak check system	Weekly
Manual precision check	Weekly
Inspect water removal system	Monthly
Inspect span gas solenoid valve	Monthly
Multipoint calibration	Monthly
Clean sample/reference filters	Quarterly
Electronic bias adjustment	Semi-Annually
Source balance adjustment	Semi-Annually
Cell wall & window inspection	Annually
CO_2 interference test	Annually
H_2O interference	Annually

Table 4. Typical NDIR Monitor Problems

Observation	Possible Cause	Diagnostic Check
CO level too low	Reference infrared source source failing	Run span gas check
	Sample lines clogged	Check with flow meter
	Decreased pressure in sample compartment of detector	Check after inspection of infrared source
	Vacuum pump failure	Inspect pump
	Amplifier failing	Completely check-out electronics system
CO level too high	Sample infrared source failing	Run span gas check
	Sample cell optics dirty	Inspect and clean if necessary
	Decreased pressure in reference compartment of detector	Run span gas check after inspection of infrared source
	Amplifier failing	Completely check-out electronics system
Abnormal positive zero drift	Moisture elimination devices inoperative	Recharge silica gel; check refrigeration unit
	Dirty optical surfaces	Clean cells as necessary; check particulate filter
	Amplifier failing	Check-out electronics system completely
		Run span check

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Table 5. QA/QC Operational Parameters

QA/QC Parameters	Actions
Calibration gas on concentration	Measurement of control samples as part of the auditing program.
Data processing errors	Data processing checks performed as a part of the auditing program.
Zero drift	Zero check and adjustment before each sampling period as part of routine operating procedure.
Span drift	Span check and adjustment before each sampling period as part of routine operating procedure.
System noise	Check of strip chart record trace for signs of noise after each sampling period as part of routine operating procedure.
Sample cell pressure variation	Reading and recording sample cell pressure at the beginning and end of a sampling period as part of routine operating procedure.
Temperature variation	Minimum-maximum thermometer placed near the analyzer, or any other temperature-indicating device, read periodically throughout the sampling period. This would usually be done as a special check.
Voltage variation	A.C. voltmeter measuring the voltage to the analyzer and read periodically throughout the sampling period. This would usually be done as a special check.

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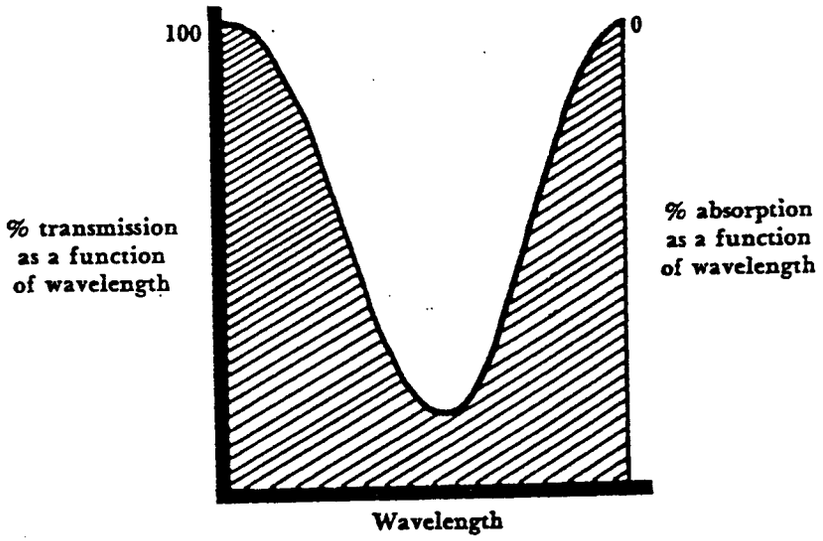

Figure 1A. Typical Absorption Curve in the IR

Gas	Location of band centers (μm)	Wave number (cm^{-1})
NO	5.0-5.5	1800-2000
NO_2	5.5-20	500-1800
SO_2	8-14	700-1250
H_2O	3.1	1000-1400
	5.0-5.5	1800-2000
	7.1-10	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

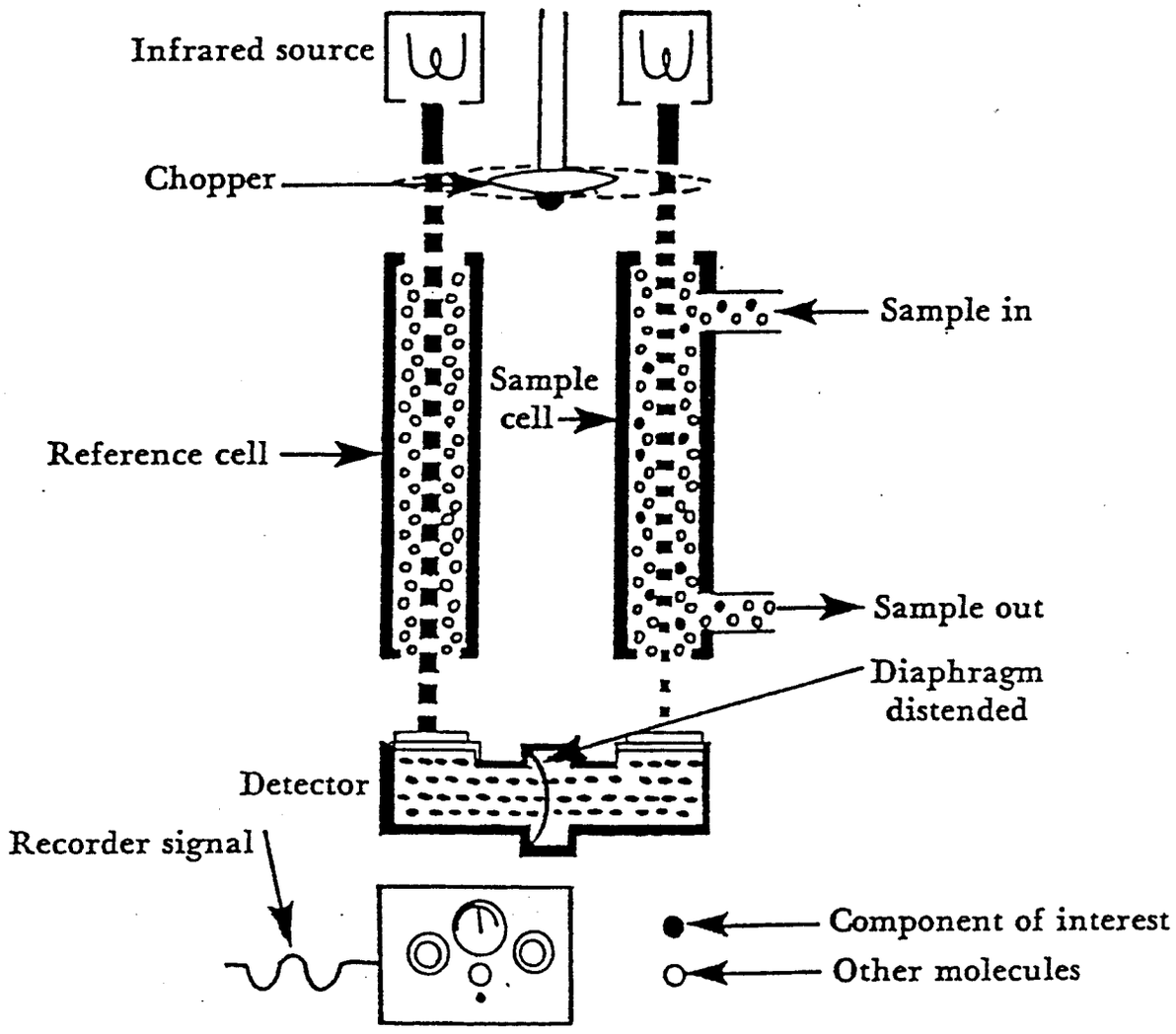

Figure 2. Major Components of a Commercially Available NDIR Instrument

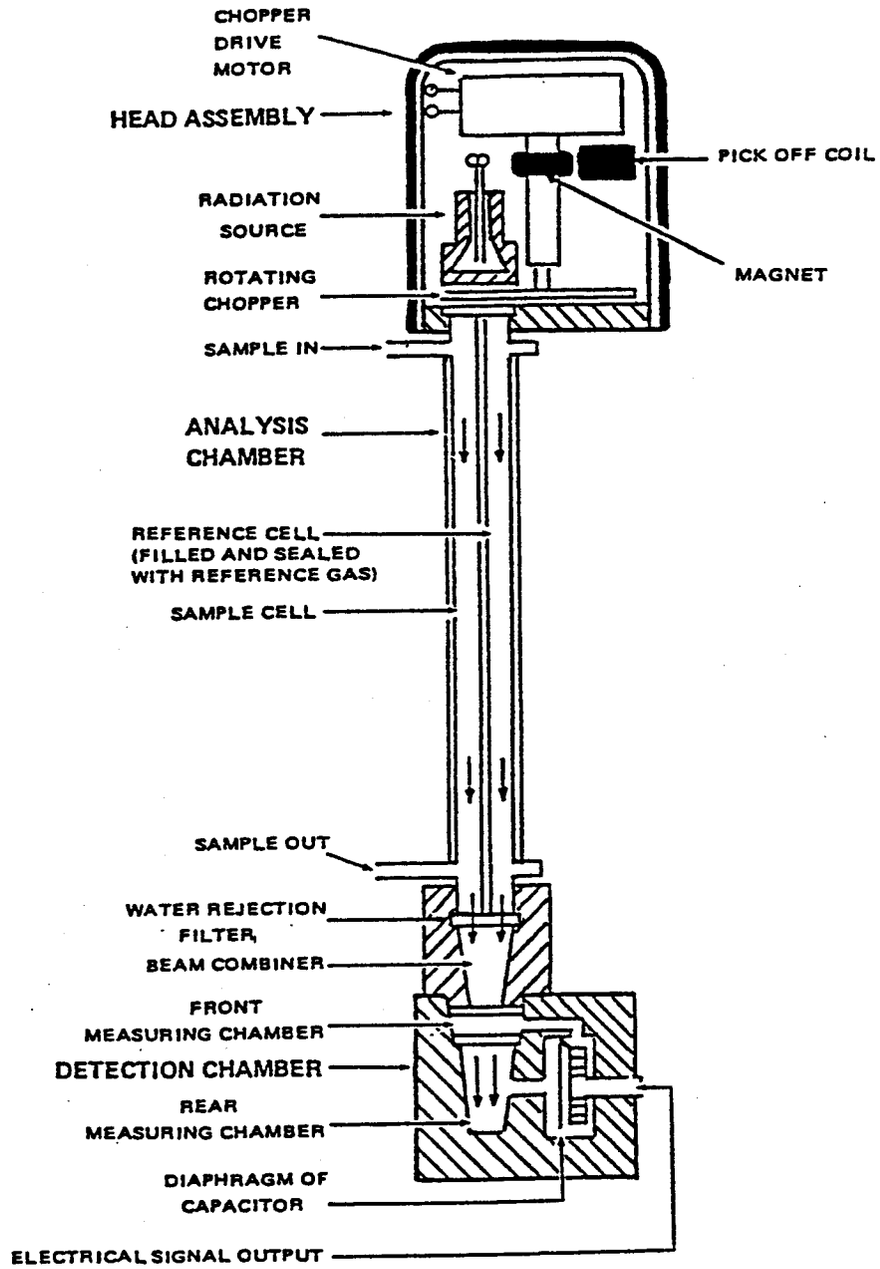

Figure 3. Front/Rear Chamber Detector Design

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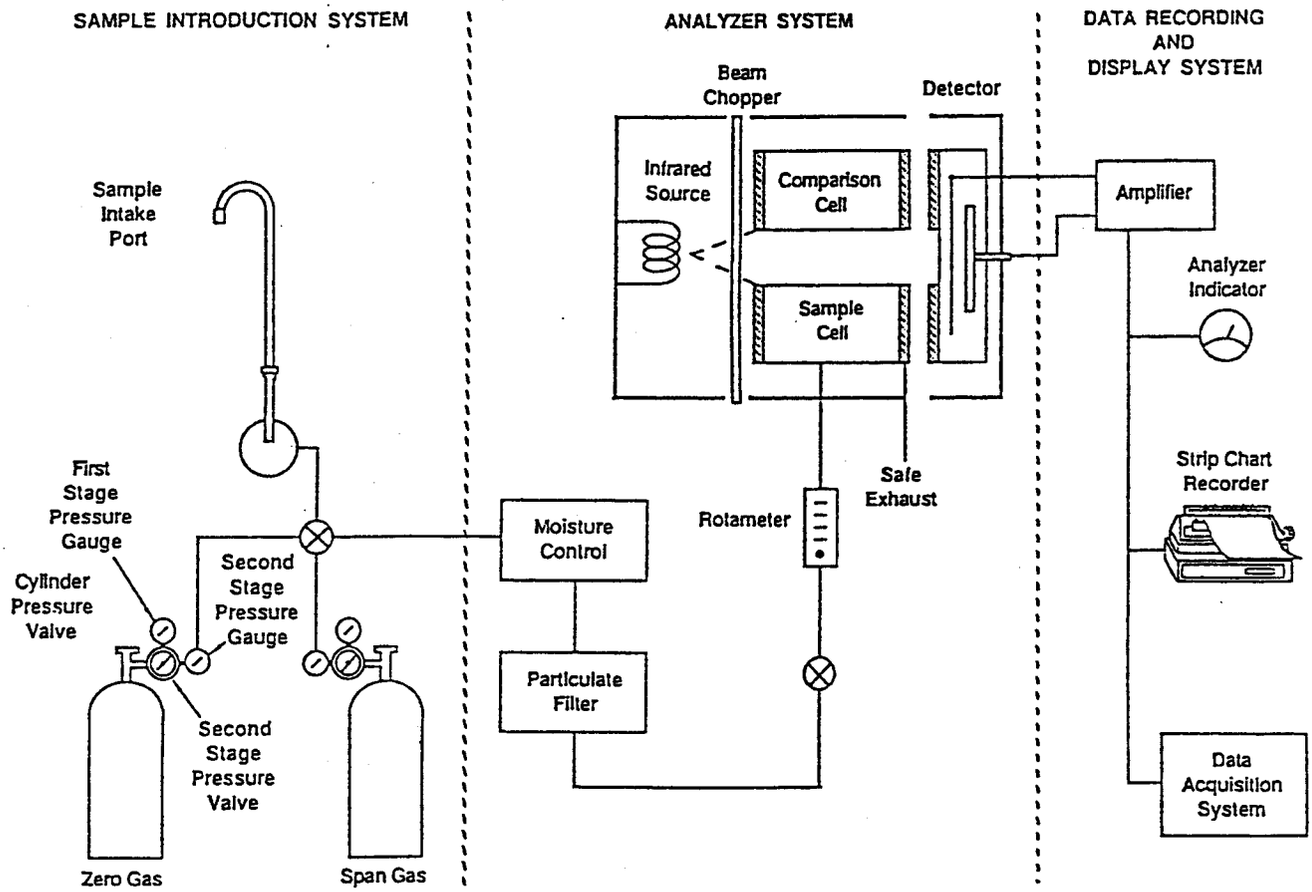

Figure 4. NDIR Calibration and Detector System

ADJUSTED ZERO AND SPAN VALUES			ANALYZER CALIBRATED
	% CHART	PPM	
ADJ. ZERO			LOCATION _____
ADJ. SPAN			S/N _____ SITE NO. _____
			DATE _____
TEMP. _____ °C PRESS _____ "Hg			DATE LAST CALIBRATED _____
RANGE _____ TIME CONSTANT _____			

INPUT		ANALYZER RESPONSE	
ppm	% CHART	%CHART	ppm

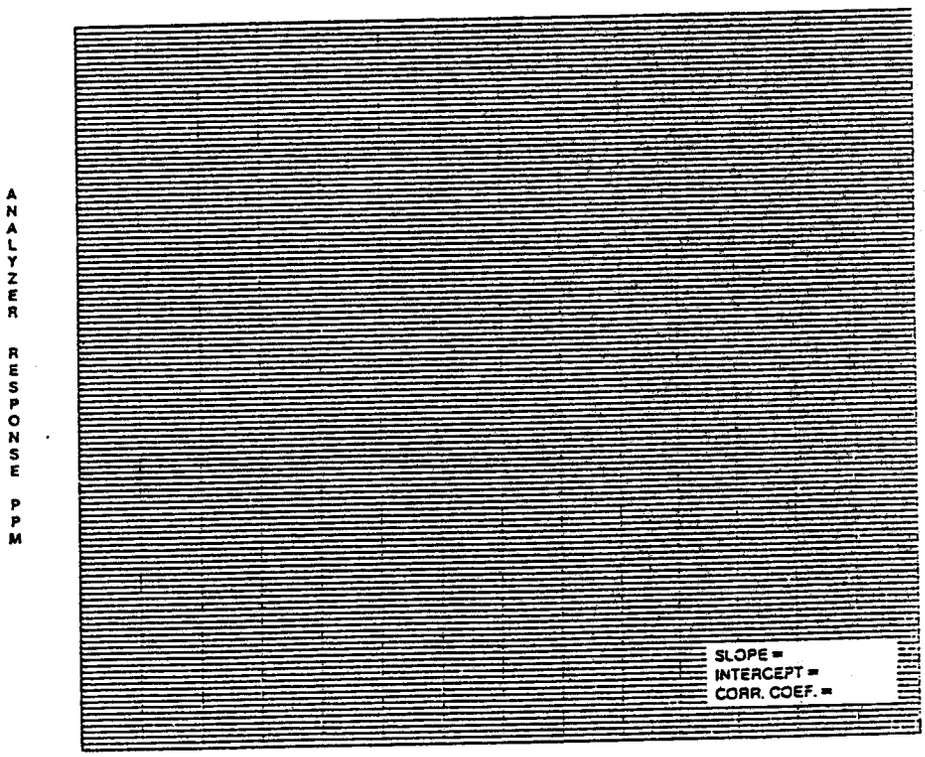

Figure 5. Multipoint Calibration Data Sheet

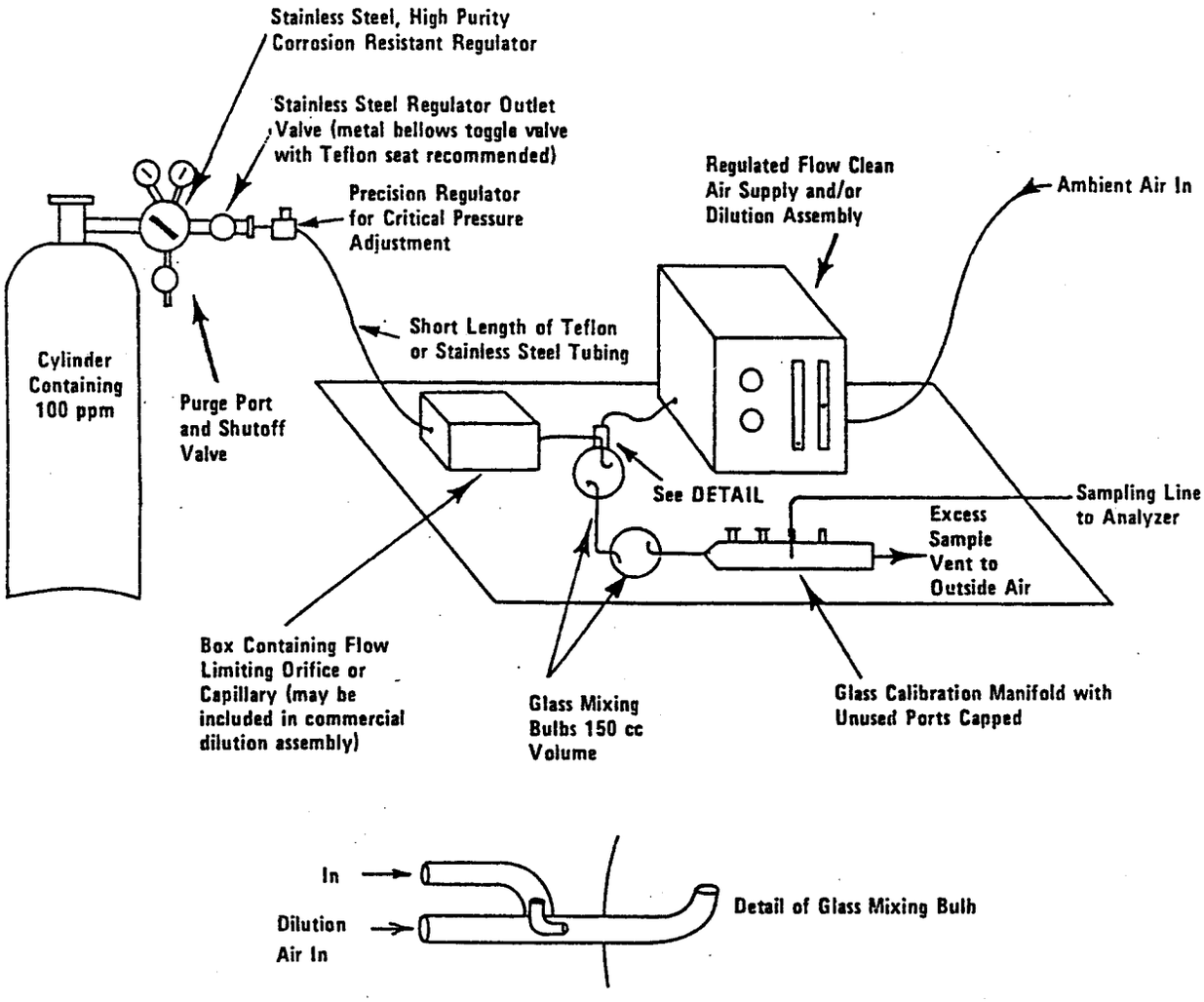

Figure 6. Assembly for Dilution of CO from Cylinder for Use in Calibration or Span Check

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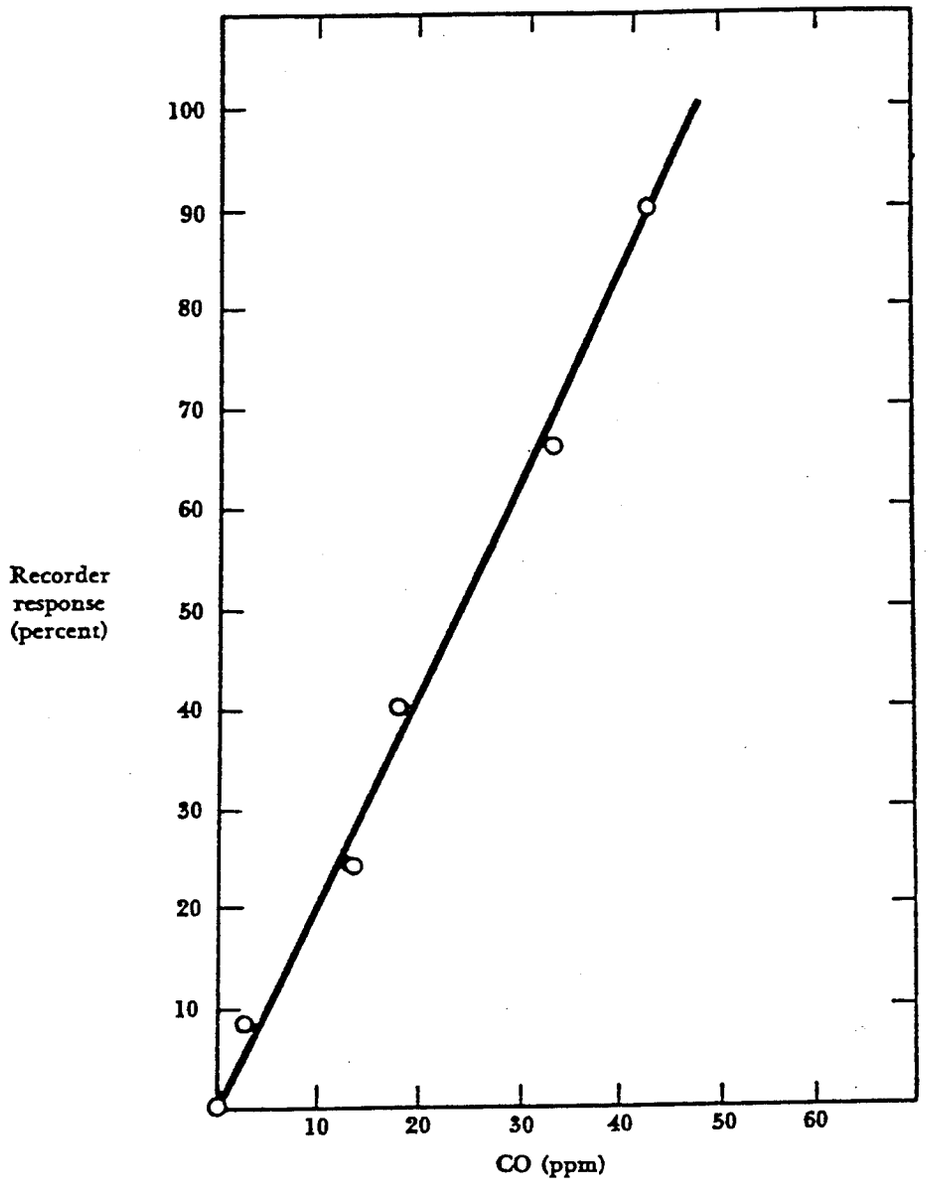

Figure 7. NDIR Calibration Curve

Monthly Maintenance Check List

SITE NUMBER _____ TECHNICIAN _____

ANALYZER S/N _____

DATE	READING: DIAL/CHART (ppm)				FLOW SETTING					PARTIC-ULATE FILTER	CYL PRESSURE	
	ZERO		SPAN		SAMPLE		REFERENCE				ZERO	SPAN
	UNADJ.	ADJ.	UNADJ.	ADJ.	UNADJ.	ADJ.	UNADJ.	ADJ			#	#

OPERATOR INSTRUCTIONS:

1. DAILY: ZERO/SPAN/PRECISION CHECK
2. EACH VISIT: CHECK FLOW SETTING;
   CHART TRACE
3. WEEKLY: REPLACE PARTICULATE FILTER;
4. MONTHLY: INSPECT WATER TRAP FILTER;
   INSPECT SPAN GAS SOLENOID VALVE - DATE LAST CHECKED _____
   ZERO AIR _____ ZERO AIR WITH SPAN GAS _____
5. QUARTERLY: CLEAN SAMPLE/REFERENCE FILTERS; MULTI POINT CALIBRATION.
   SPAN GAS TO SPAN GAS INLET _____ SPAN GAS TO SAMPLE INLET _____
6. SEMI-ANNUALLY: ELECTRONIC BIAS ADJUSTMENT - DATE LAST CHECKED _____
   SOURCE BALANCE ADJUSTMENT - DATE LAST CHECKED _____
7. ANNUAL: INSPECT CELL WALLS AND WINDOWS - DATE LAST CHECKED _____
   CO_2 INTERFERENCE TEST - DATE LAST CONDUCTED _____
   H_2O INTERFERENCE TEST - DATE LAST CONDUCTED _____

DATE	COMMENTS OR MAINTENANCE PERFORMED

Figure 8. Monthly Maintenance Check Sheet

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Method IP-3B

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO_2) IN INDOOR AIR USING GAS FILTER CORRELATION (GFC)

Method IP-3B

DETERMINATION OF CARBON MONOXIDE (CO) OR CARBON DIOXIDE (CO_2) IN INDOOR AIR USING GAS FILTER CORRELATION

1. Scope

This document describes a procedure for determination of CO and CO_2 concentrations in indoor air using gas filter correlation (GFC). This procedure provides automatic and continuous measurement of CO and CO_2 in indoor atmospheres. Analyzers employing the GFC measurement principle rely on the properties of CO and CO_2 to absorb infrared energy at distinctive wavelengths (i.e., 4.7 μ and 2.0 μ, respectively).

2. Applicable Documents

2.1 ASTM Standards

D1356 Definition of Terms Relating to Atmospheric Sampling and Analysis
D1357 Recommended Practice for Planning the Sampling of the Atmosphere
D3195 Recommended Practice for Rotameter Calibration
D1914 Recommended Practice for Conversion Units and Factors Relating to Atmosphere Analysis
D3249 Recommended Practice for General Ambient Air Analyzer Procedures
E1 Specification for ASTM Thermometers
E180 Recommended Practice for Development of Precision Data for ASTM Methods for Analysis and Testing of Industrial Chemicals

2.2 Other Documents

Laboratory and Indoor/Ambient Air Studies (1-10)
U.S. Environmental Protection Agency Technical Assistance Document (11)

3. Summary of Method

3.1 GFC spectrometry is based upon comparison of the detailed structure of the infrared absorption spectrum of the measured gas to that of other gases also present in the sample being analyzed. The technique is implemented by using a high concentration sample of the measured gas, i.e., CO and CO_2, as a filter for the infrared radiation transmitted through the analyzer, hence the term GFC.

3.2 The basic components of the GFC CO/CO_2 spectrometer are shown in Figure 1. Radiation from an IR source is chopped and then passed through a gas filter alternating between CO and N_2 due to rotation of the filter wheel. The radiation then passes through a narrow bandpass interference filter and enters a multiple optical pass cell where absorption by the sample gas occurs. The IR radiation then exits the sample cell and falls on an IR detector.

3.3 The CO/CO_2 gas filter acts to produce a reference beam which cannot be further attenuated by CO and CO_2 in the sample cell. The N_2 side of the filter wheel is transparent to the IR radiation and therefore produces a measure beam which can be

absorbed by CO and CO_2 in the cell. The chopped detector signal is modulated by the alternation between the two gas filters with an amplitude proportional to the concentration of CO and CO_2 in the sample cell. Other gases do not cause modulation of the detector signal since they absorb the reference and measure beams equally. Thus the GFC system responds specifically to CO and CO_2.

3.4 With the improved rejection of interferences afforded by the GFC technique, it is possible to increase the sensitivity of the analyzer. This is achieved by the multiple pass optics (white cell) used in the sample cell which leads to a large path length, and thus an improved sensitivity, in a small physical space. This allows full scale sensitivity down to 1 ppm CO with a lower detectable limit (LDL) of 0.020 ppm CO to be achieved.

4. Significance

4.1 The GFC method of measuring CO/CO_2 offers improved specificity and sensitivity over conventional NDIR techniques. The GFC analyzers provide a wide dynamic range with a reported sensitivity of 0.1 ppm CO. This technique employs the reference principle and affords the lower sensitivities needed for indoor air monitoring.

4.2 There are several GFC analyzers available for measuring CO or CO_2. The GFC analyzer described in this method is the Thermo Environmental Corp. (TECO) model 48 GFC CO Analyzer, (Thermo Environmental Corp., Instruments Division, 108 S. Street, Hopkinton, MA 01748). This analyzer meets the specifications as outlined in Table 1. The specific information is provided as guidance to be referred to in addition to specific model users manuals.

5. Definitions

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

6. Interferences

6.1 The microcomputer circuitry upon which the GFC analyzer described herein (Thermo Environmental Corp., Model 48 GFC CO Analyzer) is based eliminates many disadvantages inherent in analog systems and provides for increased stability, accuracy, and flexibility. Digital computations are insensitive to drift with time or temperature, therefore sources of instrument drift or error due to the electronics are minimized.

6.2 Because infrared absorption is a non-linear measurement technique, it is necessary for the instrument electronics to transform the basic analyzer signal into a linear output. In instruments employing analog electronics, this is accomplished with an additional circuit which generates a function approximating the basic analyzer's calibration curve over a limited range of gas concentrations. With the analyzer, approximations are not necessary since the exact calibration curve is stored in the computer's memory and is used to

accurately linearize the instrument output over any desired range. The analyzer is linearized in this way up to a CO concentration of 1000 ppm.

6.3 The analyzer is designed to perform a variety of tasks by using appropriate information stored in the instrument's program memory. For example, the microcomputer is used to process signals from both a pressure and temperature transducer to make corrections to the instrument output, resulting in concentration measurements which are unaffected by changes in the temperature or pressure of the gas being sampled.

7. Apparatus

7.1 Commercially available GFC CO analyzer - For measurement of CO, the analyzer should be EPA reference or equivalent monitor using GFC and provide a continuous CO monitoring system equipped with IR source, sample and reference gas cells, detector, adequate power supply, amplifier/control unit, meter, and recording system. The analyzer must meet or exceed manufacturer's specifications. See Table 2 for a listing of commercially available GFC CO analyzers. The listing is an excerpt from U.S. EPA's list of designated Reference and Equivalent Methods.

7.2 Commercially available GFC CO_2 analyzer - Analyzer should provide a continuous CO_2 monitoring system equipped with IR source, sample and reference gas cells, detector, adequate power supply, amplifier/control unit, meter, and recording system. The analyzer must meet or exceed manufacturer's specifications. Table 2 also includes commercially available GFC CO_2 analyzers.

7.3 Teflon® particulate filter - 5-10 μm pore size, 2" diameter Teflon® element.

7.4 Flowmeters and controllers - In order to obtain an accurate dilution ratio, in the dilution method used for calibration, the flow rates must be regulated to 1%, and be measured to an accuracy of at least 2%. The meter and controller can be two separate devices, or combined in one device. The users manual for the meter should be consulted for calibration information. Additional information on the calibration of flow devices can be found in the Quality Assurance Handbook (1). It should be noted that all flows should be corrected to 25° C and 760 mm Hg, and that care should be exercised in correcting for water vapor content.

7.5 Mixing chambers - A chamber constructed of glass, Teflon®, or other nonreactive material, and designed to provide thorough mixing of CO or CO_2 and diluent air for the dilution method.

7.6 Output manifold - The output manifold should be constructed of glass, Teflon®, or other nonreactive material, and should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent indoor air from entering the manifold.

8. Reagents and Materials

8.1 CO or CO_2 concentration standard - Cylinder of CO or CO_2 (depending on monitoring needs) in air containing an appropriate concentration of CO or CO_2 suitable for the selected operating range of the analyzer under calibration. The assay of the cylinder must be traceable either to a National Bureau of Standards (NBS) CO or CO_2 in Air Standard Reference Material (SRM) or an NBS/EPA approved gas manufacturer's Certified Reference Material (CRM). A recommended protocol for certifying CO or CO_2 gas cylinders against a CO or CO_2 SRM or CRM is given in the Quality Assurance Handbook (1). The gas cylinder should be recertified on a regular basis (best source).

8.2 Dilution gas (zero air) - Air, free of contaminants which will cause a detectable response on the CO or CO_2 analyzers. The zero air should contain <0.1 ppm CO/CO_2 (best source). Since the analyzer is virtually interference free, it is only necessary to insure that CO/CO_2 has been removed. It should be noted that zero air as supplied in cylinders from commercial suppliers typically contains CO/CO_2 concentrations in the 0.1 - 0.3 ppm range. Thus, cylinder air should be scrubbed of the residual CO/CO_2 prior to its use in the analyzer as a dilution gas or a zero standard. Room air which has been scrubbed of CO/CO_2 can be used as the zero air source. It is not necessary to remove SO_2, NO, NO_2, CO_2, water vapor, or hydrocarbons, since the analyzer does not respond to these molecules. If water vapor is not removed, it might be necessary to correct the flow measurement data when calculating the dilution ratio of the span CO/CO_2 reference. (A platinum on alumina catalyst, operated at 250°C, has been found to be a convenient oxidizer to convert CO to CO_2. If it is desired to remove water vapor, SO_2, etc., a photolytic ozone generator can be used to convert NO to NO_2. This can be followed by a heatless air drier to remove water vapor, NO_2, SO_2, hydrocarbons, and ozone. The oxidizer should then be used to remove the CO. An alternative to the heatless air drier could be Perma-Pure® Drier, followed by silica gel, followed by activated charcoal. It has also been reported that a substance sold as Purafil is successful in removing NO, and can be substituted for the ozonator.)

8.3 Pressure regulators for CO/CO_2 standard cylinders - The regulator used must have a nonreactive diaphragm and internal parts, as well as a suitable delivery pressure, best source.

8.4 Sampling line - Teflon®, borosilicate glass or similar tubing with an O.D. of 1/4" and a minimum I.D. of 1/8" is required for all sampling lines, best source.

9. Systems Maintenance

This chapter describes the periodic maintenance procedures that should be performed on the analyzer to ensure proper, uninterrupted operation. Certain components such as the sample pump, solenoid valves, and source have a limited life and should be checked on a regular calendar basis and replaced if necessary. Other operations, such as cleaning the optics and checking the calibration of the pressure and temperature transducers should also be performed on a regular basis. What follows is a check and/or cleaning procedure for

these elements. Replacement procedures for components found to be defective by these checks are given in the manufacturer's instruction manual.

9.1 Cleaning the Optics

Best results will be obtained if the optics are cleaned prior to recalibration. The cleanliness of the mirrors should also be checked any time the Test INT intensity frequencies give a result less than 10,000 Hz, since one source of low output is light attenuation due to dirt on the mirrors. The procedure for cleaning the mirrors is outlined here.

9.1.1 Turn off power and disconnect power line.

9.1.2 Remove field mirror, (the field mirror is the rear mirror), by removing the four allen head screws holding it to the main bench (use a 9/64 allen wrench). Remove the relay mirror (the relay mirror is the front mirror, accessible through the front door), by removing the three allen head screws holding it to the main bench (use a 9/64 allen wrench).

9.1.3 Carefully clean each mirror using a "Q-tip" and methanol. Rinse with distilled or ionized water. Dry by blowing clean dry air over the mirror.

9.1.4 Reassemble following the above procedure in reverse. It is not necessary to realign any mirror following cleaning.

9.1.5 Calibrate following the procedure of Section 10.

9.2 Source Replacement

The source control system of the analyzer has been designed to operate the wire wound resister source conservatively in order to increase its life. Nevertheless, the source does have a finite life. Since the source is relatively inexpensive and easily replaced, it is recommended that the source be replaced after one (1) year of continuous use. This will prevent loss of data due to source failure. If a source is to be replaced on an "as needed" basis, it should be replaced when any one of the following conditions occurs.

9.2.1 The source should be replaced if there is no light output.

9.2.2 The source should be replaced if after cleaning the optics, the Test INT (intensity) frequencies remain below 10,000 Hz.

Note: Since the analyzer is a ratio instrument, and since replacing the sources does not affect the calibration, it is not necessary to recalibrate the analyzer every time the source is replaced.

9.3 Detector Frequencies

The analyzer measures intensity ratios and not absolute values. Therefore a large range of detector output frequencies are acceptable for proper operation of the instrument. The nominal values are between 10,000 and 30,000 Hz. These frequencies can be monitored by energizing the Test INT pushbutton. Degradation of detector frequencies below the acceptable range indicates either a dirty mirror or a weak source. If cleaning the mirrors does not increase the detector frequencies to their proper range, replace the source.

9.4 Pressure Transducer

By energizing the Test P/T (pressure/temperature) pushbutton, the LED display will show the pressure in mm Hg as determined by the pressure transducer. The pressure transducer has a zero and span adjust. The zero can be adjusted by disconnecting the tubing from the pressure transducer and connecting a vacuum pump known to produce a vacuum less than 1 mm Hg. The zero potentiometer is then adjusted for a reading of zero mm Hg. If the pump is then disconnected, but the transducer not connected to the bench, the display should read the current local barometric pressure. If this valve does not agree with a known accurate barometer, adjust the span potentiometer. Note that if the expected pressure changes are small (i.e., the only changes expected are barometric weather changes and not altitude changes) an error in the zero setting will not introduce a measurable error if the span is adjusted correctly. Thus if only a barometer is available, and not a vacuum pump, only adjust the span. If a barometer is not available, a rough check could be made as follows. Obtain the current barometric pressure from the local weather station or airport. Since these pressures are usually reported corrected to sea level, it might be necessary to correct to local pressure by subtracting .027 mm Hg per foot of altitude. Do not try to calibrate the pressure transducer unless the pressure is known accurately. Note that it is possible for the atmospheric barometric pressure from room to room or in a building to be different from the outside atmospheric pressure as a result of the positive pressure developed by the air-conditioning and/or heating systems.

9.5 Temperature Transducer

By energizing the Test P/T pushbutton twice, the LED display will show the temperature in °C. The transducer used is a thermistor. In order to calibrate the temperature transducer, remove it from the bench and tape it to a calibrated thermometer. Adjust the temperature adjustment potentiometer so that the LED displayed value agrees with the value on the calibrated thermometer. Since the thermistors used on the analyzer are interchangeable to an accuracy of ± .2°C, and have a value of 10K ohms at 25°C, an alternative procedure is to hook up an accurately known 10K resistor to the thermistor input on the mother board, and adjust for a reading of 25°C on the digital display. Note that a 1°C change corresponds to a ± 5% change in resistance, thus this alternative procedure can be quite accurate as a check; however, it clearly is not NBS traceable.

9.6 System Leaks and Pump Check Out

There are two major types of leaks, external leaks, and leaks across the solenoid seals.

9.6.1 External leaks - In order to test for the presence of leaks around the fittings, disconnect the sample input line and plug the sample fitting. The flow as read on the rotameter should slowly decrease to zero. The pressure as read on the LED display should drop to below 250 mm Hg. If the pump diaphragm is in good condition and the capillary not blocked, it should take less than one minute from the time the inlet is plugged to the time the reading below 250 mm Hg is obtained.

9.6.2 Leaks across the solenoid valve - In order to check for leaks across the solenoid valves, plug in the span inlet line, engage the "Run-Span" pushbutton, and check the leaks according to the procedure in Section 9.6.1. If the pressure drops below 250 mm Hg, the valve associated with the span line is okay. Next plug the zero inlet in, engage the "Run-Zero" pushbutton, and check the leaks according to the procedure in Section 9.6.1. If this pressure also drops below 250 mm Hg, the valve associated with the zero line is okay.

9.7 Digital to Analog Converter Test

By energizing the Test DAC (digital to analog converter) pushbutton, the analog outputs will track the digital output from -23 ppm to 1000 ppm going from -2.3% full scale to +100% full scale. If a recorder trace is made, giving a straight line, the analog outputs are operating properly. Any excursions from a straight line indicate a probable lost bit or bad recorder.

9.7.1 To adjust the zero on a recording device, enter the Test Z/FS (zero/full scale) mode. This will output zero volts on the analog outputs. To adjust the span on recording device, engage the button a second time. This will output the full scale voltage (10.000 V unless otherwise specified) on the analog outputs.

9.7.2 To adjust the zero and span on the D/A board, monitor the analog output with an accurate voltmeter. Enter the Test Z/FS mode and adjust (for analog output #1) on the D/A board for zero volts, or any small offset voltage desired. Do the same for analog output #2. Now engage the Test Z/FS pushbutton a second time and adjust (analog output #1) for 10.000 volts (or for 10.000 volts plus the zero offset). Do the same for analog output #2.

10. Analyzer Calibration

Prior to calibration, the analyzer is allowed to stabilize for one hour. Perform the service checks recommended by the manufacturer. Figure 2 provides a flow schematic for calibration of the analyzer.

10.1 Analyzer Connection

Connect the analyzer and the equipment of Section 7 as shown in Figure 2. If an optional sample line filter is used, the calibration must be performed through this filter. Insure that the flowrate into the output manifold is greater than the total flow required by the analyzer, and any other flow demand connected to the manifold.

10.2 Zero Adjust

10.2.1 Allow sufficient time for the analyzer to warm up and stabilize.

10.2.2 Adjust the dilution system of Figure 2 so that zero air alone is present in the output manifold. Since not all flow controllers have a positive shut off, it might be necessary to disconnect the CO/CO_2 input line and cap it. Allow the analyzer to sample zero air until a stable reading is obtained and adjust the zero using the ZERO thumbwheel switches. Adjust for an average reading of zero.

10.2.3 If a strip chart recorder is used to obtain a record of the analog output, it is recommended that the system (i.e., either the analyzer or the recorder) be adjusted to obtain a zero trace at 5% of scale. This is to allow observation of zero drift and/or zero noise. This offset can be achieved by using the zero offset capability of the recorder or by adjusting the analog output of the analyzer to obtain the desired offset.

10.2.4 Record the stable zero air response as Z.

10.3 Span Adjust

Note: The following discusses the span adjustment and concentration of CO, this also applies to span adjustment and concentration when sampling for CO_2 using the Thermo Environmental CO_2 GFC Analyzer, 41/41 H.

10.3.1 Select the operating range of the analyzer. The full scale analog outputs of the analyzer are given in Section 11.3.7.

10.3.2 Adjust the zero air flow and the CO flow from the standard CO cylinder to provide a diluted CO concentration of approximately 80% of the upper range limit (URL) of the analyzer. The total air flow must exceed the total demand of the analyzer connected to the output manifold to insure that no indoor air is pulled into the manifold vent. Allow the analyzer to sample this CO concentration standard until stable response is obtained. The exact CO concentration is calculated from:

$$[CO]out = ([CO]std \times Fco)/(Fd + Fco)$$

where:
[CO]out = diluted CO concentration at the output manifold ppm.
[CO]std = concentration of the undiluted CO standard ppm.
Fco = flow rate of the CO standard corrected to 25°C and 760 mm Hg, liters per minute.
Fd = flow rate of the dilution air corrected to 25°C and 760 mm Hg, liters per minute.

10.3.3 Adjust the analyzer SPAN thumbwheels to obtain a recorder response as indicated from:

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

where:
URL = nominal upper range limit of the analyzer's operating range.
Zco = analyzer's response to zero air, % scale.
Note: If the instrument is zeroed first, use of the span switches will not affect the zero setting.

10.3.4 Record the CO concentration and the analyzer's response.

10.4 Additional Concentration Standards

Generate several additional concentrations (at least five others are suggested) by decreasing Fco or increasing Fd. Be sure the total flow exceeds the analyzer's total flow demand. For each concentration generated, calculate the exact CO concentration using the equation in

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Section 10.3.2. Record the concentration and the analyzer's response for each concentration.

10.5 Calibration Curve

Plot the analyzer's response versus the corresponding CO concentrations. Connect the experimental points using a straight line, preferably determined by linear regression techniques. The calibration curve is used to reduce subsequent sampling data.

10.6 Frequency of Calibration

In order to generate data of the highest confidence it is recommended that a multipoint calibration be performed every three (3) months, any time any major disassembly of components is performed, or any time the zero or span checks give results outside the limits described in Section 10.7 below.

10.7 Periodic Zero and Span Checks

In order to achieve data of the highest confidence, it is suggested that periodic zero and span checks be performed.

10.7.1 Periodically challenge the analyzer with zero air. The output of the zero air supply should be greater than the flow demand of the analyzer. In addition, an atmospheric dump bypass should be utilized to ensure that the zero air gas flow is being delivered at atmospheric pressure. Record the analyzer's response in percent of scale as Ao. Compute the zero drift from the following equation:

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

Z = recorder response at the calibration for zero air, % scale.
Note: For convenience, zero air can be plumbed directly to the zero air input bulkhead port, and the zero check performed by engaging the "Run-Zero" pushbutton.

10.7.2 Periodically challenge the analyzer with a CO level of approximately 80% of the URL. The 80% URL level may be obtained by dilution of a higher level of CO using a system similar to that of Figure 4, or by using a low level cylinder of CO containing CO in air at a concentration of approximately 80% of the URL. In either case, the cylinder of CO should be checked against a National Bureau of Standards (NBS) CO in Air Standard Reference Material (SRM) or a NBS/EPA approved gas manufacturer's Certified Reference Material (CRM). It should also be rechecked periodically to check for stability. This is especially true for a cylinder of low level CO. The Quality Assurance Handbook should be referred to for the procedure of checking the cylinders. Record the analyzer's response in % of scale as A80. Compute the span error from the following equation:

$$\text{Span Error, } \% = ([A80 - Z)URL/100] - [CO]) \times 100/[CO]$$

where:
Z = Recorder response obtained at the last calibration for zero air, % scale
[CO] = Span concentration
URl = Nominal upper range limit of analyzer's operating range

Note: For user convenience, the span gas can be plumbed directly to the span input bulkhead fitting. By engaging the "Run-Span" pushbutton, span gas will flow into the instrument.

10.7.3 The latest copy of the Quality Assurance Handbook for Air Pollution Measurement Systems should be consulted to determine the level of acceptance of zero and span errors.

10.7.4 For detailed guidance in setting up a quality assurance program, the user is referred to the Code of Federal Regulations and the EPA Handbook on Quality Assurance.

11. Analyzer Operation

11.1 Analyzer Description

As illustrated in Figure 3, the instrument can be most conveniently discussed by separating it into the following operational components.

- Optical bench
- Correlation wheel and chopper motor
- Source and source power supply
- Detector, preamplifier, and bias supplies
- Input signal conditioning board
- DC power supply
- Microcomputer
- Temperature controller
- Flow components (pump, valves, flowmeter, and plumbing)
- Temperature and pressure transducers

11.1.1 Optical Bench - The optical bench is of the white cell design. The use of the white cell multipass optical bench allows one to achieve a long path length, with a large acceptance angle, in a small physical package. The bench has been designed for easy disassembly for cleaning. The source, detector, correlation wheel, and chopper motor mount rigidly to the bench. No realignment should be necessary after routine cleaning.

11.1.2 Correlation Wheel and Chopper Motor - The correlation wheel consists of two hemispherical cells, one fitted with CO (or CO_2 when using the Model 41/41H analyzer) and the other with N_2. Integral with the correlation wheel is the chopper pattern necessary to produce the high frequency (360 Hz) chop necessary for the infrared detector. The correlation wheel is rotated by a synchronous motor.

11.1.3 Source and Power Supply - The infrared source is a special wire wound resistor. It is heated by passing a highly regulated DC voltage through the resistor. Replacement, when necessary, is straightforward.

11.1.4 Detector, Preamplifier, and Bias Supply - The detector used on the analyzers (Model 48 and 41/41H) is a solid state device with an integral cooler. It is mounted directly onto the optical bench. The output of the detector is fed into a preamplifier prior to its transmission to the input signal conditioning board. The bias voltage necessary to operate the detector is generated by a separate bias voltage power supply. Table 2 outlines specifications for the GFC CO analyzer.

11.1.5 Input Signal Conditioning Board - The input signal conditioning board takes the output signal from the preamplifier, and separates the signal into two components, one component being the signal coming from the CO half of the correlation cell, the other due to the N_2 half of the correlation cell. This board includes the sensors and associated circuitry for determination of the wheel position, as well as an AGC (automatic gain control) circuit. Finally, it contains two V-F's (voltage to frequency) converters to digitize the two signals.

11.1.6 DC Power Supplies - The DC power supply board generates the necessary regulated DC voltages. In addition, it contains the driving circuitry for the solenoids.

11.1.7 Microcomputer - In the analyzed microcomputer the pulse train outputs of the input signal conditioning board feed directly into computer controlled counters. In addition, the pulse train output of the pressure transducer and the temperature transducer system are fed directly into the same computer controlled counter. The software operates on this information to determine the sample concentration, to output diagnostic data, and to output the computed sample concentration to the front panel digital display and rear panel analog recorder jacks. The software contains sophisticated algorithm to minimize noise, increase sensitivity, insure that the output is linear, to correct for changes in temperature and pressure, and to check for information.

11.1.8 Temperature Controller - The analyzer contains a temperature transducer to measure the temperature and to correct for temperature changes. However, in order to insure that the optical bench is above the dew point to avoid water condensation, the optical bench is operated at a temperature slightly above ambient. Meaningful output data will be generated even if the bench has not stabilized.

11.1.9 Flow Components - The analyzer operates at nominal atmospheric pressure. Figure 4 summarizes the flow schematic. A downstream pump and capillary control the sample flow through the optical bench, which is monitored by a rotameter. The nominal flow is 1 liter per minute, with valves between 1/2 - 2 liters per minute. The span, zero, and sample solenoids are operated by successive engagements of the RUN pushbutton on the front panel. The control signals for the solenoids go through the microcomputer.

11.1.10 Temperature and Pressure Transducer - Temperature and pressure must be measured if one wants to compensate for changes in atmospheric values. The pressure is measured by a strain gauge pressure transducer. The temperature is measured by a thermistor.

11.2 Analyzer Installation

The installation of the analyzer includes unpacking the instrument, connecting sample, zero, span, and exhaust lines to the instrument, and attaching the dual analog outputs to a suitable recording device. Installation should always be followed by a multipoint calibration using the procedure outlined in Section 11.4. See Appendix C-3 of this Compendium, Placement of Stationary Active Monitors, for a discussion of factors regarding monitor placement.

11.2.1 Unpacking the Analyzer - The analyzer is shipped complete in one container. In addition to the basic analyzer, a six-foot line cord and an instruction manual are included in the shipping container.

11.2.1.1 Remove the analyzer from the shipping container and set it on a table or bench which will allow easy access to both the front and rear of the instrument.

11.2.1.2 Snap open latches holding the cover to the instrument. Remove the cover from the main frame of the instrument to expose the internal components.

11.2.1.3 Check for possible damage during shipment.

11.2.1.4 Check that the printed circuit boards are tightly inserted in their connectors.

11.2.2 Assembling the Analyzer

11.2.2.1 Connect the sample air to be measured to the bulkhead connector labeled "SAMPLE" on the rear panel of the instrument. Care should be taken to ensure that the sample is not contaminated by dirty, wet, or incompatible materials in the sample lines. Teflon®, borosilicate glass, or similar tubing with an O.D. of 1/4" and a minimum I.D. of 1/8" is required for all sampling lines. The length of the tubing should be held to a minimum. For best results, the tubing between the manifold and the analyzer should be less than ten feet. [CAUTION: Sample gas should be delivered to the instrument at atmospheric pressure. It may be necessary to employ an atmospheric dump bypass plumbing arrangement to accomplish this.]

11.2.2.2 Connect a source of gas of interest free air to the bulkhead labeled "ZERO" on the rear panel of the instrument. Generation of CO/CO_2 free air is discussed in Section 8.2.

11.2.2.3 Connect a source of CO span gas (i.e., use CO_2 span gas for CO_2 analyzer) to the bulkhead connector labeled "SPAN" on the rear panel of the instrument.

11.2.2.4 Connect the rear panel bulkhead labeled "EXHAUST" to a suitable vent. take care to verify that there is no restriction on this line.

11.2.2.5 Connect a recording device to the output channels of the instrument. Unless otherwise specified, the recorder signals are 0-10 VDC.

11.2.2.6 Install the power cord to the rear of the instrument. Plug the male end into an appropriate outlet. Check for proper voltage requirements.

11.2.2.7 The analyzer can be operated either with or without a particulate filter. If a filter is used, it should be a Teflon® filter-holder with a 5-10 micron Teflon® filter. In order to satisfy all EPA requirements for precision and level 1 span checks (see reference 2), it is recommended that the filter be installed between the sample-span solenoid and the optical bench. The flow scheme of the analyzer has been designed to allow for this type installation.

11.3 Analyzer Operation

Analyzer operation is illustrated in the flow diagram provided in Figure 4. A description of the controls follows.

11.3.1 Power Switch - Controls power to the electronic circuits, pump, chopper motor, and solenoid valves. When turned on, the power "ON" light integral with the switch will be lit; there also should be an audible sound from the pump. The instrument automatically goes into the startup mode.

11.3.2 Sample Flowmeter - The flowmeter shows the flow rate through the optical bench. The meter should read between 1/2 to 2 liters per minute (1-4 scfh). The flow rate is set by a capillary. It can only be changed by using a different sized capillary.

11.3.3 LED Display - Depending upon the mode of operation, the display will show the CO concentration in PPM, O, or FSCALE, DAC ramp, detector frequencies, temperature in degrees Celsius, pressure in millimeters Hg, various status diagnostics, or the previous hourly average CO concentration.

11.3.4 CO Run and Test Mode Entry Pushbuttons - Allows the operator to change the mode of operation of the instrument. A LED (light emitting diode) above the pushbutton indicates the active mode. There are eight (8) pushbuttons.

11.3.4.1 Remote Mode - This pushbutton is used to engage (LED above the "ON") or disengage (LED above the pushbutton "OFF") the remote options if installed.

11.3.4.2 Test Z/FS (Zero/Full Scale) - First actuation into this mode sets the instrument to digital zero. The recorder output levels may then be adjusted to O V or to some offset level. Engaging the pushbutton a second time sets the instrument to digital full scale. The full scale levels of the recorder outputs can then be adjusted.

11.3.4.3 Test DAC (Digital to Analog Converter) - This function is used to test for proper operation of the analog outputs and any recorder which may be connected. Actuation of this pushbutton results in the generation of a "ramp" on the analog outputs. Initial entry into this mode displays -23 ppm and outputs -2.3% full scale on the analog outputs for 30 seconds. The DAC is then caused to change its output sequentially through all its possible states causing the digital display to count from -23 to +1000 ppm while the analog outputs change from -2.3% full scale to +100% full scale in steps of 0.1% FS. This process takes approximately seven minutes for completion. A straight line ramp on the recorder chart indicates proper functioning of both the instrument and recorder. Both the digital display and analog output ramp can be stopped at any intermediate value by engaging the pushbutton a second time. Engaging the pushbutton a third time causes the ramp to continue. This allows calibration of the recorder at any of the intermediate values.

11.3.4.4 Test INT (Intensity) - Actuation of this button causes the instrument to display the infrared light intensity in Hz measured by the IR detector. The initial actuation displays the intensity as digitized by the first V-F (voltage to frequency) converter. The second engagement displays the intensity as digitized by the second V-F converter. Both readings should be nominally the same, reading at least 10,000 Hz. A low reading is an indicator of either a weak IR source or of low reflectance of the mirrors in the optical bench. Therefore, the need to clean the optics and the status of the V-F converters can be ascertained without dismantling any part of the instrument.

11.3.4.5 Test P/T (Pressure/Temperature) - Initial entry into this mode caused the pressure to be displayed in millimeters Hg. If this pushbutton is engaged a second time, the temperature in degrees Celsius will be displayed.

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11.3.4.6 Test STAT (Status) - This function allows the user to determine which options have been selected by the internal circuit board switches without the need to open the instrument and interpret the switch settings. Successive engagement of the pushbutton indicates the full scale ranges in ppm of analog outputs #1 and #2, the time responses of analog outputs, the status (whether on or off) of the eight internal switches, and additional status functions if in the troubleshooting mode.

11.3.4.7 Test H.A. (Hourly Average) - First actuation of this button displays the average CO concentration for the previous hour whether the hourly average analog output interrupts are engaged or not. The second actuation displays the minutes past the hour presently assumed by the instrument. If the pushbutton is then held in, the time will increment, allowing the user to set the beginning time of the average.

11.3.4.8 RUN - This pushbutton cancels all test diagnostic modes and puts the instruments into the sample monitoring mode. If no diagnostic tests are desired, use of this button is all that is required to "drive" the instrument. The digital display shows the CO concentration in ppm. There are three RUN modes, indicated by lights and labels in the display, and operated by successive engagements of the pushbutton:

11.3.4.9 Run-Zero - The solenoids switch so that zero gas flows into the optical bench.

11.3.4.10 Run-Span - The solenoids switch so that span gas flows into the optical bench.

11.3.4.11 Run-Sample - The solenoids switch so that sample gas flows into the optical bench. Note that "Run-Sample" is the default mode. Thus when the instrument is first turned on (or when power comes on again after a power failure) the instrument automatically goes into the "Run-Sample" mode. If the analyzer is inadvertently left in a diagnostic or calibration mode, data will be lost for only one hour, since the instrument will automatically default to the "Run-Sample" mode one hour after the last actuation of any switch.

11.3.5 Zero - When calibrating the instrument, three thumbwheel switches are used to set the zero reading of the analyzer.

11.3.6 Span - Three thumbwheel switches are used to set the instrument to the concentration of a span gas source. If the instrument is zeroed first, use of the span switches will not affect the zero setting.

11.3.7 Range - The analyzer has two independent analog outputs with independently selectable ranges and time responses. The first range thumbwheel switch selects the range for output #1 (the upper terminals on the rear panel), while the second switch selects the range for output #2. The selected full scale ranges can be displayed by use of the Test STAT function. The number code on the thumbwheel switches correspond to the following ranges:

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

Switch Setting	Full Scale Range (PPM) (cont.)
5	50
6	100
7	200
8	500
9	1000

11.3.8 Time - These two thumbwheel switches select the time response/hourly averaging options for analog outputs #1 and #2 respectively. The selected time responses for analog outputs #1 and #2 can be displayed by use of the Test STAT function. The number code on the thumbwheel switches corresponds to the following:

Setting	Time Response (60 Hz)	Time Response (50 Hz)
0	10 sec. CO average	12 sec. CO average
1	20 sec. CO running average	24 sec. CO running average
2	30 sec. CO running average	36 sec. CO running average
3	60 sec. CO running average	60 sec. CO running average
4	90 sec. CO running average	96 sec. CO running average
5	120 sec. CO running average	120 sec. CO running average
6	300 sec. CO running average	300 sec. CO running average
7	1 hr. CO continuous average (c.H.A.)	1 hr. CO continuous average (c.H.A.)
8	1 hr. & 60 sec. integrated CO averages, time multiplexed, 60 sec. averages periodically blanked (b.H.A.)	1 hr. & 60 sec. integrated CO averages, time multiplexed, 60 sec. averages periodically blanked (b.H.A.)
9	1 hr. & 60 sec. integrated CO averages, time multiplexed 60 sec. averages delayed (d.H.A.)	1 hr. & 60 sec. integrated CO averages, time multiplexed 60 sec. averages (d.H.A.)

11.3.8.1 For time switch settings 0 through 6, the analog output updates every 10 seconds (12 seconds for 50 Hz). If the switch setting is 7, the analog output gives the average for the previous hour setting at the time when the minute time (as displayed upon second actuation of the Test H.A. pushbutton) is equal to one.

11.3.8.2 If the switch setting is 8, the analog output gives during the first 10 minutes of every hour, the CO average for the previous hour, and during the remaining 50 minutes, updating every 60 seconds, the current 60 second CO integrated average.

11.3.8.3 If the switch setting is 9, the analog output gives during the first 10 minutes of every hour, the CO average for the previous hour, and during the remaining 50 minutes, sixty (60) second integrated CO averages for the present hour, time compressed in the ratio 5:6. Therefore, even while the hourly average is being output, the analyzer continues to monitor CO and stores the 60 second averages to be updated every 50 seconds for the remaining 50 minutes of the hour. The hourly average routines are discussed more fully in the manufacturer's instruction manual.

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11.3.8.4 The digital display indicates the CO average corresponding to the time specified by switch settings 0 through 6 for analog output #1, updating every 10 seconds (12 seconds for 50 Hz) as indicated by a blinking decimal point. If the time switch for analog output #1 is set to 7, 8, or 9, the digital display indicates 60 second running averages updating every 10 seconds (12 seconds for 50 Hz).

11.4 Analyzer Startup

11.4.1 The source turns on, all electronics are turned on, the detector cooler goes on, the chopper motor and sample pump go on, the heater in the pressure transducer goes on, the program initializes itself.

11.4.2 During the few minutes it takes for the source etc. to stabilize observe that the power switch is energized, the LED display first displays the word "HELLO" followed by the word "CO" (during this time, approximately 2 minutes, the analog outputs will give 0 volts.) The instrument will then automatically go into the "RUN SAMPLE" mode.

11.4.3 The analyzer has been designed so that the Test diagnostic modes can be utilized without disturbing the analog outputs. Therefore, if one enters the Test STAT of H.A. modes, the instrument continues to output the CO values at the analog outputs. Entering the Test Z/FS or DAC modes does affect the outputs, however, the microcomputer continues to store the CO data for use when returning to the RUN mode. If one enters the Test INT or P/T modes, the analyzer "latches" onto the current CO value and continues to output that value until the instrument is returned to the RUN mode. The analyzer then enters a wait period of approximately 25 seconds before updating to the current CO value.

11.5 Analyzer Shutdown

De-energize the power switch on the front panel. The analyzer is now powered down.

11.6 Loss of Power

If a power failure occurs or if the analyzer is turned off momentarily, the instrument automatically goes into the start-up mode upon resumption of power. Note that if any of the hourly average modes are being used, upon power up the timer will be reset to zero, thus the average will not necessarily be in synchronization.

11.7 Analyzer Electronics and Microcomputer System

In order to understand the operation of the analyzer, a general knowledge of the electronics and software is necessary. The electronics can conveniently be broken down into the following components:

- DC power supply and solenoid driver
- Bias source and cooler power supply
- Detector and preamplifier
- Input signal conditioning board
- Digital electronics
- Temperature controller

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11.7.1 DC Power Supplies - The DC power supply outputs the regulated and unregulated DC voltages necessary to operate the digital electronics, the bias supply, the detector and preamplifier, the input signal conditioning board, and the temperature controller. The transformer used is field jumpable for 110 and 220 volt service. It outputs +24 volts unregulated and ±15 volts and +5 volts regulated. Regulation is achieved by use of monolithic voltage regulators. The DC board also contains the driving circuit necessary to energize the solenoids. The logic on/off signals are received from the microcomputer.

11.7.2 Bias, Source and Cooler Power Supplies - The solid state detector used needs a bias voltage of approximately -100 volts DC. Both the cooler and source need a high current, low voltage source. The bias supply contains a high current 18 volt regulated power supply. This 18 volts is also used for an oscillator, the output of which goes to a step-up transformer to generate the high voltage. This high voltage then passes through a rectifying circuit to form the -100 volt bias needed for the detector.

11.7.3 Detector and Preamplifier - The detector used is a photo conductive, lead-selenide (PbSe) device, with an internal thermo-electric cooler. The PbSe detector operates through use of the internal photoelectric effect. That is, its conductivity is proportional to the high intensity hitting it. One characteristic of this device is that it has a high conductivity even with no light. The background conductivity increases with increasing temperature. Thus in order to reduce the background conductivity, the detector is cooled. In order to distinguish the signal from background, the source is chopped. Thus the output of the detector includes an AC component due to the background conductivity. It should be noted that the AC component is very small compared to the DC component. The output of the detector passes through a coupling capacitor which only passes the AC component. The AC component is then amplified. The output signal is an AC signal, with a low frequency component and a high frequency component. The low frequency component is at 30 Hz, and is due to the 30 Hz rotation of the correlation wheel. The high frequency component is at 360 Hz and is due to the mask on the correlation wheel which divides the wheel into 12 sectors. The output of the preamplifier is fed through a shielded cable to the input signal conditioning board.

11.7.4 Input Signal Conditioning Board - The input signal conditioning board contains the circuitry necessary to operate the AGC (automatic gain control), the rectifier, and the demodulation circuitry. In addition, it includes the necessary components to digitize the signal output.

11.7.5 Microcomputer System - The microcomputer system is a multiboard system interconnected by use of a mother board. A detailed discussion of these boards is provided in the manufacturer's Instruction Manual. The boards are broken up into functional forms as follows:

- Microprocessor
- Memory
- Counter
- Peripheral Interface
- Display Driver
- Digital/Analog

- Switch
- Span-Zero Buffer Board
- General Purpose Interface

11.7.6 Temperature Controller - Two 50 watt 100 ohm resistors (400 ohm for 220 V) mounted on the optical bench are used to heat the optical bench above the dew point, to avoid moisture condensation on the mirrors. A thermistor is used to determine the bench temperature, with op-amp and the solid state relay used as the control elements to control the current into the heaters.

12. Method Safety

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

13. Performance Criteria and Quality Assurance (QA)

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

13.1 Standard Operating Procedures (SOPs)

13.1.1 SOPs should be generated by the users to describe and document the following activities in their laboratory: 1) assembly, calibration, leak check, and operation of the specific sampling system and equipment used; 2) preparation, storage, shipment, and handling of the sampler system; 3) purchase, certification, and transport of standard reference materials; and 4) all aspects of data recording and processing, including lists of computer hardware and software used.

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

13.2 Quality Assurance Program

The user should develop, implement, and maintain a quality assurance program to ensure that the sampling system is operating properly and collecting accurate data. Established calibration, operation, and maintenance procedures should be conducted on a regularly scheduled basis and should be part of the quality assurance program. Maintenance procedures provided in Section 9, calibration procedures in Section 10, and operation procedures in Section 11 of the method and the manufacturer's instruction manual should be followed and included in the QA program. Additional QA measures (i.e., trouble-shooting) are provided by the manufacturer as well as further guidance in maintaining the sampling system which is beyond the scope of this document.

14. References

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2. 40 CFR Part 58, Appendix A, B.

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

Table 1. Specifications for GFC CO Analyzer

Ranges	0-1, 2, 5, 10, 20, 50, 100, 200, 500, 1000 ppm
Noise	0.05 ppm RMS - with time constant = 30 seconds
Minimum Detectable Limit	0.10 ppm
Zero Drift, 24 hours	± 0.2 ppm
Span Drift	± 1% Full Scale
Rise, Fall Times (0-95%) (at 1 lpm flow, 30 second response time)	1 minute
Precision	± 0.1 ppm
Linearity	± 1%
Flow Rate	0.5 - 2 lpm
Rejection Ratio	Negligible interference from water and CO_2
Operating Temperature	Performance specifications maintained over the range 15-35°C (may be operated safely over the range 5-45°C)
Power Requirements	105 - 125 VAC, 60 Hz 220 - 240 VAC, 50 Hz 100 Watts
Physical Dimensions	17"W x 8 3/4"H x 23"D
Weight	45 lbs.
Dual Outputs (Standard)	Individually selectable to 0-10mv, 0-100mv, 0-1V, 0-5V, 0-10V; digital display; 1 hour integrated value. Other outputs available upon request (4-20ma, IEEE488)

Table 2. Commercially Available GFC CO Analyzers Designated by U.S. EPA as Reference Methods

Identification	Manufacturer	Fed. Vol.	Reg. Pg.	Notice Date
Dasibi Model 3003 Gas Filter Correlation CO Analyzer, operated on the 0-50 ppm range, with a sample particulate filter installed on the sample inlet line.	Dasibi Environmental Corp. 515 West Colorado St. Glendale, CA 91204	46	20773	4/07/81
Thermo Electron Model 48 Gas Filter Correlation Ambient CO Analyzer, operated on the 0-50 ppm range, with a time constant setting of 30 seconds.	Thermo Electron Instruments, Inc. 8 West Forge Parkway Franklin, MA 02038	46	47002	9/23/81
Monitor Labs 8830 CO Analyzer operated on the 0-50 ppm range, with a five micron Teflon® filter element installed in the rear-panel filter assembly.	Monitor Labs, Inc. 10180 Scripps Ranch Blvd. San Diego, CA 92131	53	7233	3/07/88
Dasibi Model 3008 Gas Filter Correlation CO Analyzer, operated on the 0-50 ppm range, with a time constant setting of 60 seconds, a particulate filter installed in the analyzer sample inlet line, with or without use of the auto zero or auto zero/span feature.	Dasibi Environmental Corp. 515 West Colorado St. Glendale, CA 91204	53	12073	4/12/88

Commercially Available GFC CO Detection Devices

Detection Device I.D.	Manufacturer	Portability
Gas Analyzer DEFOR	Westinghouse Elec. Process & Environmental Measuring Technology Orrville, OH 44667 (800)628-1200	Stationary
CO_2 Analyzer Model 41/41H	Thermo Environmental Instruments, Inc. 8 West Forge Pkwy. Franklin, MA 02038 (508)520-0430	Stationary

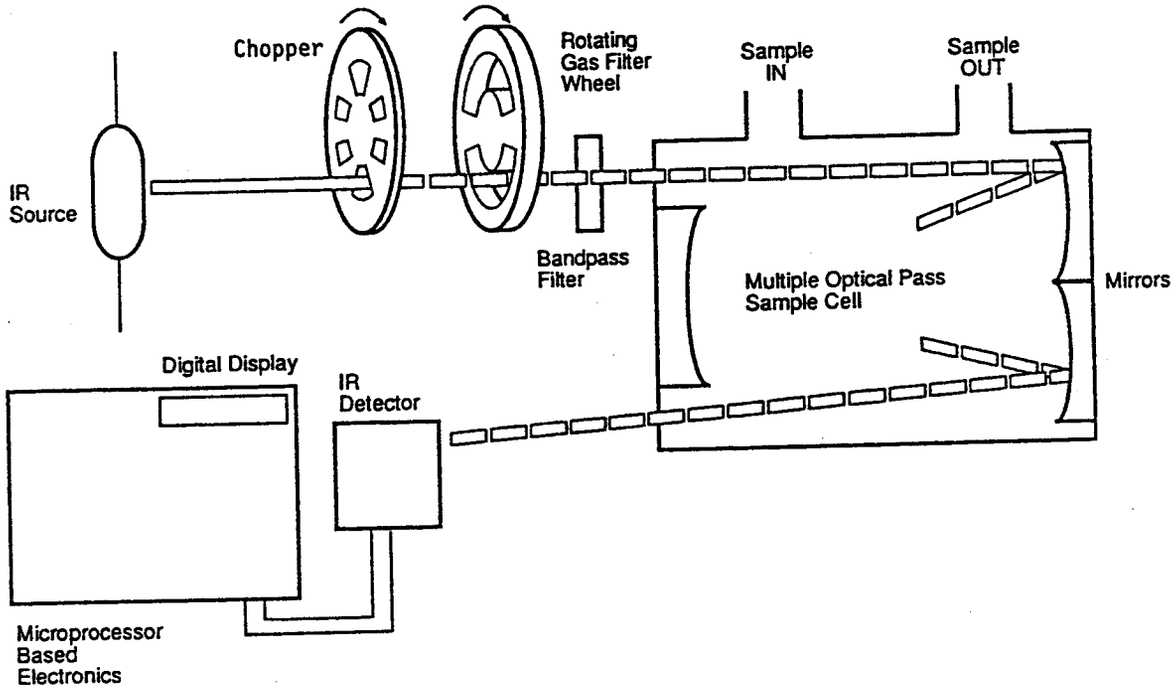

Figure 1. Gas Filter Correlation Basic Components

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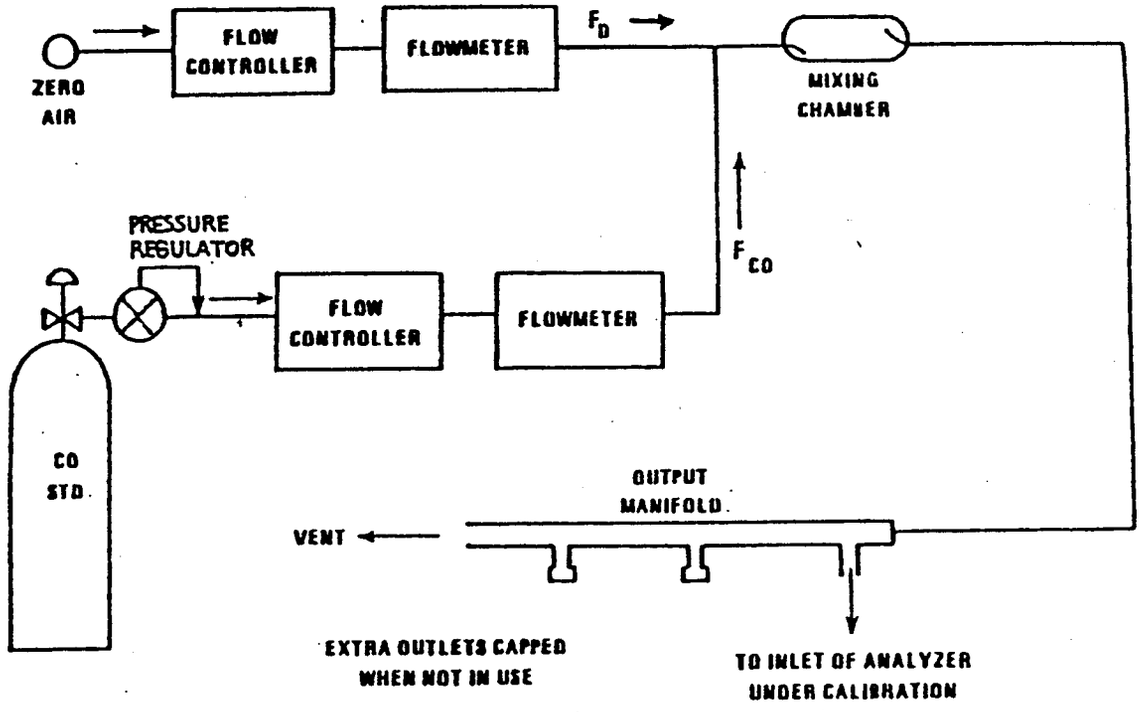

Figure 2. Flow Schematic of Calibration System

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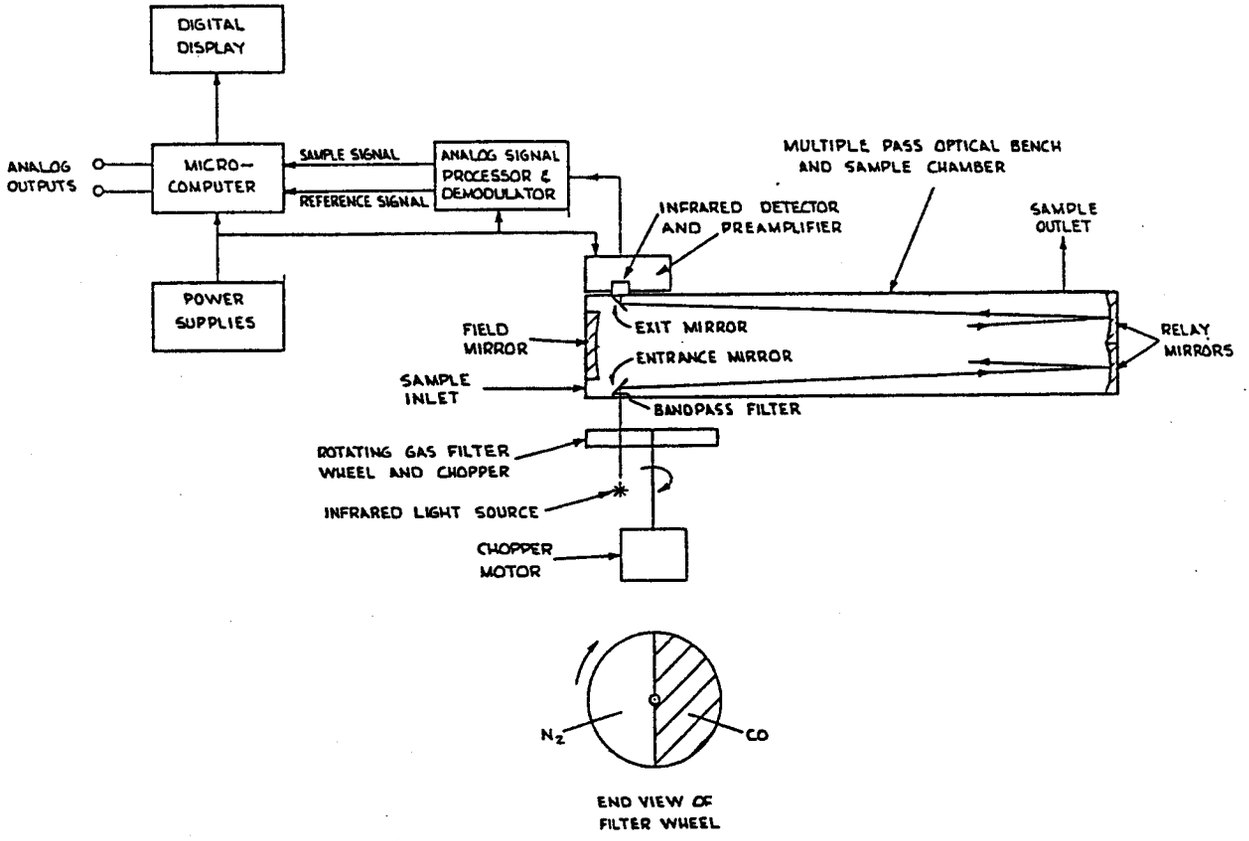

Figure 3. Block Diagram of a Gas Filter Correlation Spectrometer

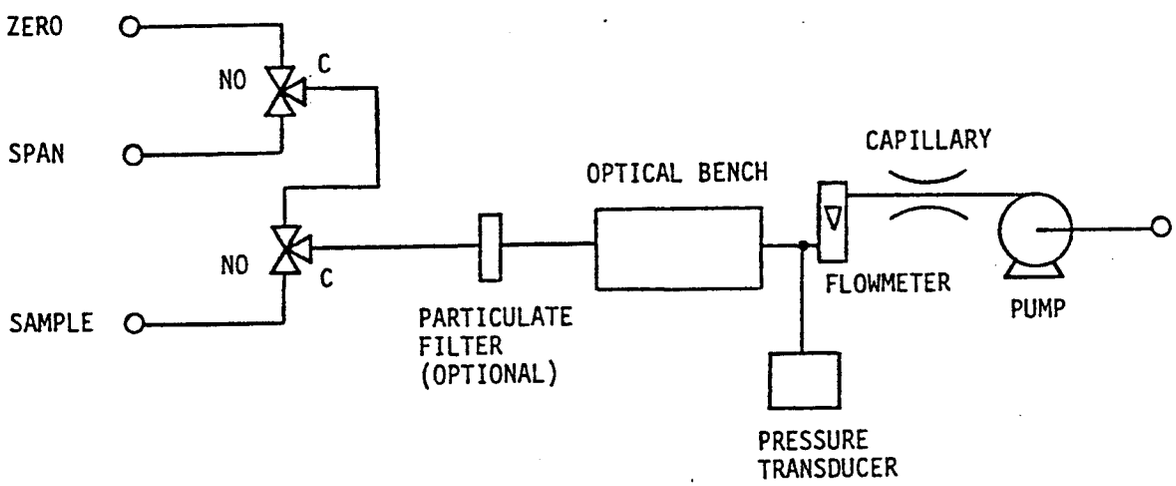

Figure 4. Flow Schematic for Calibration of GFC Analyzer

Method IP-3C

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

Method IP-3C

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

1. Scope

1.1 This document describes a method for determination of CO only, employing electrochemical oxidation. This method utilizes a small, portable, personal exposure monitor (PEM) which can be attached to an individual (i.e., to directly assess exposure levels). With the PEMs, CO levels are measured in an individual's breathing zone, on a continuous real-time basis. Electrochemical CO monitors can also be used as area monitors.

1.2 Measurement of CO by electrochemical oxidation relies on oxidation of CO to CO_2 to produce an electrical signal related to the CO concentration in sample air.

1.3 An Appendix detailing the use of a portable air sampling system (PASS) for the determination of CO is also included.

2. Applicable Documents

2.1 ASTM Standards

D1356	Definition of Terms Relating to Atmospheric Sampling and Analysis
D1357	Recommended Practice for Planning the Sampling of the Atmosphere
D3195	Recommended Practice for Rotameter Calibration
D1914	Recommended Practice for Conversion Units and Factors Relating to Atmospheric Analysis
D3249	Recommended Practice for General Ambient Air Analyzer Procedures
E1	Specification for ASTM Thermometers
E180	Recommended Practice for Development of Precision Data for ASTM Methods for Analysis and Testing of Industrial Chemicals
D3162-78	Standard Test Method for Carbon Monoxide in the Atmosphere (Continuous Measurement by Nondispersive Infrared Spectrometry)

2.2 Other Documents

Laboratory and Indoor/Ambient Air Studies (1-11)
U.S. Environmental Protection Agency Technical Assistance Document (12)

3. Summary of Method

3.1 The electrochemical CO monitor samples either by diffusion or by use of a small diaphragm type pump which maintains a constant flow rate. The monitor employs an electrochemical measuring principle in which CO is converted to CO_2 in a liquid cell, thus freeing electrons to generate a small electrical current that is amplified, measured, and recorded. Figure 1 provides a schematic of a standard CO PEM.

3.2 In the monitor, the sample is transported to an electrochemical cell where CO is oxidized to CO_2. Oxidation of CO produces a current and subsequent signal that are

proportional to the CO concentration in the sample air. The electrical signal can be displayed directly or integrated inside the instrument to give readings in parts per million. This process is illustrated in Figure 2.

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

3.4 The following information details the operating principles of a CO PEM manufactured by General Electric (GE) Co. (1,2) and discusses basic principles of determining CO by electrochemical oxidation.

3.4.1 The GE monitor employed solid polymer electrolyte (SPE) technology (formerly patented by GE) using a membrane with deionized water stored on one side. Figure 2 provides a complete illustration of the GE CO monitor. The deionized water was stored in a plastic reservoir cell. The sample containing CO was continuously pumped past the other side of the membrane. The pump operated up to 40 hours with a precision of 2 ppm with zero and span checks performed before and after field service. When the sample entered the 100% relative humidity environment of the saturated membrane, CO (present in the sample) combined with water in the following reaction:

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$$

3.4.2 The resulting hydrogen ions ($2H^+$) passed through the membrane freeing up electrons ($2e^-$). A sensor electrode was mounted on the sampling side of the membrane and a counter electrode was mounted on the water reservoir side of the membrane. The electrons freed by the above reaction moved from the sensor electrode to the counter electrode through an external circuit, generating an electric current that was amplified. At the water reservoir side of the membrane, the hydrogen ions and electrons combined to form water as shown in the following reaction:

$$2H^+ + 2e^- + 1/2\ O_2 \rightarrow H_2O$$

3.4.3 When both of the reactions in Section 3.4.1 and Section 3.4.2 are combined, the following reaction occurred, causing CO in the sample to be oxidized to CO_2:

$$CO + 1/2\ O_2 \rightarrow CO_2$$

For each CO molecule oxidized, two electrons traveled through the external circuit. The resulting current generated was directly proportional to the CO concentration present in the sample.

3.4.4 After amplification, the CO concentration was read directly in parts per million by a liquid crystal display (LCD) system. The continuous electrical signal was recorded in internal memory of the GE monitor configured as discussed in Section 4.2.

3.4.5 The reaction was affected by temperature. A thermistor mounted in the sensing cell altered the gain of the amplifier circuitry, forming a temperature compensation network. Chemical interferents (e.g., nitrogen dioxide) were removed from the sample with a chemical filter consisting of an oxidant (e.g., potassium permanganate on activated alumina) before entering the sensing cell.

3.4.6 Although the GE CO PEMs are no longer manufactured, the information provided may be helpful in understanding the electrochemical oxidation process of CO to CO_2. Additionally, one could use the technology to develop a CO PEM or modify an existing one to meet specific monitoring needs.

4. Significance

4.1 Over the last decade, various small, portable personal monitors capable of measuring air pollution exposures of people as they go about their daily lives have been introduced. Several manufacturers offer light-weight personal monitors for carbon monoxide that are hand-held, belt-mounted, or can be carried on a shoulder strap like a camera or portable radio. Passive CO detectors also have been developed by several companies. However, minimal data concerning the performance and evaluation of these monitors are available. The sections describing the CO monitors have been generalized into standard procedures applicable to most of the currently available instruments. For use in the Compendium, the authors have relied on information provided from manufacturer's operating and instructional manuals.

4.2 At this writing, there is little documentation (i.e., research/test data, human exposure studies, etc.) available for CO monitors used for personal monitoring in non-industrial atmospheres except for the CO PEM manufactured by the Aircraft Division of General Electric (GE) Co. (1,2) from 1978 to 1984. The GE Co. Monitor is no longer produced. The GE CO detector was evaluated in two studies conducted by the U.S. Environmental Protection Agency (1,2). As part of the study, the GE CO sensing systems were adapted with microprocessor data loggers. The data loggers were used to automatically manipulate and store numerical data from the instruments for later examination and retrieval. For the study, the CO monitors were termed "COED" monitors for carbon monoxide exposure dosimeters. The COED monitors were used in Denver, Colorado and Washington, DC for human exposure studies conducted 1982-1983. The COED-I, which consisted of the GE monitor and a Magus Group microprocessor-based data logging and control package, was used successfully to obtain more than 1600 24 hour human CO exposures in these two cities. The COED-II, which consisted of the GE monitor and a HP41CV programmable calculator and interfacing electronics, was evaluated briefly, but data was not published due to problems with some instruments. The tests proved that the GE monitor was suitable for personal monitoring applications (1,2).

4.3 Although the GE monitors are no longer produced, the technology behind the CO monitor provides a means to adequately determine indoor CO concentrations. Table 1 provides the GE monitor's performance characteristics. Other small, portable electrochemical CO monitors are available. Though research validating other models' applicability to this method has not been conducted, additional models that may be usable are included in Table 2.

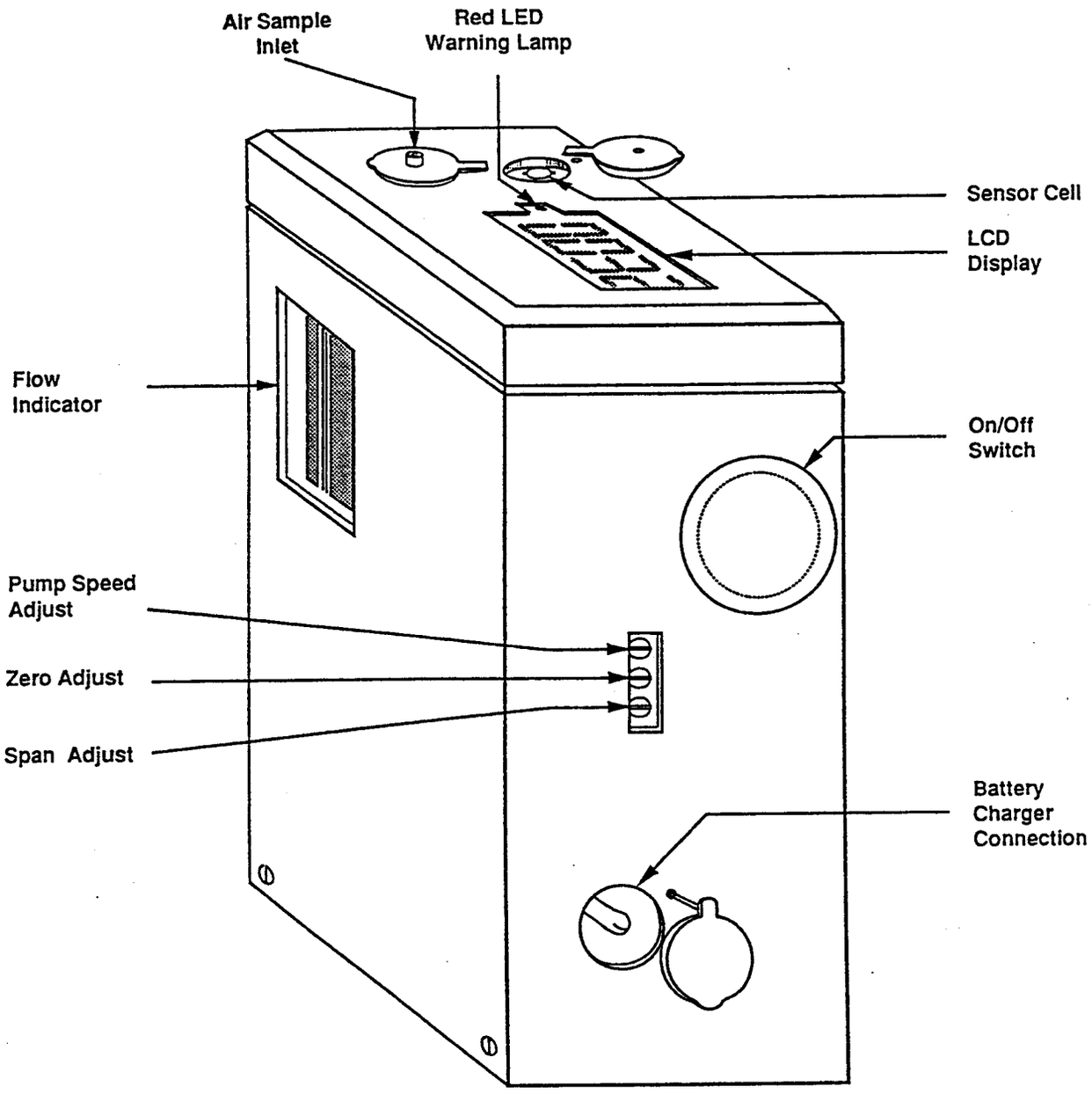

Figure 1. CO Personal Exposure Monitor

Note: Some models report erroneous zero when sensor cell is exposed to nitrogen for more than a few minutes. Users manual will specify zero procedure and what zero gas is recommended for that model.

8.2 Calibration and span gases - pressurized cylinders with CO concentrations corresponding to the CO dosimeter range of operation. Some models have available calibration kits with calibration gases, connecting tubing, and pressure regulators. The cylinders should be traceable to a NBS/SRM or to a NBS/CRM.

8.3 Multistage pressure regulators - standard, two-stage, stainless steel diaphragm regulators with pressure gauges for gas cylinders.

8.4 Battery charger - capable of recharging the CO monitor.

8.5 Thermometer - used to measure area monitoring temperature.

8.6 Barometer - used to measure barometric pressure of monitoring area.

9. Systems Maintenance

All necessary maintenance activities are included in the manufacturer's operating instructions. Because a majority of the CO monitors produced may not be uniform (e.g., pump/pumpless, filter/no filter, etc.), the maintenance practices vary from one monitor to the next. However, the following provides a brief summary of general maintenance practices standard for all CO monitors.

9.1 Periodic Maintenance

The CO monitor should be properly maintained to ensure successful operation. Periodic maintenance is conducted to reduce system failures and maintain calibration integrity of the monitor. Periodic maintenance should include inspection of the battery pack, filter (optional), pump (if applicable), and the important support equipment. As with the NDIR analyzer, instrument calibration should be checked on a schedule established after the monitor has operated for a period of time. The sensitivity and linearity should also be checked. These instrument checks should be done at least on an annual basis. However, when any major component is changed the linearity and selectivity of the instrument should be confirmed. A log of these settings and a service and repair log should be kept to assist in evaluating maintenance difficulties.

9.2 Routine Maintenance

Regular checks of the instrument and its operation are mandatory. Even though a system may provide excellent quality data initially, without routine maintenance and system checks the quality of the data will degenerate with time.

9.3 Preventive Maintenance

The preventive maintenance program of the CO monitoring system should contain a troubleshooting guide and diagnostic chart to assist operators in identifying and correcting instrument problems.

9.4 Troubleshooting the Monitor

9.4.1 The manufacturer's instruction manual generally contains troubleshooting guidelines that cover most troubles which may occur.

9.4.2 The troubleshooting guidelines should only be used after the analyzer cannot be calibrated or aligned according to manufacturers' specifications or cannot be operated properly.

9.4.3 The manufacturer's troubleshooting guide provides the user with a logical sequence to follow while investigating problems

10. CO Monitor Calibration

It is essential that zero, span and multipoint calibrations be performed frequently. Daily zero and span checks and weekly multipoint calibration is recommended. Proper calibration is vital to this equipment's accuracy. The instrument is calibrated by introducing into it a known concentration of gas being monitored, and adjusting the span control to correspond to the known analysis of the gas. The operator should not attempt to calibrate or use the instrument until the operating manual is thoroughly read. The CO monitor should be calibrated when the instrument is received, any maintenance is performed and any components are replaced. The following information refers to the GE COED and is provided as guidance in addition to specific model's users manuals.

10.1 CO Monitor Zero Calibration

10.1.1 Ensure that the cell assembly is stabilized and the batteries are charged and functioning properly.

10.1.2 Place the battery switch to on position and pump switch (if applicable) to off position.

10.1.3 Connect zero gas supply to CO monitor. Do not connect gas supply directly to monitor. Use appropriate tubing (i.e., Teflon®, Tygon®, or polyproylene tubing) and tee fittings for interconnections.

10.1.4 Start the zero gas flow from the cylinder into the monitor by turning the pressure regulator. For pump-fitted models, flow is generally maintained at approximately 100 mL/min at cylinder pressures greater than 50 psig.

10.1.5 Place the monitor pump switch to ON position (if applicable). The battery switch is still in the ON position. The monitor self-test (warning lights and audible alarm activated) may occur momentarily.

10.1.6 If the monitor reads 0 to 2 ppm after about three minutes, it is zeroed properly. If the reading is not in the 0-2 ppm range, adjust the dosimeter potentiometer for 0 ppm.

10.1.7 Release the pressure regulator to stop flow of the zero air calibration gas. Disconnect tubing and fittings.

10.2 CO Monitor Span Calibration

10.2.1 For span calibration of the CO monitor place the battery switch to ON position and the pump switch (if applicable) to the ON position. Connect span gas cylinder to instrument with appropriate tubing and fittings.

10.2.2 Start the span gas flow into the monitor. Note the CO concentration as written on the analysis tag attached to the cylinder (nominally 50-60 ppm CO).

10.2.3 After approximately three minutes, adjust the span potentiometer to achieve the same ppm CO reading as that of the span gas.

10.2.4 Release pressure regulator to stop flow of span calibration gas. Disconnect tubing and the fittings from the CO dosimeter and gas cylinder, and battery switches.

10.3 CO Monitor Multipoint Calibration

10.3.1 A multipoint calibration should be conducted on initial use, on a weekly basis and whenever maintenance which affects the monitor is performed.

10.3.2 Perform a manual zero and span calibration as in Sections 10.1 and 10.2.

10.3.3 Introduce intermediate span gases with concentrations of 20%, 40% and 60% of full scale in succession. A stable reading at each intermediate span point should be reached before proceeding to the next one. Intermediate span points will be introduced from individual cylinders.

10.3.4 Plot the monitor's response versus the corresponding CO concentrations. Connect the experimental points using a straight line, preferably determined by linear regression techniques. The calibration curve is used to reduce subsequent sampling data.

11. CO Monitor Operation

11.1 Once the monitor has been properly zeroed and the span checked, it is ready to analyze indoor CO concentration. Figure 2 provides a flowchart on CO monitor operation. The following information refers to the GE COED and is provided as guidance in addition to a specific model's users manuals.

11.2 Place the pump switch (if applicable) on. If the instrument is equipped with a self-test feature, lights/alarms will be activated when the monitor is started.

11.3 Verify sample flow (i.e., flowrate recommended by the manufacturer) on flow indicator scale. Adjust monitor as required to obtain proper flow rate.

11.4 Place CO monitor in shirt/pocket or secure to user's clothing. If CO monitor is to be used as an area monitor, see Appendix C-3 of this Compendium, Placement of Stationary Passive Monitors, for a discussion of factors regarding monitor placement.

11.5 After the desired sample period, turn the pump switch off. Recharge the battery after each sampling period to prevent damage.

12. Method Safety

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

13. Performance Criteria and Quality Assurance (QA)

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

13.1 Standard Operating Procedures (SOPs)

13.1.1 SOPs should be generated by the users to describe and document the following activities in their laboratory: 1) assembly, calibration, leak check, and operation of the specific sampling system and equipment used; 2) preparation, storage, shipment, and handling of the sampler system; 3) purchase, certification, and transport of standard reference materials; and 4) all aspects of data recording and processing, including lists of computer hardware and software used.

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

13.2 Quality Assurance Program

The user should develop, implement, and maintain a quality assurance program to ensure that the sampling system is operating properly and collecting accurate data. Established calibration, operation, and maintenance procedures should be conducted on a regularly scheduled basis and should be part of the quality assurance program. Calibration procedures provided in Section 10, operation procedures in Section 11, and maintenance procedures in Section 9 of this method and the manufacturer's instruction manual should be followed and included in the QA program. Additional QA measures (e.g., trouble shooting) as well as further guidance in maintaining the sampling system are provided by the manufacturer.

13.2.1 The latest copy of the Quality Assurance Handbook for Air Pollution Measurement Systems (13) should be consulted to determine the level of acceptance of zero and span errors.

13.2.2 For detailed guidance in setting up a quality assurance program, the user is referred to the code of Rederal Regulations (14) and the EPA Handbook on Quality Assurance.

14. References

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Monitors," EPA Contract No. 68-02-4035, Research Triangle Park, NC, Northrop Services, Inc. - Environmental Sciences, 1984.

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10. "Application Notes for Neotronics Exotox and Neotox CO Personal Exposure Monitors," Neotronics, Gainesville, GA, 1988.

11. List of Designated Reference and Equivalent Methods, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, April 12, 1988.

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

13. *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II--Ambient Air Specific Methods*, EPA 600/4-77-0272, May 1977.

14. 40 CFR Part 58, Appendix A, B.

Table 1. Performance Characteristics of the GE CO Montior

Useful ranges: 0 to 1000 ppm CO

Lower detectable limit: 1 ppm CO

Accuracy: LCD direct readout; 0-500 ppm ± 10%

Warm-up time: 15 seconds (after full battery charge)

Response time: within 2 minutes to 90%

Operating temperature with specified accuracy: 1-40°C (34-104°F)

Attitude: within 45° of vertical

Relative humidity range: 0-95%

Span drift: less than ± 10% (1 week)

Zero drift: less than ± 2 ppm (10 hours)

Table 2. Commercially Available Electrochemical CO Monitors

Identification	Manufacturer	Data Logger
Neotox	Neotronics of NA Inc. Box 370 Gainesville, GA 30503 (800)535-0606	not available
Exotox 550FHC or 550FCS Multi-gas Monitor	Neotronics of NA Inc. Box 370 Gainesville, GA 30503 (800)535-0606	included
CO-82	GASTECH 8445 Central Ave. Newark, CA 94560-3431 (415)794-6200	optional
1140 or 4140 CO Analyzer Series or 5100 Series PEM	Interscan Box 2496 Chatsworth, CA 91313 (800)458-6153	optional
Model 170 CO Indicator	MSA Instrument Division Box 427 Pittsburgh, PA 15230 (800)672-4678	included
Tritector Model CGS-100	ENMET 2308 S. Industrial Highway P.O. Box 979 Ann Arbor, MI 48106 (313)761-1270	not available
Model 190 Personal CO Monitor	National Draeger, Inc. 101 Technology Dr. Box 120 Pittsburgh, PA 15230 (412)787-8383	included

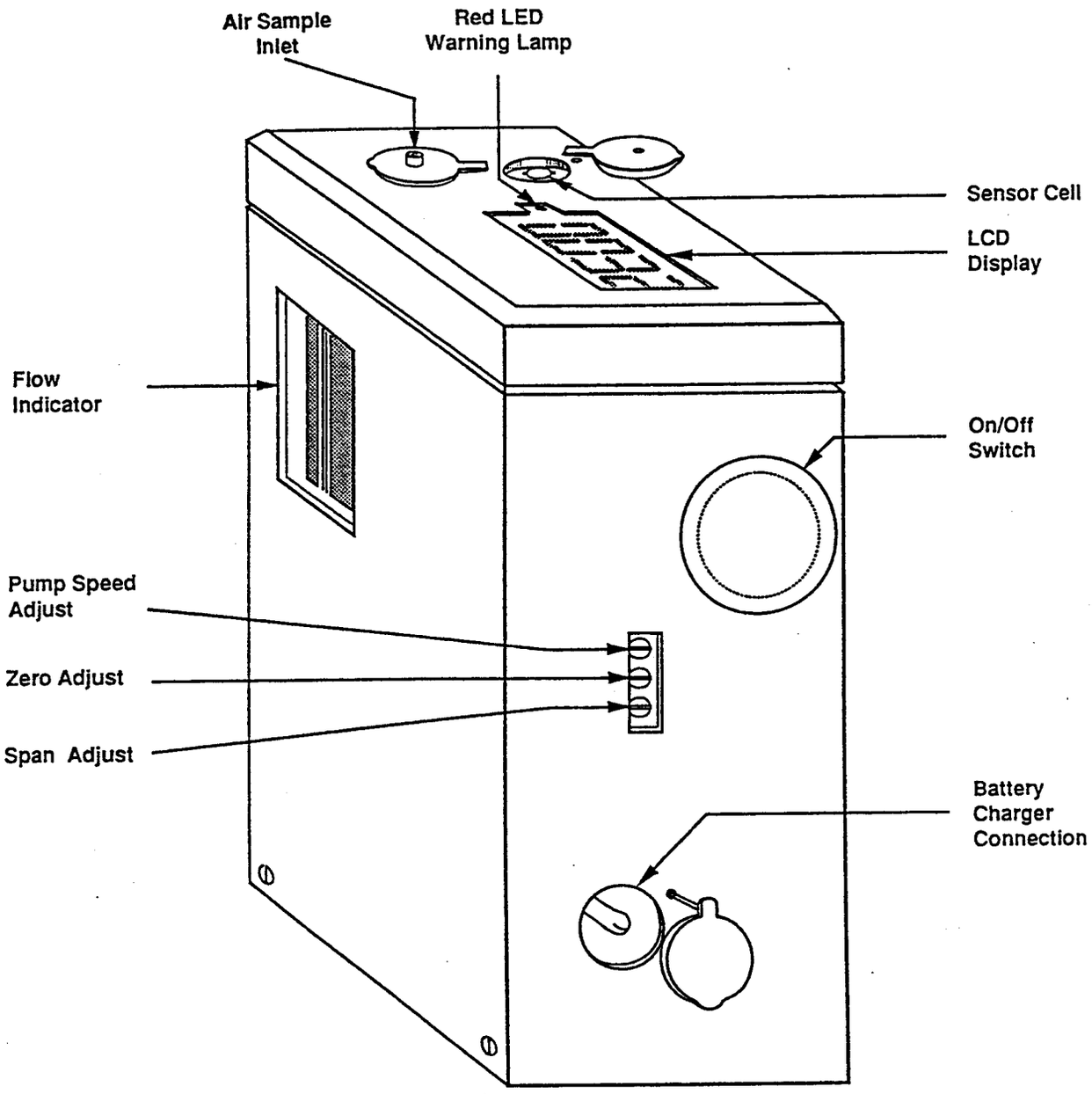

Figure 1. CO Personal Exposure Monitor

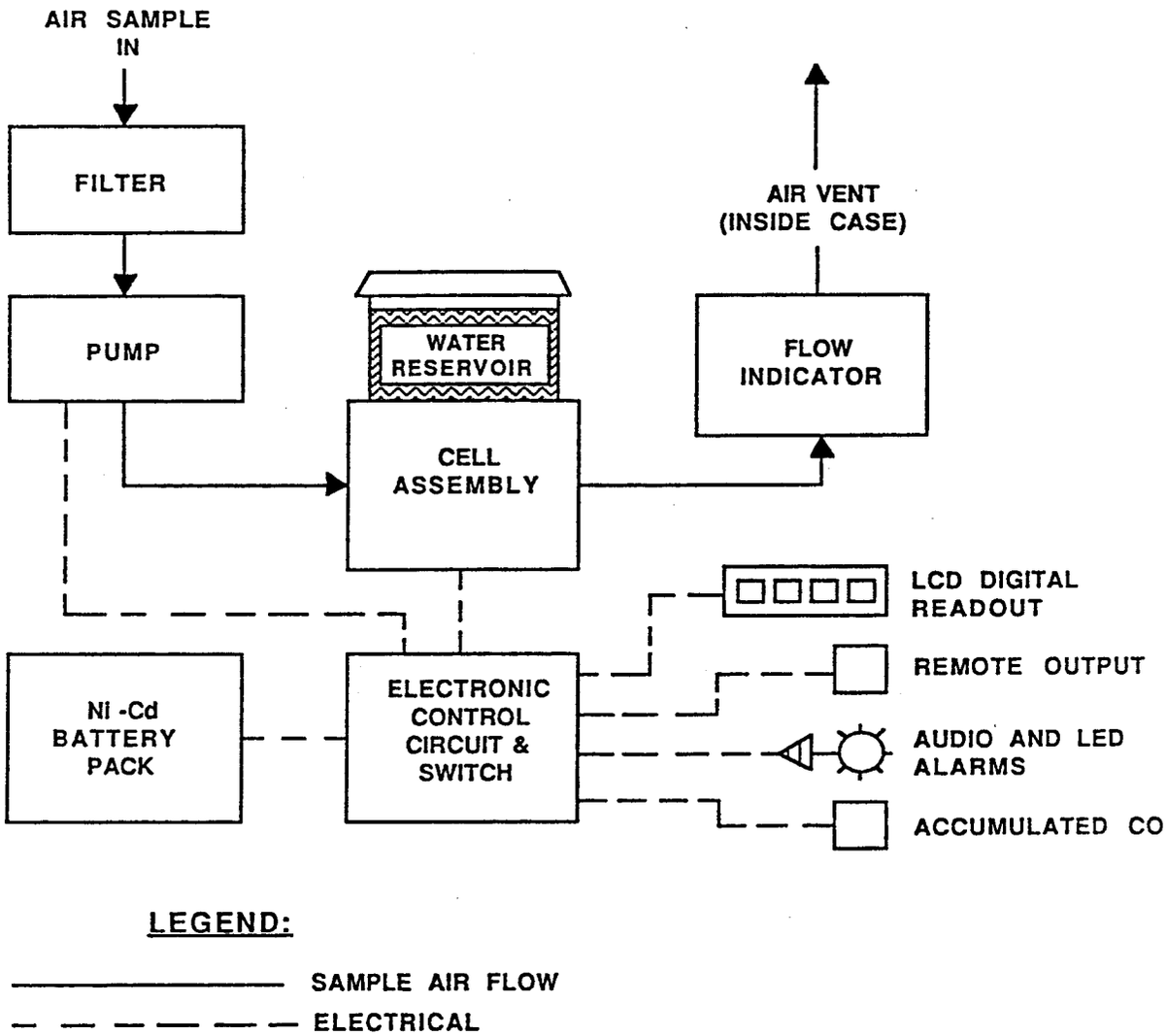

Figure 2. CO Monitor Functional Schematic

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OPERATING PROCEDURES FOR A PORTABLE CO DETECTION SYSTEM

1. Scope

1.1 This procedure is intended to screen indoor air environments for carbon monoxide. Screening is accomplished by monitoring CO within an area onsite using a portable detection system (Portable Air Sampling System (PASS), R. Jay Equipment Co, Winston-Salem, NC, (919) 741-3582, or equivalent). This procedure is not intended to yield quantitative or definite qualitative information regarding the substance detected. Rather, it provides a profile of the occurrence and intensity of CO which assists in placement of fixed-site monitors and the selection of individuals for the use of personal exposure monitors.

1.2 The PASS is contained within an ordinary briefcase which allows environmental measurements to be made unobtrusively without affecting behavior of occupants (See Figure A-1). The CO monitoring system is comprised of a sampling pump and a detector utilizing an electrochemical measurement principle. During normal operation, the output of the detector feeds directly to a data logger. The PASS also monitors for nicotine and respirable suspended particulate (RSP) matter. The temperature and barometric pressure of the environment are also monitored. Data is stored on a microcomputer within the briefcase and can be transferred to a computer for data analysis at a later time. For the benefit of the user, this write-up describes only the PASS operations of the CO detection system. However, there is mention of other parts in the system (i.e., power supply) because they are interconnected in the current design.

2. Applicable Documents and References

2.1 Operator's Manual for Portable Air Sampling System (PASS), R. Jay Equipment Co., Winston-Salem, NC, (919) 741-3582, September, 1988.

2.2 Guy B. Oldaker III and Fred C. Conrad, Jr., "Estimation of Environmental Tobacco Smoke on Air Quality Within Passenger Cabins of Commercial Aircraft," Research and Development Dept., Boyman Gray Technical Center, R. J. Reynolds Tobacco Co., Winston-Salem, NC 27102, October, 1987.

2.3 United States Patent Abstract, Patent No. 4,786,472, November 22, 1988.

3. Summary of Method

3.1 Sample air is introduced into the system through an inlet port. Air from the inlet port is passed through Tygon tubing to a diaphragm pump. The pump then passes the sample air from the inlet port to an electrochemical sensor cell where CO is oxidized to CO_2. The oxidation of CO produces a voltage signal proportional to the CO concentration present in the air sample. Data generated from the CO oxidation are obtained and stored in a

microcomputer over discrete periods of time (e.g., at about one minute intervals). Figure A-1 provides a complete illustration of the PASS.

3.2 The PASS CO detection system employs an electrochemical sensor cell that provides an analog signal proportional to the level of CO being monitored. The analog signal is connected to the PASS data logger. The sensor head consists of durable glass reinforced polypropylene junction box that is coupled to the gas sensor and signal conditioning circuitry. The PASS CO sensor operates on the same principle (i.e., electrochemical oxidation) as the GE CO monitor described in Section 3.4 of Method IP-3C. In the PASS sensor, sample air combines with water in the following reaction: $CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$ (at the anode). The hydrogen ions and electrons combine to form the following reaction: $1/2\ O_2 + 2H^+ + 2e^- = H_2O$ (at the cathode). When both of the reactions are combined, the following reaction occurs, causing CO in the sample to be oxidized to CO_2: $CO + 1/2\ O_2 \rightarrow CO_2$. When CO is oxidized, electrons travel through a circuit which produces a current directly proportional to the CO concentration in the air sample. Table A-1 provides operating specifications for the CO sensor.

4. Significance

4.1 Recent interest towards studying the nature, characteristics and quality of indoor air has developed. Of particular interest is sampling and analysis of indoor air in a specific setting over a fairly long period of time. However, for a realistic and representative assessment of the indoor air, it is often necessary to measure several substances over a range of known conditions. Unfortunately, the sampling and collection of air samples often involve noisy, large, obtrusive equipment. Such equipment often does not provide realistic or representative assessments of a particular setting due to the fact that the obtrusive nature of the equipment can tend to affect human behavior during data collection periods.

4.2 The PASS provides a flexible system for sampling air in a wide variety of indoor environments. The portable device is self contained, is easily operated, and is unobtrusive. The device can measure more than one substance as well as relative conditions of the environment such as temperature, relative humidity and atmospheric pressure. The device can be operated over relatively long periods of time. Thus, it is possible to monitor environmental air for predetermined substances on a continuous basis while having the ability to identify short term changes in concentration of particular substances.

4.3 The PASS has been commercially available for three years and can be purchased from the reference provided in section 1 of this appendix. The CO monitoring device has been purchased from various foreign countries as well as industrial parties in the United States.

4.4 For purposes of the Compendium, the PASS is presented as a means to screen indoor environments in order to locate fixed-site monitors. The fixed-site monitors employ NDIR spectrometry based on federal reference methods. To meet the needs of the user, this Appendix provides information on the PASS to inform the user of its capabilities and to furnish the information necessary to construct a similar instrument.

5. Definitions

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

6. Interferences

6.1 When sample air passes through the monitoring system, the sensor cell may tend to become dry. Interferences may occur if the sensor cell is allowed to become dry.

6.2 Daily calibration of the CO monitoring system is recommended until the operator becomes familiar with and documents the drift typical of the individual PASS.

6.3 The PASS is powered by two battery packs (i.e., one for the data logger and one for the sampling pumps) and can be operated continuously for at least 20 hours. It is strongly recommended that operators check voltages of batteries before each use of the PASS for sampling. Voltages are deemed adequate if above 12 volts for the battery pack serving the data logger and above 5 volts for the battery pack serving the sampling pumps. These voltage limits were selected to guarantee the availability of sufficient power to collect one one-hour sample. In the event that either of these limits is not met, all cells are replaced. While conservative, this practice is supported by the fact that the cost of batteries is insignificant when compared to the cost of lost data and more important lost time.

7. Apparatus

7.1 Briefcase or portable container - appropriate housing which allows for easy movement of the sampling system and its components. An example of a suitable container is a hard sided leather briefcase (National Luggage, Montreal, Canada, or equivalent). The sampling components should be held in place with an appropriate material (i.e., a machined polymethylmetha-crylate sheet or polyurethane foam).

7.2 Carbon monoxide detector - a suitable means of detecting CO such as an electrochemical sensor cell where CO is oxidized to CO_2 producing an electrical current proportional to CO concentration in the air sample (Neotronics Ltd., Gainesville, GA, (800) 535-0606, Model Otox 2001 or equivalent).

7.3 Tygon tubing - used to connect sampling components, with an inner diameter of 1/4" (Tygon by Norton Co, Akron, OH).

7.4 Carbon monoxide pump - used to draw in sample air to detection system (Gillian Instrument Corporation, 8 Daives Highway, Wayne, NJ, (201) 831-0440, P/N 10037, or equivalent).

7.5 Data logger - data storage means that provides for collection and storage of data relating to the following sampling parameters: CO values, time periods over which known

quantities of sample air pass through pumps and amount of voltage used by the pumps (Campbell Scientific, Inc., Logan, UT, (801) 753-2342, 21x Micrologger, or equivalent).

7.6 Relative humidity probe - used to monitor relative humidity of the sampling environment (Rotronic Instrument Corp., Huntington, NY, (801) 753-2342, MP-100F Relative Humidity Probe, or equivalent).

7.7 Cassette recorder - used to record sampling data (Campbell Scientific, Inc., Logan, UT, (801) 753-2342, Model RC35, or equivalent).

7.8 Cassette interface cable - provides for sampling data input into a computer (Campbell Scientific, Inc., Logan, UT, (801) 753-2342, C-20 Cassette Interface, or equivalent).

7.9 Flowmeter - 500 mL/min capability used to calibrate CO sampling pump (SKC South, Inc., P. O. Box 2016, Appomattox, VA 24522, (804) 352-7149, Film flowmeter, Cat. No. 307-2000, or equivalent).

7.10 Brass sampling port - sample air is introduced into the detector through the sampling port, suitable ports are Swagelok brass bulk head reducer tube fittings. The other portion of the fittings are machined and polished to a square or circular shape for aesthetic purposes (Crawford Fitting Co., 29500 Solon Rd, Solon, OH 28213, Part # B-400-R1-4, or equivalent)

7.11 Power source - the PASS is powered by two battery packs. One battery pack (i.e., four D cells each rated 1.5 V) powers the CO monitoring system pump. The second battery pack (i.e., eight AA cells pack rated at 1.5 V) powers the data logger and CO monitoring system detector. Experience has shown that Duracell™, non-rechargeable alkaline cells are used in the batteries for reasons of cost, availability, reliability, and power capacity. Other cells having comparable power capacity should be acceptable.
Note: All cells must be alkaline.

8. Reagents and Materials

8.1 Gas cylinder containing 0.5 ppm CO in air, working standard, certified, cylinder size AL (Scott Specialty Gases, Rt. 611, Plum-steadville, PA, 18949, (215) 766-8861, or equivalent).

8.2 Gas cylinder containing 50 ppm CO in air, working standard, certified, cylinder size AL (Scott Specialty Gases, Rt. 611, Plumsteadville, PA, 18949, (215) 766-8861, or equivalent).

8.3 Two-stage regulator for CO cylinder - two (2) required, one for each cylinder, used with non-corrosive, high purity gases (Scott Specialty Gases, Plumsteadville, PA 18949, (215) 766-8861, Model 18, or equivalent).

8.4 Gas sampling bag - 22 L, 16" X 29" with on 1 off valve (Calibrated Instruments, 731 Saw Mill River Rd, Ardsley, NY 10502, (914) 693-9232, or equivalent).

8.5 Twp piece tubing connectors, that are different sizes, used to connect flowmeter to sampling port for pump calibration (Cole-Palmer Instrument Co., 7425 N. Oak Parks Ave, Chicago, Il 60648, (312) 647-7600, Cat. No. J-6289-10 (12/Pkg), or equivalent).

8.6 Port connector for CO port - brass port connector (Charlotte Valve and Fitting Co., 7838 North Tryon St., Charlotte, NC 28213, (704) 598-7040, Part #B-401-PC, or equivalent).

9. PASS Preparation

9.1 Calibration of the CO monitoring system should be done just before the PASS is used for sampling. The operator should allow sufficient time because calibration can take up to 1.5 hours if both zero and span potentiometer require significant adjustment. The operator should check that sufficient battery voltage is available to power both the data logger and the pump within the PASS.

9.2 During sampling, measurements are recorded by the data logger at 60 second intervals. To facilitate calibration of the CO system the interval is changed to 1 second. (Note that this change in the program causes loss of the PASS identification number. The operator must re-enter the PASS identification number at the completion of calibration.) The interval change is accomplished with the following procedure. First, key in the sequence: * 1 A. The programmed sampling interval is displayed (usually 60). The operator should then key in the sequence: * 1 A, and return to recording mode by keying in the sequence: * 0.

9.3 Pump Calibration

9.3.1 The CO sampling pump should next be calibrated to a flow rate of 500 mL/min at standard conditions of temperature and pressure. The flowmeter is connected directly to the CO sampling port with the appropriate size tubing connector. Alternately, the flowmeter can be connected to the tubing leading to the CO pump by carefully disconnecting the CO pump tubing from the CO port fitting inside the briefcase.

9.3.2 The CO pump is a non-compensating, voltage regulated pump. It is very sensitive to the pressure drop of the calibration device. A soap-film flowmeter or similar device is highly recommended. Operators should use consistently the same tubing and fitting for all calibrations. The tubing and fitting should be sized to minimize the pressure drop.

9.3.3 After activating the CO pump with the slide switch under the handle, the pump flow rate is adjusted at the potentiometer labeled "PUMP" just below the label "CARBON MONOXIDE DETECTOR." The voltage supplied to the CO pump is next displayed by keying in the sequence: * 6 7 A. This voltage should be carefully recorded, as in the future, CO pump calibration can be accomplished without a flowmeter by simply adjusting the CO pump voltage to this value.

9.3.4 Once set, the CO pump voltage should not change unless the "PUMP" potentiometer is inadvertently adjusted. No change in the CO pump voltage or flow rate is noted over a two-month testing period. Set the data logger to display the CO concentration (ppm) by keying in the sequence: * 6 3 A.

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9.4 Calibration Materials

9.4.1 Two gas sampling bags and two calibration gases are required for calibration. Concentrations of 0.5 ppm and 50 ppm carbon monoxide in air (Working Standard Certified) should be used. Purchase of 0.5 ppm CO rather than 0 ppm CO is recommended so that the detector response to CO is measured on the low end of the calibration range. Preparation of calibration gases takes the supplier a minimum of two weeks; delivery can add another week. Therefore, gases should be ordered as far in advance as possible. The exact concentration of each cylinder of gas is provided by the supplier and that concentration should be used by the operator during calibration.

9.4.2 For the supplier, 0.5 and 50 ppm are target concentrations. Blended and analyzed calibration gases may end up with concentrations, for example, of 0.491 and 49.98 ppm CO. For ease of reference, 0.5 and 50 ppm will be used within these instructions to denote the low and high concentrations of CO used for calibration.

9.5 Calibration Procedure

9.5.1 Fill the two gas sampling bags 1/2 to 2/3 full of CO. Do note overfill bags, as a sudden burst of gas may cause a fluctuation in the flow rate and the CO detector response. Turn "ON" the PASS with the handle switch. Open the valve of the 0.5 ppm gas bag and quickly connect the bag to the CO pump inlet. Place the gas bag in a fixed position on a surface; do not allow either the bag or tubing to develop crimps during calibration as these may cause fluctuations in the flow rate which in turn influence the CO detector response.

9.5.2 Operators should ensure that bags remain as stationary as possible to prevent pressure (and therefore, flow rate) fluctuations during calibration. Wait ten minutes. If necessary, adjust the "ZERO" potentiometer until the CO concentration of the 0.5 ppm gas provided by the supplier is displayed on the data logger. After adjustment of the potentiometer, continue to observe the display concentration to be sure a stable reading is obtained. Remove the gas bag and quickly close the valve on the bag to prevent contamination by indoor air.

9.5.3 Operators may wish to note that within the program provided with the PASS that the last entry on the line labeled "READ CO ANALYZER" is "-2." The CO monitoring system is incapable of producing negative readings. To avoid difficulty in setting the "ZERO", the system is electronically offset by 2 ppm. With the exception of the program line mentioned above, no indication is given by the PASS that adjustments of CO concentration data are made. Again the exact concentration of each cylinder of gas as provided by the supplier is the value used during calibration.

9.5.4 The 50 ppm CO can be introduced immediately after the bag containing the 0.5 ppm CO has been removed. It is important that the operator wait the full 10 minutes before setting the "SPAN" potentiometer to the nominal value of the high concentration.

9.5.5 Operators are encouraged not to be tempted into short-cutting the calibration procedure by introducing gases for periods less than 10 minutes. When 0.5 ppm CO gas is introduced, a stable reading may be obtained before the entire ten minute period elapses. When the 50 ppm gas is introduced, on the other hand, the CO monitoring system initially responds rapidly; however, this rate slows substantially as the final, stable reading is

approached. Adjustments made to calibration before 10 minutes have elapsed and therefore before a final, stable reading has been obtained can lead to inaccurate CO measurements or to extra time being spent in calibration. Consequently, calibration is completed most quickly and accurately if the full ten minutes elapse before the "SPAN" potentiometer is adjusted. The 22 liter gas sampling bag filled to 1/2 to 2/3 full contains enough gas for ten minutes of sampling.

9.5.6 Following adjustment of the "SPAN" potentiometer, allow the PASS to sample indoor air for approximately 5 minutes to allow the detector to return to low levels without expending the calibration gas. If any adjustments to either potentiometer are made, then the entire process beginning with the introduction of the 0.5 ppm CO gas followed by the 50 ppm gas and then indoor air must be repeated until neither potentiometer requires adjustment. Last, turn "OFF" the PASS and reset the sampling interval to 60 seconds (or the desired time interval) by keying in the sequence: * 1 A 60 A. Return the PASS to the recording mode by entering: * 0.

9.6 Transporting the PASS

9.6.1 The PASS is a fairly rugged piece of equipment; however, it is intended for use in indoor environments. Consequently, operators should ensure that PASS is not exposed to extreme environmental conditions including precipitation, and temperatures below 40°F (4°C) and above 100°F (40°C).

9.6.2 The PASS is designed to be unobtrusive. There are occasions when this aspect can be a disadvantage. Operators should be aware that the technology may disturb people sensitive to suspicious activities. However, experiences to date indicate that questions seldom arise when PASS's are checked through security at airports located in the United States. When questions have arisen, the PASS documentation (for example, the operator's manual) has proven to be invaluable in demonstrating the true nature and purpose of the system.

9.6.3 Operators in the United States should note that because the PASS includes the 21X Micrologger, U.S. laws require an export license be obtained in order to carry or to ship the PASS to certain foreign nations. An application for an export license may be obtained from the U.S. Department of Commerce. Failure to comply with the law may result in fines and permanent confiscation of the entire PASS. It is therefore highly recommended that operators seek legal counsel in considering export of the PASS.

9.7 Locating the PASS

The selection of sampling location is governed by the objective of obtaining a sample that represents exposure to CO. Unfortunately, ideal locations seldom exist; instead, users typically must compromise in selecting locations. Guidelines relative to the selection of sampling location are as follow:

- PASS's should be positioned at least two feet from walls and as far from corners as practical.
- PASS's should be placed from two to seven feet above the floor, for example, on tabletops, unoccupied seats, desktops, filing cabinets, ledges, etc.

- PASS's should be positioned such that the air being sampled has an unobstructed path to the inlet ports. The narrow side of the briefcase containing the inlet ports should be flush with or extend beyond the surface the PASS is placed on. The exhaust ports should be unobstructed. Obstruction of ports may cause variable pump flow and/or pump failure.
- PASS's should be placed as far as practical from the direct influence of ventilation sources such as ducts, open doors or windows, or fans.
- PASS's should not be exposed to the direct influence of sidestream or mainstream smoke, or other sources of CO.
- Sampling operations should be as unobtrusive as possible in order not to influence the behavior of occupants.
- Technicians should have as clear a view of the indoor environment as practical to facilitate observations.
- PASS's should not be moved once positioned, and
- Technicians should not smoke during sampling operations in order to avoid inconsistent results.

10. PASS Operating Procedures

10.1 The PASS remains closed for sampling. PASS operation involves simply moving the exterior switch to the "on" position. In performing this operation, it is important that the switch be fully engaged, because it is often very difficult to determine unobtrusively whether the PASS is indeed operating. The "on" direction of the switch is indicated by a green label affixed beneath the switch plate; this label is uncovered when the switch is moved toward the "on" position.

10.2 As a fail safe measure, it is strongly recommended that operators record the start and stop times for all sampling periods. By doing this, operators ensure that volumetric results for the nicotine and particulate matter samples may still be obtained in the event of loss of power to the data logger in the interim between sampling and data retrieval.

11. Observations and Recordkeeping

11.1 Clearly, observation and recordkeeping practices will depend on the nature of the monitoring survey. For the purpose of this document, PASS is employed for characterizing environments with respect to exposure to CO. Presented in the following paragraphs are guidelines which PASS operators may consider in implementing such investigations.

11.2 The following subject areas may be considered in connection with observation and recordkeeping practices. These include: PASS location in the environment sampled; sources of CO other than cigarettes; characteristics of the heating, ventilating, and air conditioning (HVAC) system; and substantial deviations from the guidelines listed in Section 9.7.

11.3 The HVAC system can have a profound effect on results; therefore, it is important to obtain as thorough a characterization of the HVAC system as practical. Of prime importance is estimating the volume of the environment served by the HVAC system. Additionally, operators should attempt to identify locations of air supplies and returns, fans,

and other factors affecting ventilation, such as doors and windows. Often, the degree of air mixing can be assessed based upon the manner in which cigarette smoke disperses. The inclusion of detailed guidelines regarding the characterization of HVAC systems is, unfortunately, beyond the scope of this document. A sampling data sheet is provided in Figure A-2.

12. Data Retrieval and Interpretation

Several methods exist for transferring data from the data logger. This document addresses only data transfer operations involving use of a cassette recorder. This method was incorporated in the PASS approach because it allows information to be recovered easily from the field.

12.1 Voltage Checks

12.1.1 The data logger consumes power in controlling operation of the cassette recorder during data transfer. If the battery pack serving the data logger has gone through periods of extended use, insufficient power may be available to transfer data successfully. In addition, it is also possible that the data logger, if in this condition, may lose stored data in the process of attempting transfer. Because of the above concerns, it is recommended that PASS's be placed in the alternate power mode, if possible, before transfer operations are initiated. A cable and associated transformer (charger) with plug is provided with each PASS for this purpose. The transformer having the plug goes to any convenient wall socket with 120V 60Hz rating; and the other plug goes to the jack located on the PASS's front panel and below the data logger's keyboard. In the alternate power mode, battery power is not used by the data logger and is only used by the CO detector.

12.1.2 If the batteries serving the data logger have been used extensively, and additionally, if alternate power is unavailable, operators should check the battery pack voltage before attempting transfer. Checking entails keying the sequence: *6 5 A. Power for data transfer is not recommended.

12.1.3 The operator may find the data logger's display to be clear before checks can be made. This condition does not necessarily indicate that data are lost and therefore transfer is no longer worthwhile. As the last portion of available battery power is consumed, the display is affected before the data logger's memory. If the "LOG 1" signal can be returned to the display after connection is made to the alternate power supply, then it is highly likely that the data and the program have been retained.

12.2 Data Transfer From Logger

Data stored in the data logger are transferred to a cassette tape, which may then be taken to another location where transfer to computer may be performed. The data transfer procedures are described below.

12.2.1 Cassette Recorder Preparation - A data tape (as distinguished from a program tape) is inserted into the cassette recorder and the tape is then rewound. When rewound, most of the tape will appear on the left spool as viewed from the front of the cassette recorder. Operators should ensure that recording is started beyond the header on the tape.

With the tape rewound, disconnect the plug labeled "ear" from the jack on the cassette recorder. Next, engage the key labeled "Record" and allow the tape to advance several seconds before stopping. In addition to ensuring that the header will not interfere with recording of data, this operation also erases any information which may have existed on the tape from earlier uses, thereby preventing interference with data transfer which otherwise could result. The volume control on the cassette is then set to the "5" position.

12.2.2 Logger and Cassette Recorder Connection - The data logger and the cassette recorder are connected with a cable having at one end one large plug and at the other end three small plugs. The small plug labeled "EAR" is inserted into the jack labeled "EAR" on the cassette recorder. The remaining two plugs are inserted into the jacks labeled "DC 6V" and "MIC"; these connections can be made in only one manner. The large plug is then connected to the data logger at the socket labeled "SERIAL I/O" located above the keyboard.

12.2.3 Sampling Data Transfer With Cassette Tapes - The following steps detail the data transfer procedure:

12.2.3.1 On the data logger's keyboard, key in the sequence: * 8 A. Record the number displayed by the logger. This number is important because it allows the data transfer operation to be easily repeated in the event that the first attempt at transfer is unsuccessful. The number refers to the memory location of the first data point.

12.2.3.2 Continue the process by keying an "A" and recording the number displayed by the data logger. This number is important for the same reason described above and corresponds to the memory location of the final data point. Next, key in the sequence: A 1.

12.2.3.3 On the cassette recorder, simultaneously engage the keys labeled "RECORD" and "PLAY". Therefore enter "A" on the logger's keyboard. Data transfer should then occur.

12.2.3.4 The progress of data transfer may be observed from the data logger's display. (Data transfer is also indicated by blocks of noise produced by the cassette recorder.) Transfer, which involves blocks of data, is complete when the displayed number no longer changes and is equal to the second number recorded earlier, namely, the location of the final data point. The cable is then disconnected from the cassette recorder and data logger. The cassette recorder must be disconnected from the cable in order to check that data transfer was successful.

12.2.3.5 Rewind the cassette tape, engage the "PLAY" key on the cassette recorder, and listen for blocks of noise signifying the successful transfer of blocks of data. If no noise occurs, repeat the data transfer procedure with the following modifications.

12.2.3.6 On the logger's front panel, key in the sequence: * 8 A and enter the number recorded in step 12.2.3.1.

12.2.3.7 Next, key in "A" and enter the number recorded in step 12.2.3.2. Proceed as described in 12.2.3.3.

12.2.4 Data Storage on Cassettes - Two considerations relating to bookkeeping should be observed if cassette tapes are to be used to store multiple sets of data. First, operators

should record the cassette recorder's tape counter readings corresponding to data sets. For obvious reasons, numbering should start from the totally rewound position with the counter reset to "000". Second, operators should provide spacers (that is, periods of no data) between adjacent sets of data. Spacers are added to the recording at the conclusion of transferring a set of data from the data logger to the cassette recorder. Accordingly, after transfer is completed, disconnect the plug labeled "ear" from the corresponding jack on the cassette recorder and allow the tape to run at least 5 seconds before replacement. (Used tapes may be cleaned by the same process.)

12.2.5 Sampling Data Transfer with Computers - Data transfer from the cassette to computer file requires either a Campbell Scientific, Inc. C20 Cassette Interface or a PC201 "Clock-SI0 Tape Read Card & Software for IBM-PC," or equivalent. Descriptions relating to the use of these devices are beyond the scope of this document. Operators are referred to the appropriate literature from the software manufacturer. It is the PASS operator's responsibility to implement the transfer operations to computer systems.

13. Sample Calculations

13.1 The following paragraphs presume that the data have been transferred to a computer. Figure A-3 illustrates the appearance of transferred PASS data and identifies the data entries. This table was obtained through use of a PC201 board and a Compaq portable PC and includes data from nicotine and RSP sampling. LOTUS 1-2-3® software was used to label the columns.

13.2 The data record provides valuable information regarding the quality of the data and samples. Operators are encouraged to scan visually data records before initiating calculations in order to obtain a general assessment of the quality of the overall sample. The temperature, barometric pressure, and CO concentration entries represent one set of data deserving attention. With experience, operators can scan the record in a matter of seconds and assure that unusual data are absent.

13.3 The voltage to the sampling pump of the CO monitoring system should be checked for consistancy 1) throughout the sampling period and 2) relative to its value for the last calibration. If the voltage has changed since the last calibration, operators should assume that the calibration of the CO monitoring system has changed as well. Operators may have to quantify the change in calibration in order to ensure the acceptable quality of the recorded CO concentration data. Experience has shown that voltages to CO sampling pumps are constant and generally change as a result of unintentional adjustment of the associated potentiometer on the PASS's control panel.

13.4 Sampling Times - Sampling times are calculated from the data record by summing the number of minute entries for each block of data. Data blocks are readily distinguished by their accompanying clock times or dates. For the example in Figure A-3, sampling time was 10 minutes.

13.5 Carbon Monoxide Concentration Data - Carbon monoxide data are readily manipulated with Lotus 1-2-3 software. Statistics often computed include maximum,

minimum, and mean concentrations. Graphics software allow for strip chart type records to be produced.

Table A-1. CO Sensor Operating Specifications

Range: 0-50 ppm, 0-100 ppm, 0-500 ppm

Signal Outputs Available: 2 to 4 mA, 4 to 20 mA, 0-1 Volt

Input Voltage: 8-30 Volts DC (at head)

Power Consumption: < 1 Watt

Operating Temperature: -15°C to +50°C

Humidity: 0-99 %RH, non-condensing

Sensor Life: 12 months guaranteed, 24-36 months typical

Housing: Industrial Junction

Size (Mounting): 120 mm/120 mm/70 mm

Cable Entry Size: 20 mm

Outputs: 2-10 mA loop, 4-20 mA loop, 0-1 Volt

Connections: 2 wire (current outputs), 4 wire (voltage outputs)

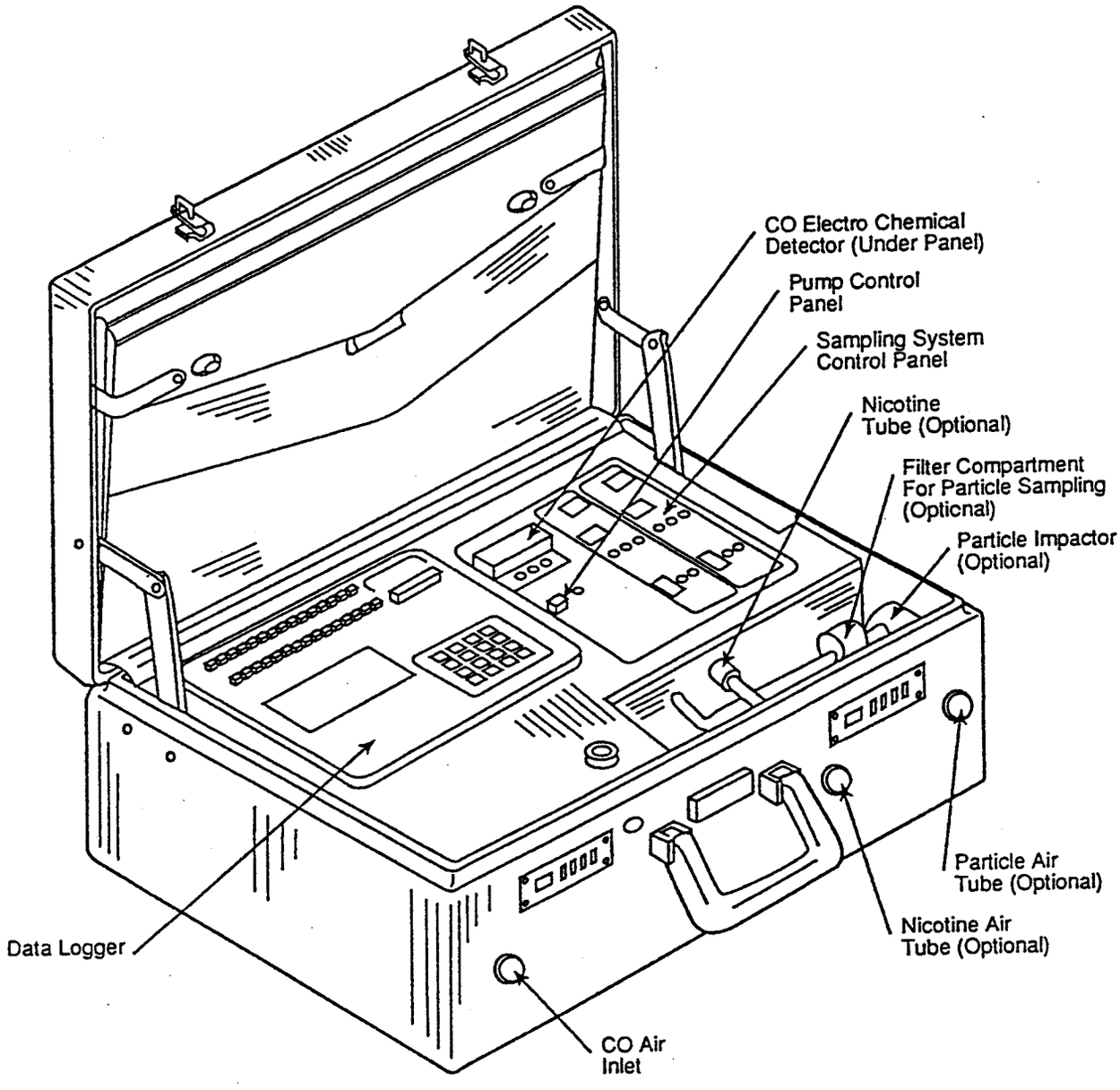

Figure A-1. Portable Air Sampling System

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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, ^{o}C
BAR PRESS	=	Barometric pressure, torr.
CO	=	Carbon monoxide, ppm.
21X VOLT	=	Voltage, v, to batteries serving 21x data logger.
SKC VOLT	=	Voltage, v, to batteries serving nicotine and particulate matter pumps.
CO VOLT	=	Voltage, v, to batteries serving CO pump.
NIC FLT	=	Fault status of nicotine pump.
TPM FLT	=	Fault status of particulate matter pump.

Figure A-3. Example Data Table

Chapter IP-4

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR

- **Method IP-4A - Perfluorocarbon Tracer (PFT)**
- **Method IP-4B - Tracer Gas**

1. Scope

1.1 Method IP-4A is a description of the sampling and analytical protocol for air exchange rate (AER) using perfluorocarbon tubes (PFT) and passive samplers (i.e., capillary adsorption tubes - CATS). This methodology was developed by Brookhaven National Laboratory as an inexpensive way of measuring AER in large-scale field studies. The PFT emitters are utilized indoors to measure the rate of air exchange which occurs over time. This method may be used with multiple PFT source types to allow inter-compartmental flows as well as whole-house AERs to be calculated. The emitters are placed in the dwelling of interest a day in advance of the passive samplers. The source emissions are collected on the passive samplers which are analyzed by a gas chromatograph coupled with an electron capture detector (GC-ECD) for the air exchange rate. If more than one source/sampler is used in a single dwelling, the average of all the calculated AERs is computed.

1.2 Method IP-4B describes the determination of the air exchange rate by the release of sulfur hexafluoride (SF_6) tracer gas. The ambient air is subsequently sampled by commercially available automated syringe samples and analyzed for trace amounts of SF_6 by gas chromatography with electron capture detection or monitored on-site by tracer gas monitors. This concentration-decay technique (also called tracer-gas dilution) has been designated as a standard practice by the American Society for Testing and Materials. In this technique, a small amount of tracer gas is injected into the indoor airspace and thoroughly mixed. Indoor concentrations "decay" with time as the exfiltrating air removes the tracer. The general procedure involves releasing tracer gas at one or more points at sufficient quantities to produce useful initial concentrations. The method of release and quantities involved depend on the internal volume of the structure, the configuration of the air-handling system, estimates of allowable versus useful concentrations, and the sensitivity of the detection system.

2. Applicability

2.1 For some time, it has been a primary focus of the U.S. EPA to compile the missing exposure data needed to complete the risk equation. The data from exposure measurements help to evaluate progress in the efforts to control environmental pollution and provide guidance for modifying approaches to make them more effective. Ultimately, the effectiveness of the regulatory process on reducing pollutant levels may be judged by exposure measurements.

2.2 In addition to measuring mass and elements, total exposure assessment studies should be organized to provide background information on indoor and outdoor air pollutant concentrations. Emphasis should be placed on collecting information on indoor air

pollutant concentrations or the relationship between indoor and outdoor air levels. Air infiltration rates are a critical component in the process of determining the influence of outdoor pollution on indoor concentrations.

2.3 Air infiltration represents an important part of the heating and cooling load of residential, commercial and industrial buildings. The heat loss associated with air leakage through the enclosure of a typical house may be as much as 40% of the total heat load. Considerable energy savings can be realized by reducing the air infiltration in a structure.

2.4 Air leakage is also an important parameter in indoor-outdoor air pollution relationships.

Method IP-4A

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR USING PERFLUOROCARBON TRACER (PFT)

Method IP-4A

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR USING PERFLUOROCARBON TRACER (PFT)

1. Scope

1.1 This document describes the protocol for the measurement of an integrated air exchange rate (AER) between the outside and inside of detached dwellings over periods ranging from approximately 10 hours to several weeks. Perfluorocarbon tracer (PFT) emitters are utilized indoors to measure the rate of air exchange which occurs over time. This method may be used with multiple PFT source types to allow calculation of both inter-compartmental flows within houses and whole-house AERs.

1.2 The methodology was developed by Brookhaven National Laboratory as an inexpensive way of measuring AER in large-scale field studies. It is currently employed in the Particle Total Exposure Assessment Methodology (P-TEAM) program conducted by the U.S. Environmental Protection Agency (U.S. EPA) and in a 5000 building home measurements study. The Danish Building Research Institute and the Helsinki University of Technology have established analytical labs which offer full AER services. In addition, there are several groups in England who are in the process of establishing AER service facilities.

1.3 The equipment described herein can be utilized to measure air exchange on neighborhood or urban to regional scales. Neighborhood scale monitoring requires measurements to identify the contributions of specific sources. Urban/regional scale measurements would identify important reactant areas.

2. Applicable Documents

2.1 ASTM Standards

D 1356 Definitions of Terms Related to Atmospheric Sampling and Analysis
E 355 Recommended Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

Ambient Air Studies (1,2)
U.S. EPA Technical Assistance Document (3)

3. Summary of Method

3.1 Air exchange rate (AER) is measured by using the perfluorocarbon tracer (PFT) system. It is designed to measure the integrated rate of exchange of air between the outside and inside of detached dwellings, as well as the exchange between zones in multizone structures. The system is capable of measuring average air exchange rates over periods ranging from about 8 hours to several weeks (4-7).

3.2 Each dwelling can be treated as a single box with AER calculated as if interior partitions are nonexistent or it can be compartmentalized. Perfluorocarbon tracer (PFT) gas is released from one to several locations inside each dwelling chosen to provide uniform PFT dispersion throughout the structure. The tracer gas is allowed to equilibrate in the

dwellings and is then collected inside capillary adsorption tubes (CAT) by diffusion onto activated charcoal spherules. The diffusion rate, and hence the sampling rate, is set by controlling the geometric dimensions of the CAT. The impact of temperature on diffusion rates is generally ignored. Sampling rates are calculated for 25°C. The CAT samplers are located around each dwelling and their PFT burdens are averaged for the calculations. The AER for each home is calculated using laboratory measurements of the collected PFT, field measurements of the structure volumes, and the sampling duration.

3.3 The laboratory analysis (4-7) of PFT collected in the CATs is performed on a gas chromatograph system equipped with an electron-capture detector (GC-ECD). The GC-ECD is first calibrated with PFT standards then a calibration curve is constructed and used to determine the type(s) and amount(s) of PFTs present in the sample.

3.4 For analysis, the samples are thermally desorbed into a 95% nitrogen-5% hydrogen carrier gas stream through a Nafion column to remove water vapor, which can produce an interfering ECD response as well as degrade the ECD performance. The sample then passes through a special catalytic column to oxidize potentially interfering fluorochlorocarbon compounds; it then flows to a precolumn to effect a coarse separation. Sample compounds continue to flow to a Porapak QS adsorbent column trap where earlier eluting compounds pass through; PFTs are retained, and later eluting compounds are vented via a time-programmed switching valve before they reach the QS trap.

3.5 After all PFTs have been trapped, the flow is reversed by a time-programmed switching valve, and heat is electrically applied to the trapping column to release the adsorbed PFTs. The PFTs now flow to a second catalytic column which mimics the first catalytic column, and finally to a main chromatographic column which separates the compounds prior to detection by the ECD. When a compound reaches the ECD, it induces a voltage signal which is sent to a data acquisition/reduction system.

3.6 The detection system consists of a dedicated integrator which receives the signal, transforms it for graphical presentation, and finally calculates concentrations of the unknown PFTs using the stored calibration curve.

3.7 The limit of detection (LOD) for AERs depends on the LOD of the GC-ECD, the sampling rate of the CAT tubes, the sample duration, the emission rates of the PFT sources, the house volume and the true integrated air exchange rate. Most GC-ECD systems can detect PFT quantities as low as 1 picoliter (pL) with 30% precision. The minimum PFT air concentration LOD is controlled by this and the sample exposure time, and the effective sampling rate (4-7).

3.8 The PFT source is inexpensive and reusable. It is small, ready for use as received, and always emitting tracers. The passive sampler (CAT) is also very small and can be located inconspicuously throughout a dwelling. The CATS are reusable providing an analytical check of the remaining PFT background is negligible. The PFT/CATs operate for the desired time without supervision. Additionally, the PFT source has a high affinity for

reaction with electrons and a low atmospheric background which allows analysis by GC-ECD to be carried out with little interference and very low detection limits.

4. Significance

4.1 The measurement of exposure serves as a critical parameter in environmental protection. The data from exposure measurements help to evaluate progress in the efforts to control environmental pollution and provide guidance for modifying approaches to make them more effective. Ultimately, the effectiveness of the regulatory process on reducing pollutant levels may be judged by exposure measurements.

4.2 In the early 1980's the U.S. EPA began to undertake programs to find the missing exposure data needed to complete the risk equation. The application of personal monitors became an effective means to measure the exposures of individuals throughout their daily activities. Besides measuring the individual's exposure to pollutants, the idea to estimate the exposures of entire populations was formulated. Since the measurement of exposures of everyone in a large metropolitan area is expensive, a simpler approach was to combine probability sampling with environmental monitoring. In this manner, the exposures of a representative probability sample of the population could be used to make inferences about exposures of the entire population.

4.3 This initial concept was applied in exposure studies involving volatile organic chemicals (VOC). A number of these studies have now been completed including carbon monoxide personal exposure monitoring. The VOC and carbon monoxide exposure field studies were the beginning of a newly emerging field of total human exposure assessment. However, the need to consider size characteristics and chemical composition in the control of airborne aerosols has been a matter of continuing concern to the U.S. EPA since the establishment of the total suspended particle ambient air quality standards in 1971. More recently, the Science Advisory Board of the U.S. EPA has made a recommendation that calls for exposure assessment studies to assess man's exposure to environmental pollutants, including the determination of sources and their relative contribution to personal exposure.

4.4 In addition to measuring mass and elements, total exposure assessment studies should be organized to provide background information on indoor and outdoor air pollutant concentrations. Emphasis should be placed on collecting information on indoor air pollutant concentrations or the relationship between indoor and outdoor air levels, especially since there has been very little attention given to indoor pollutant concentrations. Air infiltration rates are a critical component in the process of determining the influence of outdoor pollutant concentrations on indoor concentrations.

4.5 The PFT method is less intrusive than alternative methods. The PFT uses a passive sampler which requires no pumps (8-23).

5. Definitions

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

within this document at the point of use. Additional definitions, abbreviations, and symbols are provided in Appendices A-1 and B-2 of this compendium.

6. Interferences

6.1 The PFT sources are temperature sensitive. Therefore, careful placement of the sources within a dwelling is necessary. Best results are obtained when the sources are deployed in different areas of a dwelling according to the permeation rates. Haphazard placement will lead to inaccurate measurement (See Section 10).

6.2 The PFT sources and passive samplers measure minute concentrations (ppt), therefore it is very important to keep the PFT containers and the samplers well separated. The samplers are not temperature sensitive, but extreme, abrupt changes in temperature exposure should be avoided. Sampling periods are restricted to a two hour minimum and several months maximum.

6.3 Electron capture detectors are sensitive to halogenated organic compounds. The most important potential interferents in the home are freon-type refrigerants. The GC system is designed to remove these compounds by control of their travel times through the system.

7. Apparatus

7.1 Perfluorocarbon Tracer (PFT) Source - PFT sources as seen in Figure 1 consist of a 6.6 mm inside diameter by 32 mm long cylindrical aluminum shell filled with 0.4 mL of a single PFT liquid and is slightly flared at both ends to facilitate the insertion of an oversized silicone rubber plugs. The PFT liquid takes about two hours to reach equilibrium. A code number is engraved onto the aluminum shell for identification of the PFT source, silicone rubber plug type, and the number of the source (Russell Dietz or ISC Chemicals Ltd., England).

7.2 Capillary Adsorption Tubes (CATs) - CATs are constructed of glass tubes which contain a measured amount of an adsorbent as illustrated in Figure 2. The outside diameter (OD) of the tube is 6.4 mm and it is 6.4 cm long with a 45° taper ground at the ends to about 1/3 the wall thickness (to prevent cutting of "0"-rings in the desorption apparatus). The adsorbent, a granular (small beads) Ambersorb material (usually activated charcoal), is held in place by stainless steel screens (9.5 mm OD; 150 mesh) which are friction-fitted into place. A special PFT impermeable polyurethane cap is used to seal each end of the CAT before and after sampling. An identification number is either hand-engraved using a diamond-tipped vibrator or fired into the glass using powdered lead glass black numbered decals (manufactured by Russell Dietz).

7.3 Gas Chromatograph/Electron Capture Detector (GC-ECD) - Equipped with a Nafion column, two catalytic columns, a pre-column, a QS adsorbent column trap, and a main chromatographic column.

7.4 Computer Integrator - Programmed to receive standard data and produce a calibration curve based on retention times, time windows, minimum areas, type of curves, etc.

8. Reagents

The GC-ECD carrier gas is of the highest quality reagent grade 95% nitrogen - 5% hydrogen carrier gas.

9. PFT Sources Available Commercially

9.1 There are four PFT sources in use today. These are listed below along with the properties which make them appealing for use as a gaseous tracer.

Conservative gaseous tracers

Properties

- Non-depositing
- Low atmospheric background
- Non-scavenged
- Limited industrial use
- Non-reactive
- Sensitively detectable

Perfluorocarbon tracers (PFTs)	Emission Type	Emission Rate	Permeation Rate @ 25°C nL/min	Lifetime,yrs.
PDCB (P [a]- dimethylcyclobutane	1	Highest	36-50	2.9-2.1
PMCP (P - methylcyclopentane)	8	Next to highest	40-55	2.6-1.9
PMCH (P - methylcyclohexane)	2	Next to lowest	24-35	4.0-2.7
PDCH (P - dimethylcyclohexane)	3	Lowest	12-20	7.2-4.3

[a]P as in PDCB means "perfluoro".
[b]nL/min represents nanoliters/minute (10^{-9}/min).

9.2 PFT sources are advantageous over other methods in that they are used as received; they are always emitting tracer and they may be placed in any orientation. They are inexpensive and reusable. The PFT makes use of a passive sampler instead of an active one. Additionally, the PFTs high affinity for reaction with electron and low atmospheric background makes them some of the most sensitive compounds for detection on the ECD.

9.3 Although PFTs are ready for use when purchased, it is important to present how PFTs are made. There are two basic processes that have been used commercially for the production of PFTs, here restricted to the family perfluoroalkylcycloalkanes because they have the maximum response to the ECD. Other perfluoroalkanes and other perfluorocarbons are two or more orders-of-magnitude poorer in detection capability.

9.3.1 One process, cobalt trifluoride catalyzed fluorination, is available from ISC Chemicals Limited in England. The purity of their tracers has been from 85 to 99%, with a limited amount of the other existing and identified PFTs as impurities, generally less than 1%.

9.3.2 The other process for making PFTs is the dimerization of perfluoroalkenes at high pressures (up to 3000 atmospheres) and moderate temperatures (400°C). Originally patented by E.I. DuPont in Wilmington, Delaware, more than 19 years ago, the technique was used at one time to make the PDCB. They abandoned the technology more than five years ago and other small companies can now produce a number of the dimerization products, generally perfluorodialkylcyclobutanes, but at costs up to ten times or more those of the PFTs from ISC. However, the PDCB is a potential continental scale tracer because it has the highest ECD response of any of the PFTs and has a low ambient concentration. Recently, the Flora Corporation in North Carolina has indicated an interest in supplying tracers made by this process.

10. Placement of PFT Sources and Passive Samplers

10.1 Choosing PFT Sources

10.1.1 The choice of PFT source types with zone location is important in multizone structures. Because of the stack effect in all houses, a source placed on the second floor will have a very low concentration in the basement. To improve the precision of its measurement in the basement, the second floor-tracer selected should be one with the highest emission rate and the highest detectability, i.e., the earliest eluting tracer on the gas chromatograph (GC) column.

10.1.2 Thus, the choice for the second floor tracer in a 3-zone study is either Type 1 or Type 8 (see Section 9). The same reasoning extended to the other floors dictates that Type 2 be used on the first floor and Type 3 in the basement, as illustrated in Figure 3. The use of Type 1 in one zone and Type 8 in another zone in a 3-zone building should be avoided because those two tracers elute very close to each other and are therefore difficult to quantify without using special GC conditions. In stacked 4-zone structures, when both Types 1 and 8 must be used, the correct choice for the uppermost zone is Type 1, followed by Type 8 in the next lower zone, Type 2 in the next, and Type 3 in the lowest zone.

10.2 Placement of PFT Sources

Described herein is the placement of sources in family-type dwellings. The AER method can be used for other dwelling types (i.e., industrial, laboratories, offices, etc.).

10.2.1 The PFT sources should be shipped separately from the samplers. Each source shell is engraved with a code, the first number of which identifies it as one of the 4 available PFT types, i.e., type 1, 2, 3 (or TC), or 8.

10.2.2 The sources should be deployed one per every 500 ft^2 (46.5 m^2) of living area. Typically, in a single story ranch-type home, two sources are placed in the living room, dining room, kitchen area and one in each of the bedrooms. The same type of source should be used if the floor is to be treated as a single zone, as shown in Figure 3.

10.2.3 If the house has a basement, a different PFT type should be used since it is a separate but attached zone. For an open (unfinished) basement, one or two sources may be used; if it is divided into rooms, 2 sources should be used. Ignoring the basement by not

including any sources and samplers or using sources of the same type as the main floor, can result in errors in the determination of the living space ventilation rate.

10.2.4 Generally, a PFT source is placed within 0.5 to 1.5 meters of the floor and no closer than 1 meter to an outside wall. For example, it can be taped onto the leg of a table or end table or even on a lower portion of a hanging chandelier.

10.2.5 The emitters are placed in the building at least 8 hours in advance of the samples.

10.2.6 Since the source is sensitive to temperature, it should not be placed within a meter of a heating or cooling source, in direct sunlight or other drafty location such as a window, nor at a location where air would carry the PFT vapors outside or to another zone before they had mixed uniformly within the zone where they were placed.

Note: Since heated air rises and cooled air sinks, the PFT location should be at a vertical location not too far above or below the temperature measurement/control elevation and not be placed above a warm air source (e.g., a lamp or the top of a refrigerator) nor below a cooled air source (e.g., an air conditioner vent or a window sill).

10.2.7 Record the average temperature of the source on the Field Data Sheet illustrated in Figure 4. The daily average room temperature is usually adequate for this purpose, even in the case of one or more daily temperature set-back cycles.

10.2.8 It should be mentioned that the directions included in this method are for a typical dwelling (ACH = 0-2) Table 3 gives the number of sources needed if the building to be monitored is expected to have a higher air change per hour than a normal dwelling, i.e., an office building with higher ventilation.

10.3 Placement of Passive Samplers (CATs)

Note: DO NOT STORE THE SOURCES AND THE SAMPLERS IN THE SAME LOCATION. The sources and samplers should definitely not be shipped in the same container and, ideally, not even shipped on the same day. For example, if transported in the same car or truck, there is a possibility of contamination. During field deployment, the samplers can be placed in the engine compartment or roof rack of a vehicle (effectively outside) while the sources are maintained within the vehicle passenger compartment or trunk. To this end it is generally wise for 1 or 2 passive samplers to remain as controls, that is, to remain unopened, for each series of home infiltration measurements.

10.3.1 One or two samplers are usually deployed in each zone of the home with the same location restriction as the sources and at least 1 to 2 meters from any PFT source or source of air not representative of the room air (e.g., air from the outside or another zone). Thus, the samplers are usually placed near another inside wall location, but at least 2 cm from any wall, and not in a flowing air stream without a shelter such as an envelope or box.

10.3.2 In the bedroom zone of a ranch house or 2-story house, it is prudent to sample in the master bedroom plus one other bedroom; this provides a better average for that zone.

10.3.3 In the family zone, two samplers located as per the two-story diagram, as shown in Figure 3, give an average concentration which is better than just placing one sampler as per the one story diagram.

10.3.4 The samplers are not temperature sensitive, but extremes should be avoided. They can be placed on a table or taped to the leg of a chair or table in any orientation. The samplers have a rubber cap on each end.

10.4 Sampling Start-Up and Shut-Down

10.4.1 To initiate sampling, only one cap must be removed, the one near the numbered end, as seen in Figure 2. The sampler number, location, and time and date sampling commenced must be recorded on the Field Data Sheet shown in Figure 4.

10.4.2 At the end of the designated sampling period (e.g., one day, one week, one month, etc.), cap the sampler and record the time and date sampling ceased on the Field Data Sheet. Verify each CAT ID number upon removal from its sample location. CATs are stored in sealed ziplock bags for transport to the lab.

10.4.3 Record other information as called for on the Field Data Sheet. The volume of each zone of the house should be obtained from inside dimension measurements or estimated from outside lengths and widths, subtracting 1 foot (0.3 m) from each, but using inside ceiling heights. A separate sheet should be used for each home. House floor plan should be drawn to show location of each source and CAT for each sampling event. House Volume should be recorded on house floor plan. These data are needed in conjunction with other information (e.g., from questionnaires) about open windows, presence of fireplaces, window fans, window air conditioners, etc. to assist in interpreting the data.

11. Gas Chromatography with an Electron Capture Detection

11.1 The determination of PFTs collected via either the passive or programmable samplers is accomplished with a gas chromatograph system (Varian Instrument Corp., Floral Park, New Jersey, Model 3700 GC with a Model CDS-111 integrator-controller). The analysis includes thermal desorption, chemical and physical processing, chromatographic separation, and ECD determination of the tracer gas as illustrated in Figure 5.

11.2 Calibration of GC-ECD

11.2.1 Gas standards for calibrating the GC are prepared in the concentration range of 1 to 10,000 pL/L by first preparing 1000 ppm primary standards of PFT in helium (He) either gravimetrically or volumetrically and verifying on a thermal conductivity GC that has been calibrated with pure PFT vapors. These primary standards are then further successively diluted with ultra pure air (Scientific Gas Products, Plainfield, New Jersey) in Spectra-Seal aluminum cylinders (Airco Industrial Gases, Riverton, New Jersey).
Note: Regular steel cylinders have been found to adsorb significant amounts of the higher boiling point tracers (PMCH and PDCH), especially at concentrations of 1 and 10 pL/L, but the Spectra-Seal cylinders showed no adsorption loss (7).

11.2.2 Calibration of the GC is performed by setting flow rates of 5 and 50 mL/min on the gas cylinder standards and passing the flow through consecutive CATS tubes for different durations.

11.2.3 Quantities of from 0.05 to 5000 pL (pL = 10^{-12}) of tracer then are analyzed to calibrate the GC response for each tracer.

11.2.4 The limit of detection (LOD) for AER depends on the LOD of the GC-ECD, the sampling rate of the CAT tubes, the sample duration, the emission rates of the PFT sources, the house volume and the true integrated air exchange rate. It is recommended that GC-ECD systems which can detect PFT quantities at least as low as 1 picoliter with 30% precision be employed. The minimum PFT concentration LOD is controlled by this and the sample exposure time, and the effective sampling rate. For this instrument, the minimum detectable air concentration calculated by:

$$\text{(PFT LOD, pL/L)} = \frac{\text{(Minimum Measurable PFT Amount, pL)}}{\text{(Hours Exposed) x (Sampling Rate, L/hr)}}$$

$$= \frac{1 \text{ pL}}{24 \text{ hr x } 0.00892 \text{ L/hr}}$$

$$= 5 \text{ pL/L}$$

The maximum measurable PFT concentration can be calculated by:

$$\text{(PFT Concentration Maximum,pL/L)} = \frac{\text{(Maximum Measurable PFT Amount, pL)}}{\text{(Hours Exposed) x (Sampling Rate, L/hr)}}$$

$$= \frac{270 \text{ pL}}{24 \text{ hr x } 0.00892 \text{ L/hr}}$$

$$= 1260 \text{ pL/L}$$

Note: The highest PFT concentrations expected in normal dwellings are about 200 pL/L, so the upper limit should be of no consequence. The lowest PFT concentrations may be on the order of 1 pL/L for houses with open windows and fans in use.

11.2.5 The concentration of PFT produced by sources in a home is dependent on the number of PFT sources, their emission rates, the house volume, and the air exchange rate, as outlined by the following equation:

$$C = \frac{n \text{ x } S/V}{[n \text{ x } S/V)/R]}$$

where:
S ~ 1800 nL/hr, PMCH source @ 25°C
n = number of sources
V = house volume, m^3
R = air changes per hour (ACH)
The lowest PFT values are expected to be found in large houses with high AER rates. As an example, for a house with the following dimensions:

3.8

V = 500 m^3
R = 12 ACH
n = 6 PMCH sources,
the average PFT level is expected to be about 1.8 nL/m^3. This is about equal to the system LOD. The highest PFT levels will be found in small homes with low AER. As an example, for a house with the following dimensions:
V = 150 m^3
R = 0.5 ACH
n = 6 PMCH sources,
the expected PFT level is 144 nL/m^3 which is well below the system PFT capacity.

11.3 GC-ECD Analysis Protocol

11.3.1 Whether for initial bakeout or for thermal desorption and recovery of sampled PFTs, a special rack with 23 positions should be constructed as illustrated in Figure 4. The resistance heating wire element consists of about 10 turns of 0.8 mm OD (20 gage) nichrome wire (approximately 23 cm in length) such that 4.2 Vac (≈8.5 A or 36 W) heats the CATS tube to 450°C in 0.5 min and 1.9 Vac (≈3.8 A or 7 W) holds that temperature for another 0.5 min to effect the sample recovery; power is supplied from a transformer with a secondary rated at 6.3 Vac and 10 A (Essex/Stancor No. P-6308).

11.3.2 The tubes are placed into the rack by slipping through the heating coil (with one rack end removed) until they contact the spring-loaded "0"-ring seal pistons; the removal end, a 25-mm (1-in.) aluminum square stock, is replaced and the eccentric cam compresses the tube ends against the spring-loaded seals. The open 1.59 mm (1/16 in.) tubing ends are connected to a 24-position Scanivalve rotary valve assembly (Gilian Instrument Corp., Wayne, New Jersey) which has an electrical rotary switch to bring the desorption power to the proper tube.

11.3.2.1 Before the sample is thermally desorbed, the sampler tube is purged with carrier gas (5% H_2 in N_2) for a short period of time to remove any traces of oxygen which otherwise would react with the PFTs during the 400°C desorption recovery. The sample is purged through the precut catalyst as seen in Table 1, the dryer to remove water vapor, and the two precut columns before entering an adsorbent trap. The 10 cm long catalyst bed in the presence of the hydrogen in the carrier gas reduces any chlorofluorocarbon compounds, as well as any remaining oxygen, to their hydrogenated forms, thus rendering these interfering compounds nonelectron-capturing.

11.3.2.2 After the surviving PFTs elute from the precut column, heavier molecular weight constituents still within the column are purged to the atmosphere by reversing the direction of flow. Meanwhile, the eluted PFTs are reconcentrated within a 10 cm long Porapak QS adsorbent trap.
Note: The purpose of the QS trap on the gas chromatograph (GC) is two-fold. First, by not opening the trap until the first PFT eluting from the precut column arrives, some lighter constituents are discarded. Second, after the precut column is backflushed, the trap remains open for 1 min to further purge away light-interfering gases and then is closed.

11.3.2.3 When the Porapak QS trap has been heated to 200°C and opened, the PFTs are flushed through the main catalyst as seen in Table 1 for final cleanup before entering the main column for separation of the PFTs prior to detection in the ECD.

11.3.2.4 While this is occurring, the next sample tube can be thermally desorbed and loaded onto the QS trap once it has sufficiently cooled (about 50°C), thus almost halving the overall PFT sample recovery and analysis time by overlapping the stages.

Note: Automation of the sequential analysis of all 23 tubes in either a CATS desorption rack or a BATS lid is accomplished by using the BATS base timing capability to initiate the GC timing sequence as each new tube steps in place. Each analysis, including reporting of the peak areas, takes 10 minutes; 23 tubes are analyzed in just under 4 hours.

11.3.2.5 Figure 5 illustrates the detailed plumbing and valving used to effect the automated chemical and physical processing during the analysis of the PFT samples. Automation occurs through the use of eight external events contained within the integrator-controller. As illustrated in Table 2, one event starts and stops the recorder paper, four events operate the four valves, and three events control the heating of the sampler tube and the Porapak QS trap. Three 6-port (Valco Instrument Co., Houston, Texas, SSAC6T Shaft Seal) and one 4-port (Valco SSAC4UT Shaft Seal) valves with air operators are used. Vespel cone seals are preferred to the Teflon®-filled ceramic type because the latter have been found to bleed contaminants at temperatures above 100°C. With the exception of the sample valve, they are mounted within the GC oven.

11.3.2.6 When the recorder shuts off at 8.01 min, the analysis is complete and the report of the peak areas, which is proportional to the quantity of each tracer, is printed as well as transmitted to a magnetic tape, which can then be processed on a Tektronix 4052 desk top computer. The GC is ready for the repeat of the cycle on a 10 minute frequency. Figure 7 is a typical chromatogram.

12. Calculations

Numerous researchers have proposed models and methods for using tracer gases in the solution of those models for determining the air infiltration rate into a home or building considered as a single, well-mixed chamber or zone. Recently, however, it has been recognized that many larger, more complex buildings, especially those with multiple-zoned HVAC systems and even one- and two-story homes with basements, realistically can only best be represented by models which recognize the building as multiple-connected zones, each of which is well-mixed.

12.1 One-Zone Case

For a building considered as a single, well-mixed zone of known volume, V, containing one type of tracer of known emission rate, $R_s(t)$, such that a tracer concentration, C(t), is measured throughout the house which has an air exfiltration rate of $R_E(t)$, a simple material balance gives:

$$V \frac{dC(t)}{dt} = R_s(t) - R_E(t)C(t) \qquad (1)$$

where:
V = volume of the building (constant), m^3
$R_s(t)$ = total tracer source rate (variable), nL/h
$C(t)$ = average tracer concentration in the building (variable),$nL/m^3 \equiv pL/L$
$R_E(t)$ = air exfiltration rate (variable), m^3/h

Equation 1 is a general solution in which it is assumed that the tracer source rate, the tracer concentration, and the exfiltration rate can vary with time; it also was assumed that the tracer concentration is the ambient air, that is, the infiltrating air is negligible, which is always the case for PFT's. Equation 1 then can be solved for various modes of tracer experiments, including tracer decay, constant concentration, and constant emission rate. The PFT sources are designed to provide a constant emission rate source in the building. About 5 to 10 h after deployment, the tracer concentration will become more or less constant, dependent only on slow changes in the exfiltration rate due either to mechanical ventilation or weather changes. For these steady state assumptions [that is, $dC(t)/dt \approx 0$], Equation 1 becomes:

$$\frac{1}{n}\sum_{t=1}^{n}\frac{R_s(t)}{C(t)} = \frac{1}{n}\sum_{t=1}^{n}R_E(t) = R_s\frac{1}{n}\sum_{t=1}^{n}\frac{1}{C(t)} \qquad (2)$$

assuming that the source rate is constant, that is $R_s(t) = R_s$, over n periods of concentration. But:

$$\frac{1}{n}\sum_{t=1}^{n}\frac{1}{C(t)} = \frac{1}{n}\left(\frac{1}{C(1)} + \frac{1}{C(2)} + \ldots + \frac{1}{C(n)}\right)$$

$$= \frac{1}{n}\left(\frac{C(2)C(3)\ldots C(n) + C(1)C(3)\ldots C(n) + \ldots + C(1)C(2)\ldots C(n-1)}{C(1)C(2)\ldots C(n)}\right)$$

$$\approx \frac{1}{n}\left(\frac{n\bar{C}^{\,n-1}}{\bar{C}^{\,n}}\right) \approx \frac{1}{\bar{C}}$$

The second term in Equation 2 is the average infiltration rate, $\bar{R}_E$. Thus:

$$\bar{R}_E \approx \frac{R_s}{\bar{C}} \qquad (3)$$

The approximation in Equation 3 is because it was shown that the reciprocal of an average concentration, $\bar{C}$, which is the quantity that the passive sampler determines, is close to but not identical to the average of reciprocal concentrations.

12.2 Two-Zone Case

Examples of two-zone cases are a two-story house on a slab, a one-story (for example, ranch) with a basement or a crawl space, and any building which is ventilated with two separate HVAC systems. Figure 8 depicts the model for a one-story house (Zone 1) with a basement (Zone 2). Air can infiltrate from outside the house into each zone (R_{11} and R_{12}) and exfiltrate each zone to the outside (R_{E1} and R_{E2}). In addition, air can exchange between the zones in both directions (R_{E12} and R_{E21}). Assuming that a different tracer type is used in each zone (Tracer 1 in Zone 1, etc.), tracer material balances, assuming that steady state pertains and that there is negligible tracer in the outside air, give the following:

Zone 1

$$R_{21}C_{12} - R_{12}C_{11} - R_{E1}C_{11} = -R_{s1} \quad (4)$$

$$R_{21}C_{22} - R_{12}C_{21} - R_{E1}C_{21} = 0 \quad (5)$$

Zone 2

$$R_{12}C_{11} - R_{21}C_{12} - R_{E2}C_{12} = 0 \quad (6)$$

$$R_{12}C_{21} - R_{21}C_{22} - R_{E2}C_{22} = -Rs2 \quad (7)$$

where:

R_{12}, R_{21} = air exchange rates from Zone 1 to Zone 2 and Zone 2 to Zone 1, m^3/h,

R_{E1}, R_{E2} = air exfiltration rates from Zones 1 and 2, m^3/h,

R_{s1}, R_{s2} = rates of tracer sources in each respective zone, nL/h, and

C_{11}, C_{21}, C_{12}, C_{22} = concentration of Tracer 1 in Zone 1, etc., $nL/m^3 (\equiv pL/L)$.

The concentrations are measured with the passive samplers, and the tracer source rates are known. Thus, the four unknowns, two air exchange rates and two exfiltration rates, can be solved from the four simultaneous equations. The rate of infiltration for each zone then can be calculated from air mass balances:

$$R_{11} = R_{E1} + R_{12} - R_{21} \quad (8)$$

$$R_{12} = R_{E2} + R_{21} - R_{12} \quad (9)$$

The solutions to Equations 4 to 7 can be obtained by solving as two sets of simultaneous equations, noting that R_{21} can be solved from Equations 4 and 5 and R_{12} from Equations 6 and 7. Then R_{E1} and R_{E2} can be obtained from Equations 5 and 7, respectively. The solutions, which are given in the Appendix, also can be obtained, by any standard matrix inversion routine for use on a desktop computer. This is especially useful when the number of zones increases to three or four. Once all the flow rates have been determined, simple

material balances then can be performed for pollutants in the same building. The following equations

$$R_{21}C_{p2} + R_{11}C_{pa} - 2R_{12}C_{p1} - R_{E1}C_{p1} = -R_{p1} + k_1V_1Cp1 \quad (10)$$

$$R_{12}C_{p1} + R_{12}C_{pa} - R_{21}C_{p2} - R_{E2}C_{p2} = -R_{p2} + k_2V_2C_{p2} \quad (11)$$

where:

C_{p1}, C_{p2}, C_{pa} = concentration of pollutant in Zone 1, Zone 2, and the ambient outside air, respectively,

R_{p1}, R_{p2} = rate of the pollutant source in zone.

k_1, k_2 = rate of pollutant scavenging in each zone, and

V_1, V_2 = volume of each zone.

would then give the pollutant net source strength in each zone of the building. The solutions to the tracer and air material balance equations are:

Two-Zone Case

$$R_{21} = (R_{s1}C_{21})/(C_{11}C_{22} - C_{12}C_{21})$$

$$R_{12} = (R_{s2}C_{12})/(C_{11}C_{22} - C_{12}C_{21})$$

$$R_{E1} = R_{21}(C_{11/C21}) - R_{12}$$

$$R_{E2} = R12(C11/C12) - R_{21}$$

R_{11} and R_{12} are calculated from Equations 8 and 9 in the text.

12.3 Three-Zone Case

A typical example of a three-zone building is a two-story house with a basement. Again, assuming that a different tracer source is used in each zone and that the steady state assumption applies, a set of nine tracer material balance equations can be developed to solve for nine unknown flow terms (three exfiltration flow rates, one from each zone, and six air exchange rate terms, two leaving each zone). A set of three air mass balance equations would provide the three unknown infiltration rates. It is apparent that as the number of zones increases, the matrix solution approach with computer assistance is the only manageable way.

Three-Zone Case

Let:

$$[\ ] = [C_{11}(C_{22}C_{33}-C_{23}C_{32}) + C_{12}(C_{23}C_{31} - C_{21}C_{33}) + C_{13}(C_{21}C_{32} - C_{22}C_{31})]$$

Then:

$$R_{21} = R_{s1}(C_{21}C_{33} - C_{23}C_{31})/[\ ]$$

$$R_{31} = R_{s1}(C_{22}C_{31} - C_{21}C_{32})/[\ ]$$

$$R_{32} = R_{s2}(C_{11}C_{32} - C_{12}C_{31})/[\ ]$$

$$R_{12} = R_{s2}(C_{12}C_{33} - C_{13}C_{32})/[\ ]$$

$$R_{13} = R_{s3}(C_{13}C_{22} - C_{12}C_{23})/[\ ]$$
$$R_{23} = R_{s3}(C_{23}C_{11} - C_{13}C_{21})/[\ ]$$
$$R_{E1} = R_{31}(C_{23}/C_{21}) + R_{21}(C_{22}/C_{21}) - R_{13} - R_{12}$$
$$R_{E2} = R_{32}(C_{13/C12}) + R_{12(C11}/C_{12}) - R_{23} - R_{21}$$
$$R_{E3} = R_{13}(C_{11/C13)} + R_{23}(C_{12}/C_{13}) - R_{31} - R_{32}$$
$$R_{11} = R_{E1} + R_{12} + R_{13} - R_{21} - R_{31}$$
$$R_{12} = R_{E2} + R_{21} + R_{23} - R_{12} - R_{32}$$
$$R_{13} = R_{E3} + R_{31} + R_{32} - R_{13} - R_{23}$$

The total ACH in a house is given simply by the sum of the exfiltration rates of all zones divided by the sum of the volume of all zones. (See Section 12.2 entitled "Two-Zone Case" of the text for definition of the terms.)

12.4 N-Zone Case

It is apparent, then, that for N zones, a set of N trace material balance equations can be written to solve for N^2 unknown flow terms (N exfiltration flow rates, one from each zone, and N(N - 1) air exchange rates, that is, N - 1 leaving each zone to flow to another zone). Also, a set of N air mass balance equations would provide the N unknown infiltration rates.

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Table 1. Gas Chromatography Specification and Conditions

Main Column	1.2 m (4 ft) long packed with 0.1% SP-1000 on Carbopack C (Supelco, Inc., Bellefonte, PA)
Precut Columns	1.2 m (4 ft) long Porasil F followed by 0.3 m (1 ft) long of 0.1% SP-1000 on Carbopack C
Column Oven	140°C
Precut Catalyst	10.1 cm (4 in) long packed with palladium (Pd) (1%) on polyethylenimine/SiO_2-Royer Pd catalyst (Strem Chemicals, Inc., Newburyport, Mass.); 200°C
Main Catalyst	3.2 cm (1.24 in) long packed similarly; 200°C
Carrier Gas	5% H_2 in N_2 at 25 and 20 mL/min, respectively, through the precut and main columns
Porapack QS Trap	10.1 cm (4 in) long packed with Porapack QS
Permeation Dryer	1.2 m (4 ft) long Nafion dryer (Permapure Products Inc., Oceanport, N.J., Model MD-125-48S) located in the top of GC (~35°C)
ECD	180°C

Note: All columns (including catalyst beds and adsorbent trap) are made with 3.2 mm (0.125 in) OD stainless steel tubing.

Table 2. Gas Chromatograph[a] Sequence of Events

Event Time, min	Event Code	Event	Event Status
0.00	---	System steps to next sample tube; starts event clock	---
0.01	0.01	Recorder starts	Off
0.01	0.14	QS/sampler heating relay switches to QS trap	On
0.02	0.10	Desorption Power turned on	On
0.02	0.12	High power position	On
0.35	0.13	Low power position	Off
0.50	0.08	Sample in QS trap injected (that is, V4 on)	On
1.60	0.09	V_4 is off	Off
1.60	0.11	Desorption power turned off	Off
1.62	0.15	QS/sampler relay switches to sampler	Off
2.30	0.06	V_3 is on	On
4.95	0.04	V_2 is on	On
5.00	0.02	V_1 is on	On
5.00	0.10	Desorption power turned on	On
5.00	0.12	High power position	On
5.40	0.13	Low power position (not used for BATS tubes)	Off
5.70	0.08	V_4 is on	On
7.30	0.11	Desorption power turned off	Off
7.60	0.09	V_4 is off	Off
7.70	0.07	V_3 is off	Off
7.75	0.03	V_1 is off	Off
7.80	0.05	V_2 is off	Off
8.01	0.00	Recorder off	On

Table 3.
Number of PFT Sources Needed Per Zone to Achieve the Lower Limit of Detection When the Exposure Time Varies*

	Hours Exposed				
	8	12	24	48	168 (7 days)
Source Type					
PDCB	13	9	4	2	1
PMCP	11	8	4	2	1
PMCH	18	12	6	3	1
PDCH	37	25	13	6	2

*Assuming:

ACH	≤ 6
Vol. per zone	≈ 314 m^3 (500 ft^2 floor space with 8 foot ceilings)
GC-ECD	Limit of Detection ≤ 1 pL
PFT	minimal emission rate

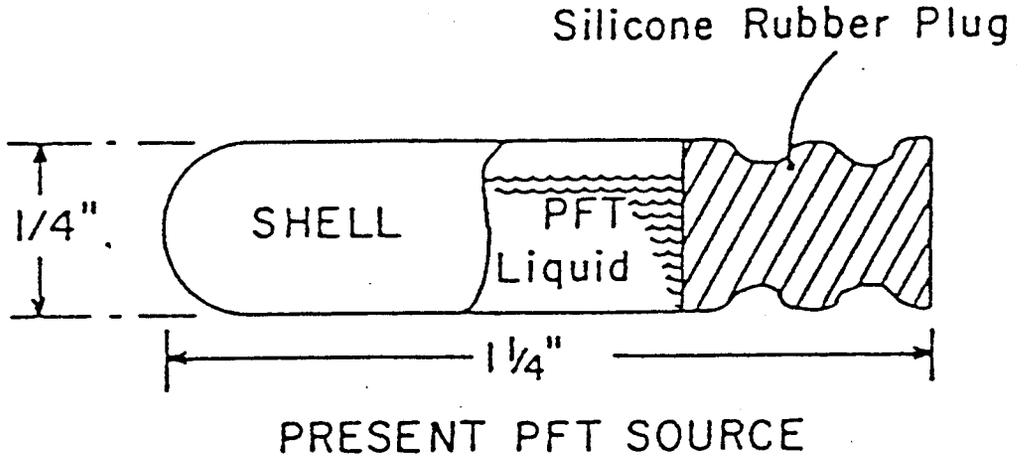


Figure 1. Diagram of the PFT Source Configuration

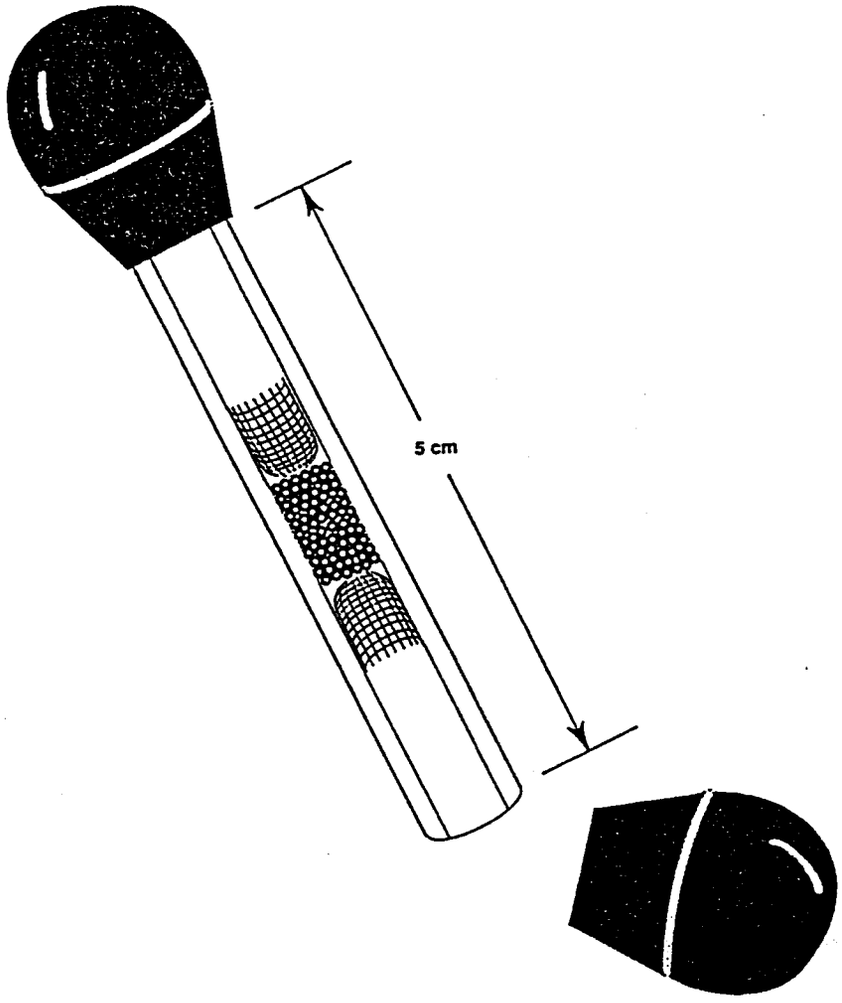
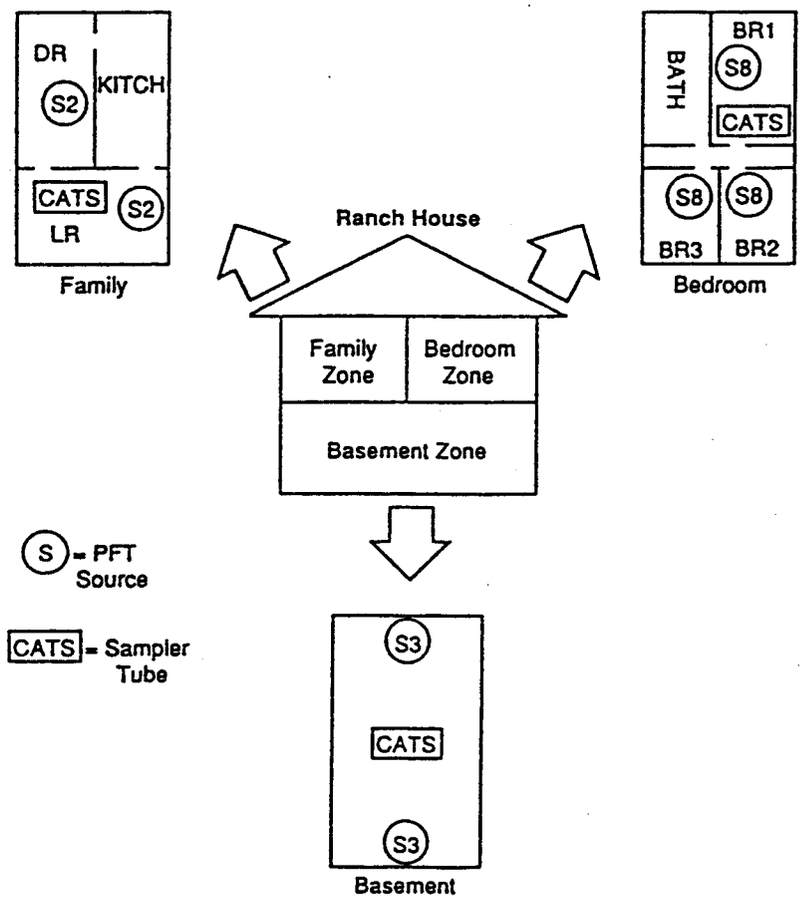


Figure 2. Diagram of a Typical capillary Adsorbent Tube (CAT)

One-Story, Ranch Style House with a Basement



Basement Zone
Sources- Place two PTF type 3 sources on opposite ends of the basement. If an obstruction exists, place a source on either side of the obstruction.
Sampler- Place the CATS in the center of the basement or within the largest open area.

Family Zone
Sources- Place two PFT type 2 sources within the two largest rooms.
Sampler- Place a CATS in the largest room.

Bedroom Zone
Sources- Place one PFT type 8 source in each bedroom.
Sampler- Place a CATS in the largest bedroom in the zone.

Figure 3A. Placement of PFT Sources

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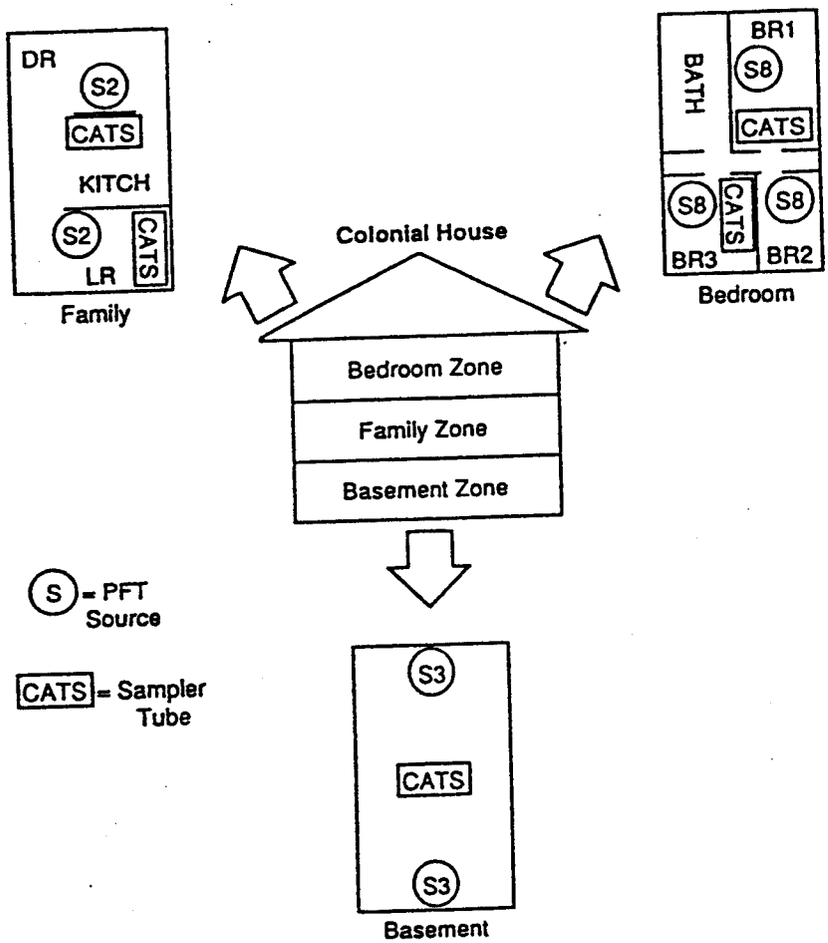
Two- Story, Colonial Style House with a Basement



Basement Zone
Sources- Place two PTF type 3 sources on opposite ends of the basement. If an obstruction exists, place a source on either side of the obstruction.
Sampler- Place the CATS in the center of the basement or within the largest open area.

Family Zone
Sources- Place two PFT type 2 sources in the rooms at opposite ends of the zone.
Sampler- Place two CATS in the largest rooms in this zone, twords the center, but away from each other and the sources.

Bedroom Zone
Sources- Place one PFT type 8 source in each bedroom.
Sampler- Place two CATS in the largest bedrooms within this zone.

Figure 3B. Placement of PFT Sources

Project Title____________________

House ID:____________ # of Zones:_____

House Description
____1 story
____2 story
____w/basement
____split level
____w/fireplace
____w/woodstove

Circle one

Start Date: / / Start Time: : am pm

Stop Date: / / Stop Time: : am pm

Zone #:_____ Zone ID:______# of Sources:______ Source Code:______

Avg. Temp. (°F):______ Volume (ft^3):______ # of CATS:______
(°C):______ (m^3):______

			Source Location	
CATS ID	Room	Item Placed On	Room	Item Placed On

Zone #:_____ Zone ID:______# of Sources:______ Source Code:______

Avg. Temp. (°F):______ Volume (ft^3):______ # of CATS:______
(°C):______ (m^3):______

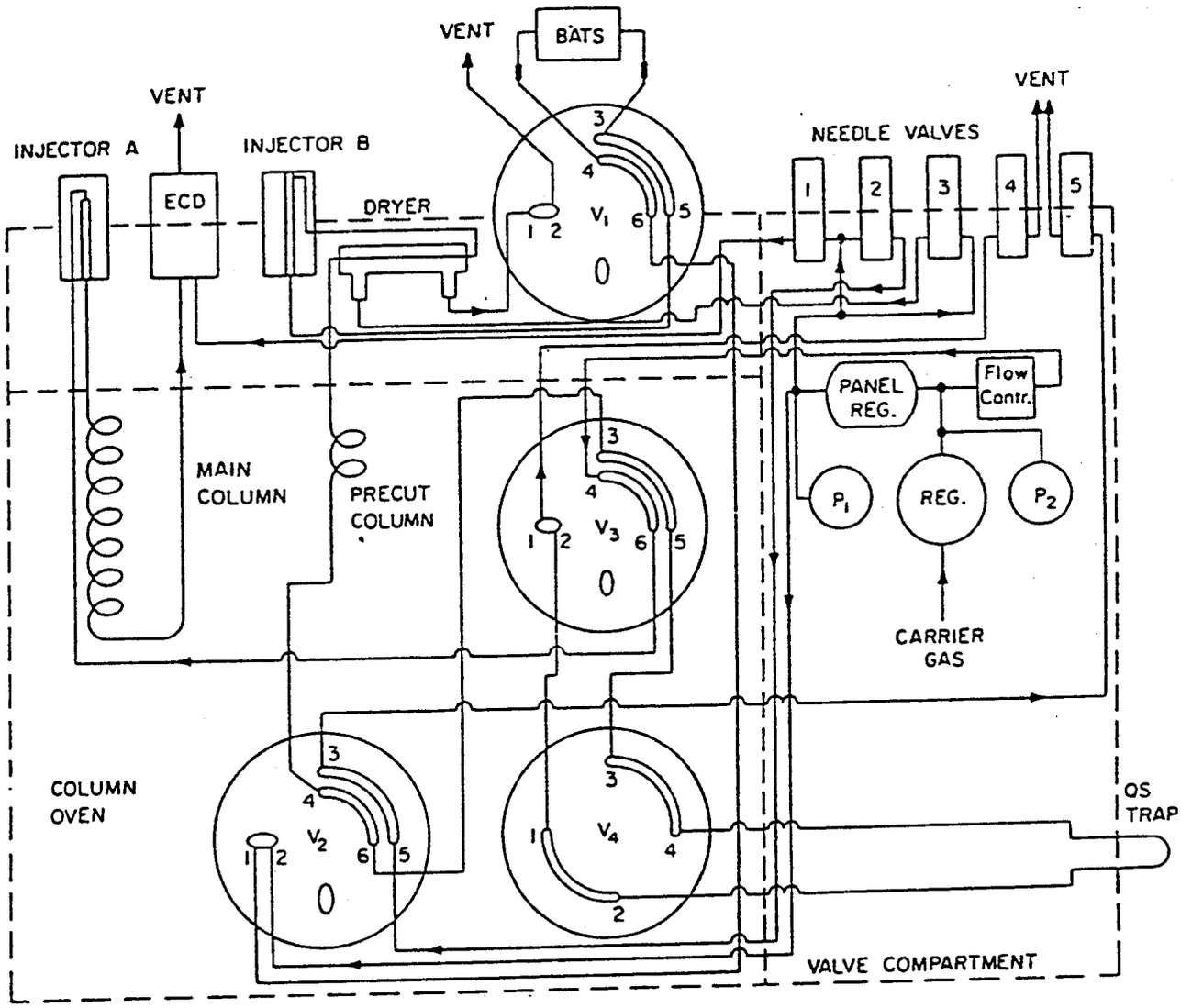
			Source Location	
CATS ID	Room	Item Placed On	Room	Item Placed On

Zone #:_____ Zone ID:______# of Sources:______ Source Code:______

Avg. Temp. (°F):______ Volume (ft^3):______ # of CATS:______
(°C):______ (m^3):______

			Source Location	
CATS ID	Room	Item Placed On	Room	Item Placed On

Figure 4. Data Sheet



V_1 = The sampler valve.
V_2 = The precut valve.
V_3 = The flow direction valve.
V_4 = The Porapak QS valve.

Each is shown in its "ON" position; in the "OFF" position, the valve slots are rotated 90° counterclockwise.

Figure 5. Schematic of Laboratory GC Analyzer

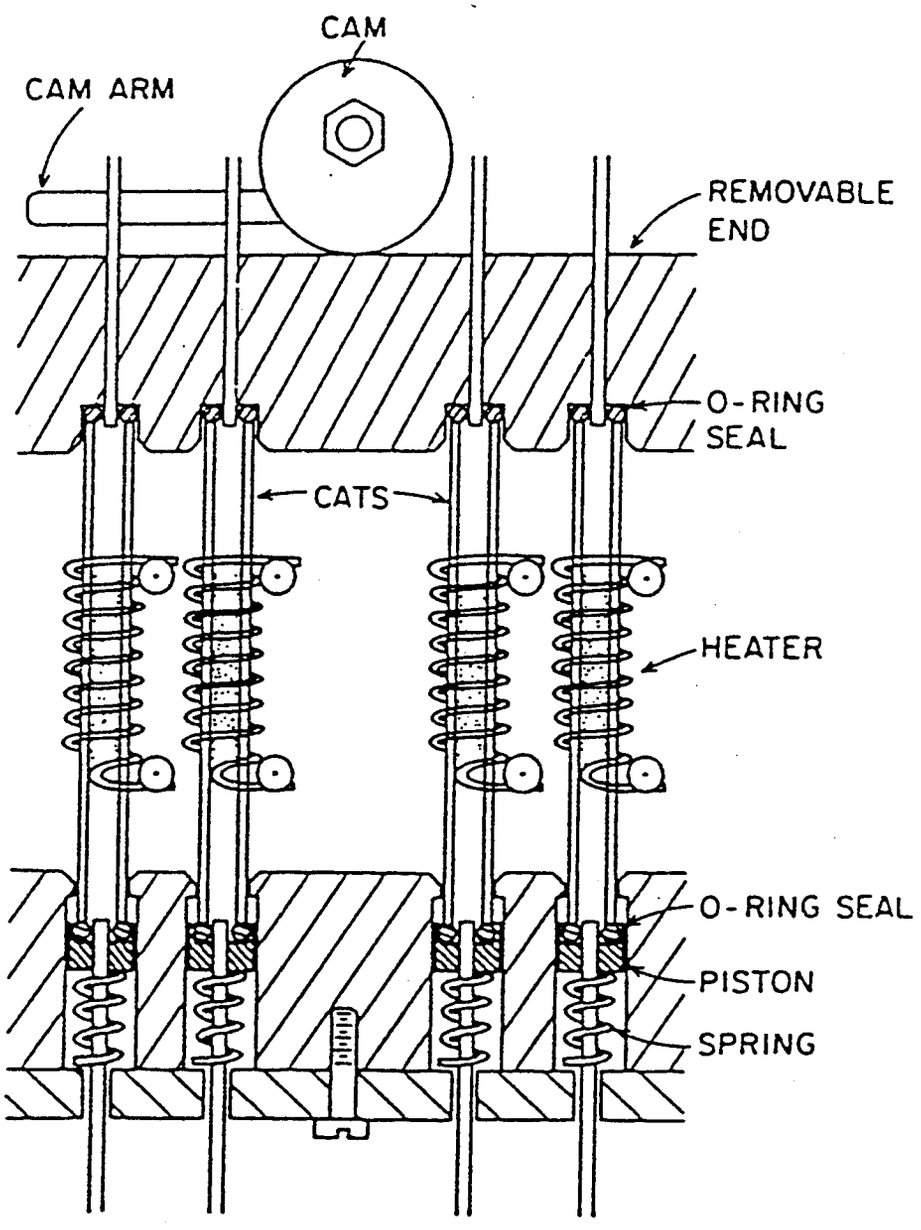


Figure 6. Passive Sampler Thermal Desorption Rack

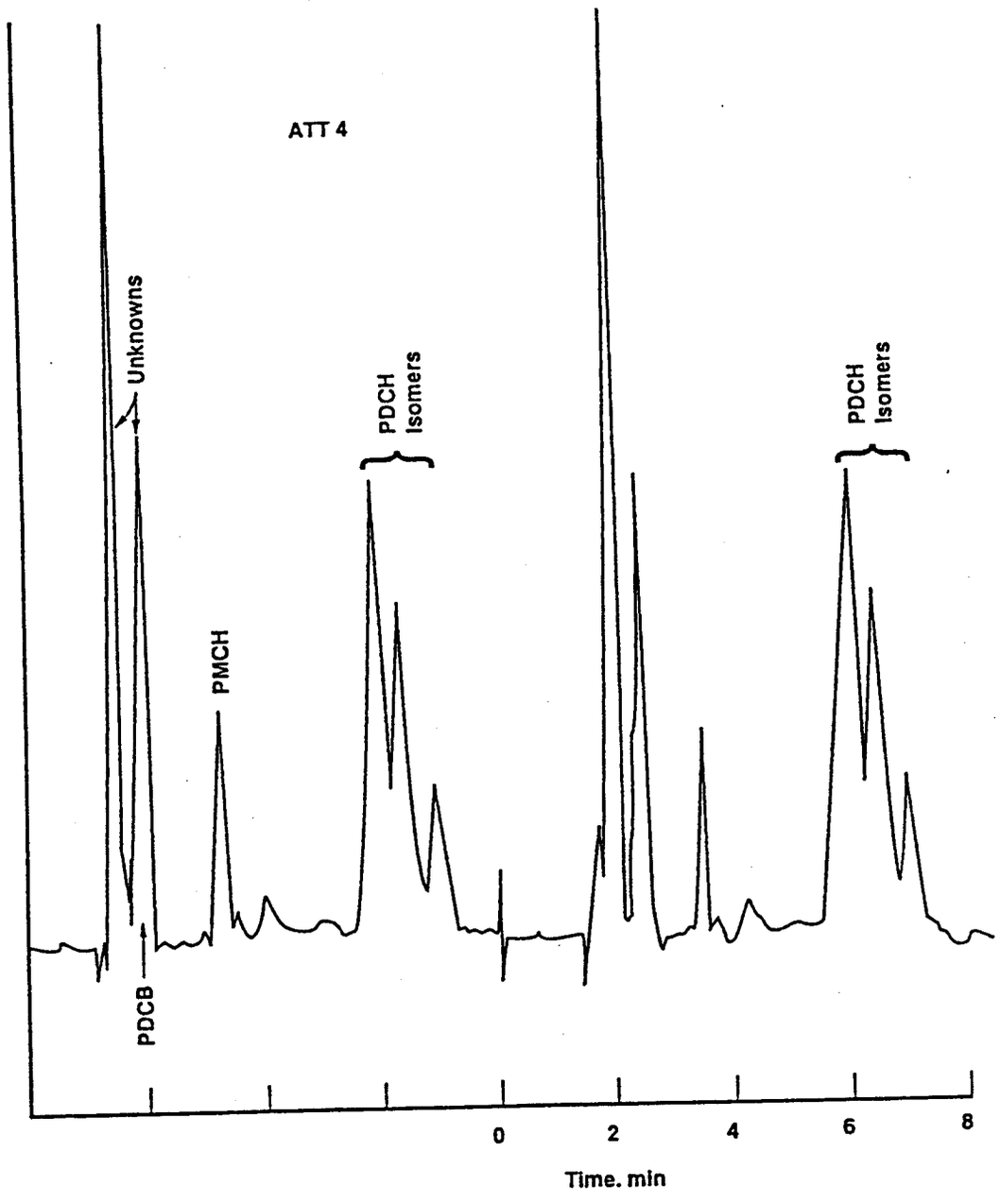
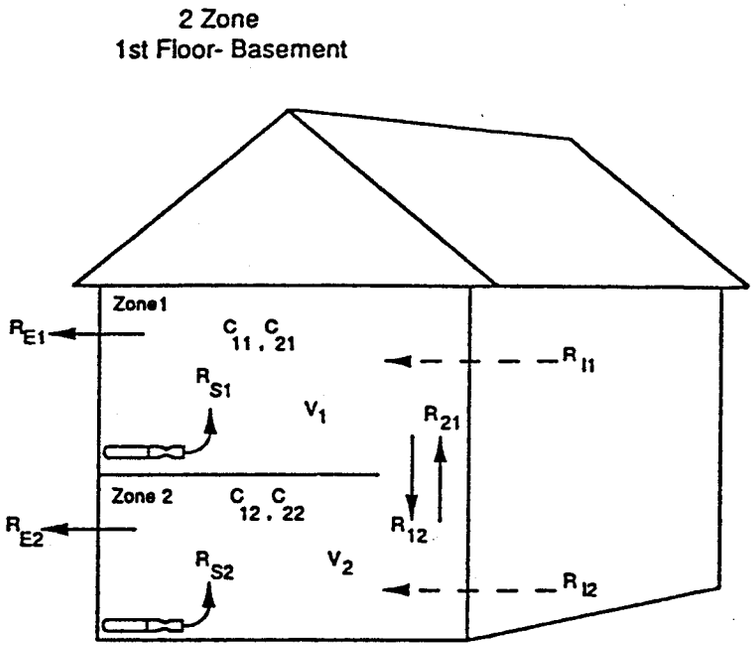


Figure 7. Chromatograms of Two 25-L Ambient Air Samples with the GC Specifications Shown in Table 1. The Unknown Peak after PDCB is PMCP.



R_{I1}, R_{I2} = Air Infilttration

R_{E1}, R_{E2} = Air Leakage

R_{12}, R_{21} =Air Exchange Between Zones

R_{S1}, R_{S2} =PFT Sources

V_1, V_2 =Zone Volumes

C_{11}, C_{21} = Connection of Tracer 1 in Zone 1

C_{12}, C_{22} = Connection of Tracer 2 in Zone 2

Figure 8. Model Considered for a Two-Zone House

Method IP-4B

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR USING TRACER GAS

Method IP-4B

DETERMINATION OF AIR EXCHANGE RATE IN INDOOR AIR USING TRACER GAS

1. Scope

1.1 This document describes the protocol for the measurement for an air exchange rate (AER) between the outside and inside of buildings under natural meteorological conditions by trace gas dilution.

1.2 The tracer gas suggested for this method is sulfur hexafluoride (SF_6). Other tracer gases are available. This document lists other tracers and discusses the advantage of using SF_6. Occasionally more than one tracer gas may be desired in an application. Situations where it may be advantageous to utilize more than one tracer gas will be discussed.

1.3 To facilitate ease of operation, convenience and accuracy, this method suggests the use of commercially available automated syringe samplers and tracer gas monitors.

1.4 This test method describes a standardized technique for determining air change rate in buildings under natural meteorological conditions by trace gas dilution.

1.5 This test method shall not be used to determine the individual contribution of various building components to the air change rates of a building.

1.6 Use of this test method requires a knowledge of the principles of gas analysis and instrumentation.

1.7 The current state of the art does not possess analytical techniques to extrapolate precisely measured air change rates to meteorological conditions different from those prevailing during measurement.

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

2. Applicable Documents

2.1 ASTM Standards

E741 Determining Air Leakage Rate by Tracer Dilution (1)
E779 Test Method for Determining Air Leakage Rate by Fan Pressurization
D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis
E355 Recommended Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

Scientific Publications (2-7)
U.S. EPA Technical Assistant Documents (8)

3. Summary of Method

3.1 This test method entails introducing a small amount of tracer gas into a structure, thoroughly mixing it, and measuring the rate of change (decay) in tracer concentration. The air change rate can be estimated from the decay rate of tracer concentration with respect to time. On-site meteorological conditions are measured concurrently. In the on-site monitor variant, after the tracer gas has thoroughly mixed, an initial air sample container is filled. The air change rate can be determined from the decay in tracer concentrations.

3.2 A quantity of tracer is released at one or more points in the test building. The amount of tracer released should be sufficient to produce an easily discernible response in the gas measuring instrument. Under no circumstances should the initial tracer gas concentration exceed the Occupational Safety and Health Administration's (OSHA) time weighted average for substances included in the latest OSHA standards.

3.3 Fans or the central air system should be used to circulate the air within the room or structure in order to mix the gas thoroughly. Connecting doors, closet doors, and the like should be opened to allow unobstructed internal air flow. Several minutes should be allowed for mixing.

3.4 Air samples from one central location or several strategic points are collected at timed intervals.

3.5 The tracer concentration of each sample is determined by a gas chromatograph equipped with an electron capture detector.

3.6 The decay in tracer gas concentration as a function of time can be related to the air exchange rate of the building at the place of collection under the current meteorological conditions.

3.7 By repeating this procedure a number of times, it is possible to characterize the effects of climatological (temperature and wind) on structural (wall, windows, floors, ceilings, doors, etc.) factors on infiltration rate.

4. Significance

4.1 Air leakage accounts for a significant portion of the thermal space conditioning load; it can introduce outdoor air contaminants in conditioned indoor air, and it can dilute indoor-generated contaminants, therefore detracting from or providing for occupant comfort.

4.2 Air leakage rates are difficult to predict analytically because they are functions of building tightness and configuration, inside-outside temperature differences, wind speed and direction, quality of workmanship in construction, and numerous other factors.

4.3 This test method describes measurements of air leakage rates. In applying the results of this test method to the design of buildings, consider that the air leakage

characteristics of a structure are affected by building operation, maintenance, and the resistance of the building components to deterioration.

4.4 The tracer dilution method has been proven to be an effective way of measuring the air leakage rate of a structure under field conditions. The measurement of air infiltration using the tracer gas dilution method and on-site gas monitor equipment requires field deployment of equipment and the use of trained technicians. It is possible to take tracer gas samples on site and analyze them at a laboratory facility. The practice of taking container samples can be performed by persons not trained in the operation of the gas monitor equipment.

4.5 As an alternative to the tracer gas method, the fan pressurization method (ASTM Test Method E779) provides an indirect way to relate the air leakage rate or air tightness to the leakage area of a structure. This test method has several differences from the tracer dilution method. It can be used to compare the relative air tightness of several buildings, to identify the leakage source and rate of leakage from different components of the same building envelope, and to determine the air leakage reduction for individual retrofit measures applied incrementally to an existing building.

4.6 When the absolute air leakage rate is needed, the tracer dilution method should be used over a wide range of wind velocities and indoor and outdoor temperature differences. It is best to use the fan pressurization method for diagnostic purposes and resolve the absolute air leakage rate with the tracer dilution method. However, the measuring equipment and techniques are relatively complicated for the tracer dilution method, and the data analysis and correlation are more involved.

4.7 In contrast with the tracer gas dilution method, two other tracer gas techniques are employed:

4.7.1 One is the constant concentration approach in which the tracer gas concentration is maintained essentially constant (order of ±10%) in a given volume. The air infiltration rate is determined from how much tracer gas must be injected to maintain the constant concentration. The constant concentration feature is particularly desirable in multi-chamber buildings, since leakage from chamber-to-chamber does not disturb the air infiltration measurement.

4.7.2 The second method is the constant injection method where, as the name implies, tracer gas injection is maintained constant over time.

4.7.3 The governing equations for both constant concentration and constant injection are different from the tracer gas dilution method.

5. Definitions

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

5.1 Air change rate - the ratio of hourly indoor air change and indoor space volume measured in identical volume units (normally expressed in air changes per hour, ACH or ACPH).

5.2 Air leakage rate - the volume of air movement per unit time across the building envelope. This movement includes flow through joints, cracks, and porous surfaces, or combinations thereof. The driving force for such air leakage in service can be either mechanical pressurization and evacuation, natural wind pressures, or air temperature differentials between the building interior and the outdoors, or combinations thereof.

5.3 Building envelope - the exterior shell enclosing the indoor space.

5.4 Exfiltration - air leakage from a building space.

5.5 Indoor space - the volume of a building that exchanges air with outside ambient air. In most cases, this volume is the deliberately conditioned space within a building, generally not including the attic space, basement space, interstitial spaces (such as a double envelope), and attached structures, unless such spaces are connected to the heating and air conditioning system.

5.6 Infiltration - air leakage into a building.

5.7 Natural ventilation - unpowered airflow through intentional building openings such as open windows and vents.

5.8 Tracer gas - a gas that can be mixed with air and measured in very small concentrations, making it possible to detect air movements and measure air changes.

5.9 Ventilation - intentional outdoor air intake through a ventilation system, with mechanical ventilation being that ventilation induced by a mechanical system.

6. Interferences

6.1 SF_6 has a low natural background concentration (typically 0.1 to 0.5 ppt.). One exception to its low natural background, however, can be in the vicinity of electrical power switching equipment which may use SF_6 as an insulating material.

6.2 Tennis balls can contain SF_6 which may pose another possible source of background interference.

7. Apparatus

7.1 This description of apparatus is general in nature, and any equipment capable of performing the test measurements within the allowable tolerances is permitted (see Tables 1 and 2).

7.2 Tracer gas monitor - a device to measure tracer gas used in the study, capable of measuring the tracer gas to within ±5% at any concentration. In this case, a gas chromatograph specifically designed for tracer gas monitoring is described.

7.3 Sampling network - consisting of tubing, tubing junctions, a pump, and possibly an aspirator. This network is used to draw samples from remote locations within a structure, blend them, and bring the blended sample to a convenient place for analysis. In general, it is best to avoid plasticized tubing, such as vinyl, and use copper, stainless steel, or possibly polypropylene or nylon. The technician should be aware that surface absorption within the sampling network can be a major source of confusion in any concentration decay measurement.

7.4 Sample containers - non-absorbent, inert, low-permeability containers (such as sample bags, syringes with needle caps, of plastic bottles) used to collect and store air samples from buildings under test. With this method syringes are utilized because of air volume accuracy and ease of injection into the chromatograph.

7.5 Pump - non-contaminating air sample pump, either manual or powered, used to fill sample containers. Plastic bottles can be filled by hand squeezing. With this method a commercially available automatic syringe sampler is utilized.

7.6 Syringes - disposable syringes may be used as sample containers if sealed or to inject gas samples when the gas monitor is a gas chromatograph. A plastic bottle containing tracer gas or tracer gas/air mix can also be used.

7.7 Circulating fans - used to circulate air within a structure, capable of circulating air over 360°. Oscillating or hassock fans are preferred. Such fans are normally unnecessary in buildings with ducted forced air systems.

7.8 Meteorology stations - portable, that records wind speed and direction, outside temperature, and (if available) relative humidity, is used to obtain on-site meteorological data.

7.9 Barometer - a device to measure local barometric pressure is useful. If one is not available, barometric pressure from the nearest weather station is obtained for the time during which measurements are performed. These data are corrected for any elevation difference between the weather station and the test structure.

7.10 Tracer gas - a cylinder or container of gas chosen from those listed in Tables 1 and 2 is necessary as a source of the tracer used in the test. On this method SF_6 is used.

7.11 Timing device - a clock, watch, chronometer, or similar device suitable for measuring elapsed time and time intervals.

8. Reagents and Materials

8.1 Tracer gas - pure form SF_6.

8.2 Nitrogen gas - high purity reagent gas as the electron capture detector carrier gas.

9. Safety Precaution

The maximum allowable concentration in air for each of the tracer gases that have been used for tracer dilution air leakage measurements is provided in Tables 1 and 2. Do not

exceed this concentration under any circumstances. Good experimental practice is to ensure that the maximum allowable concentration of the particular tracer is less than this maximum by at least a factor of four. The initial tracer gas concentration must not exceed under any circumstances the OSHA time-weighted average for substances included in the latest OSHA-controlled gases list.

10. Tracer Gas Technology

10.1 General

The implementation of tracer gas technology provides quantitative information concerning air mass or pollutant transport and dispersion which cannot be readily obtained in any other manner. Applications that have used this technology include:

- Meteorological tracing and atmospheric diffusion studies.
- Isolation of the contribution of a specific emitting source from other local sources.
- Large distance plume tracking and impact assessment.
- Determination of the transport and dispersion characteristics of a locale prior to new facility construction to assess potential new source impact on air quality.
- Examination of pollutant species dispersion, depletion or conversion.
- Characterization and assessment of gaseous effluents from nuclear generating stations.
- Evaluation of highway air pollutant emission factors in the vicinity of a major highway in an urban area.
- Studying of air movement within or around an enclosed volume for ventilation studies.
- Validation and correlation of ambient air quality advection and dispersion models.
- Infiltration measurements in structures to quantify convective energy losses.
- Assessment of mine ventilation and air flow characteristics.
- Prediction of smoke movement in building fires.
- Characterization of air transport/communication and earth media permeability assessment in underground structures.

10.2 SF_6 Tracer Gas

10.2.1 Sulfur hexafluoride is a colorless, tasteless, incombustible gas, with an inertness resembling nitrogen, unchanged even at the softening temperature of hard glass and unaffected by water or caustic potash. This gas possesses excellent properties for use as a voltage insulation.

10.2.2 SF_6 is considered to be one of the most desirable tracers. It possesses one of the highest electron capture responses (it can be detected down to 10^{-12} parts SF_6 per part air - 1 ppt); and it has a low natural background concentration (typically 0.1 to 0.5 ppt). Other factors which make SF_6 the ideal tracer gas are:

- Non-toxic, non-allergenic, non-radioactive, colorless and odorless.
- Gaseous at ambient temperatures.
- Chemically inert and thermally stable for atmospheric applications.
- Capable of rapid and controlled atmospheric release from a point or area source.

- Amenable to conventional sample collection techniques.
- Commercially available.

10.2.3 One exception to its low natural background, however, can be in the vicinity of electrical power switching equipment which may use SF^6 (or Freon C-318) as an insulating material. Tennis balls contain SF_6. Thus, in any tracer release/monitoring study, care must be taken to determine whether there are background concentrations, potential tracer gas interferences or contamination prior to performing the tracer release.

11. Release of Tracer Gas

11.1 On Site Monitor Method

11.1.1 The assumption underlying the tracer gas measurement of air change rate is that for perfect mixing with steady air flow, the loss rate of tracer gas concentration conforms to the exponential dilution law; that is, the loss rate or dilution of an escaping gas is proportional to its concentration. Mathematically, this assumption leads to Equation 1.

$$C = C_0 \exp(-It) \quad (1)$$

where:
C = tracer gas concentration at time, t
C_0 = tracer gas concentration at time = 0
I = air change rate
t = time

11.1.2 Injection and Mixing of Tracer Gas - At one or more points in the test structure, release an amount of tracer gas sufficient to produce an easily discernible response in the gas-measuring instrument. The location of release is governed by the location of air handling system(s) or mixing fans in a structure with no air-handling system. This release can be done with a gas-tight syringe or a plastic bottle filled with tracer gas.

11.1.3 In a building with ducted forced air system(s), operate the main fan(s) continuously. Introduce tracer gas into the main supply or return duct(s), preferably in the vicinity of the main fan(s).

11.1.4 Leaks in the ductwork system may produce an incremental increase in the air leakage rate. Two methods to assess this leakage are:

11.1.4.1 After beginning a test, as in 10.3.3, operate the main fan(s) only for initial mixing and shortly before sampling.

11.1.4.2 Use portable fans for mixing after initiating a test as in 10.3.3. Perform the remainder of the test as in 10.3.5.

11.1.5 In a building without central heating and air conditioning system(s), release the tracer gas at one or more points within the structure. Use fans to circulate the air and mix the gas. Take care not to affect the pressure distribution within the structure. Open all doors connecting contiguous living spaces.

11.2 Container Method

11.2.1 Injection of Tracer Gas - A predetermined quantity of the tracer gas is initially injected into the building so that the initial concentration of the tracer gas is below the safety limits listed in Tables 1 and 2 and within the optimum detection range of the gas monitor used. Graduated syringes can be used for this injection. These can be prepared before the test or filled from a bottle of compressed tracer gas at the site. The injection is accomplished by slowly walking around inside the structure, injecting gas into each room in a quantity approximately proportional to the volume of the room. The graduation on the syringe greatly aids in this process. A sample container with tracer gas/air can be used in a similar manner.

11.2.2 Mixing Tracer Gas in Dwelling - A waiting period of approximately ½ to 1 h should then be allowed for proper mixing of the tracer gas. For a building with a forced air heating system, the fan on the furnace can be turned on to assist in the mixing. Experience in dwellings without an air system suggests that natural convection currents will mix the tracer gas well. This is also true for each floor of the building (if the doors between rooms are open). In multi-story structures there seems to be higher on the upper floors. This is probably due to natural convection currents caused by rising warm air. Circulating fans can be used to assist mixing of the tracer gas.

12. Sampling

12.1 General Procedures

Collecting of SF_6 samples during periods of gaseous release may be performed by several techniques. The current state-of-the-art in this topical area encompasses:

- Grab samples (syringes)
- Sequential instantaneous samples
- Portable bagged samples (time-averaged)
- Sequential bagged samples at fixed sites (time-averaged)
- Spatially-averaged bagged samples from mobile platforms (automobiles, vans, aircraft)
- Limited semicontinuous sampling (frontal chromatography)
- Continuous detector sampling
- Time-averaged samples - evacuated containers

12.2 Sampling for On Site Monitor Method

12.2.1 Before taking gas samples, allow at least 30 minutes for mixing.

12.2.2 To test for homogeneity in tracer gas concentration, take samples from a number of building spaces. When concentrations differ by less than 5% of the average concentration measured within the structure, begin monitoring the decay of tracer concentration. In a residential structure, two or more samples from widely separated locations are required. In multi-story structures, two widely separated samples per floor are required.

12.2.3 Tracer samples may be measured at a single location by taking individual samples (grab samples) at a number of distinct locations, or by drawing samples from a number of locations through a common network (multi-point sampling).

12.2.4 When multi-point sampling is used, place sensors at strategic points within the test structure and feed to a central measuring terminal. For methods that analyze air with a single measurement device, use a sampling network to bring blended air to the analyzer. A diagram of a sampling network and a sampling junction are shown in Figures 1 and 2. Note that if the dilution rate in different rooms or floors is different, samples drawn by this method yield air leakage rates slightly less than the true average rate. For example, if one of the rooms or floors is leaking air at twice the rate of the other (1 ACPH and 0.5 ACPH), analysis of the blended samples of the two will lead to an air leakage rate estimate about 4% lower than the true average rate.

12.3 Sampling for Container Method

12.3.1 Filling Initial Sample Containers - After adequate mixing of the tracer gas, an initial air sample container is filled for each floor of living space. If it is suspected that certain volumes of the building are not in perfect communication with each other, then separate air sample containers should be filled for each volume. This is accomplished by walking around the floor, filling the sample container by means of a small pump, or hand squeezing a plastic sample bottle or syringe. This will provide an integrated sample. The important criterion is that the air sample container must be filled slowly, thus ensuring that an integrated sample is obtained.

12.3.2 Label each air sample container as follows: Identification of the building (address), time of injection, time of sample, section of building from which sample was taken (first floor, basement, etc.), meteorological conditions, and indoor temperature. A suitable alternative procedure is to record these data on a log sheet and identify the samples by numbers corresponding to log entries.

12.3.3 Decay of Tracer Gas - Wait 1 hour for the tracer gas concentration to decay. Note the activities of occupants and the operating mode of mechanical equipment during this period.

12.3.4 Fill Sample Containers - Repeat the procedure in 11.3.3 at known intervals to obtain two or more additional samples of air for each floor of the building.

12.3.5 The procedures 12.3.1 through 12.3.4 are graphically shown in Figure 3.

12.4 Sampling for the Container Method with Automatic Syringe Samplers

12.4.1 A brief overview of the latest techniques used in the collection of air samples during tracer gas experiments indicates an evolution from simple, manual sampling to programmable, automated sample collection using advanced, multi-station samplers. The design and operation of microcomputer controlled sequential syringe samplers provides reliability, efficiency, and portability at a moderate cost.

12.4.2 In order to meaningfully interpret data from pollution monitoring programs, the accuracy, reliability, and reproducibility of sampling and measuring techniques become major areas of concern. Additional demands placed on sampling programs include

minimizing personnel and equipment requirements to meet specific measurement tasks, and low maintenance and replacement costs. Typical areas of interest are indoor residential and work atmospheres (Small, 1983; Spengler and Sexton, 1983; Berglund and Johansson, 1982), industrial environments, and studies concerned with transport and fate of air pollutants.

12.4.3 An automatic sampler commercially available from Scientific Instrumentation Specialists (Moscow, Idaho 208-882-3860) contains an advanced timing system which allows automatic collection of twelve sequential, time-averaged gas samples. Rack and pinion gears driven by a stepper motor mechanically actuate each syringe. In operation, the syringe plunger remains stationary while the rack and pinion drive gradually extends the syringe body. At the end of travel, the syringe needle drives into a silicone septum, and power transfers to the next syringe. A digital clock, controlled by a quartz crystal oscillator governs the operation of the sampler. The overall time accuracy is better than + 0.001% and the station-to-station sampling time reproducibility is about + 0.01%. The time base interval (2-8 minutes) is internally selectable. An operator can pre-program the unit up to 15 days ahead of the actual operation, locate it on a suitable site, and leave it unattended. The sampler will start collecting sequential, time-averaged samples (each ranging from 2 minutes to several hours) at the pre-selected time, and upon collection of each sample, seal the syringe needle to prevent diffusion or sample contamination. The unit can be very quickly turned around for another sampling cycle. A rechargeable battery, which allows up to 50 hours of continuous operation, assures portability. An optional 115/230V A/C power supply kit is available. The unit is enclosed in a sturdy aluminum case, secured with two key locks, and easily portable by one person as the overall weight is approximately 13.5 kg, as illustrated in Figure 4.

12.4.4 For collection of SF_6 air samples, polyethylene, glass, or stainless steel syringes are recommended.

12.5 Sampling Method for Large Buildings

12.5.1 Residential infiltration measurements utilizing tracer gas are relatively straightforward to accomplish. Generally, a small amount of tracer gas is released in the structure and either the central heating system or a few optimally placed fans are used to assure a homogeneous tracer gas concentration in the structure. After this, the decay in tracer gas concentration as a function of time is monitored. In the case of electronegative gases such as SF_6 and the halocarbons, the monitoring instrument of choice is a gas chromatograph equipped with an electron capture detector. By repeating this procedure a number of times, it is possible to characterize the effects of climatological (temperature and wind) and structural (walls, windows, floors, ceilings, doors, etc.) factors on the infiltration rate.

12.5.2 Approaches are not so straightforward for large buildings. The sheer volume of the building indicates that a simple tracer release/sampling operation may not provide data which are valid for the structure as a whole. Two general approaches, however, can be undertaken. If one is more concerned about the relative contribution of a given floor to total structure infiltration (as would be the case in deciding on a retrofitting program), it

is generally sufficient to perform measurements in a manner similar to that for residential structures for each floor. An anomalously high ACPH for a given floor would imply that retrofitting should concentrate on this floor.

12.5.3 A useful improvement of this established technique is the use of multiple tracer gases to characterize air exchange between the floor immediately above and below the floor being studied. By releasing three different tracer gases on three consecutive floors and monitoring their relative concentration decays with time on all three floors, one can completely characterize infiltration across the floor ceiling and external envelope of the middle floor. This technique is identified as the "sandwich approach" and depicted in Figure 5.

12.5.4 On the other hand, to characterize the total infiltration of a large structure, it is necessary to provide a tracer supply and sampling network. In this technique (identified as the "simultaneous approach"), each floor is provided with the same tracer gas and sampled independently of all other floors. As shown in Figure 6, flexible tubing is run to each floor generally through the heating/ventilating of air-conditioning ducting or the service channel in a particular building. Sampling and gas injection are performed at one central location within the structure. Actual installation details are strongly dependent on the physical characteristics of each individual building.

12.5.5 The "simultaneous approach" allows one to obtain individual decay rates for each floor at approximately the same time. Suitable averaging then provides the average infiltration rate for the structure, thereby allowing one to study systemic variations in infiltration rate due to temperature, wind, or other factors.

13. Analytical System

13.1 Samples analyzed for SF_6 during tracer release projects use gas chromatographs with an electron capture detector. In practice these instruments should be measurement-specific units optimized for SF_6 or other selected gaseous tracers.

13.2 The SF_6 concentration can be determined by on-site monitors or in the laboratory by transporting the air sample in a suitable container.

13.3 If the automatic syringe samples (Section 11) are utilized, the samples can be injected directly into the gas chromatograph.

13.4 Any gas chromatograph with an electron capture detector can be utilized, however, tracer gas monitors specifically optimized for sulfur hexafluoride are commercially available from Systems, Science and Software (S-Cubed, La Jolla, CA; Telephone: 619/453-0060).

13.4.1 Tracer gas monitors designed and manufactured by Systems, Science and Software (S-Cubed) are capable of providing measurements of unusual sensitivity (few ppt for SF_6). Parts per trillion identification allows remote detection with a minimum of tracer gas discharge. A unique feature of the S-Cubed tracer gas monitors is the use of a gated LED display which outputs values characteristic only of the tracer gas being monitored. Spurious, anomalous, or additional chromatographic peaks are not outputted; hence, confusion over the identity of a given peak cannot occur.

13.4.2 Functionally, the monitor is a measurement specific gas chromatograph with an electron capture detector. This type of detector utilizes the high electron affinity of gases with halogen group elements to provide a measurable signal. Sulfur hexafluoride is such a gas and is an ideal tracer because it is transported and dispersed exactly as other atmospheric gases.

13.4.3 The heart of the instrument, as discussed previously, is the GC column. It separates the various gaseous components of a sample by selectively slowing down some gases relative to others. The column can be thought of as a device to elute the distinct components in a gas sample in a definite order. In the case of monitoring for SF_6 only, the column material is 5A Molecular Sieve (synthetic zeolite). Columns constructed with this material possess the unique property that SF_6 is eluted prior to oxygen. In making low level tracer determinations, this property allows easy identification of a small SF_6 peak due to the absence of an uncertain baseline disturbed by the relatively high amplitude signal corresponding to an oxygen peak.

13.4.4 For field tracer gas projects, the S-Cubed Model 215AUP Environmeter has been repeatedly selected to serve as the primary instrument. The reasons for this choice in preference to other units are:

- Instrument is designed and built for field atmospheric tracing applications (Unit is not a converted or modified laboratory bench GC).
- Monitor is portable and self-contained (power supply, carrier gas and signal output display are on-board).
- Unit has range selectable capability; peak-holding digital display of signal output is directly related to SF_6 concentration.
- Rotary shear valve with a constant volume sample loop insures consistent and reproducible sample loadings with syringe injection (grab samples) or use of a remote sampling wand.
- Monitor contains printed circuit electrometer and pulse drive circuitry for low noise electronic functions, reliability and ruggedness.
- Unit is optimized for detection of SF_6 over the range 10^{-9} to 10^{-12} parts SF_6 per part air.
- Detector cell design (concentric foil and collector geometry), ionization source (tritiated-titanium foil) and pulse drive circuitry provide three decade linear dynamic range. (Unit does not require pulse counting or other output signal conditioning).
- Unit is easily operated by non-professional personnel; it does not require operation by or supervision of an analytical chemist.
- Individual calibration curves for each operating range are provided with the unit.
- Unit complies with U.S. Nuclear Regulatory Commission or Agreement States health safety requirements for sealed radioactive sources; no film badges required.
- Transfer, possession and use of unit authorized under a general distribution radiation license. (Eliminates customer filing for a specific radiation license).

14. Calibration

14.1 State the method of calibration of the gas analyzer. If the analyzer is not provided with a manufacturer's calibration, perform an actual calibration. Use standard mixtures of at least two different concentrations in the range anticipated in an actual test, unless manufacturer's specifications allow single point calibration.

14.2 Instrument calibration should be performed on a regular basis, i.e., monthly, weekly or when in the field on a daily basis (pre- and post-test measurements). This activity uses calibration gases (SF_6 in dry nitrogen or pre-purified air). Six calibration standards are used at the analyzer manufacturing site when the initial calibration curve is generated. For field use, one, or at most two, calibration concentrations are all that are required. A mid-range standard, or two standards spanning the measurement range of interest is sufficient in most cases. However, if six point calibration is desired, gases could be maintained in the following SF_6 concentrations: 5×10^{-9}, 1×10^{-9}, 5×10^{-10}, 5×10^{-11}, 1×10^{-11}, and 5×10^{-12}. Supplementing this activity, daily pre- and post-test ambient background measurements should be made in the release area to ascertain the magnitude of this condition on the specific tracer gas being released.

15. Calculations

15.1 Calculations for On Site Method

15.1.1 Rearrange Equation 1 (Section 11.1.1) as follows:

$$I = (1/t)\ln(C_0/C) \quad (2)$$

where:
C = measured time-dependent concentration
C_0 = concentration at $t = 0$
I = air change rate
t = time

Equation 2 is the starting point for several means of calculating air change rate from concentration and time measurements.

15.1.2 Graphical Method - Plot the natural logarithm of concentration on a linear scale against time in hours on a linear scale. The measurements should fall on a straight line with time, provided the air change rate remains constant. Scatter of points is expected and a straight line may have to be faired in the "best fit" sense. A minimum of three points over 1 hour should be used to determine this straight line.

15.1.2.1 On the straight line determined in 14.1.2, choose two points with coordinates (C_1, t_1) and (C_2, t_2) where C_1 is the concentration at time i. Calculate I, the air change rate, as follows:

$$I = (\ln C_2 - \ln C_1)/(t_2 - t_1) \quad (3)$$

This technique is shown in Figure 7.

15.1.2.2 This graphical method lends itself well to field study of the data, since it is easy to plot the log of concentration as a function of time. It is less sensitive to errors in concentration than other methods. It has the further advantage that a graph provides a visual display of any departures in the exponential decay law. So long as the data fall on a reasonably straight line, one has confidence that the data obtained are valid within the assumptions necessary for the validity of the tracer dilution method. One caveat that should be observed during any measurement interval is that the data points used in determining an air leakage rate should encompass the mean winds observed during the course of the measurement.

15.1.2.3 When many data points are obtained, a least-square computer program is used to calculate a "best fit" to the straight line.

15.1.3 Finite Difference Method - Calculate the air change rate after each sampling using the finite difference form of Equation 2 as follows:

$$I = L/V = 1/(t_{i+1} - t_1) \ln C_1/C_{i+1} \quad (4)$$

where:
L = leakage rate
V = room volume
t_1 = time at "i"th interval
C_1 = tracer concentration at "i"th sample interval

For measurement over N sampling intervals, form a mean and standard deviation as follows:

$$\text{Mean } I = T = (1/N)I$$

$$\text{Standard Deviation} = S_1 = [I^2 - (I)^2/N]/[N - 1]$$

The air change rate, I = L/V, is "best fit" to the sample values of this parameter. The best fit for I is the mean, and is determined from the test data in accordance with Equation 5. This finite difference method has the advantage of simplicity, but it is very sensitive to errors in concentration or to the effects of poor mixing, especially when short sampling intervals are used.

15.1.4 Decay Time Method - Concentration decay usually occurs quickly; this allows for a rapid means of estimating I. For example, with time measured in minutes, the time for one half the initial concentration to decay is noted as $t_{\frac{1}{2}}$ and the I estimate is given by $41.59/t_{\frac{1}{2}}$. Similar ratios are given for other decay fractions and are shown in Table 3. These ratios are simply computed for C/C_0 ratios of 3/4, 2/3, 1/2, etc. The measurer has to record the time that a desired ratio is encountered.

15.2 Calculations for the Container Method

Determination of Tracer Gas Concentration - Tracer gas concentrations are determined in an off-site laboratory using gas monitor equipment. The air leakage rate I is then

determined from Equation 2. For periods from 1 to 2 hours, Equation 2 is an accurate relation for determining the air exchange.

16. Records and Reports

The report should include the following information. Include as much of this information as possible to facilitate comparison with other data at a later time.

16.1 Measurement Characterization

- Air Mixing - method of initial mixing and method of maintaining mixing during the measurement if one is used
- Air Sampling - location of sampling site, sample interval, initial sample time, and method of sampling
- Tracer Gas - type, initial concentration, method of introduction
- Detector - type and method of calibration
- Type of Calculation - finite difference, decay time, graphical, least square.

16.2 Meteorological Conditions

- Location and height of meteorological measurement
- Wind speed and direction (both maximum and average)
- Temperature and measurement technique
- Barometric pressure and measurement technique
- Relative humidity or wet bulb temperature

16.3 Test Space Characterization

- Structure Type - residential, commercial, industrial, other
- Location of structure relative to other structures (give type) and roadways
- Location of structure relative to surrounding terrain (give type, that is, gullies, mountain, mounds, cliffs, etc.)
- Structure orientation and elevation relative to other structures, roadways and surrounding terrain
- Windows - type, dimensions, number, and location in test space
- Walls - interior and exterior
- Leakage - noticeable areas
- Location of chimneys, vents, and other such specified opening
- Type and capacity of heating, ventilation, and air-conditioning systems

16.4 Test Space Operating Characteristics

- Doors - open or closed
- Windows - open or closed
- HVAC System - on or off
- Vent Fans - on or off
- Special Circumstances or Characteristics During Test - occupied, unoccupied, ingress, egress

- Indoor temperature and measurement technique
- Relative humidity and measurement technique

17. Performance Criteria and Quality Assurance

17.1 General

17.1.1 At present, insufficient data exist for purposes of precision and accuracy determination. A reasonable estimate of the uncertainty in a given air change rate determination is about 10% or less.

17.1.2 Note that the air change rate is a strong function of indoor-outdoor temperature difference and wind speed and direction. When interpreting or comparing air change rate data, the fact that a pressure and temperature dependence does exist should be considered. It can have a strong effect on the results.

17.1.3 Integral to all SF_6 tracer gas acquisition, release, field sample acquisition and tracer gas analyses, established quality control methods should be applied. This activity reflects: use of SF_6 and carrier gases which conform to manufacturers' specification; use of components and materials that are compatible with SF_6; use of standardized field operating procedures; and, the comprehensive documenting of test data.

17.2 Instrumentation

17.2.1 Automatic syringe sampler - The sequential tracer gas samplers have proven extremely effective and reliable in a variety of atmospheric tracer field studies. The samplers have been used to collect fifteen minute, thirty minute, sixty minute, or longer average air samples in a number of different environments. Data return rates of 92%, 95%, and 97% have been reported. These results and investigations are good indicators of the usefulness, flexibility, and reliability of the samplers. In particular, the high degree of success (>90% in all documented cases) points to the reliability of the sequential syringe samplers.

17.2.2 Tracer Gas Monitors

17.2.2.1 To complement the comprehensiveness of the gas chromatographic measurements, instrument calibration runs should be performed on a regular basis, i.e., monthly, weekly, or when in the field on a daily basis (pre- and post-test measurements). This activity uses calibration gases (SF_6 in dry nitrogen or pre-purified air). Section 14 discusses calibration. Supplementing this activity, daily pre- and post-test ambient background measurements should be made in the release area to ascertain the magnitude of this condition on the specific tracer gas being released.

17.2.2.2 In practice, the SF_6 analyses from the 1-hour time-averaged sequential samplers are tabulated. The results of analysis for the instantaneous grab samples are recorded on the field test sheets, i.e., aligned to site, location, and time listings. In addition, all gas chromatographic analyses (sample measurements, background concentration tests and calibration runs) are generally recorded on strip charts (chromatograms).

3 6 3

18. Acknowledgements

A special thanks is extended to the following persons for providing advice and technical information pertaining to this method.

William Turner
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7. Krasnec, J. P., and Denning, D. E., "Application of Automated, Multi-Station Sequential Samplers in Atmospheric Tracer Studies," presented at the 7th World Clean Air Congress, Sydney, Australia, 1986.

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Table 1. Gases and Techniques for Tracer Dilution Method (1)

Tracer	Measuring Apparatus	Maximum Allowable Concentration in Air (vol/vol)	Maximum Detectable Concentration, ppm	Toxicology
Hydrogen	Katharometer	4% (lower explosive limit)	200	nontoxic
Helium	Katharometer		300	nontoxic
Carbon monoxide	infrared absorption	50 ppm	5	combines with hemoglobin to produce asphyxia
	gas chromatograph with gas flame ion detector		0.4	
Carbon	infrared absorption	5000 ppm	1	nontoxic
	thermal conductivity detector		70	
Sulfur hexafluoride	electron capture gas chromatograph	1000 ppm	0.000002	nontoxic
Nitrous oxide	infrared absorption	25 ppm	1	nontoxic
Ethane	flame ionization detector	3% (lower explosive limit)	5	nontoxic
Methane	infrared absorption	5% (lower explosive limit)	5	nontoxic

Table 2. Atmospheric Constituents (1)

Compound	Average Tropospheric Background Concentrations, ppm	Typical Indoor and Urban Ambient Concentrations, ppm	Anthropogenic Sources
H_2	0.5	0.5	---
He	5.2	5.2	---
CO	0.1	5-50	combustion
CO_2	320	30-5000	combustion
N_2O	0.3	0.3-several ppm	combustion
Ethane	1.5×10^{-3}	0.1	incomplete combustion
Methane	1.5	2-5	incomplete combustion
SF_6	10^{-3}	10^{-5}	telephone switching stations

Table 3. Decay Ratios to Compute ACPH

Concentration Ratio	Decay Time, min.	I, ACPH
3/4	$t_{3/4}$	$17.26/t_{3/4}$
2/3	$t_{2/3}$	$24.33/t_{2/3}$
1/2	$t_{1/2}$	$41.59/t_{1/2}$
1/3	$t_{1/3}$	$65.92/t_{1/3}$
1/4	$t_{1/4}$	$83.18/t_{1/4}$
1/8	$t_{1/8}$	$124.77/t_{1/8}$

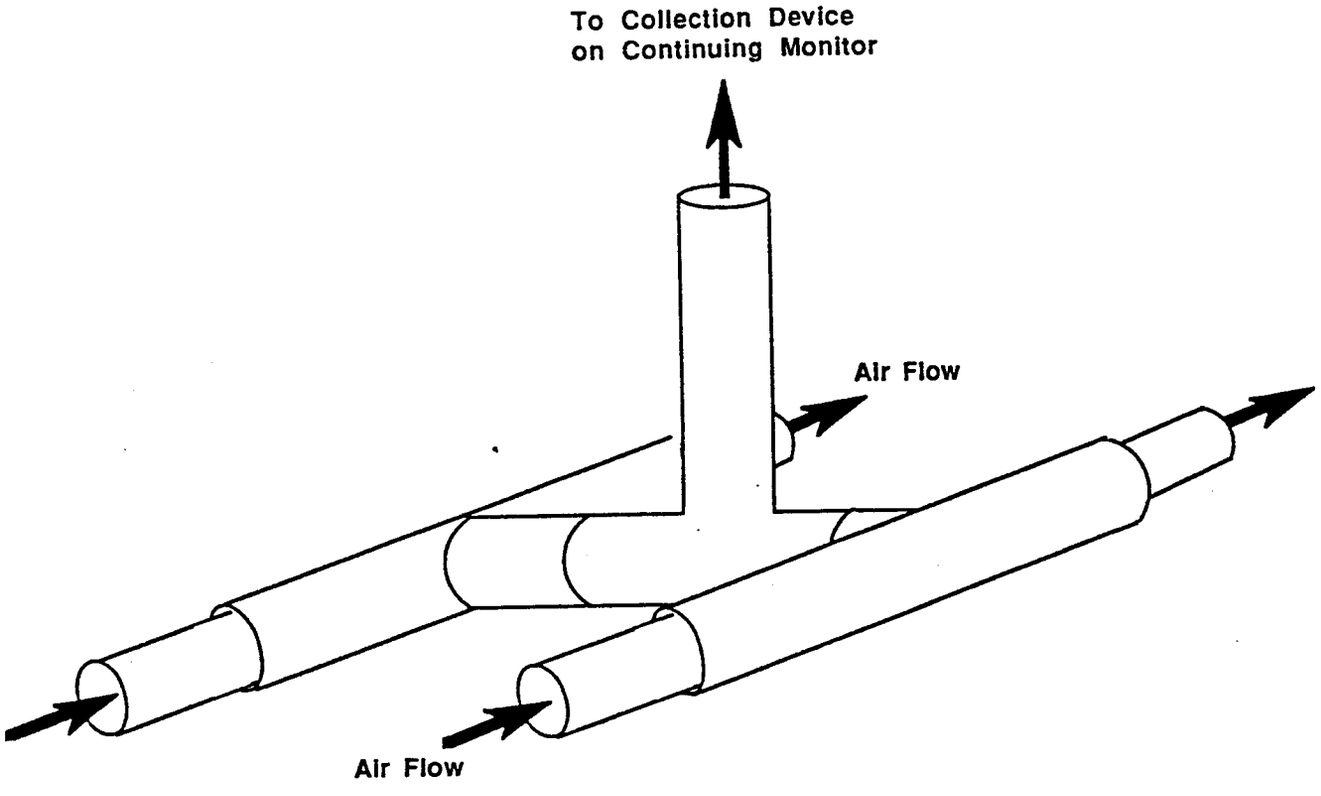

Figure 1. Four-Point Sampling Junction

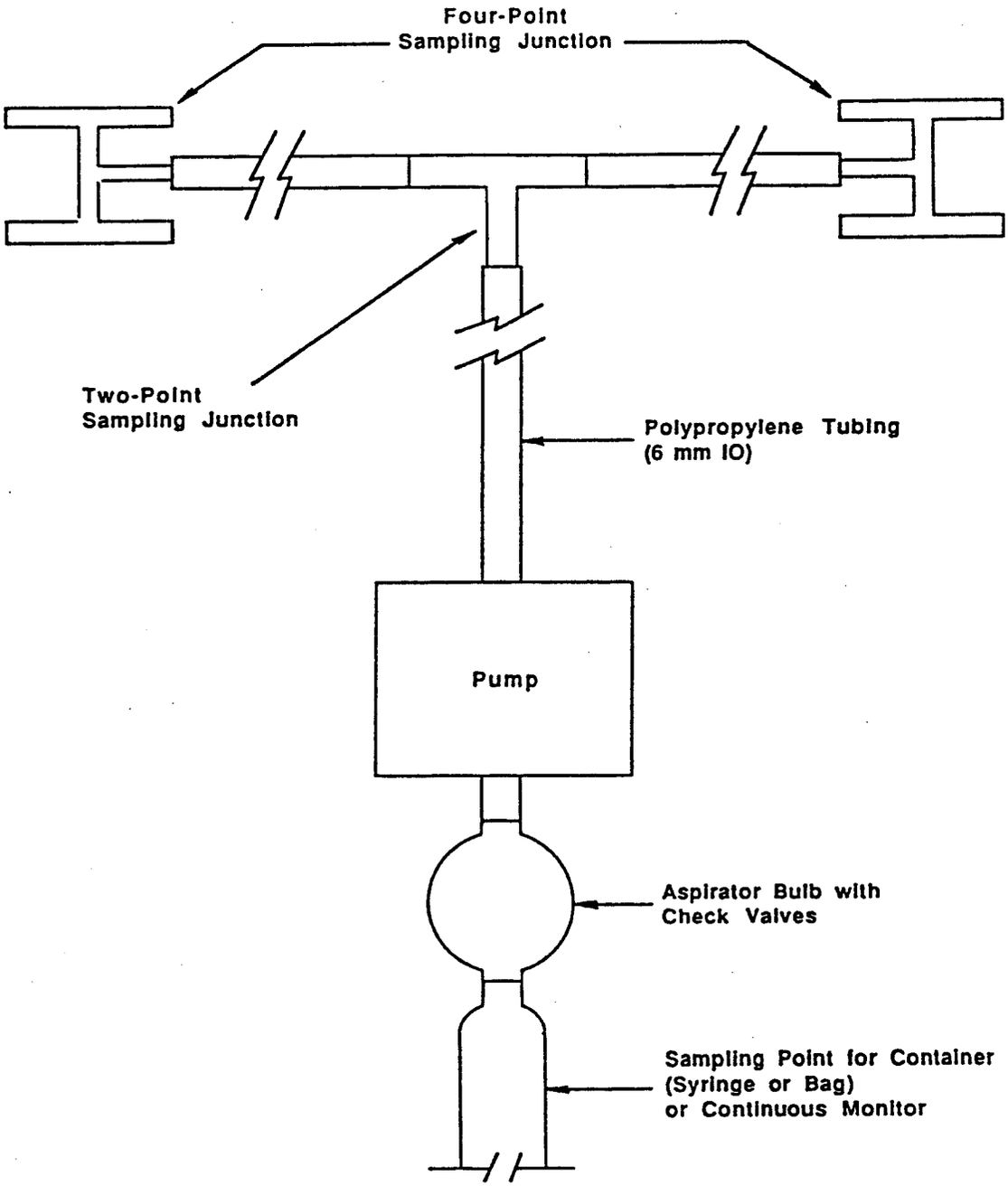

Figure 2. Symmetrical Light-Point Sampling System

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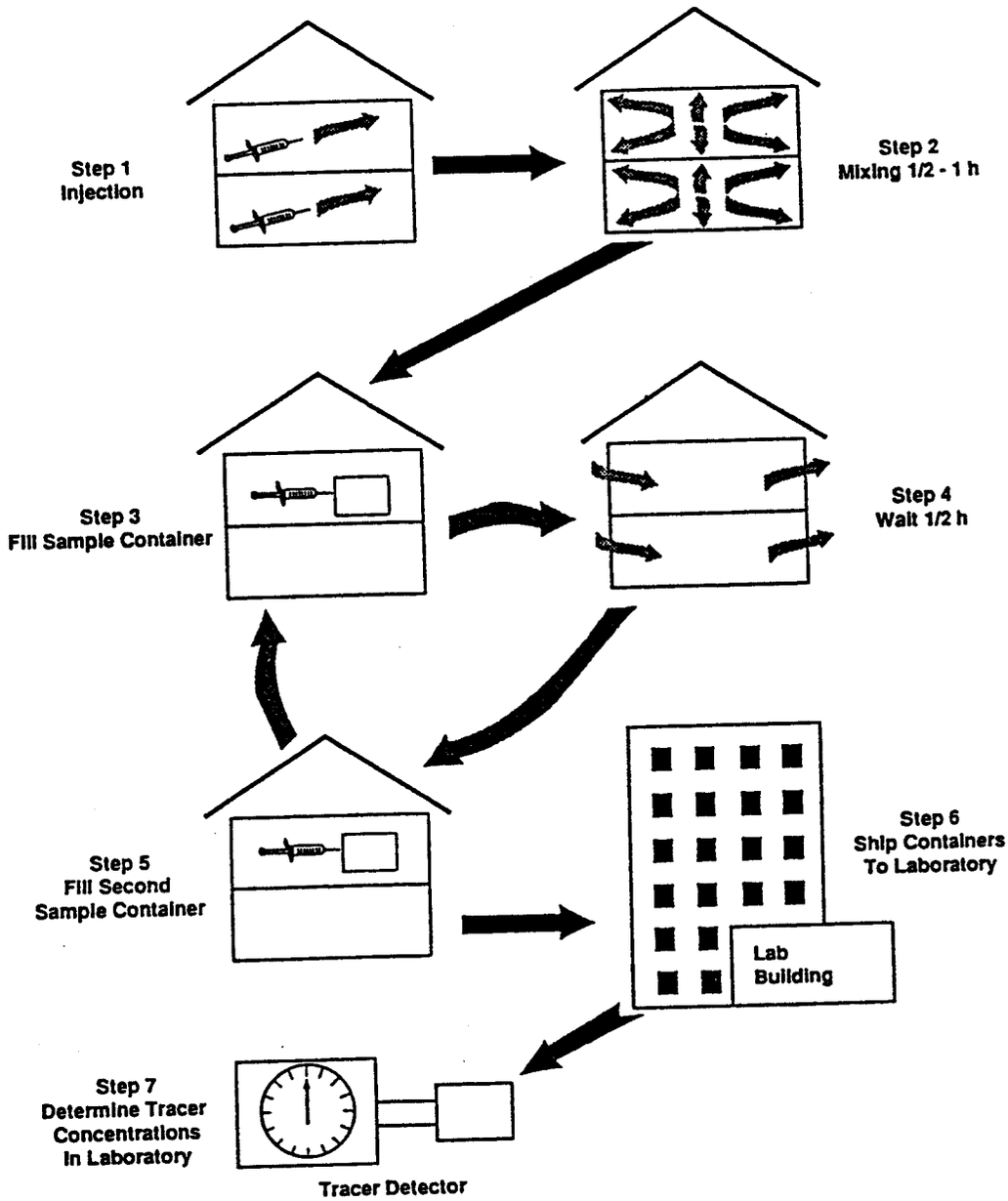

Figure 3. Procedure for Measuring Air Leakage Rate Using Sample Containers

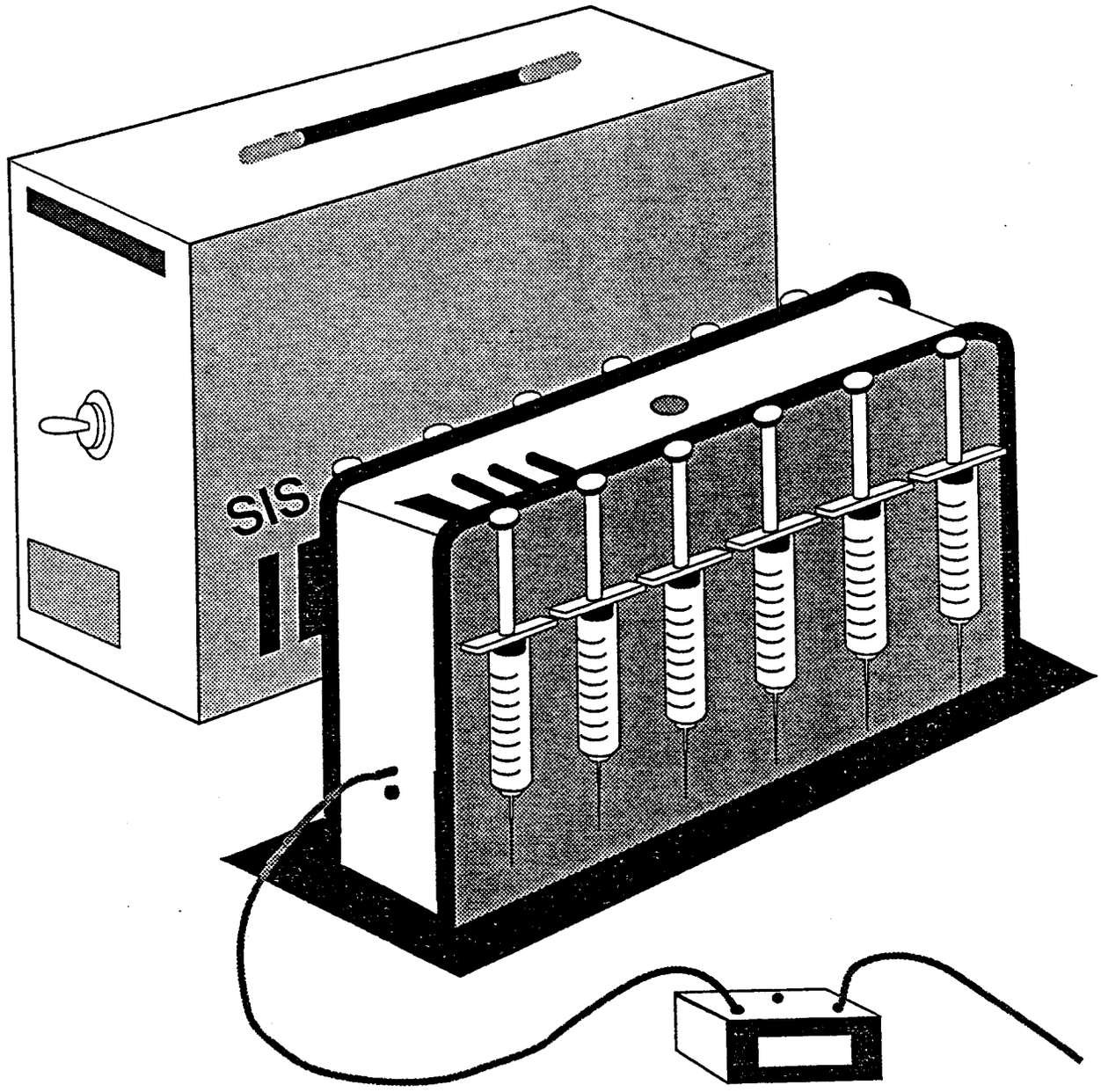

Figure 4. SIS Series 12A Multi-Station Sequential Environmental Gas Sampler

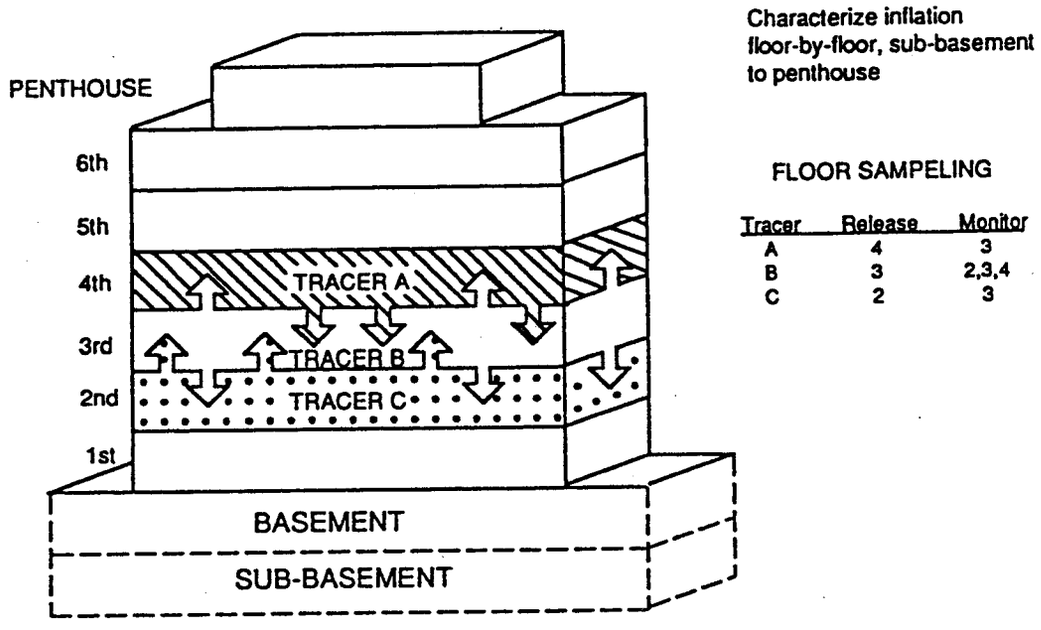

Figure 5. Multiple Tracer "Sandwich Approach" for Characterizing Air Infiltration in High-Rise Buildings

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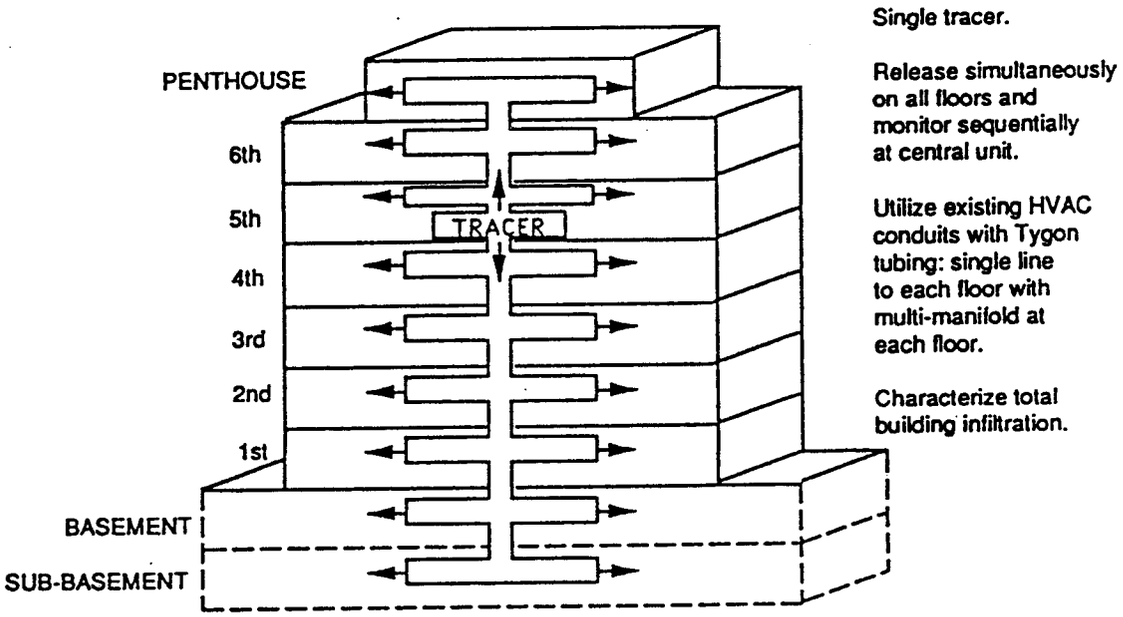

Figure 6. Single Tracer "Simultaneous Approach" for Characterizing Air Infiltration in High-Rise Buildings

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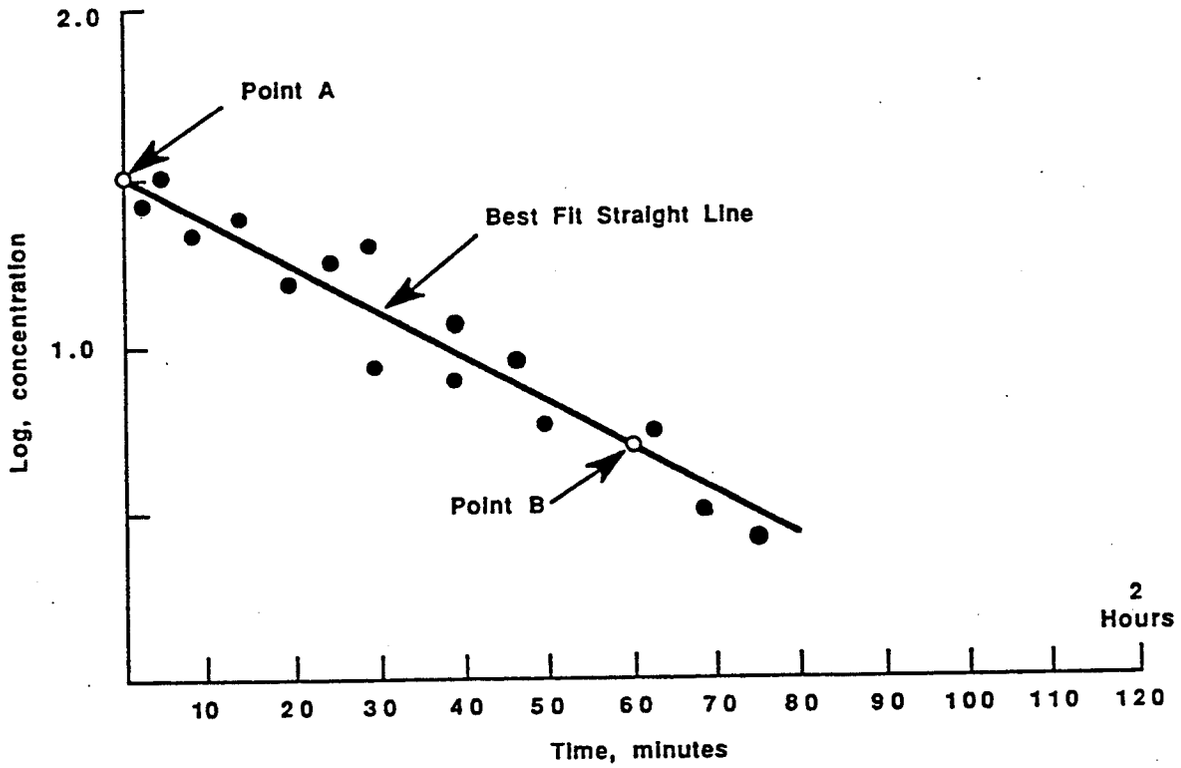


● Data Points (Natural Logarithm of Concentration Values)

○ Concentration Points 60 Minutes Apart

For $C_A = 5$ and $C_B = 2$; the exact ACH = 0.916

Graphically

$ACH = \ln C_A - \ln C_B$

$= 1.6 - 0.7$

$= \underline{0.9}$

Point A = Start
Point B = 60 Minutes

Figure 7. Graphical Determination of Air Change Rate

Chapter IP-5

DETERMINATION OF NITROGEN DIOXIDE (NO_2) IN INDOOR AIR

- **Method IP-5A - Continuous Luminox Monitor**
- **Method IP-5B - Palmes Diffusion Tube**
- **Method IP-5C - Passive Sampling Device**

1. Scope

This document describes three methods for determination of NO_2 in indoor air. An active sampling device and two passive sampling devices are discussed. The monitoring of nitrogen dioxide (NO_2) at sub-ppm and low-ppb levels is of primary concern in indoor, nonindustrial locations such as the home. The trend toward much more airtight homes which began during the energy crisis of the early 1970s has caused concern among health experts about increased levels of NO_2 in indoors. Nitrogen dioxide is a combustion product found in houses mostly due to gas or wood burning stoves, heaters and/or fireplaces. Hazardous concentrations can occur in closed environments such as kitchens and family rooms where ventilation is minimal.

2. Applicability

2.1 In the past, active sampling devices have been the method of choice for collection of NO_2 from indoor air. More specifically, Compendium Method IP-5A uses a real-time, direct measurement monitor to detect the presence of NO_2 involving the detection of fluorescent energy emitted from the reaction of NO_2 with a Luminol solution (5-amino-2,3-dihydro-1,4 phthalazine dione). As illustrated, real-time, direct measurement monitors are active sampling devices that require a mechanical pump to move the sample to the collection medium. Consequently, the sampling devices require some form of power to drive the pump and are usually heavy and bulky in appearance.

2.2 In recent years, interest has been increasing in the use of diffusion-base passive sampling devices (PSDs) for the collection of NO_2 in indoor air. PSDs are more attractive for indoor air because of their characteristics of small size, quiet operation (no pump), and low unit costs.

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

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

2.5 Compendium Method IP-5B and Method IP-5C use the diffusion principle for monitoring NO_2 in indoor air. Method IP-5B uses the Palmes tube, while Method IP-5C utilizes the passive sampling device (PSD).

Method IP-5A

DETERMINATION OF NITROGEN DIOXIDE (NO_2) IN INDOOR AIR USING A CONTINUOUS LUMINOX MONITOR

Method IP-5A

DETERMINATION OF NITROGEN DIOXIDE (NO_2) IN INDOOR AIR USING A CONTINUOUS LUMINOX MONITOR

1. Scope

1.1 Nitrogen dioxide (NO_2) is a combustion product found in houses mostly due to gas or wood burning stoves, heaters and/or fireplaces. Hazardous concentrations can occur in closed environments such as kitchens, and family rooms where ventilation is minimal.

1.2 Described herein as a method by which nitrogen dioxide can be sampled and analyzed in the air. The detection of NO_2 by chemiluminescence takes place between gas and liquid phases whereby the contact of NO_2 gas with a solution of Luminol causes direct oxidation of the solution.

1.3 The following method describes an instrument using chemiluminescence detection for the determination of NO_2.

2. Applicable Documents

2.1 ATSM Standards

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

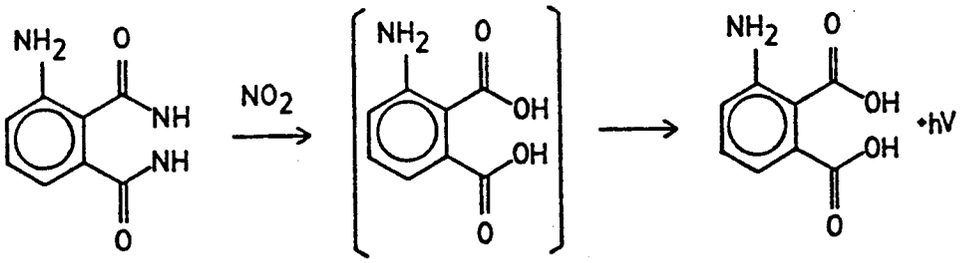
2.2 Other Documents

U.S. Environmental Protection Agency Technical Assistance Document (1)
Laboratory and Indoor/Ambient Air Studies (2-10)
Other Documents (11-12)

3. Summary Of Method

3.1 The instrument monitors NO_2 gas concentrations by the real-time, direct measurement of the fluorescent energy emitted from the reaction of NO_2 with Luminol solution (5-Amino-2,3 dihydro-1,4 phthalazine dione).

3.2 The LMA-3 NO_2 analyzer operates by detecting the fluorescent energy produced when NO_2 reacts with a solution of Luminol. In operation, sampled air is drawn through the instrument and across a fabric wick wetted with the Luminol solution. The solution is continuously replenished at the top of the wick and removed at the bottom by a small peristaltic pump. If the sampled air contains NO_2, the Luminol solution is oxidized, producing fluorescent energy according to the reaction shown on the next page.



Luminol Solution

Luminescence Emission

3.3 To detect the release of energy (hv) from the reaction, a photomultiplier tube (PMT) is positioned to view the central portion of the wick. The signal from the PMT is directly proportional to the NO_2 concentration in the sampled air. Unlike other chemiluminescent NOx detectors, the Luminox monitor measures NO_2 directly without prior conversion of NO_2 to NO. The operational block diagram for the LMA-3 NO_2 analyzer is illustrated in Figure 1.

3.4 A 500-mL polypropylene bottle serves as a reservoir to supply fresh Luminol solution continuously through the instrument. The solution is moved from the reservoir to the reaction chamber by a peristaltic pump operating at about 0.05 mL/min. The wick material is kept saturated while 1.5 L/min of sample air is drawn over the surface where reaction takes place. The emitted light from the reaction of NO_2 and Luminol is measured by a photomultiplier tube situated in front of the chamber. After leaving the wick material, Luminol is transported via the peristaltic pump into a reservoir for spent solution. Sample air drawn from the chamber and exhausted to the rear of the instrument by a small air pump.

4. Significance

4.1 Nitrogen dioxide is a reactive gas product of combustion. Household combustion sources include gas stoves, gas heating, wood burning stoves, furnaces and fireplaces. NO_2 levels in indoor air are usually equal to or lower than outdoor levels. But if combustion sources are present, then NO_2 levels can exceed outdoor concentrations. The National Ambient Air Quality Standard (NAAQS) for NO_2 for a 24-hour average is 100 $\mu g/m^3$ (~53 ppb).

4.2 Numerous investigations have documented that NO_2 concentrations may be substantially greater indoor in homes that have unvented combustion sources. Specifically, increase levels of NO_2 may be encountered in homes with gas heating, gas stoves with pilot lights and cigarette smoke.

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4.3 NO_2 has been known to cause acute lung damage at high concentrations. Concentrations at five parts per million (ppm) can cause respiratory distress. However, data on health effects of NO_2 at concentrations commonly encountered in the residential environment (500 ppb to 1 ppb) is unknown. In experimental models at these NO_2 levels, reduced efficiencies of lung defense mechanism, effects on mucociliary clearance, alveolar macrophages and the immune system have all been documented (13-14).

4.4 Consequently, the need exists for a continuous, extrasensitive NO_2 analyzer which is reliable, accurate, portable and suitable for indoor air measurements.

4.5 Historically NO_2 has been determined by colorimetric methods, and chemiluminescence methods using catalytic oxidation whereby the catalytic converter converted NO_2 to NO. In turn, NO would react with ozone and cause measurable chemiluminescence. Consequently NO would interfere with NO_2 analysis.

4.6 By using Luminol in an alkaline solution, gaseous NO_2 at atmospheric pressure reacts with the Luminol to also produce chemiluminescence. This reaction has little NO interference.

4.7 Consequently, Scintrex Ltd. applied this technology to a continuous NO_2 analyzer capable of monitoring down to the low ppb range. Recently, the monitor was extensively evaluated (10). Table 1 outlines the results of the laboratory evaluation.

5. Definitions

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

5.1 Chemiluminescence - the emission of radiation from a molecule which, after being in a vibrationally excited state, returns to its ground state.

5.2 Fluorescence - the process by which electromagnetic radiation of one spectral region is absorbed and radiated as nonthermal radiation at other wavelengths, usually longer.

5.3 Luminol - a modified solution of Luminol (5-amino-2, 3-dihydro-1,4 pthalamine dione), NaOH, NA_2SO_3 and alcohol dissolved in deionized water.

5.4 Precision - the ability of an analyzer to produce a uniform response with repeated measurements under identical conditions. The analyzer's precision is estimated by the standard deviation of a set of measurements at a uniform pollutant concentration.

5.5 Interferents - Any chemical compound which produces a response in or change of response in the analyzer is an interferent. Widely occurring compounds which may interfere include water vapor (H_2O), CO_2, oxygen (O_2), ozone (O_3) and peroxyacetyl nitrate (PAN). These compounds are known to quench various fluorescent and photochemical processes.

5.6 Limit of detection (LOD) - a limit of detection is defined as the minimum signal that may be distinguished from the background signal with a given confidence level. An LOD equal to three standard deviations of the signal for clear air (6) has been accepted.

5.7 Noise - noise (7) is the standard deviation of twenty-five consecutive measurements of zero air taken at two-minute intervals.

5.8 Lower detection limit (LDL) - lower detection limit (7) is specified as "the minimum pollutant concentration which produces a signal of twice the noise level."

5.9 Drift - drift (7) is specified as the difference between two measurements taken at the beginning and end of a specific test period (12-hour or 24-hour period).

6. Interferences

6.1 Historically, ozone has been reported in the literature (7,8) as an interference as a quenching agent to the ultraviolet light given off from the chemical reaction. An O_3 trap has been added to the analyzer to eliminate this interference.

6.2 PAN has been documented (7,9) as an interference in instruments employing the Luminol reaction. Reported relative response of the LMA-3 analyzer has been both qualitative and less than quantitative. A recent laboratory evaluation (10) indicated an average relative interference response of 0.62.

6.3 In a recent laboratory test (10), the LMA-3 analyzers illustrated measurable interference from CO_2 of 1 to 2 ppb at an NO_2 concentration level of 25 ppb (or a 5 to 7% error).

6.4 Oxygen is an effective quencher of fluorescent and photochemical reactions. Although the O_2 concentration in indoor air is largely constant and no O_2-dependent effect should be seen in the measurements, possible problems could exist during calibration. Laboratory evaluation (10) has indicated an analyzer response variation of approximately ± 0.6 ppb at an NO_2 concentration of 26.5 ppb (or 2% of the total response of the LMA-3 analyzer). Consequently, indoor air levels of O_2 should be contained as part of the calibration gas mixtures.

6.5 Water is a common interference for many fluorescent analyzers. In a recent study (10), results indicated an analyzer response variation of approximately -7 ppb at a concentration of 25 ppb of NO_2 (or a 29% error). However, since indoor air normally has a constant relative humidity, this should not affect monitor response during sampling. However, if calibration gases contain no moisture, then an error can be introduced into the analytical system. Each calibration point generated should contain approximate levels of water representing the indoor air parcel being sampled.

7. Apparatus

7.1 Sampling and Analysis

7.1.1 Chemiluminescent NO_2 monitor - Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, LMA-3 Part No. 856 000 or equivalent.

7.1.2 Rechargeable battery - back-up one 12 volt 1.5 amp-hr. gel cell. or 115 or 220 volt AC battery, best source.

7.1.3 Tubing - tubing for the liquid pump, 9.8 cm long for the waste line, 8.9 cm long for the feed line, Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 856 019 or equivalent.

7.1.4 Wick - wick for the monitor, Scintrex, Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 856 020 or equivalent.

7.1.5 Air line trap - trap protects the air pump from liquid infiltration, best source.

7.1.6 Filter cartridge - Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 200 213 or equivalent.

7.1.7 2 liter external reservoir kit - to reduce replenishing Luminol solution (optional), Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 856 018 or equivalent.

7.1.8 Carrying case - for portable operation, Scintrex Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, Part No. 856 014 or equivalent.

7.1.9 Calibrator - portable calibrator for LMA-3 monitor (optional). Provides a continuous supply of purge gas and a stable constant temperature environment for permeation device(s), Scintrex, Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, LC5-3 Luminox Calibration Source or equivalent.

7.1.10 Data logger - portable calibration controller (optional). Provides accurate dilutions of a gas standard using mass flow controllers and mixing chambers, Scintrex, Ltd., 222 Snidercroft Rd., Concord, Ontario, Canada, L4K1B5, 416-669-2280, LCC-3 Luminox Calibration Controller or equivalent.

7.2 Calibration

7.2.1 Flowmeters and controllers - In order to obtain an accurate dilution ratio, in the dilution method used for calibration, the flow rates must be regulated to 1% and be measured to an accuracy of at least 2%. The meter and controller can be two separate devices, or combined in one device. The user's manual for the meter should be consulted for calibration information. Additional information on the calibration of flow devices can be found in the Quality Assurance Handbook (15). If the calibration system uses the same type of flow meter (e.g. bubble flow meter, rotameter, mass flow meter, etc.), then no correction to standard temperature and pressure (STP) need to be made.

7.2.2 Mixing chambers - A chamber constructed of glass, Teflon®, or other nonreactive material, and designed to provide thorough mixing of NO_2 and diluent air for the dilution method.

7.2.3 Output manifold - The output manifold should be constructed of glass, Teflon®, or other nonreactive material, and should be of sufficient diameter to insure an insignificant

pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent indoor air from entering the manifold.

8. Reagents and Material

8.1 Luminol Solution

8.1.1 The Luminol solutions used by the LMA-3 NO_2 analyzer contains additives which enhance the response to NO_2, and reduce interferences from other gases such as ozone.
Note: The Luminol solutions are weakly basic and should be handled accordingly. Avoid contact with the eyes or prolonged contact with the skin. Wash with water after contact with the skin.

8.1.2 A variety of Luminol solutions have been formulated to give linear responses over different concentration ranges.
Note: The information supplied with each bottle will outline the range of linearity, rejection ratio for the ozone response as well as the PAN (peroxyacetyl nitrate) response for all of the available formulations at that time.

8.2 Calibration Gas

Note: In a recent laboratory test (10) O_2, CO_2 and water vapor were determined to cause interference to the monitor output; therefore, it is important to calibrate the LMA-3 analyzer with calibration mixtures containing indoor levels of these species.

8.2.1 Zero-air source - A source of dry zero-air that is verified to be free of contaminants that could cause detectable responses from the NO_2 analyzer will be needed. The zero-air must contain <0.1 ppb NO_2.

8.2.2 Calibration standard - NO_2 standards must be traceable (16) to a National Institute of Standards and Technology - Standard Reference Material (NIST-SRM) or a NIST/EPA approved commercially available Certified Reference Material (CRM). The NO_2 standards must be in air unless the dilution method is used. For dilution, NO_2 in nitrogen may be used if the zero-air contains O_2, CO_2 and H_2O similar to indoor air. An acceptable protocol for demonstrating the traceability of commercial cylinder gas to an NITS-SRM or CRM cylinder gas is provided in Section 14, reference 17. In order to establish a calibration curve and determine linearity of the LMA-3 analyzer, the calibration gas cylinder should correspond to 10, 20, 40, 60, and 80% of monitor full scale.

8.2.3 Span gas - pressurized cylinder containing NO_2 concentration corresponding to 80% of full scale, best source.

8.2.4 Flow control valves - used to regulate gas cylinder flow rate to analytical system, best source.

8.2.5 Multistage pressure regulators - standard two-stage, stainless steel diaphragm regulators with pressure gauges for gas cylinders.

8.2.6 Tubing - Polypropylene tubing to connect analyzer to gas cylinders when calibrating, zeroing, and spanning the instrument.

8.2.7 Thermometer - used to measure monitoring area temperature.

8.2.8 Barometer - capable of measuring barometric pressure of monitoring area.

9. Sampling System

9.1 Description

The LMA-3 NO_2 analyzer is contained in an instrument housing approximately 15" x 8" x 8" (20 x 22 x 38 cm). The instrument can be operated continuously on 110 VAC or for 2 to 3 hours with the assistance of an onboard battery. The monitor can operate at a range of either 0 to 20 or 0 to 200 ppbv, and can be connected to a strip-chart recorder or data acquisition system for permanent record of the NO_2 measurements.

9.1.1 Front Panel Controls (see Figure 2)

9.1.1.1 The power switch turns on the power to the electric and the liquid pump motor. When it is ON (upper position) the yellow LED above it will be illuminated.

9.1.1.2 The air pump switch turns on the air pump if the power is ON. A yellow LED indicates that the air pump is ON.

9.1.1.3 The backflush momentary push button initiates the backflush cycle. During the backflush, waste Luminol is pumped into the wick area to rinse out any residue, then it is pumped away. The cycle takes about 5 minutes. During this time the red LED above the backflush switch will light up. No readings may be taken during this period.

9.1.1.4 The battery charger is active any time the unit is plugged into line current. The yellow "battery charge" LED should be illuminated under this condition.

9.1.1.5 The battery low red LED indicates two warning conditions. If the unit is operating from the battery and the voltage drops below 11.6 volts, the LED will be illuminated. Secondly, if the unit is plugged in and the current acceptance of the battery exceeds 100 mA, the LED will come ON. The LED may be illuminated for a few minutes each time the unit is plugged into line current. This does not indicate a fault. It will stay ON for an extended period if the battery has been substantially discharged. If the unit is put into battery service before the light goes out, a full three hours of use should not be expected.

9.1.1.6 The three-position time constant switch is used to select 0.3, 1.0 or 3.0 seconds as the time constant for the last amplifier. The setting of 0.3 seconds provides the least amount of signal damping and is suitable for most applications. The slower settings may be selected if it is desirable to damp out noise in the signal originating from fluctuations in the NO_2 concentration, or from the instrument when measuring very low NO_2 mixing ratios.

9.1.1.7 The zero control is used to bring the displayed or output signal to zero when there is no NO_2 present.

9.1.1.8 The span control sets the photomultiplier tube high voltage (PMT HV) and hence the gain of the light detection system. It is used to change the displayed value or output voltage when a calibration source of known mixing ratio is introduced to the instrument.

9.1.1.9 The BNC type output connector provides an output voltage for use with a chart recorder or other data acquisition system. Each volt at this output corresponds to

100.00 in the display range 200, or to 10.000 in the display range 20. The output voltage extends to 5 volts even though the display shuts down above values of 2 volts.

9.1.1.10 This is a two-position toggle switch for selection of either 0 to 20 ppbv or 0 to 200 NO_2 range. This display is 4.5 digits so that the last decimal place represents 1 pptv when the instrument is in the 20 range. This display shows a single "+" sign at the left hand side when the input to the digital panel meter is above its acceptable range.

9.1.1.11 This is a three-position momentary toggle switch by which the input to the digital panel meter is chosen. If the unit is properly calibrated in the normal center position (signal), the NO_2 mixing ratio is continuously displayed. When the toggle is lifted up, the battery voltage is displayed. In order to give a true voltage reading, the battery charger is off line while this switch is held in the upper position. If the battery low light was ON due to high current acceptance, it will go out when the battery voltage is checked. When the toggle is held down, the photomultiplier high voltage will be displayed. The normal operating range for the photomultiplier is -400 to -800 volts.

9.1.1.12 The signal overload red LED indicates two fault conditions. If the light is ON steadily, then the first amplifier is overloaded. The second fault indication occurs when there is severe overloading at the first amplifier. The signal overload light will flash. This will usually be the result of the light leaking into the system from improper assembly after servicing.

9.1.2 Rear Panel Controls (see Figure 3)

9.1.2.1 These fittings are provided so that the user may attach larger fluid reservoirs for longer unattended use. They are not connected when the instrument leaves the factory.

9.1.2.2 Fittings are provided on the back panel for connecting tubing to and from the instrument. They are compression type fittings constructed on stainless steel with teflon ferrules. Suitable tubing sizes are 0.25 inch or 6 mm outside diameter.

9.1.2.3 Two access hole through the back panel are provided just below the Air Out connector. They are provided to make servicing of the wick area easier. These are normally closed with press-in chrome plated hole plugs.

9.1.2.4 This connector permits the external control of two of the LMA-3's functions: 1) operation of the air pump and 2) initialization of the backflush sequence. In addition, the circuit to the air pump indicator may also be controlled through this connector. The pin assignments are as follows:

Air pump live (A)
Air pump return (B)
Air pump LED live (C)
Air pump LED return (D)
LMA-3 supply (9.2 Volts) (E)
LMA-3 ground (F)
Ground for backflush trigger (H)
Input for backflush trigger (J)

When external control is not desired, the "shorting plug" must always be installed. The shorting plug connects pins A to B, C to D and H to J. For external control of functions

within the LMA-3 it is recommended that optical isolators or relays be used in order to avoid having to tie the grounds of the LMA-3 and the driving electronics together.

The following external functions are possible:

- Air pump control - Opening and closing the contact between pins A and B will turn the air pump OFF an ON, provided the air pump switch that is located on the front panel is turned ON.
- Air pump indicator control - Opening and closing the contact between pins C and D will turn the air pump LED OFF and ON provided the air pump switch that is located on the front panel is turned ON.
- External backflush control - For control of the backflush trigger, wire the switching device as follows: 1) pin E through a 100 k ohm resistor to normally open, 2) pin F through a 100 k ohm resistor to common, 3) pin H to common, and 4) pin J to normally closed. The switch may be held high between 20 microseconds and 10 seconds before going low again. This will put 4.6 Volts down pin H to trigger the backflush cycle. The front panel backflush control will still be usable if this wiring is used.

9.1.2.5 The BNC type output connector is provided for the convenience of the operator. It carries exactly the same signal as the Output connector on the front panel.

9.1.2.6 The power cord receptacle also carries the instrument's main fuse and a supply voltage selection card. Locate the power receptacle on the rear of the instrument. Slide the plastic window to the left to expose the fuse and voltage selector. Observe the number showing on the small circuit board which is now visible. This number should indicate the nominal value of the power supply to be used (i.e. 120 or 240 volts). If it does not indicate the proper voltage, pull it out and re-orient it so that the desired figure shows when the board is re-installed. There are also positions which indicate 100 or 220 volts. These are not used on this instrument. If they are selected, the power circuits will be supplied as if 120 had been selected (for 100) or if 240 had been selected (for 220). The instrument is shipped with the voltage selector in the 120 position and a 0.2 amp slo-blow fuse installed. To inspect or change the main fuse, pull the small lever marked "Pull Fuse".

Note: If 240 volt service is required the main fuse must be changed to 0.1 amp slo-blow. Four spare fuses are supplied with the instrument, two of each value. Once the proper voltage selection and fusing have been verified, the plastic window may be slid to the right and the power cord inserted in the receptacle.

9.1.2.7 The LMA-3 may be operated from lead-acid type batteries of larger capacity than the rechargeable batteries built-in to the instrument. The nominal voltage of the external battery should be 12 volts. When the plug is pushed into the jack, the internal battery is disconnected from the power circuit and the external battery takes its place. If the external battery is of much higher capacity, then the built-in battery charger will not provide enough current to recharge the battery in a reasonable amount of time. For this reason, large external batteries should be recharged separately.

Note: When connecting an external battery, make sure the LMA-3 is turned OFF and is not plugged in to line current. First, clamp the jaws onto the external battery (red to positive and black to negative) and then plug the cable into the back of the LMA-3.

9.1.3 Inside display area - The inside display area contains several distinct functional areas. They are:

- Detection assembly
- Liquid/air handling components
- Power supplies/signal processing

9.1.3.1 The detection assembly contains the photomultiplier tube (PMT), the air passage and wick plates and the liquid and air fittings.

9.1.3.2 Air passage plate - The function of this plate is to direct the sample air onto the wick. The air passage plate incorporates a window which admits light to the PMT detector. The air pathway in the plate is convoluted in order to stop ambient light from reaching the PMT detector.

9.1.3.3 Wick plate - The wick plate is fastened directly to the air passage plates. The wick itself consists of a strip of absorbent material held to the plate by bars at the top and bottom. The liquid fittings project from the left side of the detector assembly. The upper fitting carries a slow continuous feed of the Luminol solution to the top of the wick and the lower fitting carries away the expended solutions to a waste bottle. The air fittings face the rear of the instrument. The upper AIR IN fitting is oriented upwards to facilitate the attachment of the PFA Teflon® air tubing by means of a teflon compression fitting. The lower AIR OUT fitting is a simple nipple over which the tygon outlet tubing is pressed.

9.1.3.4 Liquid/air handling components - The miniature air pump is attached to the top right side of the instrument frame. The pump draws air through the air passage circuit and then exhausts the sampled air through the AIR OUT fitting located in the rear panel. A trap is provided in the air line to protect the air pump from liquid that may escape from the detector assembly as well as from particulates in the sample air. The trap is located between the detector assembly and the air pump and consists of two stages, a liquid trap and a particulate trap. The liquid trap is a round chamber, mounted high on the inside wall of the LMA-3, which captures by means of gravity any large amounts of liquid in the air line. The second trap is a disposable cartridge air filter, located beneath the liquid trap, which captures any particulates in the air being sampled. The liquid pump is a two-channel peristaltic pump, mounted on the left portion of the center bulkhead. When the power is turned ON, the roller assembly can be seen to rotate at approximately 3 rpm. The direction of the rotation coincides with the direction of the liquid flowing through the tubing. The liquid lines can be traced quite easily. It can be observed that the liquid lines run from the Luminol supply bottle, through one side of the pump, to the top fitting on the wick plate, then from the bottom fitting on the wick plate to the other side of the pump, and finally to the waste bottle.

9.1.3.5 Power supplies/signal processing - The main power supplies are controlled from the sealed power supply section that can be seen in the left rear corner of the case. Housed inside are two printed circuit boards. The power circuit board provides voltages

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for logic circuits, power for running the motors, charging the battery, and supplying the photomultiplier high voltage circuitry. The second board carries the main power transformer with its secondary fuse and the timer circuit for controlling the air and liquid pump motors during the backflush operation. The backup battery is located underneath the rear chassis and cannot be seen from above. Any time the unit is plugged in to line current, the battery is automatically charged.

9.1.3.6 Signal processing - The remainder of the electronics lie forward of the center bulkhead. One printed circuit board is devoted to the high voltage power supply for the photomultiplier while the other carries the signal generation and temperature compensation circuits. The normal switches, potentiometers and indicator lights are found in this area as well as the self-contained liquid crystal digital voltmeter attached to the front panel.

9.2 Operating Procedures

9.2.1 Installation

9.2.1.1 Install the instrument in an upright position.

Note: The instrument can be operated continuously on an angle of up to 30 degrees from vertical in any direction. It can also tolerate momentary tipping in any direction of up to 60 degrees from vertical.

9.2.1.2 Before operating, ensure that the air INLET and OUTLET parts on the back panel, are not obstructed.

9.2.2 Internal Reservoir (see Figure 4)

9.2.2.1 Confirm that the instrument is turned OFF and unplugged.

9.2.2.2 Remove the top cover of the instrument.

9.2.2.3 Working with one bottle at a time, pull the tubing from the top of the bottle and remove the bottle from the instrument.

9.2.2.4 The Luminol fluid may then be emptied or replenished as appropriate by removing the lid from the bottle.

Note: The "feed" bottle sits in the well closest to the front and the "waste" bottle sits to the rear.

9.2.2.5 Replace the bottle and push the tubing back onto the fitting.

9.2.2.6 Proceed with the second bottle as described above.

9.2.2.7 Replace the instrument cover and tighten the cover fastener located on the rear panel.

9.2.3 External Reservoirs

Note: An external reservoir kit is commercially available. To install the external reservoirs, the following sequence of steps are outlined below.

9.2.3.1 Confirm that the instrument is turned OFF and unplugged.

9.2.3.2 Loosen the instrument cover fastener located on the rear panel and slide the cover off.

9.2.3.3 Loosen the fittings on top of the standard liquid bottles so that the black plastic fitting may be pulled out.

9.2.3.4 Remove the standard bottles from the instrument.

9.2.3.5 Plug the black tubes into the bulkhead fittings on the rear panel and finger tighten the fitting caps.

9.2.3.6 Tubes from the external reservoirs are attached to the LIQUID IN and LIQUID OUT fittings on the rear panel.

Note: The liquid lines should be kept as short as possible and very small inner diameter so that fresh solution will reach the wick quickly after liquid changes and so that the backflush cycle will operate correctly.

9.2.3.7 Replace the instrument cover and tighten the cover fastener located on the rear panel.

9.2.4 Powering the Unit and Sampling

9.2.4.1 If line current is available, plug the LMA-3 into the power source. The yellow battery charge light emitting diode (LED) should be illuminated.

Note: Because the battery is charged with a "float" voltage, the unit may be safely left plugged into the power source without damaging the battery.

9.2.4.2 Turn the power switch ON. The yellow LED above the switch should be illuminated. The digital panel meter will also be activated and will show a four digit number approximately equal to zero.

9.2.4.3 Insure that the liquid pump motor is operating. In operation, the loading on the pump is uneven as a result of the work involved in compressing the pump tubing with each successive roller.

Note: The motor will sound alternately as if it is straining then running free. This is normal as long as the rotation does not significantly slow during the high load periods. The rotation speed of the pump should be approximately 3 rpm. After the liquid pump has been operating for about 10 minutes, you should be able to see plugs of liquid traveling down the waste tubing to the waste bottle.

9.2.4.4 Turn ON the air pump switch.

Note: You should now hear a fairly loud buzzing noise. This noise may be muffled by attaching a short length of one-quarter inch plastic tubing to the AIR OUT port. Tubing (preferably 0.030" wall x 0.25" OD teflon) may also be attached to the AIR IN port to deliver sample gas from a remote location or to muffle the air pump noise. Figure 5 illustrates the air flow through the LMA-3 NO_2 analyzer.

9.2.4.5 Check the battery voltage and photomultiplier tube high voltage (PMT HV) using the momentary DISPLAY SELECT switch. The battery voltage should be between 11.6 and 13.5 volts depending upon its state of charge. The PMT HV will normally be in the -400 to -800 volt range.

9.2.4.6 Select the appropriate DISPLAY RANGE and TIME CONSTANT. Where the NO_2 levels are very low, or if fast fluctuations in the signal are undesirable, choose a longer time constant setting.

9.2.4.7 Operate the instrument for 30 minutes in order to insure stable operation, then commence sampling at designated location.

9.2.5 Backflushing

9.2.5.1 As the LMA-3 operates, a certain amount of evaporation takes place in the reaction cell. Eventually this action leaves a solid residue which can block the detector window and reduce the readings. Recent field studies (10) have demonstrated that the LMA-3, when operated continuously for several days, will provide erratic responses. To eradicate the residue and erratic responses, a backflush cycle has been incorporated into the LMA-3 to dissolve and flush the residue into the waste bottle. The backflush cycle should be performed on a daily basis.

9.2.5.2 When the BACKFLUSH switch is pressed the backflush cycle will commence, shutting down the air pump and reversing the liquid pump at a higher than normal rate. This action draws liquid from the waste bottle and pumps it into the air passages. After about 2 1/2 minutes, the liquid pump returns to the normal direction of rotation at high speed. This quickly empties the air passages of liquid. After another 2 1/2 minutes, the liquid pump returns to its normal speed and the air pump restarts.

9.2.5.3 Backflush the system each time the reservoir is refilled (about every three days during continuous operation, or if a decrease in sensitivity is observed). Backflushing is recommended every 24 hours if the instrument is to be operated without daily calibration.

9.2.5.4 Ensure there is at least one-half inch of liquid in the waste bottle.

9.2.5.5 Place the three-way switch in the BACKFLUSH mode for about two minutes. The red LED above the BACKFLUSH button will remain lit during the cycle.

Note: If for any reason the instrument power is turned OFF during a backflush cycle, make sure that the AIR PUMP switch is in the OFF position before turning the power back ON. Run the instrument in this mode (normal liquid flow, air pump OFF) for at least 6 minutes before putting the air pump back ON or initiating another backflush.

9.2.5.6 When the fluid lines are full and the reaction chamber flooded, place the three-way switch in the PRIME position for approximately 2 minutes to clear sampling lines of fluid.

9.2.5.7 Return the three-way switch to the NORMAL position.

9.2.5.8 The LMA-3 signal will take 10 to 30 minutes to return to normal after a backflush operation.

Note: The backflush cycle should be initiated, whenever any of the conditions listed below are met:

- Each time the reservoir is refilled, or
- If a decrease in sensitivity is observed, or
- Daily if the analyzer is operated continuously.

10. Analytical Systems

10.1 System Description

10.1.1 The analytical system consists of a reducing agent, Luminol solution, with NO_2 gas acting as an oxidizing agent. A microphotometer measures the relative transmittance of the fluorescent energy emitted from the oxidation reaction of the Luminol.

10.1.2 A photomultiplier tube serves as the microphotometer by viewing the reaction site which is a cloth wick saturated in Luminol solution upon which the gas liquid reaction occurs.

10.1.3 The signal from the wick provides a measure of the NO_2 mixing ratio.

10.1.4 The signal is inputted to an analog to digital converter, a liquid crystal digital (LCD) voltmeter, and onto an LCD screen.

10.1.5 The analog can also be inputted to a strip recorder or to data acquisition instrumentation.

10.2 Systems Performance Criteria

10.2.1 Calibration - Calibrate the NO_2 air monitor every time the Luminol solution is changed or if the monitor has not been used for twelve or more hours.

10.2.2 Manual Zero and Span Calibration

10.2.2.1 Prior to operating the analyzer, an initial calibration must be performed. The following provides procedures to measure NO_2 concentrations in indoor air using the NO_2 LMA-3 continuous monitor.

Note: Follow the manufacturer's detailed instructions when calibrating a specific analyzer.

10.2.2.2 Assemble the analyzer as discussed in Section 9.2.4.

10.2.2.3 Connect zero gas to the analyzer at the AIR IN port.

10.2.2.4 Open the gas cylinder pressure valve.

10.2.2.5 Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired delivery pressure.

Note: If the air flow is pressurizing the unit, a "T" connection can be used to direct excess air to the atmosphere. Connect one end of the "T" to the AIR IN port and leave the other end open to the atmosphere.

10.2.2.6 Set the sample flow rate as read by the rotameter (read the widest part of the float) to the value that is to be used during sampling (2 Lpm is recommended).

10.2.2.7 Let the zero gas flow long enough to establish a stable trace. Allow at least 5 minutes for the analyzer to stabilize.

10.2.2.8 Adjust the zero control knob until the trace corresponds to the line representing 5% of the strip chart width above the chart zero or baseline. The above is to allow for possible negative zero drift. If the strip chart already has an elevated baseline, use it as the zero setting.

10.2.2.9 Let the zero gas flow long enough to establish a stable trace. Allow at least 5 minutes. Mark the strip chart trace as adjusted zero.

10.2.2.10 Disconnect the zero gas.

10.2.2.11 Connect the span gas with a concentration corresponding to approximately 80% of full scale, depending upon the Luminox solution, to the "T" connection.

Note: The calibration gas should contain O_2, CO_2 and H_2O in concentrations expected in indoor air.

10.2.2.12 Open the gas cylinder pressure valve. Adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired pressure.

10.2.2.13 Set the sample flow rate, as read by the rotameter, to the value that is to be used during sampling, which should be approximately 2 Lpm.

10.2.2.14 Let the span gas flow until the analyzer stabilizes.

10.2.2.15 Adjust the span control until the deflection corresponds to the correct percentage of chart, as computed by:

$$\text{Correct percentage of chart} = [C_s(\text{ppb})]/[C_f(\text{ppb})] \times 100 + 5\ \%\ \text{zero offset}$$

where:
C_s = concentration of NO_2 span gas, ppb
C_f = full scale reading of analyzer, ppb

As an example where the % zero offset is 5 and the correct percentage of chart for the span gas of 40 ppb would be:

$$40\ \text{ppb}/50\ \text{ppb} \times 100 + 5 = 85$$

10.2.2.16 Allow the span gas to flow until a stable trace is observed. Allow at least 5 minutes. Mark the strip chart trace as adjusted span.

10.2.2.17 Disconnect the span gas.

10.2.2.18 Repeat Section 10.2.2.8 through Section 10.2.2.17 and if no readjustment is required, go to Section 10.2.3. If a readjustment greater than 1 ppb is required, repeat Section 10.2.2.8 through Section 10.2.2.9.

10.2.2.19 Lock the zero and span controls.

10.2.2.20 Record final zero and span potentiometer setting.

10.2.3 Multipoint Calibration

10.2.3.1 A multipoint calibration is required when the analyzer is first purchased, the analyzer has had maintenance which could affect its response characteristics, or when results from the auditing process show that the desired performance standards are not being met.

10.2.3.2 A multipoint calibration required calibration gases with concentrations corresponding to approximately 10, 20, 40, 60, and 80% of full scale. The calibration gases should be certified to be within ±2% of the stated value and purchased in high pressure cylinders with inside surfaces of a chromium-molybdenum alloy of low iron content or other appropriate linings. The cylinders should be stored in areas not subject to extreme temperature changes nor exposed to direct sunlight.

Note: Each span gas cylinder should contain O_2, CO_2 and H_2O in concentrations expected in indoor air.

There are two acceptable methods for dynamic multipoint calibration of the LMA-3 analyzer. They are:

- the use of individual certified standard cylinders of NO_2 for each concentration needed, and
- the use of one certified standard high concentration cylinder of NO_2, diluted as necessary with zero-air, to obtain the various calibration concentrations needed.

The equipment needed for calibration can be purchased commercially, or can be assembled by the user as illustrated in Figure 6. When a calibrator or its components are being purchased, certain factors must be considered:

- traceability of the certified calibration gases to an NIST-SRM (16,17) or a NIST/EPA-approved commercially available Certified Reference Manual (see Section 8.2),
- accuracy of the flow-measuring device or devices (rotameter, mass flow meter, bubble meter),
- maximum and minimum flows of dilution air and calibration gases, and
- ease of transporting the calibration equipment from site to site.

10.2.3.3 For an individual cylinder multipoint calibration, assemble the monitor and calibration system as illustrated in Figure 6.

10.2.3.4 Perform a manual zero and span calibration as in Section 10.2.2 and record the adjusted zero and span concentrations and their respective chart values.

10.2.3.5 Connect the span gas with a concentration value corresponding to 80% of full scale to the analyzer system.

10.2.3.6 Open the gas cylinder pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired pressure.

10.2.3.7 Set the sample flow rate as read by the rotameter (read the widest part of the float) to the value to be used when sampling, normally 2 Lpm.

10.2.3.8 Let the span gas flow long enough to establish a stable trace on the strip chart recorder; allow a least 5 minutes. Mark the chart trace as an unadjusted span.
Note: No adjustments are made at this point.

10.2.3.9 Disconnect the span gas.

10.2.3.10 Connect zero gas to the analyzer.

10.2.3.11 Open the gas cylinder pressure valve and adjust the secondary pressure valve until the secondary pressure gauge reads approximately 5 psi more than the desired pressure.

10.2.3.12 Set the sample flow rate as read by the rotameter to the value that is used when sampling, usually 2 Lpm.

10.2.3.13 Let the zero gas flow long enough to establish a stable zero trace on the strip chart recorder; allow at least 5 minutes. Mark the chart trace as an unadjusted zero.

10.2.3.14 Repeat Section 10.2.3.5 through Section 10.2.3.13 for each of the calibration gases with concentrations corresponding to approximately 60, 40, 20 and 10% of full scale in that order.

10.2.3.15 Fill in the information required and construct a calibration curve of analyzer response as percent of chart versus concentration in ppb. Draw a best fit, smooth curve passing through the zero and minimizing the deviation of the remaining upscale points from the curve. The calibration curve should have no inflection points, i.e., it should either be a straight line or bowed in one direction only. Curve fitting techniques may be used in constructing the calibration curve by applying appropriate constraints to force the curve through the zero. This procedure becomes quite involved; however, the most frequently used technique is to graph the curve (see Section 10.2.3.28 through Section 10.2.3.30).

10.2.3.16 Recheck any calibration point deviating more than ±1.0 ppb NO_2 from the smooth calibration curve. If the recheck gives the same results, have the calibration gas reanalyzed. Use the best fit curve as the calibration curve.

10.2.3.17 For a dynamic dilution multipoint calibration, assemble the analyzer and dynamic dilution system as illustrated in Figure 6.

10.2.3.18 Adjust the zero air flow from the dilution system to the analyzer. The flow must exceed the total demand of the analyzer connected to the output manifold to ensure that no ambient air is pulled into the manifold vent.

Note: Zero and calibration gases should contain O_2, CO_2 and H_2O in concentrations expected in indoor air.

Note: In lieu of connecting analyzer to manifold, one may fill Tedlar® bags with generated standards to be sampled by the LMA-3 NO_2 analyzer.

10.2.3.19 Allow the analyzer to sample the zero air until a stable response is obtained; adjust the analyzer zero control to within ±0.5 ppb of zero base line.

Note: Offsetting the analyzer zero adjustment to +5% of scale is recommended to facilitate observing negative zero drift. On most analyzers this should be done by offsetting the recorder zero.

10.2.3.20 Determine the 80% of monitor full scale. Example: For an analyzer with an operating range of 0 to 50 ppb, the 80% value would be:

$$0.80 \times 50 = 40 \text{ ppb}$$

10.2.3.21 Adjust the NO_2 flow from the standard NO_2 cylinder to generate a NO_2 concentration of approximately 80% of the monitor full scale. Measure the NO_2 flow and record.

10.2.3.22 Measure the dilution air flow and record.

10.2.3.23 Calculate the generated NO_2 standard by the following equation:

$$(NO_2)_{gen} = [(NO_2)_{std}(Q_{NO_2})]/[Q_{dil} + Q_{NO_2}]$$

where:

$(NO_2)_{gen}$ = concentration of NO_2 generated, by dilution, ppb
$(NO_2)_{std}$ = concentration of NITS-SRM or CRM NO_2 gas standard, ppb
Q_{NO_2} = flow rate of NO_2 standard, L/min
Q_{dil} = flow rate of dilution air flow, L/min

Note: If wet test meter or bubble meter is used for flow measurement, the vapor pressure of water at the temperature of the meter must be subtracted from the barometric pressure.

Note: If both the NO_2 and the zero-air flow rates are measured with the same type of flow meter (e.g. bubble flow meter, rotameter, mass flow meter, wet test meter, etc.) correction to standard temperature and pressure (STP) is not necessary. However, if this is not the case, then the flow of NO_2 gas and dilution gas must be corrected to STP by the following equation:

$$Q_{NO_2} = (Q_1)\,[(P_{bar}/760)(298/T + 273)]$$

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where:
Q_{NO_2} = flow rate of NO_2 standard corrected to STP, L/min
Q_1 = uncorrected flow rate of NO_2 standard, L/min
P_{bar} = barometric pressure, mm Hg
T = temperature of gas being measured, °C

10.2.3.24 Allow the analyzer to sample until the response is stable; adjust the analyzer span until the required response is obtained, and record the NO_2 recorder response. After the zero and 80% points have been set, without further adjusting the instrument, generate four approximately evenly spaced points between zero and 80% by increasing the dilution flow (Q_{dil}) or by decreasing the NO_2 flow (Q_{NO_2}). For each concentration generated, calculate the NO_2 concentrations and record the results for each point.
Note: If substantial adjustments of the span control are necessary, recheck the zero and span adjustments by repeating Section 10.2.2.

10.2.3.25 Construct a calibration curve of monitor response as percent of chart versus concentration in ppb. Draw a best fit, smooth curve passing through the zero and minimizing the deviation of the remaining upscale points from the curve. The calibration curve should have no inflection points, i.e., it should either be a straight line or bowed in one direction only. Curve fitting techniques may be used in constructing the calibration curve by applying appropriate constraints to force the curve through the zero. This procedure becomes quite involved; however, the most frequently used technique is to graph the curve.

10.2.3.26 Recheck any calibration point deviating more than $\pm 1.0 + 0.02\ C_c$ ppb from the smooth calibration curve. If the recheck gives the same results, have that calibration gas reanalyzed. Use the best fit curve as the calibration curve.

10.3 Analytical Procedure

The analytical procedure is concurrent with the operating procedures. Therefore, it is recommended to follow procedures outlined in Section 9.2 and Section 10.2 for analysis.

11. Systems Maintenance

11.1 Periodic Maintenance

Proper maintenance is necessary for successful monitor performance. Periodic maintenance should be performed to reduce equipment failure and maintain calibration integrity of the instrument. Instrument calibration should be checked on a schedule established after the analyzer has operated for a period of time. The sensitivity and linearity should also be checked. These instrument checks should be done at least on an annual basis. However, when any component (i.e., detector or pump) is changed, the linearity and selectivity of the instrument should be confirmed. The settings of the zero and span controls of instruments which operate continuously should be checked as often as required. A log of these settings and a service and repair log should be kept to assist in evaluating maintenance difficulties.

11.2 Routine Maintenance

Regular checks of the instrument and its operation are mandatory. Even though a system may provide excellent quality data initially, without routine maintenance and system checks the quality of the data will degenerate with time. Follow all routine maintenance procedures specified in the manufacturer's instruction manual.

11.2.1 Sampling system - The sampling system to which the analyzer is connected must be checked at regular intervals according to a maintenance schedule based on the components used in the specific application. Sampling system maintenance normally includes the following steps:

- checking the entire system for leaks and proper flow rates,
- cleaning and/or renewing sample system components,
- ensuring that calibration cylinders are shut off when not in use,
- ordering filled and assayed cylinders at intervals which include ample lead time to ensure continuous supply of calibration gas,
- checking operation of pumps, recorders, motors, timers and other commercial components by referring to manufacturer's instructions,
- checking and/or cleaning the entire sampling system, including the sample cell in the analyzer, when abnormal sample conditions occur, such as when slugs of water, dirt or oil are introduced.

11.2.2 Daily servicing - Automatic 80% full scale span (40 ppb) and zero precision checks should be performed utilizing the instrument's automatic zero/span standardization feature (if so equipped) and individual secondary standard gases of NO_2 in air with the above concentrations. In addition, backflushing should be performed daily, immediately before daily zero/span precision check.

11.2.3 Each visit servicing - Verify that the zero and span potentiometer settings are at the proper position. Likewise, verify that the sample flow is correct. Plot the daily zero, precision check, and span values on their respective days. If any of the zero and span values exceed 5% of stated value, perform a manual zero and span check and adjust the analyzer to the correct zero and span values using the front panel zero and span potentiometer, respectively. If there is insufficient range in the span potentiometer, a multipoint calibration must be performed.

11.2.4 Weekly servicing - Perform a leak check weekly and whenever the loosening or tightening of a fitting is involved in maintenance procedures. Using an individual cylinder, introduce a 20% of full scale (10 ppb) intermediate span gas at ambient pressure upstream of the sample pump as a precision check. Maintain the same excess flow each time the manual precision check is performed. The manual precision check should be within 10% of value. If not, investigate the cause and initiate repairs.

11.2.5 Biweekly servicing - Field evaluation (10) of the LMA-3 illustrated erratic results when the pump tubing was not changed at approximately two-week intervals. Therefore, changing of pump tubing biweekly will eliminate this source of analytical error.

11.2.6 Cleaning - Clean the upper chamber when there is an accumulation of liquid in the chamber or if large amounts of residue plug the cartridge filter.

Note: Usually minute amounts of liquid can evaporate, but if liquid stays in the chamber it may leak into and ruin the air pump.
Disassemble the trap as follows:

11.2.6.1 Confirm that the instrument is turned OFF and unplugged.

11.2.6.2 Loosen the instrument cover fastener, located on the rear panel, and slide the cover off.

11.2.6.3 Remove the "feed" and "waste" bottles from the instrument.

11.2.6.4 Remove the two phillips head retaining screws from the outside of the case and pull away the panel. The upper side trim panel on the air pump side of the instrument must be removed.

11.2.6.5 Pull the air tubes off of the trap. Separate the filter cartridge from the upper chamber.

11.2.6.6 Remove the two flat head screws which hold the chamber to the side of the instrument case. Lift the chamber out of the instrument.

11.2.6.7 Observe and note the relative positions of the air tubes and the mounting holes before disassembling the chamber.

11.2.6.8 Unscrew the two black end pieces from each other.

Note: It may be necessary to soak the unit in water to loosen the chemical residues that can bind the pieces to the center tube.

11.2.6.9 After cleaning the chamber, re-assemble it. The ends should be screwed together firmly by hand. Check the relative positions of the tubes. As mounted in the instrument, the longer black tube should point straight upwards and the short tube should point towards the front of the instrument. Adjust end pieces or switch them accordingly.

11.2.6.10 Reassemble in the reverse order of disassembly.

Note: Pass tygon tubing through the clamp on the side panel, and make sure the tubing rises sharply from the detector assembly.

12. Standard Operating Procedures (SOPs), Quality Assurance (QA) and Performance Criteria

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

12.1 Standard Operating Procedures

12.1.1 SOPs should be generated by the users to describe and document the following activities in their laboratory:

- assembly, calibration, leak check, and operation of the specific sampling system and equipment used,
- preparation, storage, shipment, and handling of the sampler system,
- purchase, certification, and transport of standard reference materials, and
- all aspects of data recording and processing, including lists of computer hardware and software used.

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

12.2 Quality Assurance Program

The user should develop, implement, and maintain a quality assurance program to ensure that the sampling system is operating properly and collecting accurate data. Established calibration, operation, and maintenance procedures should be conducted on a regularly scheduled basis and should be part of the quality assurance program. Calibration procedures and operation procedures in Section 9.2, and maintenance procedures in Section 11 of this method and the manufacturer's instruction manual should be followed and included in the QA program. Additional QA measures (e.g., trouble shooting) as well as further guidance in maintaining the sampling system should be provided by the manufacturer.

12.2.1 Precision Check

12.2.1.1 A periodic precision check is used to assess the data. A one-point check on the analyzer is carried out at least once every 2 weeks at a NO_2 concentration between 8 and 10 ppb.

12.2.1.2 The analyzer must be operated in its normal sampling mode, and the precision test gas must pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling. The standards from which the precision check test concentrations are obtained must be traceable to a NITS-SRM or a commercially available CRM; the standards used for calibration may be used for the precision check. They must conform to specifications outlined in Section 8.2.

Note: All gas standards should contain O_2, CO_2 and H_2O in concentrations expected in indoor air.

12.2.1.3 Connect the analyzer's sample inlet line to a precision gas source that has a concentration between 8 and 10 ppb NO_2 and that is traceable to a NITS-SRM or a CRM as illustrated in Section 9.2.3. If a precision check is made in conjunction with a zero/span check, it must be made prior to any zero and span adjustments.

12.2.1.4 Allow the analyzer to sample the precision gas for a least 5 min or until a stable recorder trace is obtained.

12.2.1.5 Record this value and mark the chart as "unadjusted" precision check.

12.2.1.6 The expected response of the LMA-3 analyzer should be within 10% of the precision calibration gas standard.

12.2.2 Performance Audit

12.2.2.1 An audit is an independent assessment of the accuracy of data generated by an analyzer.

12.2.2.2 Independence is achieved by having the audit performed by an operator other than the one conducting the routine field measurements and by using audit standards, reference materials, and equipment different from those routinely used in monitoring.

12.2.2.3 The audit should be an assessment of the measurement process under normal operations, that is, without any special preparation or adjustment of the system. Routine quality assurance checks conducted by the operator are necessary for obtaining and reporting good quality data, but they are not to be considered part of the auditing procedure.

12.2.2.4 Proper implementation of an auditing program will ensure the integrity of the data and assess the accuracy of the data.

12.2.2.5 A performance audit consists of challenging the continuous analyzer with known concentrations of NO_2, containing O_2, CO_2 and H_2O in concentrations expected in indoor air, within the measurement range of the analyzer. Known concentrations of NO_2 can be generated by using individual cylinders for each concentration (see Section 10.2.3) or by using one cylinder of a high NO_2 concentration and diluting it to the desired levels with zero-air (see Section 10.2.3.17). In either case, the gases used must by traceable to a NITS-SRM or a commercially available CRM.

12.2.2.6 A dynamic dilution system must be capable of measuring and controlling flow rates to within ±2% of the required flow. Flow meters must be calibrated under the conditions of use against a reliable standard such as a soap bubble meter or a wet test meter; all volumetric flow rates should be corrected to STP at 25°C (77°F) and 760 mm Hg (29.92 in Hg); but if both the NO_2 and the zero air flow rates are measured with the same type device at the same temperature and pressure, the STP correction factor in the audit equations can be disregarded.

12.2.2.7 The analyzer should be challenged with at least one audit gas of known concentration from each of the following concentrations within the measurement range of the analyzer being audited:

Audit Point	NO_2 Concentration Range, ppb
1	3 to 7
2	8 to 12
3	18 to 22
4	28 to 32
5	38 to 42

The difference in NO_2 concentration (ppb) between the audit value and the measured value is used to calculate the accuracy of the analyzer.

12.2.2.8 All measurement of audit concentrations should fall within ±10% of the audit value as a precision check.

12.3 Performance Criteria

12.3.1 Specific performance criteria have been discussed and are outlined in Table 1.

12.3.2 The lower detection limit of the method is 5 ppt_v.

12.3.3 The sensitivity of the method is 1 second for a 20% change in NO_2 mixing ratio.

12.3.4 The precision of the method is linear up to about 5 ppm_v, provided that a flow rate of 0.1 mL/min is maintained through the system.

13. Method Safety

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

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Table 1. Laboratory Performance Parameter Results of the LMA-3 NO_2 Extrasensitive Monitor Evaluation

Performance Parameter	Results
Mean Noise	0.003 ppb
Mean Precision (0% FS)	0.003 ppb
Mean Precision (20% FS)	0.040 ppb
Mean Precision (50% FS)	0.065 ppb
Mean Precision (80% FS)	0.105 ppb
Limit of Detection	0.009 ppb
Lower Detection Limit	0.005 ppb
Mean Daily Zero Drift	-0.00 ppb
Mean Daily Span Drift (20% FS)	-1.3%
Mean Rise Time	1.8 min
Mean Fall Time	0.2 min

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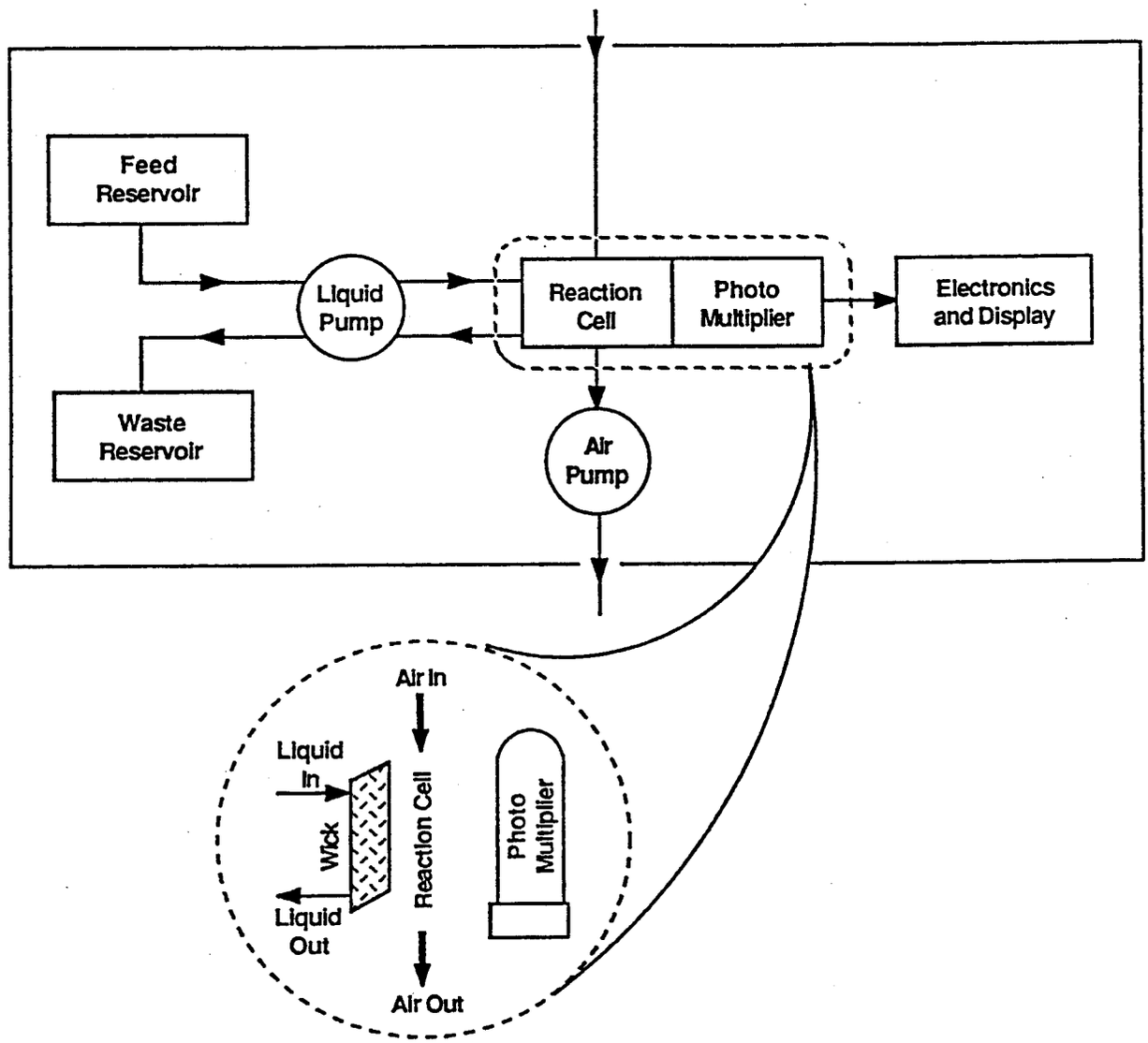

Figure 1. Operational Block Diagram of the LMA-3 NO_2 Analyzer

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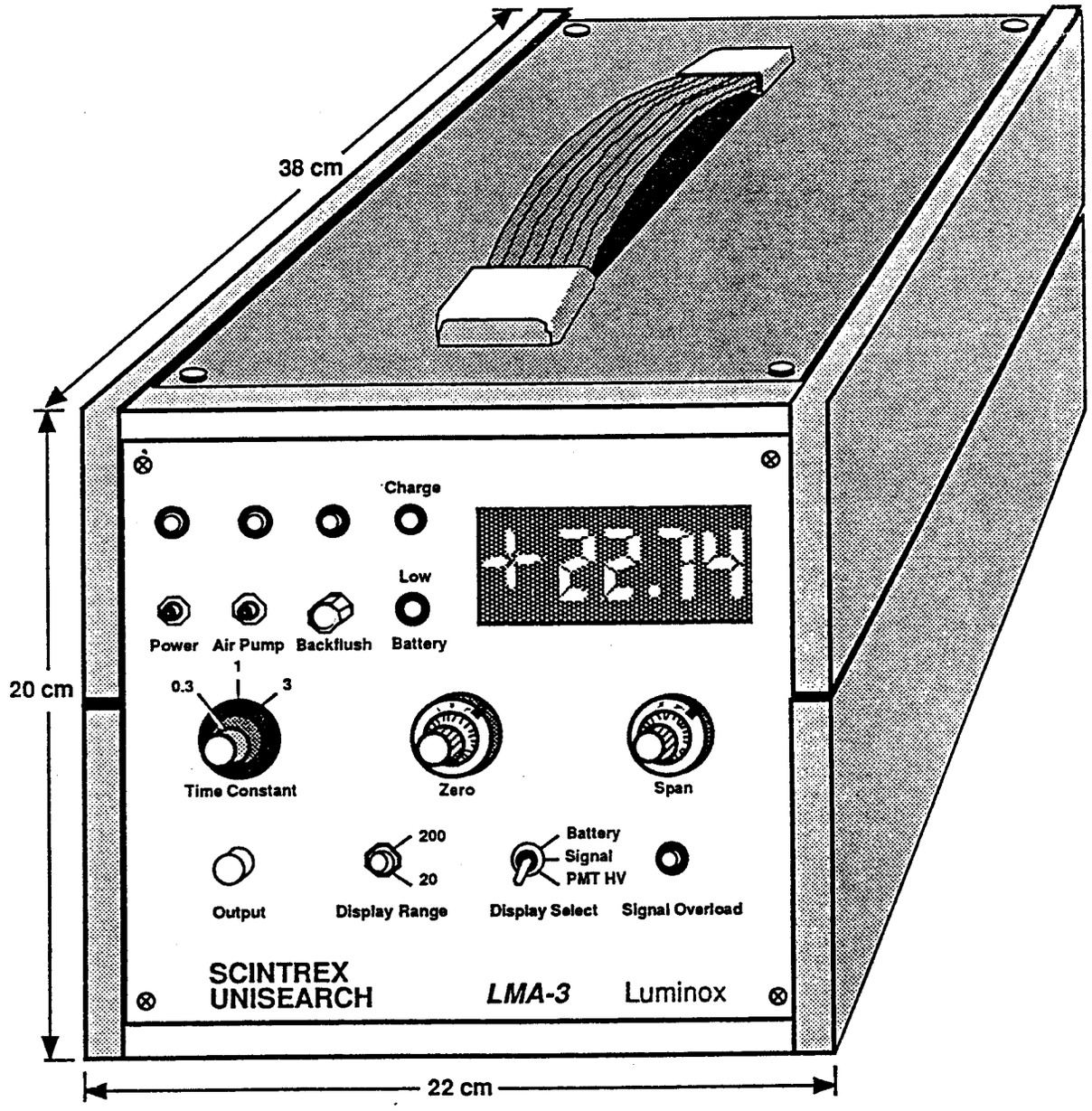

Figure 2. Front View LMA-3 NO_2 Analyzer

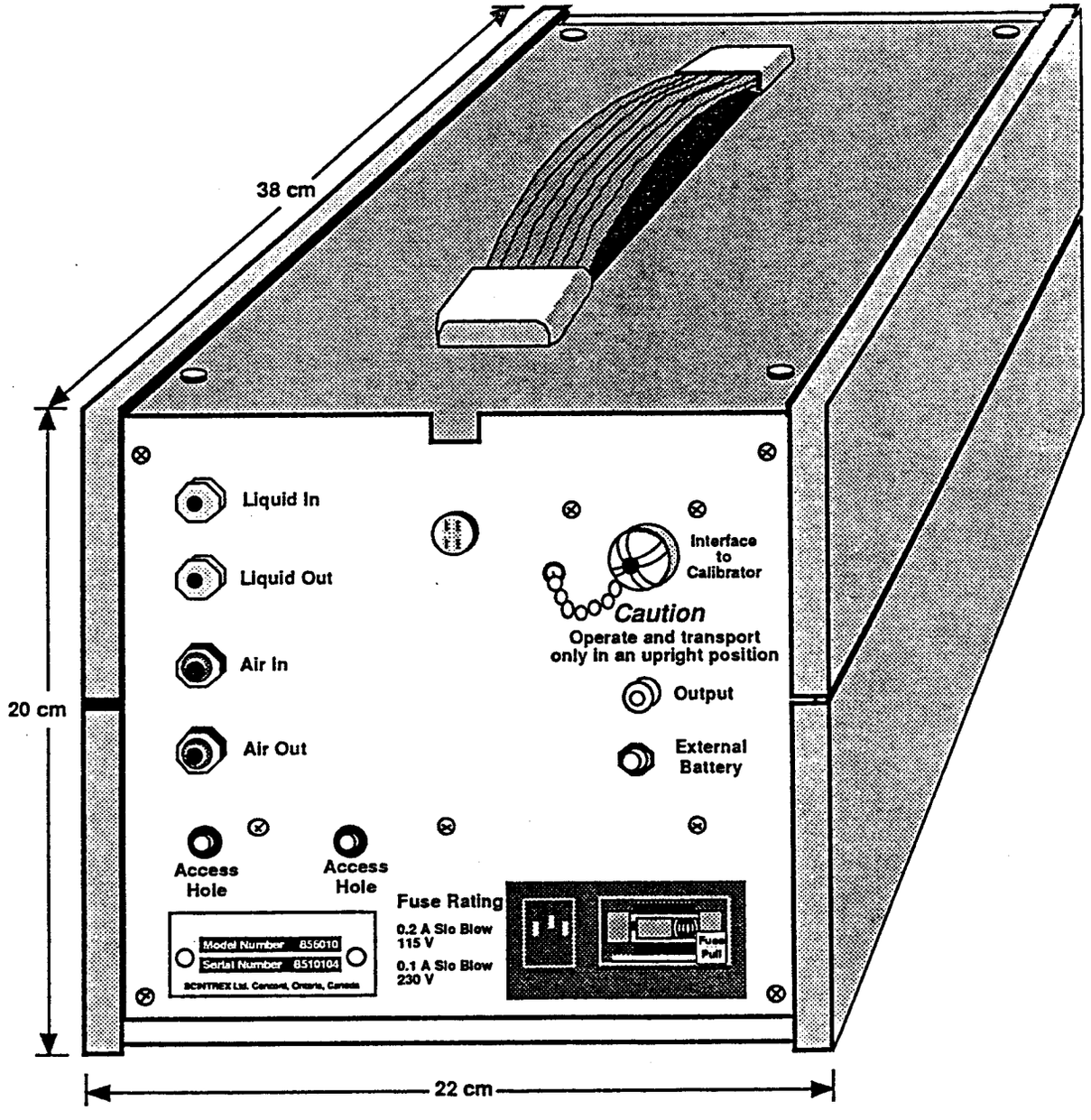

Figure 3. Back View LMA-3 NO_2 Analyzer

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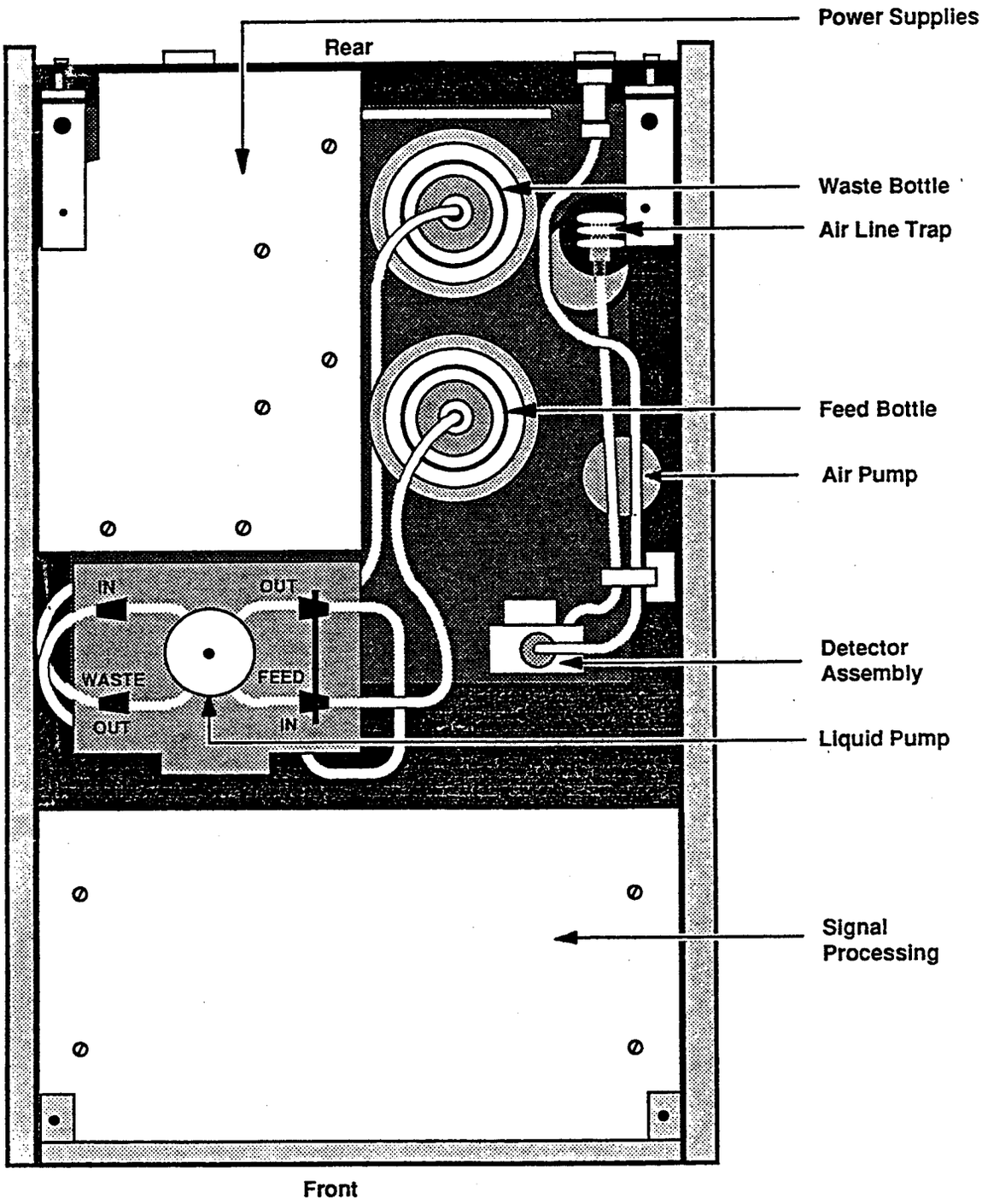

Figure 4. Top View LMA-3 NO_2 Analyzer

420

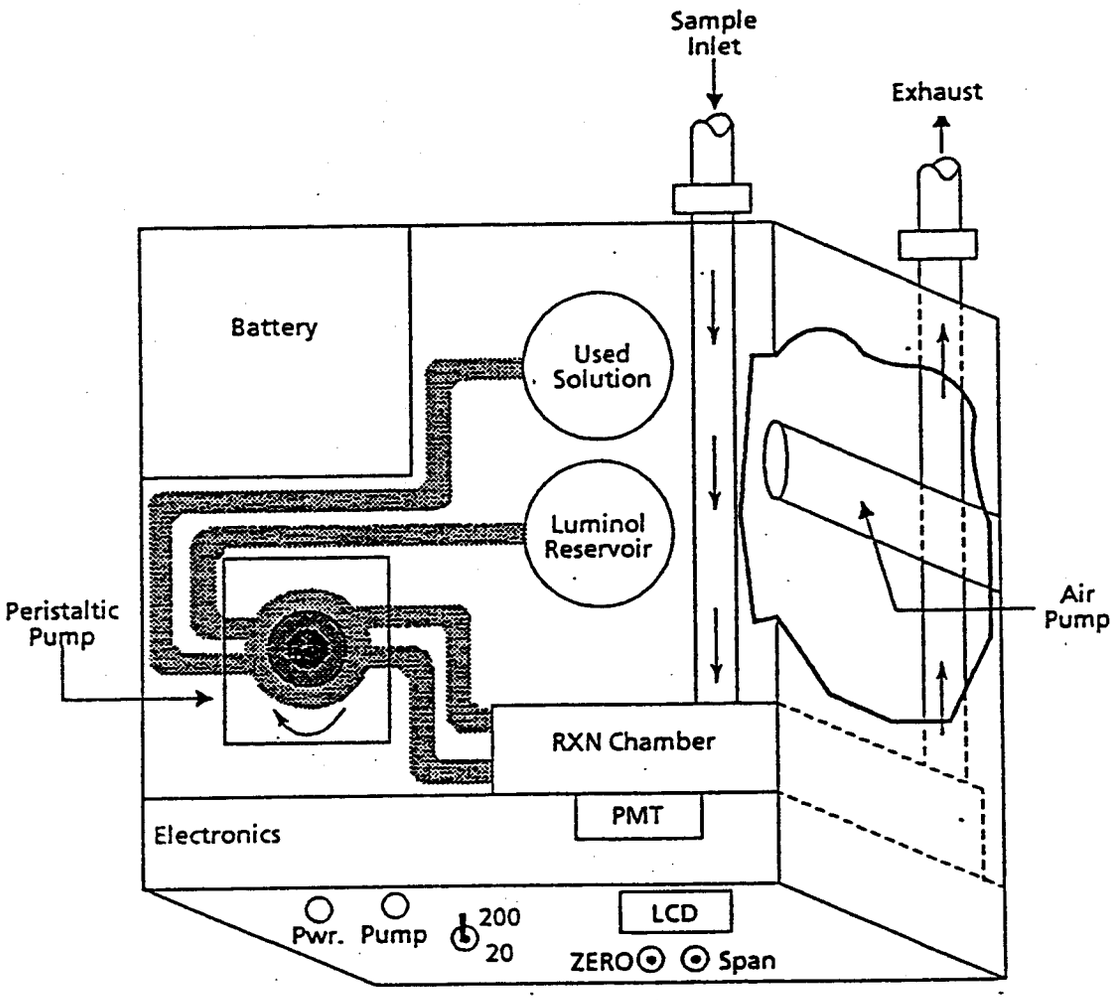

Figure 5. Sample Air through the LMA-3 NO_2 Analyzer

1/30

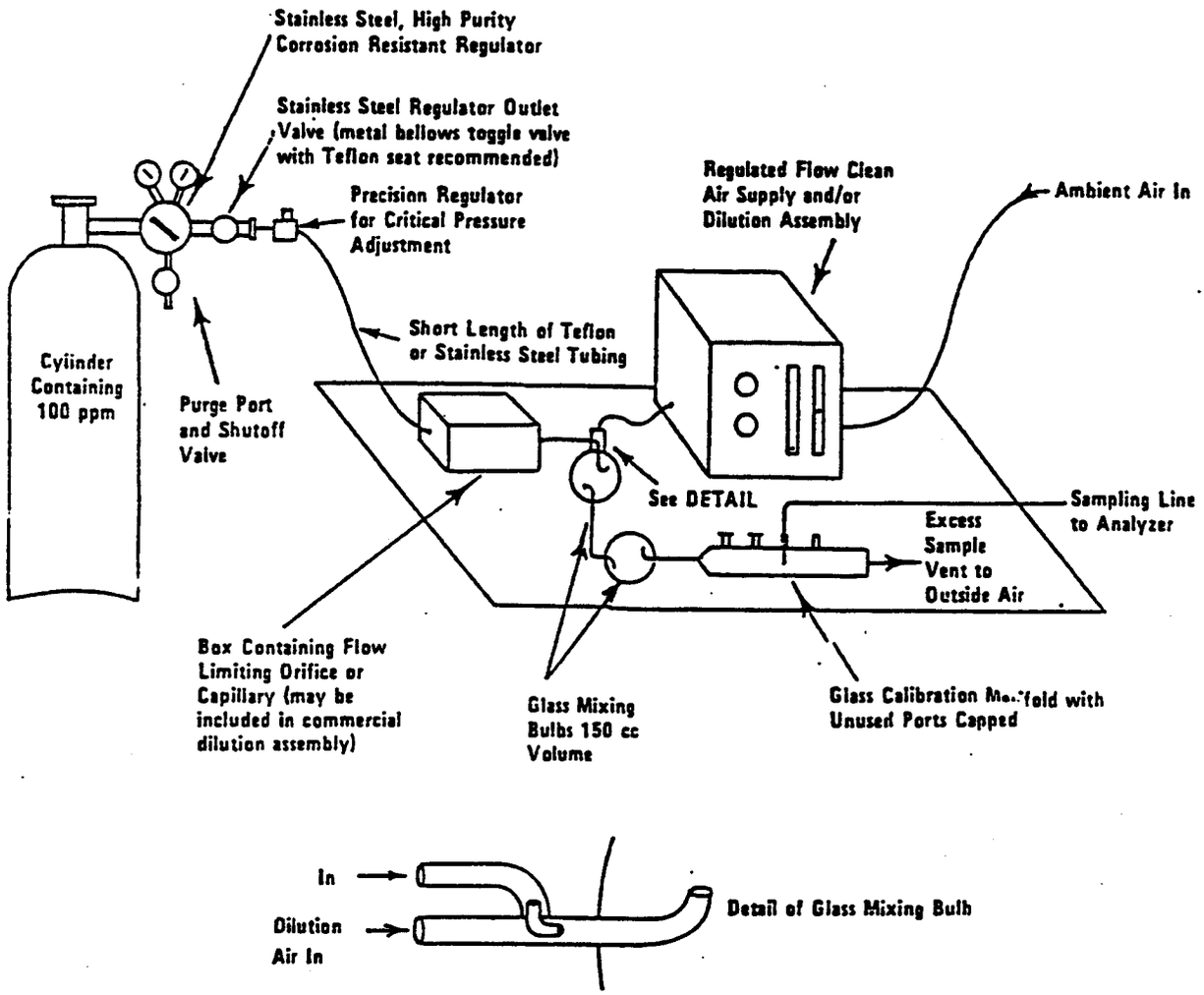

Figure 6. Assembly for Dilution of NO_2 from Cylinder for Use in Calibration or Span Check

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