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PART 1 OF 2

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

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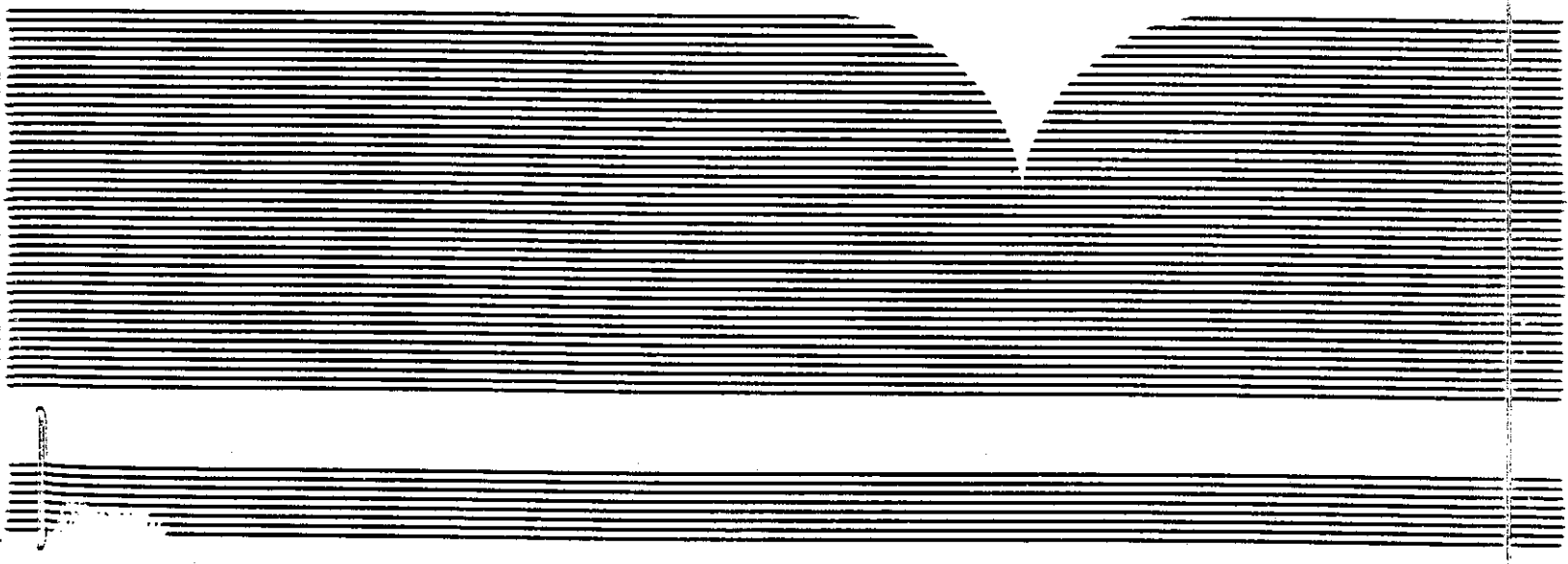

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Compendium of Methods for the Determination of Air Pollutants in Indoor Air

by

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16. ABSTRACT

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

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FOREWORD

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

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

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

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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

1. Scope
2. Applicable Documents
3. Summary of Method
4. Significance
5. Definitions
6. Interferences and Limitations
7. Apparatus
   - 7.1 Sample Collection
     - 7.1.1 Subatmospheric Pressure
     - 7.1.2 Pressurized
   - 7.2 Sample Analysis
     - 7.2.1 GC-MS-SCAN Analytical System
     - 7.2.2 GC-MS-SIM Analytical System
     - 7.2.3 GC-Multidetector Analytical System
   - 7.3 Canister Cleaning System
   - 7.4 Calibration System and Manifold
8. Reagents and Materials
9. Sampling System
   - 9.1 System Description
     - 9.1.1 Subatmospheric Pressure Sampling
     - 9.1.2 Pressurized Sampling
     - 9.1.3 All Samplers
   - 9.2 Sampling Procedure
10. Analytical System
    - 10.1 System Description
      - 10.1.1 GC-MS-SCAN System
      - 10.1.2 GC-MS-SIM System
      - 10.1.3 GC-Multidetector (GC-FID-ECD-PID) System
    - 10.2 GC-MS-SCAN-SIM System Performance Criteria
      - 10.2.1 GC-MS System Operation
      - 10.2.2 Daily GC-MS Tuning
      - 10.2.3 GC-MS Calibration
        - 10.2.3.1 Initial Calibration
        - 10.2.3.2 Routine Calibration
    - 10.3 GC-FID-ECD System Performance Criteria (With Optional PID)
      - 10.3.1 Humid Zero Air Certification
      - 10.3.2 GC Retention Time Windows Determination

10.3.3 GC Calibration
10.3.3.1 Initial Calibration
10.3.3.2 Routine Calibration
10.3.4 GC-FID-ECD-PID System Performance Criteria
10.4 Analytical Procedures
10.4.1 Canister Receipt
10.4.2 GC-MS-SCAN Analysis (With Optional FID System)
10.4.3 GC-MS-SIM Analysis (With Optional FID System)
10.4.4 GC-FID-ECD Analysis (With Optional PID System)
11. Cleaning and Certification Program
11.1 Canister Cleaning and Certification
11.2 Sampling System Cleaning and Certification
11.2.1 Cleaning Sampling System Components
11.2.2 Humid Zero Air Certification
11.2.3 Sampler System Certification With Humid Calibration Gas Standards
12. Performance Criteria and Quality Assurance
12.1 Standard Operating Procedures (SOPs)
12.2 Method Relative Accuracy and Linearity
12.3 Method Modification
12.3.1 Sampling
12.3.2 Analysis
12.4 Method Safety
12.5 Quality Assurance
12.5.1 Sampling System
12.5.2 GC-MS-SCAN-SIM System Performance Criteria
12.5.3 GC-Multidetector System Performance Criteria
13. Acknowledgements
14. References

Appendix A - Availability of Audit Cylinders from U.S. Environmental Protection Agency (USEPA) to USEPA Program/Regional Offices, State/Local Agencies and Their Contractors

Appendix B - Operating Procedures for a Portable Gas Chromatograph Equipped with a Photoionization Detector

Appendix C - Installation and Operating Procedures for U.S. Environmental Protection Agency's Urban Air Toxic Pollutant Program Sampler

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	Disadvantages
• Somewhat lower equipment cost than GC-MS	• Multiple detectors cost to calibrate
• Less sample volume required for analysis	• Compound identification not positive
• More sensitive (ECD may be 1000 times more sensitive than GC-MS	• 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.

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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)	$1,3\text{-}(CH_3)_2C_6H_4$	106.17	139.1	-47.9	
p-Xylene (1,4-Dimethylxylene)	$1,4\text{-}(CH_3)_2C_6H_4$	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)	$1,2\text{-}(CH_3)_2C_6H_4$	106.17	144.4	-25.2	
1,3,5-Trimethylbenzene (Mesitylene)	$1,3,5\text{-}(CH_3)_3C_6H_6$	120.20	164.7	-44.7	108-67-8
1,2,4-Trimethylbenzene (Pseudocumene)	$1,2,4\text{-}(CH_3)_3C_6H_6$	120.20	169.3	-43.8	95-63-6
m-Dichlorobenzene (1,3-Dichlorobenzene)	$1,3\text{-}Cl_2C_6H_4$	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)	$1,2\text{-}Cl_2C_6H_4$	147.01	180.5	-17.0	95-50-1
p-Dichlorobenzene (1,4-Dichlorobenzene)	$1,4\text{-}Cl_2C_6H_4$	147.01	174.0	53.1	106-46-7
1,2,4-Trichlorobenzene	$1,2,4\text{-}Cl_3C_6H_3$	181.45	213.5	17.0	120-82-1
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3-butadiene)					

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

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

Table 2. (cont.)

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

Table 2. (cont.)

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

Table 3. General GC and MS Operating Conditions

Chromatography

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

Temperature Program

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

Mass Spectrometer

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

FID System (Optional)

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

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

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

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

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

Table 5. (cont.)

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

Table 6. GC-MS-SIM Calibration Table

*** External Standard ***

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

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

Peak Num	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	
0		1 PP	11.225	Mass	41.00	amu	ALLYLCHLORID	761	8247 pptv	*
1		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	
5		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	

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

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

Table 7. (cont.)

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

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

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

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

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

Table 9. GC-MS-SIM Calibration Table

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

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

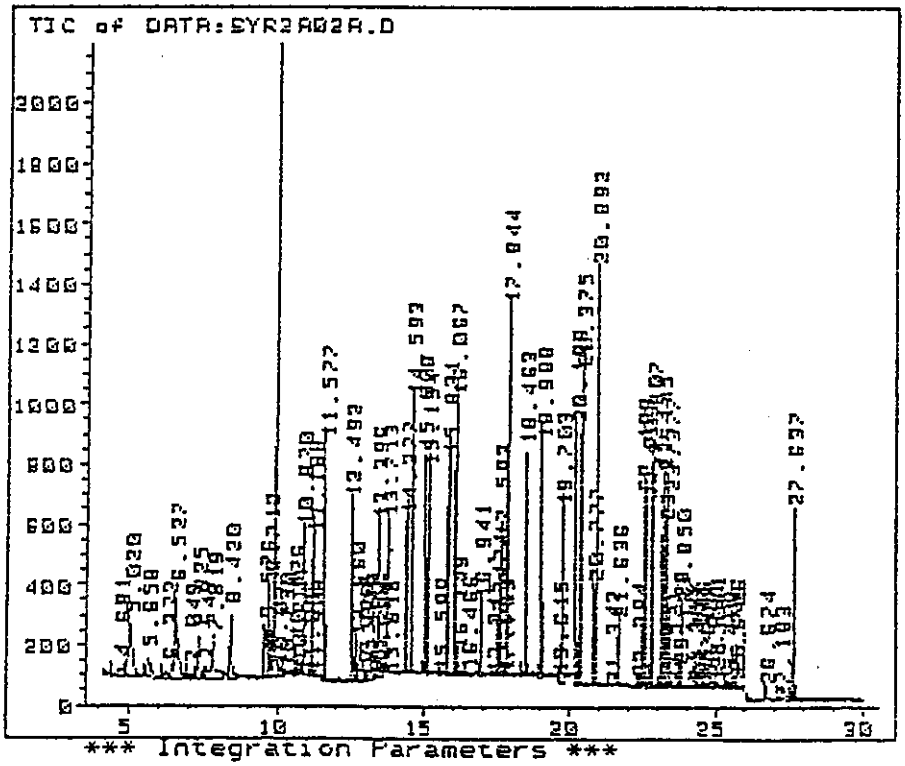
Table 10. Example of Hard-Copy of GC-MS-SIM Analysis

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

Name Info: SYR 1
Misc Info:
Operator : JDP

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

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




```
*** 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.)

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

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

Peak Num	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	967.3 pptv	
22		1 BP	17.475	Mass	75.00 amu	t-1,3DICHLPR	1626	689.2 pptv	
23		1 BB	17.594	Mass	97.00 amu	1,1,2CHLETHA	2721	1772 pptv	
24		1 BV	17.844	Mass	91.00 amu	TOLUENE	14417	2733 pptv	
25		1 PB	18.463	Mass	107.00 amu	EDB	4070	1365 pptv	*
26		1 PH	18.989	Mass	166.00 amu	TETRACHLETHE	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	

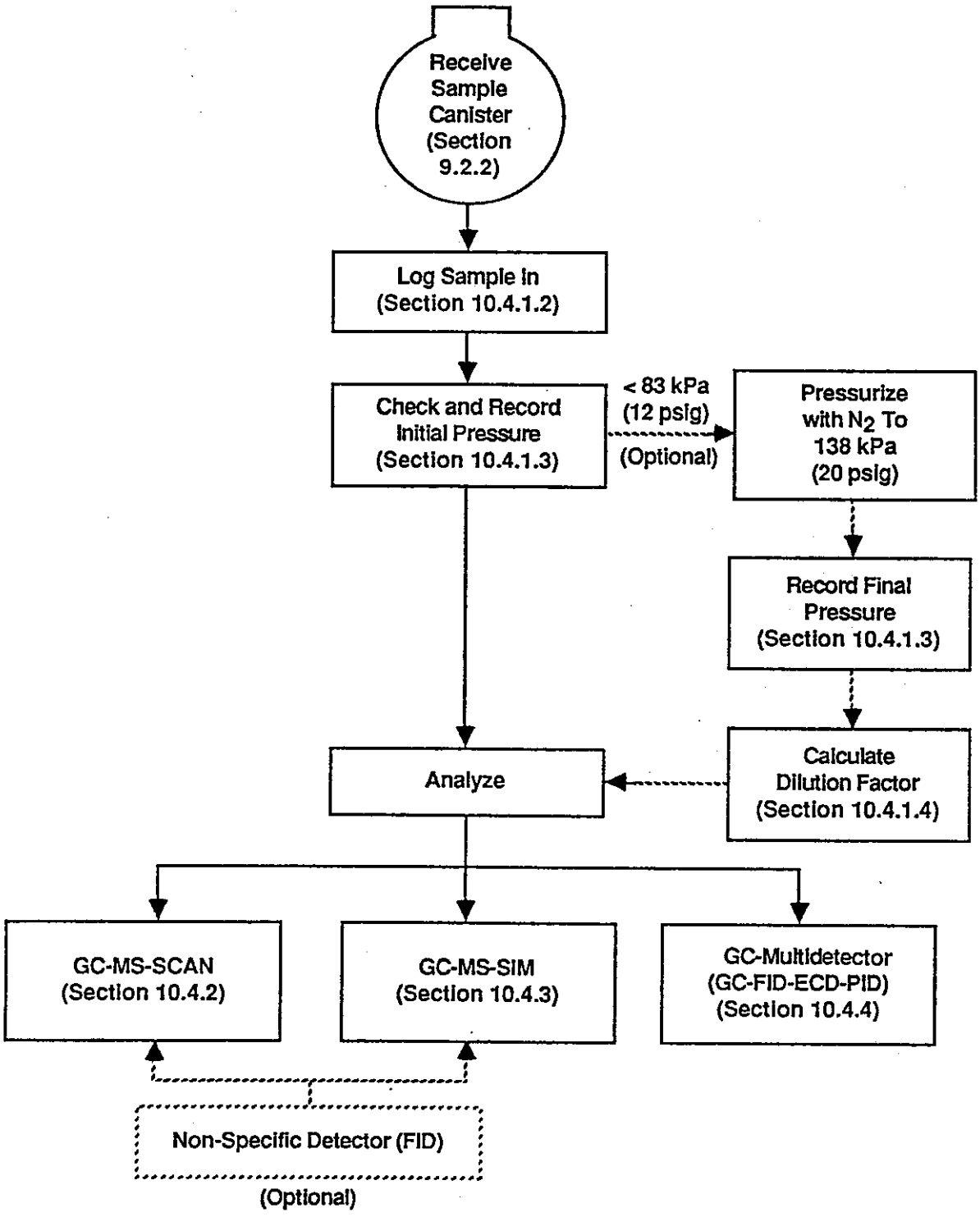


Figure 1. Analytical Systems Available for Canister VOC Identification and Quantitation

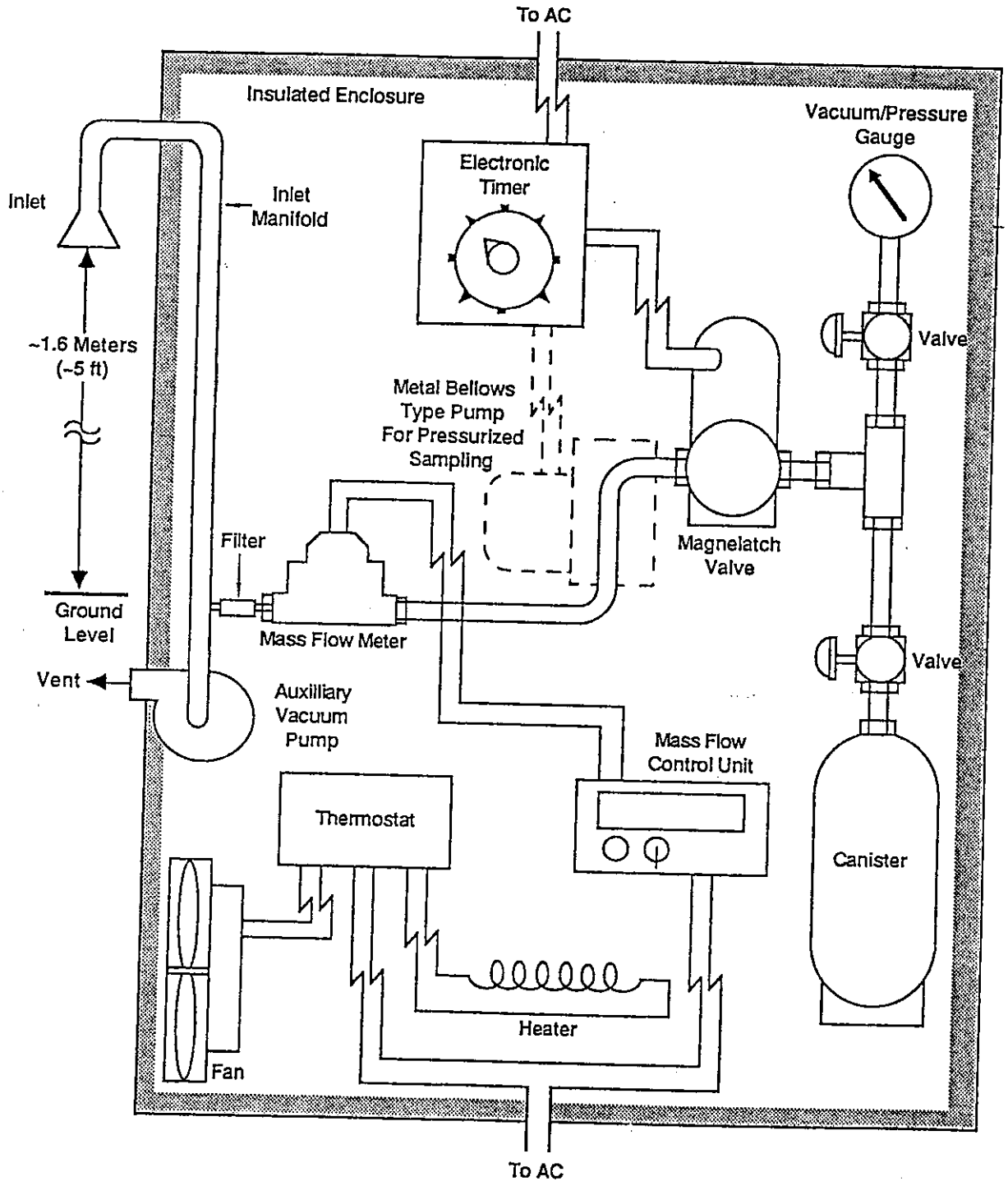


Figure 2. Sampler Configuration for Subatomic Pressure or Pressurized Canister Sampling

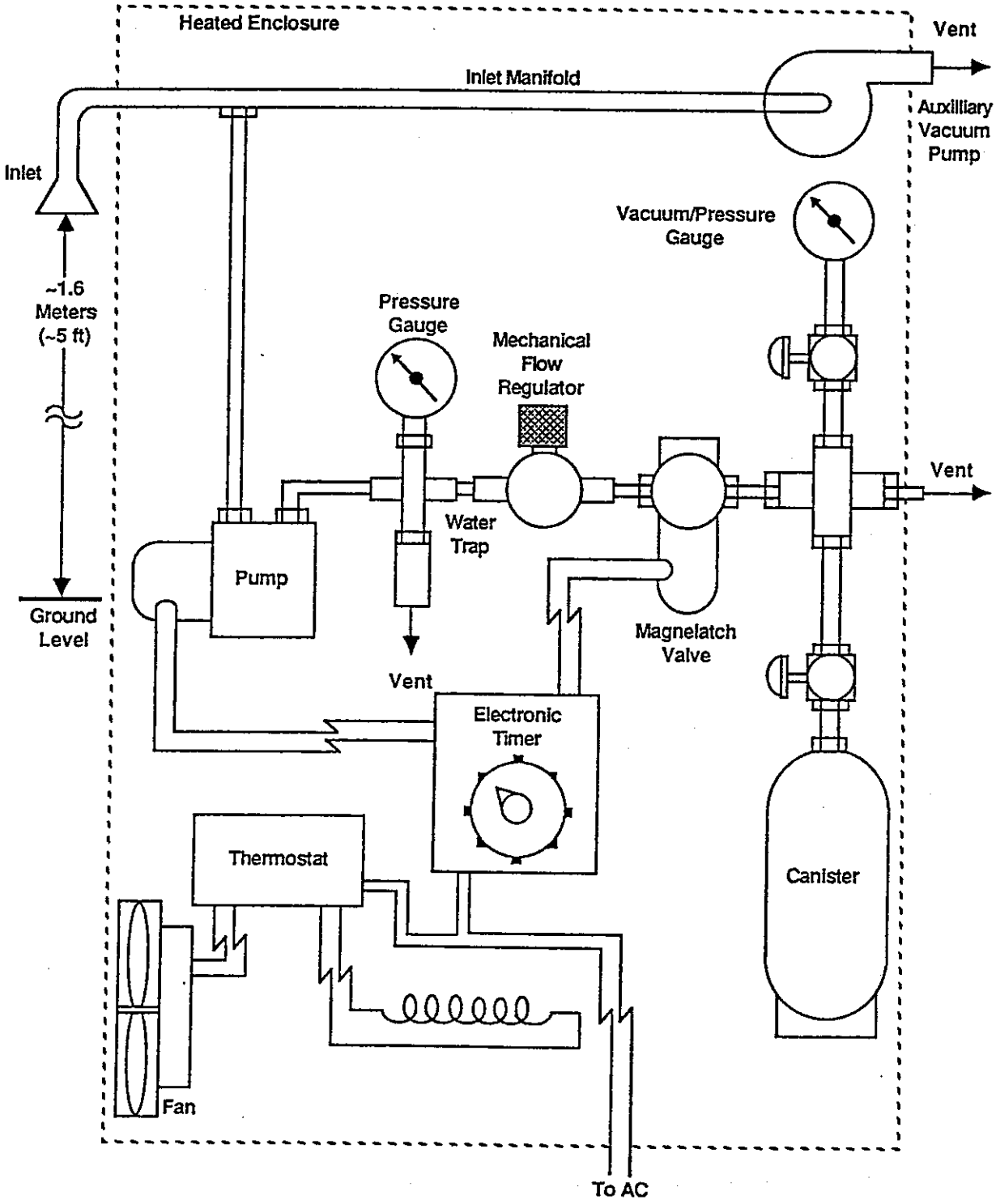


Figure 3. Alternative Sampler Configuration for Pressurized Canister Sampling

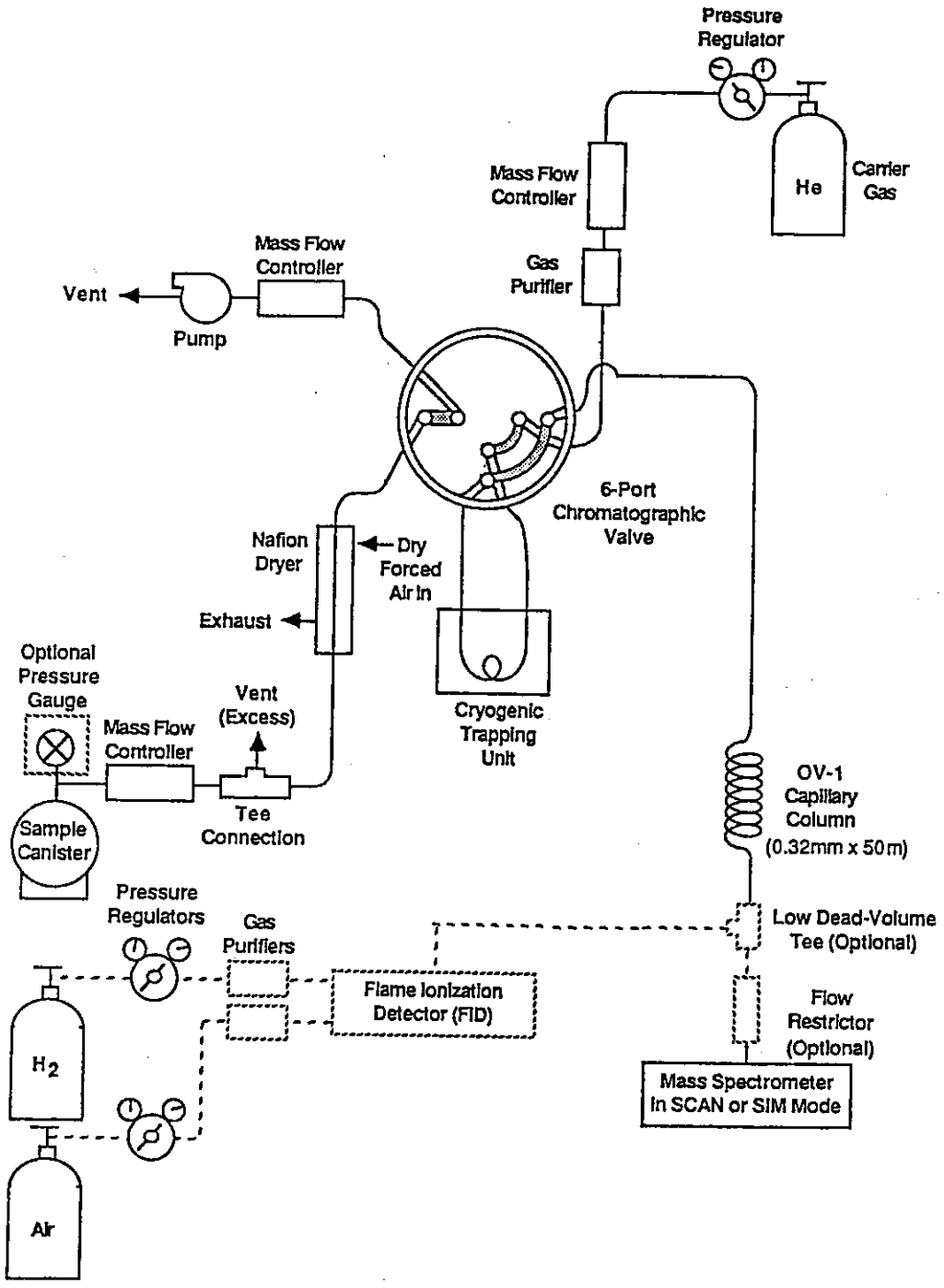


Figure 4. Canister Analysis Utilizing GC-MS-SCAN-SIM Analytical System with Optional Flame Ionization Detector with the 6-Port Chromatographic Valve in the Sample Desorption Mode

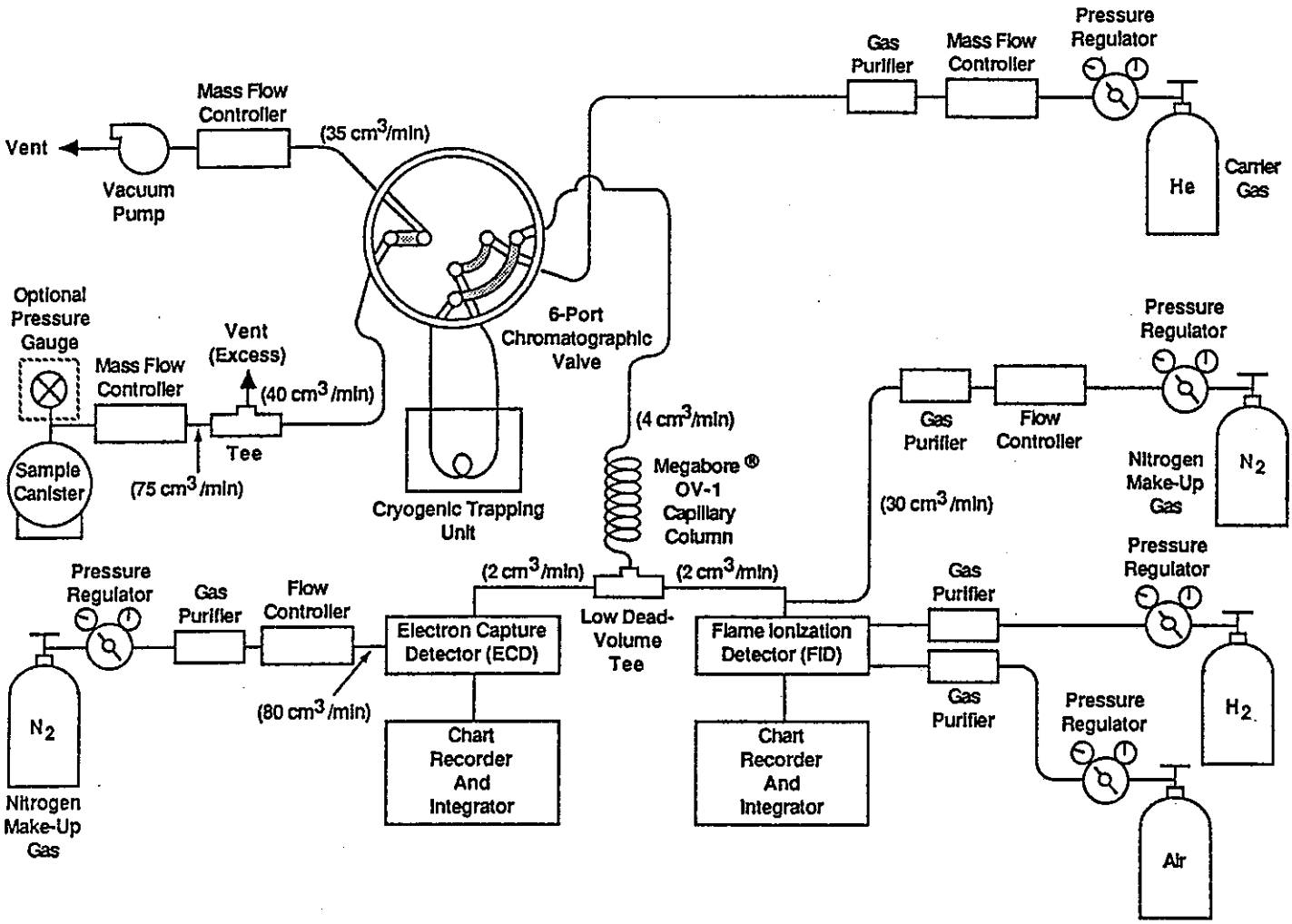


Figure 5. GC-FID-ECD Analytical System with the 6-Port Chromatographic Valve in the Sample Desorption Mode

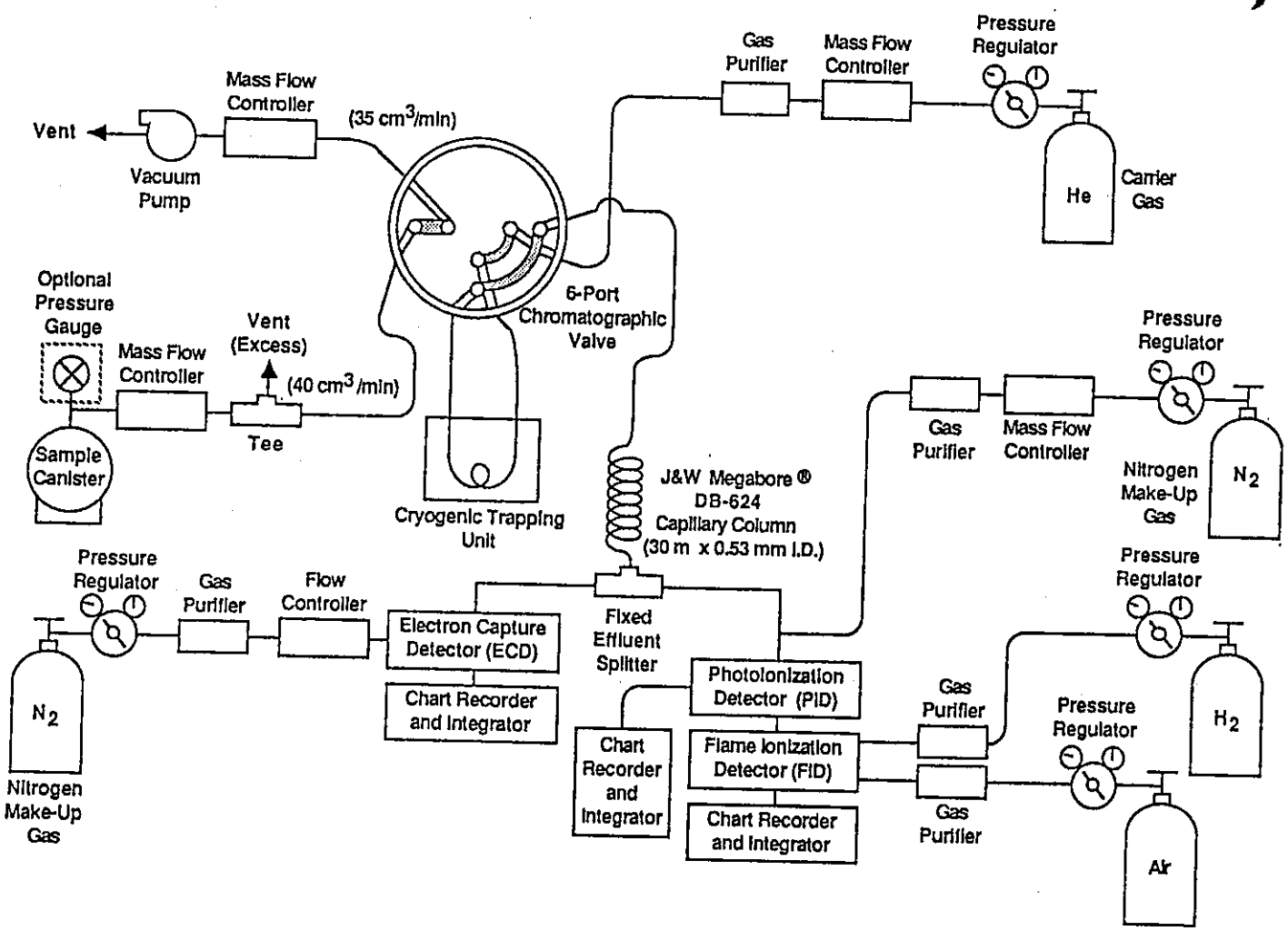


Figure 6. System Configuration Associated with the GC-FID-ECD-PID Analytical System with the 6-Port Chromatographic Valve in the Sample Desorption Mode

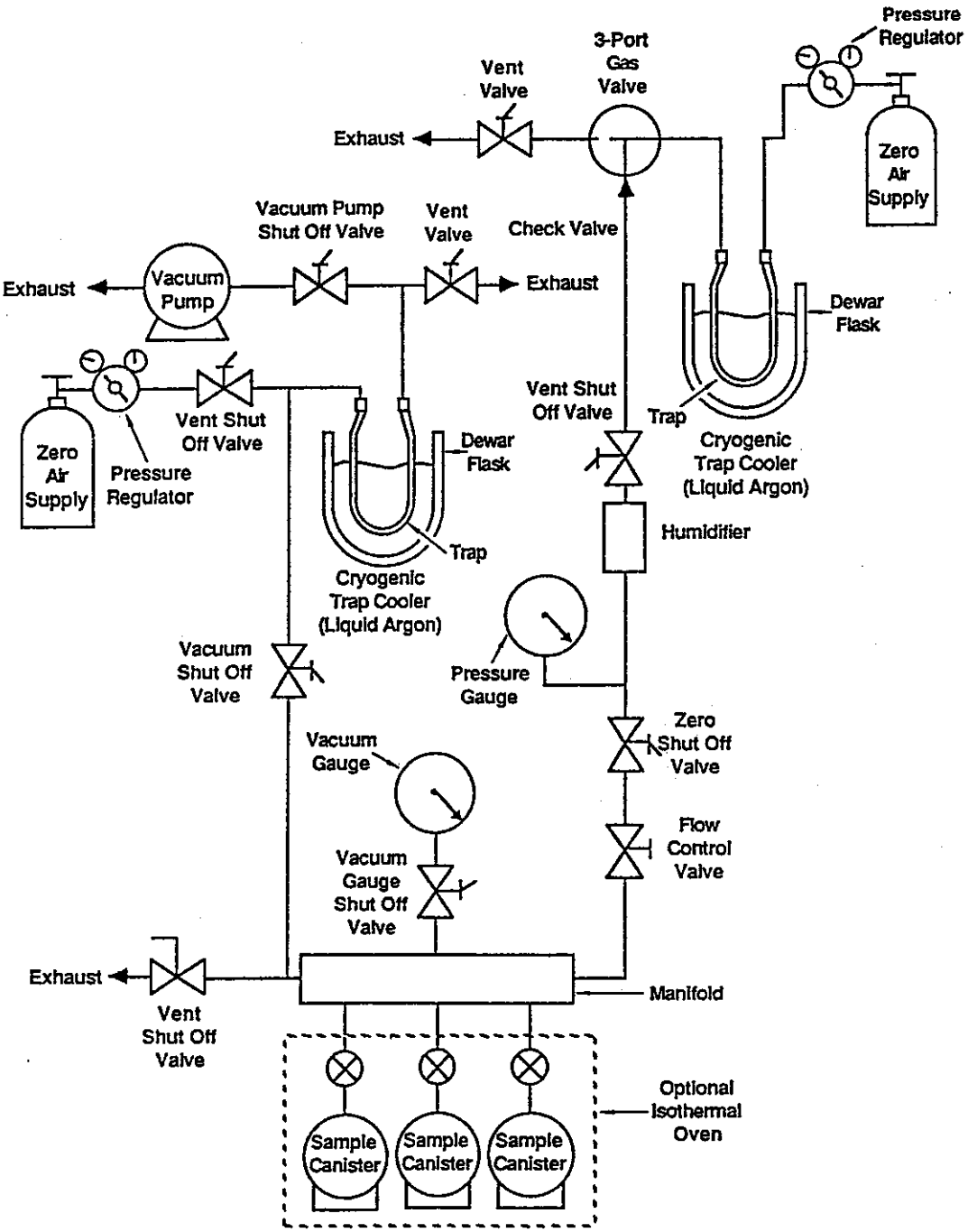


Figure 7. Canister Cleaning System

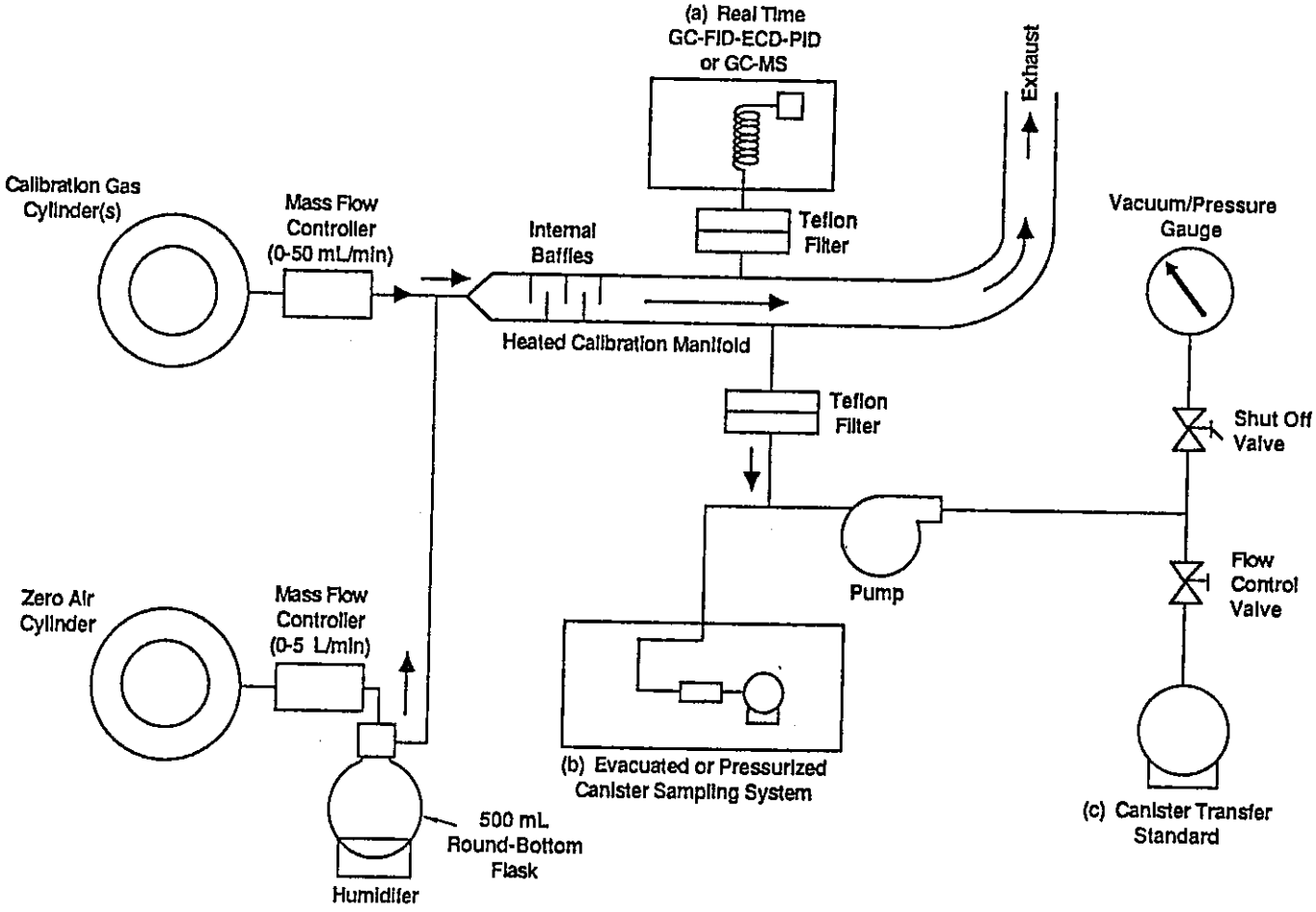
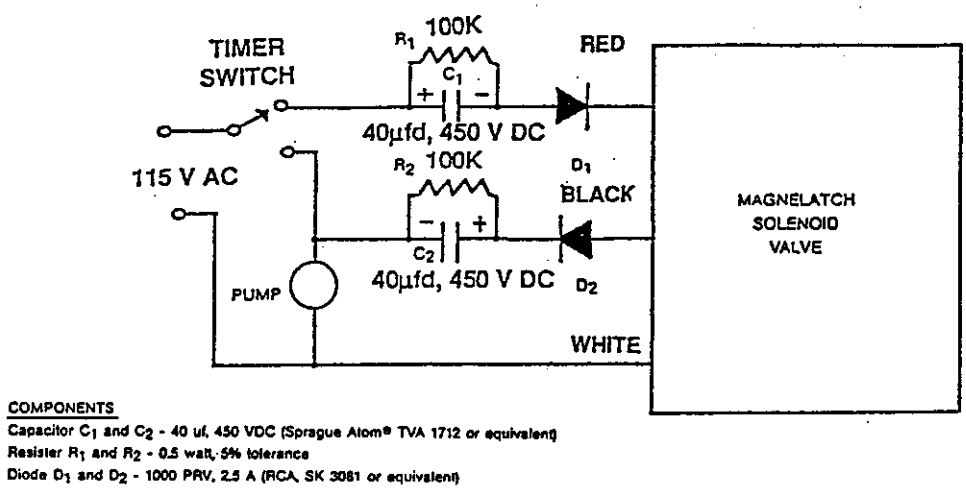
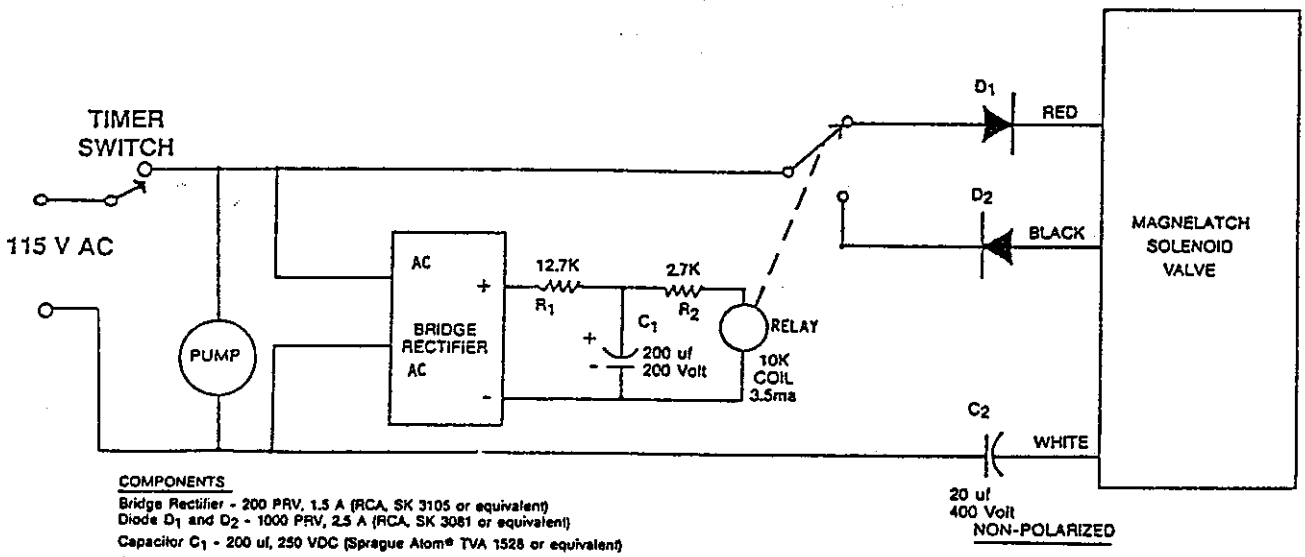


Figure 8. Schematic of Calibration System and Manifold for a) Analytical System Calibration, b) Testing Canister Sampling System and c) Preparing Canister Transfer Standards



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			X	X
STOP				

PRESSURE

CANISTER PRESSURE	
X	

SAMPLING TIMES

	LOCAL TIME	ELAPSED TIME METER READING
START		
STOP		

FLOW RATES

MANIFOLD FLOW RATE	CANISTER FLOW RATE	FLOW CONTROLLER READOUT

SAMPLING SYSTEM CERTIFICATION DATE: _____
QUARTERLY RECERTIFICATION DATE: _____

C. LABORATORY INFORMATION

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

_____
SIGNATURE/TITLE

* ATTACH DATA SHEETS

Figure 10. Canister Sampling Field Data Sheet

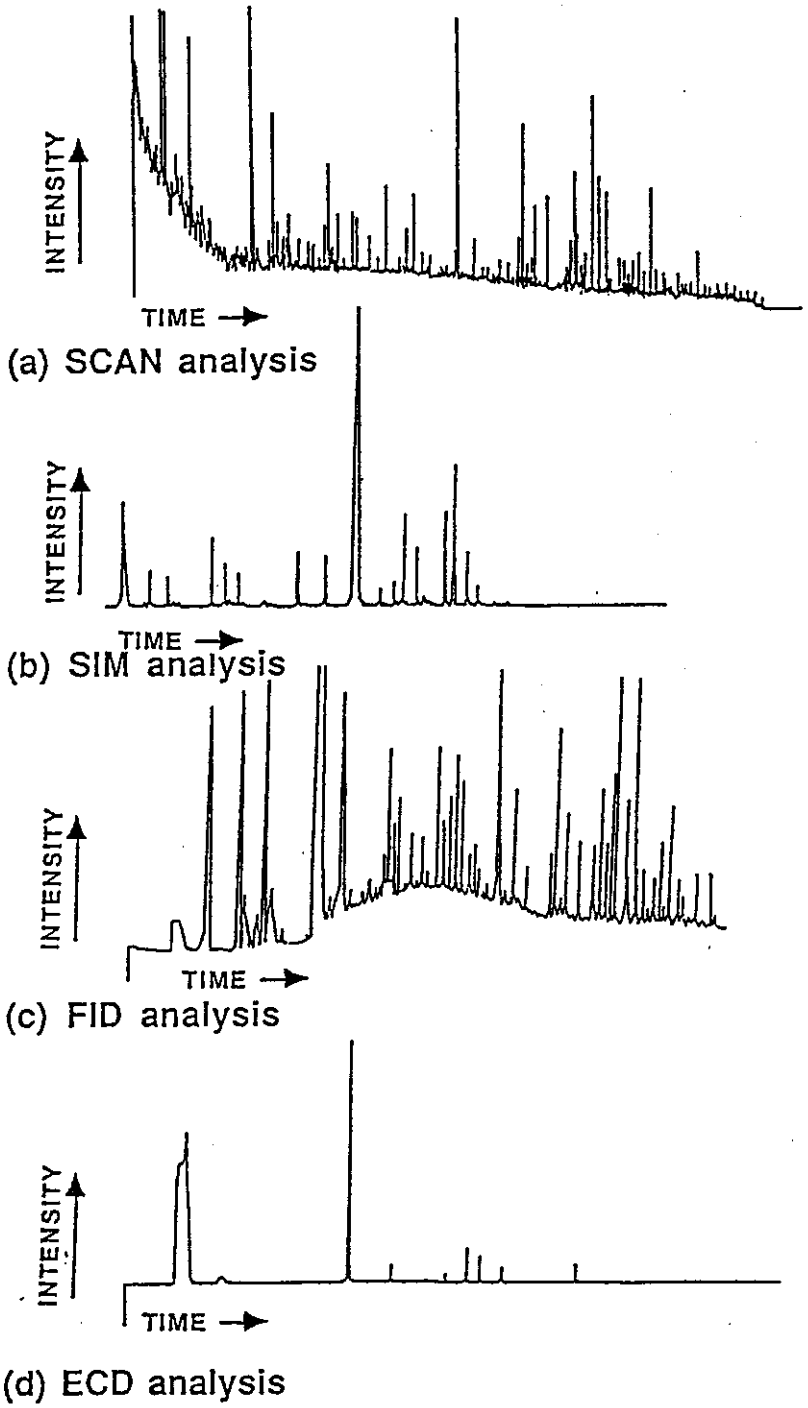


Figure 11. Typical Chromatograms of a VOC Sample Analyzed by GC-MS-SCAN-SIM Mode and GC-Multidetector Mode

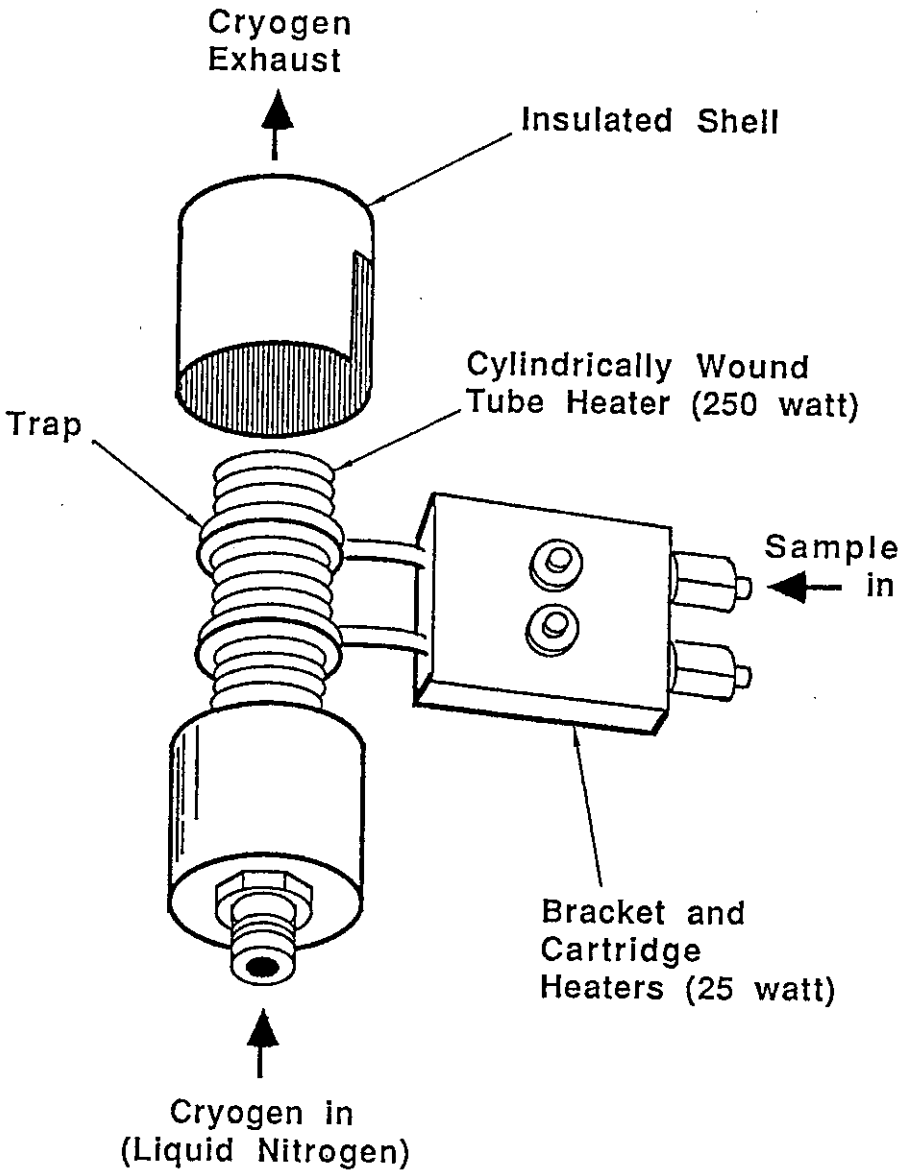


Figure 12. Cryogenic Trapping Unit

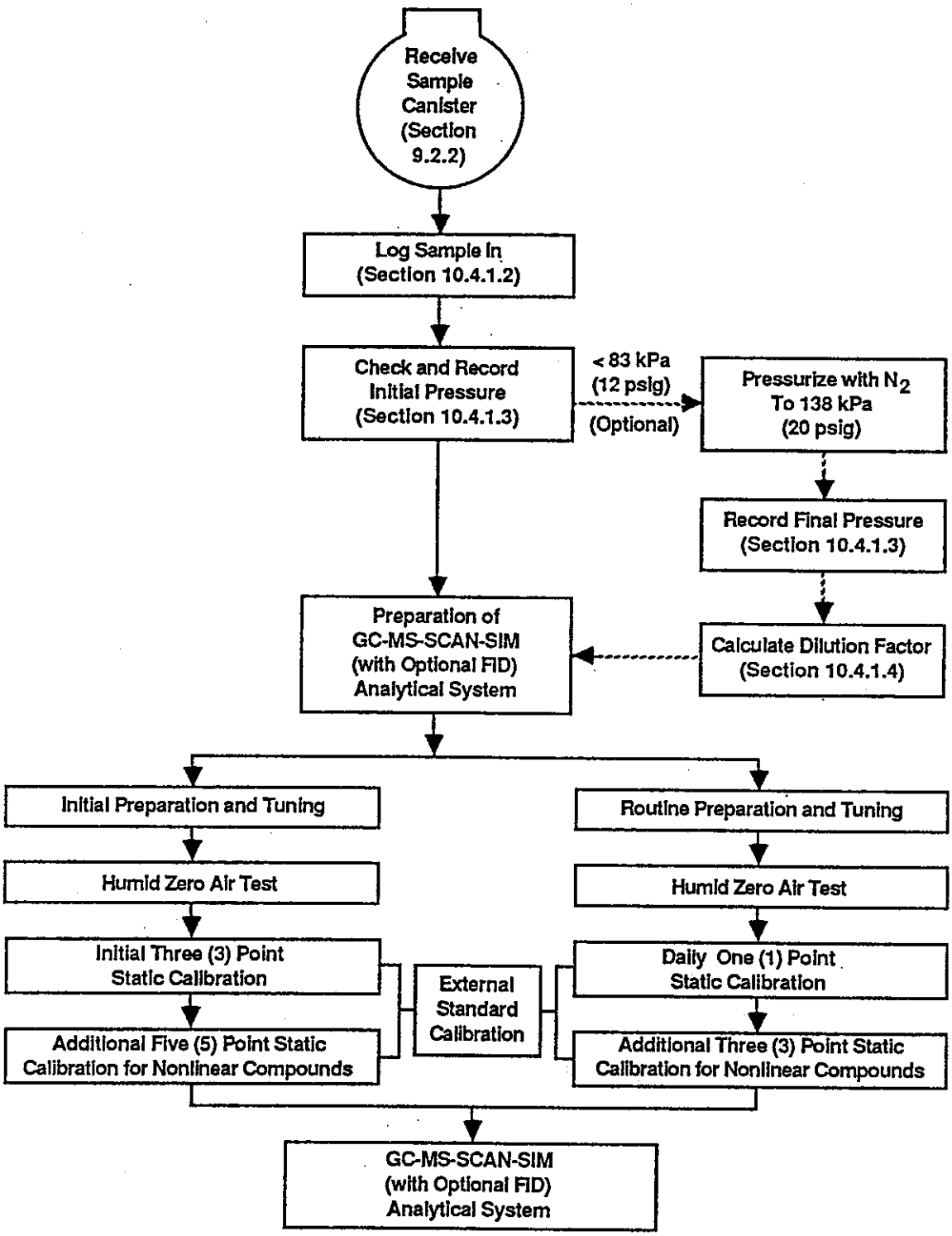


Figure 13. Flowchart of GC-MS-SCAN-SIM Analytical System Preparation (with Optional FID System)

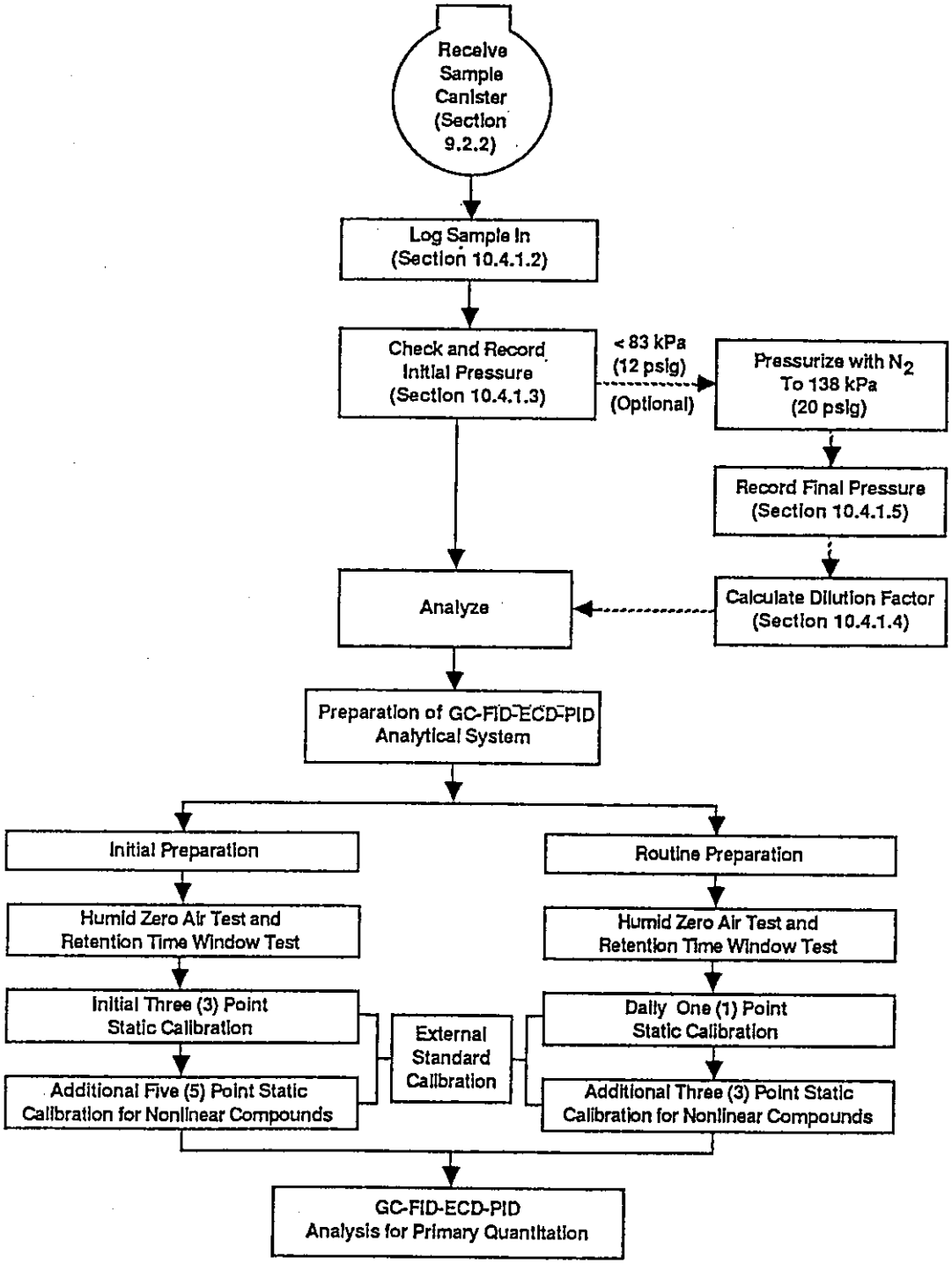


Figure 14. Flowchart of GC-FID-ECD-PID Analytical System Preparation

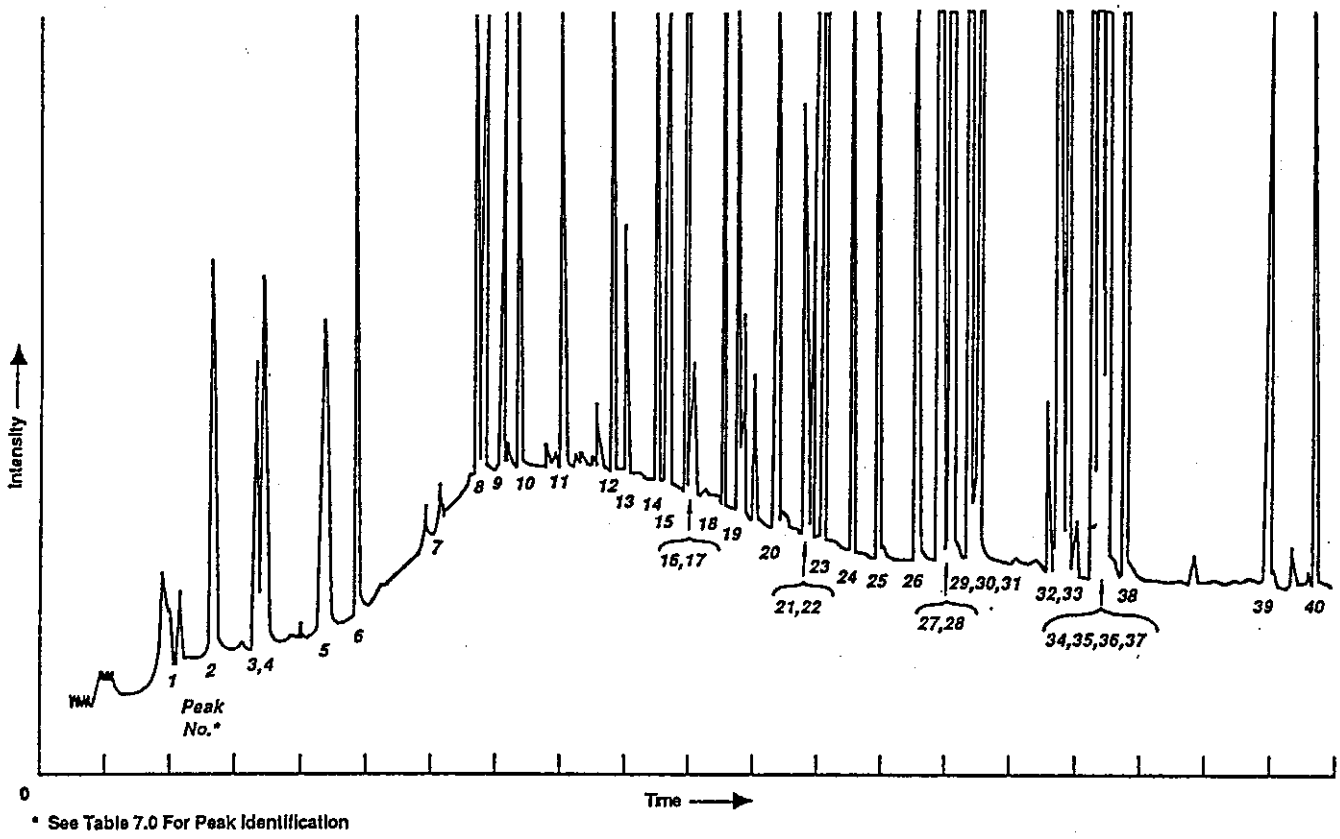


Figure 15. Typical FID Response to Selective VOCs

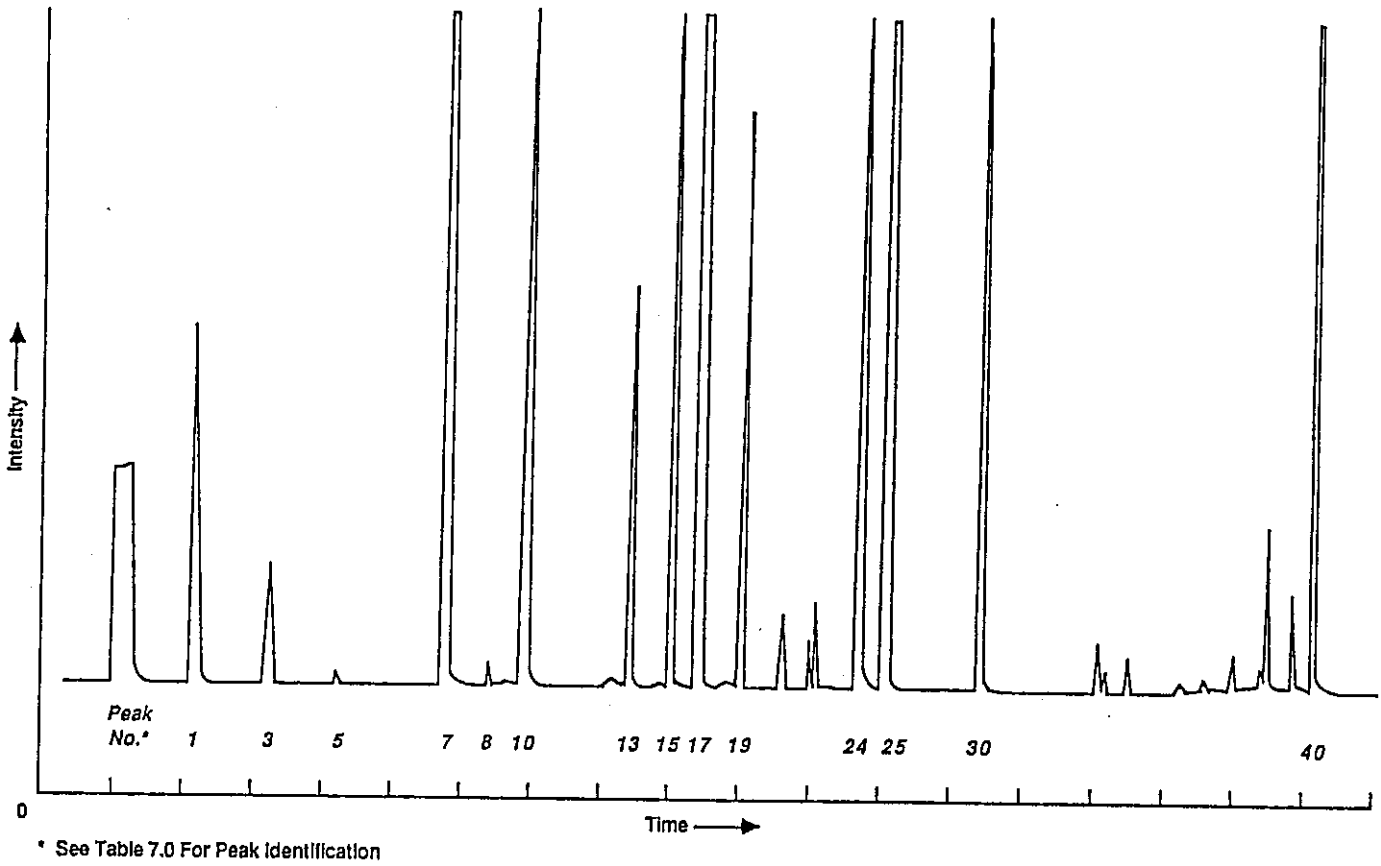
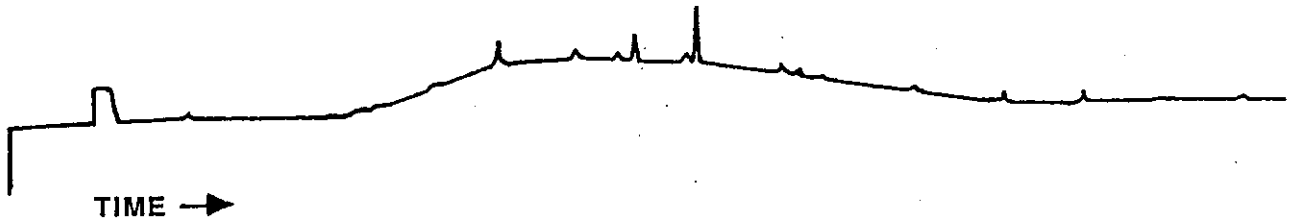
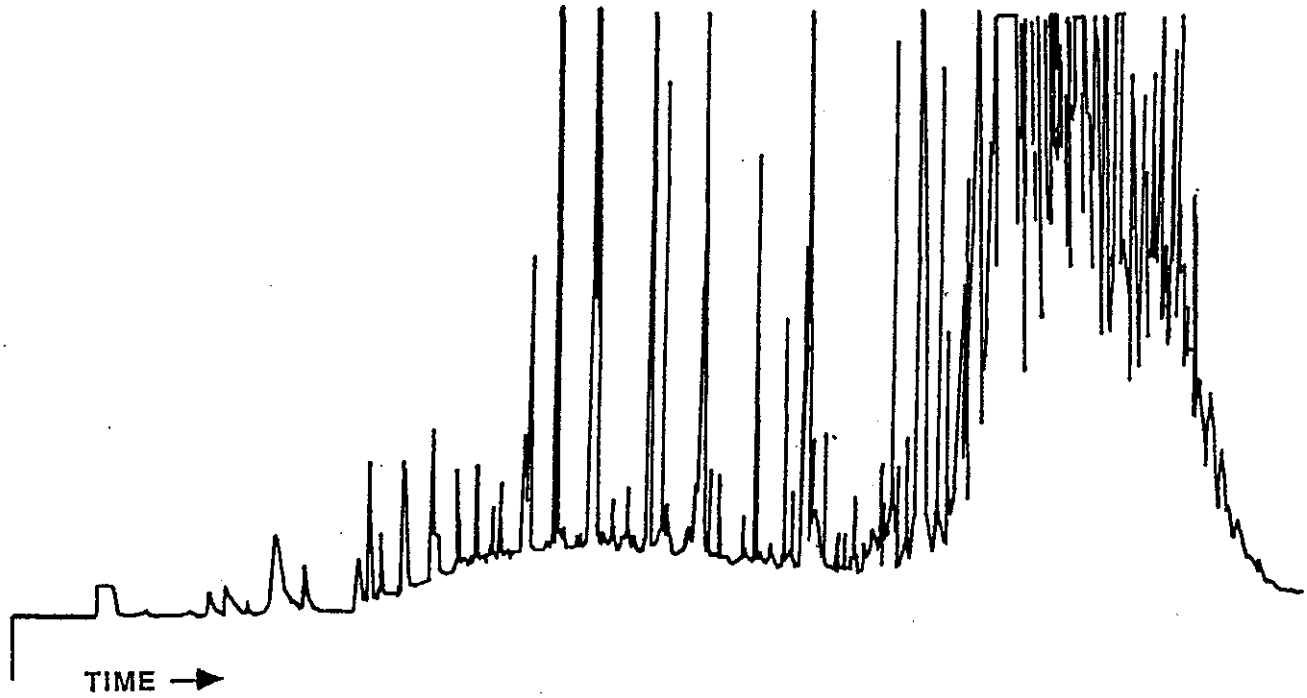


Figure 16. Typical ECD Response to Selective VOCs



(a). Certified Sampler



(b). Contaminated Sampler

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

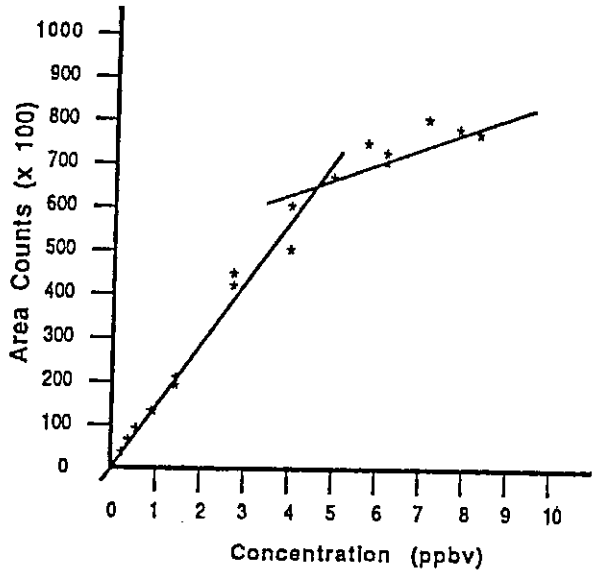


FIGURE 18(a). NONLINEAR RESPONSE OF TETRACHLOROETHYLENE ON THE ECD

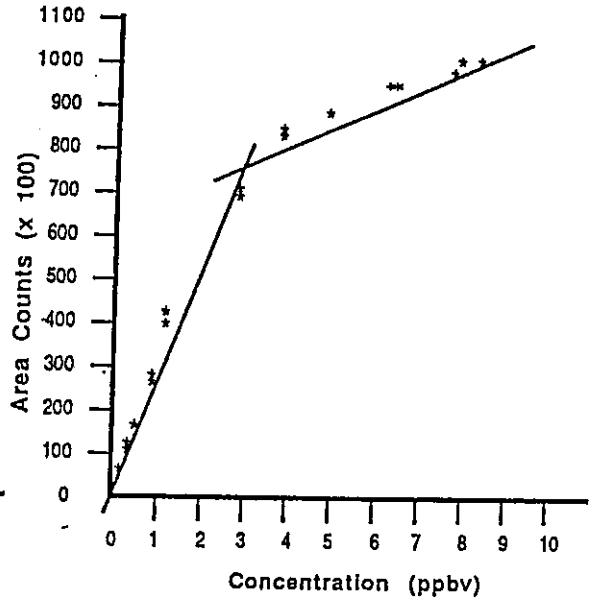


FIGURE 18(b). NONLINEAR RESPONSE OF CARBON TETRACHLORIDE ON THE ECD

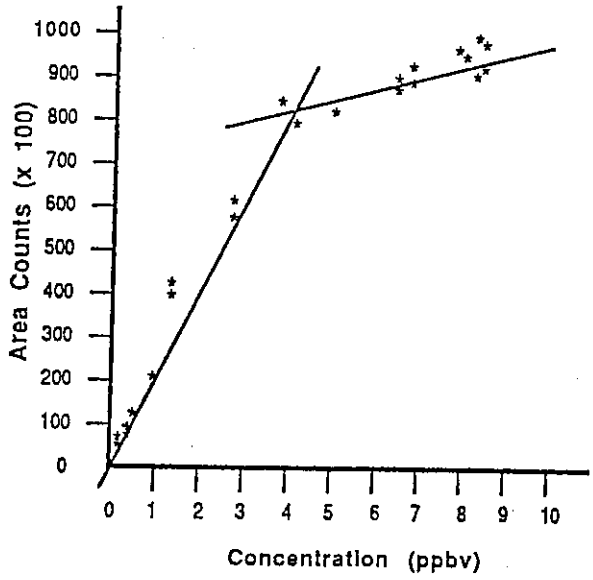


FIGURE 18(c). NONLINEAR RESPONSE OF HEXACHLOROBUTADIENE ON THE ECD

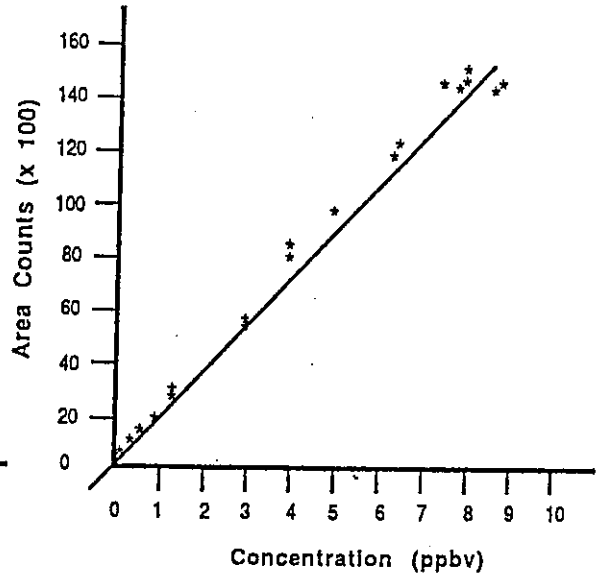


FIGURE 18(d). LINEAR RESPONSE OF CHLOROFORM ON THE ECD

Figure 18. Response of ECD to Various VOCs

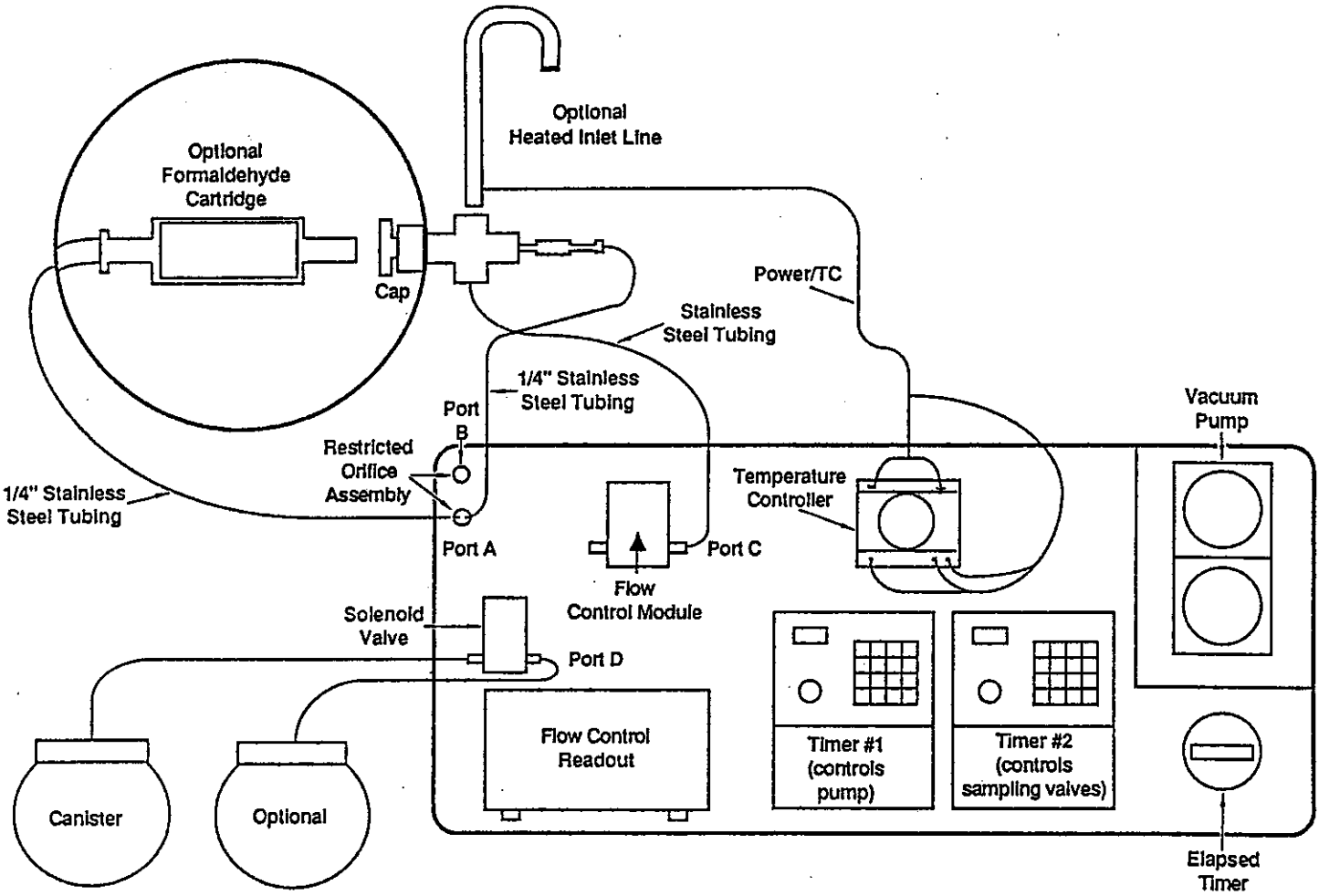


Figure 19. U.S. Environmental Protection Agency UTAP, Schematic of Sample Inlet Connections Sampler

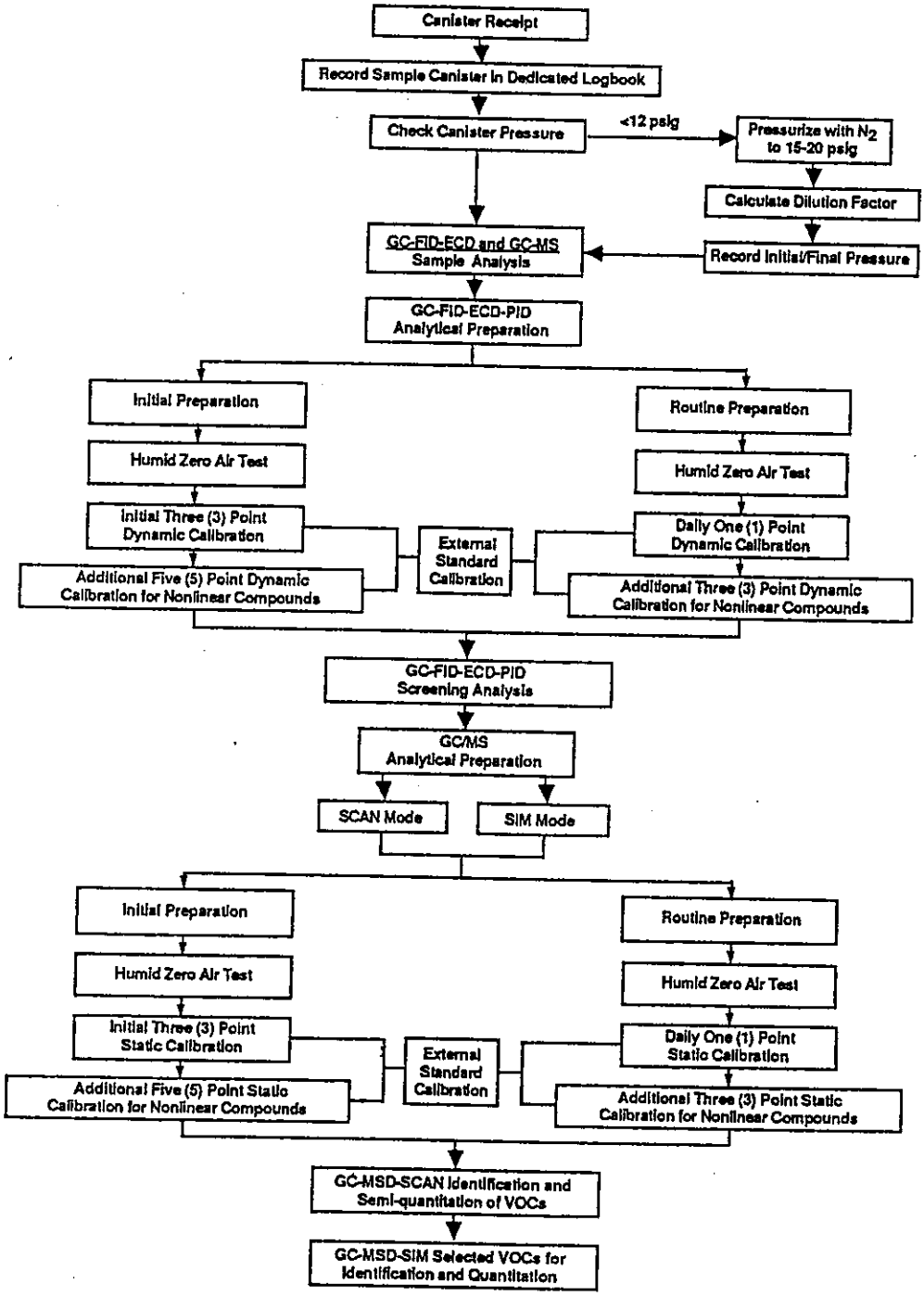


Figure 20. Flowchart of Analytical Systems Preparation

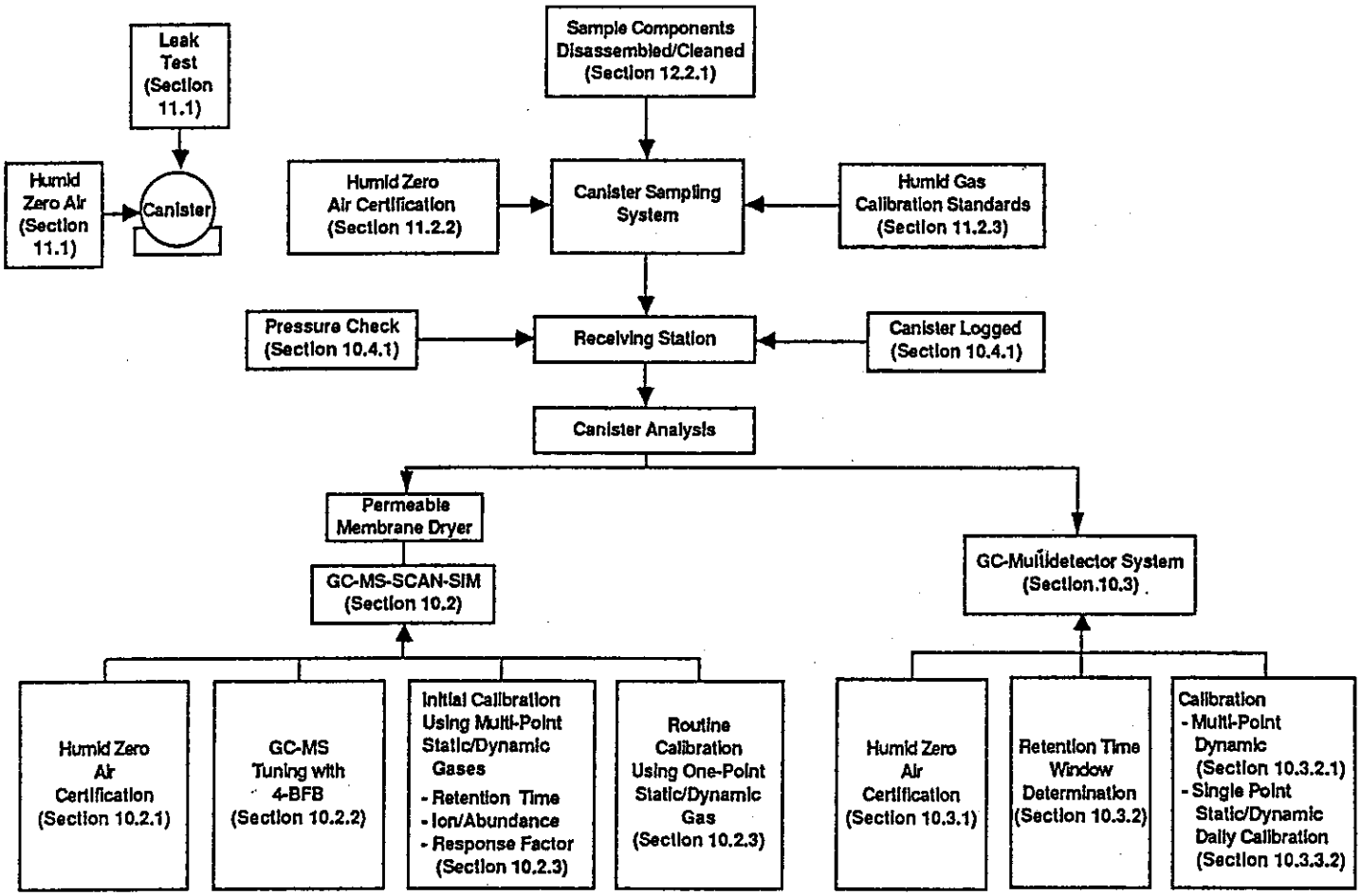


Figure 21. System Quality Assurance/Quality Control (QA/QC) Activities Associated with Various Analytical Systems

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

1. Availability of Audit Cylinders

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

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

2. Audit Cylinder Certification

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

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

3. Audit Cylinder Acquisition

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

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

3.2 The audit cylinders may be acquired by contacting:

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

Table A-1. Available USEPA Performance Audit Cylinders

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

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

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

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

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

1. Scope

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

2. Applicable Documents

2.1 ASTM Standards

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

2.2 Other Documents

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

3. Summary of Method

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

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

4. Significance

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

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

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

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

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

5. Definitions

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

6. Interferences

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

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

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

7. Apparatus

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

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

8. Reagents and Materials

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

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

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

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

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

9. Procedure

9.1 Instrument Setup

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

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

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

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

9.2 Sample Collection

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

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

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

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

9.3 Sample Analysis

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

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

10. Performance Criteria and Quality Assurance

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

10.1 Standard Operating Procedures

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

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

10.2 Quality Assurance Program

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

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

10.2.3 Blanks, Duplicates, and System Performance Samples

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

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

10.3 Method Precision and Accuracy

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

10.4 Range and Limits of Detection

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

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

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

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

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

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

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

Table B-2. Commercially Available Portable VOC Detection Instruments

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

Table B-3. Portable Gas Chromatograph Sampling Data Sheet

DATE: LOCATION: TIME:

CHROMATOGRAPHIC CONDITIONS:

COLUMN 1: COLUMN TYPE:

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

COLUMN 2: COLUMN TYPE:

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

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

SITE PLAN (indicate sampling locations):

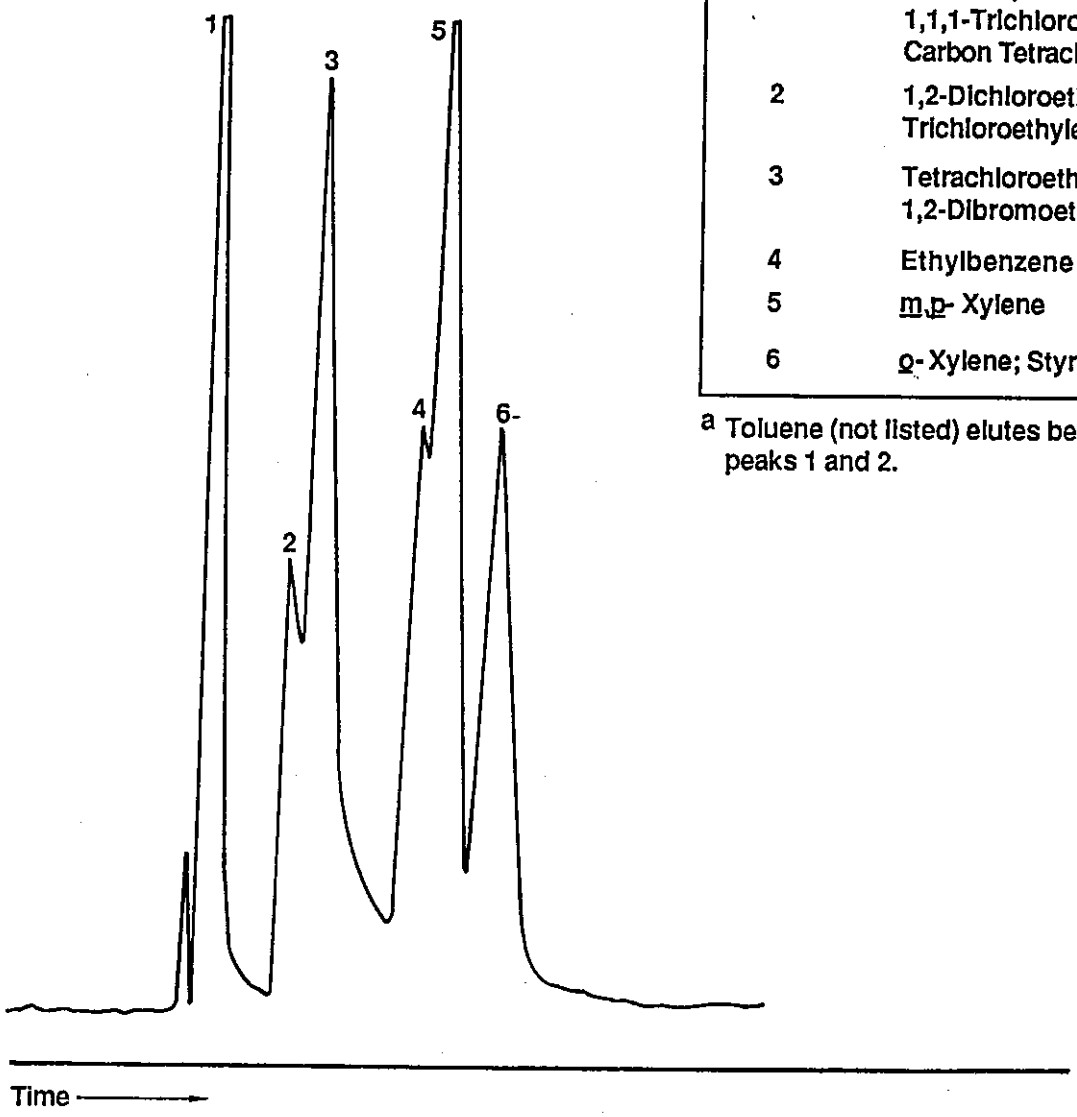
DATE SIGNATURE

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

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

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

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



Peak Assignments For Standard Mixture

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

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

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

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

1. Scope

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

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

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

2. Summary of Method

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

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

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

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

3. Sampler Installation

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

3.2 Electrical Connections (Figure C-1)

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

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

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

3.3 Pneumatic Connections

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

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

4. Sampler Preparation

4.1 Canister

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

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

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

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

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

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

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

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

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

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

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

4.1.11 The canister valve(s) are fully opened.

4.2 Timers

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

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

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

4.2.3 The elapsed time meter is set to 0.

4.3 Sampler Check

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

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

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

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

4.3.1.4 Both timers are set to "AUTO".

4.3.1.5 Both timers are initially OFF.

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

4.3.1.7 Elapsed time meter is set to 0.

4.4 Sampler Recovery (Post Sampling)

4.4.1 The valve on the canister is closed.

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

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

5. Timer Setting

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

5.1.1 Pressing the reset button,

5.1.2 Entering the correct day number and time of day,

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

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

5.2 Timer Reset

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

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

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

5.3 Date and Time Entry

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

5.4 ON and OFF Entry

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

5.5 ON and OFF Verification

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

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

Table C-1. Net Flow Controller Setting

DATE	1 CANISTER	2 CANISTERS

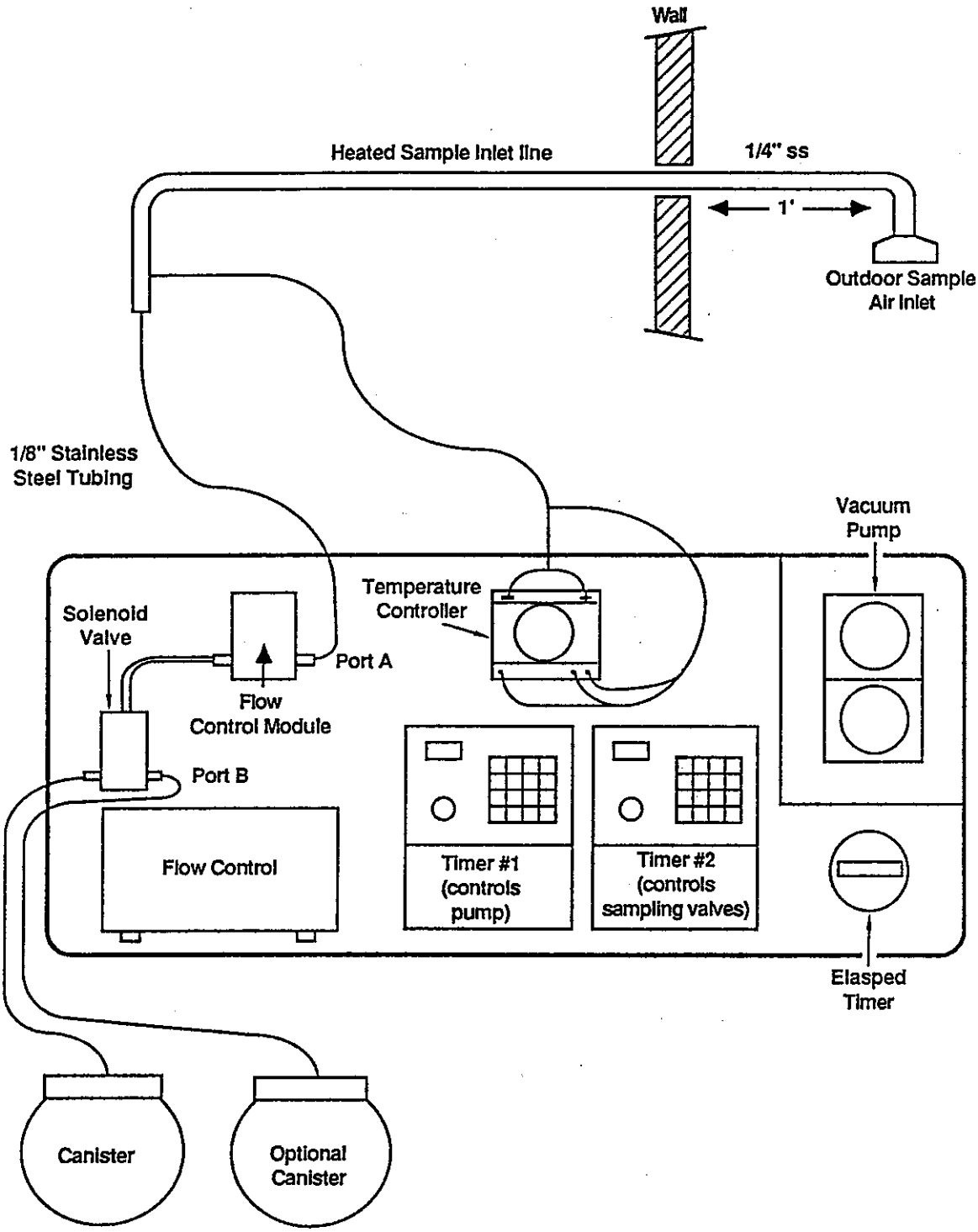


Figure C-1. Alternative 24-Hour Air Toxic Sampling System

Method IP-1B

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

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Appendix - Availability of Audit Gases

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

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

12.2.8 Turn on the master power switch to the chromatograph.

12.2.9 Set manifold temperature to 105 ± 5°C.

12.2.10 Set ionization temperature to 260°C.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

12.4.6 Select one scan to check the % RA.

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

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

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

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

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

12.5 Calibration of the GC-MS-DS System

12.5.1 External Standard Calibration Procedure

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

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

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

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

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

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

12.5.1.6 A RF is determined for each compound of interest.

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

12.5.1.8 Calculate three sets of RFs for each ion of interest for each target compound by the following equation:

$$\text{Response Factor (RF)} = A_i/C_i$$

where:
A_i = area counts for most intense ion, and
C_i = nanograms of standard deposited on cartridge

12.5.1.9 Tabulate these RFs.

12.5.1.10 If several RFs in a particular assay can be identified as outliers by their lack of correspondence to the other values obtained, discard that set of RFs.

12.5.1.11 If the ratio of response to concentration is a constant over the working range (< 10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio of RF can be used in place of a calibration curve.

12.5.1.12 If the set of three RFs does not appear to be consistent, immediately check the desorption unit, gas chromatograph, and mass spectrometer for the presence of an air leak or some other problem, rectify the problem, and repeat the series of three cartridges. Note: If substantial nonlinearity is present in the calibration curve a nonlinear least squares fit (e.g., quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where:
Y = peak, area counts

X = quantity of component, ng
A, B, and C are coefficients in the equation

12.5.1.13 Initiate quantitation of the calculated RFs for target compounds and creation of the library in the data system to obtain ion peak areas and scan numbers automatically for each ion of each compound.

Note: The data system should include information about compound ions, the scan number at which the compound should be sought, and the Method file. The Method file contains information needed to designate a mass range in which to search for ions of the target compounds and establishes parameters required for peak area quantitation.

12.5.1.14 Create a library file for the target compounds within the data system.

12.5.1.15 Verify the correctness of all information entered (RFs, amount added to cartridge, etc.) for the ion of a compound by inspecting the terminal display.

12.5.1.16 When both a Quantitation List and a Library have been created, obtain calculated Response Factors by making a correlation between the ion of the compound and a library entry number.

12.5.1.17 Correlate all ions to a library entry.

12.5.1.18 Store RFs in a Response list of the computer.

Note: The computer, using a QUAN program, will automatically calculate ng/cartridge for targeted compounds.

12.5.1.19 Transfer all data acquired to a nine-track magnetic tape for archiving and possible further reference.

12.5.2 Internal Standard Technique Using Relative Response Factors (RRFs)

12.5.2.1 To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standards can be suggested that is applicable to all samples. The compounds recommended for use as surrogate spikes have been also used successfully as internal standards, because of their generally unique retention times.

12.5.2.2 Prepare five calibration standards, containing all the target compounds, spiked on clean Tenax® tubes as outlined in Section 15.3.

12.5.2.3 To each of these tubes, add a known concentration of an internal standard, as outlined in Section 10.6.2.

12.5.2.4 Analyze each tube according to Section 12.5.

12.5.2.5 Tabulate peak height or area responses against concentration for each compound and internal standard. Calculate relative response factors (RRF) for each target compound and the internal standard using the following equation.

Note: Table 1 contains primary quantitation ions to be used for each target compound and internal standard.

$$RRF = (A_x/A_{is})(C_{is}/C_x)$$

where:
A_x = area response for the compound to be measured
A_{is} = area response ion for the internal standard
C_{is} = concentration of the internal standard, ng
C_x = concentration of the compound to be measured, ng

12.5.2.6 Initiate quantitation of the RRFs for the target compounds and creation of the library in the data system.

12.5.2.7 If the RRF value over the working range is constant (< 10% RSD), the RRF can be assumed to be invariant and the average RRF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RRF.

13. Receipt of Samples

13.1 Receive all Tenax® cartridge tubes in a sealed can with the appropriate Chain-of-Custody sheet after standards have been loaded on them.

13.2 Match the Chain-of-Custody Sheet with the corresponding sample to ensure no mixup has occurred.

13.3 Check each Chain-of-Custody Sheet carefully for the following items: 1) a signature of a person relinquishing custody, 2) the amounts of standards loaded on the cartridge, 3) the temperature and volume collected amounts, and 4) the Tenax® batch number.

13.4 Do not analyze any sample that has no Chain-of-Custody sheet or is missing any of the above information.

13.5 Put all cans of samples in the cartridge freezer when received.

13.6 Log each sample in the appropriate notebook as received.

13.7 Place each Chain-of-Custody sheet in the project notebook (with all other information regarding that particular sample) after signing and dating it.

13.8 Store any used cartridges in sealed cans so they can be recycled, cleaned, and used again.

14. GC-MS-DS Analysis of Tenax® Adsorbent Tubes by Thermal Desorption

14.1 Description of Analytical Process

14.1.1 The instrumental conditions for the analysis of volatile organics on Tenax® sampling cartridge are outlined in Table 4. The thermal desorption chamber and the six port Valco valve are maintained at 275°C during analysis. The mass spectrometer is set to scan the mass range from approximately 35-350. The helium purge gas through the desorption chamber should be 10 mL/min. The nickel capillary trap on the inlet manifold should be cooled with liquid nitrogen.

14.1.2 Initially, the thermal desorption unit is cold while the Tenax® traps are placed inside while flowing helium through them. This allows oxygen to be purged from the trap, reducing oxidative degradation of Tenax®.

14.1.3 Then, during the thermal desorption cycle, helium gas continues to flow through the cartridge to purge the organic vapors on the Tenax® into the liquid nitrogen capillary trap.

14.1.4 After the desorption has been completed, the six-port valve is rotated and the temperature on the capillary loop is rapidly raised (greater than 100°C/min); the carrier gas then introduces the vapors onto the high resolution GC column. The bonded phase fused silica capillary column is temperature programmed from 40°C (5 min hold) to 240°C at 4°C/min and held at the upper limit for a minimum of 15 min.

14.1.5 The column is programmed to a temperature to allow the elution of all of the organic compounds while the mass spectrometer is scanning. Data are recorded by the computer for subsequent processing. Quantitation is performed by the method of response factors (see Section 12.5), where the proportionate system responses for analyte and standard are determined prior to the analysis of the sample and this relative system response is used to determine the quantity of compound present on the sample cartridge.

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

14.2 Desorption Process

Note: The following outlines typical steps associated with thermal desorption using the NuTech device. They are presented as a guideline to follow when using general equipment.

14.2.1 Remove the sealed paint can containing the desired cartridge from the freezer. Note: Use the freezer in the laboratory designated for cartridge storage ONLY for this purpose. Inadvertent storage of containers of solvent in this freezer will result in contamination of all cartridges stored in the freezer and will compromise the analysis, since organic solvents are frequently target compounds for quantitative analysis. Verify that the laboratory personnel are not involved in any process which requires the presence of open containers of organic solvents as the fumes of organic solvents will hopelessly contaminate a Tenax® cartridge exposed to this atmosphere for only a few seconds, thus compromising the quantitative and/or qualitative assay.

14.2.2 Open the sealed lid of the paint can, using a flat-bladed screwdriver, beverage can opener, or other convenient tool for this purpose.

Note: The cartridge will be in a stainless steel culture tube with a Teflon-lined screw cap.

14.2.3 Remove a single culture tube from the paint can and place in the wooden cartridge holder in front of the gas chromatograph.

14.2.4 Seal the paint can and replace in the freezer.

14.2.5 Release the Teflon cap of the desorption chamber.

14.2.6 Remove the cartridge from the culture tube using forceps.

Note: DO NOT TOUCH THE CARTRIDGE WITH YOUR HANDS! The slightest trace of organic compounds present on the fingertips can be sufficient to compromise the analysis. If the cartridge is inadvertently touched, make careful note of the circumstances in both the instrument log and the project notebook.

14.2.7 Insert the cartridge immediately into the desorption chamber.

14.2.8 Close the Teflon cap of the desorption chamber.

14.2.9 Initiate the timing of the eight-minute desorption cycle.

14.3 Injection Procedure

14.3.1 At the end of the eight-minute desorption cycle, turn the desorption unit valve to the INJECT mode (down).

Note: The following sets are automatic on some commercially available instruments.

14.3.2 Initiate heating of the nickel trap.

14.3.3 Begin acquisition of data system.

14.3.4 Turn off the trap after it has heated to 240°C.

14.3.5 Press the "start run" key on the GC microprocessor simultaneously with the <CR> key on the data-system terminal. This starts the GC temperature program and the data acquisition program.

14.3.6 Turn the thermal desorption unit valve back to desorb and remove the Tenax® cartridge.

14.3.7 At the end of the run, the GC will recycle and cool to 30°C, and the data acquisition will stop automatically after 4500 scans have been acquired.

14.3.8 The analysis may be stopped before 4500 scans by pressing the "stop run" key on the GC microprocessor. The data acquisition may then be stopped by typing [<CTRL>D] on the data system terminal and then typing [E<CR>STOP<CR>].

14.3.9 Repeat this procedure for each Tenax® cartridge to be analyzed.

14.4 Data Tabulation and Storage

14.4.1 Data from GC-MS runs are normally processed by the data system in an automated program which locates the compounds of interest in the data set, quantifies those compounds for which calibration data are available, and prints a report. A typical report will present the quantification parameters and result for those compounds present and quantifiable. The report will typically list those compounds which were searched for in the sample, indicate which ones were not found, print the identifying characteristics and quantification results for those which were found, and present comments for the operator's benefit, such as the criteria which caused a peak to be rejected or the center scan for any search which failed. The information in the report can also be saved in a DS file for archival storage and DS transfer purposes.

14.4.2 The library in the data system should contain a file composed of one entry for each compound of interest. For each entry, the library contains the compound name, its mass spectrum from the Mass Spectral Data Base, its absolute retention time, and its

retention time relative to perfluorotoluene, the retention time marker, as determined from authentic standards. Response lists (RL) are compound specific DS files containing the quantitative calibration data for each of the target compounds.

14.4.3 The automated procedure attempts to locate chromatographic peaks corresponding to target compounds by a reverse library search using the following criteria for scan window:

- for internal standards: ± 100 scans from library scan number
- for single compounds: ± 20 scans from the calculated scan
- for isomer groups: -20 and +20 scans from the calculated scans for the earliest and latest eluting members of the group, respectively
- Peak identification: peak 1/2-width ≥ 5 scans, purity ≥200, fit ≥700
- Peak selection: the scan list is partitioned in order of increasing distance from the center of the scan window, except for isomer groups

14.4.4 The automated procedure begins by attempting to locate the two retention time markers (PFT and 1,2-dichlorobenzene) and the internal standards ($toluene_{d8}$). If the early eluting standard, PFT, is not located a warning message is printed and the procedure is terminated. If only the late eluting internal standard is not found, the procedure uses the scan number calculated from the library retention time for this standard as a default value. Note: Alternatively, the operator may specify scan numbers for the internal standards and then initiate the remainder of the automated procedure. The procedure cycles through the compounds in the library list attempting to locate each compound in turn.

14.4.5 If one or more peaks are identified in the search for a target compound, the resulting scan list is partitioned to order the scans in increasing distance from the center of the search window. The mass spectra in the partitioned list are sequentially compared to the library entry for the target compound in order to the mass weighted purity, fit and rfit. The following ratio ranges are tested:

- Fit/purity: >0.99, <1.30
- Rfit/purity: >0.99, <1.05

If rfit/purity passes but fit/purity exceeds 1.29 the spectrum is enhanced, reprocessed through the library comparison, and tested against the above criteria.

14.4.6 If the mass spectrum at the peak maximum passes either of the above tests, the procedure attempts to quantify the peak. If the target is a single compound, only the first peak to pass the qualitative criteria is processed further. If the target is an isomer group, all peaks detected by the search are processed through the qualitative filters and all that pass these filters are quantified. If no peaks are found by the search or pass through the qualitative filters, a "not found" entry is placed in the report.

Note: The failure of a peak to satisfy these criteria does not necessarily prove the absence of the compound in the sample. Interfering compounds or low levels of the compound of interest may cause the test values to fall outside of the acceptance range. It is also possible to obtain acceptable values for fit/purity and rfit/purity, but have a questionable identification. If the absence of a particular compound is of crucial importance and the DS procedure fails to locate the compound, or for any compound which has a fit, purity, or rfit

less than 700, manual inspection of the data by a person skilled in the interpretation of GC-MS data is necessary for confirmation.

14.5 Qualitative Peak Identification

14.5.1 Relative intensities of major ions in the reference spectrum (ions greater than 25% of the most abundant ion) should be present in the sample spectrum.

14.5.2 The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% of the standard spectra, the corresponding sample ion abundance must be between 30 and 70%).

14.5.3 Molecular ions present in reference spectrum should be present in sample spectrum.

14.5.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

14.5.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

14.5.6 If in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (e.g., unknown aromatic, unknown hydrocarbon, unknown chlorinated compound). If a probable molecular weight can be distinguished, include it.

14.6 Peak Quantification

The procedure attempts to quantify peaks which have been qualitatively identified. Quantification is based on integration of the extracted ion current profile (EICP) of a quantitation mass or ion for the compound. This mass has been previously selected for each compound based on its spectral uniqueness, intensity, and lack of potential interferences from known coeluting compounds. Currently used masses are listed in Table 1.

14.7 Sample Quantitation

14.7.1 Sample quantitation is performed by the data processing system for all desired ions of all target compounds.

14.7.2 Utilizing the QUAN package of the data system involving compound identification and response factor to obtain quantitation data of the target compounds by the following equation:

$$X_A = [(A_A)(\mu g_{STD})]/[A_{STD})(RRF)]$$

where:

X_A = amount of target compound, μg
A_A = area of ion of analyte, counts
μg_{STD} = mass of standard applied to tube, μg

A_{STD} = area of standard, counts
RRF = relative response factor (see Section 12.5.2)

14.7.3 The computer, upon request, will print out peak number, m/e, scan, time, relative retention time, area and amount.

14.7.4 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = [(X_A - B_A)(1000\ L)]/[(m^3)(V_S)(R_A)]$$

where:
C_A = calculated concentration of target compound, ng/L
X_A = defined in Section 14.7.2
B_A = amount of target compound on blank, μg
V_S = calculated in Section 11.3.21
R_A = recovery factor, if applicable

15. Generation of Known Concentrations Procedures

15.1 Three procedures are discussed for generating known concentrations of targeted VOCs to be used for direct injection into the GC-MS-DS for calibration or depositing upon Tenax® tubes to be used in calibration of the entire GC-MS-DS analytical system. They are: 1) preparation of known concentrations utilizing static dilution bottles, 2) use of flash vaporization technique for loading targeted VOC standards upon Tenax® tubes and 3) use of permeation tube system for generating known concentrations of VOC standards upon Tenax® tubes. The standards preparation procedures are based on U.S. Environmental Protection Agency SOPs (41,45).

15.2 Flash Vaporization (see Figure 5)

15.2.1 Principle

15.2.1.1 A dilute solution of one or more organic compounds in methanol is injected into a heated zone in a helium stream. The methanol and the solute compounds are rapidly vaporized and then swept onto a sorbent cartridge. Methanol has little affinity for Tenax® sorbent and is rapidly eluted from the cartridge.

15.2.1.2 The solute compounds remain in the sorbent bed when the cartridge is removed from the flow system, and may subsequently be desorbed from the cartridge and delivered to an analytical instrument for analysis.

15.2.1.3 Since the quantity of each compound in the cartridge can be determined from its concentration in the solution and the volume of solution injected, this method may be used to spike quantitative standards on sorbent cartridges.

15.2.2 Interferences

15.2.2.1 Contamination of the methanol solvent with compounds to be calibrated, or with compounds producing similar instrumental responses, will result in false high or false positive responses.

15.2.2.2 Contamination of a compound used as a standard will result in a decreased response. Contamination of one compound with another one to be used in the same solution will result in incorrect responses for both compounds.

15.2.2.3 Chemical reaction between two compounds in a standard mixture will result in low responses for both. Absorption of a compound into the matrix of sorbent particles will probably result in part of it being retained in the cartridge during desorption, with consequent decreased response.

15.2.3 Flash Vaporization Assembly

15.2.3.1 Assemble the flash vaporization unit, as illustrated in Figure 5.

15.2.3.2 Adjust the helium flow to 30 mL/min and the heating mantle to 310 ± 10°C.

15.2.3.3 Allow the helium to flow for approximately 30 minutes to equilibrate the system.

15.2.4 Syringe Cleaning

15.2.4.1 Rinse individual syringe with methanol and acetone.

15.2.4.2 Dry in a vacuum syringe cleaner for ~30 seconds. (A heat gun is used to heat the barrel of the syringe during vacuum drying).

Note: Syringes must be rigorously cleaned after each injection to remove traces of sample. Even if more than one injection is needed from any given source a freshly cleaned syringe must be used for each injection. Failure to do so will probably result in erratic responses.

15.2.5 Helium Volume Required

15.2.5.1 The volume of helium required to elute methanol from a sorbent cartridge is determined by using a thermal conductivity detector.

15.2.5.2 Several different flow rates are tried to find one which results in as sharp a methanol peak as possible without sweeping volatile solutes out of the cartridge before it can be removed from the system.

15.2.6 Preparation of Standard Gas Concentration

15.2.6.1 Set the helium flow to 30 mL/min and the heater to 310° ± 10°C.

15.2.6.2 Place a clean (see Section 10.2) Tenax® cartridge in line.

15.2.6.3 Pass helium through the cartridge for a period of 5 minutes.

15.2.6.4 Using a heated syringe retrieve from the individual standard flask an aliquot by the following procedure:

15.2.6.4.1 Pull a 1 μL sample of methanol into the syringe.

15.2.6.4.2 Next draw a 1 μL plug of air.

15.2.6.4.3 Then pull the calculated quantity of standard solution into the syringe.

15.2.6.4.4 Finally, continue to pull another 1 μL plug of air.

Note: This insures that the sample solution is flushed completely out of the needle by the methanol plug during injection.

15.2.6.5 With the aliquot of the standard in the syringe, inject smoothly, at the standard injection point, the syringe contents over a period of about 5 seconds.

15.2.6.6 Allow the helium containing the injection standard to pass through the cartridge for 50 minutes or until 1500 mL of helium has passed.

15.2.6.7 Remove the cartridge from the system, cap and store at 5°C.

15.2.7 Calculation of Deliverable Concentration

15.2.7.1 The approximate volume of solution to be injected is calculated by working backward from the size of the spike to be placed in the sorbent cartridge.

15.2.7.2 For example, if a 500 ng spike is needed, it could be done by injecting 10 µL of methanol containing 50 ng/µL of solute. Therefore, 10 µL x 50 ng/µL solution = 500 ng.

15.2.7.3 A solution containing 50 ng/µL of solute is prepared by dissolving 5 mg of neat compound in a 100 mL volumetric flask and diluting to mark with methanol.

15.2.7.4 If the density of the neat compound is 0.9726 g/mL (0.9726 mg/µL), then the measured neat compound would be

$$5 \text{ mg}/(0.9726 \text{ mg}/\mu\text{L}) = 5.14 \ \mu\text{L}$$

15.2.7.5 Therefore, 5.14 µL of solute measured with a syringe would produce 50 ng/µL solution when diluted to 100 mL with methanol.

15.2.7.6 It is not practical to measure fractions of microliters, so usual practice would be to dissolve 5 µL of sample in 100 mL of methanol to produce a concentration of

$$(0.9726 \text{ mg}/\mu\text{L} \times 5 \ \mu\text{L})/100 \text{ mL} = 0.0486 \text{ mg/mL} = 48.63 \text{ ng}/\mu\text{L}$$

A 10 µL aliquot of this solution would contain 486.3 ng.

15.2.7.7 No correction for impurities in the neat sample is needed if manufacturer's determined purity is 98% or better.

15.2.7.8 As an example, a typical column evaluation mixture can be prepared as follows:

Standard	Density, g/mL	Volume, µL	Weight, mg	Deliverable Volume, µl	Spiked on Cartridges, ng
Ethylbenzene	0.867	11.0	9.54	3	286
p-Xylene	0.861	12.0	10.33	3	310
Acetophenone	1.028	10.0	10.28	3	308
2-Nonanone	0.821	12.0	9.85	3	296

These compounds should be 98% pure or better, and purity should be checked by capillary GC. Each compound is measured into a 100 mL volumetric flask using a microsyringe. The flasks are filled to the mark with spectrographic grade methanol and the contents mixed thoroughly. The solution must be used within half a day. Three microliters of those solutions, when injected into the flash vaporization unit in the manner specified above, will

deposit approximately 300 ng of each compound on a sorbent cartridge as shown in the table above.

15.3 Static Dilution Bottle

15.3.1 Principle

15.3.1.1 A quantity of liquid organic compound is injected into a two-liter round bottom helium-filled flask through a septum cap. After injections are completed, the flask is agitated and heated to achieve complete vaporization.

15.3.1.2 Aliquots of the resulting vapor are then delivered to sorbent cartridges or analytical instruments. The weight of each compound delivered is calculated from 1) the density of the liquid, 2) the volume of liquid injected into the known volume of the bottle, and 3) the volume of the vapor aliquot removed.

Note: The quantity of any compound injected into the dilution flask must be substantially less than that which would result in a partial pressure equal to its vapor pressure at ambient temperature. Vaporization of liquid aliquots injected into the bottle must not result in a large positive pressure, and removal of vapor aliquots from the flask must not result in a substantial vacuum. If these precautions are not taken erratic responses will occur.

15.3.2 Interferences

15.3.2.1 Contamination of a compound used as a standard will result in decreased response. Contamination of one compound with another one used in the same vapor mixture will result in an incorrect response for both compounds.

15.3.2.2 Adsorption of vapor molecules on the walls of the bottle or on the septum will result in loss of material, with a consequent decrease in response. This is especially likely when new, freshly annealed bottles are used. Contamination of apparatus can result in adsorption loss or provide unexpected sources of compounds in a mixture.

15.3.2.3 Chemical reactions between compounds can deplete them from the mixture and might also result in unexpected reaction products. Use of a syringe for consecutive injections from the same bottle without cleaning after each injection will probably result in erratic responses due to buildup of sample residues in the syringe.

15.3.3 Applicability

15.3.3.1 The static dilution bottle technique for preparing standards has been validated for the following 22 substances:

Acetophenone	3,4-Dichloro-1-butene
Benzonitrile	Perfluorotoluene
1,1,1,2-Tetrachloroethane	Fluoroiodobenzene
1,4-Dioxane	1-Ethenyl-4-chlorobenzene
1-Chloro-2,3-epoxypropane	3-Chloro-1-propene
1,3-Dichlorobutane	1,4-Dichlorobutane
1,4-Dichlorobenzene	1,2,3-Trichloropropane
cis-1,4-Dichloro-2-butene	1,1-Dichloroethane

2-Chlorobutane	1-Methyl-4-(1-Methyl-ethyl)-benzene
2-Chloroethoxyethene	Butylbenzene
1-Methylethylbenzene	1,3,5-Trimethylbenzene

15.3.3.2 Amounts used have ranged between 0.3 and 4 μL of liquid samples. Repeatability of daily injections of a mixture of the 22 compounds into the GC-MS is about ± 10% relative standard deviation. Precision depends on the substance introduced, the skill of the individual producing the flask standard, and the skill of the operator of the instrument used to analyze the flask contents. Accuracy has not been established.

15.3.4 Flask Cleaning

15.3.4.1 Wash the two-liter flask with detergent and water.
15.3.4.2 Rinse several times with deionized water.
15.3.4.3 Dry in an oven at 300°C for 4 hours.

15.3.5 Syringe Cleaning

15.3.5.1 Rinse individual syringes with methanol and acetone.
15.3.5.2 Dry in a vacuum syringe cleaner for ~30 seconds. (A heat gun is used to heat the barrel of the syringe during vacuum drying.)
Note: Syringes must be rigorously cleaned after each injection to remove traces of sample. Even if more than one injection is needed from any given source a freshly cleaned syringe must be used for each injection. Failure to do so will probably result in erratic responses.

15.3.6 Flask Calibration

15.3.6.1 Place 30 3-mm glass beads inside the flask and weigh on an analytical balance to an accuracy of 0.01 g.
15.3.6.2 Fill the flask with deionized water to the level of the septum cap.
15.3.6.3 Weigh the flask containing the glass beads and water on an analytical balance to an accuracy of 0.01 g.
15.3.6.4 The weight of the water required to fill the bottle is the difference between the two weights, as calculated below:

$$V_f = (Wt_f - Wt_i)$$

where:
V_f = volume of flask, mL
Wt_f = final weight of flask with beads and water, g
Wt_i = initial weight of flask with beads, g

15.3.7 Preparation of a Standard Gas Solution in a Flask

15.3.7.1 Two methods have been used to load the dilution flask with organic components for standards: 1) direct injection of each compound separately into the flask and 2) a single direct injection of a previously prepared mixture of compounds.

Note: These methods have been shown to produce indistinguishable results.

15.3.7.2 The first method involves injecting each compound (one at a time) into the flask. The flask is inverted after each injection with the syringe in place through the septum, in order for the beads to remove any liquid remaining on the syringe needle. The second method involves preparing a master solution by injecting 1 mL of each component into a culture vial fitted with a septum cap. After all the compounds have been added, the vial is agitated to produce a homogeneous liquid mixture. The vial is then recapped with a new septum. Aliquots of this master solution are removed and injected into the dilution flask as needed in the same manner as indicated above.

15.3.7.3 Retrieve a clean, dry two liter flask containing 70 3 mm glass beads.

15.3.7.4 Flush the flask with helium for a period of five minutes.

15.3.7.5 At the end of the flushing process, immediately cap with a Mininert septum cap.

15.3.7.6 Place the two liter flask on a magnetic stirring apparatus and set at the maximum speed.

15.3.7.7 Using the syringes, inject the calculated volume of each compound (one at a time) or from the mixture solution into the flask while the glass beads are agitated by the stirring bar at the maximum setting of the magnetic stirrer.

15.3.7.8 Invert the flask after each injection with the syringe in place through the septum, in order for the beads to remove any liquid remaining on the syringe needle.

15.3.7.9 After all substances have been introduced, place the flask in the oven at 60°C for 30 minutes to equilibrate.

15.3.7.10 Store the flask in the oven at 60°C until needed. Bottles are stable for one week after preparation.

Note: The technique of injecting a solution of targeted compounds rather than individual injection of specific compounds is preferred if many substances are involved, because it is more rapid, and the master solution can be used over a long period if it is refrigerated at 0°C. Before use, the refrigerated solution is allowed to sit at room temperature for about an hour. It is recommended that a total less than 90 µL of liquid be injected and a total less than 20,000 µL of gas be removed.

15.3.8 Withdrawal of an Aliquot

15.3.8.1 Remove the flask from the oven and place on the magnetic stirrer for approximately 15 seconds.

15.3.8.2 Place the syringe to be used in the extraction procedure in the oven at 60°C to prevent condensation in the syringe during delivery.

15.3.8.3 Using the heated syringe, insert its needle through the septum and pump three times slowly.

15.3.8.4 After the third pump, fill the syringe to approximately 25% greater volume than needed.

15.3.8.5 After a 5-second pause, withdraw the needle from the Mininert septum valve.

15.3.8.6 Flush the excess sample from the syringe, then draw a small quantity of air into the syringe to retard diffusion of sample through the syringe tip.

15.3.8.7 The aliquot sample must be used immediately.

15.3.9 Delivery of an Aliquot

15.3.9.1 If the sample is to be injected into a clean sorbent cartridge, the tip of the needle is inserted to the center of the sorbent bed. Then the plunger is depressed over a 10 second period while the needle tip is being withdrawn about half the distance to the end of the bed.

15.3.9.2 If the sample is injected directly into the analytical instrument, injection is made in the normal manner unless column-head freeze-trapping (cryofocusing) is being employed, in which case the plunger is depressed over about a 10 second period.

15.3.9.3 If a sample is too large to be injected in one step, two or more injections may be made. This causes no complication for injection into a sorbent cartridge, but cryofocusing must be employed when multiple injections are made directly into a gas chromatograph.

15.3.10 Calculation of Deliverable Concentration

15.3.10.1 Volumes to be introduced into the 2 liter flask are calculated by working backwards from the quantity of material to be delivered.

15.3.10.2 For example, if a 500 ng delivery is needed, it could conveniently be accomplished by using a 50 μL syringe containing 10 ng/μL of compound. Therefore,

$$50\ \mu L \text{ syringe} \times 10\ ng/\mu L \text{ solution} = 500\ ng$$

15.3.10.3 If the typical volume of the flask is 2.065 L, then to get that concentration (10 ng/μL) in the flask, one would have to add 20.65 mg of liquid compound to the flask. The calculation would therefore involve:

$$10\ ng/\mu L \times 2.065\ L = \text{quantity of liquid needed to develop a flask concentration of } 10\ ng/\mu L.$$

$$10\ ng/\mu L \times 2.065\ L = 20.65\ mg$$

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.

Tubes should initially be allowed to equilibrate for 24 hours. After small changes in temperature (1 to 5°C), the tube should be allowed to equilibrate for at least half an hour.

15.4.2 Applicability

15.4.2.1 A permeation tube system has been developed for application of loading known standards onto Tenax® cartridges for use in determining the relative response factor and the column performance evaluation (CPMX) of the GC-MS-COMP system in conjunction with the flash vaporization system.

15.4.2.2 In addition, the permeation tube system is used for generating external standards [perfluorobenzene (PFB) and perfluorotoluene (PFT)] to be loaded by syringe onto the Tenax® tube to determine relative retention times, relative response factors and stability of the GC-MS-DS system and for generating deuterated standards used in the evaluation of breakthrough volumes associated with Tenax®.

15.4.3 Permeation Generator Assembly

15.4.3.1 A permeation system consists of four main parts (see Figure 18): 1) a temperature-controlled chamber containing permeation tubes, 2) a mixing chamber, and 3) permeation tube storage chamber. A stream of nitrogen flows through the system. The amounts of compounds transported downstream remain constant once the system has become equilibrated with the compounds to be loaded. The amount of compounds can be determined by measuring the time and the gas flow through the cartridge.

15.4.3.2 The permeation system may be used to load any volatile compound that will permeate at a constant rate under controlled conditions, and to inject a calibration standard onto a sorbent via syringe.

15.4.4 Preparation of Standard Gas Concentration

Note: The following routine should be followed when Tenax® cartridges are loaded with deuterated standards via a permeation system: 1) determine the number of cartridges to be loaded, 2) select the permeation tubes, 3) determine the loading conditions to be used, 4) equilibrate the system, 5) load the cartridges, 6) calculate the amounts of compounds loaded, 7) ensure the integrity of the loading procedure, and 8) pack and store the cartridges.

15.4.4.1 Determination of the Number of Cartridges to be Loaded

15.4.4.1.1 Obtain a copy of the field sampling schedule from the Monitoring Coordinator or Program Manager.

15.4.4.1.2 Determine the number of deuterated standards and external standards required to satisfy the sampling objectives.

15.4.4.2 Selection of the Permeation Tubes

15.4.4.2.1 Check the permeation notebooks (located in the laboratory) to see which permeation tubes are available for the needed standards.

15.4.4.2.2 Select only the permeation tubes whose permeation rates are stable.

Note: A permeation rate is considered stable when the mean permeation rate has a coefficient of variation (CV) of less than 10%. The mean permeation rate is calculated using the last five individual permeation rates. Do not use permeation tubes with permeation rates below 100 ng/min or above 1×10^5 ng/min.

15.4.4.2.3 In a bound notebook assigned for the specific project, prepare a table including: 1) the numbers of the tubes to be used, 2) the names of the compounds, and 3) the corresponding mean permeation rates.

15.4.4.3 Determination of the Permeation System Conditions

15.4.4.3.1 For any compound, calculate the amounts needed to be loaded onto a Tenax® cartridge using the following formula:

$$G = (P)(t)[F_1/(F_1 + F_2)]$$

where:
G = amount loaded of compound onto Tenax® tube, ng
P = permeation rate of specific compound, ng/min
t = total time of loading of compound onto Tenax® tube, minutes
F_1 = flow rate through the Tenax® cartridge, mL/min
F_2 = exhaust flow rate, mL/min
Note: The four variables G, t, F_1, and F_2 determine the loading conditions. Any three may be fixed and the fourth one calculated from the equation.

15.4.4.3.2 The following restrictions must be followed to minimize error: 1) do not load for less than two minutes, 2) do not load with a cartridge flow below 50 mL/min or above 150 mL/min, 3) do not operate the system with a total flow below 250 mL/min.

15.4.4.3.3 If the GC-MS-DS system needs to operate in the range of 200-500 ng per analyte, then the analyst must generate standards concurrent with that range. Fixing three of the four variables of the above equation will enable calculation of the needed loading onto the Tenax® tube.

15.4.4.3.4 As an example, the following calculations are provided to assist the user in determining operating parameters of the permeation tube system in generating standards on QA/QC checks.

OBJECTIVE: To load chlorobenzene and chloroform onto a cartridge in the range of 200-500 per analyte.

GIVEN: G = 200 ng per analyte
F_1 = 80 mL/min
t = 4 min
P = 270 ng/min for chlorobenzene
= 520 ng/min for chloroform

Chlorobenzene

$$G = (P)(t)[F_1/(F_1+F_2)]$$

$$200 \text{ ng} = (270 \text{ ng/min})(4 \text{ min})[(80 \text{ mL/min})/(80 \text{ mL/min} + F_2)]$$

$$F_2 = \{[(270 \text{ ng/min})(4 \text{ min})(80 \text{ mL/min})]/200 \text{ ng}\} - 80 \text{ mL/min}$$

$$F_2 = 352 \text{ mL/min}$$

Now, since all tubes are in the permeation device together, the flow (F_2) for chloroform will be 352 mL/min. Therefore, the loading on the Tenax® tube for chloroform must be calculated to verify that it falls within the 200-500 ng per tube loading.

Chloroform

$$G = (P)(t)[F_1/(F_1 + F_2)]$$

$$G = (520 \text{ ng/min})(4 \text{ min})[(80 \text{ mL/min})/(80 \text{ mL/min} + 352 \text{ mL/min})]$$

$$G = 385 \text{ ng}$$

All values obtained are within the acceptable range.

15.4.4.4 Equilibration of the Permeation System

15.4.4.4.1 Locate the chambers in which the selected permeation tubes are stored.

15.4.4.4.2 With a long glass hook, remove the selected permeation tubes from the storage chamber and transfer immediately to the loading chamber of the permeation system.

Note: Failure to wear nylon gloves when handling permeation tubes may result in skin damage and/or contamination of the permeation tubes.

Note: Perform this operation as quickly as possible. The tubes contain toxic materials, some of which are cancer suspect agents.

15.4.4.4.3 Direct nitrogen flow to the side where the Tenax® cartridge will be loaded.

Note: When a cartridge is not being loaded, a dummy cartridge is placed in the loading position.

15.4.4.4.4 Allow the system to equilibrate for 90 minutes before loading cartridges with the generated test atmospheres.

15.4.4.5 Loading of the Tenax® Cartridges

Note: Be sure the background of the Tenax® cartridges is acceptable before loading them.

15.4.4.5.1 Divert the nitrogen flow to the side that will not be used for loading cartridges.

15.4.4.5.2 Insert the Tenax® cartridge into the chamber.

15.4.4.5.3 Direct the test atmospheres gas flow through the cartridge.

15.4.4.5.4 Concurrently, start the stopwatch.

15.4.4.5.5 Calculate the time needed to load the amounts desired as follows:

$$t = (G/P) \times [(F_1 + F_2)/F_1]$$

Do the calculation based only on the compound whose permeation tube has the highest or lowest permeation rate.

15.4.4.5.6 At the calculated time rotate the two stopcocks to direct gas flow away from the cartridge being loaded.

15.4.4.5.7 Handling the cartridge with a Kimwipe®, remove the cartridge and return it to its culture tube. Seal the tube.

15.4.4.5.8 Label the tube. Include the following information: 1) project number, 2) deuterated standard mixture followed by a number indicating the order of loading, and 3) the date.

15.4.4.5.9 Prepare a Chain-of-Custody sheet with the information concerning amount loaded on the tube.

15.4.4.6 Storage of the Deuterated Standard Cartridges

15.4.4.6.1 Secure the cartridge inside the Kimax® tube with a glass wool plug to avoid breakage during transport.

15.4.4.6.2 Label the top of the screw cap with the following symbol: D*.

Note: * The star indicates that deuterated standards have been loaded onto the cartridge. This symbol will also be added to the participant's code.

15.4.4.6.3 Store the cartridges in a sealed paint can in the freezer until they are ready to be sent to the field.

15.4.4.7 Calculations of the Amounts Loaded

15.4.4.7.1 For every compound, calculate the amount loaded onto a cartridge using the general formula:

$$G = (P)(t)[F_1/(F_1 + F_2)]$$

15.4.4.7.2 Deliver the loaded permeation tubes to the GC-MS-DS for use in the quality assurance program.

16. Calibration of Personal Sampling Pump

16.1 The pump is calibrated so the flow controller is set at the desired sampling rate at standard conditions for the Tenax® sorbent sampling tube.

16.2 Sampling pumps are calibrated at the beginning and at the conclusion of each sampling period. To ensure quality volumetric results, pump calibration is recommended at random points throughout each study.

16.3 Assemble the personal sampling pump calibration system (see Figure 19). Connect a soap-film flowmeter of suitable volume (typically 1 liter) with Tygon tubing to the back-end of the active sampler, as illustrated in Figure 19.

Note: With higher sampling rates, a considerable pressure drop through the tube can result. To minimize this effect, a larger capacity pump would be necessary for higher sampling rates (i.e., >5 L/min).

16.4 Record the barometric pressure and ambient temperature on the sampling data sheet.

16.5 Thoroughly wet the surface of the flowmeter before any measurements are recorded. Measure the time for a soap-film bubble to travel a known volume with a stopwatch. Perform five replicate measurements and compute the average time. Calculate the standard volume (V_S) in liters from the equation:

$$V_S = (V_a \times P_b \times 298)/[(T + 273) \times 760]$$

where:
V_S = volume corrected to standard conditions of 298°K and 760 torr, L
V_a = actual volume measured with the soap-film flowmeter, L
T = temperature at calibration, °C
P_b = barometric pressure at calibration, torr
760 = standard pressure, torr
298 = standard temperature, °K

16.6 The standard flow rate (Q_S) is then calculated with the equation:

$$Q_S = V_S/R$$

where:
Q_S = standard flow rate, L/min
V_S = volume corrected to standard conditions, L
R = average time obtained from soap-film measurement, minutes

16.7 Once the flow has been set, record calibration date in laboratory logbook.
Note: Set flow rate of pump and indicate flow rate on a sticker attached to the pump.

17. Performance Criteria and Quality Assurance

17.1 This section summarizes quality assurance (QA) measure and provides guidance concerning performance criteria which should be achieved within each laboratory. In many cases the specific QA procedures have been described within the appropriate sections of this protocol. Figure 20 summarizes these performance criteria discussed in this protocol.

17.2 Standard Operating Procedures (SOPs)

17.2.1 Each user should generate SOPs describing the following activities as they are performed in their laboratory: 1) assembly, calibration, and operation of the sampling system, 2) preparation, handling and storage of Tenax® cartridges, 3) assembly and operation of GC-MS system including the thermal desorption apparatus and data system, and 4) all aspects of data recording and processing.

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

17.3 Tenax® Cartridge Preparation

17.3.1 Each batch of Tenax® cartridges prepared should be checked for contamination by analyzing one cartridge immediately after preparation. While analysis can be

accomplished by GC-MS, many laboratories may choose to use GC-FID due to logistical and cost considerations.

17.3.2 Analysis by GC-FID is accomplished as described for GC-MS except for use of FID detection.

17.3.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria the entire lot should be rejected.

17.4 Sample Collection

17.4.1 During each sampling event at least 10% of all field samples should accompany the samples to the field and back to the laboratory, without being used for sampling, to serve as a field blank. The average amount of material found on the field blank cartridge may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data for that component must be identified as suspect.

17.4.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) will be collected, preferably at different flow rates. If agreement between parallel samples is not generally within ± 25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples one should consider using a reduced flow rate and longer sampling interval if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest may be required.

17.4.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 20% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater. The frequency of use of backup cartridges should be increased if increased flow rate is shown to yield reduced component levels for parallel sampling. This practice will help to identify problems arising from breakthrough of the component of interest during sampling.

17.5 GC-MS Analysis

17.5.1 Performance criteria for MS tuning and mass calibration have been discussed. Additional criteria may be used by the laboratory if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC-MS system.

17.5.2 Chromatographic efficiency should be evaluated using spiked Tenax® cartridges since this practice tests the entire system. In general, a reference compound such as perfluorotoluene should be spiked onto a cartridge at the 100 nanogram level. The cartridge is then analyzed by GC-MS. The perfluorotoluene (or other reference compound)

peak is then plotted on an expanded time scale so that its width at 10% of the peak can be calculated. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The asymmetry factor should be between 0.8 and 2.0. The asymmetry factor for any polar or reactive compound should be determined using the process described above. If peaks are observed that exceed the peak width or asymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings and is necessary. Some laboratories may choose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature. Such schemes cannot be conducted by placing the substances onto Tenax® because many of the compounds (e.g., acids, bases, alcohols) contained in the test mix are not retained, or degrade, on Tenax®.

17.5.3 The system detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where:

DL = calculated detection limit injected, ng
A = the intercept of the slope
S = the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required)

In general, the detection limit should be 20 nanograms or less and for many applications detection limits of 1-5 nanograms may be required. The lowest level standard should yield a signal to noise ratio, from the total ion current response, of approximately 5.

17.5.4 The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation should be 25% or less.

17.5.5 A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present in ambient air (e.g., perfluorotoluene). The integrated ion intensity for this compound helps to identify problems with a specific sample. In general the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any sample giving a value greater than ±2 standard deviations from the mean (calculated excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

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Table 1. Compounds Identified and Quantified by Automated GC-MS-DS Procedure with Typical Detection Limits in Full Scan Mode

Compound	Quantitation Mass (m/z)	Detection Limits (ng)
perfluorotoluene (internal standard)*	217	0.3
benzene*	78	2.6
methylbenzene*	91	2.0
1,2-dimethylbenzene*	106	0.5
1,3,5-trimethylbenzene	120	2.5
ethylbenzene*	91	1.6
ethylbenzene*	104	1.7
(1-methylethyl) benzene	105	1.1
butylbenzene	91	0.7
1-methyl-4-(1-methylethyl) benzene	119	4.0
chlorobenzene*	112	1.7
bromobenzene	156	14.1
1,2-dichlorobenzene*	146	12.4
1-ethenyl-4-chlorobenzene	138	2.0
trichloromethane	83	2.7
tetrachloromethane*	82	2.1
bromochloromethane*	130	2.1
bromotrichloromethane*	163	1.6
dibromomethane*	174	4.5
tribromomethane*	171	8.5
1,1-dichloroethane*	63	5.7
1,2-dichloroethane	62	3.8
1,1,1-trichloroethane*	99	1.7
1,1,2-trichloroethane*	85	2.1
1,1,1,2-tetrachloroethane	31	0.9
1,1,2,2-tetrachloroethane	83	6.5
pentachloroethane*	167	1.8
1,1-dichloroethane*	961	6.9
trichloroethene*	132	0.8
tetrachloroethene	166	2.6
bromoethane*	108	7.8
1,2-dibromoethane*	107	3.3
1-chloropropane*	42	1.7
2-chloropropane*	43	3.4
1,2-dichloropropane	63	4.0
1,3-dichloropropane	76	9.6
1,2,3-trichloropropane	753	4.7
1-bromo-3-chloropropane	158	1.6
3-chloro-1-propene	41	1.6

Table 1 (cont'd)

Compound	Quantitation Mass (m/z)	Detection Limits (ng)
1,2-dibromopropane*	121	14.4
2-chlorobutane	57	3.5
1,3-dichlorobutane	55	0.5
1,4-dichlorobutane	55	8.2
2-3-dichlorobutane*	90	5.1
1,4-dichloro-2-butane (cis)	752	1.9
3,4-dichloro-1-butane	75	6.5
tetrahydrofuran	72	1.2
1,4-dioxane	88	3.9
1-chloro-2,3-epoxypropane	71	8.1
2-chloroethoxyethene	631	8.2
benzaldehyde*	77	5.9
acetophenone	105	2.9
benzonitrile	103	1.3
ISOMER GROUPS		
1,3- & OR 1,4-dimethylbenzene	106	0.5
1,2- & OR 1,3-dichlorobenzene*	146	1.3
2- & OR 3- & OR 4-chloro-1-methylbenzene*	126	0.5
SURROGATE GROUPS AND INTERNAL STANDARDS		
4-bromofluorobenzene (BFB)	95	
chlorobenzene-d_5	117	
1,4-dichlorobenzene	150	
1,4-difluorobenzene	114	

* Compounds used to calibrate GC-MS-DS on a daily basis either by direct injection or on spiked adsorbent tubes.

Table[a] 2. Breakthrough Volumes[b] and Safe Sampling Volumes[b] for Tenax-GC and Tenax-TA

	Tenax-GC breakthrough volume[b]	Tenax-TA breakthrough volume[b]		Tenax-GC safe sampling volume[c]	Tenax-TA safe sampling volume[c]	
	38°C	20°C	35°C	38°C	20°C	35°C
Acetaldehyde	0.6	0.6	0	0.3	<1	<1
Acrolein	4	5	2	1.7	2	<1
Acrylonitrile	-	8	3	-	3	1
Allyl chloride	-	8	3	-	3	1
Benzene	19	36	15	8.2	14	6
Benzyl chloride	300	440	200	130	175	80
Bromobenzene	300			130		
Carbon tetrachloride	8	27	13	3.5	11	5
Chlorobenzene	150	184	75	6.5	5	2
Chloroform	8	13	5	4	5	2
Chloroprene	-	26	12	-	10	5
Cresol	440	570	240	191	230	95
p-Dichlorobenzene	510	820	330	221	290	130
1,4-Dioxane	-	58	24	87	23	10
Ethylene dibromide	60	77	35	26	30	14
Ethylene dichloride	-	29	12	-	12	5
Ethylene oxide	-	0.5	0.3	-	<1	<1
Formaldehyde	-	0.6	0.2	-	<1	<1
Hexachlorocyclo-pentadiene	-	2000	900	-	800	360
Methyl bromide	0.8	0.8	0.4	0.4	<1	<1
Methyl chloroform	-	9	4	-	3	2
Methylene chloride	3	5	2	1.5	2	<1
Nitrobenzene	-	520	240	-	200	95
Perchloroethylene	-	100	45	-	40	18
Phenol	-	300	140	-	120	55
Propylene oxide	3	3	1	1.5	1	<1
Trichloroethylene	21	45	17	8.5	18	7
Vinyl chloride	0.6	.06	.03	.03	<1	<1
Vinylidene chloride	-	4	2	-	2	<1
Xylene	200	177	79	89	70	32

[a]See Section 18, reference 58.
[b]Breakthrough volumes expressed as liters/gram of sorbent.
[c]Safe sampling volume = {[Breakthrough volume (L/g)]/1.5} x 0.65 grams of sorbent.
[d]Breakthrough volumes for other chemicals can be extrapolated on the basis of boiling points for chemicals in the same chemical class.

Table 3. Commercially Available Thermal Desorption Units

Company	Address	Number	Model Comments
Tekmar Co.	PO Box 371856 Cincinnati, OH 45222-1856 (800) 543-4461	5010GT	1. 1/4 or 5/8 in. tubes 3 to 7-inches long, glass or metal. 2. Desorption temperatures to 420°C.
Nutech Corp.	2806 Cheek Rd. Durham, NC 27704 (919 682-0402	320	1. Uses glass sorbent tubes.
Chrompack	1130 Rt. 202 South Raritan, NJ 08869 (800) 526-3687	TCT	1. Desorption temperatures to 300°C. 2. 1/4-in. OD x 3.0 in.
Chemical Data Sys., Inc.	7000 Limestone Rd. Oxford, PA 19363 (215) 932-3636	330	1. Desorption temperature to 350°C. 2. 1/4-in. OD x 3-in. long or 1/2 in.
Perkin-Elmer	2772 N. Garey Ave. Pomona, CA 91767 (714) 593-3581	ATD-50	1. Desorption temperatures to 250°C. 2. 1/4-in. OD x 3-in. long tubes. 3. Up to 50 samples processed automatically.
Envirochem, Inc.	Box 180 Kemblesville, PA 19347 (212) 255-4474		1. Desorption temperatures to 300°C. 2. 6-mm OD x 11.5-cm long tubes.

Table 4. Typical Operating Conditions for a GC-MS-DS

Thermal Desorption Unit - NuTech Model 320 or Tekman Model 5000 or equivalent

Purge Gas	Helium @ 1.2 mL/min
Desorption Cycle	8 Minutes
Initial Desorption Temperature	25°C
Final Desorption Temperature	190°C
Thermal Desorption Unit Purge	10 mL/min

Gas Chromatography

Injection/Detector Temperature	200°C
Initial Column Temperature	30°C
Initial Hold Time	0.1 minutes
Program	4°C/min to 240°C
Final Hold Temperature	240°C
Final Hold Time	0.1 minutes
Maximum Over Temperature	245°C
Carrier Gas	Helium velocity 20 cm^3/sec at 250°C
GC-MS Interface	Direct coupling or glass jet
Sample Injection to MS	Direct Probe
Column	Hewlett-Packard OV-1 glass capillary crosslinked methyl silicone (50 m x 0.3 mm, 0.17 μm film thickness) Scientific Glass Engineering SE-30 glass capillary crosslinked methyl silicone (50 m x 0.5 mm, 0.80 μm film thickness)

Mass Spectrometer - Quadrupole Spectrometer, Electron Impact (EI)

Mass Range	35 to 320 amu
Scan Time	1 sec-10 min over entire range
EI Condition	70 eV
Mass Scan and Detector Mode	Follow manufacturer instruction for select mass selective detector (MS) and selected ion monitoring (SIM) mode
Routine Tuning	p-bromofluorobenzene
Preamp Sensitivity	10^{-7}
Emission Current	-0.45
Electron Multiplier Voltage	1000 to 1500
Mass Filter	10 amu/sec
Filter	x 100
Total Ion Current Sensitivity	1
Resolution	Normal
Display	TIC
Response	Fast

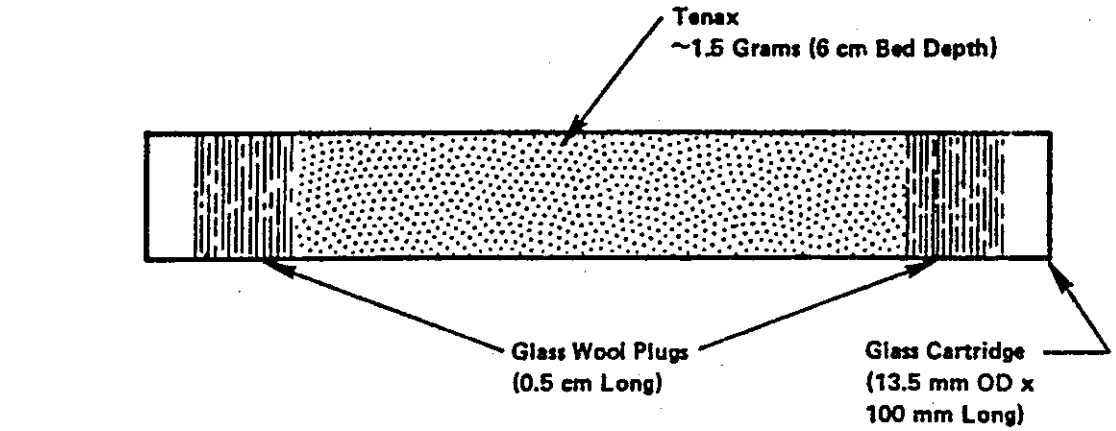
Table 5. Suggested BFB Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	15-40% of the base peak
75	30-60% of the base peak
95	base peak, 100% relative abundance
96	5-9% of the base peak
173	<2% of mass 174
174	>50% of the base peak
175	5-9% of mass 174
176	>95% but <101% of mass 174
177	5-9% of mass 176

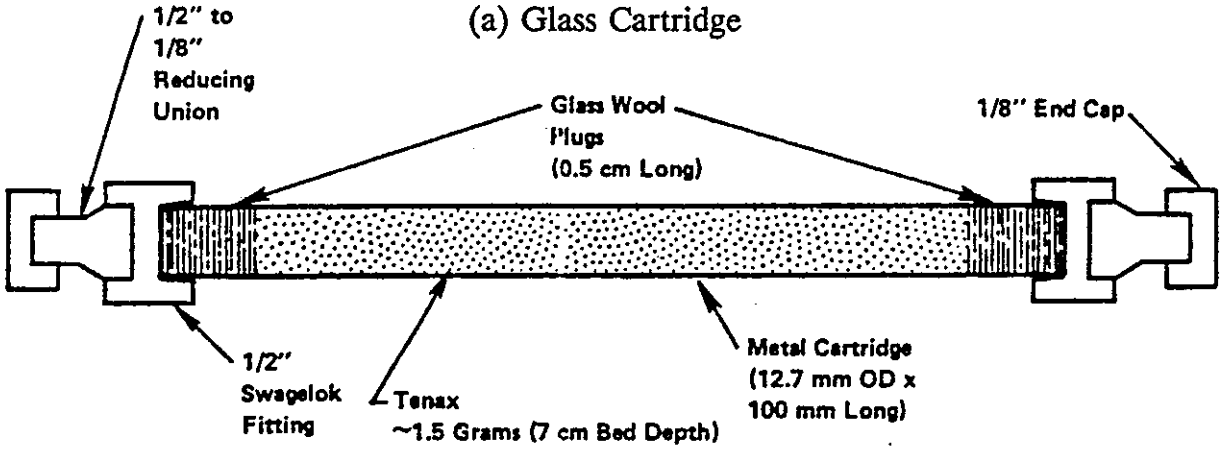
Table 6. Target Compound List Used in Response Factor (RF) Determination with Specific Mass Loading onto Spiked Cartridge

Compound	ng Loaded
Benzene	304
Chloroform	114
1,1,1-Trichloroethane	174
Carbon Tetrachloride	201
1,2-Dichloroethane	329
Trichloroethylene	403
1,1,2,2-Tetrachloroethane	409
Chlorobenzene	140
Tetrachloroethylene	323
Ethylbenzene	346
p-Xylene	344
o-Xylene	352
Styrene	362
o-Dichlorobenzene	260
p-Dichlorobenzene	260
n-Octane	288
n-Decane	292
5-Nonanone*	328
Acetophenone*	411
2,6-Dimethylphenol*	294
2,6-Dimethylaniline*	391
1-Octanol*	330
Perfluorobenzene	125
Perfluorotoluene	130

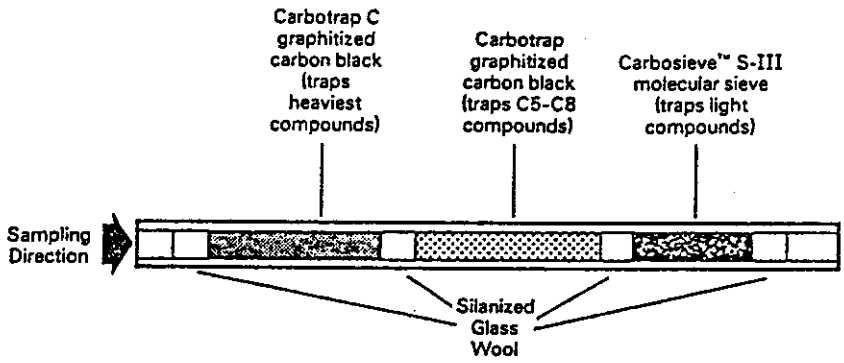
*Used in the calculation of column performance parameters; not a target compound.



(a) Glass Cartridge

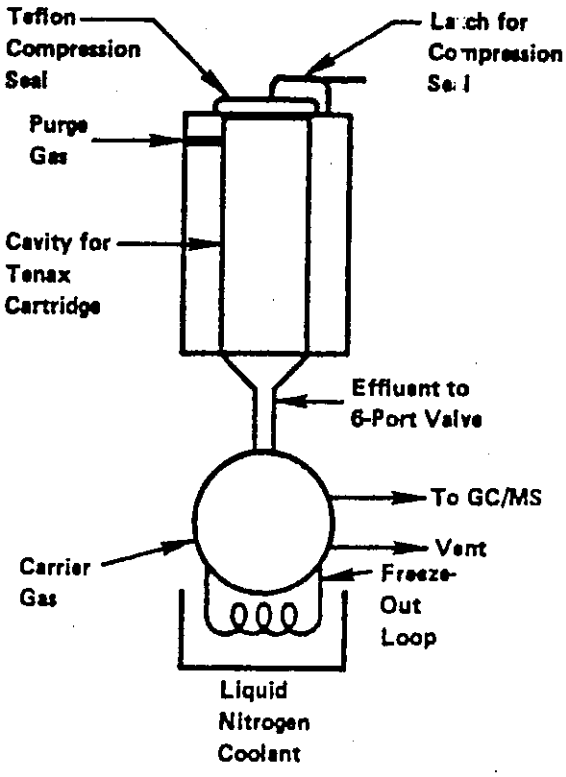


(b) Metal Cartridge

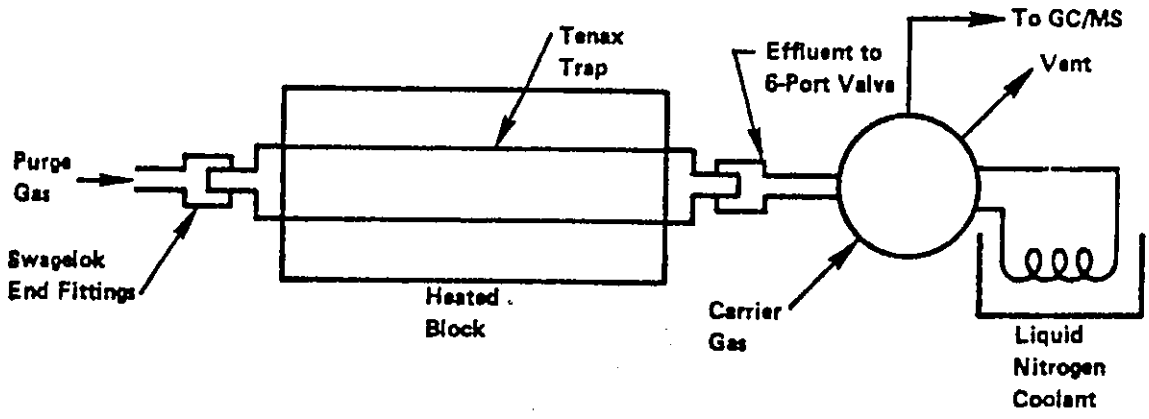


(c) Multibed Adsorbent Tube

Figure 1. Common Designs of Adsorbent Cartridges



(a) Glass Cartridges (Compression Fit)



(b) Metal Cartridges (Swagelok Fittings)

Figure 2. Tenax® Cartridge Desorption Modules

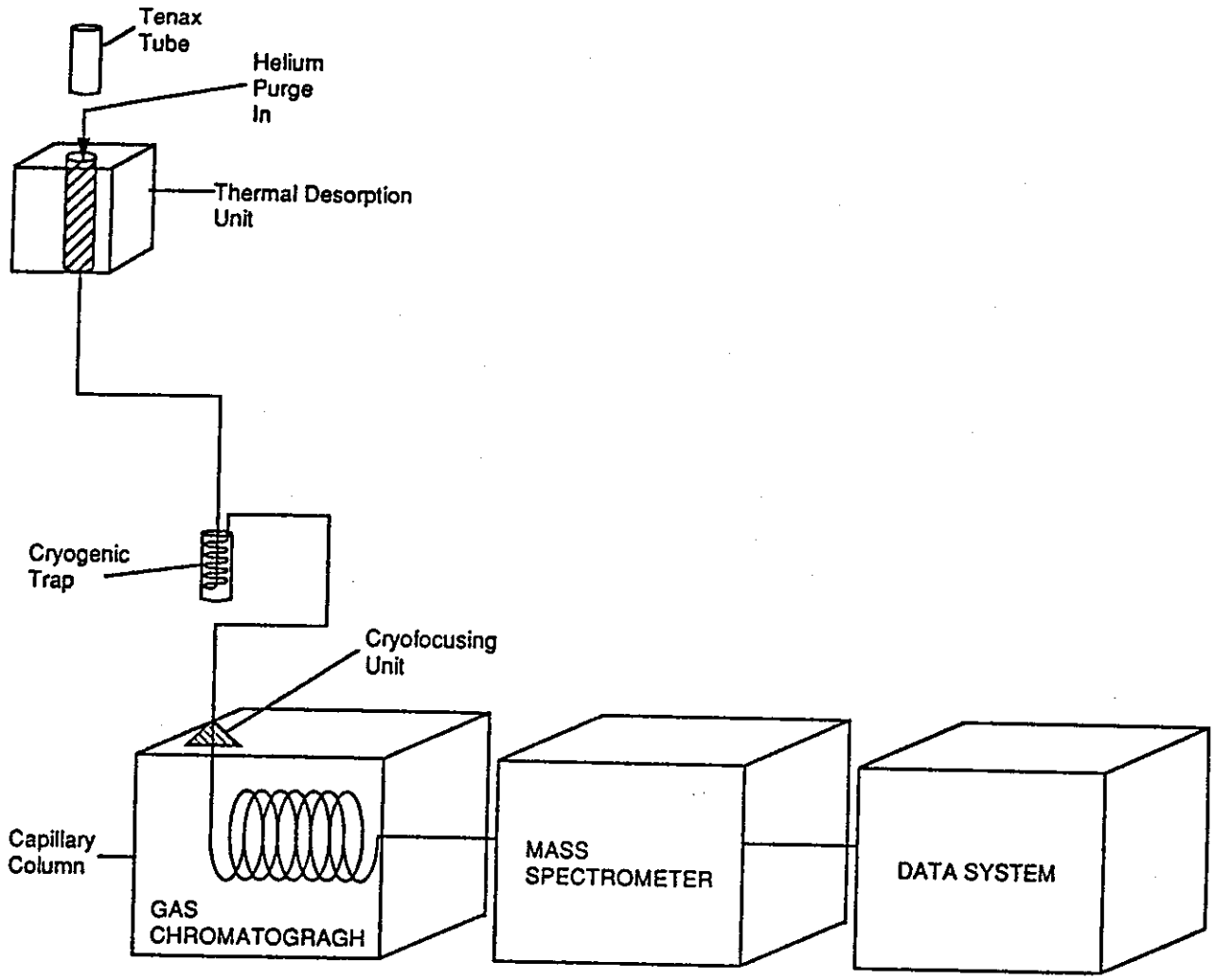


Figure 3. Typical Desorption GC-MS-DS Configuration

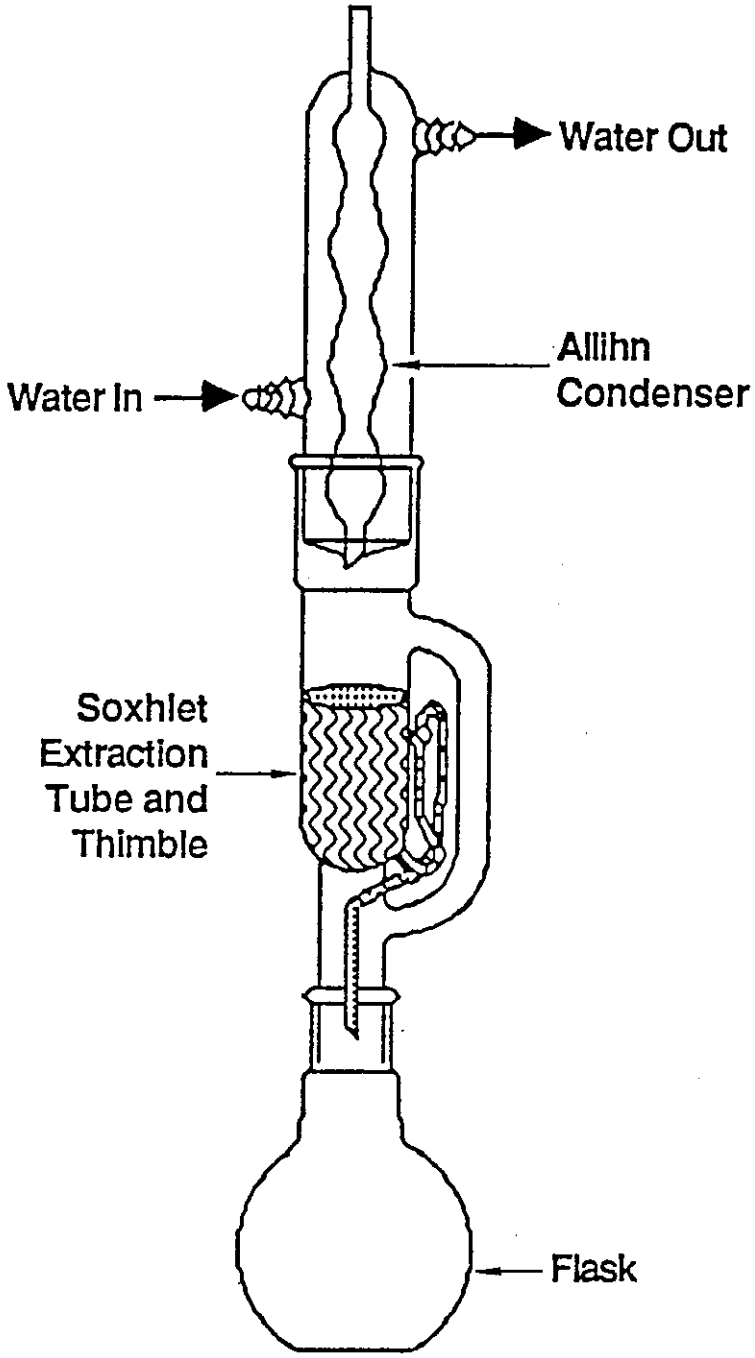


Figure 4. Soxhlet Extraction Apparatus with Allihn Condenser

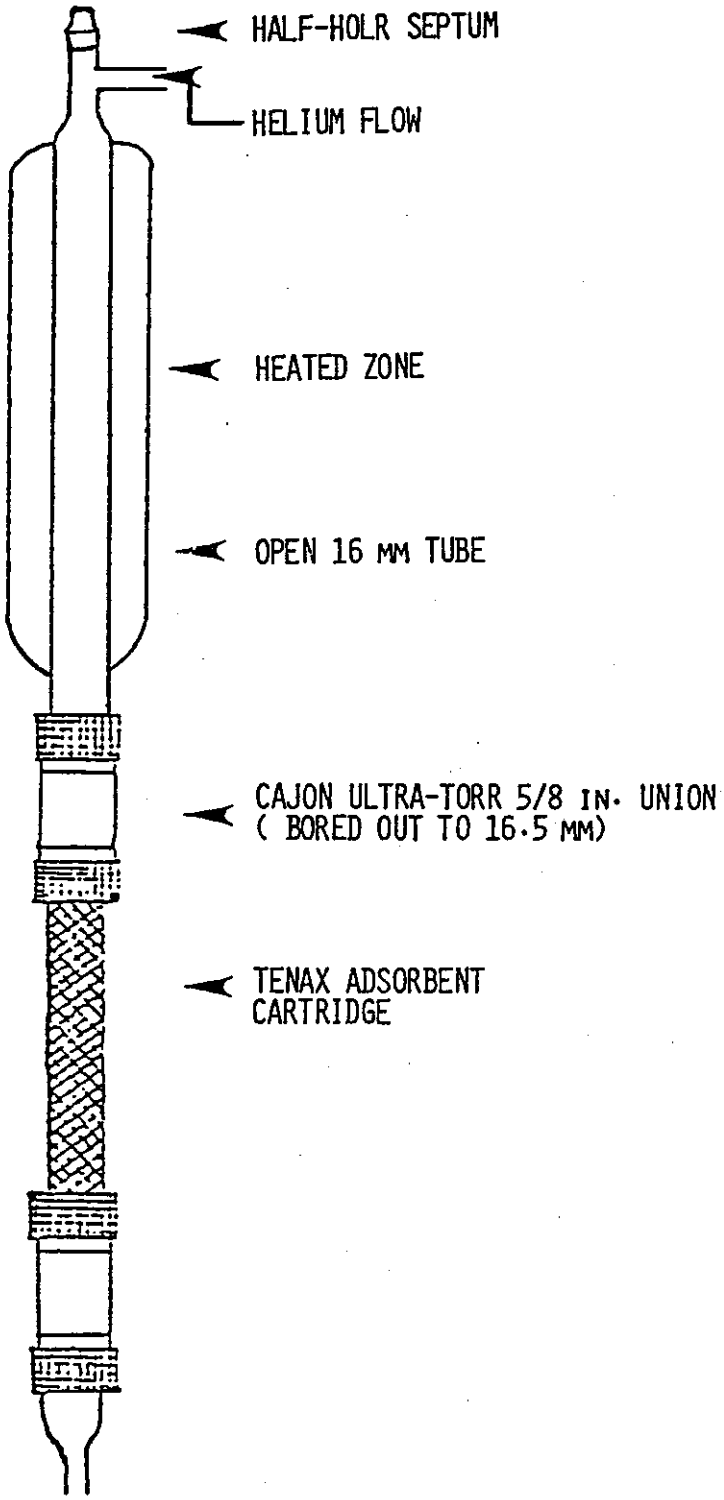


Figure 5. Flash Evaporation Unit

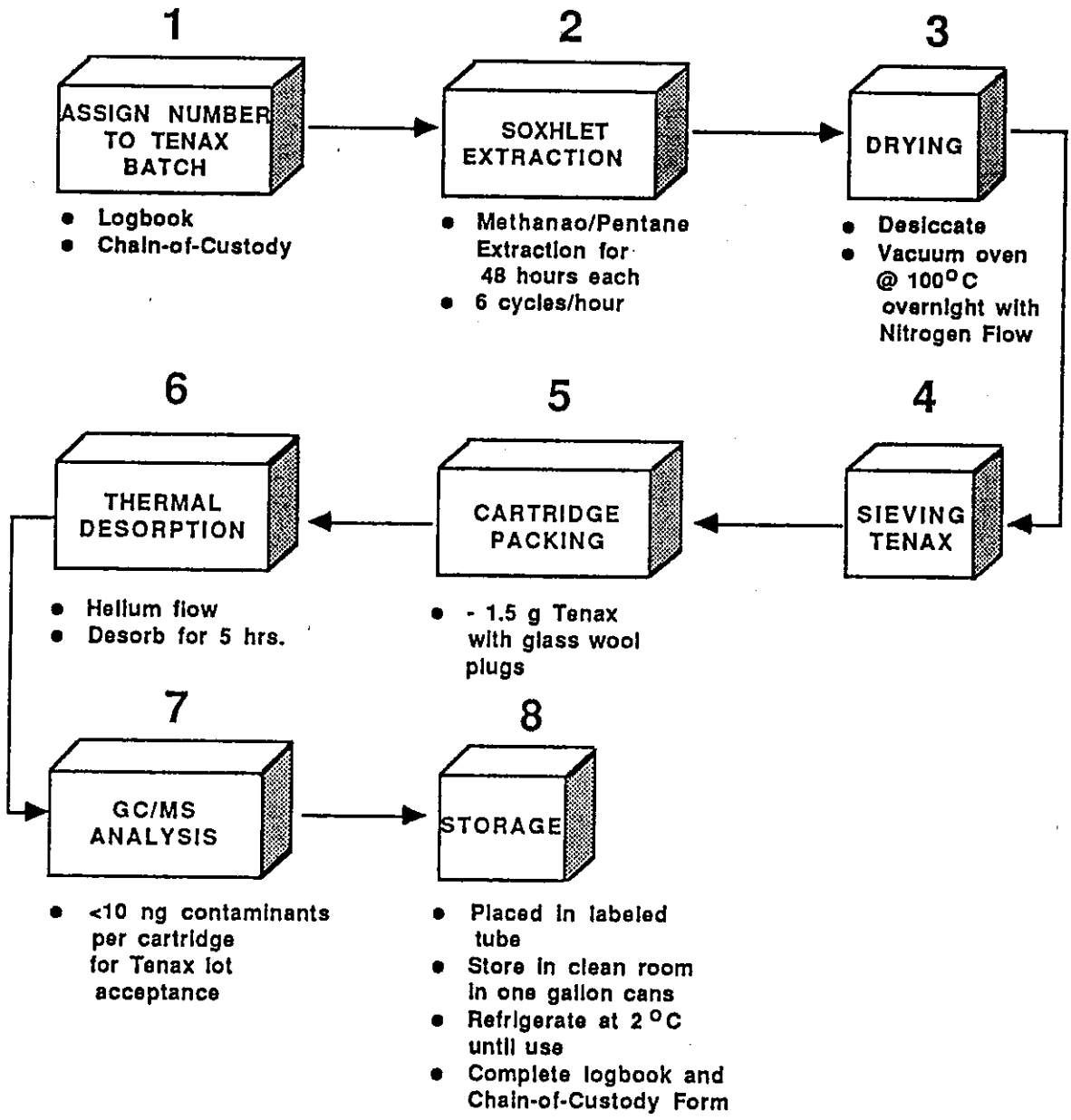


Figure 6. Tenax® Clean-Up Scheme

TENAX CLEANUP WORKSHEET

Tenax Batch No. _____ Projected Use _____
Virgin/Recycled. Recycled Source _____ No. of Cartridges _____

Extraction

Number of Soxhlet Units (circle one): 1 2 3 4 5

Methanol Extraction: Date (Hours)

Siphon Rate

Pentane Extraction: Date (Hours)

Siphon Rate

Drying

Nitrogen Chamber: Date (Hours)

Approx. Flowrate

Vacuum Oven: Date (Hours)

Pump Trap

Cooldown (Hours)

N_2 Vent Thru Act. C

Sieving/Packing

Sieve (40/60) Date:

Packing Date(s):

Cleanup

Teflon Septum; Date:

Teflon Liner; Date:

Figure 7. Tenax® Clean-Up Worksheet

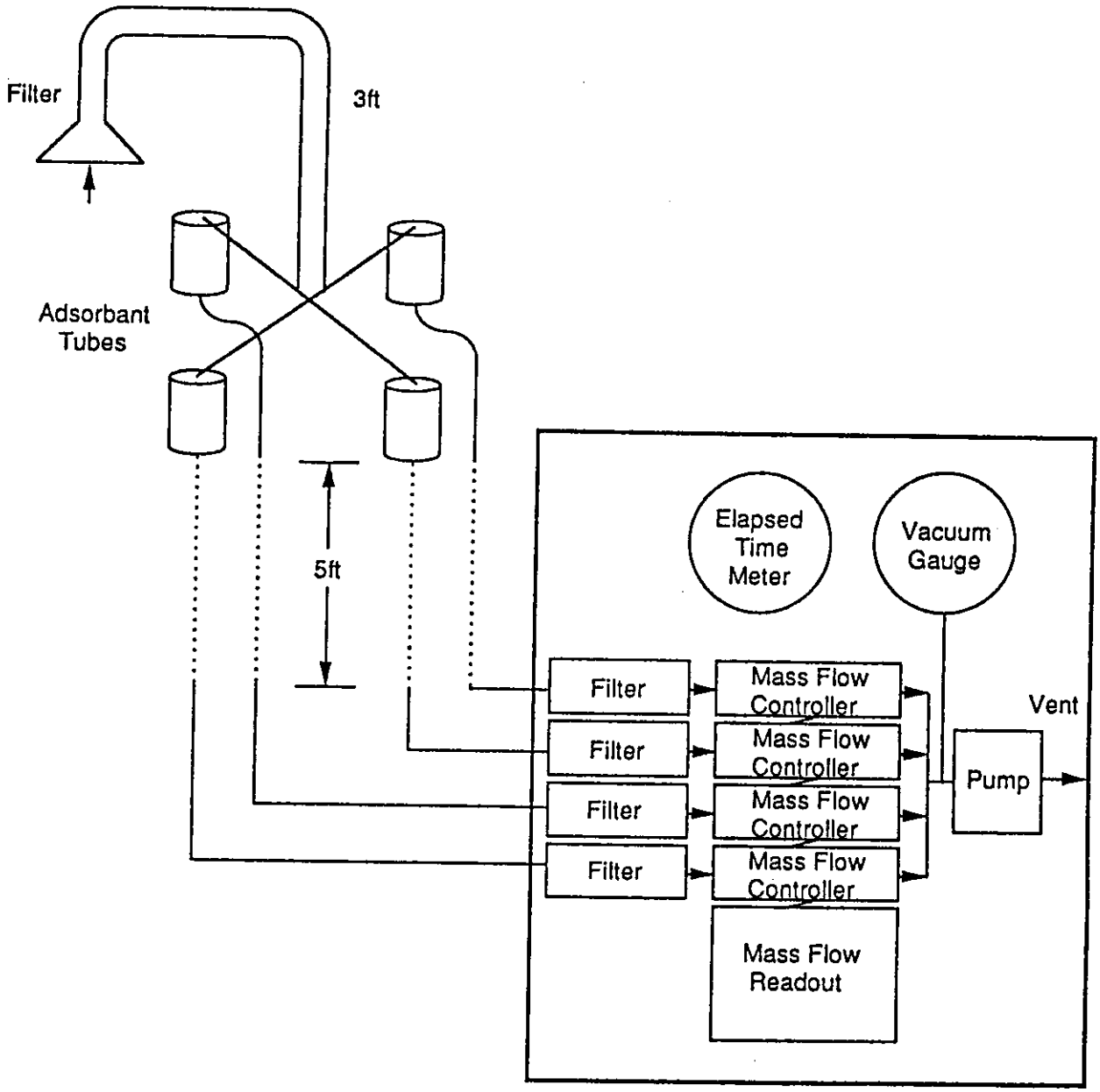


Figure 8. Flow Diagram for TAMS Toxic Air Sampler

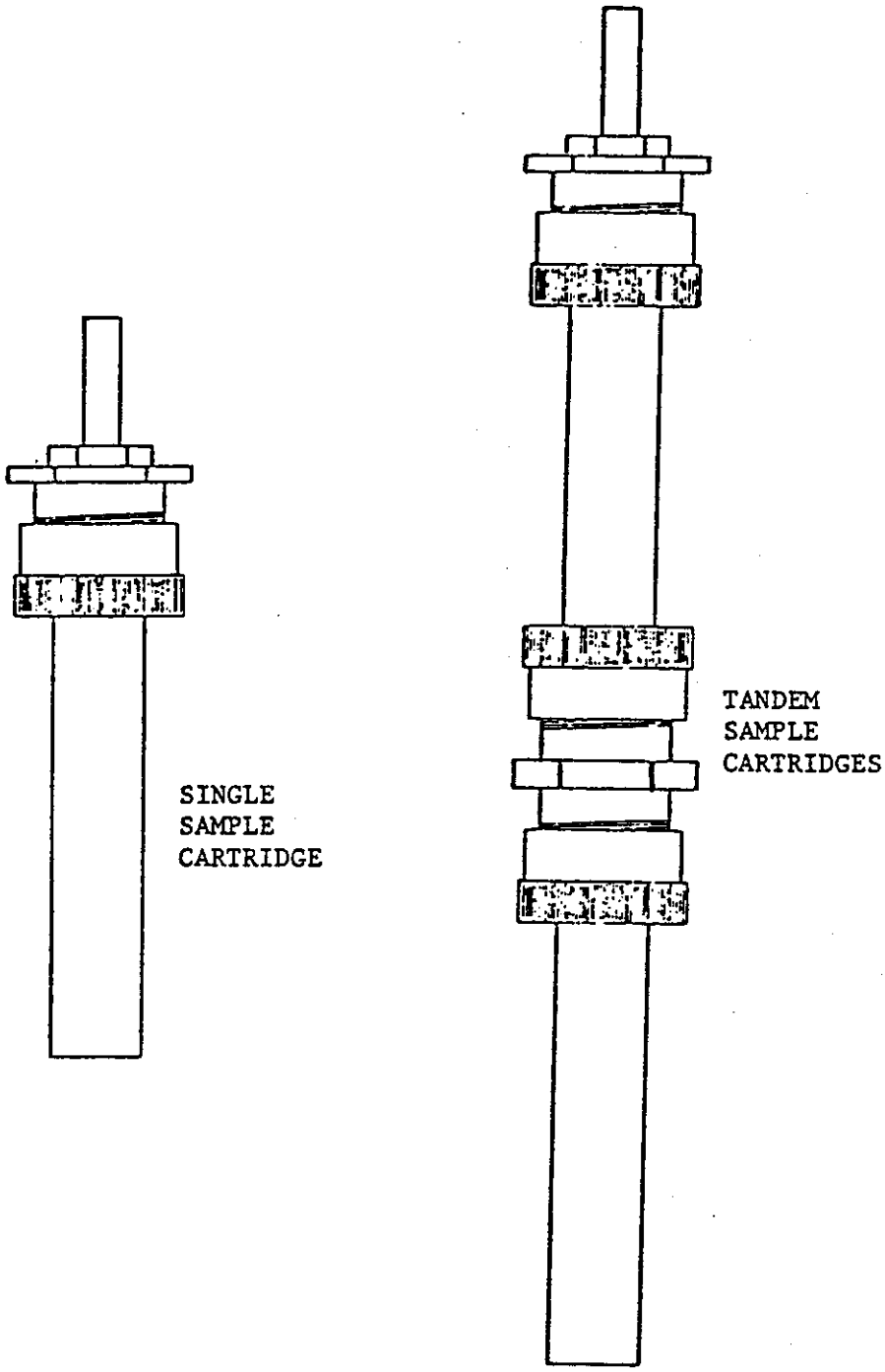
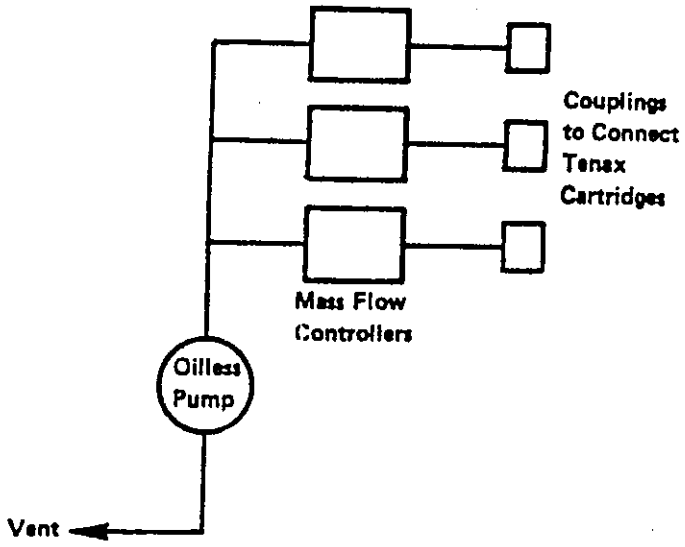
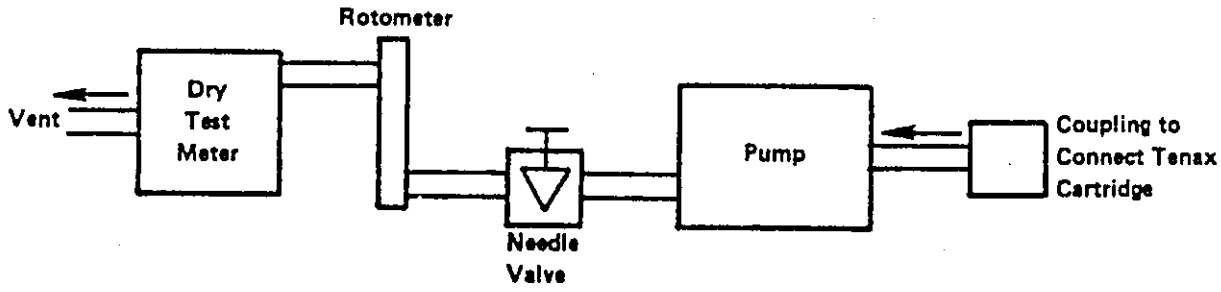


Figure 9. Single and Tandem Sample Cartridges



(a) Mass Flow Control



(b) Needle Valve Control

Figure 10. Typical Sampling System Configurations

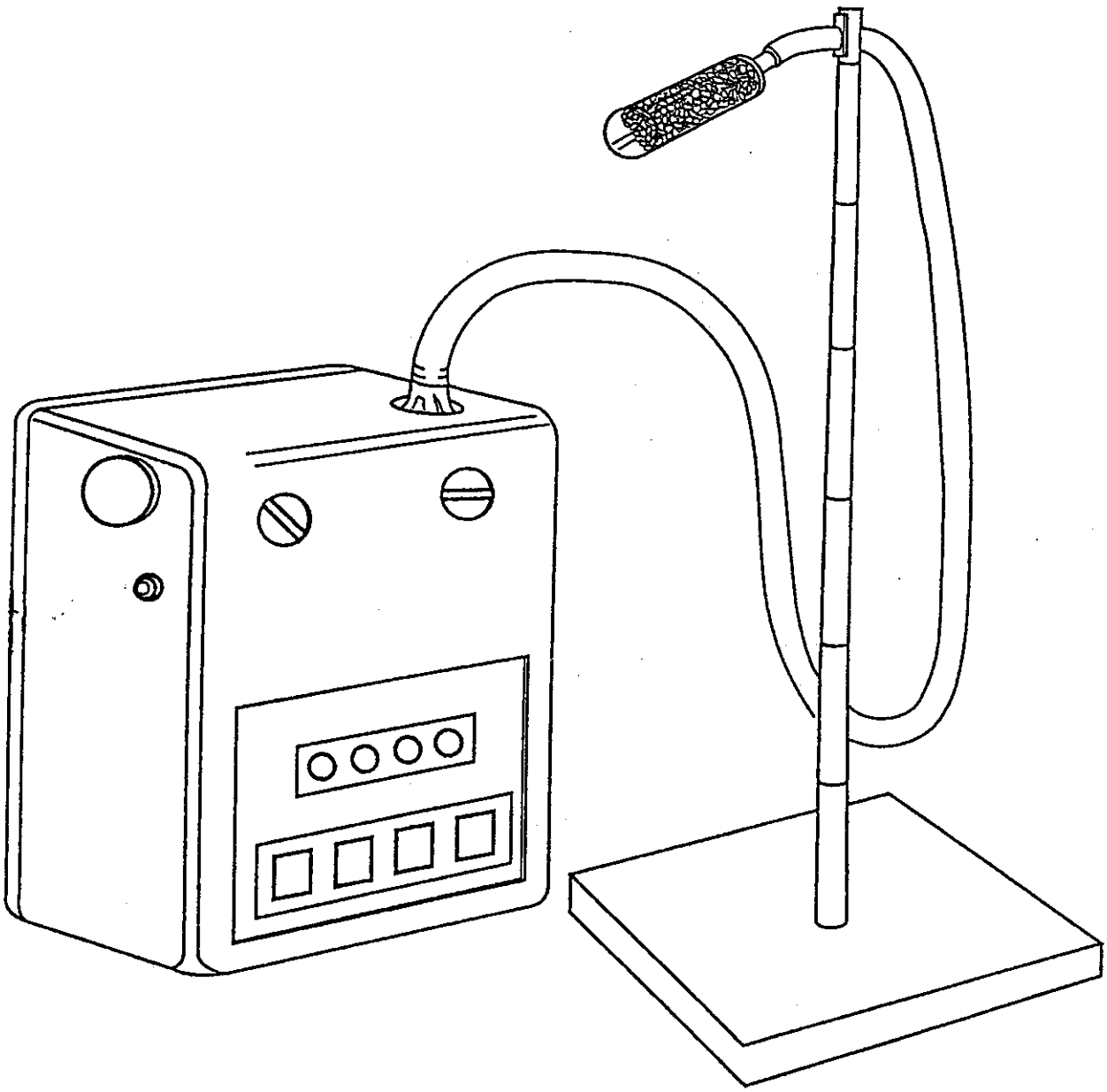


Figure 11. Adsorbent Cartridge Attached to Personal Pump

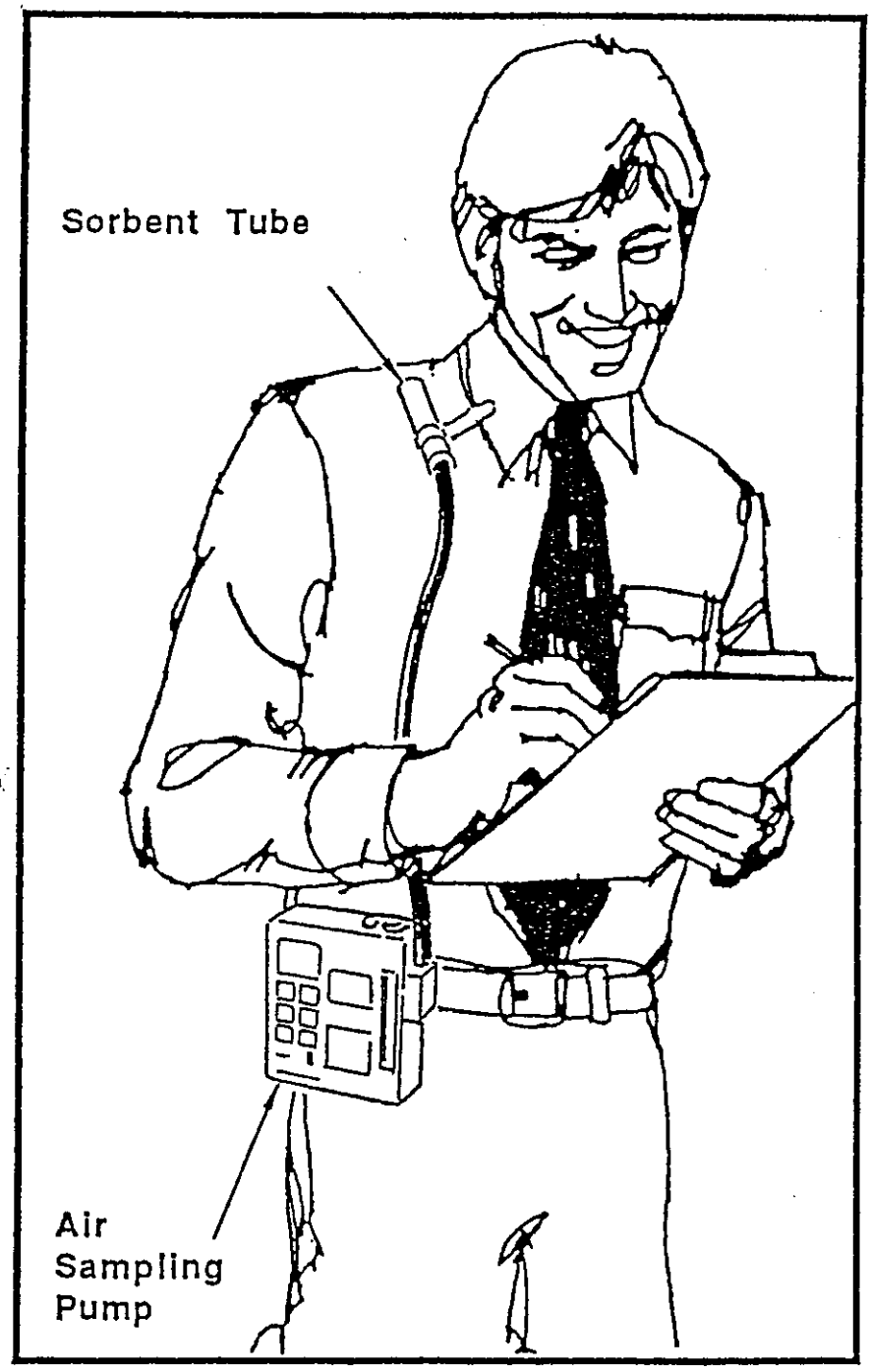


Figure 12. Personal Monitoring

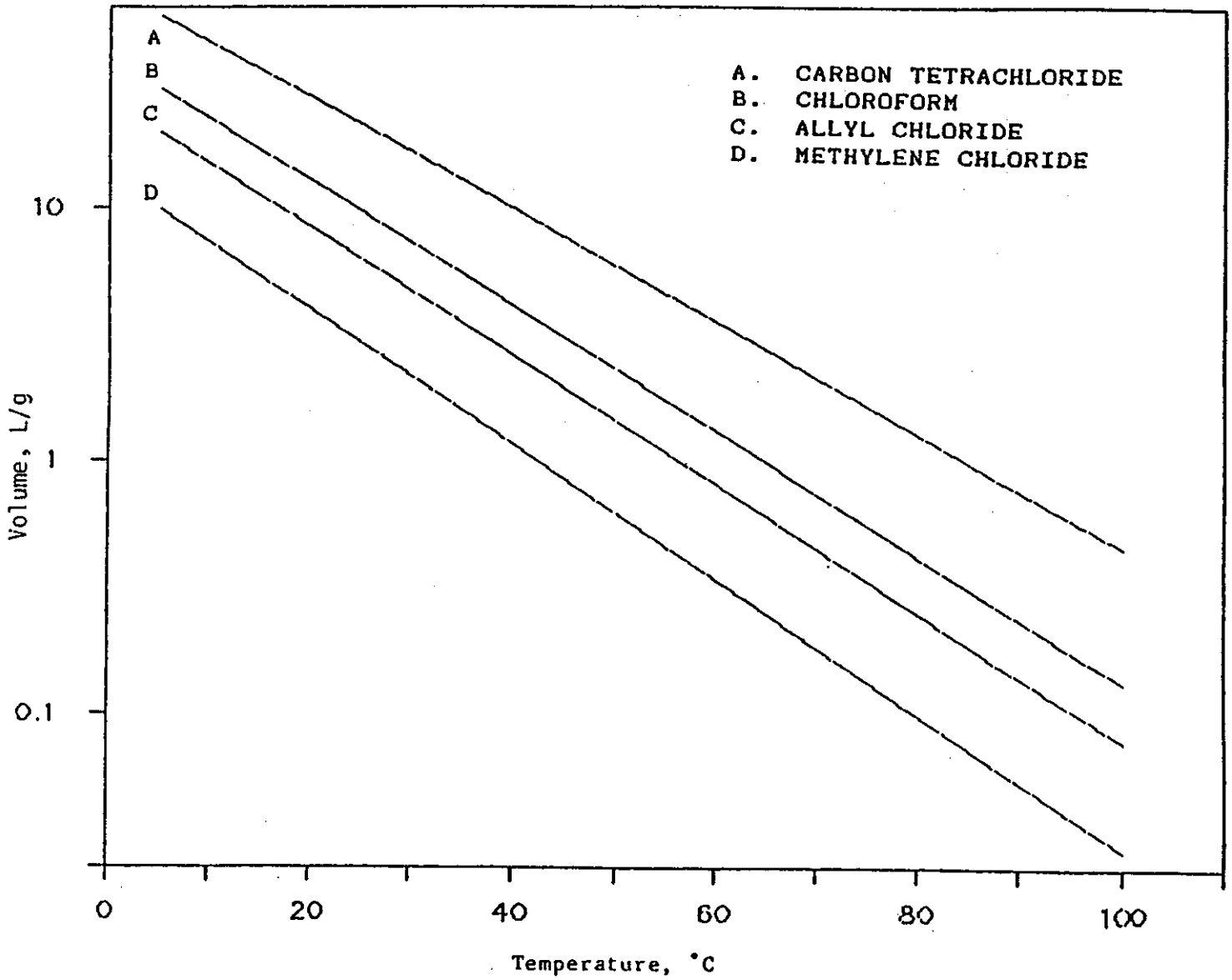


Figure 13. Breakthrough Curves for Carbon Tetrachloride, Chloroform, Allyl Chloride, and Methylene Chloride on Tenax®

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

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

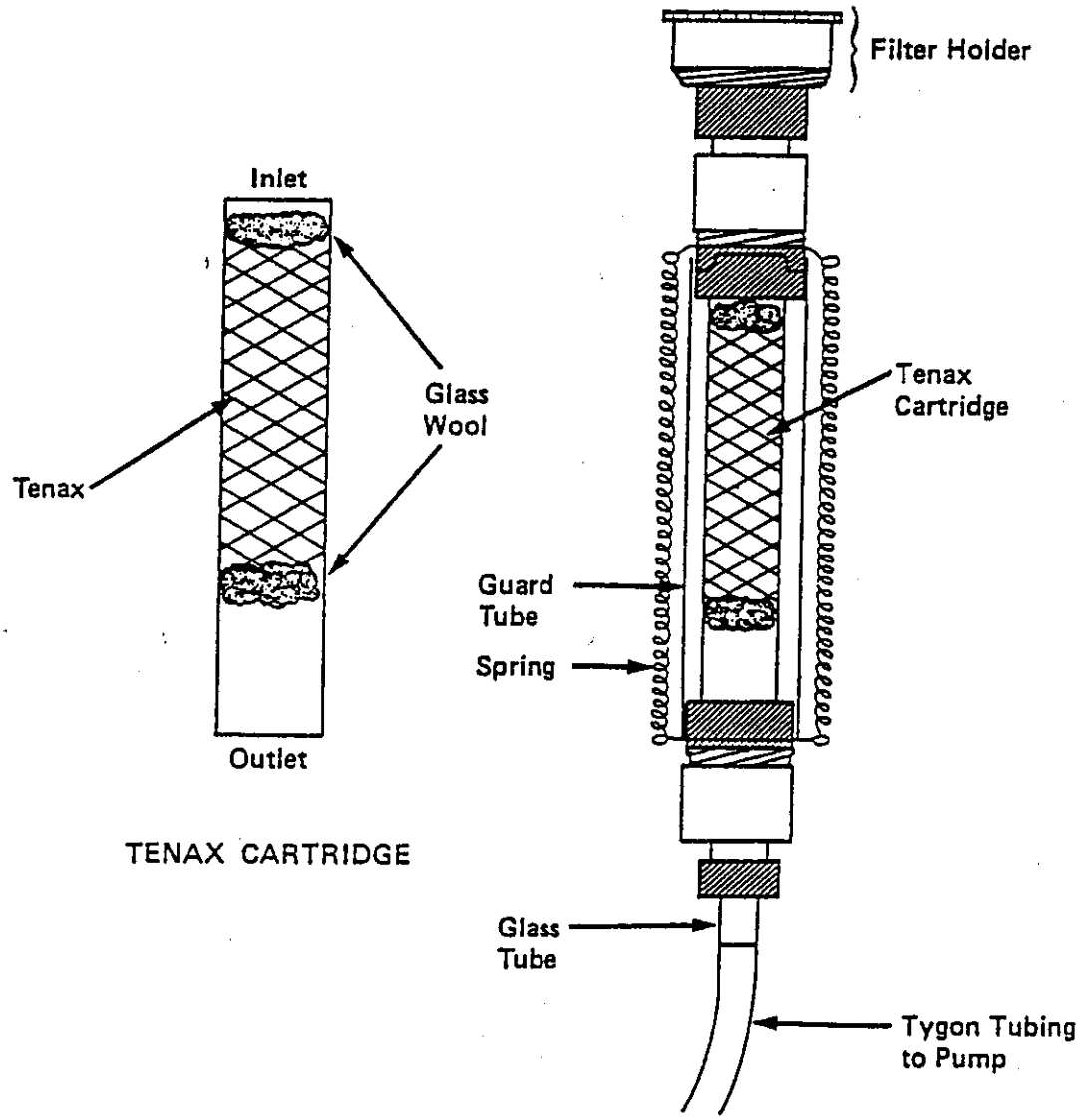


Figure 16. Optional Particulate Filter Assembly Attached to Adsorbent Cartridge

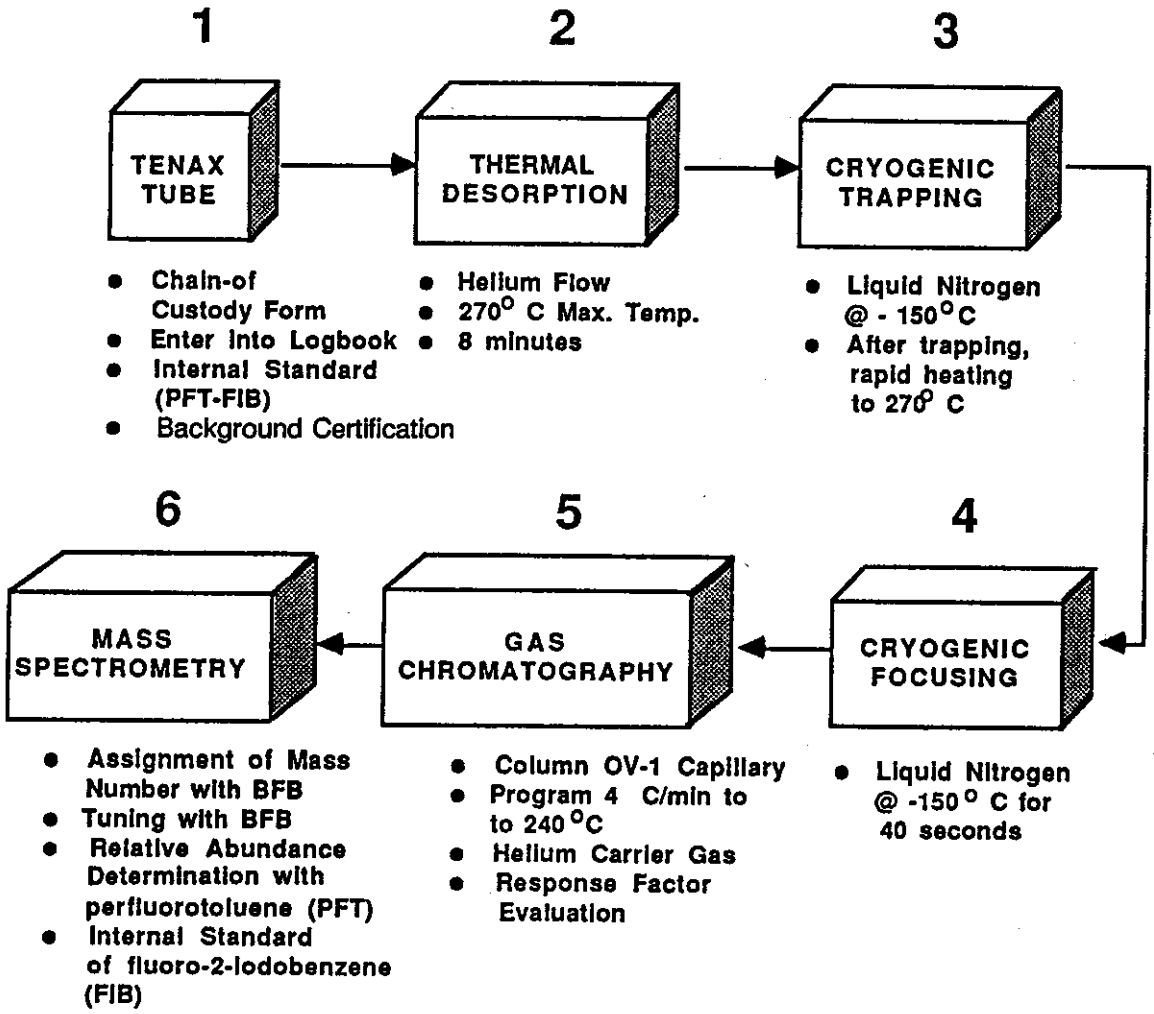


Figure 17. Specific Activities Associated with the GC-MS-DS

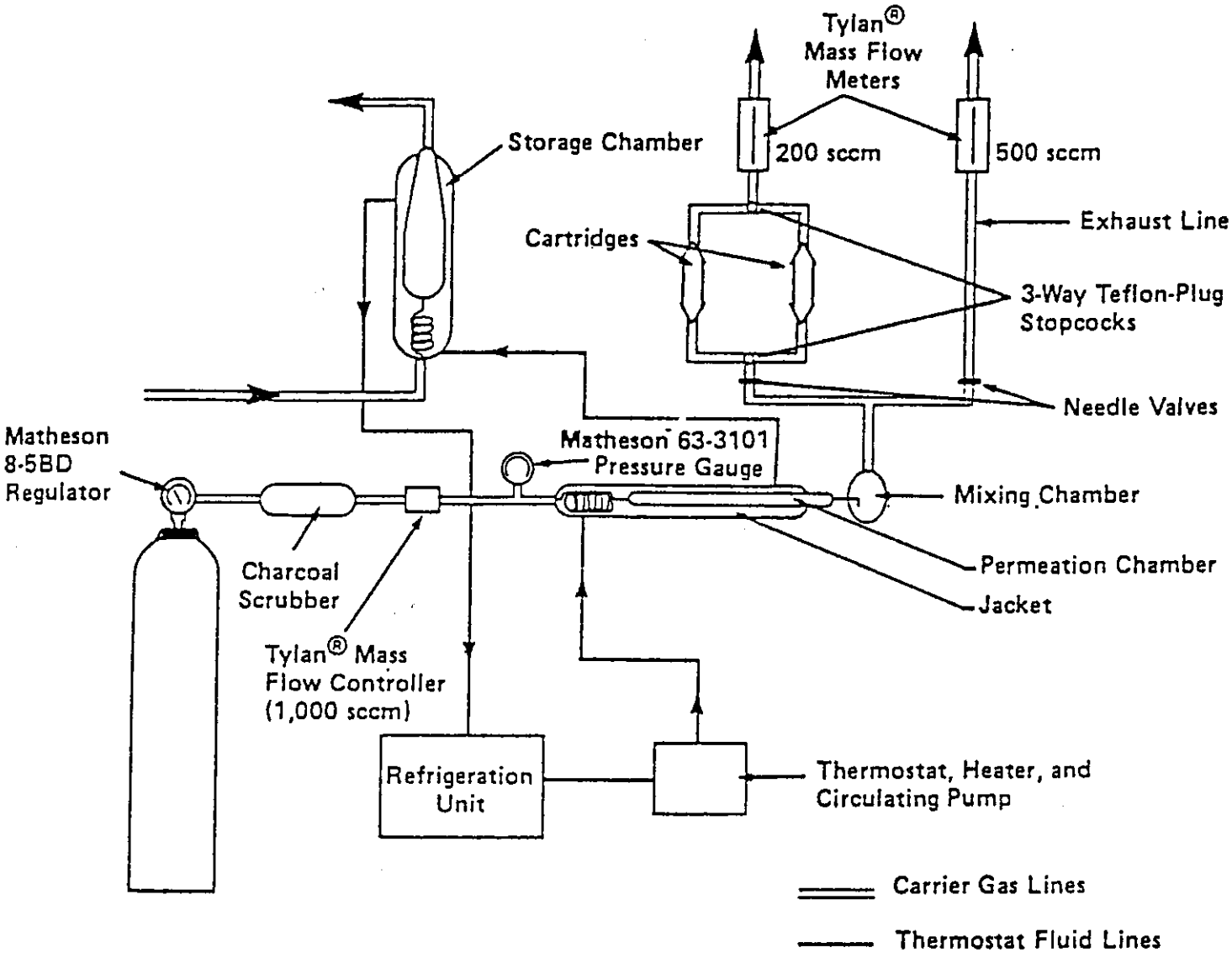


Figure 18. Permeation Tube System for Generating Standard Gas Atmospheres

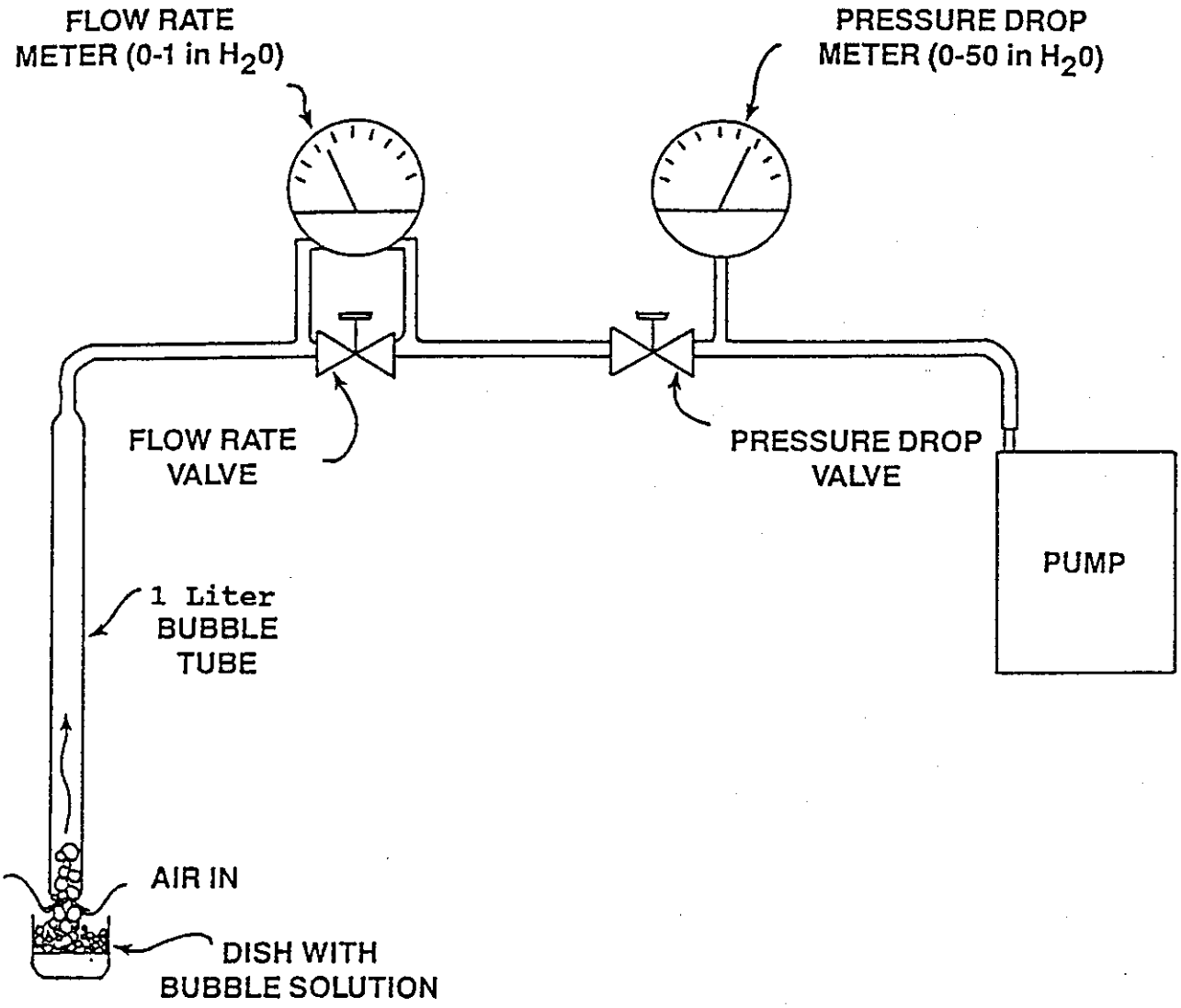


Figure 19. Calibration Assembly for Personal Sampling Pump

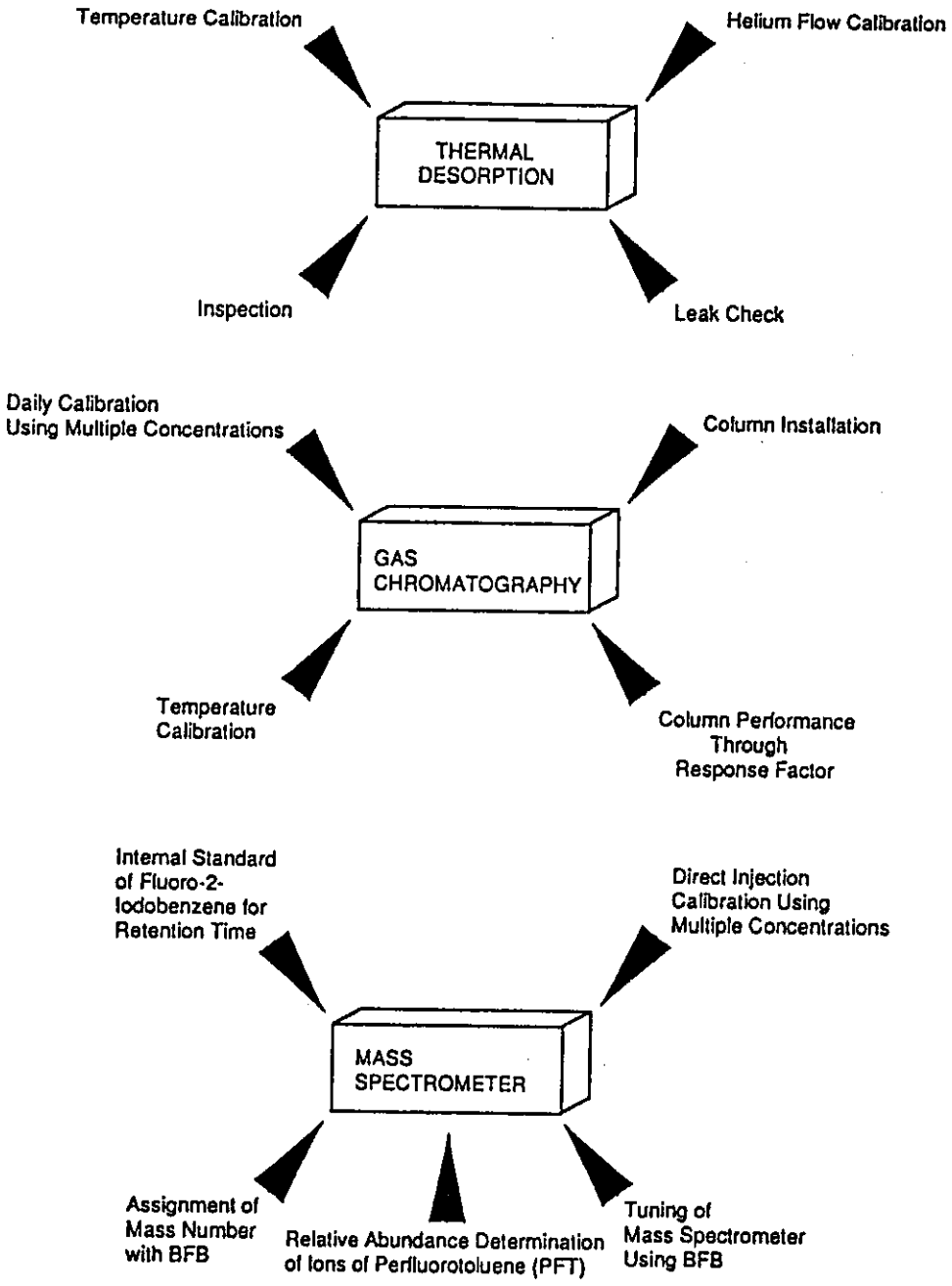


Figure 20. Performance Criteria Associated with the GC-MS-DS

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