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TECHNICAL ASSISTANCE DOCUMENT

TECHNICAL ASSISTANCE DOCUMENT FOR SAMPLING AND ANALYSIS OF OZONE PRECURSORS

Technical Assistance Document for

Sampling and Analysis of Ozone Precursors

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NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

This document contains guidance and discussion on methods applicable to the proposed revisions to Title 40 Part 58 of the Code of Federal Regulations. The proposed revisions pertain to the enhanced monitoring of ozone precursors and meteorological monitoring. The precursors addressed include volatile organic compounds, carbonyl compounds, oxides of nitrogen, and total reactive oxides of nitrogen. The meteorological parameters include surface meteorology and upper air meteorology. The document is structured in a document control format to accommodate expected revisions due to the emerging nature of the technologies discussed. The primary users of this document are expected to be Regional, State, and local Environmental Protection Agency personnel addressing the new enhanced ozone ambient air monitoring provisions.

The document consists of the following sections and appendices:

(1) Introduction

(2) Methodology for Measuring Volatile Organic Ozone Precursors In Ambient Air

(3) Methodology for the Determination of Total Nonmethane Organic Compounds In Ambient Air

(4) Methodology for Measuring Oxides of Nitrogen and Total Reactive Oxides of Nitrogen In Ambient Air

(5) Methodology for the Determination of Carbonyl Compounds In Ambient Air

(6) Meteorological Monitoring

(7) References

(A) Discussion, Issues, and Selected Procedures Related to Canister Sampling

(B) List of Materials, Equipment, and Vendors

PREFACE

The United States Environmental Protection Agency proposes to revise the air quality surveillance regulations in Title 40, Part 58 of the Code of Federal Regulations to include provisions for enhanced monitoring of ozone and oxides of nitrogen, and for additional monitoring of volatile organic compound and meteorological parameters. The proposed revisions are in accordance with congressional mandates set forth in the Clean Air Act Amendments of 1990.

This technical assistance document has been prepared to provide direction on sampling and analysis methodology to Regional, State, and local Environmental Protection Agency personnel during enhanced monitoring planning, implementation and operation activities.

This document does not circumvent the need for highly skilled technical personnel who understand and can perform the procedures described. It should not be used as a standard operating procedure.

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LIST OF ABBREVIATIONS

BFB	p-bromofluorobenzene
C	Centigrade
CAAA	Clean Air Act Amendments
CBD	central business district
CFR	Code of Federal Regulations
cm	centimeter
CMSA	Consolidated Metropolitan Statistical Area
CRM	Certified Reference Material
C18	octadecylsilane-bonded silica gel
DNPH	2,4-dinitrohpenylhydrazine
DQOs	Data Quality Objectives
ECD	electron capture detector
EPA	Environmental Protection Agency
EKMA	Empirical Kinetic Modeling Approach
F	Fahrenheit
FID	flame ionization detector
GC	gas chromatography
GC/MS	Gas Chromatography/Mass Spectrometer
GMT	Greenwich Mean Time
HCl	Hydrochloric Acid
Hg	Mercury
$HN0_3$	Nitric Acid
HPLC	High Performance Liquid Chromatography
I.D.	inside diameter
L	liter
LST	Local Standard Time
m	meter
mg	milligram
mL	milliliter
mm	millimeter
MSA	Metropolitan Statistical Area
MSD	mass selective detector

LIST OF ABBREVIATIONS
Continued

N_2	Nitrogen
ng	nanogram
NAAQS	National Ambient Air Quality Standard
NAMS	National Air Monitoring Stations
NIST	National Institute of Standards and Testing
nm	nanometer
NMOC	Nonmethane Organic Compounds
NOAA	National Oceanographic and Aeronautic Administration
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NO_x	Oxides of Nitrogen
NO_y	Total Reactive Oxides of Nitrogen
NWS	National Weather Service
O_2	Oxygen
O_3	Ozone
O.D.	outside diameter
PAMS	Photochemical Assessment Monitoring Stations
PAN	Peroxyacetyl Nitrate
PDFID	Preconcentration Direct Flame Ionization Detection
PID	photo-ionization detector
PLOT	Porous Layer Open Tubular
ppbC	parts per billion Carbon
ppbv	parts per billion volume
ppmC	parts per million Carbon
ppmv	parts per million volume
psig	pounds per square-inch gauge
QA	quality assurance
QC	quality control
RF	response factor
RRF	relative response factor

LIST OF ABBREVIATIONS
Continued

SIM	selective ion monitoring
SIP	State Implementation Plan
SLAMS	State and Local Air Monitoring Stations
SODAR	Doppler sound detection and ranging
SOPs	standard operating procedures
SRM	Standard Reference Material
UAM	Urban Airshed Model
UHP	Ultra High Purity
UV	ultraviolet
VOCs	volatile organic compounds
WCOT	Wall Coated Open Tubular
μg	microgram
μL	microliter
%RSD	percent relative standard deviation

SECTION 1.0

INTRODUCTION

The Environmental Protection Agency (EPA) is proposing to revise the ambient air quality surveillance regulations in Title 40 Part 58 of the Code of Federal Regulations (40 CFR Part 58)[1] to include provisions for enhanced (1) monitoring of ozone (O_3) and oxides of nitrogen (NO_x), (2) monitoring of volatile organic compounds (VOCs), (3) monitoring selected carbonyl compounds, and (4) monitoring of meteorological parameters. The revisions require States to establish additional air monitoring stations as part of their existing State Implementation Plan (SIP) monitoring network. The EPA's authority for proposing the enhanced monitoring regulations are provided for in Title I, Section 182 of the Clean Air Act Amendments of 1990 (CAAA).

The principal reasons for requiring the collection of additional ambient air pollutant and meteorological data are: (1) the lack of successful attainment of the National Ambient Air Quality Standard (NAAQS) for O_3, and (2) the need to obtain a more comprehensive air quality database for O_3 and its precursors. Data acquired from enhanced ambient air monitoring networks will have a variety of uses, including:

- Developing and evaluating new O_3 control strategies;
- Determining NAAQS attainment or non-attainment for O_3;
- Tracking VOCs and NO_x emissions inventory reductions;
- Providing photochemical prediction model input;
- Evaluating photochemical prediction model performance;
- Analyzing ambient air quality trends; and
- Characterizing population exposure to VOCs and O_3.

1.1 PURPOSE

The purpose of this document is to support the proposed revisions to the 40 CFR Part 58. The document provides technical information and guidance to Regional, State, and local Environmental Protection Agencies responsible for measuring O_3 precursor compounds in ambient air. Sampling and analytical methodology for speciated VOCs, total nonmethane organic compounds (NMOC) and selected carbonyl compounds (i.e., formaldehyde, acetaldehyde and acetone) are specifically addressed. The document also addresses methodology for measuring NO_x, discusses issues associated with total reactive oxides of nitrogen (NO_y), and provides technical direction for measuring the meteorological parameters prescribed by the revised regulations.

The technical guidance provided for measuring volatile organic O_3 precursors is based on emerging and developing technology. Guidance for automated applications, in particular, is based to a significant extent on experience obtained from the application of this technology during an O_3 precursor study conducted by the EPA in Atlanta, Georgia, during the summer of 1990[2]. Because these methods are based on emerging technology and reflect current state of the art, they will be subject to continuing evaluation, and improvements or clarifications are anticipated in the future.

Users should consider this guidance a basic reference to assist in developing and implementing their O_3 precursor monitoring program. The method descriptions are generic in approach and should not be considered a set of final standard operating procedures (SOPs). The document is prepared in a document control format to accommodate revisions that are anticipated as the emerging technologies develop.

1.2 ORGANIZATION

The guidance provided in Section 2 of this document addresses the measurement of volatile organic O_3 precursors and includes method descriptions for manual and automated sample collection and analysis. Detailed discussions on selected topics such as which volatile organic O_3 precursors to measure, critical gas

chromatography issues, and how canister sampling should be approached are presented.

Section 3 discusses the measurement of NMOC using Method TO-12 from the Compendium of Methods for Sampling and Analysis of Toxic Organic Compounds in Ambient Air[3]. Although measurement of total NMOC has limited application to the implementation of the proposed 40 CFR Part 58 requirements, it is included because of its applications to canister cleanliness verification and potential application to alternative monitoring strategies. The alternative monitoring strategies would involve the use of an automated version of Method TO-12 complemented with an extensive canister sampling and manual VOCs speciation analysis program.

Section 4 addresses the measurement of NO_x and issues associated with NO_y.

Section 5 addresses the measurement of selected carbonyl compounds using Compendium Method TO-11 from the Compendium of Methods for Sampling and Analysis of Toxic Organic Compounds in Ambient Air[3] and includes new information on the interference of O_3.

Section 6 provides direction on meteorological monitoring, including parameters to be measured and approaches to measurement. A detailed discussion on techniques for characterizing upper atmospheric conditions is also provided.

Section 7 lists references cited in this document. These references should be consulted when more definitive information is required.

Appendix A contains detailed procedures for canister cleaning and canister sampling system certification. Precautions in the use of canisters and on sample stability in canisters are also presented.

Appendix B lists materials and equipment referred to in this document, along with vendors names.

1.3 SUMMARY OF THE MONITORING REGULATIONS

The 1990 CAAA require EPA to promulgate regulations to enhance existing ambient air monitoring networks. Existing SIP stations are identified as State and Local Agency Monitoring Stations (SLAMS) and National Air Monitoring Stations

(NAMS). The proposed new monitoring stations will be identified as Photochemical Assessment Monitoring Stations (PAMS). The U.S. EPA is also preparing a guidance document on enhanced O_3 monitoring network design entitled Enhanced Ozone Monitoring Network Design and Siting Criteria[4] which provides assistance regarding the number of PAMS required, and station location and probe siting criteria.

The monitoring revisions proposed by EPA include changes to 15 separate Sections, Subparts, or Appendices of 40 CFR Part 58, and vary in complexity and impact on State and local agencies.

The areas of the revised 40 CFR Part 58 regulations most relevant to enhanced ambient air monitoring are operating schedules, PAMS methodology, and quality assurance. Section 58.13 of 40 CFR Part 58 contains the operating schedule for SLAMS and NAMS. This section would be revised to require sampling for VOCs and carbonyl compounds on a schedule specified in Section 4.4 of Appendix D of the revised regulations.[1]

Five PAMS site types are described in the regulations. The number of PAMS required is dependent on the population of the Metropolitan Statistical Area (MSA) or Consolidated Metropolitan Statistical Area (CMSA). The specified minimum sampling schedules for VOCs and carbonyl compounds for each site type are presented in Table 1-1. The sampling schedule applicable to a specific area is dependent on population and PAMS site types. The example of an isolated area network design shown in Figure 1-1 identifies the location of the five PAMS site types referred to in Table 1-1. The PAMS site types are described below.

Type 1 PAMS characterize upwind background and transported O_3 precursor concentrations entering the MSA or CMSA. Type 2 PAMS characterize the type and magnitude of precursor emissions in the MSA or CMSA at the point where O_3 precursor concentrations are expected to be highest. Type 3 PAMS characterize O_3 precursor concentrations and ratios downwind of the sources of emissions. Type 4 and Type 5 PAMS are maximum O_3 concentration locations occurring downwind of Type 2 PAMS sites.

TABLE 1-1

ENHANCED OZONE MONITORING NETWORK SAMPLING SCHEDULE

Population of MSA/CMSA	Required Site Type	Minimum VOCs Sampling Frequency[1]	Minimum Carbonyl Compounds Sampling Frequency[1]
Less than 500,000	(1)	A	-
	(2)	A	D
500,000 to 1,000,000	(1)	A	-
	(2)	B	E
	(4)	A	-
1,000,000 to 2,000,000	(1)		-
	(2)	A	E
	(3)	B	E
	(4)	C	-
		A	
More than 2,000,000	(1)		-
	(2)	A	E
	(3)	B	E
	(4)	C	-
	(5)	A	-
		A	

[1]Frequency Requirements Are As Follows:

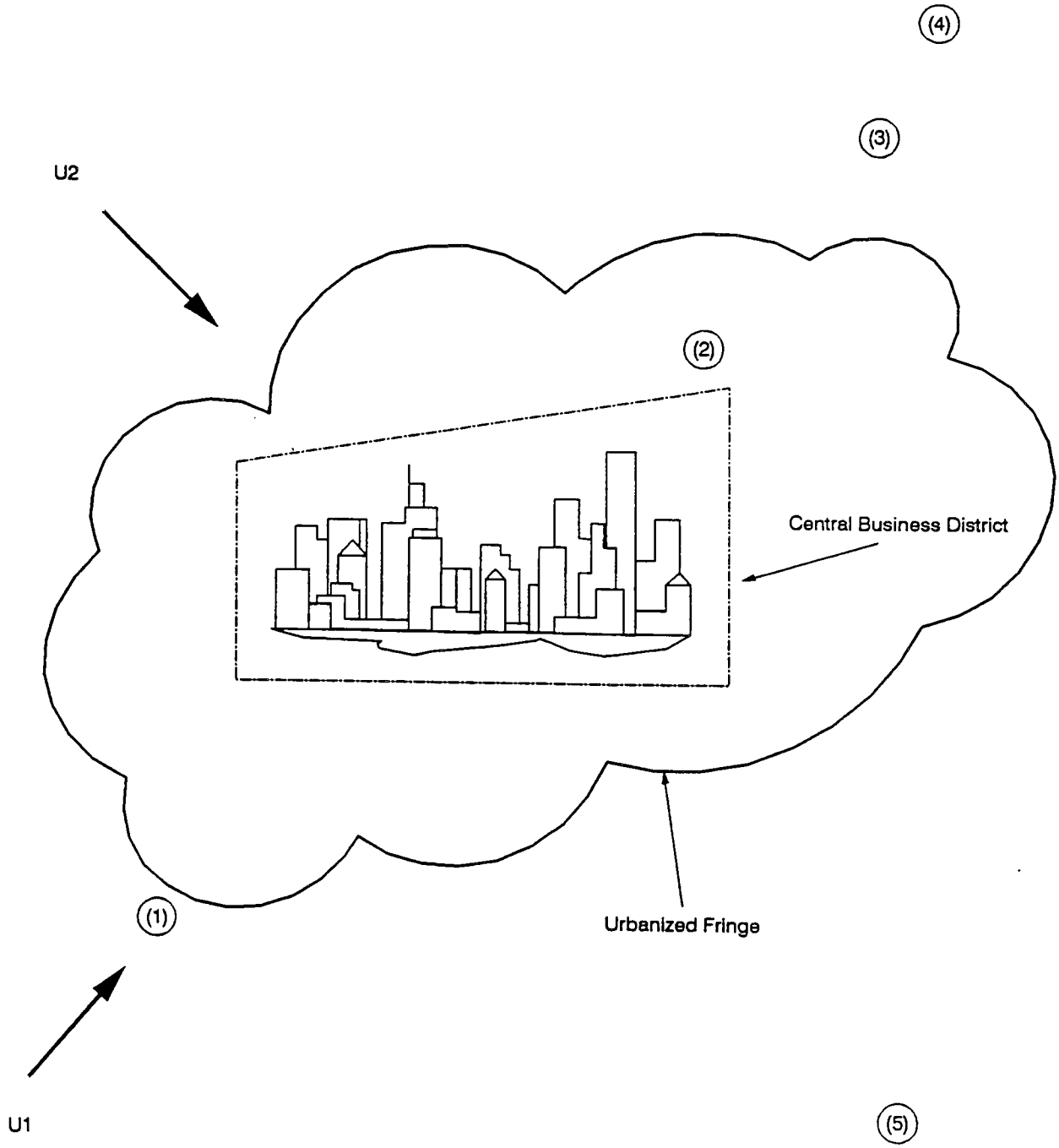
A = Eight 3-hour samples every third day and one 24-hour sample every sixth day during the monitoring period.

B = Eight 3-hour samples, every day during the monitoring period and one 24-hour sample every sixth day year-round

C = Eight 3-hour samples, every day and one 24-hour sample every sixth day during the monitoring period.

D = Four 6-hour samples, every third day during the monitoring period.

E = Four 6-hour samples, every day during the monitoring period.



U1 and U2 represent the first and second most predominant wind direction during the ozone season

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Figure 1-1. Isolated area network design.

Appendix A of 40 CFR Part 58 would be revised to reference this guidance document for general quality assurance recommendations for VOCs and meteorological measurements. Specific quality assurance criteria for VOCs were not included in Appendix A because the emerging nature of VOCs measurement technology has not allowed development of quality assurance criteria equivalent to those for criteria pollutants.

Appendix C of 40 CFR Part 58 would require that methods used for O_3 and NO_x be reference or equivalent methods. Because there are no reference or equivalent methods promulgated for VOCs and meteorological measurements, Appendix C of the revisions would refer agencies to this guideline document for direction. Appendix C of the revisions would also allow the use of approved alternative VOC measurement methodology. This provision would require States that choose to pursue alternatives to the methodology described herein to provide details depicting rationale and benefits of their alternative approach in their network description as required in 40 CFR Part 58, Section 58.4 - PAMS Network Establishment. This provision would also require that the proposed alternative be published in the Federal Register, subjected to public comment and subsequently approved by the Administrator of EPA.

SECTION 2.0

METHODOLOGY FOR MEASURING VOLATILE ORGANIC OZONE PRECURSORS IN AMBIENT AIR

The term VOCs generally refers to gaseous nonmethane organic compounds that have a vapor pressure greater than 10^{-2} kilopascals and, for the most part, have a carbon number in the range of C_2 through C_{12}. Many of these compounds play a critical role in the photochemical formation of O_3 in the atmosphere. Volatile organic compounds are emitted from a variety of sources. In urban areas the dominant source is automobiles. This section provides two generic method descriptions for measuring VOCs in ambient air and information and guidance to assist in the development, implementation, and use of these methods. A number of issues are addressed, including the target volatile organic O_3 precursors to be measured; gas chromatographic issues associated with identification and quantification of these precursors; and a description of the methodology used for identification confirmation by gas chromatography/mass spectrometry (GC/MS).

Measuring volatile organic O_3 precursors is a complex process involving the application of gas chromatographic techniques for qualitative and quantitative determination of individual hydrocarbon compounds and total NMOC. Two methods are presented for collecting and analyzing volatile organic O_3 precursor samples; (1) a manual method (see Section 2.3) involving the collection of integrated, whole air samples for subsequent analysis at a central laboratory, and (2) an automated method (see Section 2.4) where sample collection and analysis and data collection is performed automatically on-site. Ideally, agencies responsible for designing, implementing, and operating PAMS will satisfy their monitoring requirements by initially using some combination of the manual and automated gas chromatographic approaches, detailed in these two method descriptions. Eventually, most agencies should primarily use the automated gas chromatograph methodology; however, manual sampling and analysis capability will always be needed to verify the proper

operation of the automated systems, characterize the quality of the collected data, and address the identification of unknown compounds.

Because of the complexity of the measurement process and the numerous choices of instrumentation (e.g., sampling equipment, gas chromatographs, data acquisition hardware and software, etc.) the method descriptions in this document are presented generically. Background information on the potential benefits and limitations of the methods are provided. Users are ultimately responsible for equipment selection and set-up, method development, and preparation of SOPs for their specific systems.

2.1 IDENTIFICATION OF TARGET VOLATILE ORGANIC OZONE PRECURSORS

Volatile organic O_3 precursors are nonmethane organic compounds typically in the C_2 through C_{12} carbon number range. Figure 2-1 presents a list of typical volatile organic O_3 precursors that should be measured and reported to satisfy the requirements of the proposed revisions to 40 CFR Part 58. Users should initially consider these target compounds for developing their measurement systems and monitoring approach. As experience is gained regarding the occurrence of specific VOCs at each specific site, target compounds may be either deleted from, or added to, the list depending on their frequency of occurrence.

The compounds listed in Figure 2-1 are presented in the order of their expected chromatographic elution from a J&W® DB-1 dimethylsiloxane capillary analytical column. Compounds with lower boiling points elute first on this particular analytical column, followed by the heavier, higher molecular weight components with higher boiling points. Concentrations of target volatile organic O_3 precursors and unknown components (unidentified peaks) are calculated in units of parts per billion Carbon (ppbC). An estimate of the total NMOC in ppbC is made by summing all identified and unidentified gas chromatographic peaks. The concentration in ppbC of a compound can be divided by the number of carbon atoms in that compound to estimate the concentration of the compound in parts per billion volume (ppbv).

Acetylene	Methylcyclopentane
Ethylene	2,4-Dimethylpentane
Ethane	Benzene
Propylene	Cyclohexane
Propane	2-Methylhexane
Isobutane	2,3-Dimethylpentane
1-Butene	3-Methylhexane
n-Butane	2,2,4-Trimethylpentane
trans-2-Butene	n-Heptane
cis-2-Butene	Methylcyclohexane
3-Methyl-1-Butene	2,3,4-Trimethylpentane
Isopentane	Toluene
1-Pentene	2-Methylheptane
n-Pentane	3-Methylheptane
Isoprene	n-Octane
trans-2-Pentene	Ethylbenzene
cis-2-Pentene	p-Xylene
2-Methyl-2-Butene	Styrene
2,2-Dimethylbutane	o-Xylene
Cylcopentene	n-Nonane
4-Methyl-1-Pentene	Isopropylbenzene
Cyclopentane	n-Propylbenzene
2,3-Dimethylbutane	α-Pinene
2-Methylpentane	1,3,5-Trimethylbenzene
3-Methylpentane	1,2,4-Trimethylbenzene
2-Methyl-1-Pentene	β-Pinene
n-Hexane	Total NMOC
trans-2-Hexene	
cis-2-Hexene	

Figure 2-1. Target Volatile Ozone Precursors

2.2 CHROMATOGRAPHY DISCUSSION AND ISSUES

2.2.1 Gas Chromatography with Flame Ionization Detection

Gas chromatography with flame ionization detection (GC/FID) is the recommended technique for monitoring volatile organic O_3 precursors in ambient air. The sensitivity, stability, dynamic range, and versatility of GC/FID systems make themextremely useful for measuring very low concentrations of VOCs in ambient air. The basic components of GC/FID systems applicable to these measurements are:

- The carrier gas supply and regulation system;
- The sample concentration and injection system;
- The analytical or chromatographic separation column;
- The analytical column oven;
- The detection device; and
- The recording or integration device.

In the GC/FID technique, an air sample is taken from a canister or directly from the ambient air, and passed through the sample concentration system. The concentrated sample is then desorbed and injected onto the analytical column of the gas chromatograph. The VOCs are separated by taking advantage of each compound's distribution between the mobile phase (i.e., the carrier gas) and the stationary phase (i.e., the solid or liquid phase coating on the analytical column). The sample is introduced into the carrier gas stream just before it encounters the stationary phase of the analytical column. The mixture is separated into individual compounds based on the distribution equilibrium between the mobile and stationary phases. The compounds then elute from the column and enter the detector. The time of elution, or retention time, aids in identification because it is a characteristic of each particular compound.

Typically, a sample taken from an urban environment contains 100 to 150 detectable compounds in the C_2 through C_{12} carbon range, that may be reasonably separated into quantifiable peaks. These compounds are generally present at concentrations varying from less than 0.1 ppbC to greater than 1000 ppbC with the typical concentration being 0.1 to 50 ppbC. Detection of typical urban concentration levels generally requires that samples be concentrated cryogenically in order to selectively concentrate the compounds of interest and not the components of the sample that are not of interest (i.e., air, moisture, and carbon dioxide). Modern GC technology, coupled with sophisticated peak identification software, estimates the identity and quantity of each compound to the extent that the analytical column has been characterized and validated. The retention characteristics of the analytical column must be determined for each target compound using pure compounds or mixtures of pure compounds diluted with inert gas. The Flame Ionization Detector (FID) responds nearly uniformly to all nonmethane hydrocarbon compounds on a per carbon atom basis. This uniformity of response simplifies calibration in that a single hydrocarbon compound can be used to calibrate the detector response for all gas chromatographic peaks. The GC/FID response is calibrated using a hydrocarbon standard (e.g., propane) of known concentration. Compound identifications obtained from GC/FID may be periodically verified using more definitive techniques such as GC/MS. (See Section 2.5 for a discussion regarding the use of GC/MS for verification of compound identifications.)

An automated GC system developed and manufactured in Bilthoven, Netherlands, and marketed in the United States by Chrompack® Inc., Raritan, New Jersey, was used during the Atlanta O_3 precursor study[2] to obtain hourly VOC measurements. This system was equipped with a preconcentration adsorption trap, a cryofocusing secondary trap, and a single analytical column with a thick film liquid phase loading. In order to adequately concentrate and speciate the light hydrocarbon compounds with this configuration, large amounts of cryogen were required for cooling the preconcentration trap and operating the oven of the gas chromatograph at

sub-ambient temperatures. Much of the discussion that follows focuses on reducing the consumption of cryogen and improving the performance of the automated GC system by using alternative column(s) and column configurations.

2.2.2 Identification Issues

A GC/FID system relies primarily on retention times to make compound identifications. Gas chromatographic retention times are subject to shifting and interferences from non-target co-eluting compounds. Misidentification typically occurs when the chromatogram is complex, making peak identification difficult. Under these conditions the FID may not adequately deconvolute the peaks of interest, which increases the probability of incorrect identification and inaccurate quantitation.

The potential for identification errors can be reduced or eliminated by:

- Using relative retention times to designate reference peaks;
- Using dual column configurations to provide improved resolution (see Section 2.2.7 regarding column selection);
- Using specific detectors such as a mass spectrometer or a mass-selective detector (MSD);
- Having an experienced chromatographer conduct frequent visual inspection of the chromatograms to verify proper system operation; and
- Re-analyzing the samples on a better characterized GC system.

The effort devoted to peak identification and quantification confirmation is critical to the quality of the collected data. Users must determine the appropriate level of effort to be devoted to this activity, based on their specific needs and capabilities. Expert chromatography software packages, such as MetaChrom®[6], can be used to explore, and subsequently process, large or complex chromatographic data sets to improve qualitative and quantitative information.

In order to accommodate the large number of sample analyses required by the proposed revisions to 40 CFR Part 58, total analytical run time must be considered.

Parameters affecting analytical run time are column selection and configuration, temperature program rate, carrier gas flow, and instrument configuration. Analytical run time is most critical when automated methods of sampling and analysis are used because the analytical instrumentation must be capable of completing sample collection and analysis within a specified time period. Typical and practical analytical run times for automated applications usually do not exceed 45 minutes. For manual applications, the ultimate analytical run time is less critical and may be modified to meet the user's analytical needs.

2.2.3 Moisture Issues

The effects of moisture should be considered in any monitoring program where ambient sample preconcentration is required to increase detection sensitivity. Cryogenic techniques are commonly used for sample preconcentration of C_2 through C_{12} hydrocarbons. The collection of moisture in the cryogenic trap during sample preconcentration can cause several problems. These problems include retention time shifting of the earlier-eluting compounds[7], column deterioration, column plugging due to ice formation, FID flame extinction, and adverse effects on adsorbent concentration traps and some analytical detectors. If "cold spots" exist in the sample concentration or transfer system, water can collect and cause sample carryover or "ghost" peaks in subsequent sample analyses. This carryover may affect the data by causing chromatographic interferences which affect the resolution, identification, and quantitation of components of interest.

Moisture removal from the sample stream prior to sample concentration minimizes these problems and allows larger sample volumes to be concentrated, thus providing greater detection sensitivity. However, any device used to remove moisture from the sample can result in the loss of certain VOCs of interest and potentially introduce contaminants into the system.

Moisture can be removed from the air sample stream using a Perma-Pure® permeable membrane or equivalent drying device. The permeable membrane drying device generally consists of a copolymer of tetrafluoroethylene and fluorosil monomer

that is coaxially mounted within a larger polymer or stainless steel tube. The sample stream is passed through the permeable membrane tube, allowing water to permeate through the walls into a dry nitrogen (N_2) or air purge stream flowing through the annular space between the membrane and the outer tube. To improve drying efficiency and prevent memory effects, the dryer can periodically be cleaned using a procedure that involves heating (typically at 100 degrees centigrade for 20 minutes) and purging with dry N_2 or air.

For the manual analysis method, the incorporation of a moisture removal device is left to the discretion of the user. This decision requires a trade-off between the advantage (i.e., improved chromatographic sensitivity and reduced retention times shifting) and the disadvantages (i.e., potential contamination problems, loss of certain compounds of interest, and increased retention times shifting). For automated applications, moisture removal is critical and will be required.

2.2.4 Detector Types

Several non-specific but selective GC detectors are available for determining hydrocarbon, aliphatic, aromatic, and halogenated compounds. The FID is the most widely used and universal GC detector. The FID provides good sensitivity and uniform response based on the number of carbon atoms in the compound. The FID is well suited for ambient air analysis because a majority of VOCs in ambient air are hydrocarbons. The uniformity of response allows reasonable estimates of hydrocarbon compound concentration to be determined. This estimate of concentration is achieved by calibrating the FID response with a single representative compound (e.g., propane). The FID also has a broad linear dynamic range of response, allowing analysis of samples with concentrations ranging from nanogram (ng) to milligram (mg) quantities of hydrocarbons.

An electron capture detector (ECD) is appropriate for the analysis of electron deficient materials, particularly the poly-halogenated and nitro-substituted compounds. Many of the compounds in this select group are considered toxic VOCs. The ECD is 10 to 100 times more sensitive than the FID for specific halogenated compounds.

Using an ECD in combination with an FID can be useful in both the qualitative identification and quantitative determination of specific halogenated compounds.

The photoionization detector (PID) is useful in ambient air analysis because of its sensitivity to, and selectivity for, aromatic compounds. Although the PID has inherent stability and drift problems, its ability to detect aromatic compounds can be 10 to 20 times greater than that of the FID. Using a PID in conjunction with an FID can aid in qualifying and quantifying most aromatic compounds.

2.2.5 Calibration Standards

Calibrating a GC/FID system to measure VOCs requires two distinctly different types of calibration mixtures: a primary standard to calibrate detector response for gas chromatographic peak quantitation and a qualitative mixture of known hydrocarbon compounds to determine gas chromatographic peak retention times.

2.2.5.1 Primary Calibration Standard --

The GC/FID response is calibrated in ppbC using a propane primary calibration standard traceable to the National Institute of Standards and Technology (NIST). Standard Reference Materials (SRM) from NIST and Certified Reference Materials (CRM) from specialty gas suppliers are available for this purpose. Less expensive working standards needed for calibration over the range of expected concentrations can be manually prepared by the user or purchased from a gas supplier, provided they are periodically traced to a primary SRM or CRM. Based on the uniform carbon response of the FID to VOCs, the response factor determined from the propane SRM is used to convert area counts into concentration units for every peak in the chromatogram.

2.2.5.2 Retention Time Calibration Standard --

The retention time calibration standard is a multiple-component mixture containing all target VOCs at concentration levels from 10 to 30 ppbC for each compound. It is a working standard and is used during the initial setup of the GC/FID system to optimize critical peak separation parameters and determine individual

retention times for each of the target compounds. The retention time calibration standard is also used during the routine operation of the GC/FID system as a quality control (QC) standard for verifying these retention times. The response of GC/FID to selected hydrocarbons in this standard can be used to monitor FID performance and determine when recalibration of the FID using the primary calibration standard is necessary. The concentration of each compound in the retention time standard need not be directly traced to an SRM or CRM (as is the case for the primary calibration standard); rather it can be determined with reasonable accuracy using the FID propane carbon response factor from the calibrated GC system. The multiple-component mixture is not readily available and must either be prepared by the user or obtained as a special order from a specialty gas vendor. A general procedure for preparing the multiple-component mixture is given in the following discussion.

2.2.5.2.1 Retention Time Calibration Standard Preparation -- A stock retention time calibration standard containing the compounds of interest should be prepared at a concentration level approximately 100 times that of the anticipated working standard concentration. The stock standard can be prepared by blending gravimetrically weighed aliquots of neat liquids or by adding aliquots of gaseous standards with a inert diluent gas. The aliquot of each compound is introduced through a heated injector assembly into an evacuated SUMMA® passivated stainless steel canister. For the neat liquid aliquots, the pre-injection and post-injection syringe weights are recorded, and the difference used to determine the amount of liquid actually transferred to the canister. Following injection of all neat liquid and gaseous components, the canister is pressurized to at least 2 atmospheres above ambient pressure with clean, dry N_2. Concentrations are calculated based on the amount of compounds and diluent injected and the final canister pressure, using ideal gas law relationships.

The stock retention time calibration standard is used to prepare humidified working retention time calibration standards at the ppbC level. As indicated earlier, it is not necessary to determine exact component concentrations in the multi-component

mixture because it is not being used to determine compound specific response factors. However, the approximate concentration of the stock standard must be known in order to prepare the working retention time standards. Preparation of the working standards is accomplished by syringe injecting a gaseous aliquot of the stock standard into a SUMMA® passivated stainless steel canister, and subsequently diluting with humidified zero air. The working standard should be prepared to provide enough volume to last throughout a monitoring period (3-4 months). A 33-liter SUMMA® passivated canister pressurized to at least 3 atmospheres above ambient pressure should provide sufficient supply of the working standard.

2.2.6 Analytical System Calibration

The detector response of the analytical system should initially be calibrated with multiple level propane standards over the expected sample concentration range. The primary calibration standard is used to generate a per Carbon response factor based on propane for determining the concentration of each target VOC, as well as the summation of all detected VOCs (total NMOC). It is impractical and unnecessary to determine compound specific response factors for each of the volatile organic O_3 precursors shown in Figure 2-1, because the per Carbon response of the FID to these compounds is approximately equal. It is appropriate to measure each compound concentration in terms of ppbC using the relative response factor determined from the propane standard.

For a known, fixed sample volume, the concentration is proportional to the area under the chromatographic peak. The area is converted to ppbC using the following equation:

$$C_A = RF\ (AC)$$

Where:

RF = Response Factor

AC = Area Counts

C_A = Concentration (ppbC)

The response factor (RF) is an experimentally determined calibration constant (ppbC/area count), and is used for all compound concentration determinations. The response factor is determined by the analysis of the ppbC level NIST standard and is determined using the following equation:

$$RF = \frac{3\ (C_B)}{MAC}$$

Where:

3 = Carbon Atoms - Propane

C_B = Concentration of the NIST Propane Standard (ppbv)

MAC = Median area count, determined from three replicate analyses of the primary standard or analysis of the multi-level calibration standards

Retention time identification of target compounds is performed by analyzing the retention time calibration standard prepared as described in Section 2.2.5.2. This standard is analyzed at least in duplicate to establish the correct retention times and retention time windows for the peaks of interest.

A calibration check and retention times check of the analytical system should be performed every 2 days in order to determine system variability and overall performance. Acceptance criteria for analytical system performance (e.g., ±10%) should be established during the method development stage of the program.

The calibration and retention times check are performed concurrently using the retention time calibration standard. The retention time calibration standard is analyzed and the resulting compound concentrations and retention times are compared to the values obtained during the initial or most recent calibration of the analytical system. The compound concentrations and retention times should compare within the limits of the acceptance criteria. If they do not re-calibration of the analytical system should be performed.

2.2.7 Column Selection and Configuration

Column selection for analysis of the target volatile organic O_3 precursors is dependent to a large extent on whether the application involves manual or automated methods. However, column selection for both methods is primarily dictated by total sample analysis time and target compound resolution requirements. Other column selection factors to be considered include practical and cost considerations, such as the need to minimize cryogen consumption. Selecting columns that will provide the desired separation of the C_2 through C_4 hydrocarbons without cooling the column oven to sub-ambient temperatures will decrease cryogen consumption significantly.

Column configurations for use in enhanced monitoring programs are generally limited to single-column, single-detector, or dual-column, dual-detector applications. The simplest analytical column configuration involves the use of a single column with a single FID. However, this configuration imposes limitations on the separation of selected target volatile organic O_3 precursors. Analyzing the full range of C_2 through C_{12} hydrocarbons using a single analytical column may result in less than optimum separation characteristics for either the light or heavy hydrocarbons, depending on the analytical column chosen. For example, to improve resolution of the C_2 through C_4 hydrocarbons, a thick liquid phase column and sub-ambient column oven temperatures is desirable. However, the use of a thick liquid-phase column results in less than optimum resolution of the C_5 through C_{12} hydrocarbons, and sub-ambient column oven temperatures result in increased cryogen consumption. In order to improve the separation characteristics for the light hydrocarbons (C_2 through C_4) as well as the heavier hydrocarbons (C_5 through C_{12}), a more complex dual-column, dual-detector configuration may be considered. In this case, the two columns can be judiciously selected to provide optimum separation of both light and heavy hydrocarbons without sub-ambient column oven temperatures. Because both columns must be contained in one gas chromatographic oven for automated applications, columns must be selected that will provide the desired separation with a single oven temperature program.

Despite the limitations, users are strongly encouraged to pursue a single-column, single-detector approach during the initial operation of their enhanced monitoring program. A single-column configuration may result in less than optimum separation characteristics of either the light or heavy hydrocarbons, but is simpler to use than a dual-column configuration. As experience is gained with the GC/FID system(s), a more complex dual-column configuration should be pursued.

2.2.7.1 Column Recommendations --

Several columns applicable to either single- or dual-column applications are discussed below. The column conditions described are recommendations provided from laboratory applications or conditions determined by the column manufacturer that should provide acceptable separation of the VOCs of interest. However, these conditions must be evaluated and optimized by an experienced chromatographer to verify acceptable peak resolution prior to use. Both column configuration and column selection are left to the discretion of the users. The columns described below have been used in either a single- or dual-column configuration in conjunction with a single- or dual-FID for separation of the C_2 through C_{12} hydrocarbons.

The dual-column configuration recommended does not require the use of sub-ambient column oven temperatures and therefore results in reduced cryogen consumption. When using dual-column configurations, a single gas chromatographic column oven temperature program must be optimized for both analytical columns in order to provide the best target compound separation.

The heavy hydrocarbons (C_5 - C_{12}) maybe resolved using a 0.32 millimeter (mm) inside diameter (I.D.), 60 meter (m) J&W® DB-1 fused silica column with a 1-micron dimethylsiloxane coating. However, this column will not provide complete separation of the light hydrocarbons (C_2 - C_4) even at sub-ambient column oven temperatures. The DB-1 column has been historically and extensively used in ambient air applications. It can be used in conjunction with a 0.32 mm I.D., 50 m Chrompack® Porous Layer Open Tubular (PLOT) fused silica analytical column, with a 5-micron Al_2O_3/KCl coating. The PLOT column provides acceptable light hydrocarbon

separation under the same column oven temperature program conditions used for the DB-1 column but does not provide complete separation of C_9 - C_{12} hydrocarbons. Simultaneous use of these columns lends itself to dual-column automated applications. The PLOT analytical column is susceptible to moisture, which may cause peak retention times shifting and column deterioration; therefore, moisture must be removed from the sample using a permeable membrane dryer or other drying device. If manual sample analysis using these columns is performed, sequential analyses or the use of separate GC systems may be considered to optimize and obtain complete C_2 through C_{12} separation. Figures 2-2 and 2-3 are example chromatograms from the DB-1 and PLOT columns. It is recommended that users give primary consideration to the DB-1 and PLOT columns described above during their column selection process.

The user is encouraged to perform the initial system set-up, optimization, and check-out with a less complex single-column configuration utilizing the DB-1 for the C_4 through C_{12} hydrocarbons, since these hydrocarbons represent the majority of the target volatile organic O_3 precursors. Once this single-column application has been optimized, the second analytical column may be installed and optimization of simultaneous operation of both columns for complete C_2 through C_{12} resolution can be performed.

There are a large number of alternate column options that can be used for C_2 through C_{12} analysis for both single- or dual-column approaches. The column selection process should be based on the capability of the column to separate the target volatile organic O_3 precursors listed in Figure 2-1 in conjunction with desired overall sample analysis time. The recommended manufacturer conditions, along with the carrier gas flow rates, must be evaluated and optimized in order to verify acceptable peak resolution prior to use. When choosing alternate columns, the user should consult directly with the analytical column manufacturer or developer for advice regarding column characteristics, optimum gas chromatographic oven temperature programs, or other considerations.

Analytical Conditions	
Column:	DB1, 60m x 0.32mm
Temperature:	-60°C/2 min at 6°C/min to 180°C/3 min
Det:	FID, 300°C
Carrier Gas:	Helium, 2 mL/min

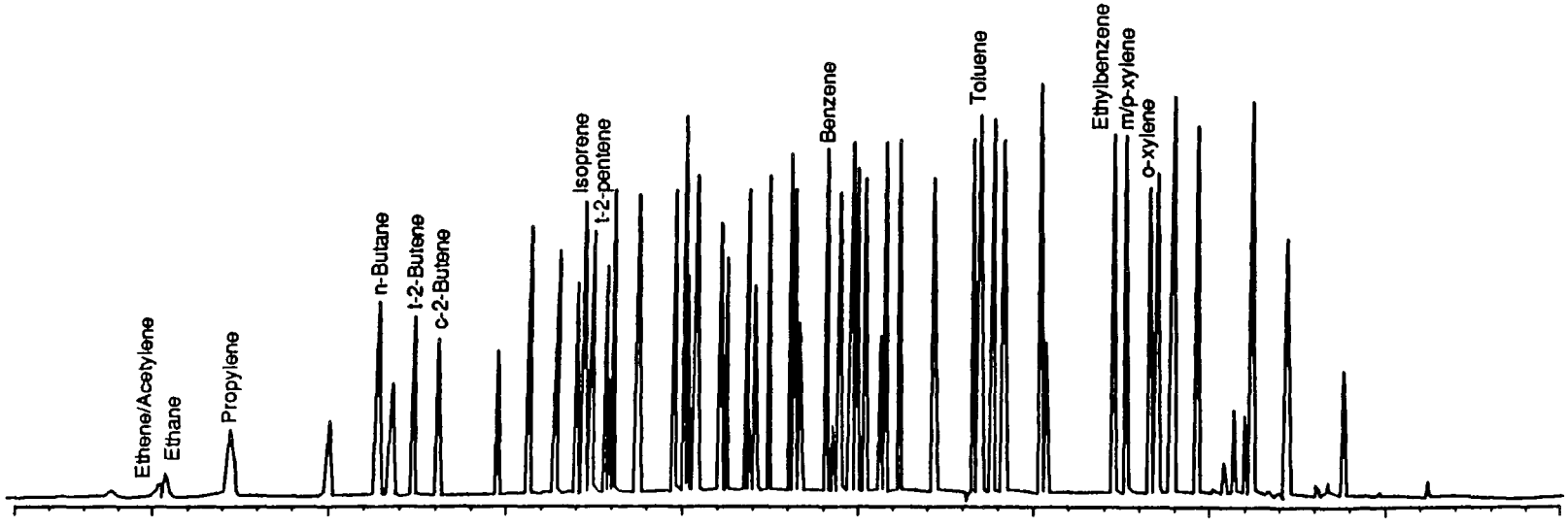

Figure 2-2. Example Chromatogram for J&W®DB1 Capillary Analytical Column.

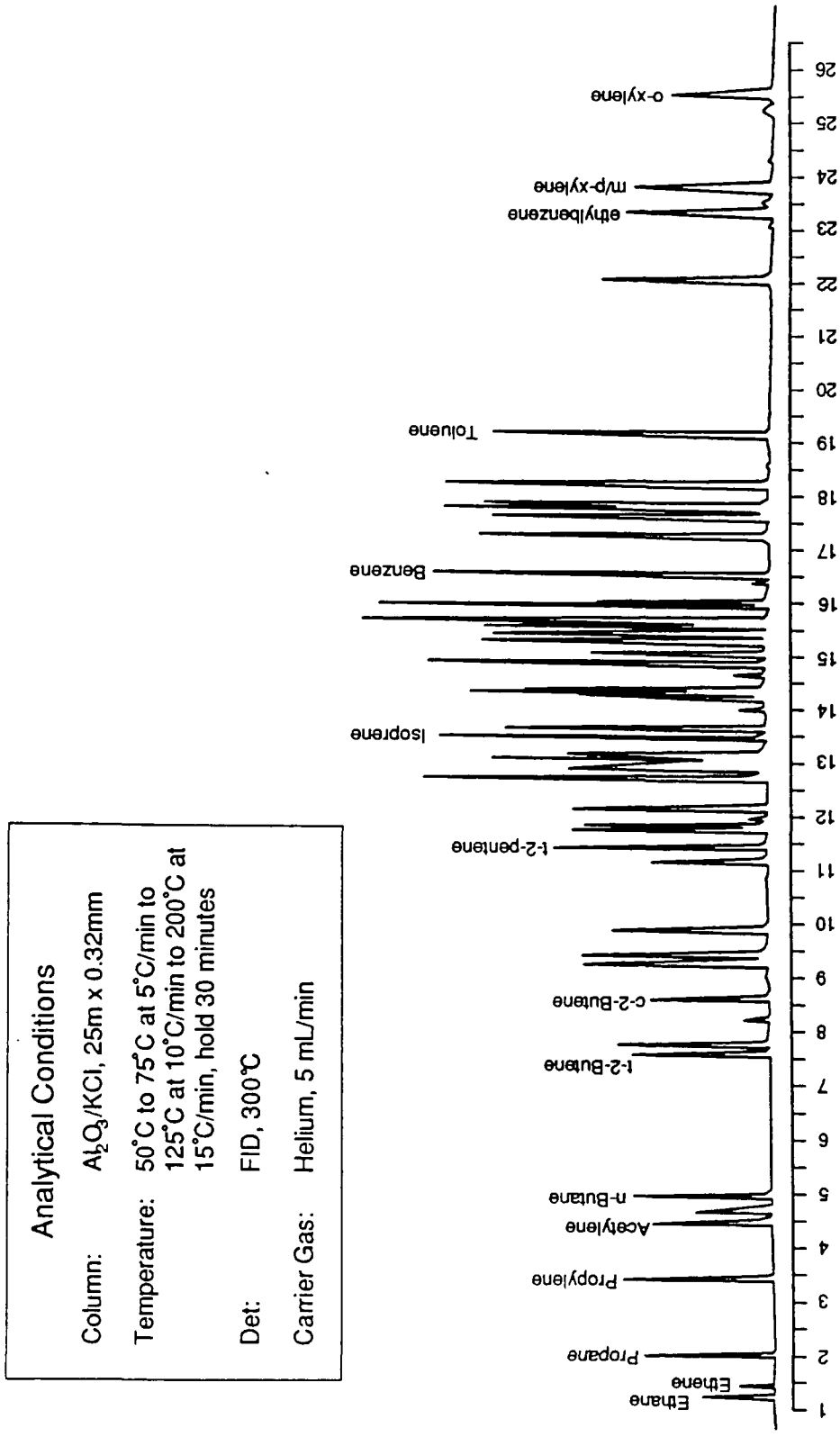

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Figure 2-3. Example Chromatogram for Chrompak® Al_2O_3/KCl PLOT Capillary Analytical Column.

The following columns are alternatives for single-column, light (C_2 - C_4) hydrocarbon separation and, in some cases, require sub-ambient oven temperature conditions:

1. J&W® DB-1 with a 5-micron dimethylsiloxane phase thickness, an internal diameter of 0.32 mm, and a length of 60 m. The recommended oven temperature program is -60 degees centigrade (°C) for 2 minutes, to 180°C at 8°C per minute. The final oven temperature is maintained for 13 minutes for a total analytical run time of 45 minutes.

2. J&W® GS-Q fused silica capillary column with an internal diameter of 0.53 mm and a length of 30 m. The recommended oven temperature program is 40°C to 200°C at 4°C per minute. The final oven temperature is maintained for 5 minutes for a total analytical run time of 45 minutes.

The following columns are alternatives for single-column, heavy (C_5 - C_{12}) hydrocarbon separation and, in some cases, require sub-ambient oven temperature conditions:

1. Chrompack® WCOT (Wall Coated Open Tubular) capillary fused silica column with a 5-micron CP-SIL 5CB dimethylsiloxane stationary phase thickness, an internal diameter of 0.32 mm, and a length of 50 m. The recommended oven temperature program is -20°C for 5 minutes, to 200°C at 7°C per minute. The final temperature is maintained for 9 minutes, which results in a total analytical run time of 40 minutes.

2. Restek® RTx-502.2 capillary fused silica column with a 3-micron phase thickness, an internal diameter of 0.53 mm, and a length of 105 m. The recommended GC oven temperature program is 35°C for 10 minutes, to 200°C at 4°C per minute. The final oven temperature is maintained for 7 minutes, which results in a total analytical run time of 58 minutes. This column is capable of separating the C_4 through C_{12} hydrocarbons without the need for sub-ambient column oven temperatures.

A combination of these light and heavy hydrocarbon separation columns may be used to accommodate dual-column approaches.

2.2.8 Data Quality Objectives

Data quality objectives (DQOs) must be established to ensure that the quality of the data collected is consistent with the overall method goals and intended use of the data. Data quality objectives reflect the level of uncertainty that the data user can tolerate from data collected. The method performance characteristics of the DQOs should include, at a minimum, detection limits, accuracy, and precision guidelines. It is the responsibility of the user to implement the steps necessary to determine and ensure that the data meet the established DQOs.

Detection limits are expressed in units of concentration and reflect the smallest volume of a compound that can be measured with a defined degree of certainty. Instrument detection limits can be assessed using a procedure specified in 40 CFR Appendix B, Part 136.1[5]. This procedure is device- or instrument-dependent and involves the replicate analysis of at least seven samples at very low ppbv concentrations. The procedure uses the standard deviation of the concentration measured from replicate sample analyses in conjunction with the Student's t-value at the 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The detection limit for hydrocarbon VOCs should be approximately 1 ppbC for each compound.

Accuracy involves the closeness of a measurement to a reference value, and reflects elements of both bias and precision. The SRM standards from NIST or CRM standards from specialty gas vendors should be used to determine the reference value and must be analyzed under conditions that duplicate the analysis method. In the absence of specific DQOs, absolute accuracy should be within 25% of a reference value. Accuracy for at least 25% of the target compounds should be determined.

Precision is a measure of the repeatability of the results. In the absence of specific DQOs, absolute precision of repeated measurements should be within 20% relative standard deviation or coefficient of variation.

2.3 MANUAL METHOD FOR COLLECTING AND ANALYZING VOLATILE ORGANIC OZONE PRECURSOR SAMPLES

The manual methodology for obtaining volatile organic O_3 precursor measurements involves collecting integrated, whole air canister samples for subsequent analysis at a central laboratory. The proposed revisions to 40 CFR Part 58 require States to obtain 3-hour and 24-hour integrated measurements of volatile organic O_3 precursors at specified sample collection frequencies based on individual PAMS site type requirements. The sample collection frequencies range from one 24-hour sample every sixth day to eight 3-hour samples every day. Specific sample collection frequencies are presented in Figure 1-1.

Application of the manual methodology to the enhanced O_3 monitoring regulations requires the collection and analysis of a large number of canister samples depending on the combination of manual and automated (see Section 2.4) approaches selected to satisfy the requirements. The extent and success of a manual monitoring program will be dependent on the number of canisters available for use, and the analytical capacity of the central laboratory involved. An integrated, well planned sampling and analysis program is necessary to address the numerous aspects of a canister-based monitoring operation, which include canister cleaning and transport; sampling frequency and procedures; analysis procedures; and data acquisition and reporting. These details must be addressed in accordance with the specific needs of the user. The intent of this section is to provide general guidance on the manual method approach. Users of manual methodology are responsible for the selection, set-up, and optimization of their specific system(s), and for the preparation of SOPs that delineate the details of each operation.

2.3.1 Sampling

This section describes the configuration and use of SUMMA® passivated canisters and associated sample collection systems. These systems provide samples for subsequent analysis at a central laboratory using a gas chromatographic analytical system with computerized data reduction and reporting capabilities.

The sample collection system should be capable of unattended sampling in order to allow collection of samples in accordance with the specified schedule presented in Table 1-1. Procedures for collecting canister samples are described below. Precautions pertaining to the use of canisters, canister cleaning procedures, and sampling system certification procedures are discussed in detail in Appendix A of this document.

Collecting time-integrated whole ambient air samples for subsequent analysis of target compounds is a widely accepted practice. Systems currently in use incorporate diverse operating approaches. The primary difference among the various approaches is the technique and associated hardware used to perform time-integration of a canister sample collection. Time-integration techniques generally involve the use of electronic and mechanical devices, either separately or in combination. Canister sampling systems can be obtained commercially or can be custom-built for a specific application.

The use of canisters to satisfy the 3-hour sampling schedules specified in Table 1-1 will require automated multiple-event canister sampling systems. Back-to-back collection of the individual 3-hour samples may not be practical using single-event systems, due to the required attendance of an operator to change the sample canisters between events. A limited number of multiple-event canister sampling systems are commercially available. Additional systems should become available as the need for them increases. Multiple-event systems can also be custom-built. A conceptual automated multiple-event canister sampling system configuration is presented in Figure 2-4.

2.3.1.1 Canister Sample Collection --

The following sections generally describe single-event canister sampling equipment and procedures that can be incorporated into multiple-event collection system operation.

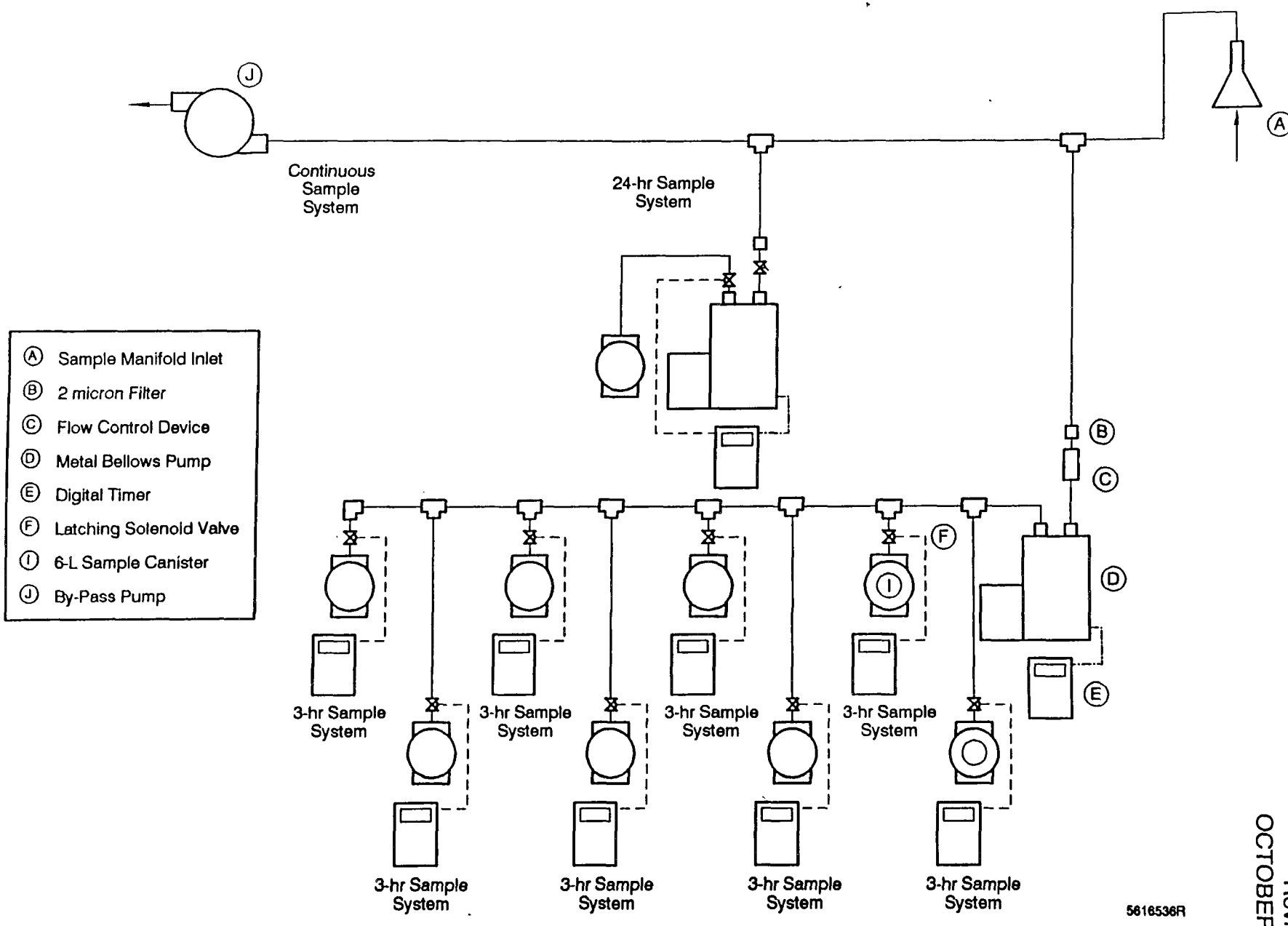


Figure 2-4. Automated multi-event canister sampling system.

2.3.1.1.1 Sampling Equipment -- A typical single-event sampling system configuration is presented in Figure 2-5. The single-event canister sampling system is comprised of the following primary components:

Sample Pump - A stainless steel bellows pump, capable of 2 atmospheres output pressure. The pump must be free of leaks and determined nonbiasing.

Sample Inlet Line - Chromatographic-grade stainless steel tubing used to connect the sampler to the sample probe and manifold assembly.

Sample Canister A SUMMA® passivated leak-free stainless steel sample containment vessel of desired internal volume with a bellows valve attached at the inlet.

Stainless Steel Vacuum/Pressure Gauge - Capable of measuring vacuum (0-30 in Hg) and pressure (0-30 pounds per square-inch gauge). Gauge should be leak-free and shown to be nonbiasing.

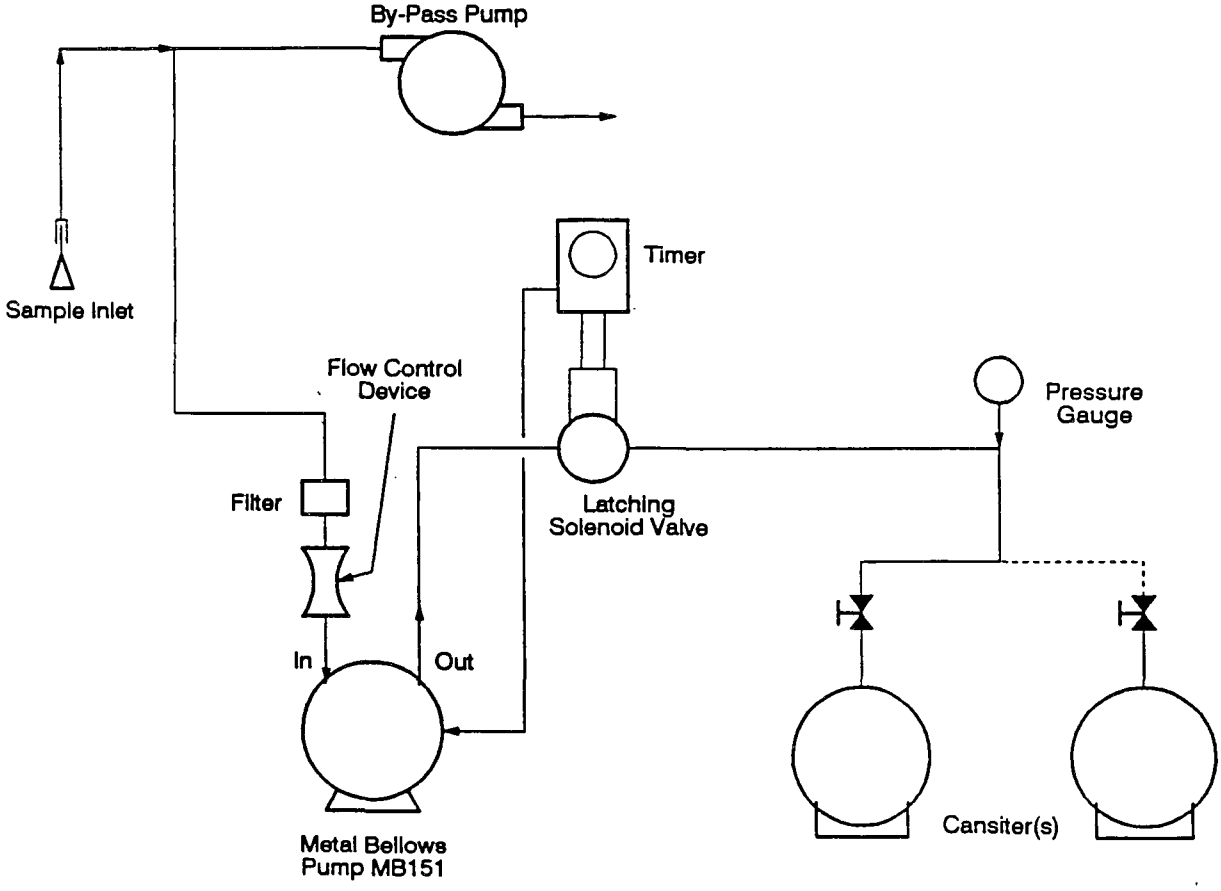
Fixed Orifice, Capillary, Adjustable Micrometering Valve or Electronic Mass Flow Controller - Capable of maintaining a constant flow rate (± 10%) over a specific sampling period under conditions of changing temperature (20-40°C) and humidity (0-100% relative).

Particulate Filter - 2 micron sintered stainless steel in-line filter.

Electronic Timer - To allow unattended operation (activation and deactivation) of the collection system.

Latching Solenoid Valve - Electric-pulse-operated, stainless steel solenoid valve, with Viton® plunger seat and o-rings.

Chromatographic Grade Stainless Steel Tubing and 316 Grade Stainless Steel Fittings - Used for system interconnections (all tubing in contact with the sample prior to analysis should be chromatographic grade stainless steel and all fittings should be 316 grade stainless steel).



Sample inlet is an inverted glass funnel.
Lines and fittings are stainless steel.

Figure 2-5. Single-event canister sampling system.

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By-pass Pump - Used to continuously draw sample air through the inlet probe and manifold assembly at a rate in excess of the sampling system total uptake. Sample is extracted from the manifold at a lower rate, and excess air is exhausted to the atmosphere.

Elapsed Time Indicator - Measures the duration of the sampling episode.

2.3.1.1.2 Sampling Procedure --

The sample is collected in a canister using a pump and flow control device. A stainless steel metal bellows style pump draws in ambient air from the sampling probe and manifold assembly at a constant flow rate to fill and pressurize the sample canister.

A flow control device is used to maintain a constant sample flow rate into the canister over a specific sampling period. The flow rate used is a function of the final desired sample pressure and the specified sampling period and assumes that the canisters start at a pressure of 5 mm Mercury (Hg) absolute. The flow rate can be calculated by:

$$F = \frac{P \times V}{T \times 60}$$

Where:

F = flow rate (mL/min)
P = final canister pressure, atmospheres absolute
V = volume of the canister (mL)
T = sample period (hours)
60 = minutes in an hour

For example, if a 6-L canister is to be filled to 2 atmospheres absolute pressure in 3 hours, the flow rate can be calculated by:

$$F = \frac{2 \times 6000}{3 \times 60} = 67.7 \text{ mL/min}$$

For automatic operation, the timer is programmed to activate and deactivate the sample collection system at specified times, consistent with the beginning and end of a sample collection period.

The use of the latching solenoid 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 sampling period. The temperature rise in the valve could cause outgassing of organic compounds from valve components. The latching solenoid valve requires only a brief electrical pulse to open or close at the specified start and stop times; therefore, the valve experiences no temperature increase. The pulses may be obtained either with an electronic timer that can be programmed for short (5 to 60 seconds) actuation pulses, or with a conventional mechanical timer incorporating an attached electric pulse circuit.

Canister sampling systems can collect sample from a shared sample probe and manifold assembly as described in Section 2.4.1.1.1 or from a system specific stainless steel sample probe and by-pass pump. If a system specific probe and by-pass pump are used, a second electronic timer should be incorporated to start the by-pass pump several hours prior to the sampling period to flush and condition the components. The connecting lines between the sample inlet line and the canister should be as short as possible to minimize internal surface area and system residence time.

The flow rate into the canister should remain relatively constant over the entire sampling period. If a critical orifice is used as the flow control device, a drop in the flow rate may occur near the end of the sample period.

Prior to field use, each sampling system should be certified nonbiasing. (Refer to Appendix A, Section A4.0 of this document for details pertaining to canister sampling system certification.) The canisters should also be determined nonbiasing or clean before each use. (Refer to Appendix A, Section A3.0 of this document for details pertaining to canister cleaning.)

The following provides specific details for operating a typical single-event sampling system.

1. Verify the correct sample flow rate using a calibrated mass flow meter or rotameter. The flow can be measured directly at the inlet of the system. The calibrated mass flow meter or rotameter is attached to the sample inlet line, prior to the particulate filter. The sampling system is activated, and the reading obtained is compared to the desired collection flow rate. The values should agree within ± 10 percent. If a mass flow controller is being used as the system flow control device, allow the system to equilibrate for 2 minutes. After 2-minute equilibration, the desired sample flow rate is attained by adjusting the system mass flow controller until the calibrated mass flow meter or rotameter indicates the correct flow rate. If the sampling system uses a micrometering valve instead of a mass flow controller as the flow control device, adjust the micrometering valve until the correct flow rate is achieved (see Figure 2-5). If the sampling system uses a fixed critical orifice assembly as the flow control device, change the orifice to a size consistent with the desired flow rate.

2. Deactivate the sampler and reset the elapsed time indicator to show no elapsed time.

3. Disconnect the calibrated mass flow meter or rotameter and attach a clean canister to the sampling system.

4. Open the canister bellows valve.

5. Record the initial vacuum in the canister, as indicated by the sampling system vacuum gauge, onto the canister sampling field data sheet.

6. Record the time of day and elapsed time indicator reading onto the canister sampling field data sheet.

7. Set the electronic timer to begin and stop sampling at the appropriate times.

8. After sample collection, record the final sample pressure onto the sampling field data sheet. Final sample pressure should be close to the desired

calculated final pressure. Time of day and elapsed time indicator readings should also be recorded.

9. Close the canister bellows valve. Disconnect and remove the canister from the sampling system.

10. Attach an identification tag to the canister. Canister serial number, sample number, location, and date should be recorded on the tag.

2.3.2 Analysis

Gas chromatographic analysis of whole air ambient samples collected in SUMMA® passivated canisters for measurement of VOCs is well established and routinely performed. The analytical system should incorporate a sample concentration trap, a gas chromatograph, appropriate analytical column(s) and detector(s), and a data acquisition system. A sample drying device may also be incorporated. The user may choose either a single analytical column with a single-FID for ease of operation or a more complex two-column, two-FID configuration to improve the resolution of the VOCs over the C_2 through C_{12} range. An alternative approach for improving C_2 through C_{12} resolution is to use two gas chromatographs with two separate specific analytical columns and oven temperature programs. Several column configuration alternatives are described in Section 2.2.7.

2.3.2.1 Analytical Equipment and Configuration --

The following sections identify and describe the primary components of the analytical system.

2.3.2.1.1 Sample Drying Device -- Sample moisture removal can be performed to prevent or reduce potential adverse effects on the sample concentration device, the analytical column(s), and the detector(s). Moisture removal allows analysis of larger sample volumes, which provide enhanced detection sensitivity. Enhanced detection sensitivity is critical to the measurement of less abundant volatile organic O_3 precursors.

Moisture should be removed from the sample stream using a permeable membrane drying device or equivalent drying system (Section 2.2.3). Nonpolar hydrocarbon compounds pass through the drier unaffected but certain polar VOCs may be removed (e.g., C_{10} terpenes). To prevent moisture build-up and memory effects, the drier must be initially and periodically cleaned using a procedure recommended by the manufacturer.

2.3.2.1.2 Sample Concentration Device -- Ambient air samples can be concentrated using commercially available or custom built adsorbent and/or cryo-focusing devices, referred to as traps. Adsorbent traps use individual or combinations of absorbent media (e.g., Carbotrap, Carbotrap C, and Carbosieve III) to achieve sample concentration. The adsorbent(s) is typically contained in a tubular housing. The sample stream is passed through the adsorbent(s) and selectively concentrated. Cryogenically cooling the adsorbent trap during the concentration process can increase the collection efficiency of the adsorbent media. Cryogenic concentration of samples can also be performed using a trap consisting of chromatographic grade stainless steel tubing packed with commercially available 60/80 mesh deactivated glass beads maintained at -185°C during sample concentration. Most sample concentration devices use the process of thermal desorption to revolatize the concentrated VOCs for transfer to the analytical column for separation.

2.3.2.1.3 Gas Chromatograph -- Commercially available GC/FID systems can be used to analyze concentrated VOC samples. Sub-ambient oven capability may be required depending on the analysis approach selected.

2.3.2.1.4 Analytical Columns -- Because of the complexity of the relationship between instrument configuration, operating parameters, sample matrix, and target compounds, the selection of the applicable analytical column(s) should be based on the specific criteria and recommendations for column selection discussed in Section 2.2.7. Consultation with GC column manufacturers for guidance in selecting

alternative columns to meet the specific requirements of a program is recommended. Column selection should be based on the capability of a column to separate the target compounds, while considering the desired overall analysis run time. Once the column configuration is selected, it is the responsibility of the chromatographer to determine the optimum analytical conditions for each critical operational parameter in order to achieve the best gas chromatographic performance.

2.3.2.1.5 Support Gases --

GC Support Cylinder Gases:

Ultra High Purity (UHP) grade helium (99.999% purity)
Hydrocarbon Free Air (< 0.1 parts per million Carbon total hydrocarbon)
UHP grade Hydrogen (99.999% purity)

Cryogen:

Liquid Nitrogen

Primary Calibration Standard:

30 ppbC propane standard diluted from an NIST stock standard

Retention Time Calibration Standard:

10 to 30 ppbC/compound calibration standard containing each of the target compounds.

2.3.2.1.6 Data Acquisition System -- The data acquisition system consists of, but is not limited to, a PC-DOS personal computer with appropriate chromatography data acquisition and peak integration software. Chromatography software is typically comprised of subroutines that perform data acquisition, peak integration and identification, hard copy output, post-run calculations, calibration, peak re-integration, and user program interfacing. Acquired data should be automatically and permanently stored on magnetic media (e.g., hard disk, floppy diskette).

2.3.2.2 Analytical System Operation --

This section provides general guidance for initial system set-up, analytical system parameter optimization, calibration, and data acquisition and reporting. Specific and detailed SOPs must be prepared by the user, with appropriate input and assistance from the system manufacturer or developer.

2.3.2.2.1 Set-up and Parameter Optimization -- A minimum period of 3 to 6 months prior to field sampling and sample analysis should be anticipated for acquisition of canisters, acquisition and/or fabrication and certification of canister sampling systems, initial equipment set up, user familiarization and development of SOPs. All systems should initially be set up in accordance with the manufacturer's or developer's operational performance specifications.

During initial setup of the GC analytical system, numerous critical parameters must be evaluated to determine optimum operating conditions for obtaining quantitative data. These parameters include, but are not limited to, selection of sample concentration flow rate; sample concentration trap collection and desorption time and temperatures; the gas chromatographic oven temperature program parameters; calibration of the detector, and gas chromatographic integration methods to be used for peak identification. These parameters should be optimized and characterized using; (1) pure compounds in air and (2) the retention time calibration standard (see Section 2.2.5.2) containing a mixture of the components of interest. Once the critical parameters are established, the retention time calibration standard is used to determine the exact retention times of the target compounds for input into the chromatography data reduction and peak integration software.

2.3.2.2.2 Calibration -- The analytical system should initially be calibrated with propane standards at concentrations over the expected sample concentration range. Analysis of the primary calibration standards should be performed every two days in order to determine analytical system variability and overall performance. Refer to Section 2.2.5 for details.

Retention time identification of target compounds is determined by analyzing individual species and the retention time calibration standard described in Section 2.2.5.2.

2.3.2.2.3 Data Acquisition and Reporting -- The data from the GC system are collected and processed with a data acquisition system selected by the user. The data acquisition system contains the algorithms to acquire, integrate, and identify the chromatographic peaks by retention times. The system should also be capable of producing a report file for every sample analyzed and interfacing with other data processing equipment. Each report file should include, at a minimum, each peaks retention time, area counts, concentration in ppbC, and the peaks name if it is an identified component. The system should calculate an estimate of the total NMOC, determined by the summation of the concentrations of all detected peaks in the chromatogram. The report files should be archived on magnetic media to allow for future processing.

To aid the chromatographer in obtaining more exact qualitative and quantitative results, additional information such as variation in retention time during an analysis should be considered. To obtain this additional information, it is recommended that the data be processed using a software package such as that designed and marketed by MetaChrom®. This software allows the user to process large and/or complex chromatographic data sets and improve data validation. Reassignment of peak identification can be performed using parameters such as reference compounds, retention times and peak search windows, and appropriate algorithms. The software program compensates for variations in sample matrix and instrument performance. The software also provides information on the presence of unknown and unidentified peaks.

2.4 AUTOMATED METHOD FOR COLLECTING AND ANALYZING VOLATILE ORGANIC OZONE PRECURSOR SAMPLES

The PAMS requirements prescribed in 40 CFR Part 58 recommends that States should obtain continuous, 3-hour measurements of volatile organic O_3 precursors at at least one site within a network. This section describes an automated sampling and analysis methodology to be used in conjunction with the manual sampling and analysis methodology described in Section 2.3. The automated methodology may provide a viable, less costly approach for obtaining volatile organic O_3 precursor measurements at all sites within a network. The automated approach (e.g., configuration, columns, detectors, etc.) described in this section is a modification of the GC approach described in Section 2.3. Exceptions and limitations have been applied to facilitate the automation of the example GC system. An automated system offers an additional advantage in its inherent capability of providing short-term (e.g., 1-3 hour) measurements on a continuing basis for long time intervals.

The following description is based on a commercially available example automated system, the Chrompack® CP-9000, and is described only in general terms. The intent is to provide guidance on configuration and operation of an automated system. It is not intended to serve as an SOP. Alternative approaches using other commercially available or custom fabricated systems are acceptable. Users must recognize that they are response for optimizing the critical parameters for their specific system (consistent with the manufacturers instructions if applicable) and are also responsible for the preparation of SOPs for their specific system.

2.4.1 Method Description

This section describes the equipment, data acquisition hardware, calibration, operation, data reporting and validation for an automated GC system. This guidance should be used to define equipment specifications and prepare SOPs consistent with the proposed 40 CFR Part 58 enhanced O_3 monitoring requirements.

The GC system must be designed for automatic sample collection, sample analysis and data collection on site. For automated, real-time analysis of target volatile

organic O_3 precursors, the GC system must be housed in a temperature-controlled shelter at the PAMS. The analytical system should incorporate a sample concentration system (for concentrating VOCs continually at a constant flow rate over a predetermined sampling time) a cryo-focusing trap (for improving the resolution capability of the gas chromatographic column); an appropriate analytical column(s); an FID detector(s); and a data acquisition and integration system.

The VOCs are collected on the sample concentration trap, thermally desorbed onto the sample cryo-focusing trap, and finally thermally desorbed onto the analytical column(s) for separation, qualitative identification, and quantification. The cycle of collection, desorption, cryo-focusing, and analysis should be completely automated. The automated system should provide the flexibility of adjusting critical sampling and analysis parameters (e.g., sample integration times, trap temperatures and flow rates, column temperatures, and support gas flow rates) in order to facilitate optimization. System flexibility will allow the evaluation and consequent use of alternate components within the system (e.g., alternate sample collection traps, cryo-focusing approaches, cooling systems, and columns). For typical automated GC applications, the system is set up to collect and analyze one sample each hour. To achieve this frequency of sampling and analysis, the cycle of sampling, refocusing, analysis, and report file generation takes approximately 1 hour and 20 minutes, with the last 20 minutes of the cycle occurring concurrently with the sample collection phase of the next hourly cycle. By overlapping the cycle activities in this way, the overall cycle time is effectively reduced to 1-hour.

2.4.1.1 Analytical Equipment and Configuration --

The automated system should consist of a sample probe and manifold, a sample drying device, a solid adsorbent primary sample collection trap, a secondary cryo-focusing trap, an analytical column(s), and FID(s). Although more complex, the two-column, two-FID configuration may be more appropriate if resolution over the full range of C_2 though C_{12} hydrocarbons is required. Several column configurations and

approaches are described in Section 2.2.7. Information identifying and describing the primary components of an automated system are presented in this section.

2.4.1.1.1 Sample Probe and Manifold -- A sample probe and manifold assembly should be used to provide a steady representative flow of air for collection and subsequent analysis. Figure 2-6 presents a sample probe and manifold assembly recommended for use at PAMS.

The sample probe is constructed of glass approximately 1 inch in outside diameter (O.D.). The inlet of the sample probe is configured as an inverted funnel approximately 4 inches in O.D. The sample manifold is constructed of glass approximately 1-1/2 inches in O.D. Ports for sample extraction are located on the sample manifold. Teflon® bushings are used as section connectors. A bleed adapter and blower are located at the exit of the sample manifold. The blower is used to pull sample air through the sample probe and manifold. The bleed adapter is used to control the rate at which the sample air is pulled through the manifold.

An excess of sample air should be pulled through the sample probe and manifold to prevent back diffusion of room air into the manifold and to ensure that the sample air is representative. Sample air flow through the sample probe and manifold should be at least 2 times greater than the cumulative flow of sample air being removed from the manifold for collection and analysis.

The vertical placement of the sampling probe and inlet funnel should be at a height of 3 to 15 meters above ground level. Because enhanced O_3 monitoring requirements involve multiple-pollutant measurements, this range serves as a practical compromise when determining suitable probe position. In addition, the probe inlet should be positioned more than 1 meter vertically and horizontally away from any supporting structure.

The probe inlet should be positioned away from nearby obstructions such as a forest canopy or building. The vertical distance between the probe inlet and an obstacle should be at least two times the height difference between the obstacle and the probe inlet. Unrestricted air flow across the probe inlet should occur within an arc

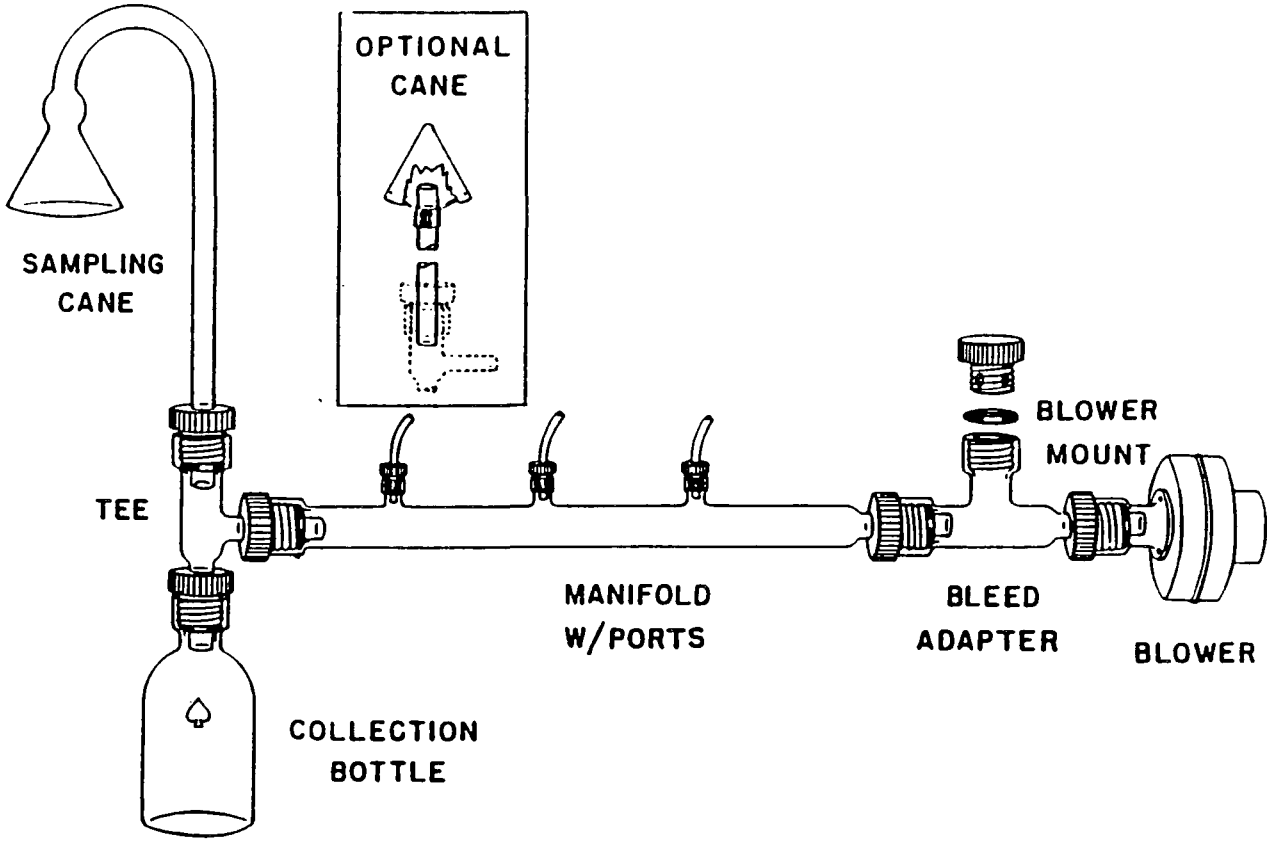

Figure 2-6. Sampling probe and manifold assembly.

of at least 270 degrees. The predominant and second most predominant wind direction must be included in this arc. If the probe inlet is positioned on the side of a building, a 180° clearance is required.

More specific details of probe positioning are presented in the "Enhanced Ozone Monitoring Network-Design and Siting Criteria Guideline Document".[4]

2.4.1.1.2 Sample Drying Device -- Sample moisture must be removed for automated applications to prevent or reduce adverse effects on the adsorbent trap, the analytical column(s), and the detector(s) as described in Section 2.2.3. Moisture removal allows analysis of larger sample volumes, which provide enhanced detection sensitivity. Enhanced detection sensitivity is critical to the measurement of less abundant volatile organic O_3 precursors.

Moisture should be removed from the sample stream using a permeable membrane drying device or equivalent drying system (see Section 2.2.3). Nonpolar hydrocarbon compounds pass through the drier unaffected but some polar VOCs may be removed (e.g., C_{10} terpenes). Although the potential loss of compounds is a disadvantage, drying the sample is still warranted based on the advantages listed above. To prevent moisture build-up and memory effects, the dryer must be initially and periodically cleaned using a procedure recommended by the manufacturer.

2.4.1.1.3 Sample Concentration Device -- Ambient air samples are concentrated using commercially available or custom built adsorbent and/or cryo-focusing devices, referred to as traps. The Chrompack® CP-9000 uses a primary adsorbent trap that is a cryogenically cooled. The primary trap is comprised of a 1/4-inch glass cartridge containing at least 1 gram of each of the following adsorbents:

- Carbotrap C (for trapping high molecular weight VOCs);
- Carbotrap (for trapping C_5 through C_8 VOCs); and
- Carbosieve III (for trapping low-molecular-weight compounds).

The three adsorbents are separated within the glass cartridge by layers of deactivated glass wool. The trap is cryogenically cooled to -20°C during the concentration process to ensure collection of the C_2 hydrocarbons. The primary trap is used in conjunction with a secondary cryogenic trap. The function of the secondary trap is to refocus the desorbed sample from the adsorbent trap prior to injection onto the analytical column. The secondary cryogenic trap is comprised of a 12 cm length of deactivated fused silica with an I.D. of 0.53 mm. It is coated with the porous polymer Poraplot U. The secondary cryogenic trap is maintained at -110°C during the sample concentration process.

2.4.1.1.4 Gas Chromatograph -- A Chrompack® CP-9000 equipped with automated control, sub-ambient oven capability, and injector assembly systems or an equivalent gas chromatograph may be used.

2.4.1.1.5 Analytical Columns -- The user should develop specific criteria for column selection and anticipated gas chromatographic operating conditions, based on parameters discussed in Section 2.2.7. For the initial operation of the automatic GC system, the less complex single-column configuration is recommended. The column selected should be capable of a reasonable separation of a majority of the compounds listed in Figure 2-1, preferably without requiring sub-ambient gas chromatograph oven temperatures. Elimination of the need for sub-ambient column oven temperatures will minimize the cryogen required to operate the GC system. Once the column is selected, it is the responsibility of the user to determine the optimum conditions for each critical operating parameter for the best performance of the column (i.e., best separation characteristics for the components of interest). Once experience is gained, a more complex dual-column, dual-FID configuration can be implemented and optimized.

2.4.1.1.6 Support Gases --

GC Support Cylinder Gases:

Ultra High Purity (UHP) grade helium (99.999% purity)
Hydrocarbon Free Air (< 0.1 parts per million Carbon total hydrocarbon)

UHP grade Hydrogen (99.999% purity)

Cryogen:

Liquid Nitrogen

Primary Calibration Standard:

30 ppbC propane standard diluted from an NIST stock standard

Retention Time Calibration Standard:

10 to 30 ppbC/compound calibration standard containing each of the target compounds as described in Section 2.2.5.2.

2.4.1.1.7 Data Acquisition System -- The data acquisition system consists of, but is not limited to, a PC-DOS personal computer with Chrompack PCI® chromatography data acquisition and integration software. Chrompack® chromatography software is comprised of subroutines that perform data acquisition, peak integration and identification, hard copy output, post-run calculations, calibration, peak re-integration, and user program interfacing. Acquired data should be automatically and permanently stored on magnetic media (e.g., hard disk, floppy diskette).

2.4.1.2 Operation --

This section provides general guidance for the initial setup of an automated GC system, preparation of operational procedures, calibration, field operation, and data acquisition and validation. Site specific and detailed SOPs must be prepared by the user, with appropriate input and assistance from the manufacturer or developer of the system.

2.4.1.2.1 Set-up and Parameter Optimization -- Users should anticipate a minimum of 3 to 6 months for initial setup, configuration, familiarization, and development of SOPs, prior to field deployment of the automated system. The system should be initially set up and tested for conformance with the manufacturer's or developer's operational specifications. Under the terms of the agreement for purchase

of the system, the manufacturer or developer should be required to provide a detailed instruction manual for operation of the system. The agreement should also require the manufacturer or developer to provide initial system setup, user training, and demonstration of adequate performance of the system in accordance with a predetermined protocol (developed cooperatively by the purchaser and the manufacturer). The initial setup, testing, and training phase of the operation should be conducted in a laboratory setting with adequate space and accessible support equipment.

During the initial set-up of the automated GC system numerous critical parameters must be evaluated to determine optimum system operating conditions. Critical parameters include, but are not limited to, the sample collection flow rate and sampling (integration) time; sample concentration and desorption times; flow rates and temperatures for the sample concentration traps; oven temperature program parameters; detector calibration; and the GC integration methods used for peak identification based on retention times. These parameters are optimized by varying the operating conditions to achieve the best resolution of the target compounds using pure component mixtures and the retention time calibration standard (see Section 2.2.5.2). Once all the critical parameters are optimized, the retention time calibration standard can be used to establish the exact retention times for each of the target compounds as input to the internal chromatography software.

The following example is typical of optimized settings for the automated hourly analysis of C_2 to C_8 hydrocarbons, using a single-column configuration in a Chrompack® CP 9000 automated GC system:

Sample collection rate and time :	10 mL/min for 30 minutes
Primary trap sample collection temperature:	-20°C
Total sample volume:	300 mL
Primary trap desorption temperature:	250 C°

Secondary trap collection rate and rate:	7 mL/min for 7 minutes
Secondary trap collection temperature:	-110°C
Secondary trap desorption temperature:	200°C
Injector temperature:	200°C
Column:	Chrompack® Al_2O_3/KCl, 0.32 m x 25 m
Column flow rate:	10 mL/min
GC oven initial temperature:	50°C
GC oven final temperature:	200°C
GC oven ramp rate:	5°C/min to 75°C, 10°C/min to 125°C, 15°C/min to 200°C
GC oven final time:	30 minutes
Detector temperature:	300°C
Detector hydrogen flow-rate:	30 mL/min
Detector air flow-rate:	300 mL/min

2.4.1.2.2 Standard Operating Procedure -- An SOP for field operation of the system should be prepared. The SOP should be based on information obtained during the set-up and familiarization period and the requirements of the specific program. The SOP should address the details of the routine operation of the system and should include:

- A detailed description of the system, including the required settings for all critical operational parameters;
- A listing of ancillary equipment and materials;

- A detailed operating procedure addressing initial start-up, calibration schedule, retention time check schedule, required maintenance, and record keeping;
- Data acquisition and reporting aspects; and
- Associated data quality issues.

2.4.1.2.3 Calibration -- The analytical system is calibrated in units of ppbC using an NIST traceable propane primary standard. (See Section 2.2.5 for details on calibration standards.) Based on the carbon response of the FID to the primary standard, a relative response factor (ppbC/area count) is determined. This factor is used to convert area counts from every peak in a chromatogram into concentration units. An estimate of the total NMOC is made by summing the concentrations of every peak (identified and unknown) detected in a sample. For an identified compound, the concentration in ppbC can be divided by the number of carbon atoms in the compound to estimate the concentration in ppbv. A minimum of three different concentrations of propane are required to develop a suitable calibration curve for determining the FID response. The three concentrations should span the working range of the analytical system. At least two replicate analyses at each concentration are recommended.

Retention time identification of target compounds is determined by analyzing the retention time calibration standard described in Section 2.2.5.2. This standard is analyzed at least in duplicate to determine the correct retention times and retention time windows for the peaks of interest.

2.4.1.2.4 Sampling Parameters -- Critical automated GC sampling parameters are closely interrelated. Determination of specific optimum sampling conditions is dependent on field conditions (i.e., expected compound concentration ranges, humidity, temperature, etc.), desired sensitivity (detection limit), cryogen consumption, and sample trapping efficiency. During the setup period, these sampling parameters should be evaluated to determine the optimum conditions for each sampling parameter. Recommended primary sampling parameters are:

- A sample collection rate of 1 each hour; and
- A sample collection (integration) time of 15-45 minutes.

For hourly sampling, the sample collection time must be limited to allow for the refocusing and analyzing cycle of the system. The refocusing and analysis cycle requires approximately 45 minutes. Shorter sampling times (no less than 15 minutes) may be used to reduce the use of cryogen. A sample collection volume of 200 to 600 mL is recommended. The sample collection volume used requires a judicious trade-off between required detection limit (the larger the sample the lower the detection limit) and potential moisture problems (the lower the sample volume the less the potential for moisture-associated problems). Integration times of up to 45 minutes may be considered by using an intermediate sample collection/integration device. This device should consist of a sample collection/integration vessel configured to provide integrated collection of one sample while a previously collected sample is being analyzed. Advantages to using an intermediate collection/integration device include longer integration times and reduced cryogen use during the concentration step of sample analysis. Intermediate sample collection/integration devices are under development and not currently commercially available.

2.4.1.2.5 Field Operation -- The automated GC system should be installed in a temperature-controlled shelter at the field location. The system should be operated in accordance with an SOP that is prepared by the user, based on the information obtained during the setup and familiarization period. The system should be serviced by a qualified operator. The operator should perform the routine operational and QC functions specified in the SOPs. Critical operational checks (e.g., calibration checks for the FID response) should be performed daily or as frequently as practical. Operational parameters should be adjusted, if necessary, so that the quality control criteria are maintained. Retention time checks should be performed twice each week or preferably every other day to provide retention time reference information for validating compound identifications. The retention time

calibration standard can also be used to track the FID response to determine when generation of a new calibration curve is necessary.

2.4.1.2.6 Confirmation Samples Analysis -- There are various levels of peak identification and quantitation confirmation that should be considered when validating data obtained from the automated GC system. These levels vary in complexity and extent of confirmation information provided. Confirmational approaches that use canister sampling technology include the following:

- Duplicate analyses on a selected number of samples on the same automated GC system;
- Secondary analysis on a better characterized GC system;
- Establishment of an exchange sample analysis and comparison program with neighboring State agencies;
- External or internal audit sample analysis; and
- Confirmation analysis of selected target compounds using a GC/MS for peak identification.

2.4.1.2.7 Data Acquisition and Reporting -- Data from the automated GC system are collected and processed using an on-site personal computer to operate the GC acquisition and integration software program. The GC software is developed and supplied by the manufacturer or developer of the system, and should contain the necessary algorithms to acquire, integrate, and identify the chromatographic peaks by retention times. The system should be capable of producing a report file for every sample analyzed and interfacing with other data processing equipment. This file should contain all the necessary information needed to identify the sample, the exact time it was collected, the chromatogram generated by the GC for the sample, and a sequentially numbered listing for all peaks from the chromatogram. This listing should contain the "name of the peak" (if the peak is one of the target compounds and has been identified by retention time) and all unidentified peaks and the associated

concentration, retention time, relative retention time to the selected reference peak or peaks, peak area, and peak width. The listing should also contain an estimate of total NMOC calculated by summing the concentrations of all of the peaks detected from the chromatogram. The report files for each day's operation should be transferred daily to magnetic media for subsequent validation, evaluation, and interpretation.

2.4.1.2.8 Data Validation -- The analyst must develop systematic procedures to determine that the quality of the data is consistent with DQOs. These procedures should include examination of the calibration, QC, and data report files. Ideally, the report file for each sample analysis should be examined by an experienced chromatographer to verify that the sample was properly collected, analyzed, and correct peak identifications were made. However, this examination may not be practical due to the large number of report files that are generated when the automated GC system is operated continuously on an hourly basis. The validation procedure in the QC section of individual site SOPs should address this issue by recommending a minimum number of files that must be examined to ensure that the system operated properly during data collection.

A computer software program such as the one designed and marketed by MetaChrom® should be considered to facilitate the data validation process. This software is designed to aid the chromatographer in generating more exact qualitative and quantitative results. The MetaChrom® software is designed to reprocess the gas chromatographic result files in order to verify the retention time identifications for each peak. In this process, retention time and peak area information are extracted from the gas chromatographic result file to create a large database matrix. Using this matrix, consistent peak identifications can be made for all result files, including both identified and unknown peaks.

2.5 GAS CHROMATOGRAPHY/MASS SPECTROMETRY

A GC system utilizing an FID cannot conclusively establish the identification of VOCs. Peak identifications are based on matching peak retention times with those obtained from previous analysis of neat compounds and mixtures of neat compounds.

The selection of neat compounds is based on prior knowledge of the compound composition expected in the sample mixture. Knowledge of the complexity of VOCs in ambient air suggests that identification only by retention times is not conclusive.

The combination of capillary chromatographic retention times with the specific ions observed by a mass spectrometer or MSD provides specificity for the identification of organic compounds. Chromatographic coelution of two compounds can be resolved by specific mass data unless the two compounds are isomers of each other and have identical or very similar mass spectra. Because of the cost of the instrumentation, use of mass-specific detection is not always possible. However, it is recommended that samples be analyzed periodically by mass spectrometric detection both to confirm peak identification and to provide identification information for the observed unknown peaks. Use of a mass-specific detector to confirm compound identification provides confidence in the identifications that are made in the course of routine chromatographic operations.

2.5.1 Identification Confirmation

In the full-scan mode, the mass spectrometer scans over a specified mass range in a period of time, then repeats the cycle. On each scan cycle, a complete mass spectrum is generated. In the full-scan mode, identification of unknown or unanticipated chromatographic peaks can be made because all of the mass spectral information is acquired and available for examination. The following steps can be taken to identify an unknown compound:

- The mass spectrum of the unknown compound can be subjected to a computerized library search for comparison to more than 42,000 mass spectra, and a successful match of acceptable quality may be obtained for the sample mass spectrum and a reference mass spectrum;
- If a reference compound for the specific analyte is not included in the library, the library search algorithm will frequently allow the experienced mass spectra interpreter to establish the class of the unknown compound and possibly the composition of the compound, although usually not the exact isomer;

- The mass spectrum of the unknown compound can be interpreted by an experienced mass spectral data interpreter, and the compound can be identified from first principles, or additional information such as functional groups, composition, and other characteristics can be obtained from the mass spectrum; and

- A quantitative value can be estimated for the unknown compound by assuming an equivalent system response to a standard, a level of quantitation that is usually accurate to within an order of magnitude.

The following criteria determine compound identification:

- The capillary retention time must be within ±0.06 relative retention time units of the retention time of the compound in either a calibration standard or the daily calibration check standard;

- The mass spectrum of the compound of interest must correspond to the mass spectrum of a standard of the compound generated on the same analytical system on which the sample analysis is being performed; and

- The major ions of the mass spectrum must maximize within two scans (one second) of each other.

If the identification criteria can be met, then the identification made by GC is confirmed.

2.5.1.1 Use of Selected Ion Monitoring Techniques --

If the mass spectrometer is programmed to look only at the regions of the chromatogram where specific peaks occur more time is spent in monitoring the masses of specific interest and consequently sensitivity is enhanced. This mode of operation, in which only a few masses are monitored per compound, is known as Selected Ion Monitoring (SIM). Because analysis of volatile organic O_3 precursors in ambient air involves very low concentrations (typically 1 to 15 ppbv), the additional sensitivity that can be gained in the SIM operating mode is frequently required. However, the SIM mode provides data only for the compounds specified -- unknown compounds cannot be identified in this mode.

2.5.2 Equipment

Gas Chromatograph/Mass Spectrometer - A gas chromatograph/mass spectrometer and data system capable of acquiring data in either the full-scan or SIM mode and of processing the data. The mass spectrometer must be capable of scanning over the mass range from 35 to 350 amu in 1 second or less, using 70 eV (nominal) ionizing energy in the electron ionization mode, and producing a mass spectrum that meets instrument acceptance criteria.

Sample Interface - A sample interface capable of taking a constant volume sample from the sample canister and cryogenically preconcentrating the sample.

Gas Chromatograph - A gas chromatograph capable of sub-ambient oven operation.

Chromatographic Columns - Chromatographic columns appropriate to provide compound separation in approximately 45 minutes of analysis time.

2.5.3 Interferences

Impurities in the gases used and solvent vapors present in the laboratory where the analysis is performed can contaminate the samples. The analytical system must be demonstrated free from contamination under the conditions of the analysis by analyzing humid zero air blanks. Use of tubing other than chromatographic grade stainless steel, non-Teflon® thread sealants, and flow controllers with rubber internal components must be avoided. High levels of VOCs can result in carryover to subsequent samples. Whenever a high VOC concentration is encountered in a sample, humid zero air should be analyzed until the absence of contamination can be demonstrated. The laboratory where analysis of VOC is performed should be completely free of volatile organic solvents.

2.5.4 Standards

Standards may be generated by dynamic dilution of certified gaseous standards or by serial dilution of a stock prepared from liquid standards.

2.5.4.1 Instrument Performance Check Standard --

A standard of p-bromofluorobenzene (BFB) in humidified zero air at a concentration that will allow collection and analysis of 20 ng of BFB (full-scan operating mode) or 1 ng of BFB (SIM operating mode) under the standard preconcentration parameters is required. The following criteria will apply:

Full-scan operating mode:

Mass	Abundance Ratio
50	8 - 40% of mass 95
75	30 - 66% of mass 95
95	base peak, 100% relative abundance
96	5 - 9% of mass 95
173	less than 2% of mass 174
174	50 - 120% of mass 95
175	4 - 9% of mass 174
176	93 - 101% of mass 174
177	5 - 9% of mass 176

SIM operating mode:

Mass	Abundance Ratio
174	100
175	4 - 9% of mass 174
176	93 - 101% of mass 174
177	5 9% of mass 176

2.5.4.2 Calibration Standards --

Multiple working standards at specific concentrations must be prepared for GC/MS calibration because response factors vary widely for compounds analyzed by this technique. Five initial working calibration standards are required. For full-scan mode, the standards should be at 0.5, 1.0, 5.0, 10.0, and 15.0 ppbv for each target analyte. For SIM mode, the standards may be prepared at the same level, or a standard at lower level may be substituted if the instrument saturates at a level of 15.0 ppbv. The calibration standards must be prepared in humidified zero air.

2.5.4.3 Internal Standard Spiking Mixture --

An internal standard spiking mixture containing bromochloromethane, chlorobenzene-d_5, and 1,4-difluorobenzene at 2 ppbv each in humidified zero air is required for performing quantitative calculations in the SIM mode. If the internal standard spiking mixture is being used in the full-scan mode, a concentration of 5 ppbv is required. The internal standard spiking mixture may be prepared from liquid standards if certified gaseous standards are not available.

2.5.5 Instrument Operating Conditions

All instrument operating conditions must be optimized by the analyst for the particular instruments and analytes being used.

2.5.5.1 Sample Concentration Conditions --

The VOCs of the canister sample are concentrated on a cryotrap cooled to approximately -185°C. A predetermined volume of sample air from the collection canister, consistent with the volume used during calibration, is passed through a cryotrap. The exact trapping flow rate and time period over which the sample is concentrated in the cryotrap will vary with the analytical system, but the total volume trapped must be the same each time. These parameters must be optimized by the analyst for the particular analytical system used. After concentration, the sample is transferred from the sample interface system to the head of the capillary column.

2.5.5.2 Desorption Conditions --

The following conditions may be used for desorption of cryogenically collected VOCs:

Desorption temperature:	180°C
Desorption gas flow rate:	carrier gas flow rate
Desorption time:	<60 seconds

2.5.5.3 Gas Chromatographic Conditions --

Gas chromatographic conditions must be optimized for each analytical system in order to provide adequate compound separation and sensitivity. Baseline separation of the three dichlorobenzene isomers and between ethylbenzene and m-/p-xylene is indicative of adequate chromatographic column resolution. It is desirable that the identical GC column be used for the GC/MS analysis as for the GC analysis. In this way, sample peak resolution will be nearly identical and confirmation or unknown compound identification will be simpler and more meaningful.

2.5.5.4 Mass Spectrometer --

The mass spectrometer must be operated at an electron energy of 70 eV (nominal). The mass range and monitoring time in the SIM mode will be determined by the target compounds selected. The analytical system must meet the specifications of the manufacturer for mass calibration in order to provide accurate mass assignments. The acceptability of the tuning conditions of the mass spectrometer is established by the analysis of the instrument performance check standard. The instrument performance check standard should be analyzed at a frequency that verifies the stability and acceptability of the tuning conditions of the mass spectrometer.

2.5.5.5 Calibration --

Prior to analyzing blanks and samples and after analyzing the instrument performance check standard, the analytical system must be calibrated at a minimum of five concentrations to establish instrument sensitivity and linearity of response. (See Section 2.5.4.2 for details on calibration standards.)

2.5.5.5.1 Multipoint Calibration -- Each calibration standard must be analyzed, adding the appropriate amount of internal standard spiking mixture to each calibration standard during the sample collection in the cryotrap. The area response for the primary ion and the corresponding concentration for each compound and internal standard are recorded. A relative response factor (RRF) for each compound of interest is calculated using the following equation:

$$RRF = [A_x/C_x] / [A_{is}/C_{is}]$$

Where:

A_x = integrated area of the primary ion for each compound to be measured

C_x = concentration of the compound to be measured, ppbv

A_{is} = integrated area of the primary ion for the internal standard

C_{is} = concentration of the internal standard, ppbv

The RRF for each compound is calculated using the values for area and concentration of the closest-eluting internal standard.

2.5.5.5.2 Acceptance Criteria for Calibration Curve -- The average RRF must be calculated for each compound by averaging the values obtained at the five concentrations used for the calibration range. The percent relative standard deviation (% RSD) for each compound must be less than 30 percent. The % RSD of the RRF

values across the working range of the calibration curve is calculated using the following equation:

$$\% \text{ RSD} = \frac{\text{Standard Deviation}}{\text{Average RRF}} \times 100$$

If some of the calibration compounds do not meet the criterion, additional standards are analyzed until the criterion can be met. If the analysis of additional calibration samples does not produce data that will meet the calibration acceptance criteria, instrument maintenance and/or repreparation of calibration standards is required.

2.5.5.5.3 Daily Calibration Check -- A check of the stability of the calibration curve must be performed every 12 hours. A calibration standard from approximately the middle of the calibration range (a 5 ppbv standard) should be used as a calibration check standard. The percent difference (% D) between the RRF calculated from the daily calibration check standard and the RRF for the original calibration curve is calculated. The % D is calculated according to the following equation:

$$\% \text{ D} = \frac{(MRRF_x - MRRF_c) \times 100}{MRRF_x}$$

Where:

$MRRF_x$ = average RRF from the initial calibration curve

$MRRF_c$ = RRF obtained from the daily calibration check standard

The % D must be within ±30% for the calibration curve to be considered valid. If % D for a given compound is not within ±30%, the analysis of the daily calibration

check standard is repeated. If the criterion cannot be met for one or more compounds after repeated analysis of the daily calibration check standard, the calibration curve is no longer valid and a new multipoint calibration curve must be generated.

2.5.5.5.4 System Performance Checks -- Internal standard signal levels and retention times must be monitored for each calibration sample, blank, and field sample analyzed. If the retention time for any internal standard changes by more than 30 sec from the most recent daily calibration check standard, the analytical system must be inspected for malfunctions and corrections must be made as indicated. The peak area for the primary ion for each internal standard must be monitored in each analysis performed. If the peak area for the primary ion changes by more than 40%, the analytical system must be inspected for malfunctions and corrections must be made as indicated. If corrections are made to the analytical system to repair a malfunction, analyses performed during the period when the analytical system was malfunctioning must be repeated, if possible. If it is not possible to repeat analyses, any data obtained from samples analyzed by the malfunctioning analytical system must be qualified and possibly rejected.

2.5.5.5.5 Frequency of Multipoint Calibration -- The multipoint calibration must be repeated when daily calibration checks no longer meet acceptance criteria. If adjustments, corrections, or repairs are made to the analytical system, the multipoint calibration curve must be regenerated if the daily calibration check no longer meets acceptance criteria.

2.5.6 Analysis Procedures

When the analytical system has been optimized and calibrated, sample analysis may be initiated. To analyze a canister sample, the canister is connected to the interface to cryogenically concentrate the VOCs of the air sample. A sample of accurately known volume is drawn from the canister through a concentration trap, which is cryogenically cooled to -185°C. During the sample collection process, the

gas chromatograph is cooled to the sub-ambient starting point of its temperature program.

2.5.6.1 Vaporization of Volatile Organic Compounds --

After the volatile organic components of the sample and the internal standard mixture are condensed on the cryotrap, the sample is injected and the cryotrap is heated to desorption temperature and swept with helium. The contents of the cryotrap are vaporized and recondensed on the head of the subambient capillary column. The canister is closed and removed from the sampling manifold. The cryotrap is heated and swept with helium until the next analysis to ensure that the cryotrap will not exhibit any carryover of components from one sample to the next.

2.5.6.2 Initiation of Analysis --

When the sample is transferred to the head of the subambient capillary column, the GC/MS scan cycle is initiated to allow full-scan analysis or the first SIM monitoring window.

2.5.6.3 Initial Review of Data --

Upon completion of the analysis, data must be checked for saturation. If the mass spectrometric peak saturated, no quantitative data can be obtained. Saturation is unusual when analyzing ambient air samples. Quantitation by a secondary ion may not be performed if the primary ion is saturated because the calculated values will not be accurate; a negative bias will be introduced and, depending upon the level of saturation, the calculated value may be biased negative by a factor of more than ten. If an analysis is performed and detector saturation is encountered, then (1) the analysis must be repeated with a diluted sample to obtain accurate quantitative values; and (2) the analysis which shows saturated compounds must be followed by analyses of blanks to demonstrate that there will be no carryover of compounds in the analytical system.

2.5.6.4 Sample Dilution --

If the concentration of any analyte exceeds the calibration range, the sample must be diluted to an appropriate level and the analysis repeated. The need for dilution is a function of the following:

- The level of dilution chosen should be sufficient to keep the concentration of the largest analyte peak in the upper half of the initial calibration range of the instrument; and
- If other sample components in the original sample analysis are within the calibration range, the concentration values for these components should be reported from the original undiluted analysis.

2.5.7 Qualitative Analysis

The compounds listed in Table 2-1 must be identified by the following factors:

- The capillary retention time must be within ± 0.06 relative retention time units of the retention time of the compound in either a calibration standard or the daily calibration check standard;
- The mass spectrum of the compound of interest must correspond to the SIM mass spectrum of a standard of the compound generated on the same analytical system on which the sample analysis is being performed; and
- Where multiple ions are monitored for a given compound, these ions must maximize within 1 second of each other.

Because SIM analysis is being performed, the mass spectra will in most cases consist of no more than three peaks. For halogenated compounds, two peaks of an isotopic cluster will be selected so that a theoretical ratio for the presence of halogen can be verified. A minimal requirement for the identification of a compound in the SIM mode is that the primary ion be present within an interval of 0.06 relative retention time units of the retention time of the authentic compound. For chlorinated compounds, the primary ion must be present at the correct retention time and the secondary ion of the isotope cluster must be present in the correct ratio to the primary ion.

Table 2-1

Primary Quantitation Ions for Compounds of Interest

Compound Name	Primary Ion	Confirmation
Propane	43	44
Propylene	41	42
Isobutane	57	58
n-Butane	57	58
Isopentane	57	72
n-Pentane	57	72
2-Methylpentane	57	72
3-Methylpentane	57	72
Benzene	78	-
Toluene	92	91
Ethylbenzene	91	106
m-/p-Xylene	91	106
o-Xylene	91	106
1,2,4-Trimethylbenzene	105	120
Isoprene	67	53
2,2-Dimethylbutane	57	71
Cyclopentane	42	70
2,3-Dimethylbutane	43	42
Methylcyclopentane	56	84
2,4-Dimethylpentane	43	85
2,2,4-Trimethylpentane	57	56
n-Heptane	43	100
Methylcyclohexane	83	98
2,3,4-Trimethylpentane	71	70
2-Methylheptane	43	57
3-Methylheptane	85	84
trans-2-Butene	41	56
cis-2-Butene	41	56
trans-2-Pentene	55	70
cis-2-Pentene	55	70
3-Methyl-1-butene	55	70
2-Methyl-1-butene	55	70
alpha-Pinene	93	121
beta-Pinene	93	69
1-Butene	41	56

NOTE: This table must be expanded by the inclusion of relative retention times (not available) and theoretical ratios between the primary and secondary ions (not calculated until a definite list of compounds is available.

2.5.8 Quantitative Analysis

Identified target compounds are quantified by the RRF method using peak areas for the primary ions. If internal standard retention times or peak areas are within the acceptable range, quantitative analysis can be performed. The concentration of the compound of interest in air (in ppbv) is calculated by the following equation:

$$C_c = \frac{(A_c)\ (C_{is})\ (DF)}{(A_{is})\ (RRF)}$$

Where:

A_c = integrated area of the primary quantitation ion for the compound of interest

C_{is} = concentration of internal standard, ppbv

DF = dilution factor, if applicable. If no dilution has been performed, the dilution factor is 1

A_{is} = integrated area of the primary quantitation ion for the nearest-eluting internal standard

RRF = relative response factor for the compound of interest from the calibration curve

2.5.9 Additional Uses

The GC/MS analytical system can also be used for primary analysis in either the full-scan mode or the SIM mode. Qualitative identification of unknown compounds is possible using full-scan GC/MS. If positive identification is possible and these tentatively identified compounds occur frequently, the GC/FID system used for routine analysis may be characterized for these compounds and they may be added to the target compound list.

SECTION 3.0

METHODOLOGY FOR DETERMINING TOTAL NONMETHANE ORGANIC COMPOUNDS IN AMBIENT AIR

Qualitative and quantitative determinations of VOCs using the GC based methodology described in Section 2.0 requires instrumentation that is expensive, complex, and difficult to operate and maintain. The method described in this section provides a similar measurement of total NMOC. Although this method is not directly applicable to the enhanced O_3 monitoring, it is included here because (1) it is a viable and effective method of post clean-up determinations of canister cleanliness; (2) it can be used for ambient total NMOC measurements of input into O_3 predictive models that do not require VOC speciation; and (3) used in combination with the manual (canister) methodology described in Section 2.3, it may provide a viable alternative to the automated methodology described in Section 2.4. The method described in this section is Method TO-12, taken from the "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air".[3] Method TO-12 involves a simple, preconcentration procedure with subsequent, direct flame ionization detection and provides accurate and sensitivity measurements of total NMOC concentrations. The instrumentation for this method can be configured for either automated in-situ measurements or for analyzing integrated samples collected in canisters.

3.1 METHOD DESCRIPTION

In recent years, the relationship between ambient concentrations of precursor organic compounds and subsequent downwind concentrations of O_3 has been described by a variety of photochemical dispersion models. The most important application of such models is to determine the degree of control of precursor organic compounds that is necessary in an urban area to achieve attainment of the NAAQS for O_3.

The more elaborate theoretical models generally require detailed organic species data obtained by multicomponent GC. The Empirical Kinetic Modeling Approach (EKMA), however, requires only the total NMOC concentration data -- specifically, the average total NMOC concentration from 6 a.m. to 9 a.m. daily at the sampling location. The use of total NMOC concentration data in the EKMA substantially reduces the cost and complexity of the sampling and analysis system by not requiring qualitative and quantitative species identification.

The method presented in this section is Compendium Method TO-12, which combines the same type of cryogenic concentration technique used in Method TO-01 for high sensitivity total NMOC measurements, without the GC columns and complex procedures necessary for species separation.

In an FID, the sample is injected into a hydrogen-rich flame where the organic vapors burn, producing ionized molecular fragments. The resulting ion fragments are then collected and detected. The FID is a nearly universal detector; however, detector response varies with the species of the organic compound in an oxygen atmosphere. Because Method TO-12 employs a helium or argon carrier gas, the detector response is nearly uniform for many hydrocarbon compounds. Thus, the historical shortcoming of the FID, varying detector response to different organic functional groups, is minimized.

Method TO-12 can be used either for direct, in-situ ambient measurements or (more commonly) for analyzing integrated samples collected in specially treated stainless steel canisters. EKMA models generally require 3-hour integrated NMOC measurements over the 6 a.m. to 9 a.m. period, and are used by State or local agencies in preparing their SIPs for O_3 control to achieve compliance with the NAAQS for O_3. For direct, in-situ ambient measurements, the analyst must be present during the 6 a.m. to 9 a.m. period, and repeat measurements (approximately six per hour) must be taken to obtain average NMOC concentration for the period. The use of sample canisters allows the collection of integrated air samples over the 6 a.m. to

9 a.m. period by unattended, automated samplers. Method TO-12 incorporates both sampling approaches.

3.2 SUMMARY OF METHOD TO-12

A whole air sample is either extracted directly from the ambient air and analyzed on site by the GC system or collected into a precleaned sample canister and analyzed off site.

The analysis requires drawing a fixed-volume portion of the sample air at a low flow rate through a glass-bead-filled trap that is cooled to approximately -185°C with liquid argon. The cryogenic trap simultaneously collects and concentrates the NMOC (via either condensation or absorption), while allowing the methane, nitrogen, oxygen, etc., to pass through the trap without retention. The system is dynamically calibrated so that the volume of sample passing through the trap does not have to be quantitatively measured, but the sample volume must be precisely repeatable between the calibration and the analytical phases.

After the fixed-volume air sample has been drawn through the trap, a helium carrier gas flow is diverted to pass through the trap in the opposite direction to the sample flow and into an FID. When the residual air and methane have been flushed from the trap and the FID baseline restabilizes, the cryogen is removed and the temperature of the trap is raised to approximately 90°C.

The organic compounds previously collected in the trap revolatilize because of the increase in temperature and are carried into the FID, resulting in a response peak or peaks from the FID. The area of the peak or peaks is integrated, and the integrated value is translated to concentration units via a previously-obtained calibration curve relating integrated peak areas to known concentrations of propane.

By convention, concentrations of NMOC are reported in units of parts per million Carbon (ppmC), which, for a specific compound, is the concentration by parts per million volume (ppmv) multiplied by the number of carbon atoms in the compound.

The cryogenic trap simultaneously concentrates the NMOC while separating and removing the methane from air samples. The technique is thus direct reading for

NMOC and, because of the concentration step, is more sensitive than conventional continuous NMOC analyzers.

3.3 SIGNIFICANCE

Accurate measurements of ambient concentrations of NMOC are important for the control of photochemical smog because these organic compounds are primary precursors of atmospheric ozone and other oxidants. Attainment of the NAAQS for ozone is therefore dependent on control of ambient levels of NMOC and other O_3 precursors.

The NMOC concentrations typically found at urban sites may reach 5-7 ppmC or above. In order to determine transport of precursors into an area, measurement of NMOC upwind of the area may be necessary. Upwind NMOC concentrations are likely to be less than a few tenths of 1 ppmC.

3.4 INTERFERENCES

In field and laboratory evaluations, water in the air sample was found to cause a positive shift in the FID baseline. The effect of this shift is minimized by carefully selecting the integration termination point and adjusting the baseline used for calculating the area of the NMOC peak(s).

When using helium as a carrier gas, FID response is quite uniform for most hydrocarbon compounds, but the response can vary considerably for other types of organic compounds.

3.5 EQUIPMENT

3.5.1 Direct Air Sampling (See Figure 3-1)

Sample manifold or sample inlet line - to bring sample air into the analytical system.

Vacuum pump or blower - to draw sample air through a sample manifold or long inlet line to reduce inlet residence time. Maximum residence time should be no greater than 1 minute.

3.5.2 Remote Sample Collection in Pressurized Canisters (See Section 2.3)

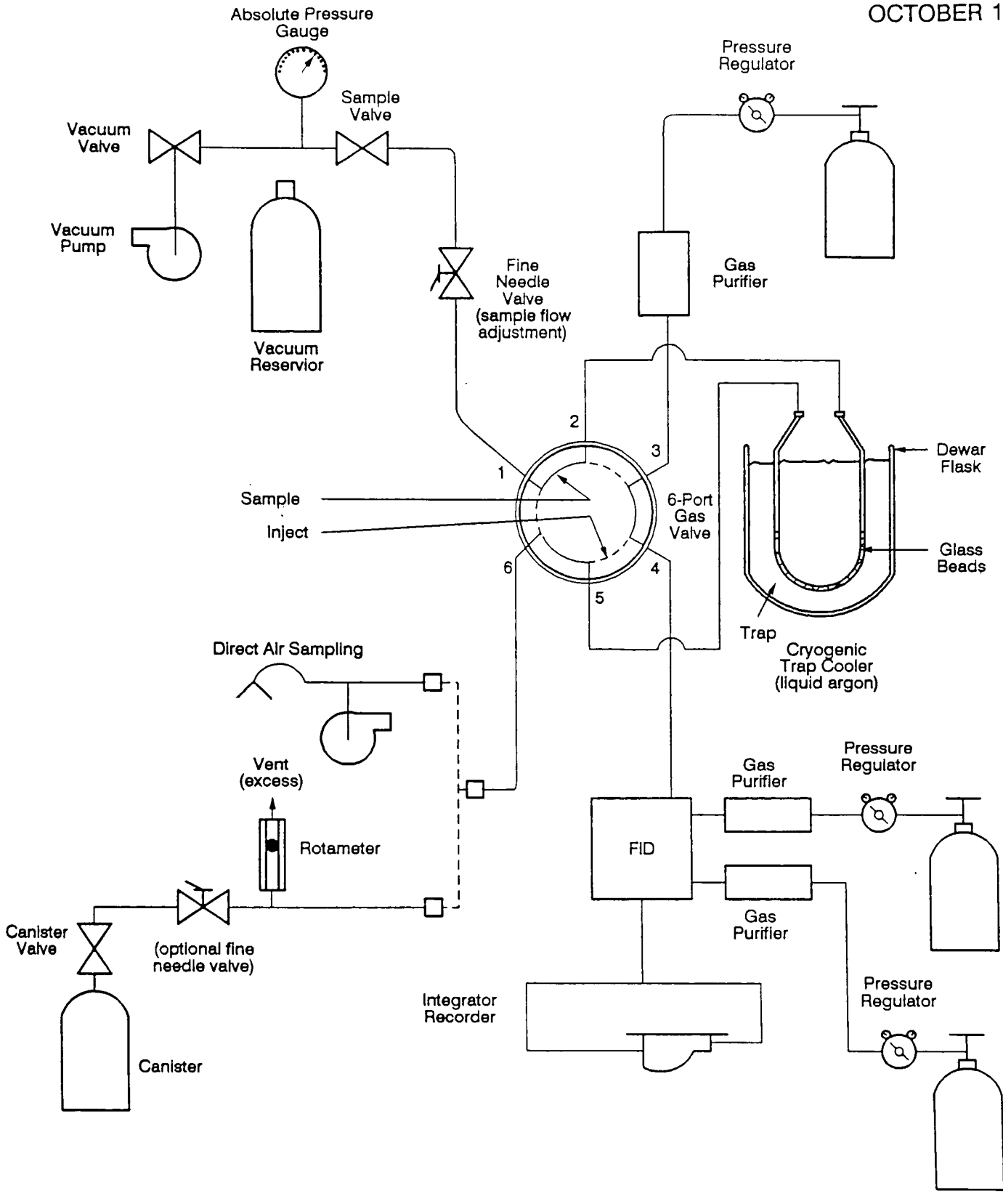

Figure 3-1. Schematic of analytical system for NMOC-two sampling modes.

3.5.3 Sample Canister Cleaning (See Section A3.0)

3.5.4 Analytical System (See Figure 3-1)

FID detector system - including flow controls for the FID fuel and air, temperature control for the FID, and signal processing electronics. The FID burner air, hydrogen, and helium carrier flow rates should be set according to the manufacturer's instructions in order to obtain an adequate FID response while maintaining as stable a flame as possible throughout all phases of the analytical cycle.

Chart recorder - compatible with the FID output signal, to record FID response.

Electronic integrator - capable of integrating the area of one or more FID response peak(s) and calculating peak area corrected for baseline drift. If a separate integrator and chart recorder are used, care must be exercised to ensure that these components do not interfere with each other electrically. Range selector controls on both the integrator and the FID analyzer may not provide accurate range ratios, so individual calibration curves should be prepared for each range to be used. The integrator should be capable of marking the beginning and ending of peaks, constructing the appropriate baseline between the start and end of the integration period, and calculating the peak area.

Trap - the trap should be carefully constructed from a single piece of chromatographic-grade stainless steel tubing (0.32 cm O.D., 0.21 cm I.D.) as shown in Figure 3-2. The central portion of the trap (7-10 cm) is packed with 60/80 mesh glass beads, with small glass wool (dimethyldichlorosilane-treated) plugs to retain the beads. The trap must fit conveniently into the Dewar flask and the arms must be of an appropriate length to allow the beaded portion of the trap to be submerged below the level of liquid cryogen in the Dewar. The trap should connect directly to the six-port valve, if possible, to minimize line length between the trap and the FID. The trap must be mounted to allow the Dewar to be slipped conveniently onto and off of the trap and also to facilitate heating the trap.

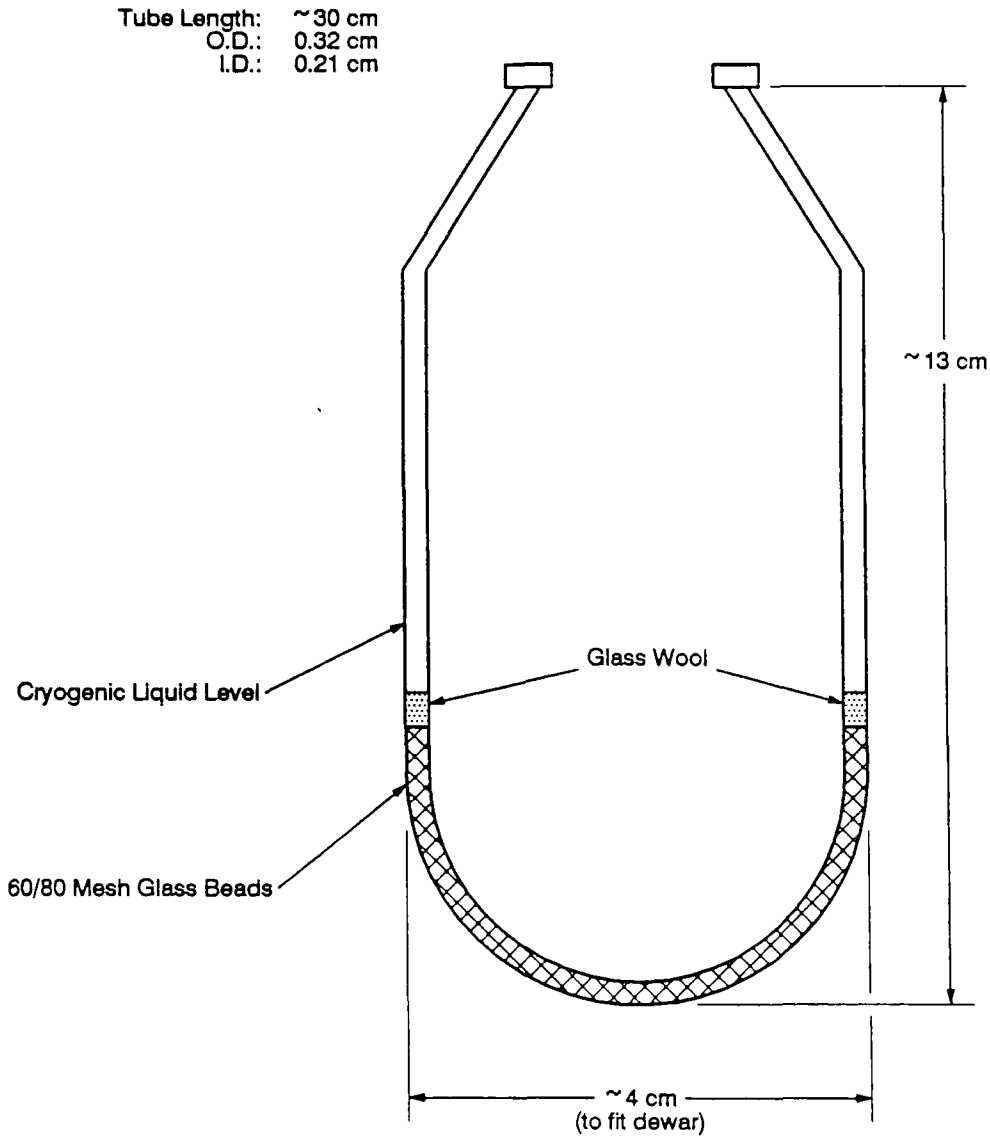

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Figure 3-2. Cryogenic sample trap dimensions.

Six-port chromatographic valve - six-port valve and as much of the interconnecting tubing as practical should be located inside an oven or otherwise heated to 80-90°C to minimize wall losses or adsorption/desorption in the connecting tubing. All lines should be as short as practical.

Multistage pressure regulators - standard two-stage, stainless steel diaphragm regulators with pressure gauges, for helium, air, and hydrogen cylinders.

Pressure regulators - optional single stage, stainless steel, with pressure gauge, if needed, to maintain constant helium carrier and hydrogen flow rates.

Fine needle valve - to adjust sample flow rate through trap.

Dewar flask - to hold liquid cryogen to cool the trap, sized to contain submerged portion of trap.

Absolute pressure gauge - 0-450 mm Hg (with 2 mm Hg scale divisions), to meter reproducible volumes of sample air through cryogenic trap.

Vacuum reservoir - 1-2 L capacity, typically 1 L.

Gas purifiers - gas scrubbers containing Drierite® or silica gel and 5Å molecular sieve to remove moisture and organic impurities in the helium, air, and hydrogen gas flows. Check the purity of gas purifiers prior to use. Gas purifiers are clean if they produce less than 0.02 ppmC NMOC.

Trap heating system - chromatographic oven, hot water, or other means to heat the trap to 80°-90°C. A simple heating source for the trap is a beaker or Dewar filled with water maintained at 80-90°C. More repeatable types of heat sources are recommended, including a temperature-programmed chromatograph oven, direct electrical heating of the trap itself, or any type of heater that brings the temperature of the trap up to 80-90°C in 1-2 minutes.

Toggle shut-off valves - leak free, for vacuum valve and sample valve.

Vacuum pump - general purpose laboratory pump capable of evacuating the vacuum reservoir to an appropriate vacuum that allows the desired sample volume to be drawn through the trap.

Vent - to keep the trap at atmospheric pressure during trapping when using pressurized canisters.

Rotameter to verify vent flow.

Fine needle valve (optional) - to adjust flow rate of sample from canister during analysis.

Tubing and Fittings - Chromatographic-grade stainless steel tubing and stainless steel fittings are used for interconnections. All such materials that contact the sample, analyte, or support gases prior to analysis should be stainless steel or other inert metal. Do not use plastic or Teflon® tubing or fittings.

3.6 REAGENTS AND MATERIALS

Gas cylinder of helium and hydrogen - ultrahigh purity grade.

Combustion air - cylinder containing less than 0.02 ppmC hydrocarbons, or equivalent air source.

Propane calibration standard - cylinder containing 1-100 ppmv (3-300 ppmC) propane in air. The cylinder assay should be traceable to an NIST SRM or to an NIST/EPA-approved CRM.

Zero air - cylinder containing less than 0.02 ppmC hydrocarbons. Zero air may be obtained for a cylinder of zero-grade compressed air scrubbed with Drierite® or silica gel and 5Å molecular sieve or activated charcoal, or by catalytic cleanup of ambient air. All zero air should be passed through a liquid argon cold trap for final cleanup, then passed through a hydrocarbon-free water bubbler for humidification.

Liquid cryogen - liquid argon or liquid oxygen may be used as the cryogen -- experiments have shown no differences in trapping efficiency between the two. However, appropriate safety precautions must be taken if liquid oxygen is used. Liquid nitrogen should not be used because it causes condensation of oxygen and methane in the trap.

3.7 DIRECT SAMPLING

For direct ambient air sampling, the cryogenic trapping system draws the air sample directly from a pump-ventilated distribution manifold or sample line. The

connecting line should be of small diameter (1/8" O.D.) stainless steel tubing and as short as possible to minimize its dead volume.

Multiple analyses over the sampling period must be made to establish hourly or 3-hour NMOC concentration averages.

3.8 SAMPLE ANALYSIS

Preanalysis and analysis procedures are contained in this section.

3.8.1 Analytical System Leak Check

1. Before sample analysis, the analytical system is assembled and leak checked.

2. To leak check the analytical system, place the six-port gas valve in the trapping position. Disconnect and cap the absolute pressure gauge. Insert a pressure gauge capable of recording up to 60 pounds per square-inch gauge (psig) at the vacuum valve outlet.

3. Attach a valve and a zero air supply to the sample inlet port. Pressurize the system to about 50 psig and close the valve.

4. Wait approximately 3 hours and re-check pressure. If the pressure did not vary more than ± 2 psig, the system is considered leak tight.

5. If the system is leak free, de-pressurize and reconnect absolute pressure gauge.

6. The analytical system leak check procedure should be performed during the system checkout, prior to a series of analyses, or if leaks are suspected. This procedure should be part of the user-prepared SOP manual.

3.8.2 Sample Volume Determination

1. The vacuum reservoir and absolute pressure gauge are used to meter a precisely repeatable volume of sample air through the cryogenically cooled trap. To do this, the sample valve is closed, the vacuum valve opened, and the reservoir is evacuated to a predetermined pressure (e.g., 100 mm Hg) at which point the vacuum valve is closed. The sample valve is then opened to allow sample air to be drawn

through the cryogenic trap and into the evacuated reservoir until a second predetermined reservoir pressure (e.g., 300 mm Hg) is reached. The fixed volume of air sampled is determined by the pressure rise in the vacuum reservoir (difference between the predetermined pressures), as measured by the absolute pressure gauge.

2. The sample volume can be calculated by:

$$V_s = \frac{(\Delta P)\ (V_r)}{(P_s)}$$

Where:

V_s = Volume of air sampled (standard mL)

ΔP = Pressure difference measured by gauge (mm Hg)

V_r = Volume of vacuum reservoir (mL), usually 1000

P_s = Standard pressure (760 mm Hg)

For example, with a vacuum reservoir of 1000 mL and a pressure change of 200 mm Hg (e.g., 100 to 300 mm Hg), the volume sampled would be 263 mm. A typical sample volume using this procedure is between 200-300 mL.

3. The sample volume determination need only be performed once during the system check-out and shall be part of the user prepared SOP manual.

3.8.3 Analytical System Dynamic Calibration

1. Before sample analysis, a complete dynamic calibration of the analytical system should be carried out at five or more concentrations on each range, to define the calibration curve. The calibration procedure should be carried out initially and periodically thereafter, and should be part of the user-prepared SOP manual. The calibration should be verified with two- or three-point calibration checks (including zero) each day the analytical system is used to analyze samples.

2. Concentration standards of propane are used to calibrate the analytical system. Propane calibration standards may be obtained directly from low concentration cylinder standards or by dilution of high concentration cylinder standards with zero air. Dilution flow rates must be measured accurately and the combined gas stream must be mixed thoroughly for successful calibration of the analyzer. The calibration standard should be sampled directly from a vented manifold or tee. The propane NMOC concentration in ppmC is three times the volumetric concentration in parts per million volume.

3. Select one or more combinations of the following parameters to provide the desired range or ranges (e.g., 0-1.0 ppmC or 0-5.0 ppmC): FID attenuator setting, output voltage setting, integrator resolution (if applicable), and sample volume. Each individual range should be calibrated separately and should have a separate calibration curve. Modern GC integrators may provide automatic ranging so that several decades of concentration may be covered in a single range. The user-prepared SOP manual should address variations applicable to a specific system design.

4. Analyze each calibration standard three times according to the procedure in Section 3.8.4. Insure that flow rates, pressure gauge start and stop readings, initial cryogen liquid level in the Dewar, timing, heating, integrator settings, and other variables are the same as those that will be used during analysis of ambient samples. Typical flow rates for the gases are: hydrogen, 30 mL/minute; helium carrier, 30 mL/minute; and burner air, 400 mL/minute.

5. Average the three analyses for each concentration standard and plot the calibration curve(s) as average integrated peak area reading versus concentration in ppmC. The relative standard deviation for the three analyses should be less than 3% (except for zero concentration). Linearity should be expected; points that appear to deviate abnormally should be repeated. Response has been shown to be linear over a wide range (0-10,000 ppbC). If nonlinearity is observed, an effort should be made to identify and correct the problem. If the problem cannot be corrected, additional points

in the nonlinear region may be needed in order to adequately define the calibration curve.

3.8.4 Analysis Procedure

1. Ensure that the analytical system has been assembled properly, leak checked, and properly calibrated through a dynamic standard calibration. Ignite the FID detector and allow to stabilize.

2. Check and adjust the helium carrier pressure to provide the correct carrier flow rate for the system. Helium is used to purge residual air and methane from the trap at the end of the sampling phase and to carry the revolatilized NMOC from the trap into the FID.

3. Close the sample valve and open the vacuum valve to evacuate the vacuum reservoir to a specific predetermined value (e.g., 100 mm Hg).

4. With the trap at room temperature, place the six-port valve in the inject position.

5. Open the sample valve and adjust the sample flow rate needle valve for an appropriate trap flow of 50-100 mL/minute.

6. Connect the sample canister or direct sample inlet to the six-port valve, as shown in Figure 3-1. For a canister, either the canister valve or an optional fine needle valve installed between the canister and the vent is used to adjust the canister flow rate to a value slightly higher than the trap flow rate set by the sample flow rate needle valve. The excess flow exhausts through the vent, which ensures that the sample air flowing through the trap is at atmospheric pressure. The vent is connected to a flow indicator such as a rotameter as an indication of vent flow to assist in adjusting the flow control valve. Open the canister valve and adjust the canister valve or the sample flow needle valve to obtain a moderate vent flow, as indicated by the rotameter. The sample flow rate will be lower and the vent flow rate will be higher when the trap is cold.

7. Close the sample valve and open the vacuum valve to evacuate the vacuum reservoir. With the six-port valve in the inject position and the vacuum valve

open, open the sample valve for 2-3 minutes to flush and condition the inlet lines(with both valves open, the pressure reading won't change).

8. Close the sample valve and evacuate the reservoir to the predetermined sample starting pressure (typically 100 mm Hg) as indicated by the absolute pressure gauge.

9. Switch the six-port valve to the sample position.

10. Submerge the trap in the cryogen. Allow a few minutes for the trap to cool completely as indicated when the cryogen stops boiling. Add cryogen to the initial level used during system dynamic calibration. The level of the cryogenic liquid should remain constant with respect to the trap and should completely cover the packed area of the trap.

11. Open the sample valve and observe the increasing pressure on the pressure gauge. When it reaches the predetermined pressure representative of the desired sample volume (typically 300 mm Hg), close the sample valve.

12. Add a little cryogen or elevate the Dewar to raise the liquid level to a point slightly higher (3-15 mm) than the initial level at the beginning of the trapping. This ensures that organics do not escape from the trap before being integrated as part of the NMOC peak(s).

13. Switch the six-port valve to the inject position, keeping the cryogenic liquid on the trap until the methane and pressure peaks have diminished (10-20 seconds). Now close the canister valve to conserve the remaining sample in the canister.

14. Start the integrator and remove the Dewar flask containing the cryogenic liquid from the trap.

15. Close the GC oven door and allow the GC oven (or alternate trap heating system) to heat the trap at a predetermined rate (typically, 30°C/min) to 90°C. Heating the trap volatilizes the concentrated NMOC. A uniform trap temperature rise rate helps reduce variability and facilitates more accurate correction for the moisture-shifted baseline. With a chromatograph oven to heat the trap, the following parameters have

been found to be acceptable: initial temperature, 30°C; initial time, 0.20 minutes (following start of the integrator); heat rate, 30°C/min; final temperature, 90°C.

16. Use the same heating process and temperatures for both calibration and sample analysis. Heating the trap too quickly may cause an initial negative response that could hamper accurate integration. Some initial experimentation may be necessary to determine the optimal heating procedure for each system. Once established, the procedure should be consistent for each analysis as outlined in the user-prepared SOP manual.

17. Continue the integration only long enough to include all of the organic compound peaks and to establish the end point FID baseline, as illustrated in Figure 3-3. The integrator should be capable of marking the beginning and ending of peaks, constructing the appropriate operational baseline between the start and end of the integration period, and calculating the resulting corrected peak area. This ability is necessary because the moisture in the sample, which is also concentrated in the trap, will cause a slight positive baseline shift. This baseline shift starts as the trap warms and continues until all of the moisture is swept from the trap, at which time the baseline returns to its normal level. The shift always continues longer than the ambient organic peak(s). The integrator should be programmed to correct for this shifted baseline by ending the integration at a point after the last NMOC peak and prior to the return of the shifted baseline to normal so that the calculated operational baseline effectively compensates for the water-shifted baseline. Electronic integrators either do this compensation automatically or they should be programmed to make the correction. Alternatively, analyses of humidified zero air prior to sample analyses should be performed to determine the water envelope and the proper blank value for correcting the ambient air concentration measurements accordingly. Heating and flushing of the trap should continue after the integration period has ended to ensure that all water has been removed. The six-port valve should remain in the inject position until all moisture has purged from the trap.

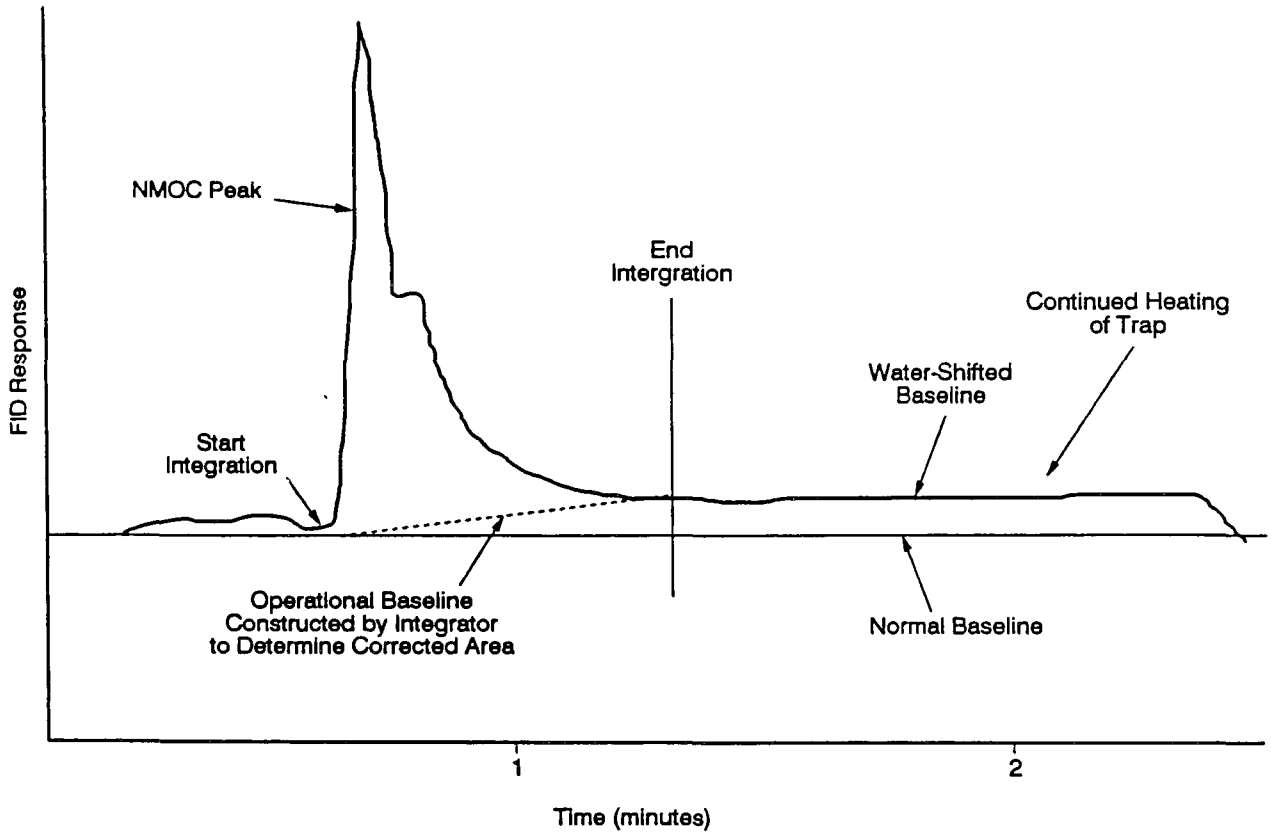

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Figure 3-3. Operational baseline and corresponding correction of peak area

18. Use the dynamic calibration curve to convert the integrated peak area reading into concentration units (ppmC). Note that the NMOC peak shape may not be precisely reproducible because of variations in heating the trap, but the total NMOC peak area should be reproducible.

19. Analyze each canister sample at least twice and report the average NMOC concentration. Problems during an analysis occasionally will cause erratic or inconsistent results. If the first two analyses do not agree within ± 5 %RSD, additional analyses should be made to identify inaccurate measurements and produce a more accurate average.

3.9 PERFORMANCE CRITERIA AND QUALITY ASSURANCE

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

3.9.1 Standard Operating Procedures

1. Users should generate SOPs that describes and documents the following activities in their laboratory:

- Assembly, calibration, leak check, and operation of the specific sampling system and equipment used;
- Preparation, storage, shipment, and handling of samples;
- Assembly, leak check, calibration, and operation of the analytical system, addressing the specific equipment used;
- Canister storage and cleaning; and
- All aspects of data recording and processing, including lists of computer hardware and software used.

2. The SOP should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

3.9.2 Method Sensitivity, Accuracy, Precision, and Linearity

The sensitivity and precision of Method TO-12 are proportional to the sample volume. However, ice formation in the trap may reduce or stop the sample flow during trapping if the sample volume exceeds 500 mL. Sample volumes below 100-150 mL may cause increased measurement variability because of dead volume in lines and valves. For most typical ambient NMOC concentrations, sample volumes in the range of 200-400 mL appear to be appropriate. If a response peak obtained with a 400 mL sample is off-scale or exceeds the calibration range, a second analysis can be carried out with a smaller volume.

The actual sample volume used need not be accurately known if it is precisely repeatable during both calibration and analysis. Similarly, the actual volume of the vacuum reservoir need not be accurately known, but the reservoir volume should be matched to the pressure range and resolution of the absolute pressure gauge so that the measurement of the pressure change in the reservoir is repeatable within 1 percent. A 1000 mL vacuum reservoir and a pressure change of 200 mm Hg, measured with the specified pressure gauge, have provided a sampling precision of ± 1.31 mL. A smaller volume reservoir may be used with a greater pressure change to accommodate absolute pressure gauges with lower resolution, and vice versa.

Some FID systems associated with laboratory chromatographs may have autoranging. Others may provide attenuator control and internal full-scale output voltage selectors. An appropriate combination should be chosen so that an adequate output level for accurate integration is obtained down to the detection limit; however, the electrometer or integrator must not be driven into saturation at the upper end of the calibration. Saturation of the electrometer may be indicated by flattening of the calibration curve at high concentrations. Additional adjustments of range and sensitivity can be provided by adjusting the sample volume used.

System linearity has been documented from 0 to 10,000 ppbC.

Some organic compounds contained in ambient air are "sticky" and may require repeated analyses before they fully appear in the FID output. Also, some adjustment may have to be made in the integrator off-time setting to accommodate compounds that reach the FID late in the analysis cycle. Similarly, "sticky" compounds from ambient samples or from contaminated propane standards may temporarily contaminate the analytical system and can affect subsequent analyses. Such temporary contamination can usually be removed by repeated analyses of humidified zero air.

3.10 METHOD MODIFICATIONS

Potential modifications to the method are contained in this section.

3.10.1 Sample Metering System

Although the vacuum reservoir and absolute pressure gauge technique for metering the sample volume during analysis is efficient and convenient, other techniques should work. A constant sample flow could be established with a vacuum pump and a critical orifice, with the six-port valve being switched to the sample position for a measured time period. A gas volume meter, such as a wet test meter, could also be used to measure the total volume of sample air drawn through the trap. These alternative techniques should be tested and evaluated as part of a user-prepared SOP manual.

3.10.2 Flame Ionization Detection System

A variety of FID systems should be adaptable to the method. The specific flow rates and necessary modifications for the helium carrier for any alternative FID instrument should be evaluated prior to inclusion in the SOP manual.

3.10.3 Range

It may be possible to increase the sensitivity of the method by increasing the sample volume. However, limitations may arise such as plugging of the trap by ice.

SECTION 4.0

METHODOLOGY FOR MEASURING OXIDES OF NITROGEN AND TOTAL REACTIVE OXIDES OF NITROGEN IN AMBIENT AIR

This section addresses the monitoring provisions of 40 CFR Part 58 for measuring NO_x and provides a general discussion of NO_y.

4.1 OXIDES OF NITROGEN

Nitric oxide (NO) and nitrogen dioxide (NO_2) are the constituents of NO_x. Oxides of nitrogen are a principal precursor to the formation of O_3.

Models such as EKMA, that are used to predict downwind concentrations of O_3 require NO_x and NMOC concentrations as inputs. The Urban Airshed Model (UAM), another type of prediction model, requires NO_x, total NMOC, and VOC speciation information as inputs.

4.1.1 Measurement of Oxides of Nitrogen

4.1.1.1 Method Description --

The NO_x compounds are typically measured using a chemiluminescent instrument. The principle of operation of this instrumentation is based on the chemiluminescent reaction of NO and O_3 specifically,

$$NO + O_3 \text{ ---> } NO_2 + O_2 + h_\nu.$$

The reaction causes electronically excited NO_2 molecules to revert to their ground state, resulting in an emission of light or chemiluminescence.

The NO is measured by blending the sample gas with O_3 in a reaction chamber. The chemiluminescence that results is monitored through an optical filter by a high-sensitivity photomultiplier. The filter and photomultiplier respond to light in a narrow-wavelength band unique to the reaction presented above. The signal developed by the photomultiplier is proportional to the NO concentration. To

determine concentration of NO_x (i.e., NO + NO_2), the sample gas is routed through an NO_2-to-NO converter. The chemiluminescent response in the reaction chamber to the converter effluent gas stream is proportional to the concentration of NO_x entering the converter.

There are basically two type of NO_2-to-NO converters. These are:

- A catalytic converter using a catalyst such as molybdenum or gold; and
- A photolytic converter using a high energy light source.

Catalytic conversion NO_2 analyzers permit accurate measurement of NO_x as long as the nitroxyl compounds occurring in the sampled atmosphere are limited to NO and NO_x. Peroxyacetyl nitrate (PAN) and nitric acid (HNO_3) are primary potential interferents to the accurate measurement of NO_x when a catalytic converter is used. A catalytic converter may partially convert HNO_3, and PAN to NO. This conversion causes artificially high values for NO_2 and NO_x. The potential for biasing the NO_x measurement because of the catalytic conversion of PAN and HNO_3 is greatest in areas where these compounds comprise a significant percentage of the total airborne compounds containing N_2 and oxygen (O_2). In this situation, the photolytic converter can be more accurate. The photolytically activated converter is a high energy light source at wavelengths from 300 nanometer (nm) to 430 nm that converts NO_2 to $NO+O_2$, which is then mixed with O_3 and measured by the chemiluminescent detector. The photolytic converter is not 100% efficient and must be calibrated to determine its efficiency.

4.1.1.2 Methods and Equipment --

Methods for measuring ambient concentrations of NO_2 that have been designated as reference or equivalent methods are presented in 40 CFR Part 53[8]. Subject to any limitations specified in the applicable designation, each method listed in 40 CFR Part 53 is acceptable for use at PAMS unless the applicable designation is

subsequently canceled. Instruments designated as reference methods for NO_2 are also approved for measuring NO, and are acceptable for determination of NO_x.

4.2 TOTAL REACTIVE OXIDES OF NITROGEN

The nitroxyl compounds in ambient air included in the group of specific compounds referred to as NO_y have not been definitively determined. This group of compounds should contain all of the oxides of nitrogen that react in the troposphere to any significant extent, and therefore, potentially contribute to the formation of O_3.

Identified NO_y constituents include:

- NO;
- NO_2;
- nitrogen trioxide;
- nitrogen pentoxide;
- nitrous acid;
- HNO_3;
- peroxynitrite;
- PAN;
- other organic nitrates; and
- aerosol nitrates.

Although the measurement of NO_y is not required by the proposed revisions to 40 CFR Part 58, NO_y is discussed because of its potential as a precursor to O_3 formation.

4.2.1 Measurement of Total Reactive Oxides of Nitrogen

There are two primary techniques to measure NO_y. These techniques are:

- Analyzing separately for each constituent using an appropriate specific method, and summing the results to determine NO_y; and

- Catalytically converting all the compounds containing N_2 and O_2 to NO and measuring the NO using a chemiluminescence instrument. Measured NO concentration is assumed to equal NO_y.

Analyzing separately for each constituent may be impractical because it requires that the user know all the compounds that are to be measured so that appropriate individual methods can be applied. Comprehensive catalytic reduction to NO usually yields NO_y concentrations higher than if the concentrations of the constituent parts of NO_y are measured separately and summed.

SECTION 5.0

METHODOLOGY FOR DETERMINING CARBONYL COMPOUNDS IN AMBIENT AIR

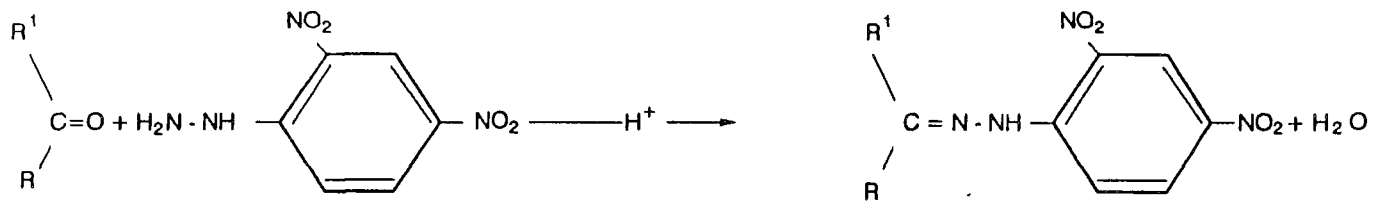
Formaldehyde and other carbonyl compounds have been shown to be major promoters in the formation of photochemical O_3. Determination of ambient formaldehyde, acetaldehyde, and acetone concentrations is a required specification of the proposed ambient air monitoring revisions to 40 CFR Part 58. Details on carbonyl sampling frequency are presented in Table 1-1. The methodology contained in Section 5.1 presents procedures for sampling and analyzing carbonyl compounds utilizing a solid adsorbent and high performance liquid chromatography (HPLC) detection. This method is sensitive and provides accurate measurements of carbonyl compounds.

5.1 METHOD DESCRIPTION

This section presents Compendium Method TO-11 which is used for determination of formaldehyde and other carbonyl compounds in ambient air, utilizing a solid adsorbent followed by HPLC detection.

Method TO-11 is a modification of Compendium Method TO-05, "Method For the Determination of Aldehydes and Ketones in Ambient Air Using High Performance Liquid Chromatography." Carbonyl compounds readily form a stable derivative with 2,4-dinitrophenylhydrazine (DNPH) reagent. The DNPH derivative is analyzed by HPLC. In Method TO-11, the DNPH reagent is coated on a solid adsorbent and used for sample collection. The method is currently based on the specific reaction of organic carbonyl compounds (aldehydes and ketones) with DNPH cartridges in the presence of an acid to form stable derivatives according to the equation shown in Figure 5-1.

The sampling method gives a time-weighted average sample. The same sampling methodology can be used for long-term (1-24 hr) sampling of ambient air where the concentration of carbonyl compounds is generally in the low (1-20) ppb



Carbonyl Group
(Aldehydes and Ketones)

2,4-dinitrophenylhydrazine
(DNPH)

DNPH - Derivative

Water

R and R^1 are organic alkyl or aromatic group (ketones) or either substituent is a hydrogen (aldehydes)

5616538R

Figure 5-1. Formation of a stable derivative.

(v/v), or for short-term (5-60 min)sampling of source-impacted atmospheres where the concentration of carbonyl compounds could reach the ppm (v/v) levels.

The sampling flow rate, as described in this document, is presently limited to about 1.5 L/min. This limitation is principally due to the high pressure drop across the DNPH-coated silica gel cartridges. Because of this limitation, the procedure is not compatible with pumps used in personal sampling equipment.

Method TO-11 instructs the user to purchase Sep-PAK® chromatographic grade silica gel cartridges and apply acidified DNPH in-situ to each cartridge as part of the user-prepared QA program. Commercially pre-coated DNPH cartridges are also available. Recent studies have indicated abnormally high formaldehyde background levels in commercially prepacked cartridges. It is advised that three cartridges randomly selected from each production lot should be analyzed for formaldehyde prior to use to determine acceptable levels. Thermosorb/F cartridges are 1.5 cm internal diameter x 2 cm long polyethylene tubes with Luer®-type fittings on each end. The adsorbent is composed of 60/80-mesh Florisil (magnesium silicate) coated with DNPH. The adsorbent is held in place with 100 mesh stainless steel screens at each end. The precoated cartridges are used as received and are discarded after use. The cartridges are stored in glass culture tubes with polypropylene caps and placed in cold storage when not in use.

Method TO-11 may involve hazardous materials, operations, and equipment. The method does not purport to address all the safety problems associated with its use. It is the responsibility of the user to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

5.2 SUMMARY OF METHOD

A known volume of ambient air is drawn through a prepacked silica gel cartridge coated with acidified DNPH at a sampling rate of 500-1200 mL/min for an appropriate period of time. Sampling rate and time are dependent upon carbonyl concentration in the test atmosphere.

After sampling, the sample cartridges are capped and placed in borosilicate glass culture tubes with polypropylene caps. The capped tubes are then placed in a friction-top can containing a pouch of charcoal and returned to the laboratory for analysis. Alternatively, the sample vials can be placed in a styrofoam box with appropriate padding for shipment to the laboratory. The cartridges may either be placed in cold storage until analysis or immediately washed by gravity-feed elution of 6 mL of acetonitrile from a plastic syringe reservoir to a graduated test tube or a 5 mL volumetric flask. The eluate is then topped to a known volume and refrigerated until analysis.

The DNPH-carbonyl derivative is determined using isocratic reverse phase HPLC with an ultraviolet (UV) absorption detector operated at 360 nm. A cartridge blank is likewise desorbed and analyzed as per Section 5.9. Formaldehyde, acetaldehyde, and acetone in the sample are identified and quantified by comparison of their retention times and peak heights or peak areas with those of standard solutions.

5.3 SIGNIFICANCE

Formaldehyde, acetaldehyde, and acetone emissions result from incomplete combustion of hydrocarbons and other organic materials. The major emission sources appear to be vehicle exhaust, waste incineration, and fuel burning (natural gas, fuel oil, and coal). In addition, significant amounts of atmospheric carbonyl compounds can result from photochemical reactions between reactive hydrocarbons and NO_x. Moreover, these carbonyl compounds can react photochemically to produce other products, including O_3, peroxides, and PAN. Local sources of formaldehyde, acetaldehyde, and acetone may include manufacturing and other industrial processes that use the chemicals. In particular, formaldehyde emissions are associated with any industrial process that results in the pyrolysis of organic compounds in air or oxygen. This test method provides a means to determine concentrations of formaldehyde, acetaldehyde, and acetone in emissions sources in various working environments and in ambient indoor and outdoor atmospheres.

5.4 INTERFERENCES

This procedure has been prepared specifically to address the sampling and analysis of formaldehyde, acetaldehyde, and acetone. Interferences in the method arise from unresolved components in the HPLC chromatogram. Organic compounds that have the same retention time and significant absorbance at 360 nm as the DNPH derivatives of carbonyl compounds will interfere. Such interferences can often be overcome by altering the separation conditions (e.g., using alternative HPLC columns or mobile phase compositions). Other carbonyl compounds can be detected with a modification of the basic procedure. In particular, chromatographic conditions can be optimized to separate acrolein, acetone, and propionaldehyde (within an analysis time of about one hour) by utilizing two Zorbax ODS columns in series under a linear gradient program. The following gradient program was found to be adequate to achieve a resolution of other potentially interfering carbonyl compounds. Upon sample injection, linear gradient from 60-75% acetonitrile/40-25% water in 30 minutes, gradient from 75-100% acetonitrile/25-0% water in 20 minutes, hold at 100% acetonitrile for 5 minutes. A reverse gradient is then necessary to reequilibrate the HPLC column. This gradient changes solvent from 100% acetonitrile to 60% acetonitrile/40% water in 1 minute, and maintains isocratic at 60% acetonitrile/40% water for 15 minutes.

Formaldehyde or acetone contamination of the DNPH reagent is a frequently encountered problem. The DNPH must be purified by multiple recrystallizations in UV grade acetonitrile. Recrystallization is accomplished at 40-60°C by slow evaporation of the solvent to maximize crystal size. The purified DNPH crystals are stored under UV grade acetonitrile until use. Impurity levels of carbonyl compounds in the DNPH are determined by HPLC prior to use and should be less than 0.025 micrograms (μg)/mL.

5.5 EQUIPMENT

Isocratic HPLC system - consisting of a mobile phase reservoir; a high pressure pump; an injection valve (automatic sampler with an optional 25-microliter (μL) loop injector); a Zorbax ODS (DuPont Instruments, Wilmington, DE) or equivalent C-18, reverse phase column or equivalent (25 cm x 4.6 mm internal diameter); a variable

wavelength UV detector operating at 360 nm; and a data system or strip chart recorder (See Figure 5-2).

Sampling system - capable of accurately and precisely sampling 100-1500 mL/min of ambient air (See Figure 5-3). The dry test meter may not be accurate at flows below 500 mL/min, and should then be replaced by recorded flow readings at the start, finish, and hourly during the collection. The sample pump consists of a diaphragm or metal bellows pump capable of extracting an air sample between 500-1200 mL/min. A normal pressure drop through the sample cartridge is approximately 14 cm Hg at a sampling rate of 1.5 L/min.

Stopwatch - for time measurement.

Friction-top metal can or a styrofoam box with air bubble padding - to contain the sample vials.

Thermometer - to record ambient temperature.

Barometer (optional) to measure barometric pressure.

Suction filtration apparatus - for filtering HPLC mobile phase.

Volumetric flasks - various sizes, 5-2000 mL.

Pipets - various sizes, 1-50 mL.

Helium purge line (optional) - for degassing HPLC mobile phase.

Erlenmeyer flask, 1 L - for preparing HPLC mobile phase.

Graduated cylinder, 1 L - for preparing HPLC mobile phase.

Syringe, 100-250 μL - for HPLC injection.

Sample vials - to contain the samples.

Melting point apparatus - to determine melting points.

Rotameters - for flow measurement.

Calibrated syringes - for precision injections and extractions.

Special glass apparatus - for rinsing, storing and dispensing saturated DNPH stock reagent (See Figure 5-4).

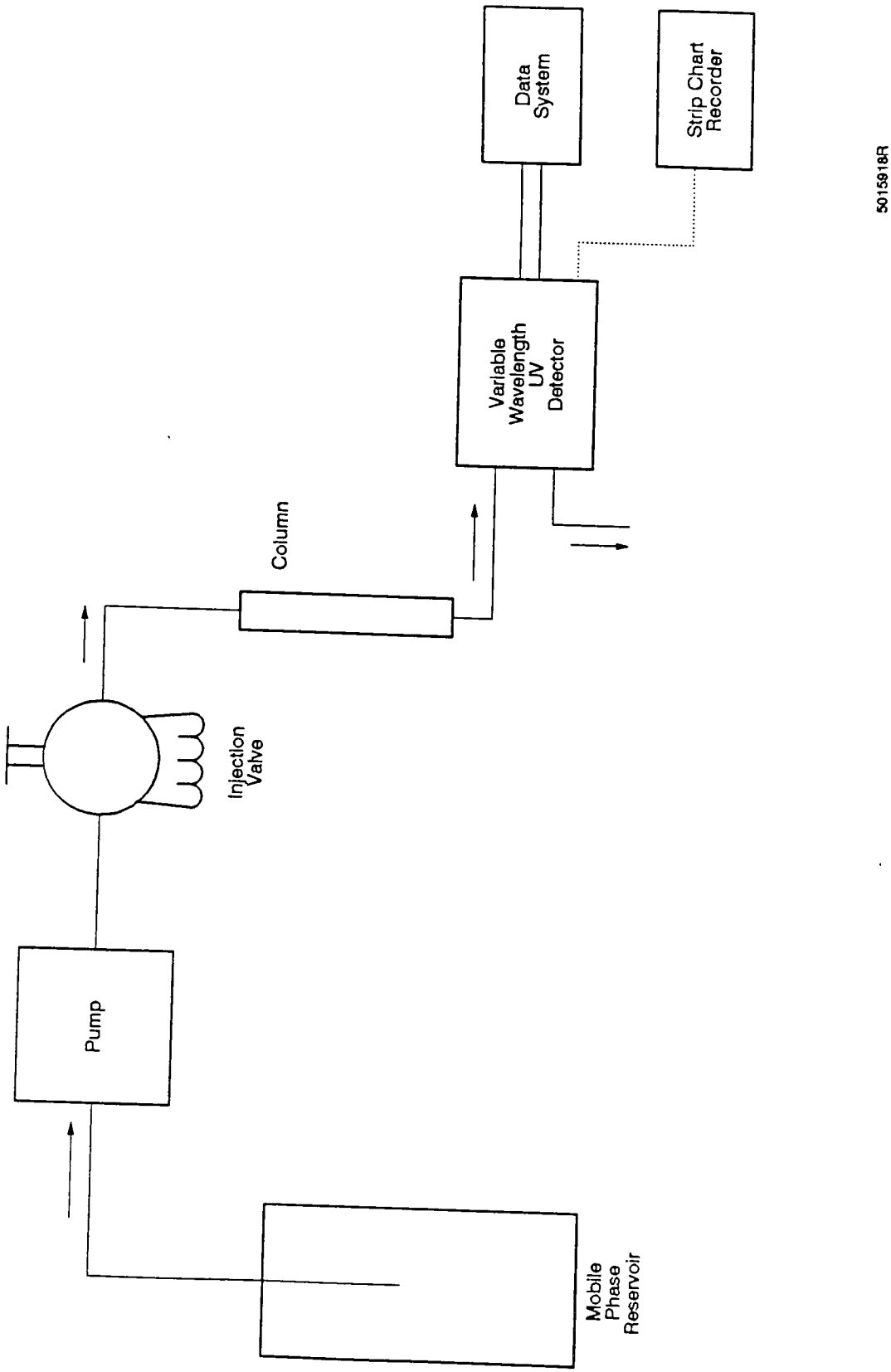
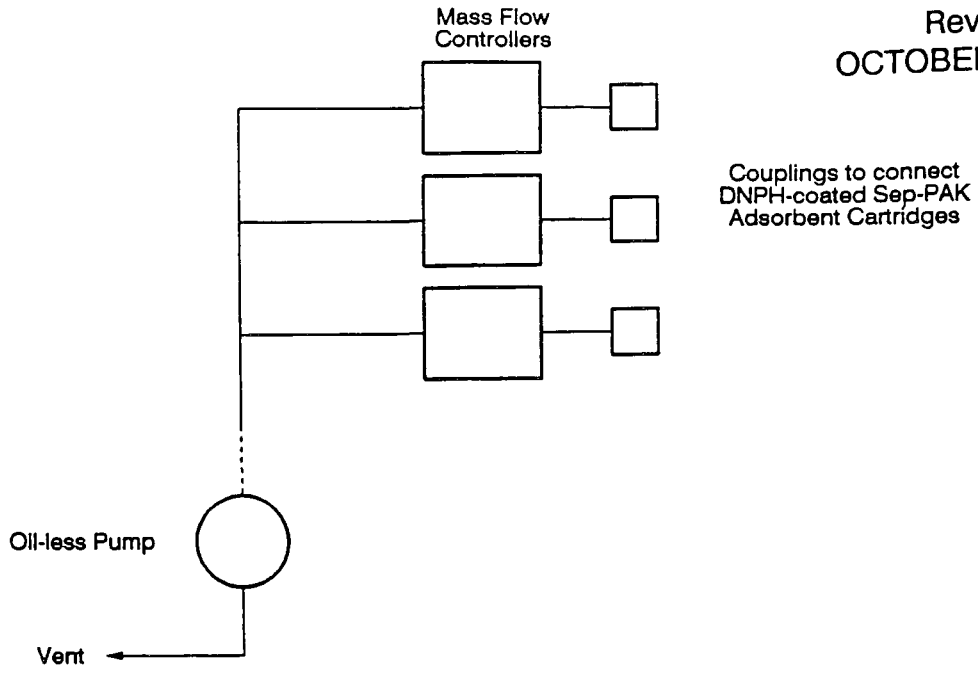
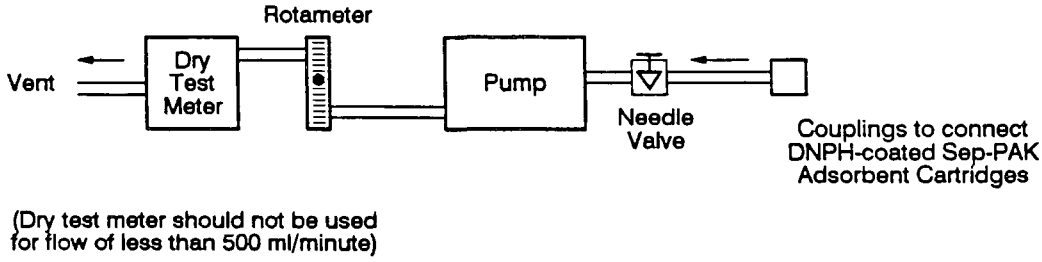


Figure 5-2. Typical HPLC System.



(a) Mass Flow Control



(b) Neddle Valve/Dry Test Meter

5015919R

Figure 5-3. Typical sampling system configurations.

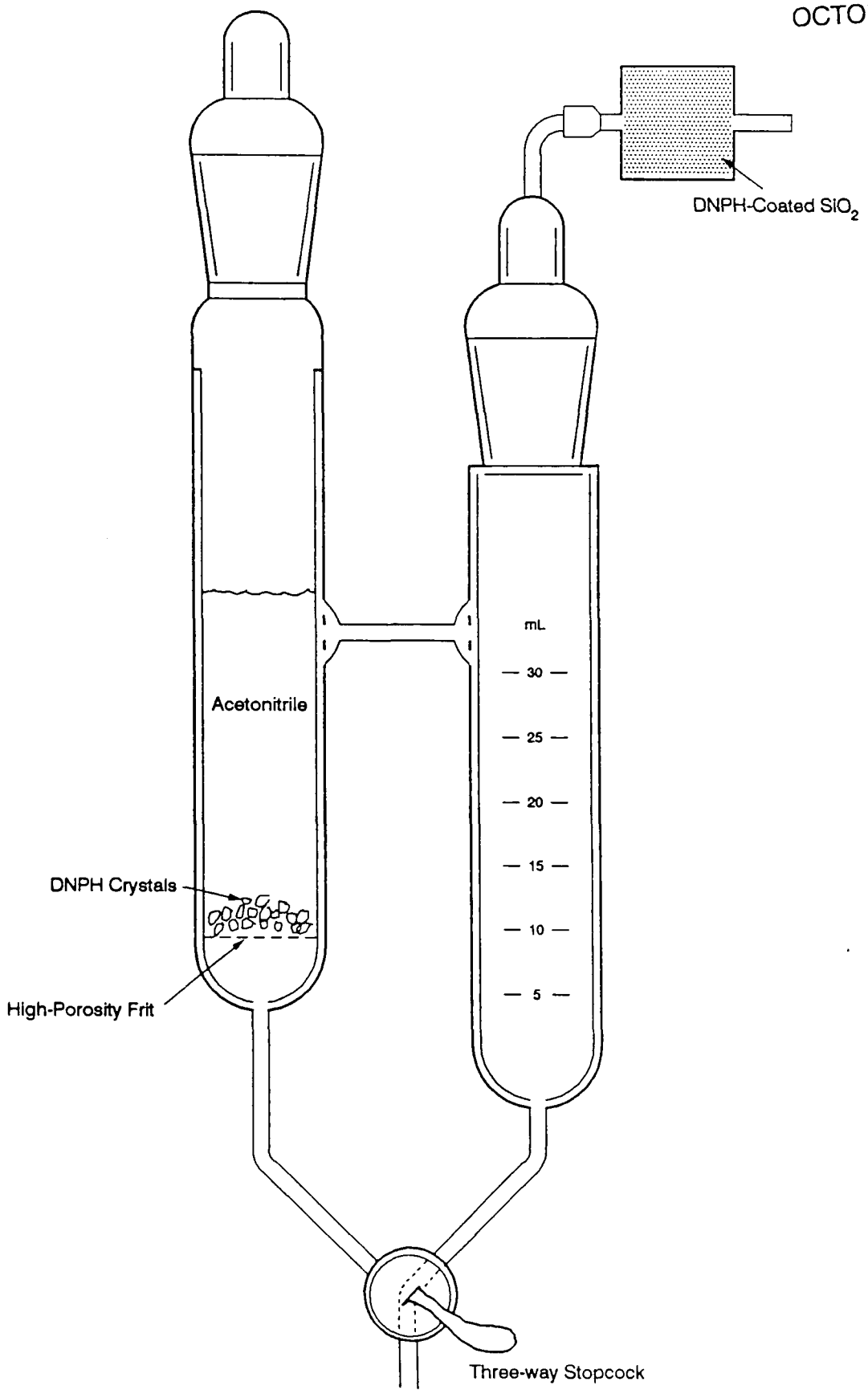


Figure 5-4. Special glass apparatus for rinsing, storing, and dispensing saturated DNPH stock solution.

Mass flow meters and mass flow controllers - for metering/setting air flow rate through sample cartridge of 500-1200 mL/min. The mass flow controllers are necessary because cartridges have a high pressure drop and at maximum flow rate, the cartridge behaves like a "critical orifice." Recent studies have shown that critical flow orifices may be used for 24-hour sampling periods at a maximum rate of 1 L/min for atmospheres not heavily loaded with particulates.

Positive displacement, repetitive dispensing pipets - (Lab-Industries, or equivalent), 0-10 mL range.

Cartridge drying manifold - with multiple standard male Luer® connectors.

Liquid syringes, 10 mL - (polypropylene syringes are adequate) for preparing DNPH-coated cartridges.

Syringe rack - to enable batch processing of 45 cartridges for cleaning, coating, and/or sample elution.

Luer® fittings/plugs - to connect cartridges to sampling system and to cap prepared cartridges.

Hot plates, beakers, flasks, measuring and disposable pipets, volumetric flasks, etc. - used in the purification of DNPH.

Borosilicate glass culture tubes (20 x 125 mm) with polypropylene screw caps - used to transport Sep-PAK® coated cartridges for field applications.

Heated probe - necessary when ambient temperature to be sampled is below 60° Fahrenheit (F) to ensure the effective collection of formaldehyde as a hydrazone.

Cartridge sampler - silica gel cartridge, Sep-PAK® coated in-situ with DNPH according to Section 5.7.

Polyethylene gloves - used to handle Sep-PAK® silica gel cartridges.

5.6 REAGENTS AND MATERIALS

2,4-Dinitrophenylhydrazine - reagent grade or equivalent. Recrystallize at least twice with UV-grade acetonitrile before use.

Acetonitrile - UV-grade, "distilled-in-glass," or equivalent.

Deionized-distilled water - charcoal filtered.

Perchloric acid - analytical grade, best source.

Hydrochloric acid - analytical grade, best source.

Formaldehyde - analytical grade, best source.

Aldehydes and ketones, analytical grade, best source - for preparation of DNPH derivative standards.

Ethanol or methanol - analytical grade, best source.

Sep-PAK® silica gel cartridge or equivalent - for sample collection.

Nitrogen - high purity grade, best source.

Charcoal - granular, best source.

Helium - high purity grade, best source.

5.7 PREPARATION OF REAGENTS AND CARTRIDGES

This section describes procedures used to prepare reagents and cartridges.

5.7.1 Purification of DNPH

This procedure should be performed under a properly ventilated hood.

1. Prepare a supersaturated solution of DNPH by boiling excess DNPH in 200 mL of acetonitrile for approximately one hour.

2. After one hour, remove and transfer the supernatant to a covered beaker on a hot plate and allow gradual cooling to 40-60°C.

3. Maintain the solution at 40-60°C until 95% of solvent has evaporated.

4. Decant solution to waste and rinse crystals twice with three times their apparent volume of acetonitrile. **Various health effects result from inhalation of acetonitrile. At 500 ppm in air, brief inhalation has produced nose and throat irritation. At 160 ppm, inhalation for 4 hours has caused flushing of the face (2-hour delay after exposure) and bronchial tightness (5 hour delay). Heavier exposures have produced systemic effects, with symptoms ranging from headache, nausea, and lassitude to vomiting, chest or abdominal pain, respiratory depression, extreme weakness, stupor, convulsions and death (dependent upon concentration and time).**

5. Transfer crystals to another clean beaker, add 200 mL of acetonitrile, heat to boiling, and again let crystals grow slowly at 40-60°C until 95% of the solvent has evaporated.

6. Repeat rinsing process as described in Step 4.

7. Take an aliquot of the second rinse, dilute 10 times with acetonitrile, acidify with 1 mL of 3.8 mole perchloric acid per 100 mL of DNPH solution, and analyze by HPLC.

8. The chromatogram illustrated in Figure 5-5 represents an acceptable impurity level of <0.025 μg/mL of formaldehyde in recrystallized DNPH reagent. An acceptable impurity level for an intended sampling application may be defined as the mass of the analyte (e.g., DNPH-formaldehyde derivative) in a unit volume of the reagent solution equivalent to less than one-tenth the mass of the corresponding analyte from a volume of an air sample when the carbonyl (e.g., formaldehyde) is collected as DNPH derivative in an equal unit volume of the reagent solution. An impurity level unacceptable for a typical 10 L sample volume may be acceptable if sample volume is increased to 100 L. The impurity level of DNPH should be below the sensitivity (ppb, v/v) level indicated in Table 5-1 for the anticipated sample volume. If the impurity level is not acceptable for intended sampling application, repeat recrystallization. A special glass apparatus should be used for the final rinse and storage according to the following procedure:

A. Transfer the crystals to the special glass apparatus (See Figure 5-4).

B. Add about 25 mL of acetonitrile, agitate gently, and let solution equilibrate for 10 minutes.

C. Drain the solution by properly positioning the three-way stopcock. The purified crystals should not be allowed to contact laboratory air except for a brief moment. Minimal contact is accomplished by placing a DNPH-coated silica cartridge on the gas inlet of the special glass apparatus.

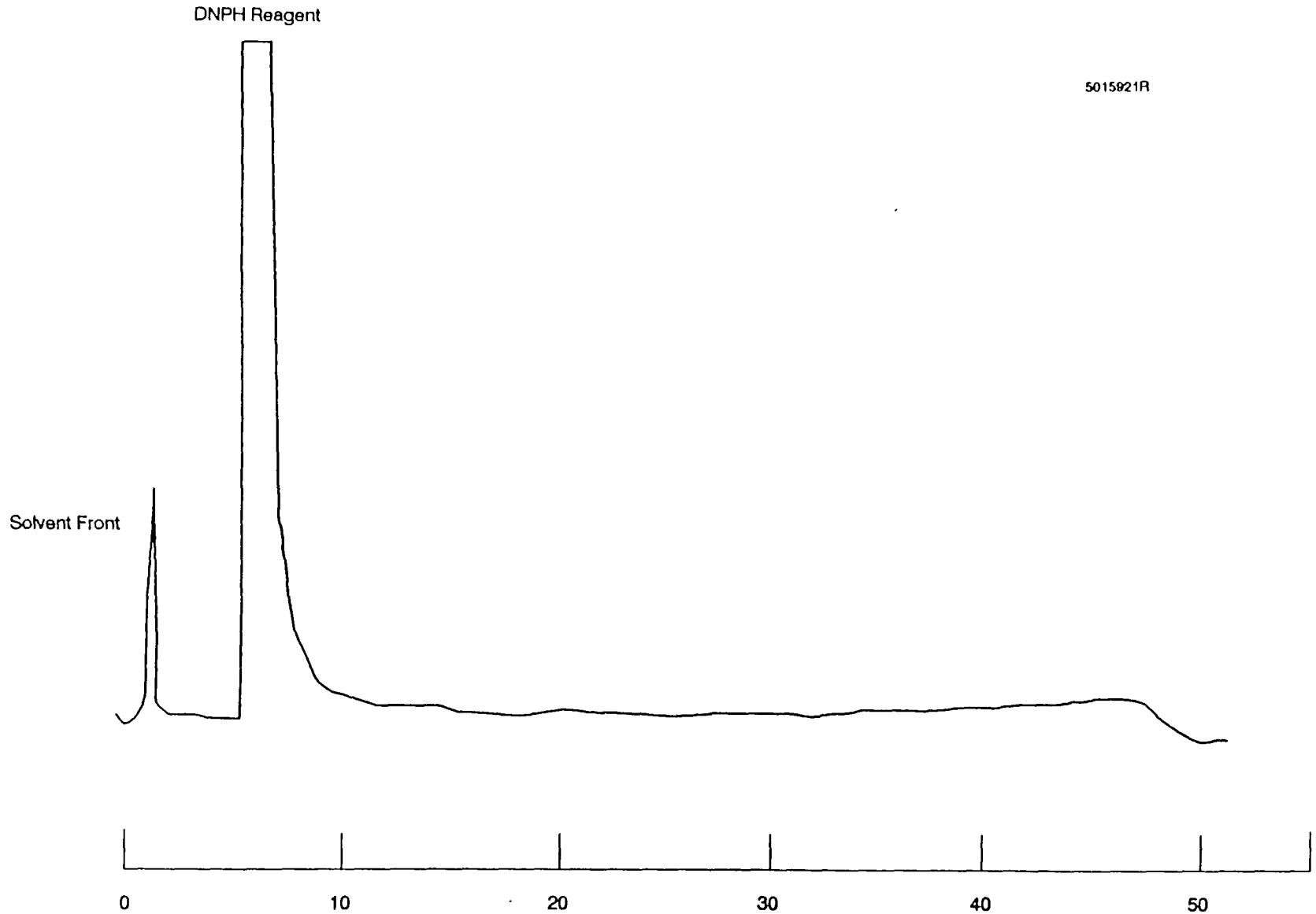


Figure 5-5. Impurity level of DNPH after recrystallization.

Table 5-1

Sensitivity (ppb,V/V) of Sampling/Analysis for Aldehydes and Ketones in Ambient Air Using Adsorbent Cartridge Followed by Gradient High Performance Liquid Chromatography

Sample Volume, L	10	20	30	40	50	60	100	200	300	400	500	1000
Compound	Sensitivity (ppb, v/v) of DNPH/HPLC Method for Carbonyls in Ambient Air											
Formaldehyde	1.45	0.73	0.48	0.36	0.29	0.24	0.15	0.07	0.05	0.04	0.03	0.01
Acetaldehyde	1.36	0.68	0.45	0.34	0.27	0.23	0.14	0.07	0.05	0.03	0.03	0.01
Acrolein	1.29	0.65	0.43	0.32	0.26	0.22	0.13	0.06	0.04	0.03	0.03	0.01
Acetone	1.28	0.64	0.43	0.32	0.26	0.21	0.13	0.06	0.04	0.03	0.03	0.01
Propionaldehyde	1.28	0.64	0.43	0.32	0.26	0.21	0.13	0.06	0.04	0.03	0.03	0.01
Crotonaldehyde	1.22	0.61	0.41	0.31	0.24	0.20	0.12	0.06	0.04	0.03	0.02	0.01
Butyraldehyde	1.21	0.61	0.40	0.30	0.24	0.20	0.12	0.06	0.04	0.03	0.02	0.01
Benzaldehyde	1.07	0.53	0.36	0.27	0.21	0.18	0.11	0.05	0.04	0.03	0.02	0.01
Isovaleraldehyde	1.15	0.57	0.38	0.29	0.23	0.19	0.11	0.06	0.04	0.03	0.02	0.01
Valeraldehyde	1.15	0.57	0.38	0.29	0.23	0.19	0.11	0.06	0.04	0.03	0.02	0.01
o-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.17	0.10	0.05	0.03	0.03	0.02	0.01
m-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.17	0.10	0.05	0.03	0.03	0.02	0.01
p-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.17	0.10	0.05	0.03	0.03	0.02	0.01
Hexanaldehyde	1.09	0.55	0.36	0.27	0.22	0.18	0.11	0.05	0.04	0.03	0.02	0.01
2,5-Dimethylbenzaldehyde	0.97	0.49	0.32	0.24	0.19	0.16	0.10	0.05	0.03	0.02	0.02	0.01

[Note: Ppb values are measured at 1 atm and 25°C; sample cartridge is eluted with 1.5 mL acetonitrile, and 25 mL are injected onto HPLC column.]

[Note: Maximum sampling flow through a DNPH-coated SEP-PAK® is about 1.5 L per minute.]

D. After draining, turn stopcock so drain tube is connected to measuring reservoir.

E. Introduce acetonitrile through measuring reservoir.

F. Rinsing should be repeated with 20 mL portions of acetonitrile until a satisfactorily low impurity level in the supernatant is confirmed by HPLC analysis. An impurity level of <0.025 μg/mL formaldehyde should be achieved, as illustrated in Figure 5-5.

G. If a special glass apparatus is not available, transfer the purified crystals to an all-glass reagent bottle, add 200 mL of acetonitrile, stopper, shake gently, and let stand overnight. Analyze supernatant by HPLC according to Section 5.9. The impurity level should be comparable to that shown in Figure 5-5.

H. If the impurity level is not satisfactory, pipet off the solution to waste, then add 25 mL of acetonitrile to the purified crystals and repeat Step F.

I. If the impurity level is satisfactory, add another 25 mL of acetonitrile, stopper and shake the reagent bottle, then set aside. The saturated solution above the purified crystals is the stock DNPH reagent.

J. After purification, purity of the DNPH reagent can be maintained by storing in the special glass apparatus.

K. Maintain only a minimum volume of saturated solution for day-to-day operation. To minimize waste of purified reagent should it ever become necessary to re-rinse the crystals to decrease the level of impurity for applications requiring more stringent purity specifications.

L. Use clean pipets when removing saturated DNPH stock solution for any analytical applications. Do not pour the stock solution from the reagent bottle.

5.7.2 Preparation of DNPH-Formaldehyde Derivative

1. Titrate a saturated solution of DNPH in 2N hydrochloric acid (HCl) with formaldehyde (other aldehydes or ketones may be used if their detection is desirable).

2. Filter the colored precipitate, wash with 2N HCl and water and let precipitate air dry.

3. Check the purity of the DNPH-formaldehyde derivative by melting point determination table or HPLC analysis. If the impurity level is not acceptable, recrystallize the derivative in ethanol. Repeat purity check and recrystallization as necessary until acceptable level of purity (e.g., 99%) is achieved.

5.7.3 Preparation of DNPH-Formaldehyde Standards

1. Prepare a standard stock solution of the DNPH-formaldehyde derivative by dissolving accurately weighed amounts in acetonitrile.

2. Prepare a working calibration standard mix from the standard stock solution. The concentration of the DNPH-formaldehyde compound in the standard mix solutions should be adjusted to reflect relative distribution in a real sample. Individual stock solutions of approximately 100 μg/L are prepared by dissolving 10 μg of the solid derivative in 100 mL of acetonitrile. The individual solution is used to prepare calibration standards containing the derivative of interest at concentrations of 0.5-20 μg/L, which spans the concentration of interest for most ambient air work.

3. Store all standard solutions in a refrigerator. They should be stable for several months.

4. Preparation of DNPH-Coated Sep-PAK® cartridges must be performed in an atmosphere with a very low aldehyde background. All glassware and plastic ware must be scrupulously cleaned and rinsed with deionized water and aldehyde-free acetonitrile. Contact of reagents with laboratory air must be minimized. Polyethylene gloves must be worn when handling the cartridges.

5.7.3.1 DNPH Coating Solution --

1. Pipet 30 mL of saturated DNPH stock solution to a 1000 mL volumetric flask, then add 500 mL acetonitrile.

2. Acidify with 1.0 mL of concentrated HCl. The atmosphere above the acidified solution should preferably be filtered through a DNPH-coated silica gel cartridge to minimize contamination from laboratory air. Shake solution, then make up to volume with acetonitrile. Stopper the flask, invert, and shake several times until the

solution is homogeneous. Transfer the acidified solution to a reagent bottle with a 0-10 mL range positive displacement dispenser.

3. Prime the dispenser and slowly dispense 10-20 mL to waste.

4. Dispense an aliquot of the solution to a sample vial and check the impurity level of the acidified solution by HPLC according to Section 5.7.1, as illustrated in Figure 5-5.

5. The impurity level should be <0.025 μg/mL formaldehyde, similar to that in the DNPH coating solution.

5.7.3.2 Coating the Cartridges --

1. Open the Sep-PAK® package, connect the short end to a 10 mL syringe, and place it in the syringe rack. Prepare as many cartridges and syringes as possible.

2. Using a positive displacement repetitive pipet, add 10 mL of acetonitrile to each of the syringes.

3. Let liquid drain to waste by gravity. Remove any air bubbles that may be trapped between the syringe and the silica cartridge by displacing them with the acetonitrile in the syringe.

4. Set the repetitive dispenser containing the acidified DNPH coating solution to dispense 7 mL into the cartridges.

5. Once the effluent flow at the outlet of the cartridge has stopped, dispense 7 mL of the coating reagent into each of the syringes.

6. Let the coating reagent drain by gravity through the cartridge until flow at the other end of the cartridge stops.

7. Wipe the excess liquid at the outlet of each of the cartridges with clean tissue paper.

8. Assemble a drying manifold with a scrubber or "guard cartridge" connected to each of the exit ports. These "guard cartridges" are DNPH-coated and serve to remove any trace of formaldehyde in the nitrogen gas supply.

9. Remove the cartridges from the syringes and connect the short ends to the exit end of the scrubber cartridge.

10. Pass nitrogen through each of the cartridges at about 300-400 mL/min for 5-10 minutes.

11. Within 10 minutes of the drying process, rinse the exterior surfaces and outlet ends of the cartridges with acetonitrile using a Pasteur pipet.

12. Stop the flow of nitrogen after 15 minutes and insert cartridge connectors into the long end of the scrubber cartridges.

13. Connect the short ends of a batch of the coated cartridges to the scrubbers and pass nitrogen through the cartridges at about 300-400 mL/min.

14. Repeat Step 11.

15. After 15 minutes, stop the flow of nitrogen, remove the dried cartridges and wipe the cartridge exterior free of rinse acetonitrile.

16. Plug both ends of the coated cartridge with standard polypropylene Luer® male plugs, and place the plugged cartridge in a borosilicate glass culture tube with polypropylene screw caps.

17. Put a serial number and lot number label on each of the individual cartridge glass storage containers and store the prepared lot in the refrigerator.

18. Store cartridges in an all-glass stoppered reagent bottle in a refrigerator until use. Plugged cartridges could also be placed in screw-capped glass culture tubes and placed in a refrigerator. Cartridges will maintain their integrity for up to 90 days stored in refrigerated, capped culture tubes.

19. Before transport, remove the glass-stoppered reagent bottles (or screw-capped glass culture tubes) containing the adsorbent tubes from the refrigerator and place the tubes individually in labeled glass culture tubes. Place culture tubes in a friction-top metal can containing 1-2 inches of charcoal for shipment to sampling location.

20. As an alternative to friction-top cans for transporting sample cartridges, the coated cartridges could be shipped in their individual glass containers. A large batch of coated cartridges in individual glass containers may be packed in a styrofoam box for shipment to the field. The box should be padded with clean tissue paper or

polyethylene-air bubble padding. Do not use polyurethane foam or newspaper as padding material.

21. The cartridges should immediately be stored in a refrigerator or in a chilled cooler upon arrival in the field.

5.8 SAMPLING

The sampling system is assembled and should be similar to that shown in Figure 5-3 above. Figure 5-3 illustrates a three-tube/one-pump configuration. The tester should ensure that the pump is capable of a constant flow rate throughout the sampling period. The coated cartridges can be used as direct probes and traps for sampling ambient air when the temperature is above freezing. For sampling ambient air below freezing, a short length (30-60 cm) of heated (50-60°C) stainless steel tubing must be added to condition the air sample prior to collection on adsorbent tubes. Two types of sampling systems are shown in Figure 5-3. For purposes of discussion, the following procedure assumes the use of a dry test meter. The dry test meter may not be accurate at flows below 500 mL/min and should be backed up by recorded flow readings at the start, finish, and hourly intervals during sample collection.

Before sample collection, the system is checked for leaks. Plug the input end of the cartridge so no flow is indicated at the output end of the pump. The mass flow meter should not indicate any air flow through the sampling apparatus.

The entire assembly, including a "dummy" sampling cartridge, is installed and the flow rate checked at a value near the desired rate. In general, flow rates of 500-1200 mL/min should be employed. The total moles of carbonyl in the volume of air sampled should not exceed that of the DNPH concentration (2 μg/cartridge). In general, a safe estimate of the sample size should be 75% of the DNPH loading of the cartridge. Generally, calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming the system is sealed.

Ideally, a dry gas meter is included in the system to record total flow. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If

the sampling period exceeds 2 hours, the flow rate should be measured at intermediate points during the sampling period. Ideally, a rotameter should be included to allow observation of the flow rate without interruption of the sampling process.

Before sampling, remove the glass culture tube from the friction-top metal can or styrofoam box. Let the cartridge warm to ambient temperature in the glass tube before connecting it to the sample train.

Using polyethylene gloves, remove the coated cartridge from the glass tube and connect it to the sampling system with a Luer® adapter fitting. Seal the glass tube for later use, and connect the cartridge to the sampling train so that its short end becomes the sample inlet. Record the following parameters on the sampling data sheet (See Figure 5-6):

- Date;
- Sampling location;
- Time;
- Ambient temperature;
- Barometric pressure (if available);
- Relative humidity (if available);
- Dry gas meter reading (if appropriate);
- Flow rate;
- Rotameter setting;
- Cartridge batch number; and

SAMPLING DATA SHEET
(One Sample per Data Sheet)

PROJECT: _____ DATE(S) SAMPLED: _____

SITE: _____ TIME PERIOD SAMPLED: _____

LOCATION: _____ OPERATOR: _____

INSTRUMENT MODEL NO: _____ CALIBRATED BY: _____

PUMP SERIAL NO: _____

ADSORBENT CARTRIDGE INFORMATION:

Type: _____ Serial Number: _____

Adsorbent: _____ Sample Number: _____

SAMPLING DATA:

Start Time: _____ Stop Time: _____

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate (Q)*, Ml/min	Ambient Temperature, °C	Barometric Pressure, mm Hg	Relative Humidity, %	Comments
Avg.							

Flow rate from rotameter or soap bubble calibrator (specify which) Total Volume Data (V_m) (use data from dry gas meter, if available)

V_m = (Final - Initial) Dry Gas Meter Reading, or ___ Liters

or

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

Figure 5-6. Sampling Data Sheet

- Dry gas meter pump identification numbers.

The sampler is turned on and the flow is adjusted to the desired rate. A typical flow rate through one cartridge is 1.0 L/min and 0.8 L/min for two cartridges in tandem.

The sampler is operated for the desired period, with periodic recording of the variables listed above.

At the end of the sampling period, the sampling parameters are recorded and the sample flow is stopped. If a dry gas meter is not used, the flow rate must be checked at the end of the sampling interval. If the flow rates at the beginning and end of the sampling period differ by more than 15%, the sample should be marked as suspect.

Immediately after sampling, remove the cartridge (using polyethylene gloves) from the sampling systems, cap with Luer® end plugs, and place it back in the original labeled glass culture tube. Cap the culture tube, seal it with Teflon® tape, and place it in a friction-top can containing 1-2 inches of granular charcoal or a styrofoam box with appropriate padding. Refrigerate the culture tubes until analysis. The refrigeration period prior to analysis should not exceed 30 days. If samples are to be shipped to a central laboratory for analysis, the duration of the non-refrigerated period should be kept to a minimum, preferably less than 2 days.

If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate (in mL/min) must be calculated according to the following equation:

$$Q_a = \frac{Q_1 + Q_2 + \ldots . Q_n}{N}$$

Where:

$Q_1, Q_2 \cdots Q_N$ = flow rates determined at beginning, end, and intermediate points during sampling.

N = number of points averaged.

The total flow rate is then calculated using the following equation:

$$V_m = \frac{(T_2 - T_1) \times Q_A}{1000}$$

Where:

V_m = total volume (L) sampled at measured temperature and pressure.

T_2 = stop time (minutes).

T_1 = start time (minutes).

$T_2 - T_1$ = total sampling time (minutes).

Q_A = average flow rate (mL/min).

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

$$V_s = V_m \times \frac{\bar{P}_A}{760} \times \frac{298}{273 + \bar{t}_A}$$

Where:

V_m = total sample volume (L) at measured temperature and pressure

$\bar{P}_A$ = average ambient pressure (mm Hg)

$\bar{t}_A$ = average ambient temperature (°C)

5.9 SAMPLE ANALYSIS

This section presents procedures for sample analysis.

5.9.1 Sample Desorption

1. Remove the sample cartridge from labeled culture tube. Connect the sample cartridge (outlet end during sampling) to a clean syringe. The liquid flow during desorption should be in the reverse direction of air flow during sample collection.

2. Place the cartridge/syringe in the syringe rack.

3. Backflush the cartridge (gravity feed) by passing 6 mL of acetonitrile from the syringe through the cartridge to a graduated test tube or to a 5 mL volumetric flask. A dry cartridge has an acetonitrile holdup volume slightly greater than 1 mL. The eluent flow may stop before the acetonitrile in the syringe is completely drained into the cartridge because of the air trapped between the cartridge filter and the syringe Luer® tip. If this happens, displace the trapped air with the acetonitrile in the syringe using a long-tip disposable Pasteur pipet.

4. Dilute to the 5 mL mark with acetonitrile. Label the flask with sample identification. Pipet two aliquots into sample vials with Teflon®-lined septa. Analyze the first aliquot for the derivatized carbonyls by HPLC. Store the second aliquot in the refrigerator until sample analysis.

5.9.2 HPLC Analysis

The HPLC system is assembled and calibrated as described in Section 5.9.3. The operating parameters are as follows:

Column:	Zorbax ODS (4.6 mm I.D. x 25 cm), or equivalent.
Mobile Phase:	60% acetonitrile/40% water, isocratic.
Detector:	ultraviolet, operating at 360 nm.
Flow Rate:	1.0 mL/min.
Retention Time:	7 minutes for formaldehyde with one Zorbax ODS column. 13 minutes for formaldehyde with two Zorbax ODS columns.

Injection Volume: 25 μL.

1. Before each analysis, the detector baseline is checked to ensure stable conditions.

2. The HPLC mobile phase is prepared by mixing 600 mL of acetonitrile and 400 mL of water. This mixture is filtered through a 0.22 μm polyester membrane filter in an all-glass and Teflon® suction filtration apparatus. The filtered mobile phase is degassed by purging with helium for 10-15 minutes (100 mL/min) or by heating to 60°C for 5-10 minutes in an Erlenmeyer flask covered with a watch glass. A constant back-pressure restrictor or a short length of 0.25 mm inside diameter Teflon® tubing should be placed after the detector to eliminate further mobile phase outgassing.

3. The mobile phase is placed in the HPLC solvent reservoir and the pump is set at a flow rate of 1.0 mL/min and allowed to pump for 20-30 minutes before the first analysis. The detector is switched on at least 30 minutes before the first analysis, and the detector output is displayed on a strip chart recorder or similar output device.

4. A 100-μL aliquot of the sample is drawn into a clean HPLC injection syringe. The sample injection loop is loaded and an injection is made. The data system, if available, is activated simultaneously with the injection, and the point of injection is marked on the strip chart recorder.

5. After approximately 1 minute, the injection valve is returned to the "inject" position and the syringe and valve are rinsed or flushed with acetonitrile/water mixture in preparation for the next sample analysis. The flush/rinse solvent should not pass through the sample loop during flushing. The loop is cleaned while the valve is in the "inject" mode.

6. After elution of the DNPH derivatives (See Figure 5-7), data acquisition is terminated and the component concentrations are calculated as described in Section 5.10.

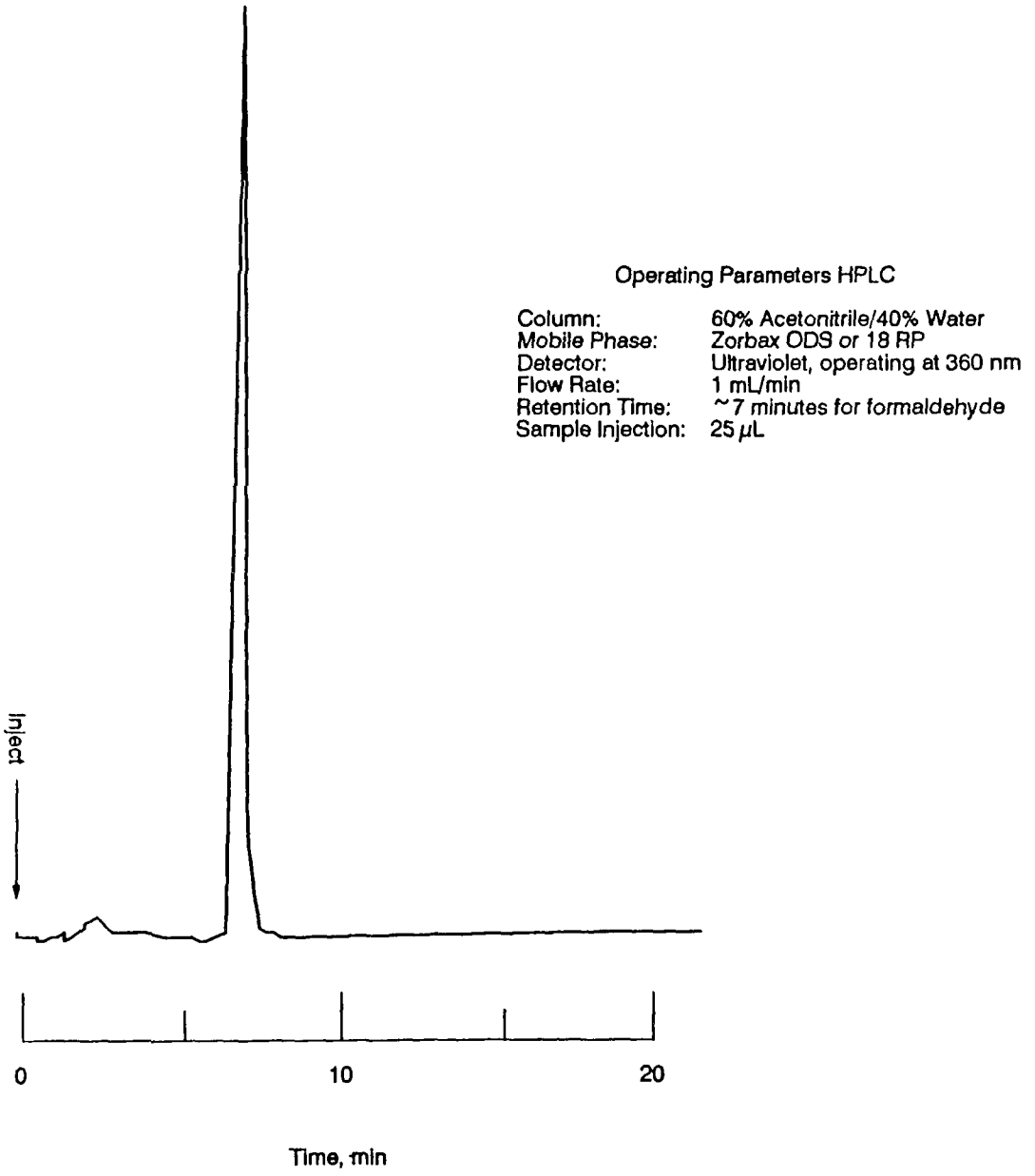


Figure 5-7. Chromatogram of DNPH-formaldehyde derivative.

7. After a stable baseline is achieved, the system can be used for further sample analyses as described above. After several cartridge analyses, buildup on the column may be removed by flushing with several column volumes of 100% acetonitrile.

8. If the concentration of analyte exceeds the linear range of the instrument, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

9. If the retention time is not duplicated (±10%), as determined by the calibration curve, the acetonitrile/water ratio may be increased or decreased to obtain the correct elution time. If the elution time is too long, increase the ratio; if it is too short, decrease the ratio. The chromatographic conditions described here have been optimized for the detection of formaldehyde. Analysts are advised to experiment with their HPLC system to optimize chromatographic conditions for their particular analytical needs.

5.9.3 HPLC Calibration

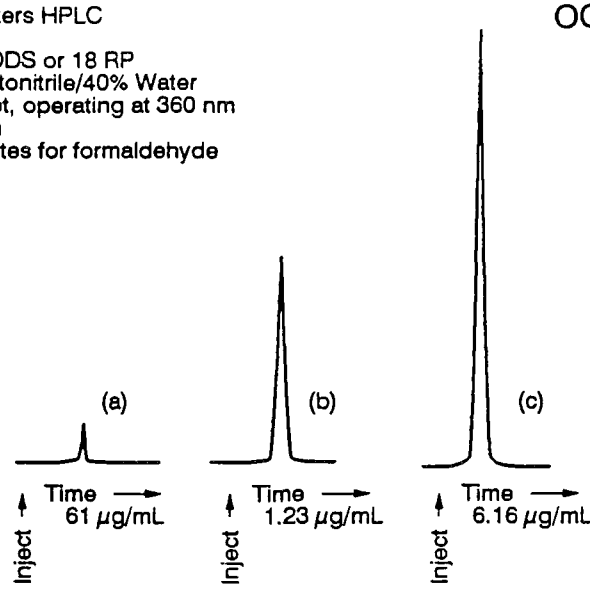
1. Calibration standards are prepared in acetonitrile from the carbonyl derivatives. Individual stock solutions of 100 μg/L are prepared by dissolving 10 mg of solid derivative in 100 mL of mobile phase. These individual solutions are used to prepare calibration standards at concentrations spanning the range of interest.

2. Each calibration standard (at least five levels) is analyzed three times and area response is tabulated against mass injected (See Figure 5-8). All calibration runs are performed as described for sample analyses in Section 5.9.2. Using the UV detector, a linear response range of approximately 0.05-20 μg/L should be achieved for 25 μL injection volumes. The results may be used to prepare a calibration curve, as illustrated in Figure 5-9. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (concentration versus are response) is obtained. The retention times for each analyte should agree with 2 percent.

3. Once linear response has been documented, an intermediate concentration standard near the anticipated levels of each component, but at least 10

Operating Parameters HPLC

Column:	Zorbax ODS or 18 RP
Mobile Phase:	60% Acetonitrile/40% Water
Detector:	Ultraviolet, operating at 360 nm
Flow Rate:	1 mL/min
Retention Time:	~7 minutes for formaldehyde
Sample Injection:	25 µL



Conc	Area Counts
.61 µg/mL	226541
1.23 µg/mL	452166
6.16 µg/mL	2257271
12.32 µg/mL	4711408
18.48 µg/mL	6953812

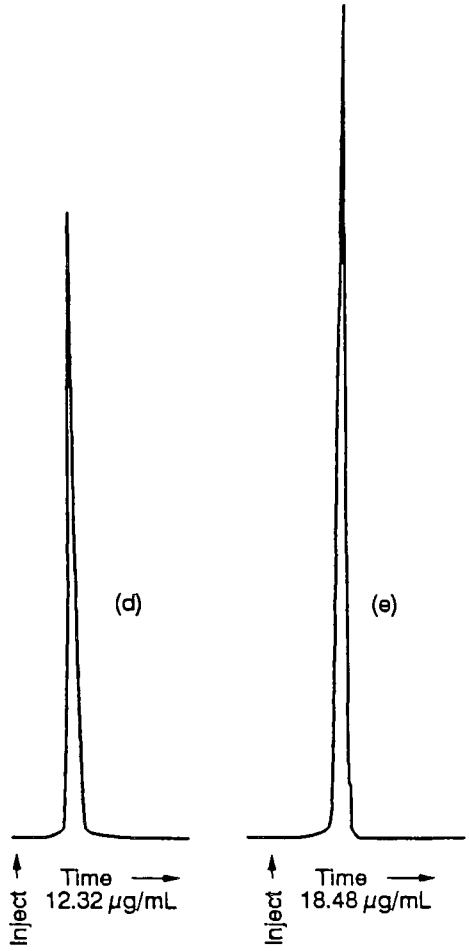


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Figure 5-8. HPLC chromatogram of varying concentrations of DNPH-formaldehyde derivative.

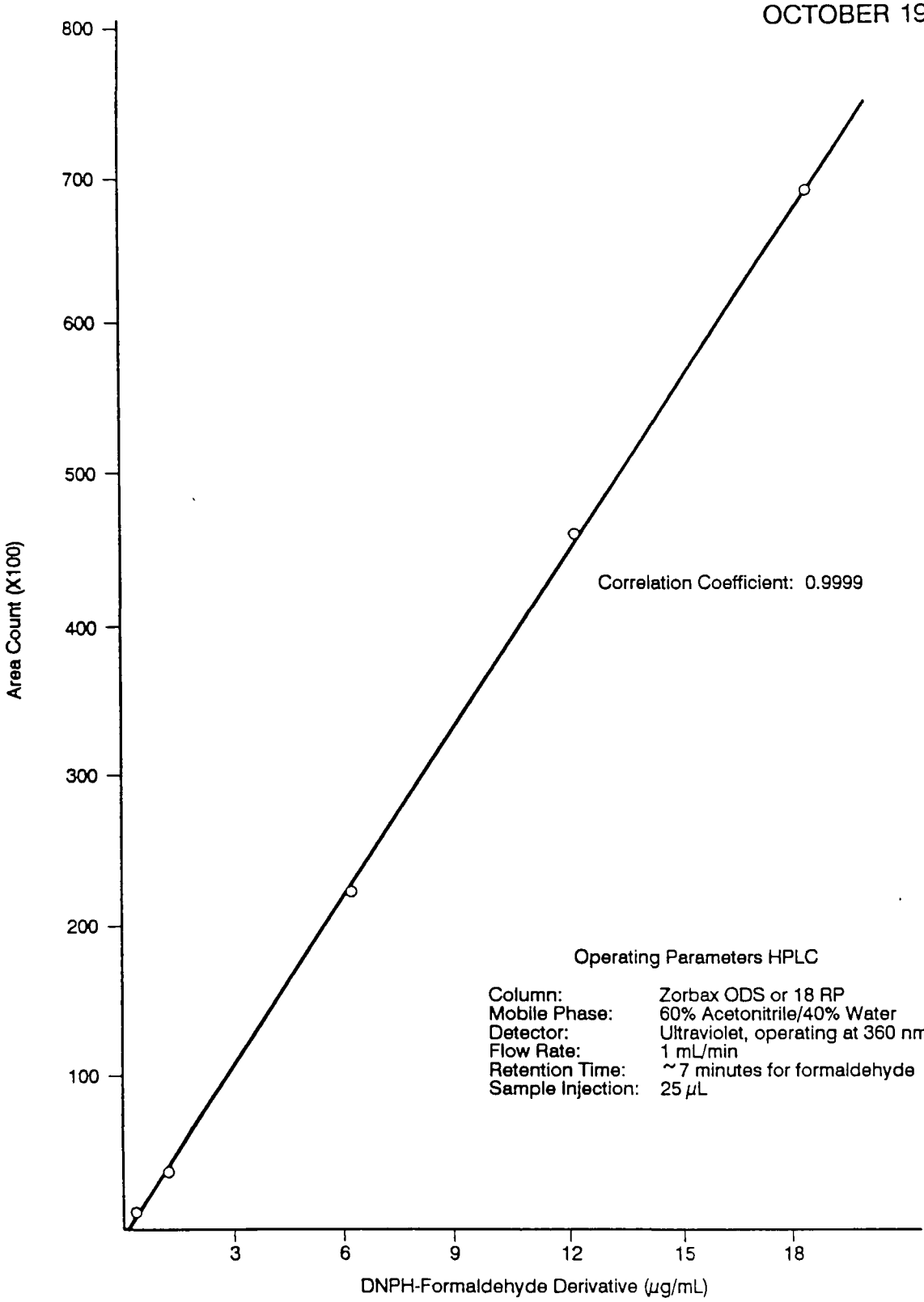

Figure 5-9. Calibration curve for Formaldehyde.

times the detection limit, should be chosen for daily calibration. The day-to-day response for the various components should be within 10% for analyte concentrations 1 μg/mL or greater and within 15-20% for analyte concentrations near 0.5 μg/mL. If greater variability is observed, recalibration may be required or a new calibration curve may be developed from fresh standards.

4. The response for each component in the daily calibration standard is used to calculate the response factor according to the following equation:

$$RF_c = \frac{C_c \times V_i}{R_c}$$

Where:

RF_c = response factor (usually area counts) for the component of interest in ng injected/response unit.

C_c = concentration (mg/L) of analyte in the daily calibration standard.

V_i = volume (μL) of calibration standard injected.

R_c = response (area counts) for analyte in the calibration standard.

5.10 CALCULATIONS

The total mass of analyte is calculated for each sample using the following equation:

$$W_d = RF_c \times R_d \times V_E / V_i$$

Where:

W_d = total quantity of analyte (μg) in the sample.

RF_c = calculated response factor.

R_d = response (area counts or other response units) for analyte in sample extract, blank corrected.

$$= [(A_s)(V_D / V_A) - (A_b)(V_b / V_s)]$$

Where:

A_s = area counts, sample.

A_b = area counts, blank.

V_b = volume (mL), blank.

V_s = volume (mL), sample.

V_E = final volume (mL) of sample extract.

V_I = volume of extract (μL) injected into the HLPC system.

V_D = redilution volume (if the sample was rediluted).

V_A = aliquot used for redilution (if sample was rediluted).

The concentrations of carbonyl compounds in the original sample is calculated from the following equation:

$$C_A = \frac{W_d}{V_m \text{ (or } V_s)} \times 1000$$

Where:

C_A = concentration of analyte (ng/L) in the original sample.

W_d = total quantity of analyte (ng) in sample, blank corrected.

V_m = total sample volume (L) under ambient conditions.

V_s = total sample volume (L) at 25°C and 760 mm Hg.

The analyte concentrations can be converted to ppbv using the following equation:

$$C_A \text{ (ppbv)} = C_A \text{ (ng/L)} \times \frac{24.4}{MW_A}$$

Where:

C_A (ppbv) = Concentration of analyte ppbv.

C_A (ng/L) = is calculated using V_s.

MW_A = molecular weight of analyte.

5.11 PERFORMANCE CRITERIA AND QUALITY ASSURANCE

This section addresses performance criteria and QA issues.

5.11.1 Standard Operating Procedures

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

- Assembly, calibration, and operation of the sampling system, with make and model of equipment used;
- Preparation, purification, storage, and handling of sampling reagent and samples;
- Assembly, calibration, and operation of the HPLC system, with make and model of equipment used; and
- All aspects of data recording and processing, including lists of computer hardware and software used.

Standard operating procedures should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

5.11.2 HPLC System Performance

The general appearance of the HPLC system should be similar to that illustrated in Figure 5-2 above. HPLC system efficiency is calculated using the following equation:

$$N = 5.54 (t_r / W_{1/2})^2$$

Where:

N = column efficiency (theoretical plates).

t_r = retention time (seconds) of analyte.

$W_{1/2}$ = width of component peak at half height (seconds).

A column efficiency of > 5,000 theoretical plates should be obtained.

Precision of response for replicate HPLC injections should be ± 10% or less, day to day, for analyte calibration standards at 1 μg/mL or greater levels. At 0.5 μg/mL level and below, precision of replicate analyses could vary up to 25 percent. Precision of retention times should be ± 2% on a given day.

5.11.3 Process Blanks

At least one field blank or blanks to equal 10% of the field samples, whichever is larger, should be shipped and analyzed with each group of samples. The number of samples within a group and/or time frame should be recorded so that a specified percentage of blanks is obtained for a given number of field samples. The field blank is treated identically to the samples except that no air is drawn through the cartridge.

5.11.4 Method Precision and Accuracy

At least one duplicate sample or duplicates to equal 10% of the field samples, whichever is larger, should be collected during each sampling episode. Precision for field replication should be ± 20% or better. Precision for replicate HPLC injections should be ± 10% or better, day-to-day, for calibration standards. At least one sample spike with analytes of interest or spiked samples to equal 10% of the field samples, whichever is larger, should be collected. Before initial use of the method, each laboratory should prepare and analyze triplicate spiked samples at a minimum of three concentration levels, bracketing the range of interest for each compound. Triplicate nonspiked samples must also be analyzed. Spike recoveries of >80 ± 10% and blank levels as outlined in Section 5.7.1 should be achieved.

5.12 DETECTION OF OTHER CARBONYL COMPOUNDS

Ambient air contains other carbonyl compounds. Optimizing chromatographic conditions by using two Zorbax ODS columns in series and varying the mobile phase composition through a gradient program will enable the analysis of other aldehydes and ketones.

5.12.1 Sampling Procedures

Same as Section 5.8.

5.12.2 HPLC Analysis

The HPLC system is assembled and calibrated as described in Section 5.12. The operating parameters are as follows:

Column:	Zorbax ODS, two columns in series
Mobile Phase:	Acetonitrile/water, linear gradient
(A)	60-75% acetonitrile/40-25% water in 30 minutes.
(B)	75-100% acetonitrile/25-0% water in 20 minutes.
(C)	100% acetonitrile for 5 minutes.
(D)	60% acetonitrile/40% water reverse gradient in 1 min.

(E)	60% acetonitrile/40% water, isocratic, for 15 minutes.
Detector:	Ultraviolet, operating at 3607 nm
Flow Rate:	1.0 mL/min
Sample Injection Volume:	25 μL

The gradient program allows for optimization of chromatographic conditions to separate acrolein, acetone, propionaldehyde, and other higher molecular weight aldehydes and ketones in an analysis time of about 1 hour. Table 5-1 above illustrates the sensitivity for selected carbonyl compounds that have been identified using two Zorbax ODS columns in series.

The chromatographic conditions described here have been optimized for a gradient HPLC system equipped with a UV detector, an automatic sampler with a 25 μL/L loop injector and two Zorbax ODS columns (4.6 x 250 mm), a recorder, and an electronic integrator. Analysts are advised to experiment with their HPLC systems to optimize chromatographic conditions for their particular analytical needs. Highest chromatographic resolution and sensitivity are desirable but may not be achieved.

The carbonyl compounds in the sample are identified and quantified by comparing their retention times and area counts with those of standard DNPH derivatives. Formaldehyde, acetaldehyde, acetone, propionaldehyde, crotonaldehyde, benzaldehyde, and o-, m-, p-tolualdehydes can be identified with a high degree of confidence. The identification of butyraldehyde is less certain because it coelutes with isobutyraldehyde and methyl ethyl ketone under the stated chromatographic conditions. Concentrations of individual carbonyl compounds are determined as outlined in Section 5.10.

Performance criteria and Quality Assurance (QA) activities should meet the requirements outlined in Section 5.11.

5.13 OZONE INTERFERENT

Laboratory tests conducted by EPA have determined that O_3 present in ambient air interferes with the measurement of carbonyl compounds concentrations when using Method TO-11 procedures. Ozone reacts with carbonyl compounds collected on the DNPH-coated silica cartridges. Carbonyl compound losses have been estimated to be as great as 48% on days when the ambient O_3 concentration reaches 120 ppbv. To eliminate this interference problem, an O_3 scrubber has been developed. This section presents the ozone scrubber equipment and procedures for use.

5.13.1 Equipment

Figure 5-10 presents the O_3 scrubber schematically. The equipment required to perform O_3 removal includes:

Copper Tubing - A 36 inch length of 1/4-inch O.D. copper tubing is used as the body of the O_3 scrubber. The tubing should be coiled into a spiral approximately 2 inches in O.D.

Potassium Iodide Solution - The inside surface of the copper coil is coated with a saturated solution of potassium iodide to provide the ozone scrubbing mechanism.

Cord Heater - A 24 inch long cord heater, rated at approximately 80 watts, is wrapped around the outside of the copper coil to provide heat to prevent condensation of water or organic compounds from occurring within the coil.

Thermocouple - A Chromel-Alumel (Type K) thermocouple is located between the surface of the copper coil and the cord heater to provide accurate temperature measurement and control.

Temperature Controller - A Type K active temperature controller is used to maintain the O_3 scrubber at 66°C as referenced by the Type K thermocouple.

Fittings - Bulkhead unions are attached to the entrance and exit of the copper coil to allow attachment to other components of the sampling system.

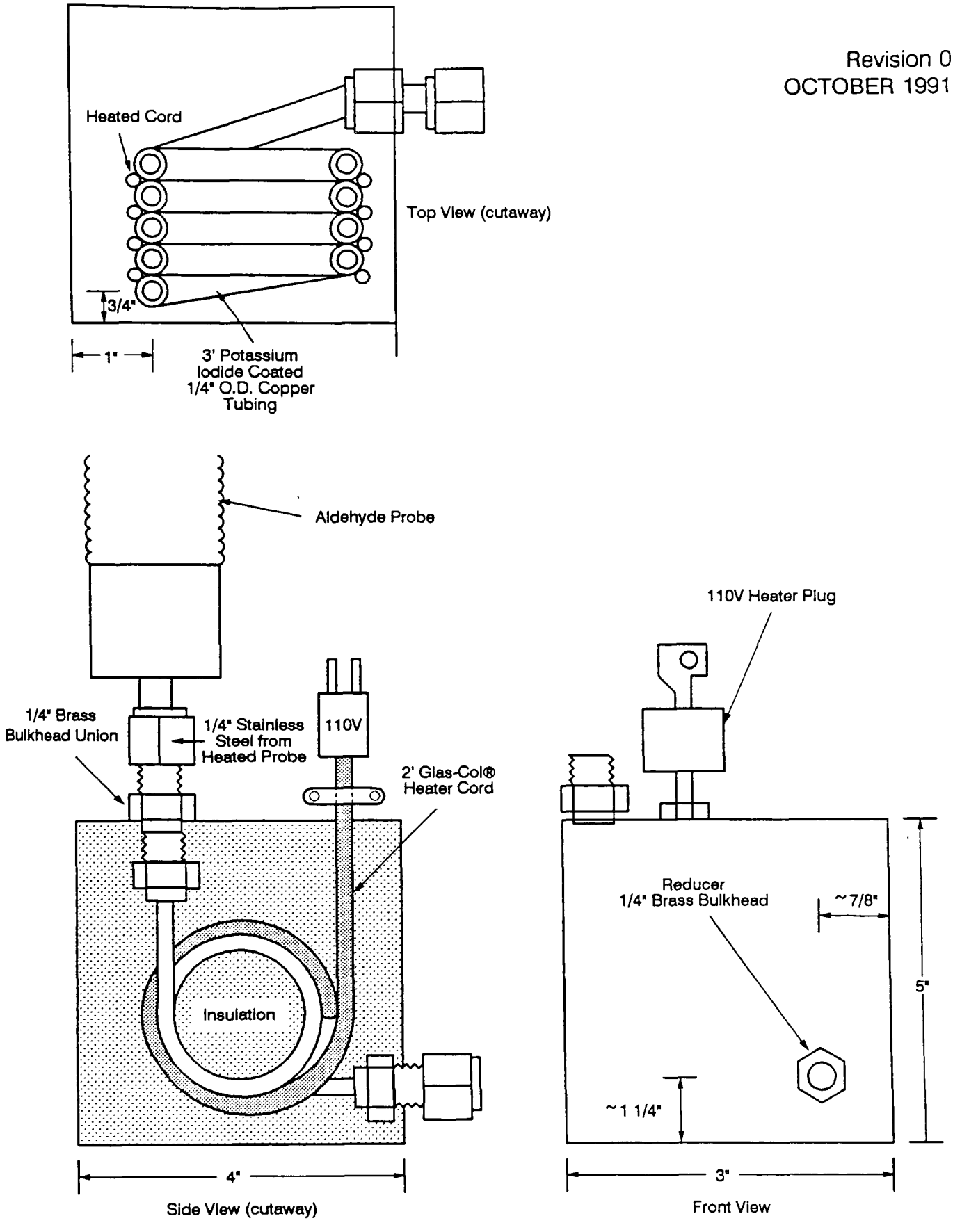

Figure 5-10. Crossectional view of the O_3 scrubber assembly.

Chassis Box - The scrubber assembly is housed in a conveniently sized aluminum chassis box.

5.13.2 Procedure

Position the O_3 scrubber assembly between the sample inlet probe and the DNPH collection cartridges. Set the temperature controller to maintain the scrubber at 66°C. After placement and temperature control are complete, sampling is conducted as described in Section 5.8.

5.14 ALTERNATIVE SUBSTRATE

A number of cartridge devices containing solid sorbents coated with DNPH have been employed for the sampling and analysis of carbonyl compounds. These techniques have met with varying degrees of success. Solid sorbents that have been used include XAD-2®, silica gel, glass beads, Fluorisil, glass fiber filters, and octadecylsilane-bonded silica gel (C18). The use of the C18 substrate coated with DNPH is discussed below.

5.14.1 Advantages of C18 Substrate

The EPA has determined that O_3 reacts with formaldehyde collected on solid sorbents coated with DNPH. The loss from silica gel DNPH tubes has been estimated to be as much as 48% when O_3 concentrations reach 120 ppbv. Preliminary data show that the C18 cartridges may be less prone to O_3 interferences than the silica gel.

5.14.2 Disadvantages of C18 Substrate

Several disadvantages of the C18 cartridge have been observed. One of the major disadvantages is seen in the breakthrough volume for the higher molecular weight aldehydes. Losses depend on the sampling flow rate, sample volume, and compound concentration. The C18 cartridges also appear to have a lower capacity for aldehydes in general. The usefulness of C18 depends on sample volume and compound concentration. Problems with background levels of acetone and certain aldehydes have also been noted. Care must be exercised during the purification of reagents and preparation of the cartridges in order to minimize the presence of these

potential interferents. Batches of cartridges that are prepared or purchased commercially must be subjected to rigorous quality control before being used.

SECTION 6.0

METEOROLOGICAL MONITORING

Surface and upper air meteorology play an important role in the formation and transport of O_3. Consequently, meteorology has an impact on population exposure to O_3. In order to support monitoring objectives associated with model inputs and performance evaluations, meteorological monitoring is required at each PAMS. Surface meteorological measurements should begin within the first year of network operation. Upper air meteorological data for determining mixing heights should be collected for approximately 10 to 20 key days per year corresponding to specific model input requirements. Upper air meteorological measurements should begin as soon as practical after regulation promulgation or the date nonattainment designation is made, whichever comes later.

6.1 MEASUREMENT - SURFACE METEOROLOGY

Ground level meteorological variables to be measured as part of enhanced O_3 network monitoring are as follows:

- Wind direction;
- Wind speed;
- Ambient temperature;
- Barometric pressure;
- Relative humidity; and
- Solar radiation.

These variables are to be monitored at a height of 10 m above ground level.

6.1.1 Equipment

The equipment examples presented in this section are routinely used to measure the meteorological parameters listed. Any equipment meeting performance specifications (e.g., accuracy, precision, resolution, etc.) required by EPA may be used. The EPA meteorological equipment specifications are presented in the "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV - Meteorological Measurements[9]".

Wind Direction - Wind direction measurements are performed using an air foil vane wind direction sensor. This sensor provides azimuth data for use in micrometeorological characterization.

Wind Speed - Wind speed measurements are performed using a 3-cup anemometer. This device provides information on horizontal wind velocity.

Ambient Temperature - Representative ambient temperature measurements are performed using a resistance temperature sensor housed in a motor aspirated radiation shield. These devices provide continuous ambient air temperature measurement with negligible radiation errors for temperature and differential temperature.

Barometric Pressure - Barometric pressure measurements are performed using an atmospheric pressure sensor. This device provides information on barometric pressure of the atmosphere in which it is located.

Relative Humidity - Relative humidity measurements are performed using a relative humidity sensor. This device provides information on relative humidity of the atmosphere in which it is located.

Solar Radiation - Solar radiation measurements are performed using a pyranometer or solarimeter. This device provides information on total sun and sky radiation.

A meteorological tower is used to locate the wind direction, wind speed, ambient temperature, barometric pressure, relative humidity, and solar radiation

sensors at the required monitoring height of 10 m. The sensors are attached to a boom located at the top of the tower. There are 3 basic tower designs available:

- Fixed Tower - the tower is a continuous structure from ground level to the 10-meter height. Access to the sensors requires that the tower be climbed;
- Tilt-over Tower - the tower is a continuous structure from ground level to the 10-meter height, but is hinged at point that allows the tower to be tilted over. The tilting action allows ground level access to the sensors; and
- Telescopic Tower - the tower is constructed of three sections, each approximately 4 meters in length. The top section is smallest in diameter and fits inside the middle section which, in turn, fits inside the base section. The top of the telescopic tower can be positioned at the 10-meter height. The top may also be positioned at a height of 4 meters, to provide for ladder access to the sensors.

6.1.2 Procedure

Operating procedures for surface meteorological equipment will vary with manufacturer and sensor style. Specific procedures of operation should be obtained from the manufacturer. Generally applicable procedures are contained in the "Quality Assurance Handbook for Air Pollution Measurements Systems: Volume IV - Meteorological Measurements[9]".

6.2 UPPER AIR METEOROLOGY - MIXING HEIGHTS

The mixing height is the maximum depth of the atmosphere from the surface up to a vertical height below which thorough mixing of pollutants can occur. The degree of dispersion within this mixed layer is a function of the atmospheric turbulence. Mechanical mixing, a function of wind flow and surface roughness, and thermal mixing, a function of surface heating or cooling, are the main factors that produce atmospheric turbulence.

Numerous studies have been performed to estimate mixing heights. Daytime mixing heights have been determined by means of instrumented aircraft. Mixing

heights were defined by utilizing three parameters: temperature, turbulence, and aerosol concentration. Strong correlations were demonstrated during the daytime between the temperature profile and the depth of the aerosol layer. These studies, along with other related studies, have led to the use of radiosonde data and surface temperature to estimate the daytime mixing height. The criterion for defining the nocturnal mixing layer or the top of the surface based stable layer is less straightforward. The stable layer height has been shown to correspond to the height of the low-level nocturnal wind-speed jet. The determinations of the mixing height are complicated by the presence of clouds, changing air masses, and the influences of large bodies of water or terrain.

The use of mixing heights information in dispersion model plume rise can be limited because of the possibility of elevated inversions at the top of mixing layers. Nearly one-half of a plume that normally would disperse upward would be reflected toward the ground if a strong inversion occurred just above the plume height. This situation could lead to maximum pollutant concentrations. Some of the plume will penetrate the top of the mixing layer depending on the strength of the inversion and the buoyancy of the plume, but this occurrence is not routinely treated in dispersion models.

An infinite series term in the gaussian equation accounts for the effects of the restriction on vertical plume growth at the top of the mixing layer. The method of image sources is used to account for multiple reflections of the plume from the ground surface and at the top of the surface mixing layer.

Mixing heights will be required as input to photochemical air quality models. The models will be applied in determining transport and boundary conditions, and to evaluate emission reductions in O_3 nonattainment areas.

Vertical temperature profiles can be used to estimate mixing heights. These temperature profiles are obtained from radiosonde balloon measurements, tethersondes, or aircraft. These temperature profiles are derived from 0 and 1200 Greenwich Median Time (GMT) upper air sounding measurements, obtained from

radiosonde releases at National Weather Service (NWS) stations. This balloon sensor also measures humidity, wind speed and direction, and pressure at incremented height levels. Tethersondes are balloon sensors tethered to a ground station that measures atmospheric parameters during their vertical ascent. Measurements with this system have been recorded at heights of 1500 meters. Tethered balloon measurements should be taken during moderate to light wind conditions when the balloon would not present an aviation hazard.

In this case, the mixing height is not measured directly but is calculated approximately from the vertical temperature profile or the lapse rate. In the mixing layer, the lapse rate is assumed to be roughly dry adiabatic (unsaturated conditions). Therefore, the mixing height is estimated in terms of this adiabatic process. The urban morning mixing height is interpreted as the height above ground at which the dry adiabatic extension of the morning minimum surface temperature plus 5°C intersects the 1200 GMT vertical temperature profile. The minimum temperature is determined between 0200 and 0600 local standard time (LST). Because NWS upper air measuring stations are located in rural areas, 5°C is added to account for the nocturnal and early morning "heat island" effects. The afternoon mixing height is calculated similarly except the maximum temperature determined between 1200 and 1600 LST is used.

Routine estimates of mixing height can be made using alternative National Oceanographic and Aeronautics Administration (NOAA) methods that employ an adiabatic temperature modification to determine the convective height and surface friction velocity, Monin-Obukhov length, and empirical expressions are used to estimate the nocturnal or mechanical mixed depth.

On-site meteorological measurement programs utilizing these instruments may help provide much needed data for input to air quality models. Existing NWS upper air data are available for large-scale atmospheric motions. Much improvement is needed in terms of the spatial scale of meteorological measurements for special air pollution studies, particularly for neighborhood or Central Business District (CBD)

urban O_3 studies. Enhancement of current upper air data would provide the means of achieving more accurate wind field and mixing height characterizations. Special studies carried out by State and local agencies, academia, and private researchers should include as an integral part of the monitoring plans, recording of upper air wind and temperature data beyond data already available from the NWS or previous air pollution studies.

Because balloon techniques require maintenance and operation, long-term measurement programs using this type of sensor could result in considerable costs. However, costs could be minimized by renting equipment or using a type of balloon sensor requiring fewer personnel for maintenance and with lower material costs. The sensor could be restricted for use only during critical pollution episodes or relevant months of the year.

6.2.1 Measurements

Mixing heights can be determined from direct measurements or estimated from vertical temperature profile measurements. The following is a description of methods used to perform these measurements. The equipment and approaches presented are only recommendations. Alternative measurement devices and approaches may be used based on approval of local regulatory agencies.

6.2.1.1 Direct Measurements --

Remote sensing devices such as acoustic sounders can be used to obtain direct measurements of mixing heights. These devices are commonly known as Doppler Sound Detection and Ranging (SODAR) systems. These devices are effective tools for remote measurement of meteorological variables at heights up to several hundred meters above the surface. The SODAR systems operate on a fundamentally simple principle; however, the systems that control the operations can be complex. The SODAR systems transmit a strong (typically 100-300 watts) acoustic pulse into the atmosphere and listen for the portion of the transmitted pulse that returns. Monostatic acoustic SODAR systems measure temperature structures by using the same acoustic driver to both transmit the pulse and receive the return signal. A bistatic system uses

different antennas to transmit and receive. Monostatic systems generally have collocated antennas, while a bistatic configuration requires an antenna separation distance based on the desired measurement height.

6.2.1.2 Vertical Temperature Profile Measurements --

Upper air sounding measurements can be made to obtain vertical temperature profiles. Alternatively, existing upper air sounding measurements can be obtained from NWS reporting stations. These vertical temperature profiles can be used to estimate mixing heights needed as input to air quality models. The upper air sounding measurements can be made by several means, including:

- Untethered balloons measuring wind speed and direction, pressure, temperature, and humidity by means of sensors that transmit readings by radio to a ground station. This method is commonly used by the NWS.
- Tethered balloons or wiresondes can measure similar atmospheric data. The tether carries signals from the sensor attached to the balloon. Many atmospheric soundings have been recorded using tethered systems, especially by research laboratories.

6.2.2 Mixing Height Measurements

The following procedures are approaches that may be used to measure or determine mixing heights and other upper air data.

6.2.2.1 Doppler SODAR Measurement Approach --

The SODAR approach provides another more direct method for determining mixing height data. The SODAR is a tool for remote measurement of meteorological variables at heights up to several hundred meters above the surface. The SODAR systems are being used more often than in the past for developing meteorological databases required for input to air quality models. The SODARs have been accepted in a few cases for on-site meteorological measurement programs. The applicability of SODAR data must be approved for use on a case-by-case basis.

The SODAR system measurements of wind speed and direction have been the subject of performance demonstrations. Some of these demonstrations have been encouraging. However, measurements of mixing heights through interpretation of SODAR facsimile charts have been more ambiguous and thus are not as reliable as more standard methods for estimating mixing heights.

Successful SODAR operation requires several factors that are unrelated, such as low background noise and optimum meteorological conditions. The level at which 90% data recovery can be achieved varies between daytime and nighttime because of the proximity of noise sources. Theoretically, SODAR daytime range should be superior to night time range.

Meteorological conditions can have a profound effect on SODAR operations. Incident acoustic energy from the SODAR is scattered by a volume of air depending on small temperature and wind speed discontinuities and the direction of propagation. The SODAR detects the backscatter based on the strength of the return signal expressed by velocity and thermal structure functions. Strong return signals can be produced within a convective or stable layer; therefore, the backscattering varies diurnally, seasonally, and synaptically.

The SODAR systems perform best for pronounced temperature differences and perform poorly during stable to neutral conditions. Summer periods result in the greatest thermal structure functions and thus provide the best SODAR range statistics. On the downside, precipitation can enhance noise or destroy the SODAR antenna diaphragm or dish. Other drawbacks include the instrument range and interpretation of data. A convective layer appears on the facsimile chart as a series of spikes. Elevated stable layers are not always strong enough to produce distinct traces. Both of these types of layers may also be out of range of the instrument. Facsimile charts are commonly set at 500 or 1000 meters.

The SODAR data are useful provided a well trained expert interprets the facsimile charts. Strong signals indicating the presence of atmospheric "targets" do not by themselves define mixing heights. Close scrutiny and analysis by a trained

person experienced in meteorology and instrumentation would be required to infer mixing height information through the analysis of time-height patterns of signal strength.

Wind speed and direction can be determined for many heights. For air quality models, particularly dispersion models, wind data at plume height or stack height may be determined by selecting a single measurement height representative of an average plume height or stack height. If model input data are required for heights exceeding the SODAR range, wind speeds can be determined based on a logarithmic profile based on data available from at least three levels. The SODAR system produces a vector-averaged wind speed. Wind direction substitution should come from a level that is at least 100 m high. The cut-off level for model input should be the highest level in which data capture is at least 80 percent. If the data are reviewed and validated, mean wind data values can be used as in put to air quality models.

Mixing heights can be analyzed using the facsimile charts produced by SODAR. Although these data are applicable to air quality models on a case-by-case basis, it is not recommended for routine model use. The primary reason for this is the SODAR's inability to detect signals from atmospheric "targets" for all possible mixing height ranges. The translation of the SODAR facsimile information into usable data is primarily for use in a regulatory context or for model evaluation studies.

Use of a Doppler SODAR system in an on-site program should be closely coordinated with the reviewing agency. An overall operational plan, including QA procedures, should be prepared prior to data collection and data use. The details of the operational plan will differ based on the specific SODAR instrument chosen.

The SODAR equipment siting criteria should be followed closely to obtain return signals with sharp atmospheric peak frequencies. To identify potential noise interferences, the following steps should be taken before siting:

- Determine acceptable noise levels survey to concur with manufacturer's minimum noise requirements.

- Identify potential noise sources.
- Perform a quantitative noise survey to concur with manufacturer's minimum noise requirements.

During siting, orientation of SODAR antennas may depend on how independent air parcel measurements are to be made combined with the complexity of the terrain. The instrument should be aligned with "true north," based on techniques described in the "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV, Meteorological Measurements[9]". The following steps should be considered part of the overall operation of the SODAR equipment.

Siting and Installation:

- Noise survey - qualitative followed by quantitative, if necessary;
- Identification of potential reflection targets;
- Disturbance potential; and
- True north alignment.

Operation and Maintenance Quality Control:

- Specifications of the manufacturer;
- Initial settings of 15 minutes for averaging period and at least 300 m for height;
- Collocated tower (at a minimum height of 10 m); and
- Standard Operating Procedures.

Timely and thorough data review:

- Daily; Weekly; and Monthly procedures.

Quality Assurance Plan:

- Major elements are QC procedures, periodic audits (conducted at 6 month intervals), and data validation.

Data Validation:

- Should be carried out, on a component-specific basis prior to using the data in a model for regulatory purposes. Management plan should incorporate timely review and archiving of data.

Data Use:

- An upper bound should be established where data capture is at least 80%, for developing model inputs. Mixing height may be acceptable on a case-by-case basis.

Data Capture Requirements:

- Valid hours defined as at least three complete valid levels for 30 minutes out of an hour (two 15-min values), must be available 90% of the time.

6.2.2.2 Vertical Temperature Profile Measurement Approach --

Radiosonde balloon techniques and operations involve tethered balloons. The tethered balloon technique has limitations, including manual operation and general safety problems. These systems should be sited as far from aircraft routes or airports as possible. Caution should be taken while using during adverse weather conditions, such as lightning or high winds.

SECTION 7.0

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APPENDIX A

DISCUSSION, ISSUES, AND SELECTED PROCEDURES RELATED TO CANISTER SAMPLING

A1.0 CANISTER SAMPLING ISSUES

The use of canister sampling for collecting and consequently determining concentrations of VOCs in ambient air is an integral part of the sampling strategy and recommended monitoring requirements specified in the proposed revisions to 40 CFR Part 58. The technology utilizes stainless steel canisters with interior surfaces conditioned by the SUMMA® process. The SUMMA® process is a proprietary treatment that passivates the internal surfaces of the canister to minimize surface reactivity. This process allows stable storage for many of the compounds of interest. Passivated stainless steel canisters in a variety of volumetric sizes are commercially available from several manufacturers.

An important advantage of the canister based methodology is that the collected whole air sample can be divided into portions for replicate analyses (permitting convenient assessment of analytical precision) and reanalyses using different analytical systems for specific peak identification and confirmation. General canister sampling procedures are described in Section 2.3 of the document.

A2.0 PRECAUTIONS IN THE USE OF CANISTERS

The canister sampling technique is not without potential problems. Primary problem areas associated with canister sampling include contamination and sample stability. If not controlled, these problems can significantly reduce the quality and usefulness of the data obtained using the canister sampling technique. The general discussion and guidance presented below are intended to provide users with information that should minimize these problems.

A2.1 CONTAMINATION

Contamination may cause additional, unsampled compounds to appear in the sample or increase the concentrations of sampled compounds. Contamination may also cause losses of sampled compounds or may introduce compounds that interfere with gas chromatographic sample analysis. Contamination can originate from the sample canisters, canister cleanup systems, components in the sampling systems or

analytical system, and improper canister storage practices. These problems become more significant as analytical sensitivities are lowered.

To minimize collection system contamination, canisters should be purchased from a reputable supplier who uses high-quality manufacturing and final cleaning procedures. Purchase requirements should specify contamination-free valves and criteria for maximum residual concentrations of target compounds. New canisters should be inspected carefully for proper welding and fittings and should always be blanked (filled with humidified zero air and analyzed) before use to check for contamination. Canisters with excessive contamination should be returned to the supplier or cleaned repeatedly until usable. Some contaminated canisters may appear uncontaminated immediately after cleaning but will outgas contaminants upon storage for several weeks. All canisters in routine use should be blanked frequently, and particularly after extended periods of storage, to be sure that significant contamination does not appear.

Canisters used for ambient or low-level measurements should be segregated from those used for higher-level concentrations or for higher-molecular-weight compounds. Higher-molecular-weight compounds are more difficult to remove from the internal canister surface.

Canister cleanup systems should be constructed of clean, high-quality stainless steel components, contain suitable cryogenic traps, and be operated systematically and meticulously to avoid system contamination from vacuum pump oil, poor quality zero air, water used in humidification systems, room air, or other sources.

Sampling and analytical systems should be constructed of clean, high quality components, with particular attention paid to pumps, valves, flow controllers, or components having any non-metallic surface. Before installation and at periodic intervals, samplers should be carefully tested for contamination or compound loss by analyzing collected samples of zero air and known concentrations of target compounds. This procedure is termed "certification" and allows the potential contamination characteristics of each specific sampling system to be assessed. A

canister sampling system certification protocol, as presented in Section A4.0, should be implemented to ensure that the status of each sampler is known prior to use.

Equipment found to be contaminated should be tested further to attempt to identify the source of the contamination. Contaminated components should be replaced or cleaned, and the system recertified. Minor contamination can often be reduced by purging the system extensively with humidified zero air.

The entire measurement system (sampling and analytical) should be checked regularly for additive and subtractive biases to ensure that measurements obtained are representative. Such checking involves extensive and continual testing of the analytical systems, sampling systems, sample canisters, and canister clean up systems. Program checks also involve using humidified zero air and standards of known concentration, to perform canister blanks and system audits. Collection of samples from collocated systems and other quality assurance techniques should also be performed. This effort represents a substantial overhead for a monitoring project, but there is no other way to ensure that the resulting data are credible.

A2.2 SAMPLE STABILITY

While many compounds have been shown to be stable in canisters over one or more weeks of storage, it is not known how these results extend to the variety of conditions that may be encountered. These conditions include variable quality of the canisters and their SUMMA® treatment, variable moisture content in the sample air, previous history or residual contamination of the canister, sample pressure in the canister above or below atmospheric pressure, storage temperatures, and canister age.

Current information appears to indicate that hydrocarbon VOCs with vapor pressures above 0.5 mm Hg at 25°C store well in canisters. Substituted hydrocarbons, particularly the halogenated hydrocarbons with similar vapor pressure properties, also store well in canisters. Laboratory tests indicate that many oxygenated hydrocarbons such as aldehydes, ketones, and alcohols have less desirable storage properties. As a general rule, organic compounds that are soluble

in water do not store well in canisters. Target analytes for which there is little stability information or for which storage stability characterization is questionable should be specifically tested for storage stability in the canisters that will be used and under typical conditions of use. Sample stability is addressed in more detail in Section A5.0.

A2.3 CANISTER LEAKAGE

There are three potential sources of canister leakage. These sources are:

- Faulty canister welds;
- Leakage at the connection of the valve to the canister; and
- Leakage through the valve.

A faulty weld is a manufacturing defect. Faulty welds are fairly rare and can be detected by conducting leakage acceptance tests. Canisters may also sustain physical damage. Damaged canisters should be repaired and retested for leaks.

Leaks at the connection of the valve to the canister are the most troublesome type of leak. Welding the valve to the canister virtually eliminates such leaks but makes subsequent valve replacement impractical and expensive. Usually, the valve is connected to the canister using a standard tubing compression fitting. Properly installed, these fittings are very reliable. However, these fittings can loosen when an operator improperly opens and closes the valve. If the valve rotates with respect to the canister during opening and closing, small leaks in this fitting can occur. Overtightening the fitting in an attempt to prevent such movement exacerbates the problem, as does any other physical strain on the connection. Short of welding the valve to the canister, vulnerability to leakage in this connection can be greatly reduced by:

- Using an oversize fitting (e.g., 5/16-inch or 3/8-inch rather than 1/4-inch);

- Equipping the canister with a valve guard to protect the valve from physical strain; and
- Mechanically clamping or fastening the valve to the canister or valve guard to prevent rotation during opening or closing.

These measures are offered by some canister manufacturers and should be specified. Even with these precautions, periodic retesting of canisters is necessary to ensure that no significant leaks in the valve connection develop with extended use.

Leaks through the valve can occur if the valve seat has become damaged through wear or overtightening. The practice of installing a cap on the valve connection when the canister is not connected to a sampling system effectively minimizes sample or vacuum loss during periods of storage.

A canister may quickly be tested for obvious leaks by pressurizing it with zero air and submerging it in clean water to look for bubbles. To check for microleaks, the canister should be evacuated and its pressure observed for several days with a sensitive absolute pressure gauge connected. This test is performed with the canister valve open. To check the valve for leakage, evacuate the canister, check the absolute pressure, close the valve, and disconnect the pressure gauge, leaving the valve connection open. Then reconnect the pressure gauge and check the pressure several days later. The canister pressure should not increase more than a few mm Hg during that period.

Canisters with excessive leaks must be repaired and repassivated or replaced, but those with relatively minor microleaks can be used for many applications if precautions are taken. Canisters determined to have microleaks can be prepared for use just prior to sample collection and analyzed promptly after sample collection. Reduction of the pre- and post-sampling time reduces the potential for bias. Between evacuation and analysis, the canister connection should be tightly capped, and the canister should be stored in a well ventilated, non-contaminated area. Avoid storing the canisters in automobiles and laboratories where organic materials are used.

Storage or shipping containers should be of an all-metal construction, well ventilated, and should avoid the use of foam padding and other organic materials.

A2.4 HISTORICAL CANISTER LOG

A historical record should be maintained for each canister to record the type of sampling service for which the canister is employed. This record will include the dates samples were taken, type of samples taken (ambient or source sample), dates of cleaning, dates of measuring cleanliness of the canister, and dates for leak checking the canister. Canisters used for ambient sampling should not be used for source sampling, and vice versa. Canisters used for source sampling typically contain much higher concentrations of organic compounds. Corrosive gases may damage not only valve seats in the inlet canister valve, but also the interior surface of the canister itself. The SUMMA®-treatment of the interior of a stainless steel canister is designed to passivate the surface, not only to decrease any catalytic potential of the surface for chemical reaction of the components in the sample, but also to decrease the active centers for adsorption of compounds, (e.g., organic pollutants), which are found in the ambient air samples taken.

A3.0 CANISTER CLEANING

The canister cleaning procedure and equipment described in this section are recommended when obtaining integrated whole ambient air samples for subsequent analysis of VOCs. The cleaning procedure involves purging the canisters with cleaned humidified air and then subjecting them to high vacuum.

The purpose of canister cleaning is to ensure that the canister interior surfaces are free of contaminants and that the canister meets a predetermined cleanliness criterion (i.e., $\leq$0.20 ppmC NMOC). This level of cleanliness minimizes the potential for carryover of organic pollutants from one sample to the next, and helps ensure that the samples collected are representative.

A3.1 EQUIPMENT

The equipment required to clean canisters includes a source of clean, humidified air to pressurize the canisters to a pressure of 20 psig, and a vacuum system for evacuating the canisters to 0.5 mm Hg absolute pressure. Air from a standard oil-less air compressor will contain pollutants from the ambient air. In addition, various VOCs will be found in the compressed air because of the lubricants used in the air compressor. Hydrocarbon-free air may be purchased in cylinders and humidified before being used in the cleaning process; however, this approach may be cost-prohibitive. Figure A3-1 presents the schematic of a canister cleanup system that is suitable for cleaning up to 16 canisters concurrently. This, and any alternative system must include a vacuum pump capable of evacuating the canisters to an absolute pressure of 0.5 mm Hg. The equipment is designed so that one manifold of eight canisters is undergoing the pressurization portion of the cleaning cycle while the other manifold of eight canisters is undergoing the vacuum portion of the cleaning cycle.

The following equipment is incorporated in a canister cleaning system.

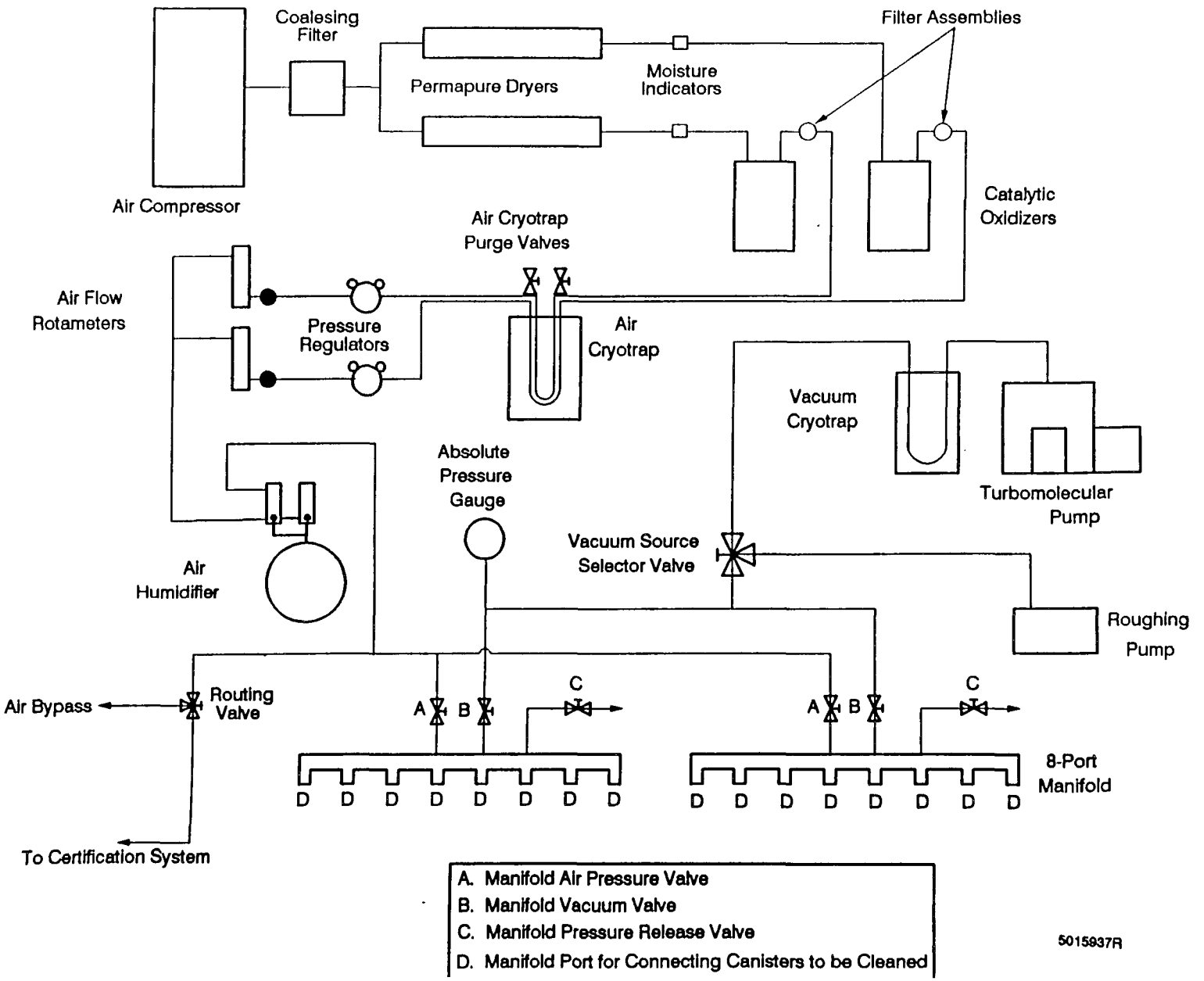
Air Compressor - A shop or laboratory oil-less air compressor used to provide the air supply for the canister cleanup apparatus.

Coalescing Filter - A coalescing filter designed to remove condensed moisture or hydrocarbon contaminants present in the air supplied from the air compressor.

Permeation Dryers - Permeation dryers used to dry the air prior to introduction into the catalytic oxidizers. Two permeation dryers are installed in parallel.

Moisture Indicators - Visual moisture indicators installed in the transfer lines between the permeation dryers and the catalytic oxidizers to monitor the performance of the permeation dryers.

Catalytic Oxidizers - Catalytic oxidizers installed in the clean-air system to oxidize any hydrocarbon contaminants that may be present in the air supplied by the air compressor. For best results and most efficient operation of the catalytic oxidizers, manufacturer's specifications should be strictly followed.


Coalesing Filter
Filter Assemblies
Permapure Dryers
Moisture Indicators
Air Compressor
Catalytic Oxidizers
Air Cryotrap Purge Valves
Air Flow Rotameters
Pressure Regulators
Air Cryotrap
Vacuum Cryotrap
Turbomolecular Pump
Absolute Pressure Gauge
Vacuum Source Selector Valve
Air Humidifier
Roughing Pump
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To Certification System
A. Manifold Air Pressure Valve
B. Manifold Vacuum Valve
C. Manifold Pressure Release Valve
D. Manifold Port for Connecting Canisters to be Cleaned
5015937R

Filter Assemblies A 5-micron sintered stainless steel filter installed in the filter housing assembly downstream of each catalytic oxidizer to trap any particulate material that may be present in the air stream leaving the catalyst bed of the oxidizer.

Air Cryotrap and Purge Valves - The air cryotrap allows the cleaned air supply lines to be subjected to cryogenic temperatures to condense (1) water formed during the oxidation of hydrocarbons, (2) any remaining unoxidized hydrocarbons, and (3) other condensables. Air cryotrap purge valves are used to purge these condensed components from the air cryotrap, as described in the operating procedure described below.

Pressure Regulators - A high purity dual stage pressure regulator installed in each branch of the air supply line so that the maximum pressure attained during the cleanup procedure is controlled at 20 psig.

Flow Controllers - The flow control devices shown in the canister cleanup schematic (Figure A3-1) are metering valves. The flow rates are set not to exceed the maximum recommended flow rate through the catalytic oxidizers.

Air Flow Rotameters - Rotameters installed in the air supply lines to allow monitoring of the flow rates through the catalytic oxidizers.

Air Humidifier - The air humidifier shown in Figure A3-1 is a SUMMA®-passivated, double-valve stainless steel canister with an inlet dip tube that projects to the bottom of the sphere. HPLC-grade water is placed in the canister prior to use. Two rotameters are connected to control air flow so that about 80% of the flow rate can be directed to the humidifier (to bubble through the water to become saturated), while the other 20% bypasses the humidifier. This procedure allows the humidification apparatus to supply cleaned, dried air that has been humidified to a relative humidity of ~80 percent.

Manifold Air Pressure Valves - Manifold air pressure valves used to isolate the air supply system from the manifold, or to make the pressurized air available to the manifold.

Eight-Port Manifolds - Eight-port manifolds designed to allow up to eight canisters at a time to be connected. Fewer canisters may be connected to the manifold if the vacant ports are sealed off with a plug fitting.

Roughing Pump - The roughing pump shown in Figure A3-1 is a high-capacity diaphragm vacuum pump used to remove the moist cleaning air from the canisters while evacuating the canisters to about 100 mm Hg absolute. The high moisture content of the cleaning air contained in the canisters will not impede the function of this diaphragm style pump, but will impede the performance of the high-vacuum pump.

High-Vacuum Pump - A high-vacuum pump capable of reducing the pressure in the canisters to 0.5 mm Hg absolute. High moisture content will impede the performance of the high-vacuum pump.

Vacuum Cryotrap - A U-shaped trap located in the vacuum manifold that is sized to fit inside a Dewar flask filled with cryogen. The purpose of this trap is to condense water vapor from the air that is pulled from the canisters during the vacuum cycle and prevent back-diffusion of organic vapors from the high-vacuum pump into the canisters during the vacuum cycle of the cleaning procedure.

Vacuum Source Selector Valve - The vacuum source selector valve is a multiposition valve used to route either the roughing pump or the high vacuum pump to the eight-port manifold assemblies or isolates both pumps from the manifold assemblies.

Compound Absolute Pressure Gauge - An absolute pressure gauge used to measure the pressure attained in the canisters during the vacuum and pressurization cycles of the cleaning procedure. The absolute pressure gauge must be able to measure absolute pressures from 40 psig down to 0.5 mm Hg absolute.

Air Bypass Valve - The air bypass valve is used to allow for a 1.0 L/min flow of air to be maintained through the catalytic oxidizers when the cleaning system is not in use. This flow prevents the oxidizers from overheating when the clean up system is not in use.

Manifold Valves The manifold vacuum valve and the manifold pressure valve are used to apply vacuum or pressure to the canisters, as required during the cleaning procedure.

Manifold Ports - The manifold ports permit connection of the canisters to the manifold. Fittings that mate directly with the canister valve fittings are used. These connections will not leak during the pressurization portion or the vacuum portion of the cleaning procedure.

A3.2 CLEANING PROCEDURE

The cleanup system is prepared for use by checking the position of all the valves. All valves should be closed initially, with the exception of the air bypass valve. Fill both the air source and vacuum pump vacuum flasks with cryogen and actuate the high-vacuum pump. Ensure that these vacuum flasks remain filled with cryogen throughout all cleanup activities. The inlet bellows valve on the humidifier is opened and the valve on the wet air rotameter is also opened. Close the valve on the dry air (bypass) rotameter to allow the air to become humidified. Allow the system to stabilize for 10 minutes. After preparing the cleanup system, canister cleaning is performed using the following procedure.

1. Connect the canisters to be cleaned to the cleaning manifolds. Record the canister numbers and pre-cleanup concentrations, if available, as determined by the last analysis, in the appropriate cleanup and canister history log book. Record data pertinent to the vacuum and pressure cleanup cycles as they are completed.

2. Remove collected moisture from the air cryotraps by opening and immediately closing the air cryotrap purge valves. Removal of the collected moisture should be performed at the beginning of each pressure cycle, so that the cryotraps do not plug with ice.

3. Release pressure from the canisters by opening all the canister bellows valves and then opening the manifold pressure release valve. When venting is complete, leave the canister bellows valves open and close the manifold pressure release valve.

4. Begin the first vacuum cycle by actuating the roughing pump, placing the vacuum source selector valve in the roughing pump position, and opening the manifold vacuum valve.

5. Evacuate the canisters to approximately 100 mm Hg, as indicated by the absolute pressure gauge.

6. Position the vacuum source selector valve in the high-vacuum pump position.

7. Evacuate the canisters to 0.5 mm Hg absolute pressure (or less) and maintain the vacuum for 30 minutes.

8. Close the manifold vacuum valve after the 30-minute high-vacuum period has been completed.

9. Begin the first pressure cycle by purging the air cryotraps (refer to Step 2) and then closing the air bypass valve. Open the manifold air pressure valve. Using the air flow control valves, adjust the air flow rate to the manufacturer's recommended optimum flow rate for the oxidizers, as indicated by the air rotameters.

10. Check the pressure regulators to verify that they are set to deliver a final pressure of 20 psig. Fill the canisters to 20 psig. As the final pressure is attained, the flow rates indicated on the air rotameters will drop to zero, regardless of the setting on the flow controllers because the pressure in the canisters and the pressure at the exit of the regulators reach equilibrium.

11. Close the manifold air pressure valve when filling is complete. Open the air bypass valve and adjust the air flowmeters to 1.0 L/min.

12. Release the pressure from the canisters after they have been under a 20 psig pressure for 30 minutes by opening the manifold pressure release valve.

13. Repeat steps 4, 5, 6, 7, and 8 for Vacuum Cycle 2.

14. Repeat steps 9, 10, 11, and 12 for Pressure Cycle 2.

15. Repeat steps 4, 5, 6, 7, and 8 for Vacuum Cycle 3.

16. Repeat steps 9, 10, and 11 for Pressure Cycle 3.

17. Close all of the bellows valves on the canisters.

A3.3 BLANKING PROCEDURE

Prior to initial use, the cleanliness of all canisters should be assessed. After the initial blanking of 100% of the canisters, the blanking frequency can be reduced. One canister on a cleaning bank of eight canisters is considered representative and should be blanked. The selection of the canister to be blanked (from the bank of eight canisters) is determined by selecting the canister with the highest pre-cleanup total NMOC concentration on the manifold. This canister is selected because the potential for compound carryover is most likely to be the largest of any of the canisters on the manifold. The blank sample is analyzed using Compendium Method TO-12 (See Section 3.0 in the main document). If this measurement meets the predetermined cleanliness criterion (i.e., $\leq$0.020 ppmC), then the other canisters on the manifold are considered clean. Blanking is a part of the overall canister cleanup procedure, and is described below.

1. Select the canister to be blanked by referencing the cleanup history logbook to determine the canister with the highest pre-cleanup total NMOC concentration.

2. Verify that all the canister bellows valves are closed. Disconnect the canister selected to be blanked.

3. Analyze the air in the canister using Compendium Method TO-12 (See Section 3.0). If the canister analysis meet the predetermined concentration criterion (i.e., $\leq$0.020 ppmC), then the blanked canister and all the other canisters on the bank of eight canisters are considered clean.

4. If the canister does not meet the concentration criterion, it is reconnected to the manifold. The entire bank of canisters is given another vacuum and pressure cycle. After the additional cycle, the same canister is blanked again.

5. After the canister is blanked and has met the concentration acceptance criterion, it is reconnected to the manifold.

A3.4 FINAL EVACUATION PROCEDURE

After cleaning and blanking, the canisters are ready for final evacuation in preparation for sample collection. The procedure for final evacuation is described below.

1. Release the pressure from the canisters by opening the manifold pressure release valve and opening all of the canister bellows valves. When venting is complete, close the manifold pressure release valve.

2. Begin final evacuation of the canisters by actuating the roughing pump, placing the vacuum source selector valve in the roughing pump position and opening the manifold vacuum valve.

3. Evacuate the canisters to approximately 100 mm Hg, as indicated by the absolute pressure gauge.

4. Activate the turbomolecular vacuum pump, checking to be sure there is liquid cryogen in the vacuum cryotrap.

5. Switch the vacuum source selector valve to the high-vacuum pump position. Allow the canisters to evacuate to 0.5 mm Hg, as indicated by the absolute pressure gauge.

6. Close the canister bellows valves on all of the canisters on the manifold. Close the manifold vacuum valve.

7. Disconnect the canisters from the manifold and remove any old identification tags. Store the cleaned canisters in the designated storage area.

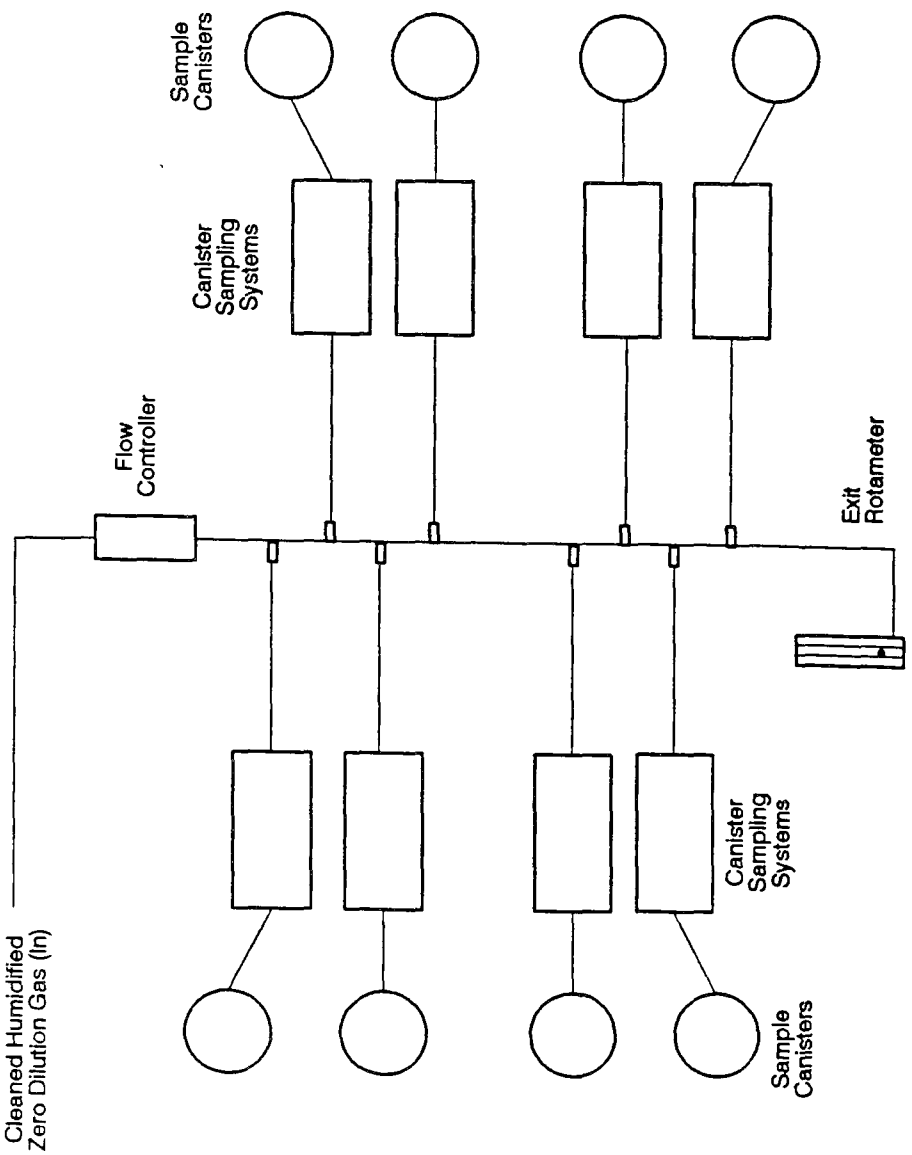
A4.0 CANISTER SAMPLING SYSTEM CERTIFICATION

Canister sampling systems should exhibit non-biasing characteristics before being used to collect samples. These sampling systems should be subjected to laboratory certification to quantify any additive or subtractive biases that may be attributed directly to the sampling system. The following procedure is recommended for certifying canister sampling systems. Alternative approaches are acceptable provided they are properly described and documented.

A challenge sample, consisting of a known concentration blend of organic compounds in clean humidified zero air, is collected through the sampling system. A reference sample is concurrently collected using a dedicated mass flow controller that has been characterized prior to each use. The samples are then analyzed using a GC system that is equivalent to or better than the GC system that will be used to analyze field volatile organic O_3 precursor samples. The percent recoveries for target challenge compounds are calculated, based on the determined reference sample concentrations. Recoveries of each of the challenge compounds should be in the range of 80-120% of the concentrations determined for the reference sample. A system-specific overall recovery should also be calculated. The overall recovery is the average of the individual compound recoveries. Each sampling system should have an overall recovery of 85-115 percent. The challenge sample percent recoveries are used to gauge potential additive and/or subtractive bias characteristics for each specific sampling system[10].

In addition to characterizing the sampling system with a blend of VOCs, the system should also be characterized using humidified zero air. A humidified zero air blank sample is collected through the sampling system to further gauge the potential for additive bias. The blank samples can be analyzed for specific target analytes, total NMOC, or both, depending on individual program requirements. Two criteria apply to the blank portion of the certification process: a determined concentration criteria of 0.2 ppbv or less for any individual target compound is required if speciation analysis of the blank sample is performed, and a total NMOC concentration criteria of 10 ppbC or less is also required.

Sampling is accomplished using dedicated manifolds for both the zero and challenge phases of the certification procedure (See Figures A4-1 and A4-2). Zero air supplied to the zero manifold should be hydrocarbon-free and humidified to approximately 70% relative humidity. The zero air should be supplied from a canister cleaning system similar to the one described in Section A3.1.


Sample Canisters
Canister Sampling Systems
Flow Controller
Exit Rotameter
Canister Sampling Systems
Sample Canisters
Cleaned Humidified Zero Dilution Gas (In)

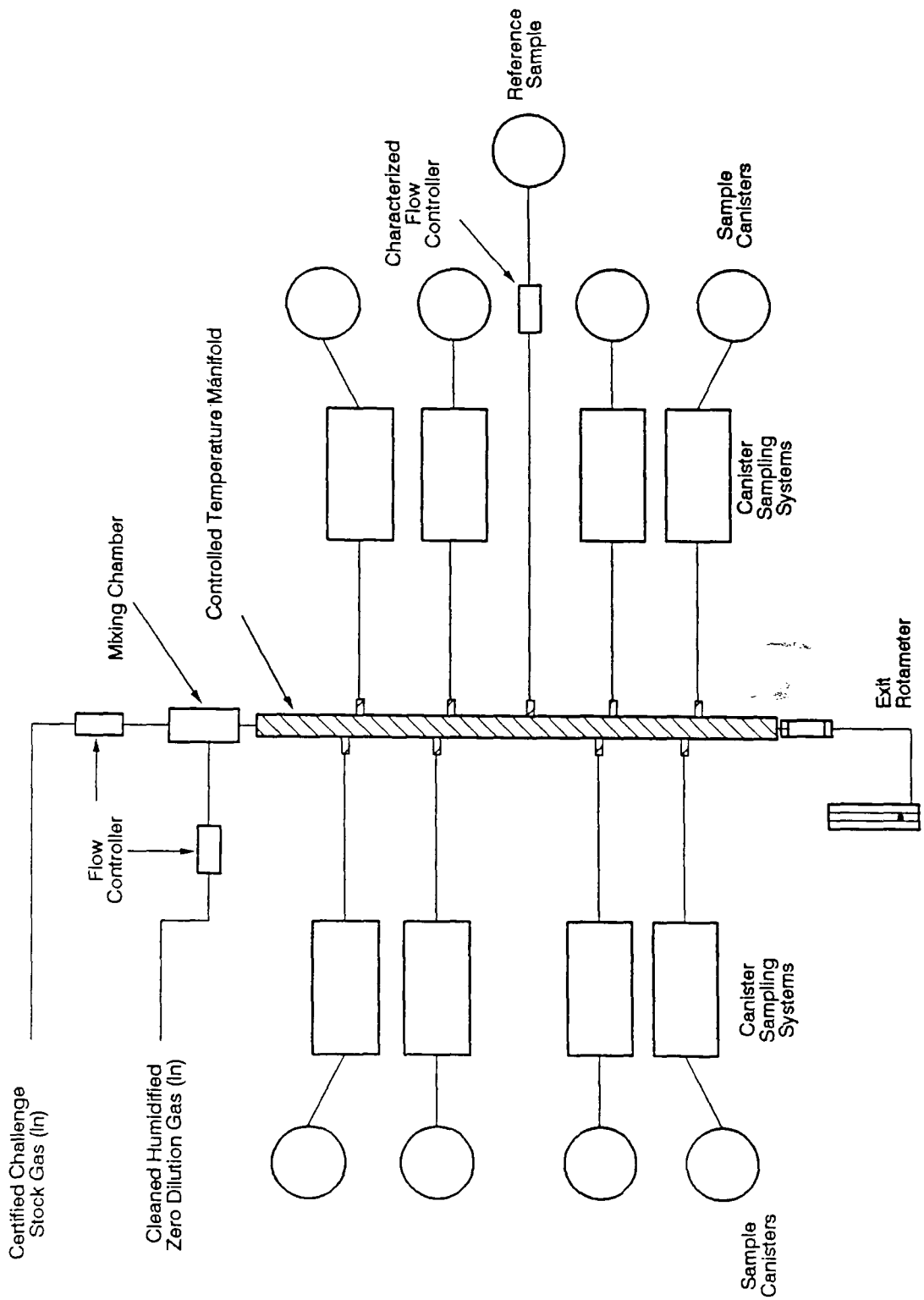


Figure A4-2. Canister sampling system certification schematic - challenge gas.

A4.1 EQUIPMENT

The equipment required to perform canister sampling system certification is described below. The equipment listed is consistent with the systems presented in Figure A4-1 and A4-2.

Mass Flow Controllers - Mass flow controllers located at the inlets to the manifolds. Mass flow controllers are used to regulate the certification pollutant, diluent, and zero air flow rates. Also, a dedicated, characterized mass flow controller is used to collect reference samples.

Mixing Chamber - A mixing chamber located between the outlets of the mass flow controllers and the inlet of the challenge manifold. The mixing chamber is a stainless steel vessel with opposed inlet and outlet ports that cause the blend of challenge gases and the diluent gas to swirl and mix prior to entering the challenge manifold. The mixing chamber is used to ensure that a homogeneous blend of challenge gas is delivered to the challenge manifold. The zero manifold does not require a mixing chamber.

Challenge Gas Manifold - A challenge gas manifold constructed of 1/8-inch O.D. chromatographic grade stainless steel tubing and 1/8-inch tee fittings. The challenge manifold is used to distribute challenge gas to the individual sampling systems being certified. The number of sample ports provided on the challenge gas manifold is determined by the number of sampling systems to be certified simultaneously.

Zero Air Manifold - A zero air manifold constructed of 1/4-inch O.D. chromatographic grade stainless steel tubing and 1/4-inch fittings. The zero manifold is used to distribute zero air to the individual sampling systems being certified. The number of sample ports provided on the zero air manifold is determined by the number of sampling systems to be certified simultaneously.

Exit Rotameter - An exit rotameter located at the outlet of both the challenge gas and zero air manifolds. The exit rotameter is used to visually indicate that an

excess of challenge gas or zero air is present in the respective manifolds during certification sample collection.

Cord Heater - A cord heater rated at 80 watts spiraled around the outside of the challenge manifold. The cord heater is used to heat the challenge manifold to 80°C. Heating the challenge manifold helps to reduce the potential for loss of challenge gas compounds to the walls of the challenge manifold. The zero manifold is not heated.

Temperature Controller - A temperature controller used in conjunction with the cord heater to actively regulate the challenge manifold temperature at 80°C.

A4.2 CERTIFICATION PROCEDURE

The procedure to perform canister sampling system certification is presented below.

1. Perform a positive pressure leak check of all sampling system fittings. Attach source of pressurized air to the inlet of the system. Coat the fittings with indicating bubble solution to locate leaks. Repair any leaks found. Perform a negative pressure leak check. Attach an evacuated canister to the exit of the sampling system. Open the canister bellows valve and record the initial vacuum, indicated by the sample pressure gauge. Close the canister bellows valve and view the sample pressure gauge and determine whether vacuum is maintained. The system is leak free if the vacuum is maintained. If vacuum is not maintained, the system is not leak free. Repair leaks and retest the system.

2. Connect the sampling systems and the reference sample flow controller to the zero manifold and purge them with humidified zero air for 48 hours. The purge air should be simultaneously routed to the challenge manifold to clean and prepare it for challenge sample collection. Terminate the humidified zero air flow at the end of the 48 hour period.

3. Purge the sampling systems, reference system, and manifold with dry zero air for 1 hour to removed accumulated moisture. During the dry purge, determine the certification flow requirements using the following equation:

$$Q_T = [((Q_s \times N_1) + (Q_R \times N_2)) \times F_1]$$

Where:

Q_s = Individual sampling system collection flow rate (mL/min)

N_1 = Number of sampling systems

Q_R = Reference system collection flow rate (mL/min)

N_2 = Number of reference systems

F_1 = 2.0; Excess flow factor

Q_T = Total required flow rate (mL/min)

4. Determine the pollutant and diluent flows required to generate the desired concentration of challenge gas using the following equations:

Step 1

$$F_2 = C_1 / C_2$$

Where:

C_1 = Desired challenge gas concentration (ppbv)

C_2 = Concentration of the stock cylinder (ppbv)

F_2 = Dilution factor (for use in next equation)

Step 2

$$Q_P = F_2 \times Q_T$$

Where:

Q_T = Total required flow rate

Q_P = Pollutant flow rate (mL/min)

Step 3

$$Q_D = Q_T \; Q_P$$

Where:

Q_D = Diluent flow rate (mL/min)

5. Generate and deliver the challenge gas to the challenge manifold and sampling systems. Condition the challenge manifold with the challenge gas for 10 minutes, with the sampling systems off. Condition the challenge manifold an additional 10 minutes with the sampling systems on, and in the bypass mode. Connect a clean evacuated canister to each sampling system.

6. Collect the challenge and reference samples. Conduct challenge sample collection according to the normal specified operation of the sampling system.

7. Connect the sampling systems to the zero manifold and purge with zero air, humidified to 100% relative humidity, for 48 hours. Dry the manifold and samplers with dry zero air for 1 hour. Adjust the zero air stream to 70% relative humidity. Condition the zero manifold for 10 minutes with the sampling systems off. Condition the zero manifold an additional 10 minutes with the sampling systems on, and in the bypass mode. Connect a clean evacuated canister to each sampling system.

8. Collect the humidified zero air blank samples. Conduct the blank sample collections using the same sampling system operating procedures used during the challenge sample collection.

9. Analyze the zero and challenge samples and calculate the % recoveries.

A5.0 SAMPLE STABILITY

Sample stability refers to the representativeness of the ambient air sample contained in a canister after sample collection and storage. For the sample to be stable, the compound matrix and concentrations of the sample must not change significantly with time. There are at least four ways that the concentration of target compounds in an ambient air sample may change after sampling:

- Chemical reaction of a compound with another compound or with itself;
- Adsorption or desorption on the interior surfaces of the canister or on particulate matter in the sample from the ambient air;
- Dilution of the sample with another gas or liquid after sampling; and
- Stratification of the sample in the canister.

A number of studies[11,12,13] have shown that a wide range of VOCs are stable in canisters for at least 30 days. Most of the reported studies were performed in SUMMA®-treated stainless steel canisters at pressures above atmospheric pressure. SUMMA® passivation of the interior surfaces of the canisters is designed to passivate the surfaces to minimize catalytic activity on the surface and to reduce the number and activity of adsorption sites on the canister's interior walls.

A5.1 POSITIVE PRESSURE SAMPLES

Samples obtained so that the final sample pressure is above atmospheric pressure (typically 5 to 20 psig) are considered positive pressure samples. Positive pressure samples are the least likely to be affected by the attainment of adsorption equilibrium in the canister after sampling. The only precaution recommended in this regard is that after sampling, no sample is withdrawn until the sample has been in the canister for at least 24 hours to allow the adsorption equilibria to stabilize.

A5.2 DILUTED SAMPLES

Samples may be diluted by adding pressurized, clean air, N_2, or other gaseous diluent. It is recommended that at least 24 hours elapse between dilution of a sample and removal of an aliquot for analysis.

A5.3 REPEATED ANALYSES

At least 24 hours must elapse between removal of aliquots from a sample canister. If repeated analyses are performed on the contents of a canister, 24 hours should elapse between successive removals of aliquots for analysis. If samples are

removed from the canister without letting the adsorption equilibria within the canister stabilize, the measured concentrations may change.

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APPENDIX B

LIST OF
MATERIALS, EQUIPMENT, AND VENDORS

Vendor	Product
ACE Glass, Inc. 1430 N. West Boulevard Vineland, NJ 08360 (609) 692-3333	Glass Sampling Manifold Assembly
AllTech Associates 2051 Waukegan Road Deerfield, IL 60015 (800) 642-4667	Chromatographic Grade Stainless Steel Tubing Supplies and Standards
Andersen Samplers, Inc. 4215-C Wendell Drive Atlanta, GA 30336 (800) 241-6898	Sample Canisters and Canister Sampling Systems
Climatronics 104 Wilbur Place Bohemia, NY 11716 (516) 567-7300	Meteorological Equipment
J&W Scientific 91 Blue Ravine Road Folsom, CA 95630 (916) 985-7888	Analytical Columns
MET ONE Instrument 479 California Avenue Grants Pass, OR 97526 (503) 471-7111	Meteorological Equipment
Nutech 2806 Cheek Road Durham, NC 27704 (919) 682-0402	Sample Canisters and Canister Sampling Systems
Perma-Pure Products P. O. Box 2105 Toms River, NJ 08754 (201) 244-0010	Permeation Drier

Vendor	Product
Restek Corporation Perm Euger Indust. Pk 110 Benner Circle Bellefonte, PA 16823 (814) 353-1300	Analytical Columns
Scientific Instrumentation P. O. Box 8941 Moscow, ID 83843 (208) 882-3860	Sample Canisters and Canister Sampling Systems
Supelco Incorporated Supelco Park Bellefonte, PA 16823-0048 (814) 359-3441	Chromatographic Grade Stainless Steel Tubing Supplies and Standards
Waters Associates 34 Maple Street Milford, MA 01757 (800) 252-4752	Carbonyl Sample Cartridges