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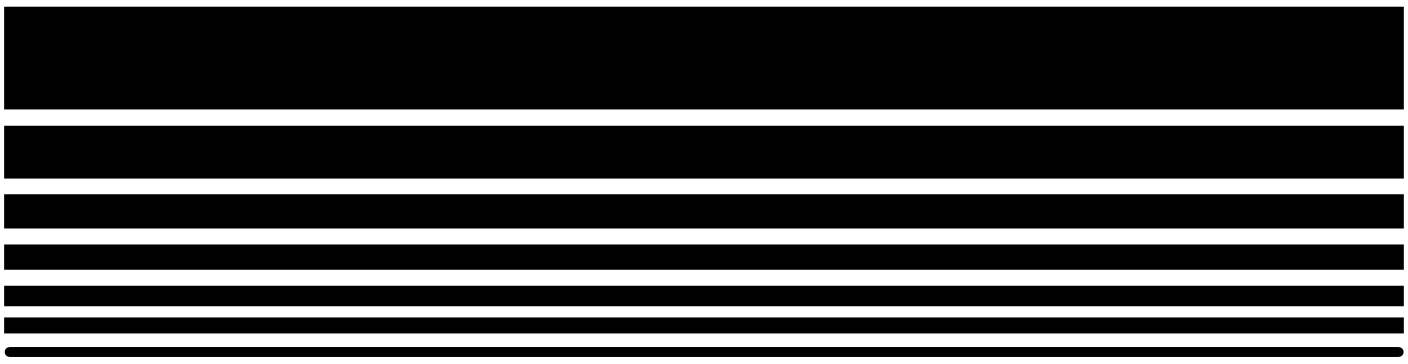
Research and Development

TECHNICAL ASSISTANCE DOCUMENT FOR SAMPLING AND ANALYSIS OF OZONE PRECURSORS



Technical Assistance Document for Sampling and Analysis of Ozone Precursors

September 30, 1998

U.S. Environmental Protection Agency
National Exposure Research Laboratory
Human Exposure and Atmospheric Sciences Division
Research Triangle Park, North Carolina, NC 27711

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Section 1.0
Introduction

Section 182 (c)(1) of the 1990 Clean Air Act Amendments (CAAA) required the Administrator to promulgate rules for enhanced monitoring to obtain more comprehensive and representative data on ozone air pollution. The Environmental Protection Agency (EPA) has revised 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 monitoring of ozone (O_3), oxides of nitrogen (NO_x), volatile organic compounds (VOCs), selected carbonyl compounds, and monitoring of meteorological parameters. The revisions require States to establish Photochemical Assessment Monitoring Stations (PAMS) as part of their existing State Implementation Plan (SIP) monitoring networks in ozone nonattainment areas classified as serious, severe, or extreme.

The principal reasons for requiring the collection of additional ambient air pollutant and meteorological data are the lack of successful attainment of the National Ambient Air Quality Standard (NAAQS) for O_3, and the need to obtain a more comprehensive air quality data base for O_3 and its precursors. Analysis of the data will help the EPA understand the underlying causes of ozone pollution, devise effective controls, and measure improvement. Data acquired from enhanced ambient air monitoring networks will have a variety of uses, which may include:

- Developing, evaluating, and refining 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 Technical Assistance Document (TAD) for Sampling and Analysis of Ozone Precursors was initially published in October 1991. The document was intended to provide guidance to those responsible for implementing PAMS. Since the initial publication, there has been a draft revision in October 1994 to Sections 2.0, 4.0, and 5.0 and a revision to Section 6.0 in June 1995, all of which were included in Appendix N of the PAMS Implementation Manual. Since these revisions, there have been significant advances in the methodology used to measure the components and parameters of interest at PAMS. These advances have necessitated this revision of the TAD.

The purpose of this document is to provide guidance in support to the enhanced ozone monitoring revisions in 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, as required by PAMS, and discusses issues associated with the collection of total reactive oxides of nitrogen (NO_y) and meteorological measurements.

The technical guidance provided for measuring O_3 precursors is based on emerging and developing technology. Guidance for automated applications, in particular, is based on experience obtained from the application of this technology during the beginning years of PAMS implementation. Because these methods are based on emerging technology and reflect state-of-

the-art, they will be subject to continuing evaluation and improvements or clarifications in the future.

Users should consider this guidance a basic reference to assist in developing and implementing their PAMS monitoring program. The technical assistance 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 are presented on selected topics such as which volatile organic O_3 precursors to measure, critical chromatography issues, moisture control, data validation, Quality Control and Quality Assurance, AIRS data entry, and how canister sampling should be approached.

Section 3 discusses the measurement of total NMOC using Method TO-12 from the Compendium of Methods for Sampling and Analysis of Toxic Organic Compounds in Ambient Air.[2] Measurement of total NMOC by Method TO-12 has limited application to the implementation of the 40 CFR Part 58 requirements, but Method TO-12 is included because of its applications to canister cleanliness verification, application to alternative monitoring strategies, and use in O_3 prediction models. Alternative monitoring strategies involve the use of canister and/or automated 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-11A from the Compendium of Methods for Sampling and Analysis of Toxic Organic Compounds in Ambient Air and includes new information regarding the methodology and issues

associated with the measurement of carbonyl compounds. Section 6 provides guidance for PAMS meteorological monitoring, which is essential to the PAMS program. Note that all sections of this Technical Assistance Document are intended to be independent. Figures, tables, and text are therefore repeated as necessary.

1.3 Summary of the Monitoring Regulations

The 1990 CAAA required 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 enhanced O_3 monitoring stations are a subset to SLAMS and identified as Photochemical Assessment Monitoring Stations (PAMS).

The monitoring revisions by EPA required changes to 15 separate Sections, Subparts, or Appendices of 40 CFR Part 58, and varied 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, NAMS, and PAMS. This section requires sampling for VOCs and carbonyl compounds according to the monitoring period and minimum monitoring network requirements specified in Sections 4.3 and 4.4 of Appendix D of the revised regulations.[1]

Unlike the SLAMS and NAMS design criteria which are pollutant-specific, PAMS design criteria are site specific. Design criteria for the PAMS network are based on selection of an array of site locations relative to O_3 precursor sources and predominant wind direction associated with peak O_3 events. Four PAMS site types are described in the regulations. The number and type of monitoring sites and sampling requirements is dependent on the population of the Metropolitan Statistical Area (MSA) or Consolidated Metropolitan Statistical Area (CMSA). The specified minimum sampling requirements for VOCs and carbonyl compounds for each site type are presented in Table 1-1. Monitoring for O_3 and NO_X (including NO and NO_2)

Table 1-1 . PAMS Minimum Monitoring Network Requirements

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

[1]Whichever area is larger.

[2]Frequency requirements are as follows:

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

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

C = Eight 3-hour samples on the 5 peak O_3 days plus each previous day, eight 3-hour samples every sixth day and one additional 24-hour sample every sixth day during the monitoring period.

D = Eight 3-hour samples every third day during the monitoring period.

E = Eight 3-hour samples on the 5 peak O_3 days plus each previous day and eight 3-hour samples every sixth day during the monitoring period.

F = Eight 3-hour samples on the 5 peak O_3 days plus each previous day, eight 3-hour samples every sixth day and one additional 24-hour sample every sixth day during the monitoring period.

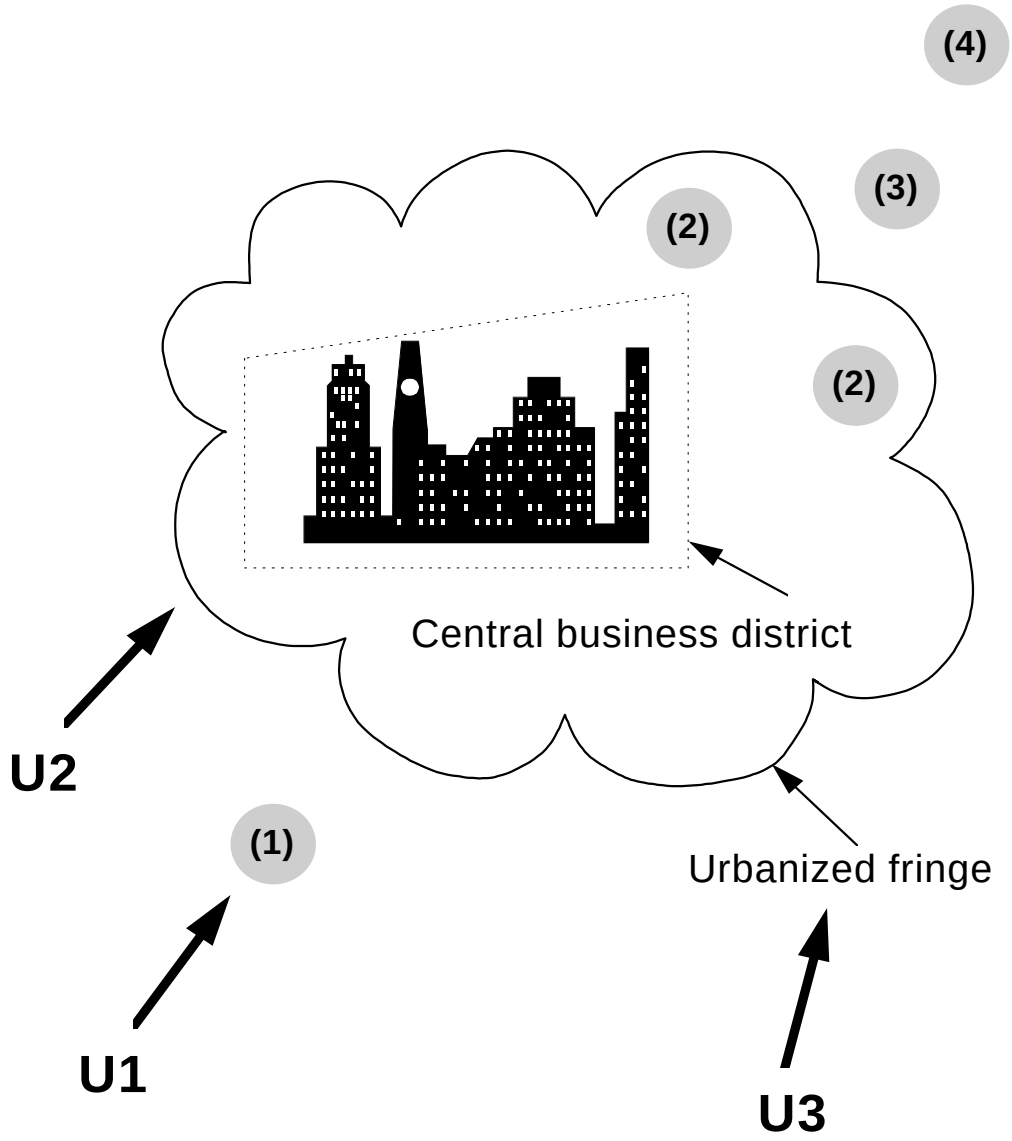
requires continuous measurements. The sampling schedule applicable to a specific area is dependent on population and PAMS site types. Specific monitoring objectives are associated with each sampling location. An example of an isolated area network design shown in Figure-1-1 identifies the location of the four PAMS site types referred to in Table 1-1.

The EPA has also prepared a guidance document on enhanced O_3 monitoring network design and siting criteria[3] which provides assistance regarding the number of PAMS required, station location, and probe siting criteria. The PAMS site types are described below.

Type (1) PAMS characterize upwind background and transported O_3 and precursor concentrations entering the MSA or CMSA and are used to identify those areas subjected to overwhelming transport. Type (2) PAMS monitor the magnitude and type of precursor emissions in the area where maximum O_3 precursor emissions are expected and are also suited for monitoring urban air toxic pollutants. Type (3) PAMS characterize O_3 precursor concentrations occurring downwind from the area of maximum emissions. Type (4) PAMS characterize extreme downwind transported O_3 and its precursor concentrations exiting the area and identify those areas which are potential contributors.

Appendix A of 40 CFR Part 58 references the Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV (Revised March, 1995) - Ambient Air Specific Methods[4] for general quality assurance recommendations for PAMS. Quality assurance procedures for VOC, NO_X, O_3 , and carbonyl and meteorological measurements must be consistent with EPA guidance. This guidance, and other information from appropriate sources, including Section 2.8 of this document, should be used by States in developing a Quality Assurance program.

Isolated Area Network Design



Note:
U1 and U2 represent the first and second most predominant high ozone day morning wind direction.
U3 represents the high ozone day afternoon wind direction.

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(1), (2), (3), and (4) are different types of PAMS sites (See Table 1-1).

Figure 1-1. Isolated Area Network Design

Appendix C of 40 CFR Part 58 requires that methods used for O_3 and NO_X be reference or equivalent methods. Because there are no reference or equivalent methods promulgated for VOC and carbonyl measurements, Appendix C of the revisions refers agencies to this guideline document for direction.

Appendix C of the revisions would also allow the use of approved alternative VOC measurement methodology (including new or innovative technologies). This provision requires States that 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 58.40 - PAMS Network Establishment.

1.4 References

1. U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40, Part 58. Ambient Air Quality Surveillance, Final Rule Federal Register, Vol. 58, No. 28, February 12, 1993.

2. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Compendium Method TO-12. *Method for the Determination of Non-Methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID)*. EPA-600/4-89/017. Research Triangle Park, NC: U.S. Environmental Protection Agency, 1988.

3. *Photochemical Assessment Monitoring Stations Implementation Manual*. EPA-454/B-93-051. Research Triangle Park, NC: U.S. Environmental Protection Agency, 1994.

4. *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV - Ambient Air Specific Methods*. EPA 600/4-77-27a. U.S. Environmental Protection Agency, 1977. Revised March, 1995.

Section 2.0

Methodology for Measuring Volatile Organic Compound Ozone Precursors in Ambient Air

In accordance with the provisions for the enhanced O_3 ambient monitoring network requirements specified in 40 CFR Part 58, Subpart E,[1] this section provides guidance and method descriptions for measuring volatile organic compounds (VOCs) that are considered to contribute to the formation of ozone in the right atmospheric conditions. Information and guidance are provided to assist in the development, implementation, and use of these methods for designing a VOC measurement program consistent with the requirements of the enhanced O_3 monitoring rule. Areas addressed include:

- A review of the network monitoring requirements;
- A list of target VOCs to be measured;
- Chromatography issues associated with peak identification and quantification;
- Automated and manual methodology for collecting and analyzing samples;
- The minimum requirements of a Quality Assurance (QA) and Quality Control (QC) program;
- Guidance for validating data from automated GC systems; and
- Submitting data into the AIRS AQS data base.

Measuring VOCs is a complex process involving the application of gas chromatographic techniques for qualitative and quantitative determination of individual hydrocarbon compounds and an estimation of total non-methane organic compound (TNMOC) content in ambient air. Two methods are presented for collecting and analyzing VOC samples: an automated method (Section 2.4) and a manual method (Section 2.5). Ideally, agencies responsible for designing, implementing, and operating

their O_3 monitoring networks will satisfy their monitoring requirements by using some combination of the automated and manual gas chromatographic approaches. Even if agencies primarily choose the automated methodology, manual sampling and analysis capability are needed to fulfill the 24-hour sample requirement; verify the proper operation of the automated systems; characterize the quality of the collected data; address the identification of unknown compounds; and enhance the representativeness of the monitoring network.

Users are ultimately responsible for equipment selection, set-up, parameter optimization, and preparation of Standard Operating Procedures (SOPs) for their specific network. 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 presented are generic. Background information on the potential benefits and limitations of the methods are also provided.

2.1 Network Monitoring Requirements

The minimum sampling frequency requirements for speciated VOC monitoring are prescribed in 40 CFR Part 58, Subpart E, Appendix D - Network Design for State and Local Air Monitoring Stations (SLAMS), National Air Monitoring Stations (NAMS), and Photochemical Assessment Monitoring Stations (PAMS). Section 4.3 - Monitoring Period requires, at a minimum, that O_3 precursor monitoring be conducted annually throughout the months of June, July, and August when peak O_3 values are expected. Section 4.4 - Minimum Monitoring Network Requirements specifies the minimum required number and type of monitoring sites and sampling frequency requirements based on the population of the affected MSA/CMSA or nonattainment area, whichever is larger. These monitoring requirements are outlined in Table 1-1. The minimum speciated VOC sampling frequency requirements are summarized by site type below:

- Site Type 1 - Eight 3-hour samples every third day and one additional 24-hour sample every sixth day during the monitoring period; or eight 3-hour samples on the five peak O_3 days plus each previous day and eight 3-hour samples and one 24-hour sample every sixth day, during the monitoring period.

- Site Type 2 - (population less than 500,000) - Same as Site Type 1.

- Site Type 2 - (population greater than 500,000) - Eight 3-hour samples every day during the monitoring period and one additional 24-hour sample every sixth day year around.

- Site Type 3 - (population greater than 500,000) - Same as Site Type 1.

- Site Type 4 - (population more than 2,000,000) - Same as Site Type 1.

Either of the two VOC methods (automated or manual) described in this section is capable of satisfying the sampling frequency and sample integration requirements. Samples collected for either method should represent a time-integrated average for the required sampling period. It is important to understand that the 3-hour sample integration period is a maximum requirement in the sense that samples can be collected more frequently at shorter sampling intervals (i.e., three 1-hour periods) but not less frequently for longer sampling intervals.

The manual methodology, where samples are collected in canisters, is primarily applicable to the less frequent sampling required for site Types 1, 3, and 4 (i.e., eight 3-hour samples every third day or during peak O_3 events) and the 24-hour sample requirement. The automated method, which allows for direct on-line sample collection, is primarily applicable to the more frequent sampling requirements for Site Type 2 (eight 3-hour samples every day during the monitoring period). The automated method provides a viable option for the continuous collection of hourly samples. Though not required, continuous collection of hourly samples also offers a more definitive assessment of the temporal and diurnal distribution of VOCs. Although it is possible to use the manual methodology for Site Type 2 sampling requirements, it is not practical due to the large number of SUMMA® canisters required.

2.2 Target Volatile Organic Compound Ozone Precursors

For the purposes of this document, the term VOCs refers to gaseous aliphatic and aromatic nonmethane organic compounds that have a vapor pressure greater than 0.14 mm Hg at 25EC, and generally 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 may be automobiles. Table 2-1 presents the target VOCs which could be measured and reported to satisfy the requirements of 40 CFR Part 58, Subpart E. Users should consider these target compounds in developing their measurement systems and monitoring approach, and initially report and submit results for these compounds into the Aerometric Information Retrieval System (AIRS) as described in Section 2.6.2 of this document. The VOCs listed in Table 2-1 were selected primarily based on their abundance in urban atmospheres and their potential role in the formation of O_3. Polar compounds are not included on the target list due to their surface adsorption characteristics and the difficulty in measuring these compounds using the methodology designed for nonpolar hydrocarbons. The methodology described in this document is designed to measure the more abundant non-polar hydrocarbons or VOCs.

The target list in Table 2-1 is not definitive or all-encompassing, but should be used as a guideline for implementation that should evolve as the monitoring program matures. As experience is gained in the collection of data regarding the abundance of specific VOCs at each site, target compounds may be deleted from the list depending on the frequency of occurrence. If additional compounds are identified and occur at high frequency, they should be added to the list of PAMS target compounds.

The compounds listed in Table 2-1 are presented in the order of their expected chromatographic elution from a J&W® DB™-1 non-polar dimethylsiloxane capillary analytical column. The AIRS parameter code for each compound is also given in Table 2-1. Compounds

Table 2-1. Target Volatile Organic Compounds

AIRS Parameter Code	Target Compound Name	AIRS Parameter Code	Target Compound Name
43203	Ethylene	43249	3-Methylhexane
43206	Acetylene	43250	2,2,4-Trimethylpentane (isooctane)
43202	Ethane	43232	*n*-Heptane
43205	Propylene	43261	Methylcyclohexane
43204	Propane	43252	2,3,4-Trimethylpentane
43214	Isobutane	45202	Toluene
43280	1-Butene	43960	2-Methylheptane
43212	*n*-Butane	43253	3-Methylheptane
43216	*trans*-2-Butene	43233	*n*-Octane
43217	*cis*-2-Butene	45203	Ethylbenzene
43221	Isopentane	45109	*m/p*-Xylene
43224	1-Pentene	45220	Styrene
43220	*n*-Pentane	45204	*o*-Xylene
43243	Isoprene (2-methyl-1,3-butadiene)	43235	*n*-Nonane
43226	*trans*-2-Pentene	45210	Isopropylbenzene (cumene)
43227	*cis*-2-Pentene	45209	*n*-Propylbenzene
43244	2,2-Dimethylbutane	45212	*m*-Ethyltoluene (1-ethyl-3-methylbenzene)
43242	Cyclopentane	45213	*p*-Ethyltoluene (1-ethyl-4-methylbenzene)
43284	2,3-Dimethylbutane	45207	1,3,5-Trimethylbenzene
43285	2-Methylpentane	45211	*o*-Ethyltoluene (1-ethyl-2-methylbenzene)
43230	3-Methylpentane	45208	1,2,4-Trimethylbenzene
43245	1-Hexene*	43238	*n*-Decane
43231	*n*-Hexane	45225	1,2,3-Trimethylbenzene
43262	Methylcyclopentane	45218	*m*-Diethylbenzene
43247	2,4-Dimethylpentane	45219	*p*-Diethylbenzene
45201	Benzene	43954	*n*-Undecane
43248	Cyclohexane	43141	*n*-Dodecane*
43263	2-Methylhexane	43102	TNMOC**
43291	2,3-Dimethylpentane	43000	PAMHC***

* These compounds have been added as calibration and retention time standards primarily for the purpose of retention time verification. They can be quantitated at the discretion of the user.

** Total Nonmethane Organic Compounds

*** PAMS Hydrocarbons

with lower boiling points typically elute first on this analytical column, followed by the heavier, higher molecular weight components with higher boiling points. Concentrations of the target VOCs and unknown compounds (unidentified peaks) are calculated in units of parts per billion Carbon (ppbC). The concentration in ppbC for a compound can be divided by the number of carbon atoms for that compound to estimate the concentration in parts per billion volume (ppbv). The target compound list in Table 2-2 has also been separated and classified into categories based on structure. The categories include paraffins (alkanes and cycloalkanes), olefins (alkenes and cycloalkenes), aromatics (arenes), and alkynes. Because the compound proved to be unstable and decomposed in the calibration gas cylinder, 2-methyl-1-pentene was replaced on the list of PAMS target volatile organic compounds by 1-hexene. *n*-Dodecane was added as a late-eluting retention time marker.

2.2.1 Total Nonmethane Organic Compound (TNMOC) and PAMS Hydrocarbons (PAMHC)

The TNMOC measurement is the unspeciated total concentration of VOCs (typically C_2 through C_{12}) in ambient air. This measurement supplements the O_3 precursor compound measurements and is used for O_3 models that do not require speciated hydrocarbon measurement input. This estimate can be made using either the automated or manual techniques described in Sections 2.4 and 2.5, respectively. An estimate of the TNMOC in ppbC is determined as the sum of all identified and unidentified gas chromatographic peaks in the C_2 through C_{12} range as eluted from the analytical column and detected by the flame ionization detector (FID). The concentration in ppbC of TNMOC is calculated by taking the total area count measured and applying the response factor for propane, the primary calibration compound. The C_2 through C_{12} retention time window should be established and periodically verified by analyzing ethylene or acetylene (C_2) and dodecane (C_{12}). These compounds may be incorporated in the retention time or calibration standard.

Table 2-2. Target VOC Compound Classification

Alkyne	**Paraffin**
Acetylene	Isopentane
	3-Methylheptane
Aromatic	2-Methylheptane
Styrene	*n*-Octane
m/*p*-Xylene	2,3,4-Trimethylpentane (isooctane)
o-Xylene	Ethane
Toluene	Propane
Ethylbenzene	Isobutane
n-Propylbenzene	*n*-Nonane
1,2,4-Trimethylbenzene	*n*-Butane
1,3,5-Trimethylbenzene	2,2,4-Trimethylpentane
1,2,3-Trimethylbenzene	*n*-Hexane
Benzene	*n*-Pentane
Isopropylbenzene (cumene)	3-Methylpentane
m-Ethyltoluene (1-ethyl-3-methylbenzene)	2-Methylpentane
p-Diethylbenzene	Cyclopentane
o-Ethyltoluene (1-ethyl-2-methylbenzene)	2,3-Dimethylbutane
p-Ethyltoluene (1-ethyl-4-methylbenzene)	Methylcyclopentane
m-Diethylbenzene	2,4-Dimethylpentane
	2,2-Dimethylbutane
Olefin	*n*-Heptane
1-Hexene*	3-Methylhexane
1-Butene	2,3-Dimethylpentane
Isoprene (2-methyl-1,3-butadiene)	Cyclohexane
1-Pentene	2-Methylhexane
trans-2-Butene	Methylcyclohexane
cis-2-Butene	*n*-Decane
trans-2-Pentene	*n*-Undecane
cis-2-Pentene	*n*-Dodecane*
Propylene	
Ethylene	

*These compounds have been added as calibration and retention time standards primarily for the purpose of retention time verification. They can be quantitated at the discretion of the user.

Compendium Method TO-12, preconcentration direct flame ionization detector (PDFID) techniques described in Section 3.0 of this document and in Appendix C, may also be used to determine TNMOC. Method TO-12 measures carbon-containing compounds from the sample as concentrated by cryogenic trapping and thermal desorption directly into a FID. The FID response is typically calibrated using propane to give a per-carbon response in area counts per ppbC. Compounds with a carbon number greater than C_{12} may be transferred and detected using the Method TO-12 technique. Because of inherent differences between the "summation of peaks" and PDFID approaches, the two approaches do not provide equivalent TNMOC results and are not directly comparable. Since the vapor pressure of carbon-containing compounds decreases with increasing molecular weight, compounds with a carbon number above C_{12} are not expected to contribute significantly (more than a few percent) to the TNMOC value.

A subgroup of TNMOC, PAMHC is the sum of peak areas for only the PAMS target compounds. Both TNMOC and PAMHC are valuable data components and the ratio PAMHC/TNMOC may indicate the conversion of ozone precursors to carbon-containing products resulting from atmospheric chemistry.

The PAMHC parameter itself is of limited value because the PAMS target list may change by geographic area. Also, PAMHC provides a broad measure of compounds that is often not substantially different from TNMOC. PAMHC could be used by a state or agency measuring only listed compounds, and then calculating the percent of unidentified compounds as:

$$\text{Percent Unidentified} \quad \frac{\text{TNMOC - PAMHC}}{\text{TNMOC}} * 100$$

Alternatively, PAMHC can be used to determine the percentage of the total made up by the listed compounds.

$$\text{Percent Identified} \quad \frac{\text{PAMHC}}{\text{TNMOC}} * 100$$

This ratio for a given PAMS site usually stays within a range characteristic of the site, subject to seasonal variation.

2.3 Chromatography Discussion and Issues

The following section discusses the basic operating principles of the gas chromatography with flame ionization detection (GC/FID) methodology used to measure ambient VOCs either as an independent analytical system or as part of an automated sampling/analytical system. Related chromatography issues or concerns regarding peak identification and quantitation, sample moisture removal, calibration, primary and retention time standard preparation and humidification, and analytical column selection and configuration are also discussed.

2.3.1 Gas Chromatography with Flame Ionization Detection

Gas chromatography with flame ionization detection is the established analytical technique for monitoring VOCs in ambient air. The sensitivity, stability, dynamic range, and versatility of GC/FID systems make them extremely effective in measuring very low concentrations of VOCs. The gas chromatograph may be an independent analytical system or a component of an automated sampling/analytical system.

Typically, a sample taken from an urban environment contains more than 100 detectable compounds that may reasonably be separated into quantifiable peaks. These compounds are generally present at concentrations varying from less than 0.1 ppbC to greater than 500 ppbC with the typical concentration ranging between 0.1 to 50 ppbC. Detection of typical urban concentration levels

generally requires that samples be passed through a preconcentration trap to concentrate the compounds of interest and separate them from components of the sample that are not of interest (i.e., air, methane, water vapor, and carbon dioxide).

The GC/FID systems required for VOC measurement consist of the following principal components:

- Sample introduction;
- Sample conditioning for moisture removal (optional);
- Sample concentration;
- Sample focusing for optimal sample injection and improved chromatographic separation (optional);
- Gas chromatography; and
- Flame ionization detection.

An air sample may be introduced to the measurement system directly from ambient air, an integrated canister, or a calibration gas cylinder. The sample is optionally passed through a sample conditioning system for moisture removal and then concentrated using an adsorbent or glass bead trap that is cryogenically cooled using liquid nitrogen, liquid carbon dioxide, or thermoelectric closed-cycle coolers. The concentrated sample is then thermally desorbed and introduced into the carrier gas prior to being introduced to the analytical column. Sample refocusing is optional and may be performed using a cryogenically or thermoelectrically cooled secondary trap. Sample refocusing may also occur at the head of the cryogenically cooled analytical column. Sample focusing is used to concentrate the desorbed sample into a narrow band for injection onto the capillary GC analytical column. The focused sample is thermally desorbed rapidly and injected onto the analytical column of the gas chromatograph as a “plug,” which maximizes GC column resolution and results in improved C_2 and C_3 chromatographic separation and peak shape. Sample focusing is effective when low carrier gas flow

rates (1-2 mL/minute) are used. The analytical column separates the sample into individual components based on the distribution equilibrium between the mobile (carrier gas) and stationary (liquid column coating) phases. The separated components elute from the column and enter the FID, where a signal is generated based on carbon response. The time of elution and detection (retention time) is the primary basis for the identification of each compound. Retention time units are typically expressed in minutes and are specific to the conditions of the GC system used. The identification of sample components is determined by matching the known retention times of the components in a retention time standard with those in the sample. It is desirable to confirm GC peak identification periodically using a mass spectrometric detector, if available.

The FID is the most widely used, universal GC detector. As a general observation, the FID provides good sensitivity and uniform response to *n*-alkanes based on the number of carbon atoms in the compound. For unsaturated, cyclic, or aromatic hydrocarbons, the FID response is less predictable. The FID is, therefore, well suited for ambient air analysis since a majority of VOCs in ambient air are hydrocarbons. This uniformity of FID response to *n*-alkanes simplifies calibration in that a single hydrocarbon compound (e.g., propane) can be used to calibrate the detector response for all hydrocarbons.[2,3] This FID response characteristic also provides for the unique capability of estimating the concentrations of not only the target peaks (identified) but also the unidentified components of the sample. Some automated GC systems require a two-component calibration mixture (e.g., propane and benzene) due to the use of dual analytical columns. By summing all identified and unidentified chromatographic peak areas, a useful estimate of the concentration of TNMOC is provided. The FID also has a broad linear dynamic range of response, allowing for the analysis of samples with concentrations ranging from picogram (using preconcentration) to microgram quantities of hydrocarbons.

Modern GC technology, coupled with sophisticated data acquisition and processing software, provides for reasonable estimates of both the identity and quantity of the target species to the extent that the analytical column is capable of separating them and the system has been adequately characterized

and calibrated. The retention characteristics of the analytical column must be determined for each target compound using pure components or mixtures of pure components diluted with a humidified inert gas.

2.3.2 Identification and Quantification Issues

Although the peak identification and quantification expected with GC/FID systems is acceptable for meeting the objectives of PAMS, the GC/FID technique has some inherent limitations. Chromatographic systems using GC/FID rely primarily on the practical use of retention times to make compound identifications for each chromatographic peak. Commercial GC/FID systems configured for VOC analyses must be suitably designed to provide stability of system parameters to ensure consistent retention times for confident peak identification.

Gas chromatographic peak misidentifications typically occur as a result of retention time shifting and interferences due to co-eluting non-target compounds. Modern GC capillary columns are generally capable of adequately separating the targeted compounds; however, co-elution of unidentified species with the targeted species can and does occur. The identification and quantitative uncertainty resulting from co-elution will depend on the type of unidentified compound and the abundance relative to the affected target VOC. The target VOCs are exclusively hydrocarbons which are primarily emitted into the atmosphere by mobile sources and generally dominate most urban samples. Concentration estimates for substituted hydrocarbon species such as oxygenated or halogenated hydrocarbons using FID are uncertain since these compounds do not respond to the FID solely on a per carbon basis. Generally, the identification and quantification of a targeted compound will not be significantly affected unless a substituted species, at a significant concentration, co-elutes with the target compound.

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

- Ensuring that the measurement system is fully optimized and characterized as discussed in Section 2.3.7, Pre-Measurement Chromatographic System Verification;
- Designating chromatographic reference peaks and using relative retention times for peak identification (Section 2.7.1, Data Validations);
- Using dual-column configurations to provide improved resolution (Section 2.3.5, Column Configuration);
- Having an experienced chromatographer conduct visual inspection of the chromatograms at some practical frequency to verify proper system operation;
- Reviewing the chromatographic data using computer-based exploratory software designed to improve and validate the GC data and determine outliers;
- Periodically re-analyzing samples on a different well-characterized GC system to identify co-eluting compounds; and
- Periodically confirming peak identification using more definitive GC/MS techniques.

Quantitative errors can be reduced by careful attention to quality control (calibration details and system blanks), frequent response checks using canister samples containing target compound mixtures of known concentration, and periodic performance audits or proficiency studies using independent reference materials. Analytical system blank analysis of humidified, ultra zero air is performed to characterize the background concentration of VOCs present in the measurement system. If unacceptable levels of background system contamination occur the data will be quantitatively compromised. Sources of contamination can be related to the:

- Source of humidified, ultra zero air;
- Sample to trap transfer line;

- Carrier gas and filters; and
- Analytical columns.

The effort devoted to peak identification, confirmation, and quantification is important to the quality of the collected data. Users must determine the appropriate level of effort to devote to this activity based on their specific needs and capabilities.

2.3.3 Sample Moisture Issues

The accurate identification and quantitation of trace level VOCs in ambient air generally require the use of sample concentration techniques for sample enrichment to enhance instrument sensitivity. The effects of moisture must be considered in any measurement program where sample concentration is required. Cryogenic concentration techniques are commonly used, especially for light hydrocarbons. The vast difference in boiling points of the C_2 and C_{12} hydrocarbons also may require the use of sub-ambient chromatography to adequately separate the entire range of compounds. The co-collection of moisture in the concentration trap and subsequent injection of water onto the analytical column can cause a number of problems and adversely affect the overall quality of the data generated. These problems include:

- Cryogenic trap freezing which results in reduced sample flow or trap blockage;
- Chromatographic column plugging due to ice formation and subsequent retention time shifting, peak splitting, and poor peak shape and resolution which result in incorrect peak identification and peak naming;
- Chromatographic column deterioration (especially with Al_2O_3 columns);
- Baseline shifts due to elution of the water profile;
- FID flame extinction;
- Poor reproducibility and precision of the data generated;

- Competition for active sites and adverse effects on adsorbent concentration traps; and
- Suppression of the FID signal.

In addition, 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 the components of interest.

Moisture removal from the sample stream prior to sample concentration minimizes these problems and also allows larger sample volumes to be concentrated, thus providing greater detection sensitivity. Moisture related problems can be alleviated by various water management methods that include Nafion® driers (Perma-Pure® Inc., Toms River, NJ), selected condensation at reduced temperatures, selective temperature desorption, non-cryogenic hydrophobic adsorbent sample concentration traps, dry gas purging, and selective multibed sorbent trapping. However, some methods used to remove moisture from the sample may result in the loss of polar VOCs which affects the TNMOC measurement. This effect is variable, based on drier efficiency and compound selectivity. A drier that minimizes both polar VOC loss and the potential for introducing contaminants into the system should be considered.

Nafion® driers are commonly used for ambient air sample drying, and are discussed in Compendium Method TO-14.[4] The Nafion® membrane consists of a hygroscopic copolymer of tetrafluoroethylene and a perfluorosulfonic acid that is coaxially mounted within a larger Teflon® or stainless steel tube. The humid sample stream is passed through the membrane tube, allowing water to pass through the walls by a process called "perevaporation" into a dry nitrogen (N_2) or air purge stream that is counter-currently flowing through the annular space between the membrane and the outer tube. Variables that determine the drying efficiency include the surface area of the membrane used, sample flow rate or sample residence time in the dryer, pressure or vacuum of the sample and purge flow rate,

temperature, and sample humidity. Depending upon the variables affecting drying efficiency, Nafion® drier water removal efficiency ranges of 80-95% have been reported.[5,6,7]

Nafion® drying devices have shown demonstrated losses of certain polar VOCs (amines, ketones, alcohols, and some ethers).[8,9] This reduction in recovery of polar VOCs significantly affects TNMOC measurements made using a Nafion® drier. Reduction in recovery of polar VOCs by drying can reduce the TNMOC measurement by 20-30% in typical ambient air samples. Nafion® driers have also caused rearrangement of several monoterpenes (á-pinene and â-pinene) but have no effect on the recovery of isoprene.[6] Hydrocarbons, chlorinated or fluorinated hydrocarbons, esters, aldehydes, and some ethers are unaffected by the drier.[8,5,10]

Recent information[11] discusses issues reported when using Nafion® driers shortly after heating to regenerate the drier by removing residual water vapor and organic compounds, in order to improve drier efficiency. Heating can significantly affect the sample integrity of the C_4- C_6 alkenes and cause compound losses and rearrangement. The degree of loss and rearrangement is dependent on length of time and the temperature used for drier regeneration, as well as sample humidity. Isoprene may be lost without reappearance of an equivalent amount of carbon. In the case of C_6 alkenes, new, unidentified peaks may emerge in the retention time area of the original peaks. Heating had no effect on C_2-C_3 alkenes, C_2-C_{10} alkanes, cycloalkenes, and aromatics. The effects of heating are reversed if the drier is immediately purged with clean, dry nitrogen or air at a flow rate of 50 cc/minute for at least three hours. Heating of Nafion® driers for regeneration should be avoided and is not recommended for PAMS. If the drier shows a loss of efficiency as determined by recovery of the target compounds in the retention time standard, the drier should be replaced. To improve efficiency and prevent memory effects, the drier should be replaced at least seasonally or more frequently as needed. Information on the use of Nafion® drying devices is presented in EPA Compendium Method TO-14[4] or EPA Compendium Method TO-15, entitled *Determination of Volatile Organic Compounds (VOCs) in Air Collected-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)* (see Appendix A).

Sample drying using selective condensation at reduced temperatures is performed by selectively condensing moisture at a reduced temperature from the sample stream during thermal desorption from the sample concentration trap. This method of drying has been evaluated for recoveries of compounds having a wide range of volatilities and was found to give good recovery, reproducibility, and acceptable chromatography when operated at 15EC.[12]

Studies have been done incorporating the use of controlled vaporization of VOCs off glass bead traps at ambient and reduced temperatures, non-cryogenic hydrophobic adsorbent sample concentration traps, dry gas concentration trap purging at selected temperatures,[13] and dual sorbent trapping systems to selectively reduce sample moisture.[14,15,16] Techniques for drying an ambient air sample have been combined, including dry purging after collection on solid sorbent, loss of water by breakthrough when collecting on solid sorbents, and sample splitting.[17,18] These novel approaches to mitigating the effects of moisture should be evaluated to determine any limitations or negative effects prior to incorporating them into any VOC measurement system. EPA Method TO-15 (see Appendix A) has recently been added to the EPA Compendium of Methods for the Determination of Toxic Organics in Ambient Air and describes different techniques for drying ambient air samples. One of the main goals of this method was to use drying methods that would not affect polar VOCs as drastically as the Nafion® driers.

2.3.4 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 (primary calibration standard) and a qualitative mixture of known hydrocarbon compounds to determine gas chromatographic peak retention times (retention time standard).

2.3.4.1 Primary Calibration Standard

The GC/FID response is calibrated in ppbC using a propane primary calibration standard referenced to a National Institute of Standards and Technology (NIST) Standard. A propane and benzene mixture is recommended for systems that utilize dual columns or column switching configurations that use two FIDs. Standard Reference Materials (SRMs) from NIST and Certified Reference Materials (CRM) from specialty gas suppliers are available for this purpose. NIST currently has a fifteen component ambient non-methane organics in nitrogen SRM available (SRM 1800) for use as a reference or primary calibration standard. SRM 1800 contains both propane and benzene. Less expensive working standards needed for calibration verification over the range of expected concentrations can be prepared by the user or purchased from a gas supplier, provided they are periodically referenced to a primary SRM or CRM. The primary calibration standards must be humidified to reflect the ambient air matrix being analyzed. A procedure for preparing humidified standards is given in Section 2.3.4.3.1. A procedure for diluting standards is given in Section 2.3.4.3.2. Based on the uniform carbon response of the FID to hydrocarbons, the response factor determined from the propane or benzene primary calibration standard is used to convert area counts into concentration units (ppbC) for every peak in the chromatogram.

It is also feasible to incorporate the primary calibration standard into the retention time standard described below by confirming the concentration of propane and benzene in the retention time mixture using a primary SRM or CRM.

2.3.4.2 Retention Time Calibration Standard

The retention time calibration standard is a multiple-component mixture containing all target VOCs at varying concentration levels. The retention time calibration standard is a humidified working standard 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 QC standard for verifying these retention times.

The response of the GC/FID to selected hydrocarbons in this standard can be used to monitor system performance and determine when system maintenance or recalibration of the FID using the primary calibration standard is necessary. Proper operation of the FID according to the manufacturer's specifications produces a linear response across the chromatographic range. The concentration of each compound in the retention time standard need not be directly referenced to the SRM or CRM (as is the case for the primary calibration standard); rather, the concentration of each compound can be determined with reasonable accuracy using the FID propane or benzene carbon response factor from the calibrated GC system. If the propane and benzene in the retention time mixture are used for primary calibration, then both must be directly referenced to an SRM or CRM. To reference a working standard to an SRM or CRM, the analytical system is calibrated with the SRM or CRM, then the working standard is analyzed against the SRM or CRM calibration. If necessary, a correction factor for the working standard is calculated.

A multiple-component high pressure mixture containing the target VOCs can be obtained from a specialty gas supplier. Multiple-component mixtures can also be prepared by the user to confirm the peak identifications using the retention time standard. The retention time standard must be humidified for use as discussed in Section 2.3.4.3.

2.3.4.3 Calibration Standard Preparation

The primary propane and benzene calibration standards must be humidified to ensure integrity and stability. Water vapor has been shown to improve the stability of low pressure VOC gas mixtures in SUMMA® canisters.

A stock multiple-component retention time calibration standard containing the compounds of interest may 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 an inert diluent gas. The aliquot of each compound should be introduced through a heated injector assembly into an evacuated SUMMA® passivated stainless steel canister or other inert container. 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 retention time working standards at the ppbC level. It is not necessary to determine exact component concentrations in the multi-component mixture because the working retention time standard should not be 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 injection of a gaseous aliquot of the stock standard into a SUMMA® passivated stainless steel canister or other inert canister, and subsequently humidifying for use.

2.3.4.3.1 Procedure for Humidification

The relative humidity of the air in a canister is an important issue with respect to the storage stability and recovery of VOCs. A study using SUMMA® passivated canisters under varying pressures, relative humidities (RHs) and different VOC residence times has shown that humidification of canisters improves the recovery of higher molecular weight, less volatile components.[19] The study showed that RH levels above 18% were required for improved compound recovery. Another study

using SUMMA® passivated canisters showed that a relative humidity of at least 15% was necessary to ensure complete recovery of 41 chlorinated, brominated and aromatic compounds at concentrations of 2 to 4 ppbv.[20] There is some evidence that canisters lined with fused silica (SilcoCan™, Restek, Inc. Bellefonte, PA) do not have a minimum requirement for humidity, as do the SUMMA® polished canisters.[21]

The relative humidity of air taken from a humidified canister can vary over a significant range. For example, as shown in Figures B-1 and B-2 of Appendix B (also see Reference 22),[22] if 18L of air at 75% RH is sampled, the air subsequently released from the canister will vary from 33% RH at 30 psig (first sample taken) to 100% RH at 0 psig. This knowledge is important since the retention times of individual gas chromatographic peaks and the response factors of some types of gas chromatographic detectors change appreciably with sample humidity. A second concern is the loss of water-soluble VOCs either to condensed water or to water consolidated in drops on the canister interior surface. For the example given above, after the canister is filled with 18L of ambient air at 75% RH, 55% of the water in the fully pressurized canister (30 psig) will be condensed on the canister interior surface and 45% will be in the gas phase. As sample is removed from the canister the water adsorbed will be replenished by evaporation of the condensed water. The ratio of H_2O in the gas phase (maintained at the equilibrium vapor pressure by evaporation from the wall) to the amount of air in the canister will increase and the RH will increase. If the RH of the ambient sample is high enough (>70% RH) then there will still be condensed water inside the canister even when the canister pressure is reduced to atmospheric pressure. The reader can gain a better appreciation for the variation in RH of gas released from a canister by assuming various RH values for ambient air and using Figures B-1 and B-2 in Appendix B.

In general, the amount of water in a given volume of air at a specified RH is calculated by using the ideal gas law and a table of water vapor pressures (Table 2-3.)[23] The ideal gas law applied to calculating the amount of water required to humidify 6 liters of air to 100% RH at 21°C and one atmosphere (zero psig) of pressure is:

$$PV = nRT \quad \textbf{(2-1)}$$

$$n = \frac{PV}{RT}$$

Where:

n = moles of H_2O

V = canister volume, 6 L

P = vapor pressure of H_2O, atm

T = temperature in K, 21EC + 273 = 294K

R = ideal gas constant, 0.08205 L-atm/K mole

Converting the vapor pressure of H_2O in mm at 21EC to atm:

$$\frac{18.65\,mm}{760\,mm/atm} \quad 0.02454 \text{ atm}$$

Table 2-3. Vapor Pressure of Water at Various Temperatures, mm Hg

Temp EC	0.0	0.2	0.4	0.6	0.8
10	9.209	9.33	9.458	9.585	9.714
11	9.844	9.976	10.109	10.244	10.380
12	10.518	10.658	10.799	10.941	11.085
13	11.231	11.379	11.528	11.680	11.833
14	11.987	12.144	12.302	12.462	12.624
15	12.788	12.953	13.121	13.290	13.461
16	13.634	13.809	13.987	14.166	14.347
17	14.530	14.715	14.903	15.092	15.284
18	15.477	15.673	15.871	16.071	16.272
19	16.477	16.685	16.894	17.105	17.319
20	17.535	17.753	17.974	18.197	18.422
21	18.650	18.880	19.113	19.349	19.587
22	19.827	20.070	20.316	20.565	20.815
23	21.068	21.234	21.583	21.845	22.110
24	22.377	22.648	22.922	23.198	23.476
25	23.756	24.039	24.326	24.617	24.912
26	25.209	25.509	25.812	26.117	26.426
27	26.739	27.055	27.374	27.696	28.021
28	28.349	28.680	29.015	29.354	29.697
29	30.043	30.392	30.745	31.102	31.461
30	31.824	32.191	32.561	32.934	33.312
31	33.695	34.082	34.471	34.864	35.261
32	35.663	36.068	36.477	36.891	37.308
33	37.729	38.155	38.584	39.018	39.457
34	39.898	40.344	40.796	41.251	41.710
35	42.175	42.644	43.117	43.595	44.078
36	44.563	45.054	45.549	46.050	46.556
37	47.067	47.582	48.102	48.627	49.157
38	49.692	50.231	50.774	51.323	51.879
39	52.442	53.009	53.580	54.156	54.737

Substituting values in the above equation:

$$\frac{(0.02454\ \text{atm})(6\text{L})}{(0.08205\ \text{L atm/K mole})(294\text{K})}$$

$$n \quad 0.00610 \text{ moles of } H_2O \text{ required for 100\% RH in the canister.}$$

To calculate the moles of H_2O required for a given relative humidity multiply the value of *n* by the RH expressed as a fraction (e.g., 20% = 0.2) and convert to the number of mg of H_2O. Express the number of mg as an equal number of µL since 1.0 mg of water occupies 1.0 µL. Thus:

$$0.00610 \text{ moles} \times 0.2 \times 18 \frac{\text{gm}}{\text{mole}} \times 1000 \frac{\text{mg}}{\text{gm}} \times \frac{1.0\ \mu\text{L}}{1.0\ \text{mg}} \quad 22.0\ \mu\text{L}$$

The number of µL to be added for other sample volumes scales linearly with volume, e.g., for a sample volume of 18L, multiply the number of µL to be added to 6L by the ratio 18/6 = 3. Hence, the number of µL to be added to a canister in order to simulate the sampling of 18 L of sample air at 21°C and 20% RH is 66 µL. Figure 2-1 can be used to approximate the amount of water in 1 L of air at temperatures from -30EC to 40EC at 75% and 100% RH. The values in the figure also scale linearly with sample volume.

Based on the studies of SUMMA®-passivated canisters, low pressure (30 psig) calibration standards prepared in canisters ideally should have at least a certain minimum amount of water vapor ($20% relative humidity) to ensure sample integrity but not enough water to cause condensation of water vapor in the canister (#33% relative humidity). Using Equation 2-1, the amount of liquid water that must be added to a 6L canister (pressurized to 18 L with dry air) to achieve these conditions at 21°C (70°F) is between 66 and 110 µL. This range will of course

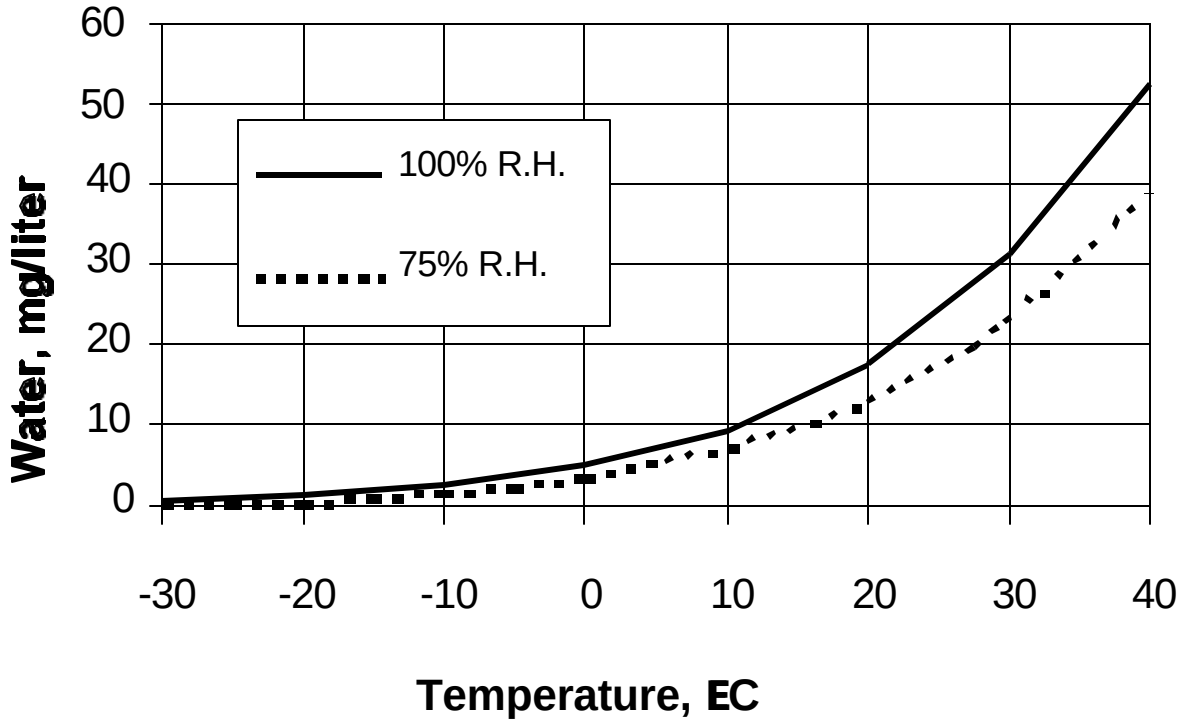


Figure 2-1. Water Content of Air at 75% and 100% Relative Humidity Over a Range of Temperatures

Amount of water is expressed as mg/liter. The density of water under standard conditions is 1 g/mL. Thus 1 mg of water occupies a volume of 1 µL. For a dry six-liter canister sample at 25EC, approximately (23 x 6) µL of water would be need to be added to achieve 100% relative humidity. Pressure is measured at the exit of the canister.

Figure adapted from Tipler, A. "Water Management in Capillary Gas Chromatographic Air Monitoring Systems." In *Proceedings of the 1994 U.S. EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants*, Research Triangle Park, NC, 1994.

vary slightly with the sample temperature (and atmospheric pressure) and should be recalculated for specific conditions. If excess water is added to the canister, water will condense inside the canister. However, the presence of condensed water is not observed to have any effect on the recovery of the non-polar PAMS target compounds and an excess of water vapor has often been used in practice when only non-polar compounds are of interest.

A detailed procedure for humidifying non-polar canister calibration standards prepared from dry stock high-pressure cylinder gases is given below. Two simple methods can be used to humidify calibration gas:

- Direct injection of water into the canister before filling with dry calibration gas; and
- Injection of water into the canister through a stainless steel union tee, then filling with dry calibration gas.

Both procedures incorporate active temperature controlled heating of the gas transfer line to 90EC. Heating ensures that the higher molecular weight compounds are transferred quantitatively and not adsorbed onto the stainless steel tubing during gas transfer. Heat also keeps the water injected through the stainless steel tee from condensing on the surfaces.

The following materials are needed:

Two-stage, non-corrosive, ultra high purity regulator - the regulator must have stainless steel diaphragms and inert seats and seals to prevent air diffusion and adsorption of low concentration trace level gases.

¼-Inch stainless steel tubing and union tee - chromatographic grade stainless steel, fused silica-lined stainless steel, or nickel are all recommended tubing material choices. A stainless steel union tee should be used.

High purity water - HPLC or spectrophotometric-grade high purity water.

Cord heater - 110 VAC rated for metal contact, with a 300-watt heat capacity minimum.

Temperature controller - active temperature controller operating on a thermocouple feedback loop.

Figure 2-2 shows the configuration of the materials for direct injection and Figure 2-3 shows the configuration of the materials for union tee injection.

Direct Injection of Water into the Canister—To humidify calibration standards by direct injection, follow these steps:

1) Insert an inert 10-mm septum into the ¼-inch nut on top of the canister valve and hand tighten to seat the septum.

2) Fill a glass syringe with the desired volume of high purity water for the canister size used. Open the canister valve slightly while quickly injecting the water, allowing the vacuum to draw the water into the canister.

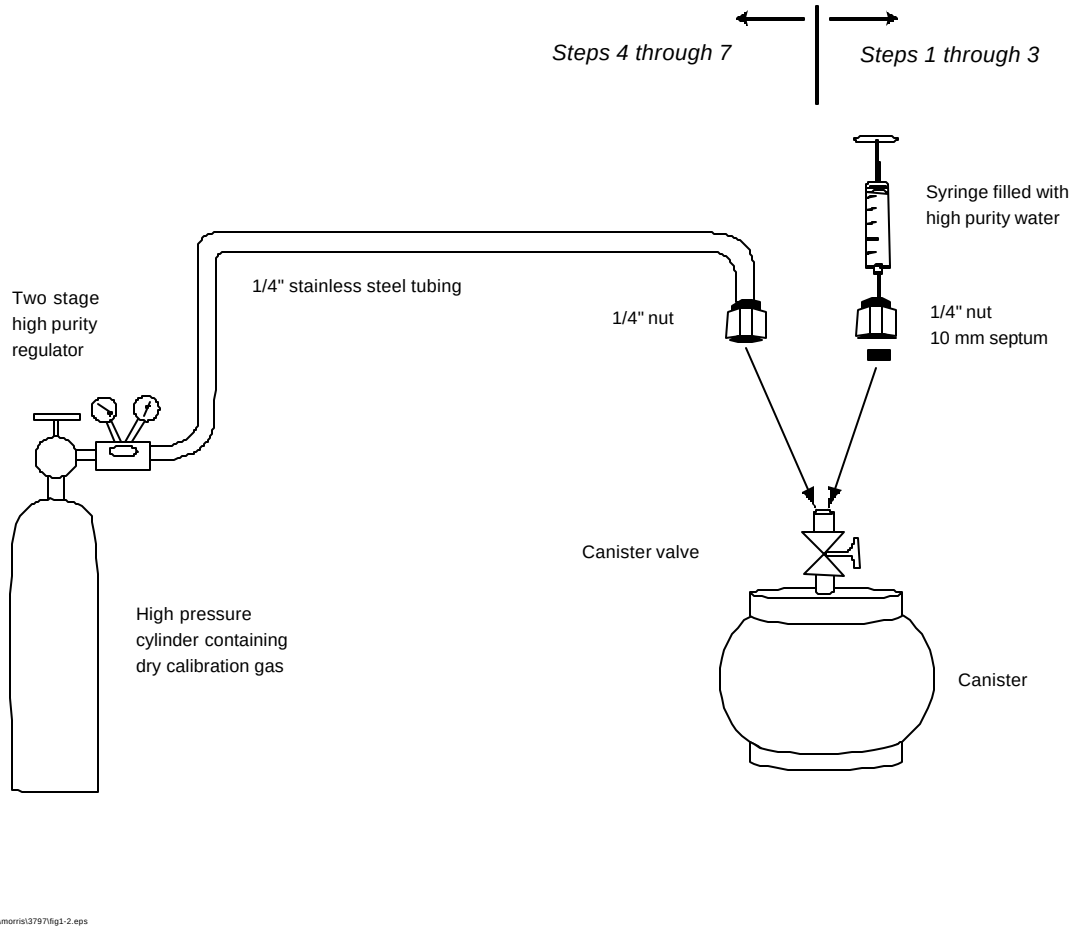
3) Close the valve and remove the cap. The canister is now ready to be filled with dry calibration gas. Any remaining water droplets in the canister valve will be carried into the canister by the flow of dry calibration gas.

4) Install the correct CGA type high purity regulator onto the calibration gas cylinder. Install a ¼-inch stainless steel male connector to connect the female NPT thread on the regulator to the ¼-inch stainless steel tubing. Install a length of ¼-inch stainless steel tubing to connect the canister to the connector fitting on the regulator.

5) Leak check the entire system by capping the ¼-inch tube outlet and pressurizing the system to the desired final canister pressure. Close the pressure regulator and monitor pressure changes. If the pressure drops, check all fitting connections.

6) Loosely attach the canister so that a complete seal is not achieved. With the valve closed, purge the entire system before use by opening and closing the pressure regulator at least three times, allowing the excess gas to escape past the incomplete seal. As an option, a stainless steel toggle shutoff valve may be installed between the canister and gas transfer tube to vent the purge gas.

7) Wrap the transfer tubing with a cord heater and plug it into the active temperature controller. Activate the temperature controller and the system to equilibrate (for 5 to 10 minutes) at a setting of about 90EC.



ols\gl\morris\3797\fig1-2.eps

Figure 2-2. Configuration of Materials to Perform Direct Injections of Water into the Canister Before Filling with Dry Calibration Gas

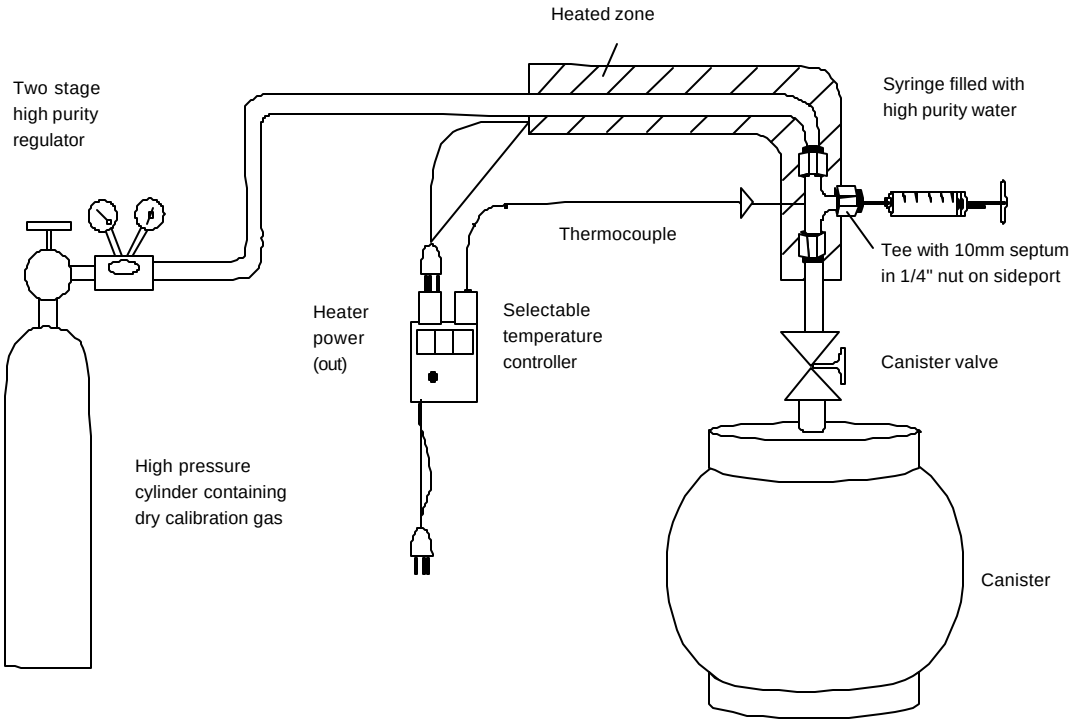


Figure 2-3. Configuration of Materials to Perform Injection of Water Through a Heated Tee While Filling with Dry Calibration Gas

8) Tighten the canister nut and set the delivery pressure gauge on the regulator to the desired final canister pressure. Fill the canister and allow it to sit overnight for static equilibration.

Union Tee Injection of Water into the Canister—To humidify calibration standards in canisters using a stainless steel union tee, follow these steps:

1) Install the correct CGA type high purity regulator onto the calibration gas cylinder. Install a ¼-inch stainless steel male connector to connect the female NPT thread on the regulator to the ¼-inch stainless steel tubing.

2) Install a length of ¼-inch stainless steel tubing to connect the canister to the connector fitting on the regulator. Install a ¼-inch stainless steel union tee at the end of the tubing and place an inert 10-mm septum in the ¼-inch nut on the side of the tee. Hand tighten the nut to seat the septum.

3) Leak check the entire system by capping the ¼-inch union tee outlet and pressurizing the system to the desired final canister pressure. Close the pressure regulator and monitor pressure changes. If the pressure drops, check all fitting connections.

4) Loosely attach the canister so that a complete seal is not achieved. With the valve closed, purge the entire system before use three times by opening and closing the pressure regulator at least three times, allowing the excess gas to escape past the incomplete seal. As an option, a stainless steel toggle shutoff valve may be installed between the canister and gas transfer tube to vent the purge gas.

5) Tighten the canister nut and wrap the transfer line and union tee with the cord heater and plug it into the active temperature controller. Activate the temperature controller and the system to equilibrate (for 5 to 10 minutes) at a setting of about 90EC.

6) Fill a glass syringe with the desired volume of high purity water for the canister size used. Open the canister valve slightly, insert the syringe into the septum and quickly inject the water.

7) Set the delivery pressure gauge on the regulator to the desired final delivery pressure and open the canister valve completely to allow the gas to fill the canister to the desired pressure.

8) When the final pressure is achieved, close the toggle valve, turn off the temperature controller, and close the regulator. Allow the canister valve to cool before closing. The valve may become hot due to thermal conductivity. **Note: Do not close the canister valve when it is hot because the Viton® ring will be distorted and the valve damaged.**

9) Allow the canister to sit overnight for static equilibration.

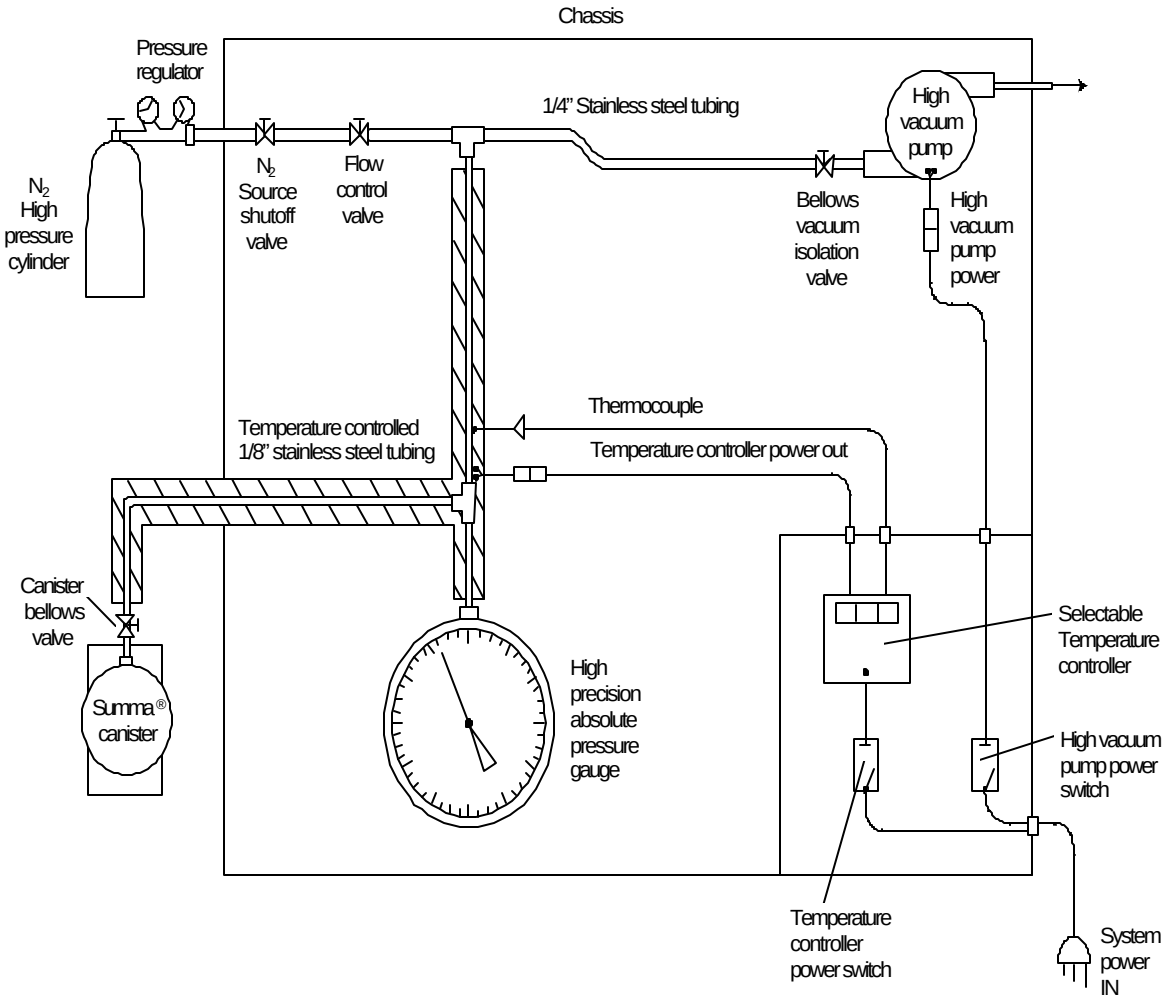
10) Calculate the volume of water to be added using equation 2-1.

2.3.4.3.2 Calibration Standard Dilution Procedure

In order to prepare multiple concentration levels from the primary calibration standard for system calibration, the calibration gas may be diluted according to the basic procedure. This dilution procedure involves volumetric dilution based on pressure and is provided here as a simplified, proven means of accurately preparing diluted calibration standards. Calibration gases may also be diluted by dynamic flow dilution, or by using commercially available dilution systems.

The primary calibration standard is initially humidified as described in Section 2.3.4.3.1. The standard is diluted with ultra high purity nitrogen. Stainless steel fittings and chromatographic grade stainless steel tubing are used for all connecting lines and fittings. The primary calibration gas is transferred into a canister for dilution. The calibration gas must be humidified as described in Section 2.3.4.3.1. The initial pressure of the canister is measured. The canister is then diluted to the desired pressure and the final canister pressure is measured. Equilibration and static mixing are allowed to take place for at least 18 hours prior to analysis. The calculated dilution factor is used to determine the final concentration value for the calibration standard.

Dilution equipment is commercially available; a dilution apparatus can also be assembled in the laboratory. The dilution apparatus shown in Figure 2-4 requires the materials described below for assembly.



o:\s\g\morris\3797\parms\chassis.ppt

Figure 2-4. Calibration Standard Dilution System

Ultra high purity grade nitrogen or air - 99.9999% purity or equivalent, hydrocarbon free.

Hydrocarbon trap - available from chromatographic supply vendors to remove trace impurities from high pressure cylinder gases.

¼-inch and C -inch stainless steel tubing and union tees - chromatographic grade stainless steel, fused silica-lined stainless steel, or nickel are all recommended tubing material choices.

Cord heater - 110 VAC rated for metal contact, with a 300-watt heat capacity minimum.

Temperature controller - active temperature controller operating on a thermocouple feedback loop.

N_2 source shutoff valve - a stainless steel bellows assembly designed valve. When the shutoff valve is closed, the dilution gas cylinder and regulator are isolated during purge evacuation of the system. When the shutoff valve is opened, the valve is used to apply dilution gas to the system for controlled introduction.

Flow control valve - a stainless steel micro-metering needle designed valve, used to introduce dilution gas into the system at a controlled flow rate.

Bellows vacuum isolation valve - a stainless steel bellows assembly designed valve. When closed, the bellows vacuum valve isolates the high vacuum pump from the system. When opened, the valve is used to apply vacuum, from the high vacuum pump, to the system.

High precision absolute pressure gauge - a compound pressure gauge used to measure the pressure in the system and the calibration canister in both positive and negative pressure modes. The pressure gauge must be able to measure pressure from 40 psig to 5 mm Hg absolute.

High vacuum pump - An oil-less diaphragm pump used to apply vacuum to the system. The pump must be able to create vacuum to 5 mm Hg absolute.

Once a dilution system is available, the basic steps for standard dilution are described below:

1) Turn the temperature controller on and allow the system to equilibrate at 100E C. Open the main dilution gas cylinder valve. Set the delivery pressure using the second gauge on the pressure regulator to approximately 10 pounds per square inch gauge

(psig) pressure over the desired final canister pressure using the pressure control knob on the regulator.

2) Zero the absolute pressure gauge by adjusting to zero.

3) Connect the calibration gas canister to be diluted to the dilution apparatus.

4) Turn on the high vacuum pump and the active temperature controller.

5) With the canister bellows valve and the N_2 source shut-off valve closed, open the bellows vacuum isolation valve. Allow vacuum throughout the system to stabilize at the lowest vacuum achievable by the pump to purge all residual gas from the system.

6) Once stabilized, close the bellows vacuum isolation valve. Open the canister bellows valve and allow the pressure in the system to equilibrate to the initial canister pressure.

7) Measure the initial pressure of the canister from the absolute pressure gauge. Record the initial canister pressure.

8) Close the flow control valve and open the N_2 source shut-off valve. Slowly open the flow control valve while monitoring the absolute pressure gauge. The slower the canister is filled, the easier it is to meet the final target pressure.

9) Continue to fill the canister until the final set point is achieved. Allow the absolute pressure gauge needle to equilibrate before reading the final pressure of the canister.

10) Once the canister has filled to the desired pressure, close the flow control valve, the N_2 source shut-off valve, and lastly the canister bellows valve. Turn off the vacuum pump and the active temperature controller.

11) Disconnect the canister, close the main valve on the dilution gas cylinder.

12) The canister should sit for at least 18 hours before analysis or further dilutions are performed to allow for static mixing and equilibration.

Calculations—The following calculations are used to determine the target final pressure (Equation 2-2) and dilution factor (Equation 2-3). The calculations do not account for barometric pressure and temperature changes, which are expected to be negligible.

$$P_{fa} \quad \frac{C_i (P_i + 14.696)}{C_f} \qquad \textbf{(2-2)}$$

where:

P_{fa}	=	Final Diluted Absolute Pressure, psia
C_i	=	Initial Concentration, ppbC
P_i	=	Initial Gauge Pressure, psig
C_f	=	Final or Target Diluted Concentration, ppbC
14.696	=	Atmospheric Pressure, psi

Example:

To dilute a 30 ppbC calibration standard in a canister with an original pressure of 5 psig (19.696 psia) to a final concentration of 15 ppbC, what is the target diluted pressure?

$$P_{fa} \quad \frac{30 \text{ ppbC } (5 \text{ psig } + 14.696 \text{ psi})}{15 \text{ ppbC}}$$

$$39.39 \text{ psia}$$

To convert psia to psig (the measured value), subtract 14.696:

39.39 psia - 14.696 = 24.70 psig

$$DF \quad \frac{P_{ia}}{P_{fa}} \qquad \textbf{(2-3)}$$

where:

P_i = Initial Gauge Pressure, psig

P_{ia} = Initial Absolute Pressure, psia = P_i + 14.696

P_f = Final Gauge Pressure, psig

P_{fa} = P_f + 14.696

DF = Dilution Factor

P_{fa} = Final Absolute Pressure, psia

Example:

Continuing with the example above, what is the dilution factor for the 30 ppbC standard which was diluted to a final pressure of 24.70 psig? What is the final concentration of the standard?

P_{ia} P_i + 14.696
5 psig + 14.696
19.696 psia

P_{fa} P_f + 14.696
24.7 psig + 14.696
39.40 psia

$$DF \quad \frac{P_{ia}}{P_{fa}}$$

$$\frac{19.696}{39.40}$$

0.499

Standard Concentration C_i * DF
0.499 * 30 ppbC
14.97 ppbC

where:

C_i = Initial concentration, ppbC

2.3.5 Column Configurations

The chromatographic column configurations generally used for VOC monitoring programs incorporate 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 overall separation of the selected target VOCs. Analyzing the full range of C_2 through C_{12} target hydrocarbons using a single analytical column may result in less than optimal separation 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 fused silica or Porous Layer Open Tubular (PLOT) column at sub-ambient column oven temperatures may be desirable. However, PLOT columns generally result in less than optimal resolution of the C_5 through C_{12} hydrocarbons. Likewise, PLOT columns increase retention times of the C_{10} through C_{12} hydrocarbons and require longer sample analysis time. If the heavier hydrocarbons are not eluted from the thick phase or PLOT columns, the TNMOC measurement may be affected, and carryover and ghost peaks may result.

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 dual-column, dual-detector configuration should be considered. In this case, two columns can be judiciously selected to provide optimal separation of both light and heavy hydrocarbons without sub-ambient column oven temperatures. Because both columns are generally contained in one gas chromatographic oven for automated applications, columns must be selected that will provide the desired separation with a single GC oven temperature program. Dual column systems may be configured with the analytical columns in parallel,

operating either concurrently or sequentially. Pre-column and post-column switching valves and the Deans®[24] switch have been used to accommodate these dual-column configurations.

2.3.6 Column Selection

Column selection for analysis of the target VOCs is dictated by the target compound resolution requirements and other practical and cost considerations, such as the need to minimize cryogen consumption and total sample analysis time. Selecting columns that will provide the desired separation of the C_2 through C_4 hydrocarbons without cooling the column oven to sub-ambient temperature decreases cryogen consumption significantly.

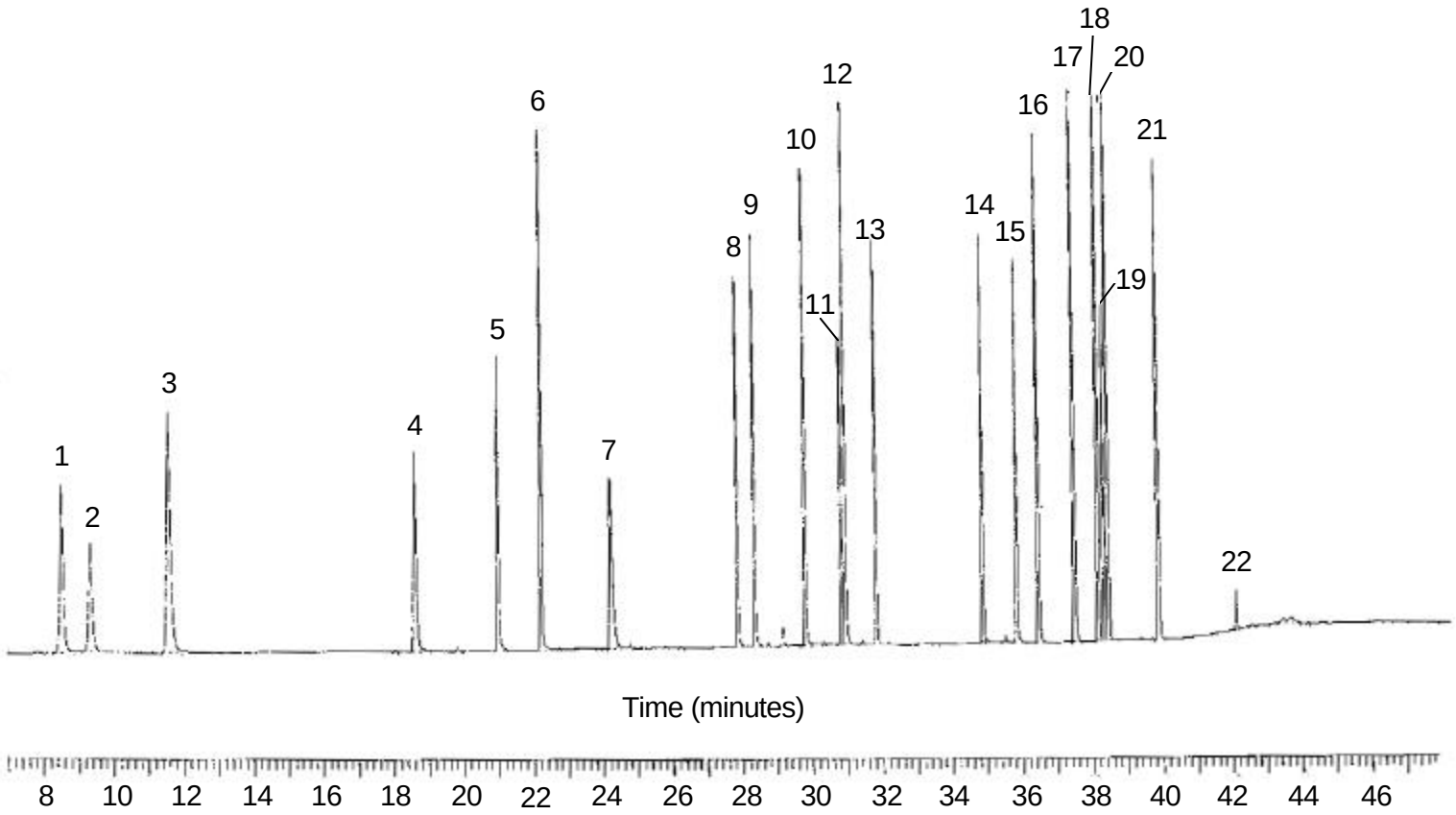
Several columns suitable for either single- or dual-column applications are discussed below. The columns described have been used in either a single- or dual-column configuration in conjunction with a single- or dual-FID for separation of the C_2 through C_{12} hydrocarbons. The column conditions described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

The C_4 through C_{12} hydrocarbons may be resolved using a 0.32 or 0.22 millimeter (mm) inside diameter (I.D.), 50 meter (m) long SGE, Incorporated BP1 fused silica column with a 1-micrometer dimethyl polysiloxane coating. This column generally does not provide adequate separation of the C_2 and C_3 hydrocarbons even at sub-ambient column oven temperatures. However, the column can provide adequate separation of the C_2 and C_3 hydrocarbons if the coating is 3 µm thick and Electronic Pressure Control is used along with sub-ambient column oven temperatures. Under these conditions, a single column can be used for all of the target hydrocarbons. Other compatible columns include the J&W DB™-1, Hewlett-Packard HP-1, Chrompack CP-SIL 5 CB, Restek RTx-1, and the Supelco SPB-1. The DB™-1 column has been historically and extensively used in ambient air applications. The SGE BP1 column can be used in conjunction with a 0.32 mm I.D., 50 m, Porous

Layer Open Tubular (PLOT) fused silica analytical column with a 5-micrometer Hewlett-Packard Al_2O_3/KCl or Al_2O_3/Na_2SO_4 coating. The Al_2O_3/Na_2SO_4 column is slightly more polar than the Al_2O_3/KCl and provides optimal resolution of the C_4 hydrocarbons. 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 and elution of C_9 through C_{12} hydrocarbons. Other compatible columns include the J&W GS-Alumina™ Al_2O_3/KCl and Al_2O_3/Na_2SO_4. However, alumina PLOT columns from different manufacturers may not be directly interchangeable and may require some method modification due to the variation in column selectivity.

Because the alumina layer is active, PLOT Al_2O_3 analytical columns are very susceptible to polar compounds such as water, which causes column deactivation and shifting of peak retention times. Moisture and other polar compounds must be removed from the sample stream using a membrane drier or other drying device. If manual sample analysis using a single PLOT Al_2O_3 column 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 and elution. Figures 2-5 and 2-6 are example chromatograms of retention time calibration standards containing the PAMS target compounds as eluted from the 0.32 mm I.D., 50 m, 5 micrometer, Al_2O_3/Na_2SO_4 PLOT and 0.22 mm I.D., 50 m, 1 micrometer, SGE, Incorporated BP1 columns. Since these columns have been successfully used by others, users should give primary consideration to these column types during their column selection process. Figure 2-7 shows a representative ambient air sample analyzed on a PLOT column; Figure 2-8 shows the same sample analyzed on a BP1 column. Peaks are numbered on the chromatograms, identified peaks are listed in Table 2-4.

Stationary phase selectivity is neither completely understood nor easily explained. Using a simplification, selectivity can be considered the ability of the stationary phase to differentiate between two compounds by virtue of a difference in their chemical and/or physical properties. Stationary phase and solute factors such as polarizability, solubility, magnitude of dipoles and hydrogen bonding influence selectivity. In many cases, more than one factor will be



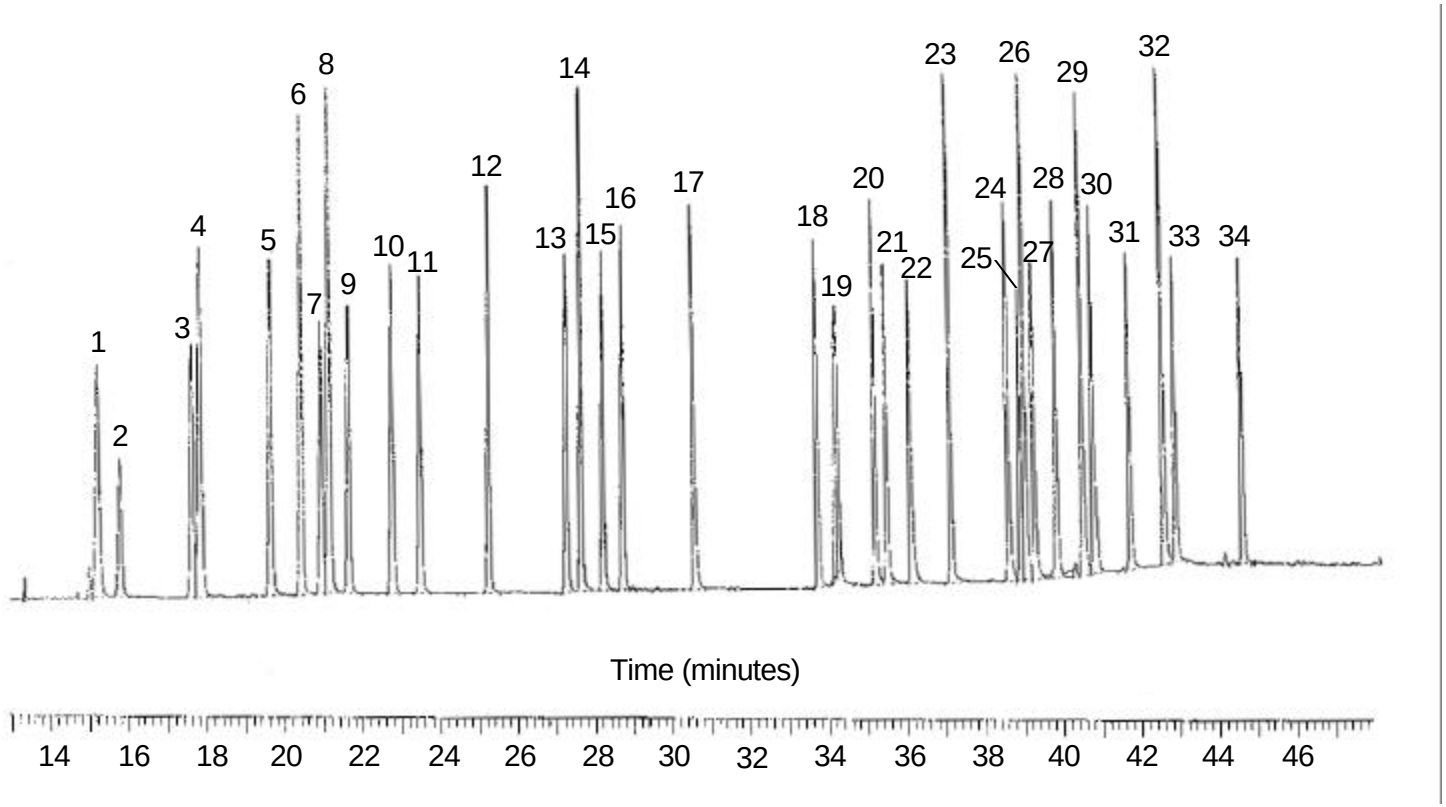
Column:	HP Al_2O_3/Na_2SO_4 50m x 0.32mm x 5µm
Carrier:	Helium, ~2.5ml/min
Initial Temp:	45ºC, 15 minutes
Rate 1:	5ºC/min
Temp 2:	170ºC
Rate 2:	15ºC/min
Final Temp:	200º C, 6 minutes

Peak #	AIRS Code	Compound Name
1	43202	Ethane
2	43203	Ethylene
3	43204	Propane
4	43205	Propylene
5	43214	Isobutane
6	43212	n-Butane
7	43206	Acetylene
8	43216	trans-2-Butene
9	43280	1-Butene
10	43217	cis-2-Butene
11	43242	Cyclopentane

Peak #	AIRS Code	Compound Name
12	43221	Isopentane
13	43220	n-Pentane
14	43226	trans-2-Pentene
15	43224	1-Pentene
16	43227	cis-2-Pentene
17	43244	2, 2-Dimethylbutane
18	43284	2, 3-Dimethylbutane
19	43263	2-Methylpentane
20	43230	3-Methylpentane
21	43243	Isoprene
22	43246	2-Methyl-1-Pentene

o:s/g/morr/3797/pams/compoun1.ppt

Figure 2-5. Example Chromatogram for the PAMS Target Compounds from the PLOT Analytical Column



Column:	SGE, Inc. BPI, 50m x 0.22mm x 1µm
Carrier:	Helium, ~2.5ml/min
Initial Temp:	45ºC, 15 minutes
Rate 1:	5ºC/min.
Temp 2:	170ºC
Rate 2:	15ºC/min.
Final Temp:	200ºC, 6 minutes

Peak #	AIRS Code	Compound Name
1	43231	Hexane
2	N/A	Unknown
3	43262	Methylcyclopentane
4	43247	2, 4-Dimethylpentane
5	45201	Benzene
6	43248	Cyclohexane
7	43263	2-Methylhexane
8	43291	2, 3-Dimethylpentane
9	43249	3-Methylhexane
10	43250	2, 2, 4-Trimethylpentane
11	43232	n-Heptane
12	43261	Methylcyclohexane
13	43252	2, 3, 4-Trimethylpentane
14	45202	Toluene
15	43960	2-Methylheptane
16	43253	3-Methylheptane
17	43233	n-Octane

Peak #	AIRS Code	Compound Name
18	45203	Ethylbenzene
19	45109	m/p-Xylene
20	45220	Styrene
21	45204	O-Xylene
22	43235	n-Nonane
23	45210	Isopropylbenzene
24	45209	n-Propylbenzene
25	45212	m-Ethyltoluene
26	45213	p-Ethyltoluene
27	45207	1, 3, 5-Trimethylbenzene
28	45211	o-Ethyltoluene
29	45208	1, 2, 4-Trimethylbenzene
30	43238	n - Decane
31	45225	1, 2, 3-Trimethylbenzene
32	45218	m-Diethylbenzene
33	45219	p-Diethylbenzene
34	43954	n-Undecane

o:s/g/morr/3797/pams/compoun2.ppt

Figure 2-6. Example Chromatogram for the PAMS Target Compounds from the BP1 Analytical Column

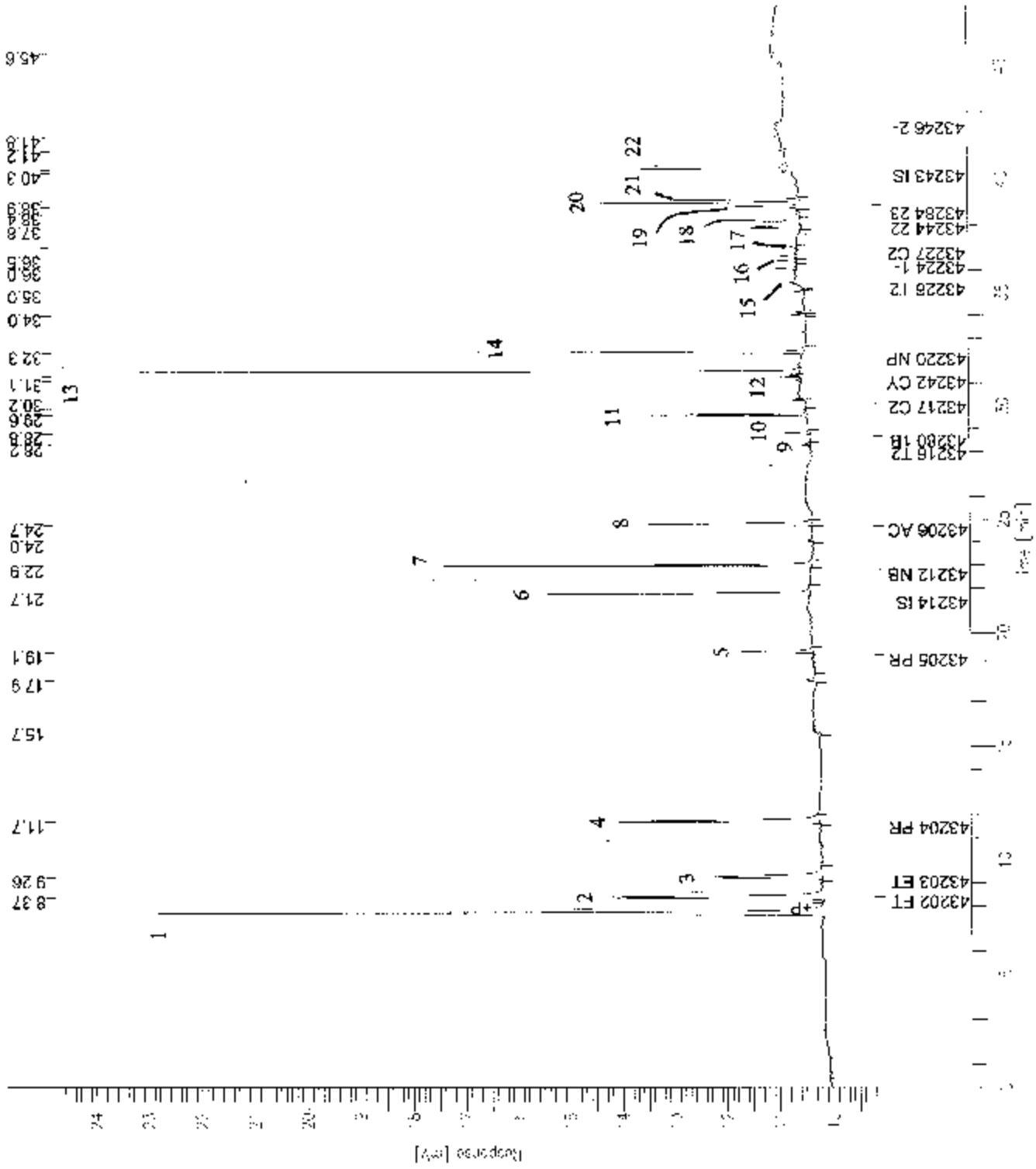


Figure 2-7. Representative Ambient Air Sample Analyzed on a PLOT Column

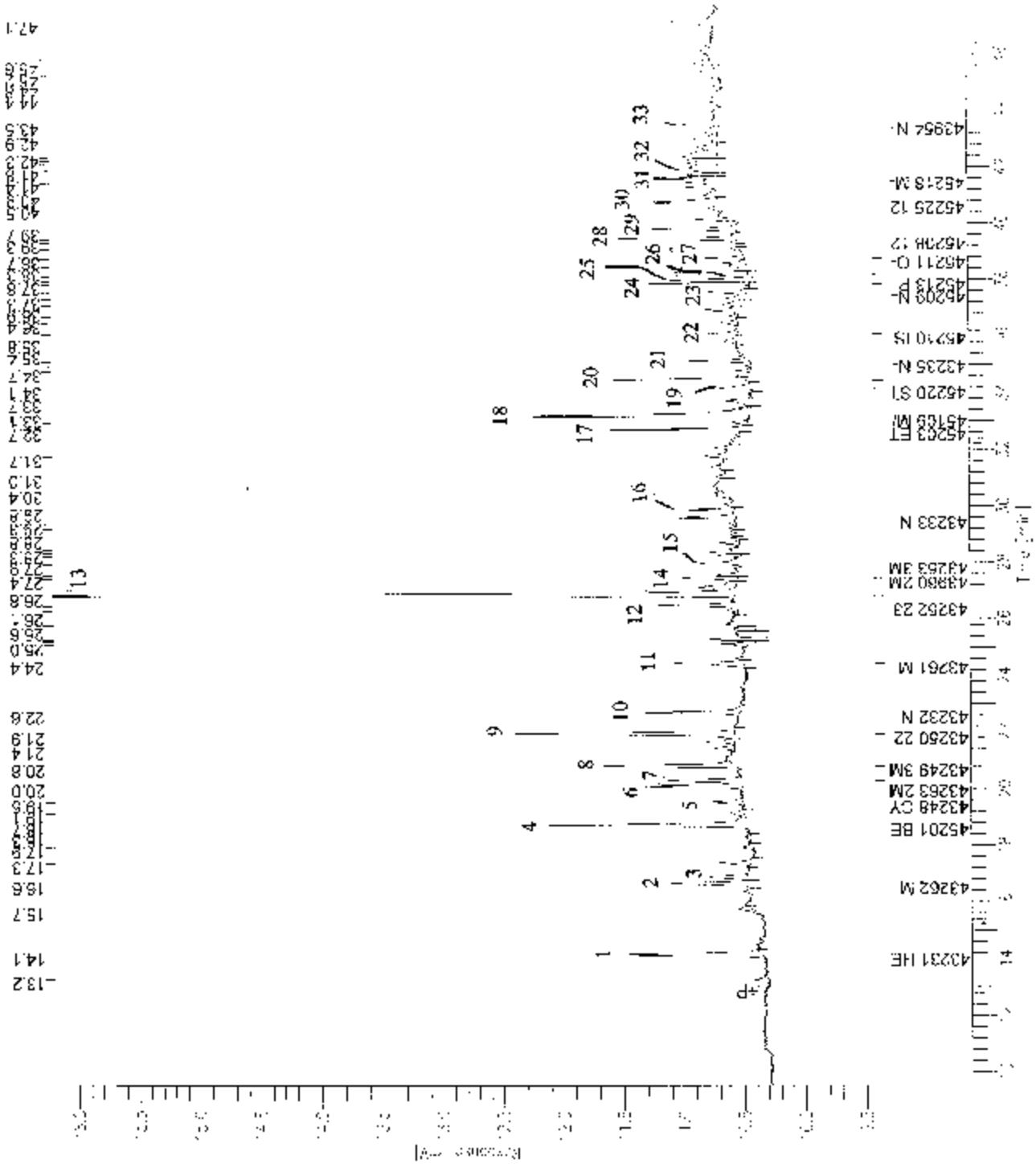


Figure 2-8. Representative Ambient Air Sample (same as Figure 2-6) Analyzed on a BP-1 Column

Table 2-4. Peak Identifications, Ambient Air Sample

PLOT Column		BP1 Column	
Peak Number	**Peak Identification**	**Peak Number**	**Peak Identification**
1	ethane	1	hexane
2	unidentified	2	methylcyclopentane
3	ethene	3	2,4-dimethylpentane
4	propane	4	benzene
5	propylene	5	cyclohexane
6	isobutane	6	2-methylhexane
7	*n*-butane	7	2,3-dimethylpentane
8	acetylene	8	3-methylhexane
9	*trans*-2-butene	9	2,2,4-trimethylpentane
10	1-butene	10	*n*-heptane
11	unidentified	11	methylcyclohexane
12	*cis*-2-butene	12	2,3,4-trimethylpentane
13	cyclopentane	13	toluene
14	isopentane	14	2-methylheptane
15	*trans*-2-pentene	15	3-methylheptane
16	1-pentene	16	*n*-octane
17	*cis*-2-pentene	17	ethylbenzene
18	2,2-dimethylbutane	18	*m/p*-xylene
19	2,3-dimethylbutane	19	styrene
20	2-methylpentane	20	*o*-xylene
21	3-methylpentane	21	*n*-nonane
22	isoprene	22	isopropylbenzene
		23	*n*-propylbenzene
		24	*m*-ethyltoluene
		25	*p*-ethyltoluene
		26	1,3,5-trimethylbenzene
		27	*o*-ethyltoluene
		28	1,2,4-trimethylbenzene
		29	*n*-decane
		30	1,2,3-trimethylbenzene
		31	*m*-diethylbenzene
		32	*p*-diethylbenzene
		33	*n*-undecane

significant, so there will be multiple selectivity influences. Unfortunately, information about most compound characteristics, such as the strength of hydrogen bonding or dipoles, is not readily available or easy to determine. This lack of physical data makes it difficult to accurately predict and explain the separation obtained for a particular column and set of compounds. Some generalizations, however, can be made. The DB1 nonpolar phase (dimethyl polysiloxane) is the most nonpolar siloxane stationary phase available. In most cases, compounds will elute from this column primarily in order of increasing boiling point. However, both vapor pressure and solubility in the stationary phase influence the exact elution order.

PLOT chromatography is accomplished through the gas/solid adsorption interactions between the solutes and the solid adsorbent coated on the column tubing wall. The aluminum oxide (Al_2O_3) surface is deactivated using KCl or Na_2SO_4. Stationary phase polarity is based on the relative retention of saturated and unsaturated hydrocarbons. The more polar column will result in unsaturated compounds being more retained relative to the saturated hydrocarbons. The Na_2SO_4 deactivation of the Al_2O_3 results in a slightly more polar column than the KCl deactivation.

There are some alternative columns that can be used to separate C_2 through C_{12} hydrocarbons for both single- or dual-column approaches. The column selection process should be based on the capability of the column to separate the VOCs listed in Table 2-1 in conjunction with desired overall sample analysis time and cryogen use. The manufacturer-recommended conditions and carrier gas flow rates should be evaluated and optimized to verify acceptable peak resolution prior to use. When choosing alternate columns, the user should consult directly with the analytical column manufacturer for advice regarding column characteristics, optimum gas chromatographic oven temperature programs, carrier gas flow rates, and other operational considerations.

The following columns are alternatives for single-column, C_2 through C_4 hydrocarbon separation and may require sub-ambient temperature conditions to achieve adequate separation:

1. J&W DB™-1 with a 5-micron dimethyl siloxane phase thickness, an internal diameter of 0.32 mm, and a length of 60 m. The recommended oven temperature program is -60EC for 2 minutes then to 180EC at 8EC 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 PLOT capillary column with an internal diameter of 0.53 mm and a length of 30 m. The recommended oven temperature program is 40EC for 4 minutes to 200EC at 10EC per minute. The final oven temperature is maintained for 5 minutes for a total analytical run time of 25 minutes. The GS-Q® column is not affected by water.

The following columns are alternatives for single-column, C_5 through C_{12} hydrocarbon separation and may require sub-ambient oven temperature conditions to achieve adequate separation:

1. 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 35EC for 10 minutes to 200EC at 4EC 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.

2. J&W DB™-624 capillary fused silica column with a 3-micron stationary phase thickness, an internal diameter of 0.53 mm, and a length of 75 m. The recommended oven temperature program is 35EC for 8 minutes to 200EC at 10EC per minute. The final temperature of 200EC is maintained for 3 minutes, which results in a total analytical run time of 27.5 minutes.

3. Restek® RTX-1 capillary fused silica column with a 3-micron dimethylsiloxane phase thickness and an internal diameter of 0.32 mm and a length of 60 m. The recommended oven temperature program is -25EC for 4 minutes then to 175EC at 4EC per minute, then to 220EC at 22EC per minute. The final oven temperature is maintained for 5 minutes for a total run time of about 60 minutes. The Electronic Pressure Control program is 18.3 psi for 5 minutes then to 37.5 psi at 0.35 psi/minute. Total program time is about 61 minutes.

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

2.3.7 Pre-measurement Chromatographic System Verification

Prior to making speciated VOC measurements using an automated GC system, the level of system operation must be thoroughly documented. Information collected during this process is important in characterizing the system operation and establishing a baseline for performance. The information from the pre-measurement system verification is used to determine system specific target analyte retention times, relative retention times, identification of co-eluting compounds and matrix effects, internal standard retention times, interferences, and detection limits.

2.3.7.1 Retention Times and Relative Retention Times

The rigorous sampling frequency requirements and large data sets associated with PAMS require the use of an automated GC system with FID, and presume the commercial availability of such systems. These systems must rely on the practical use of retention times and relative retention times for qualitative peak identification. Commercial GC/FID systems are designed to provide stable system parameters that ensure adequate peak identification based on the use of retention times.

Retention time is the time at which the component elutes from the analytical column and reaches the detection device. The retention of a compound will be determined by its distribution equilibrium between the stationary and mobile phases, i.e., the distribution ratio. Retention time units are typically expressed in minutes and this time is specific to the conditions of the GC system used.

When dealing with complex target analyte lists, as in the case of PAMS measurements, preparing multiple retention time standards that contain 10-15 target analytes that are of known retention order and well separated by retention time will simplify peak identification and retention time assignment. These standards must be analyzed to determine specific retention times for the target compounds and resolve chromatographic issues relative to the instrument conditions, analytical column(s), and chromatographic conditions used. Retention time is widely applied in chromatography

and based on the information gathered from standards. When the retention times for a GC system are verified, it is important for the system to be operated for a period to allow equilibration and retention time stabilization to occur. Several standards should be analyzed over a period of days to assess retention time variability and system stability. The retention time variability is used to establish retention time windows for each component. It is very important that standards be prepared in humidified air, at a relative humidity similar to the samples being analyzed.

The identification of sample components is determined by matching the retention times of the components in the standard with those in the sample. This procedure provides the chromatographer with a certain degree of confidence that the correct peak has been accurately identified. Peak identification by retention time is adequate for the PAMS network requirements. A compound's retention time is characteristic, though not unique. It is, therefore, possible for other compounds to have the same retention time. The presence of co-eluting compounds or missed peak identifications cannot be completely excluded. Periodic confirmation of peak identification and quantification using more definitive techniques, such as GC/MS, is encouraged.

Retention times are typically stable and reproducible, but they are subject to system variability. To account for any retention time variations, relative retention time (RRT) can be used to aid in assigning peak identifications. Many commercial GC systems incorporate the use of relative retention times for peak identification in their data acquisition and processing software. On most commercial GC systems, the use of RRT for peak identification is easy to implement. An adjusted or relative retention time can be determined by using both reference or internal standard peaks. Reference peaks are those components of the sample that are typically present in the sample matrix (reference peaks of opportunity). Internal standard peaks are components subsequently added to the sample that are uncommon to the sample matrix. The relative retention time of a target compound (a), as compared with a reference compound (b), may be calculated as:

$$RRT \quad \frac{RT_a}{RT_b} \qquad \textbf{(2-4)}$$

where:

RT_a = retention time of the target compound

RT_b = retention time of the reference peak

The relative retention time of a compound determined in this manner will vary with temperature and the analytical column stationary phase, but should otherwise be independent of other analytical conditions. The relative retention time method of peak identification works well when the target compound elutes relatively close to the reference peak used and retention time shifting is linear. The use of reference peaks in several retention time windows is only recommended to compensate for retention time shifting that is not linear. The use of too many reference peaks may actually compromise the ability of the data system to adequately identify the target peaks consistently.

A retention time reference peak should be chosen that;

- Is always or typically present in the sample matrix;
- Is in the same general retention time area or carbon number range of the chromatogram;
- Shows chromatographic behavior similar to target components (sharp peak shape); and
- Is well separated from other components in the sample matrix.

Suggested retention time reference peaks include propane, toluene, benzene, and butane, or other compounds appropriate to the individual PAMS site.

2.3.7.2 Internal Standards

When GC analysis is performed on a continuous basis at an often unattended or remote site, fluctuations in ambient temperature and other factors can cause variations in instrument performance and chromatographic retention times. Changes in ambient conditions can cause small changes or variations in carrier gas flow rate, column temperature, detector response, sample injection volumes, and sample moisture content. Use of internal standards can help to minimize the influence of GC system variability. Internal standards are often also used as reference peaks for determining relative retention times.

The internal standard should be added to the cryofocusing or adsorbent sample collection system, concurrent with sample collection, to minimize the effects of the sample matrix. The chief difficulty in using internal standards for VOC analysis lies in finding an internal standard that does not interfere with the sample constituents. Characteristics that must be considered when choosing a suitable internal standard include:

- Components that are uncommon in ambient air;
- Ease and reproducibility in handling and introducing into the GC system;
- Similar in chemical and physical properties to those compounds being analyzed;
- Moderate volatility and low vapor pressure comparable to the expected retention times and concentrations of the sample hydrocarbons;
- Does not interfere with the measurement method;
- Complete resolution from all other components present in the sample;
- Stable under the conditions and method used; and
- Does not react with components of the measurement system.

Perfluorotoluene (PFT) is a compound that meets these characteristics and has been used as an internal standard for air monitoring programs.

Separation of the internal standard compound from other compounds normally found in the sample must be accomplished using the measurement system and methods implemented by the user to accomplish sample analyses. Typical ambient air samples are very complex and contain numerous components. Verification of the internal standard performance and retention time characteristics using the GC system chosen must be determined using actual ambient air samples. A suitable internal standard can be analyzed concurrently with the sample to adjust for variations in retention time and detector response.

2.3.7.3 Identification of Co-Eluting Compounds and Matrix Effects

Another important part of pre-measurement chromatographic system verification is the determination and effect of possible co-eluting compounds and other sample matrix effects on the ability to find reference peaks, make peak identification, and ultimately to quantitate target analytes.

Blank samples that contain humidified zero air should be analyzed to establish the GC system background and determine the level of contamination or artifacts. Blank or zero air samples should not contain the target VOCs at a concentration greater than the detection limit. Any significant levels of contamination or artifacts that interfere with the retention times of target analytes must be addressed or documented prior to sample analysis. Information from the analysis of standards containing target analytes can then be used to determine where co-eluting compounds may occur. Co-elution issues can be resolved by optimizing the chromatographic conditions of the system, such as carrier gas linear velocity and column oven temperature.

Further information regarding co-eluting compounds in samples not identified by zero air analyses may be obtained using GC/MS. When used under similar conditions (column type,

temperature program, etc.), the GC/MS provides valuable information to aid the user in confirming peak identification and determining the presence of co-eluting compounds and other unknowns. When GC/MS is used for confirmation, it is important to ensure that the system sensitivity or detection limits are equivalent to the O_3 precursor GC/FID system being used.

2.3.7.4 Detection Limits

The development of methods to measure trace levels of organic compounds in ambient air and the need for the ability to measure extremely low concentration levels for risk assessment purposes requires that the analytical system detection limits for the target compounds be established for the analytical system used. The analytical detection limit must meet the measurement quality objectives given in Section 2.8. The detection limit is one of the most important performance characteristics of an analytical system. The GC system detection limit should not be determined until a complete, specific, and well defined analytical method has been developed. All sample processing steps used in the analytical method must be included in the experimental determination of the detection limit. Refer to Section 2.8 for guidance on the approach to establishing VOC detection limits for PAMS. If the analytical method detection limit does not meet the quality objectives, the sensitivity of the GC system and methodology used may not be adequate and should be re-evaluated and improved prior to use for O_3 precursor monitoring programs.

2.4 Automated Method for Collecting and Analyzing Volatile Organic Compound Ozone Precursor Samples

The minimum monitoring network requirements for enhanced O_3 monitoring are described in Section 4.4 of 40 CFR Part 58, Subpart E, Appendix D, and are also discussed in Section 2.1 of this document. The rigorous sampling frequency requirements of enhanced O_3 monitoring (e.g., eight 3-hour samples every day during the monitoring period) makes automated GC methodology a viable, cost-effective approach for obtaining VOC measurements at all sites within a network. An automated

GC system offers an additional advantage in its inherent capability to provide short-term (e.g., 1-hour) measurements on a continuous basis for long time intervals.

The following description of automated methodology is based on currently available commercial automated GC systems and is described in general terms. The intent is to provide guidance on the configuration and operation of automated GC systems, not to serve as a Standard Operating Procedure (SOP). Alternative approaches using custom fabricated automated systems are acceptable. This guidance should be used to define equipment specifications and prepare system specific SOPs consistent with the 40 CFR Part 58 enhanced O_3 monitoring requirements. The users must recognize that they are responsible for optimization and characterization of the critical parameters for their specific GC system (consistent with the manufacturers' instructions, if applicable).

The GC system must be capable of automated sample collection, analysis, and data acquisition on site and must be housed in a temperature-controlled shelter. The primary components of an automated GC are a sample introduction system, sample conditioning system (for moisture removal), sample concentration system (for sample enrichment), cryofocusing trap (as an option for improving peak shape and resolution), gas chromatograph with FID(s), and a data acquisition and processing system. Commercially available systems incorporate many variations of the primary components of an automated GC system.

The purpose of Section 2.4 is to describe the sample collection, sample analysis, system operation, system calibration, and system specifications for an automated GC system. The sample probe and manifold, sample introduction, sample conditioning, and sample concentration systems are discussed in Sample Collection, Section 2.4.1. Sample cryofocusing, gas chromatography, and data acquisition and processing are discussed in Sample Analysis, Section 2.4.2. This guidance should be used to define automated GC specifications for procurement and to develop and implement a network monitoring program consistent with the 40 CFR Part 58 enhanced O_3 monitoring requirements.

2.4.1 Sample Collection

Samples collected for automated analysis should represent a time-integrated average for the required sampling period. In the case where an integrating canister is used to collect the sample, the canister should be filled at a constant flow rate over the full integration period minus the time required to transfer a sample to the primary trap and purge and evacuate the canister. In the case where the sample is collected directly onto the primary concentration trap, the sample should be collected at a constant flow rate for the full integration period minus the time required to desorb the sample onto a secondary trap or onto the analytical column and perform system operations to accommodate the next sample collection. The minimal sample integration time required to constitute a 1-hour sample is 40 minutes. Additional provisions must be made to meet the 24-hour sample requirement. A manual approach to 24-hour sample collection and analysis is discussed in Section 2.5.

The O_3 precursor compounds are collected from a sample manifold with a probe and introduced into the automated GC system. Water may be removed from the sample stream as discussed in Section 2.3.3 and then the VOCs concentrated onto a primary sample collection trap. The concentrated sample is thermally desorbed onto a secondary cryofocusing trap (optional) or onto the head of the cooled GC column to focus the desorbed sample into a small volume or "plug." The sample volume is then desorbed for analysis by the GC/FID system.

2.4.1.1 Sample Probe and Manifold

A sample probe and manifold assembly should be used to provide a representative air sample for collection and subsequent analysis. Sample probe and manifold assemblies are commercially available or can be custom fabricated. Examples of typical sample probe and manifold assemblies are presented below. If automated calibration techniques that periodically flood the manifold with calibration standards are to be applied for the criteria pollutants, a separate manifold would be required to support the VOC and carbonyl components of the PAMS program.

The sample probe is constructed of glass that is approximately 1 inch in outside diameter (O.D.). The inlet of the sample probe is configured with an inverted funnel, approximately 4 inches O.D. The sample manifold is constructed of glass, approximately 1 and ½ inches O.D. The manifold has ports used for sample distribution. The number of ports located on the manifold must be equal to or greater than the total number of monitoring systems to which sample will be delivered. To reduce the potential for bias, the port nearest to the inlet of the manifold should be reserved for VOC sampling.

Teflon® bushings are used to connect sample lines to the manifold. Because the manifold and ports are constructed of glass, care must be taken to not place excessive stress on the assembly to avoid breakage. For VOC sampling, the sample lines should be constructed of 1/8 inch O.D. stainless steel tubing. The 1/8 inch tubing is flexible and will accommodate the flow rates typically associated with VOC sample collection. The sample lines should be kept as short as possible to reduce sample transfer time.

A blower and bleed adapter are located at the exit end of the sample manifold. The blower is used to pull sample air through the probe and manifold and the bleed adapter is used to control the rate at which the sample air is pulled through the manifold. An excess of sample air is 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 of outside ambient air. Sample air flow through the sample probe and manifold should be at least two times greater than the total air flow being removed for collection and analysis by all systems on the manifold.

The vertical placement of the sample probe and inlet funnel should be at a height of 3 to 15 meters above ground level. Because the O_3 monitoring requirements involve multiple-pollutant measurements, this range serves as a practical compromise for probe position. In addition, the probe inlet should be positioned more than 1 meter, both vertically and horizontally, away from the housing 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 any obstacle should be a 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 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 degree clearance is required. More specific details of probe positioning are presented in the "PAMS Implementation Manual."[25] The glass probe should be reinforced or supported along the straight vertical axis of the assembly. Typically this support is provided by routing the probe shaft through a rigid section of metal or plastic tubing that is secured to the housing structure.

The manifold can be positioned in either a horizontal or vertical configuration. Figure 2-9 presents the manifold assembly in the vertical configuration. Figure 2-10 presents the manifold assembly in the horizontal configuration. If the horizontal configuration is used, the sample ports must point upward so that material that may be present in the manifold will not be transferred into the sample lines.

With continuous use the sample probe and manifold can accumulate deposits of particulate material and other potential contaminants. The sample probe and manifold should be cleaned to remove these materials. The recommended frequency for cleaning is quarterly. To clean the assembly, disconnect the sample lines and blower from the manifold. The sample lines and blower are not cleaned. For safety, electric power to the blower should be terminated until the cleaning process is completed. Disassemble the individual components by disconnecting the probe, manifold, collection bottle, and coupling devices from each other. The individual components should then be cleaned using heated high purity distilled water and a long handled bottle brush. The components should then be rinsed with the distilled water and allowed to dry completely before reassembling. If required, mild glass cleaner or detergent can be used to clean particularly dirty components. However, care should be taken to select cleaners and detergents that are advertised to have low organic compound content and the number of rinses performed should be increased to ensure that all associated residues are removed.

2.4.1.2 Sample Introduction

The air sample can be introduced to the automated GC system directly from the air sample manifold using a mass flow controller or other flow control device at a constant flow rate over the prescribed sample integration time. As an alternative, the air sample may be collected into an integrating canister at a constant flow rate over the prescribed sample integration time,

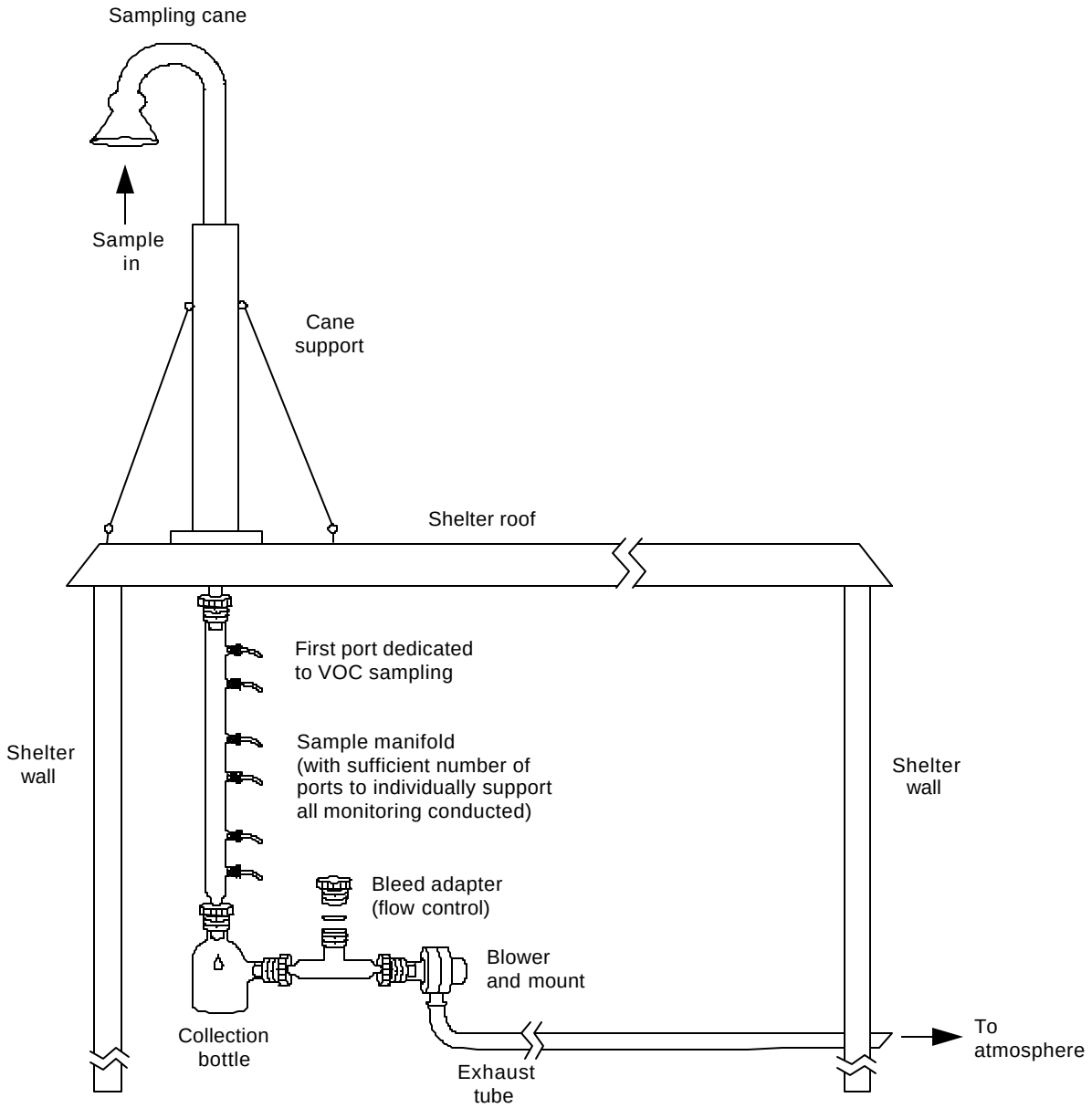
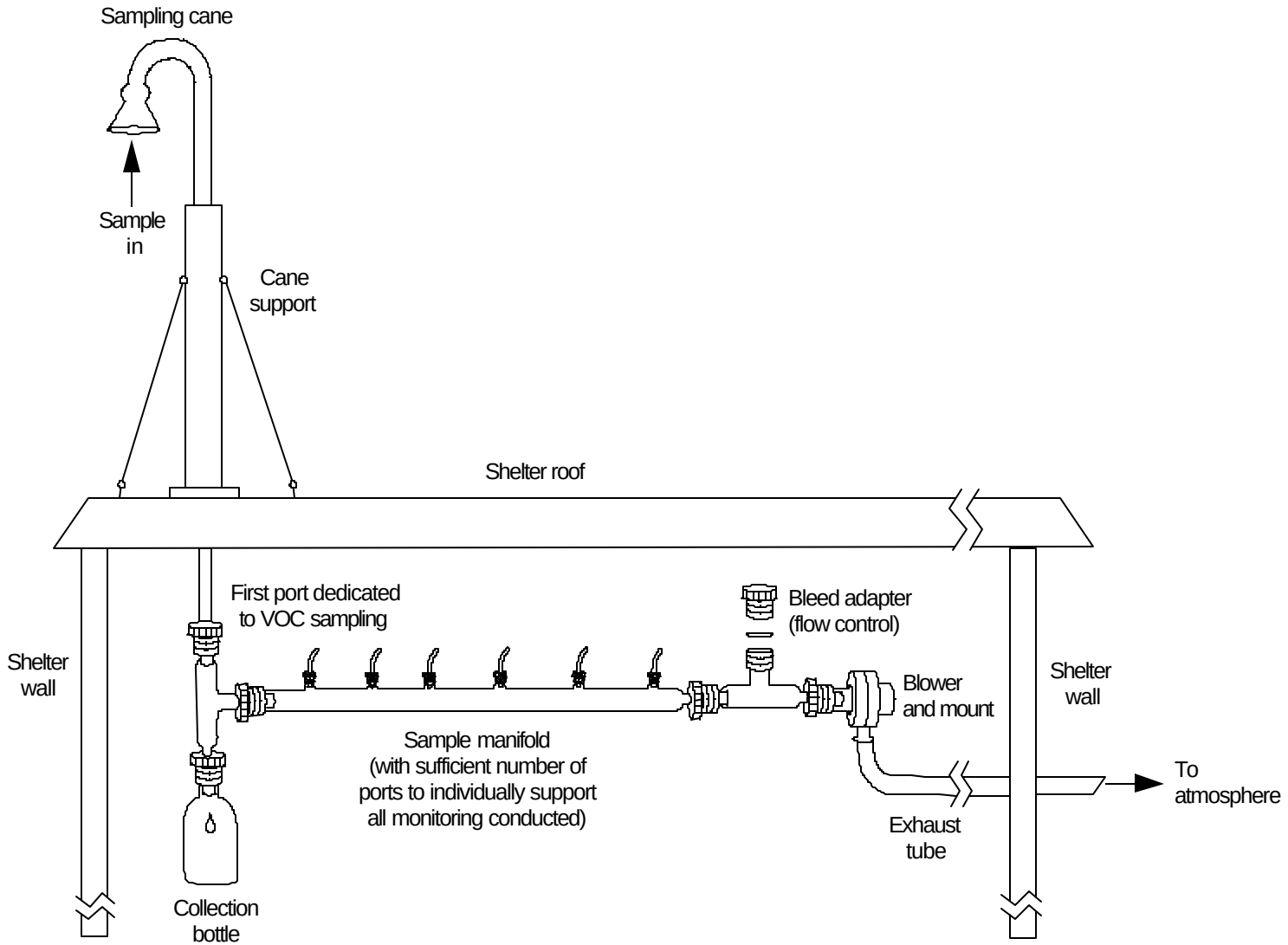


Figure 2-9. Vertical Configuration



o/s/g/mon/3797/pams/shelt2.ppt

Figure 2-10. Horizontal Configuration

and then supplied to the sample concentration trap at the end of the integrating period. For purposes of calibration and proficiency studies, and to meet the 24-hour sampling requirements, samples may also be introduced directly from pressurized SUMMA® canisters.

2.4.1.3 Sample Conditioning

Moisture is removed from the sample stream for automated GC analysis to prevent or reduce the detrimental effects of moisture on the primary concentration trap, analytical column(s), and detector(s) as described in Section 2.3.3. Moisture removal also allows for analysis of larger sample volumes, which provides lower detection limits, and is crucial to the measurement of very low concentration VOCs.

Some commercially available automated GC systems incorporate the use of Nafion® membrane sample drying devices. New developments in moisture removal include controlled temperature vaporization, selective temperature condensation, hydrophobic concentration traps, and micro-scale purge-and-trap. The loss of polar VOCs may result from moisture removal using some of these techniques and this loss of polar VOCs may significantly affect the TNMOC measurement. The user must characterize the effects of their particular sample conditioning method on the TNMOC measurement and target VOCs of interest.

2.4.1.4 Sample Concentration

Ambient air samples are primarily concentrated using multi-bed sorbent or cryogenically-cooled deactivated glass bead traps. Sampling time and flow rate are typically used to determine the total volume concentrated onto the primary trap. Multi-bed sorbent traps (Carbotrap® and Carbosieve®) or cryogenically cooled glass bead traps are required to efficiently collect the complete range (C_2 through C_{12}) of VOCs for O_3 precursor monitoring.

Samples are collected onto sorbent traps at ambient temperature or the traps are cooled using liquid cryogen (H_2, CO_2, Ar) or Peltier® electronic cooling devices to improve collection efficiency. Ideally, sorbent traps selectively adsorb only the trace VOCs and do not interact with the atmospheric constituents (i.e., CO_2) or introduce any contaminants into the system. Sorbent traps may also be designed to eliminate water vapor by using hydrophobic sorbent materials.

Sample concentration using glass bead traps requires a trapping temperature of -185EC. Trapping at a temperature above -185EC will result in the loss of early-eluting C_2 compounds such as acetylene, ethane, and ethylene. Trapping at a temperature below -185EC can result in the collection of methane and oxygen, and can have an adverse effect on chromatography. These traps are typically cooled using liquid cryogen (N_2 or Ar). This cooling process is commonly known as cryogenic concentration or cryotrapping, and is the oldest and best known of the techniques for collecting C_2 through C_{12} VOCs. The glass beads provide surface area for collection of the VOCs at the cryogenic trapping temperature.

2.4.2 Sample Analysis

Following sample collection and concentration, the sample is thermally desorbed directly onto the analytical column(s). The analytical column may be cryogenically cooled to aid in focusing the desorbed sample into a narrow band prior to chromatographic separation. The analytical column chromatographically separates the sample into components for subsequent detection by the FID. The signal from the FID is then acquired and processed using a PC-based data acquisition and processing system.

2.4.2.1 Sample Focusing or Cryofocusing

The sample cryofocusing step is optional and may not be employed in all commercially available automated GC systems. The secondary cryofocusing trap is used to focus the desorbed

sample from the concentration trap into a "plug" for injection onto the analytical column. Cryofocusing improves the peak separation and in particular the resolution of C_2 and C_3 hydrocarbons. This technique is especially helpful when the sample is desorbed from the concentration trap at low flow rates.

Cryofocusing traps incorporate the use of fused silica tubing that is cooled using liquid cryogen. The fused silica tubing is wide-bore (0.32 mm I.D.) or megabore (0.53-mm I.D.) deactivated fused silica tubing that is cooled to approximately -185EC. Cryofocusing traps may be packed to increase the surface area and improve the focusing of the sample band.

2.4.2.2 Gas Chromatography

The gas chromatograph contains the analytical column(s) of choice for PAMS VOC analysis. Refer to Sections 2.3.5 and 2.3.6 for guidance on column configuration and selection. Commercially available GC systems are typically configured with the appropriate analytical column(s) to separate the VOCs of interest. However, the user must determine if the system meets the enhanced O_3 monitoring requirements and specifications (Section 2.4.4) prior to procurement. The user must also characterize the performance of the system operation prior to use. Commercial GC systems may incorporate the use of single or dual-column configurations (in series or parallel) that may require sub-ambient oven temperature programs. It is important to note that systems that eliminate the need for sub-ambient column oven temperatures reduce the overall cryogen consumption of the system. New developments in carrier gas electronic pressure programming and control have greatly improved peak resolution and retention time stability for some automated GC systems.

Automated GC systems employ the use of a PC-based data acquisition and processing system for peak integration and quantitation. Data acquisition and processing systems are comprised of hardware and software that perform data acquisition, peak detection and integration, peak identification by retention time, post-run calculations and quantitation, calibration, peak reintegration, user program

interfacing, and hard copy output. Data are automatically stored on magnetic media (e.g., hard disk or floppy diskette).

The GC data acquisition and processing software is developed and supplied by the GC manufacturer and should contain the necessary algorithms to acquire, integrate, and identify the chromatographic peaks by retention time. The system should be capable of producing an electronic and hard copy report file that contains the information needed to identify the sample and a listing of all peaks detected in the chromatogram. This listing should contain the peak name if it is a target compound. All detected peaks (both target and unidentified) should be reported with a concentration, in ppbC, and a retention time. The listing should also contain the TNMOC estimate calculated by summing the concentrations of all peaks (both target and unidentified) detected in the chromatogram. See Section 2.6.1 for a more detailed discussion on data processing capabilities of automated GC systems.

2.4.2.3 Analytical System Calibration

The detector response of the analytical system should be calibrated with multiple level propane primary standards over the expected sample concentration range. Benzene is suggested as a second primary standard to calibrate dual-column systems. These dual-column systems employ a Deans®[24] switch or other column switching techniques. Benzene may also be used to quantitate the target compounds when using a single-column approach. The primary calibration standard is used to generate a response factor per carbon atom for determining the concentration of each target VOC, as well as the TNMOC. It is impractical and unnecessary to determine compound specific response factors for each of the target VOCs presented in Table 2-1 because the carbon response of the FID to these compounds is approximately linear.

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

$$C_A \quad RF\,(AC) \qquad \textbf{(2-5)}$$

where:

C_A = Concentration (ppbC)

RF = Response Factor, ppbC/area count

AC = Area Counts

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 primary standard using the following equation:

$$RF \quad \frac{3\,(C_B)}{MAC} \qquad \textbf{(2-6)}$$

where:

3 = Carbon Atoms in Propane (6 when benzene is used as a second calibration standard)

C_B = Concentration of the NIST Propane Standard (ppbv)

MAC = Mean Area Count, determined from the analyses of multiple levels or multiple injections of the primary standard

The retention time of target compounds is determined by analyzing the retention time calibration standard as described in Section 2.3.4.2. This standard is analyzed in triplicate, at a minimum, to establish the correct retention times and retention time windows for the peaks of interest.

The primary standard (Section 2.3.4.1) is used to perform a calibration check of the analytical system in order to determine system variability and overall performance. The calibration and

retention time checks may be performed concurrently using the retention time calibration standard. The compound concentrations and retention times should compare within the limits of the data quality objectives established for the monitoring program. If they do not, the analytical system should be recalibrated.

2.4.3 System Operation

This section provides guidance and general operating considerations for initial system set-up, optimization of sampling parameters, and field operation for automated GC systems.

2.4.3.1 Initial System Set-up

During the initial set-up of the automated system several parameters must be evaluated to optimize the operating conditions. Critical parameters include, but are not limited to, the sample collection flow rate and sample integration time, sample concentration and desorption conditions, oven temperature program parameters, detector calibration, and the peak detection and integration methods used by the data acquisition and processing system. These parameters are optimized by varying the operating conditions to achieve the best resolution and detection of the target VOCs using primary calibration and retention time calibration standards.

Prior to making VOC measurements using an automated GC system, the baseline performance of the system must be thoroughly documented. The information from the system baseline characterization is used to determine system specific target compound retention times, relative retention times, identification of co-eluting compounds and matrix effects, internal standard retention times, interferences, and detection limits. Subsequent calibrations and retention time QC checks should be verified against the system baseline to identify trends or excursions from acceptable performance. See Section 2.3.7 for a discussion of pre-measurement system characterization.

Users should anticipate a minimum of six months for initial setup, configuration, familiarization, and development of SOPs prior to the field implementation of an automated GC system. The system should initially be set up by the manufacturer and demonstrate adequate system stability and performance. Under terms of agreement for purchase, the manufacturer should be required to provide a detailed instruction manual for system operation and to meet the specifications as defined by the user. For a set of primary system specification guidelines see Section 2.4.4.

2.4.3.2 Sampling Parameters

Determination of optimum sampling parameters is dependent on field conditions (i.e., expected compound concentration ranges, humidity, temperature, etc.), desired sensitivity, cryogen consumption, and sample trapping efficiency. During the setup period, these sampling parameters should be evaluated to determine the optimum conditions for each. Primary sampling parameters are the sample collection frequency (1 sample each hour) and the minimum sample collection or integration time (40 minutes).

For hourly sampling, the minimum sample collection or integration time is 40 minutes. A sample collection volume of 200 to 600 mL is recommended. The sample volume used requires a trade-off between the required detection limit and potential moisture interference problems. Longer sample integration times may be implemented by using an intermediate sample collection or integration device. This device usually consists of a sample integration vessel configured to provide integrated collection of one sample while the previously collected sample is being analyzed. Advantages to using an intermediate sample integration device include longer integration times and reduced cryogen use during the concentration step of sample analysis.

2.4.3.3 Field Operation

The automated GC system should be installed in a temperature-controlled shelter at the field location. Detailed SOPs for field operation of the automated GC system must be developed. The SOPs should be based on information obtained during the set-up and familiarization period and the requirements of the monitoring program. Refer to QA/QC Section 2.8.3.1 for a more detailed discussion of SOP development. The system should be maintained by a qualified operator who should perform the routine operational and quality control functions as specified in the SOPs. Critical operational checks should be performed as frequently as practical. Operational parameters should be adjusted, if necessary, so that the data quality objectives are met. It is recommended that all adjustments to the operational parameters be documented in a laboratory notebook. Primary calibration and retention time checks should be performed routinely according to the minimum QC requirements given in Section 2.8. Retention time calibration checks are performed 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 recalibration is necessary.

2.4.4 System Specifications

A set of primary specifications is provided below to conduct the evaluation for procurement of an automated GC/FID system. It is imperative that the enhanced O_3 monitoring network requirements for this type of system be compared against vendor offers to ensure that appropriate systems are procured. Primary system specifications are presented below. Additional system specifications may be added at the discretion of the user.

- The automated GC/FID system must be able to meet the sampling frequency requirements as prescribed in 40 CFR Part 58, Subpart E, Appendix D, and the sample integration requirements as discussed in Section 2.1 of this document (minimum sample integration time of 40 minutes to comprise a 1-hour sample). The manual methodology described in Section 2.5 is required for collection of the one 24-hour sample every sixth day.

- Cryogen consumption is a primary consideration for system procurement. Transport and delivery of liquid cryogen to the site may be impractical. The amount of liquid cryogen consumed by the system will determine the frequency of site visits and impact the cost for site operation and the level of data capture. Systems that utilize electronic cooling devices should be strongly considered if all other user specified requirements are satisfied.

- To avoid cross contamination, the system must demonstrate system background levels that are below the 0.2 ppbC estimated detection level for each VOC target species and 3 ppbC for TNMOC.

- The system must demonstrate the ability to separate the target VOCs of interest (C_2 through C_{12}) and provide an adequate estimate of the TNMOC value. Refer to Section 2.2.1 for a discussion of TNMOC.

- To ensure adequate peak identification and quantitation by retention time, the system must incorporate operating parameters that provide stable retention times. Observed retention time drift must be less than 0.1 minutes.

- The sample conditioning device, used to remove moisture from the sample stream and reduce the effects of moisture on the system, must minimize both polar VOC losses and the potential for introducing contaminants into the analytical system.

- The minimum level of quantitation (LOQ) must be 3.0 ± 0.2 ppbC for propane and correspond to an FID signal that is 3 to 5 times the baseline noise.

- The system should incorporate microprocessor control and battery backup capability to ensure that all programmed control activities for sample collection and analysis will be retained should the system power be interrupted. The system should automatically resume all operations once power is restored to the system to improve the level of data capture. Although not a requirement, the capability to log and report system interruptions (date, time, and type of failure) is advantageous.

- The system operation should be flexible enough to allow sample collection and analysis parameters to be easily modified to meet changes in network monitoring frequency and sample integration times as required.

- Expedient and responsive vendor support is a key consideration. The user should specify that the vendor maintain an adequate supply of replacement parts and a staff of qualified service technicians to ensure that the minimum number of sampling events are missed should a system failure occur. The user should specify that the vendor guarantee that parts and components be delivered to the site within 2 working days

from the placement of the order. The user should also specify that the response to automated GC system service calls be received within 24 hours of placement and the system be placed in acceptable working order within 7 days of the service request.

- The vendor must provide an in-depth, detailed manual covering all aspects of the automated GC/FID system (i.e., operation, maintenance, etc.), initial system setup, user training, and demonstrate adequate system performance.

2.5 Manual Method for Collecting and Analyzing Volatile Organic Compounds

The manual methodology for obtaining volatile organic compound (VOC) measurements involves collecting time-integrated, whole air canister samples for subsequent analysis at a central laboratory. Under the minimum network monitoring requirements in 40 CFR Part 58, Subpart E, States must obtain 3-hour and 24-hour integrated measurements of VOCs 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 discussed in Section 2.1. A discussion of sample collection methodology is provided in EPA Compendium Method TO-15 (Appendix A).

Application of the manual methodology to the enhanced O_3 monitoring regulations requires the collection and analysis of a large number of canister samples. The magnitude and success of the manual monitoring program depends on the quantity of canisters available, the capabilities of the sample collection system used, the analytical capacity of the central laboratory, and the availability and skill of staff to address the needs of the specific program design. An integrated, well planned sample collection and analysis program is necessary to address the numerous aspects of a canister-based monitoring operation, which include canister cleaning and transport, sample collection procedures and frequency, analysis procedures, and data acquisition and reporting. These details must address the needs of the specific program. 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 all operations.

The intent of this section is to provide general guidance on manual methodology. The following sections generally describe multiple-event and single-event canister sampling equipment, procedures, and operation. Recommended system specifications applicable to the procurement of canister sampling systems are also presented.

2.5.1 Sample Collection

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

Canister sample collection systems should be capable of unattended operation in order to allow collection of samples in accordance with the network monitoring requirements presented in Table 1-1 (see Section 1). Procedures for collecting canister samples are described in Section 2.5.1.1 and Section 2.5.1.4. Precautions pertaining to the use of canisters, canister cleaning procedures, and sample collection system certification procedures are discussed in detail in Section 2.5.3.

Collecting time-integrated whole ambient air samples for subsequent analysis of target VOCs is a widely accepted practice. Samples collected should represent a time-integrated average for the required sampling period (i.e., collected at a constant flow rate over the full collection period). Sample collection 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 canister sample collections and multiple- or single-event sample collection capabilities. Time-integration techniques generally involve the use of electronic and/or mechanical devices. Canister sampling systems are available commercially or can be custom built by the user for a specific application.

Multiple-event sample collection systems are needed to meet the 3-hour, around-the-clock collection frequency. 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.

2.5.1.1 Multiple-event Sample Collection Equipment

A typical multiple-event sample collection system configuration is presented in Figure 2-11. The multiple-event canister sample collection system is comprised of the following primary components:

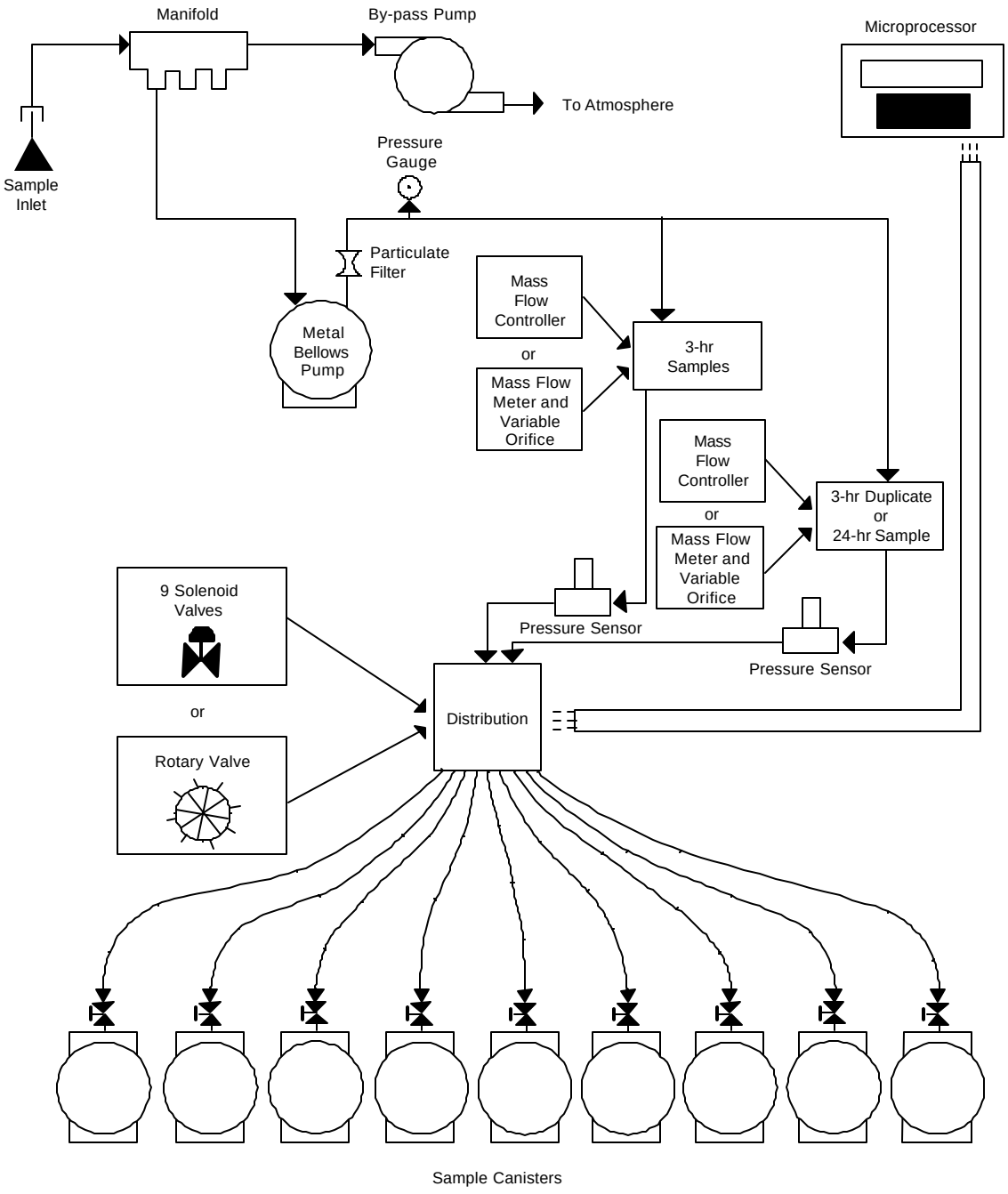


Figure 2-11. A Typical Multiple-event Sample Collection System

Inlet probe and manifold assembly - Constructed of glass (see Figures 2-9 and 2-10) or stainless steel. Used as a conduit to transport sample air from the atmosphere at the required sampling height and distribute it for collection.

By-pass pump - A single- or double-headed diaphragm pump, or a caged rotary blower. Used to continuously draw sample air through the inlet probe and manifold assembly at a rate in excess of the sampling system total uptake. All excess sample air is exhausted back to the atmosphere.

Sample pump - A stainless steel bellows pump, capable of 2 atmospheres above ambient output pressure. Used to extract sample air from the manifold assembly and deliver it to the sample canister during collection.

Sample inlet line - Chromatographic-grade stainless steel tubing. Used to connect the sampler to the manifold assembly.

Sample canisters - SUMMA® passivated stainless steel sample vessels of desired internal volume with a bellows valve attached at the inlet of each unit. Used to contain the collected sample air for transportation and analysis.

Electronic pressure sensor - A pressure measurement device capable of measuring vacuum (0-30 in Hg) and pressure (0-30 pounds per square-inch gauge). Used to measure initial and final sample canister pressures.

Adjustable orifice and mass flow meter assembly or electronic mass flow controller - An indicating flow control device(s). Used to maintain a constant flow-rate (± 10%) over a specific sampling period under conditions of changing temperature (20-40EC) and humidity (0-100% relative).

Particulate filter - Two micron sintered stainless steel in-line filter. Used to remove particulate material larger than 2 microns from the sample air being collected.

Microprocessor - An event control and data acquisition device. Used to allow unattended operation (i.e., activation and deactivation of each sampling event) of the sampling system and to record sampling event specific process data (i.e., start and end times, elapsed times, initial and final sample pressures, etc.).

Solenoid valves or a multi-port rotary valve - Eight electric-pulse-operated or low temperature coil, stainless steel body solenoid valves with Viton® plunger seat and o-rings or one multi-port stainless steel body rotary valve with Viton® o-rings. Used to provide access to or isolation of the sample canister(s).

Stainless steel tubing and fittings - Isolation and interconnection hardware. Used to complete 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.

2.5.1.2 Multiple-event Sample Collection Procedure

Samples are collected in individual canisters using a single pump and one or more flow control devices. 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 each sample canister during each specific sampling event.

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

$$F \quad \frac{P \times V}{T \times 60} \qquad \textbf{(2-7)}$$

Where:

F = flow rate (mL/min)

P = final canister pressure, atmospheres absolute

V = volume of the canister (mL) at one atmosphere pressure

T = sample period (hours)

60 = minutes in an hour

For example, if 6-L canisters are to be filled to 1.5 atmospheres absolute pressure each over individual 3-hour integration period (i.e., collection episode), the flow rate specific to each period is calculated as follows:

$$F \quad \frac{1.5 \text{ atm} \times 6000 \text{ mL/atm}}{3 \text{ hr} \times 60 \text{ min/hr}} \quad 50 \text{ mL/min}$$

During operation, the microprocessor control device is programmed to activate and deactivate the components of the sample collection system, consistent with the beginning and end of each individual sample collection period.

The use of individual electric-pulse-operated or low temperature coil solenoid valves avoids any substantial temperature rise that would occur with conventional coil solenoid valves. The temperature rise associated with conventional coil solenoid valves could cause outgassing of organic compounds from valve components into the samples.

Electric-pulse-operated solenoid valves require only a brief electrical pulse to open or close at specified start and stop times. The valve, therefore, experiences no temperature increase. The pulses may be obtained either from the microprocessor directly, if it can be programmed for short (5 to 60 seconds) actuation pulses, or by incorporating an attached electric pulse circuit.

Low temperature coil solenoid valves incorporate a low current draw circuit design to lift the plunger and valve seat assembly (i.e., open the valve) when the coil is energized. A spring returns the plunger and valve seat assembly (i.e., closes the valve) automatically when the coil is not energized. Because no electric-pulse circuit is required, the low temperature coil solenoid valves are much simpler in design and considered more reliable.

Canister sampling systems can collect sample from a shared sample probe and manifold assembly as described in Section 2.4.1.1 or from a dedicated stainless steel sample probe, manifold

assembly, and by-pass pump. If a dedicated probe, manifold assembly, and by-pass pump are used, provisions should be made (i.e., using a separate timer device, etc.) to start the by-pass pump several hours prior to the first sampling event of a multiple-event collection period to flush and condition the sample collection system components. The connecting lines between the sample inlet and each canister should be kept as short as possible to minimize internal surface area and system residence time.

The flow rate into each canister should remain relatively constant over the entire collection period of each sampling event. If an adjustable orifice(s) is used as the flow control device(s), a drop in the flow rate will occur near the end of the each sample collection period as pressure in the canister increases. Typically this condition occurs when canister pressure exceeds one-half atmosphere above ambient pressure. Consequently, care must be taken to select a sample flow rate that will yield a final pressure that will not significantly exceed 22-24 psia (i.e., ~8-10 psig) at the end of the sample collection interval.

Prior to any field use, each sample collection system should be certified as nonbiasing, meaning that the sample collection system does not add to or subtract from the concentrations of the samples collected using it. (Refer to Section 2.5.1.7 for details pertaining to canister sampling system certification). The canisters should also be determined to be clean before each use. (Refer to Section 2.5.2 for details pertaining to canister cleaning.) Each adjustable orifice and mass flow meter assembly, or mass flow controller, used as a flow control device should be calibrated against a primary flow measurement standard (i.e., a bubble flow meter, etc.). The calibration qualifies the relationship between indicated flow versus measured flow. Multiple calibration points of comparison, spanning the entire range of the flow control device in increments of 10% of the device range, should be used. For example, if a mass flow meter having a 0-100 mL measurement range is being calibrated, comparisons would be made at 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mL. Calibration curves that mathematically define the relationship between the flow rates indicated by the flow control device and corresponding actual flow rates measured by primary flow measurement standard are generated from these comparisons. The calibration curves are used to set actual desired flow rates, based on the flow

rates indicated by the flow control devices. Pressure sensors should be calibrated against a primary pressure measurement standard (i.e., manometer or absolute pressure gauge), and should also be calibrated using the same process described above. Calibration of the flow control and pressure measurement devices should be performed prior to any field deployment. A calibration check should then be conducted periodically according to a program specific QA/QC schedule as developed by the user. The calibration check should consist of performing a single point comparison at a representative setting (e.g., a flow rate typically used for sample collection). The recommended frequency for performing calibration checks is biannually (two calibration checks per year).

The following procedure provides generic steps for operating a typical multiple-event sampling system:

1. Set the sample collection system to the desired sample collection flow rate(s) (i.e., referencing the corresponding calibration curve(s) and considering the canister volume and the desired final canister pressure).

2. Program the microprocessor event control system to begin and stop sampling consistent with user specific collection frequency requirements.

3. Attach all sample canisters to the sample collection system.

4. Open all the canister bellows valves.

5. After sampling, record the initial and final sample pressures in each canister (i.e., referencing the corresponding calibration curve(s)), and the start and end time of each collection event onto the sampling field data sheet. The microprocessor event control and data acquisition system should automatically store these data for each collection event. Final sample pressure should be close to the desired calculated final pressure.

6. Close all of the canister bellows valves.

7. Attach an identification tag to each canister documenting the canister serial number, sample event number, sample type, location, and collection date.

8. Disconnect and remove each canister from the sample collection system.

An in-depth SOP, specific to the exact sample collection system utilized, must be developed.

2.5.1.3 Multiple-event System Specifications

Multiple-event sample collection systems will be required if canisters are used to meet the network monitoring requirements for VOC measurements in a practical, non-labor intensive manner.

A set of primary specifications is provided below to direct the evaluation and procurement of multiple-event sample collection systems. It is imperative that the site requirements for this type of system be compared against vendor offerings to ensure that appropriate systems are procured. Primary collection system specifications are presented below. However, additional collection system specifications may be added at the discretion of the user.

- An in-depth, detailed manual describing all aspects of the sample collection system (i.e., operation, maintenance, etc.) must be provided by the vendor.

- The overall size of the sample collection system, including canisters, should be kept as compact as possible. The sample collection systems are usually installed into existing sampling site shelters where many other parameters (i.e., criteria pollutant concentrations, meteorological conditions, etc.) are also being measured. Each of the other parameters requires separate instrumentation and consequently the shelters can become very crowded.

- The sample collection system should meet all applicable electrical and safety codes, operate on standard 110 Vac power, and incorporate a main power fuse or circuit breaker. Specific potential electrical hazard and/or other safety considerations should be detailed in a supplied users manual.

- The overall configuration, and components comprising that configuration, should allow for simple operation, maintenance, and service of the sample collection system. Materials used in the construction of components of the sample collection system should exhibit nonbiasing characteristics, i.e., the materials should neither contribute to nor take away from the measured organic content. The components themselves should generally conform to the descriptions presented in Section 2.5.1.1. All surfaces that

come in direct contact with sampled air should be constructed of glass, stainless steel, or Viton®. The use of Teflon® or other plastics or polymers should be avoided because the absorption/ desorption characteristics of these materials increase the potential for sample bias.

C The sample collection system should be able to be certified as nonbiasing. The user should seek assurances and/or evidence that the sample collection system design/configuration being considered will be, or has been certified according to the recommended procedures presented in Section 2.5.1.7.

C Ideally, the sample collection system should be able to accommodate the sample collection event frequency presented in Section 2.1 and simultaneously allow a duplicate 3-hour sample collection as recommended for QC purposes. The sampling system should have the capability to collect the following during any given 24-hour period:

- Eight 3-hour time-integrated canister samples;

- One 3-hour time-integrated duplicate canister sample, collected concurrently with one of the eight 3-hour canister samples; and

- One 24-hour time-integrated canister sample, collected concurrently with the eight 3-hour samples, but <u>not</u> concurrently with the duplicate 3-hour canister sample.

It is imperative that the sample system have the collection capabilities detailed above, including the 24-hour sample collection. If not, a second sample collection system will be required to address the 24-hour sample collection and, consequently, more overall labor and space would be needed to fully address the network monitoring requirements.

The ability of the sample collection system to perform sample collections as presented above would allow the operator to visit the site only twice during the 24-hour period being characterized; once to install cleaned evacuated canisters prior to sampling and once to remove canisters containing the collected samples.

C The sample collection system must be able to perform time-integration of the canister sample collections. The sample collection system should allow for variable collection flow rates so that canisters of different internal volume may be used (refer to Section 2.5.1.2 for specifics on the relationship between canister volumes, collection duration, and collection flow rate).

- The sample collection system should incorporate a microprocessor event control and data acquisition device. At a minimum this microprocessor should be programmable to control the start and stop times of every collection event within a 24-hour sampling period. The microprocessor should also be able to simultaneously collect and store all the sample collection process data pertaining to each sampling event as follows:

  - Start and stop times for each sample collection; and

  - Beginning and ending sample canister pressures for each sample collection.

  The microprocessor should incorporate a battery backup system to address power failure situations. Battery backup is necessary to ensure fewer invalidated samples and a higher collection completion rate. The battery backup system would ensure that all programmed control activities and collection process data are retained for a predetermined interval in the event that standard power to the system is interrupted. Retaining the programmed control activities would allow sample collection to resume automatically at the next programmed event time when standard power is restored to the sample collection system. Retaining the collection process data for samples collected prior to the termination of standard power allows these samples to be qualified as valid or invalid, based on sampling start and stop times and initial and final pressures. Although not absolutely necessary, adding a miniature printer would allow for the generation of a report listing all sample collection process data.

- Expedient and responsive vendor support should be a mandatory requirement and primary consideration when procuring a multiple-event canister sample collection system. The user should specify that the vendor maintain an adequate supply of replacement parts and qualified service technicians to ensure that the absolute minimal number of sampling events is missed should a sample collection system failure occur. The user should specify that the vendor guarantee that parts/ components be delivered to the sampling site within two working days of order placement, and that a sample collection system delivered to the vendor for repair or for other problems be serviced and returned to the user within seven working days.

2.5.1.4 Single-event Sample Collection Equipment

A typical single-event sample collection system configuration is presented in Figure 2-12. The single-event sample collection system consists of the following primary components:

Inlet probe and manifold assembly - Constructed of glass (see Figure 2-4) or stainless steel. Used as a conduit to transport sample air from the atmosphere at the required sampling height and distribute it for collection.

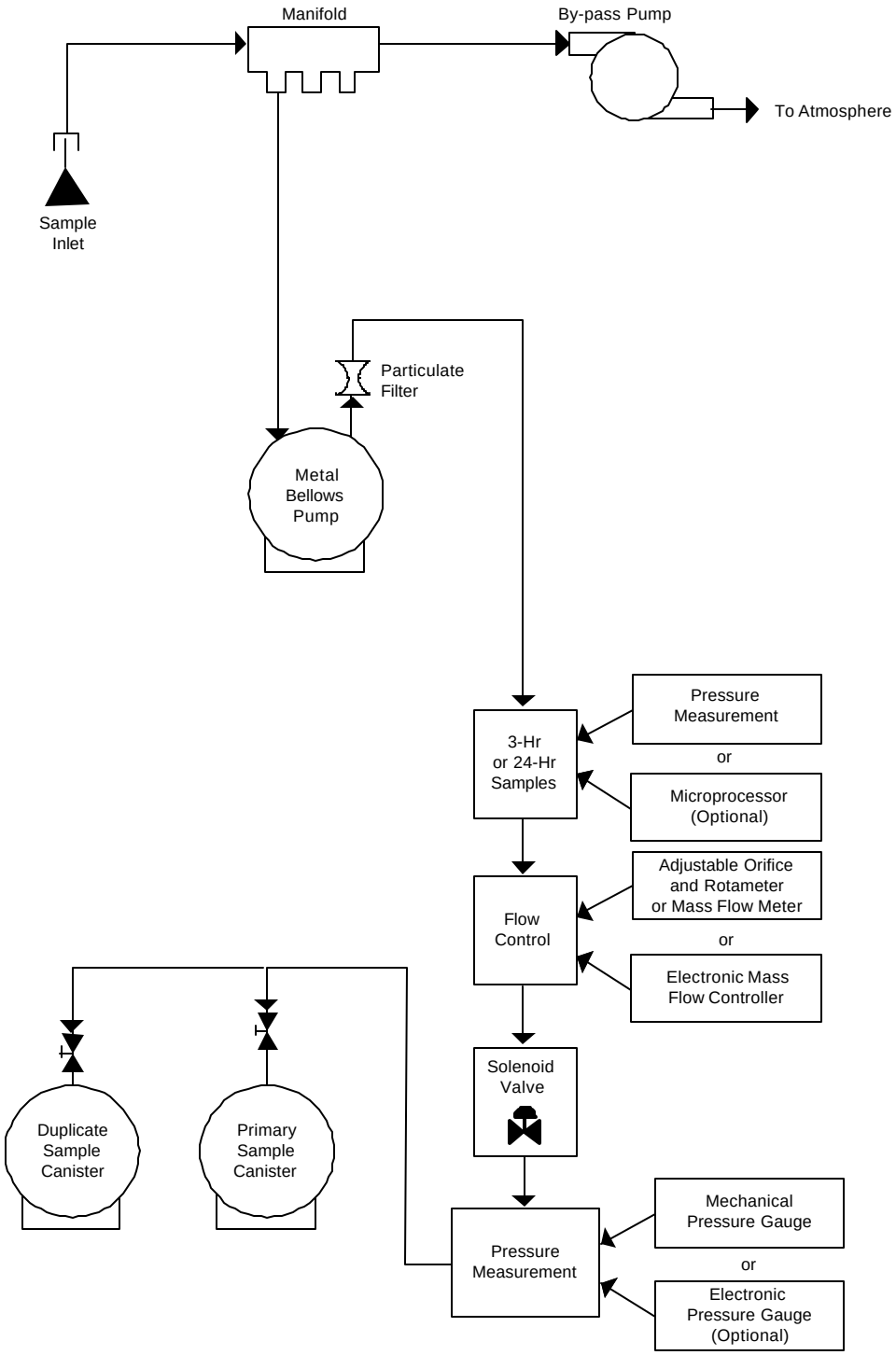


Figure 2-12. A Typical Single-event Sample Collection System

By-pass pump - A single- or double-headed diaphragm pump, or a caged rotary blower. Used to continuously draw sample air through the inlet probe and manifold assembly at a rate in excess of the sampling system total uptake. All excess sample air is exhausted back to the atmosphere.

Sample pump - A stainless steel bellows pump, capable of 2 atmospheres above ambient output pressure. Used to extract sample air from the manifold assembly and deliver it to the sample canister during collection.

Sample inlet line - Chromatographic-grade stainless steel tubing. Used to connect the sampler to the manifold assembly.

Sample canisters - SUMMA® passivated stainless steel sample vessels of desired internal volume with a bellows valve attached at the inlet of each unit. Used to contain the collected sample air for transportation and analysis.

Stainless steel vacuum/pressure gauge or electronic pressure sensor (optional) - A pressure measurement device capable of measuring vacuum (0-30 in Hg) and pressure (0-30 pounds per square-inch gauge). Used to measure initial and final sample canister pressures.

Adjustable orifice and rotameter, or mass flow meter assembly, or electronic mass flow controller - An indicating flow control device (or devices). Used to maintain a constant flow rate (± 10%) over a specific sampling period under conditions of changing temperature (20-40EC) and humidity (0-100% relative).

Particulate filter - Two-micron sintered stainless steel in-line filter. Used to remove particulate material larger than 2 microns from the sample air being collected.

Electronic timer or microprocessor (optional) - An event control device. Used to allow unattended operation (activation and deactivation) of the collection system.

Solenoid valve - An electric-pulse-operated or low temperature coil, stainless steel body, solenoid valve, with Viton® plunger seat and o-ring. Used to provide access to or isolation of the sample canister(s).

Elapsed time indicator - A time measurement device used to measure the duration of the sampling episode.

Stainless steel tubing and fittings - Isolation and interconnection hardware. Used to complete 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.

2.5.1.5 Single-event Sample Collection 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, the internal volume of the canister used, and the specified sampling period. A starting pressure of 5 mm mercury (Hg) absolute for the canisters is assumed. The flow rate is calculated using the formula presented in Section 2.5.1.2.

During 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.

Single-event sample collection systems can collect sample from a shared sample probe and manifold assembly as described in Section 2.4.1.1 or from a dedicated stainless steel sample probe, manifold assembly, and by-pass pump. If a dedicated probe, manifold assembly, 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 constant over the entire sampling period. If an adjustable orifice is used as the flow control device, a drop in the flow rate will occur near the end of the sample collection period because the orifice size is no longer critical as pressure in the canister

increases. Typically this condition occurs when canister pressure exceeds one-half atmosphere above ambient pressure. Consequently, care must be used to select a sample flow rate that will yield final pressure that will not significantly exceed 22-24 psig (i.e., ~8-10 psig) at the end of the sample collection interval.

Prior to field use, each sample collection system should be certified as nonbiasing. (Refer to Section 2.5.1.7 for details pertaining to canister sample collection system certification.) The canisters should also be demonstrated to be clean before each use. (Refer to Section 2.5.2 for details pertaining to canister cleaning.)

The following generic steps are provided for the operation of a typical single-event sample collection system:

1. Activate the sample collection system and 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, before the particulate filter. The sample collection system is activated and the indicated flow rate is compared to the desired collection flow rate. The values should agree within ± 10%. If a mass flow controller is being used as the sample collection system flow control device, allow the system to equilibrate for two minutes. After the two-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 sample collection system uses a adjustable orifice assembly as the flow control device, adjust the orifice size until the correct flow rate is achieved. If the sampling system uses a fixed orifice as the flow control device, ensure that the orifice is the correct size to provide the desired flow rate.

2. Deactivate the sample collection system and reset the elapsed time indicator to show no elapsed time.

3. Disconnect the calibrated mass flow meter or rotameter and attach a cleaned evacuated canister to the sample collection system.

4. Open the canister bellows valve.

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

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

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

8. After sample collection, record the final sample pressure on 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 sample collection system.

10. Attach an identification tag to the canister documenting the canister serial number, sample number, sample type, location, and collection date.

An in-depth SOP, specific to the exact sample collection system utilized, must be developed.

2.5.1.6 Single-event System Specifications

Although different in complexity and general application, many of the collection system specifications that apply to multiple-event collection systems also apply to single-event collection systems. To ensure that a single-event collection system meets the user's program needs, the following system specifications should be presented to, and addressed by, the candidate vendor(s) prior to procurement.

- An in-depth, detailed manual covering all aspects of the sample collection system (i.e., operation, maintenance, etc.) must be provided by the vendor.

- Although fewer canisters are utilized at a time, as compared to the multiple-event systems, the overall size of the sampling system should still be kept as compact as possible.

- The sampling system should meet all applicable electrical and safety codes, operate on standard 110 Vac power, and incorporate a main power fuse or circuit breaker. Specific potential electrical hazards and/or other safety considerations should be detailed in a supplied user's manual.

- The overall configuration, and components comprising that configuration, should allow for simple operation, maintenance, and service of the sample collection system. Materials used in the construction of components of the sample collection system should exhibit nonbiasing characteristics. The components themselves should generally conform to the descriptions presented in Section 2.5.1.4. All surfaces that will come in direct contact with sampled air should be constructed of glass, stainless steel, or Viton®. The use of Teflon® or other plastics or polymers should be avoided because the absorption/desorption characteristics of these materials increase the potential for sample bias.

- The sample collection system should be able to be certified as nonbiasing. The user should seek assurances and/or evidence that the sample collection system design/configuration being considered can or has been certified according to the recommended procedures presented in Section 4.0 of Compendium Method TO-12 (Appendix C).

- The sample collection system should be able to perform time-integration of the canister sample collections, and allow for variable collection flow rates so that different volume canisters may be used.

- Expedient and responsive vendor support should be a mandatory requirement and primary consideration when procuring a single-event canister sample collection system. The user should specify that the vendor maintain an adequate supply of replacement parts and qualified service technicians to ensure that the absolute minimal number of sampling events is missed should a sample collection system failure occur. The user should specify that the vendor guarantee that parts/components be delivered to the sampling site within two working days of order placement. The user should also specify that a sample collection system delivered to the vendor for repair or for other problems be serviced and returned to the user within seven working days.

An alternative procedure involves passive sampling into a SUMMA®-polished canister, with subsequent pressurization of the canister to 30 psig at the central laboratory. This procedure reduces the relative humidity in the canister but also dilutes the sample.

2.5.1.7 Canister Sampling System Certification

Canister sampling systems should exhibit nonbiasing 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 blend of organic compounds at a known concentration 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 concentrations determined for the reference sample. 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%. 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, TNMOC, or both, depending on individual program requirements. Two criteria apply to the blank portion of the certification process: a determined concentration criterion of 0.2 ppbC or less for any individual target compound is required if speciation analysis of the blank sample is performed, and a TNMOC concentration criterion 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 (Figures 2-13 and 2-14). 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 2.5.2.

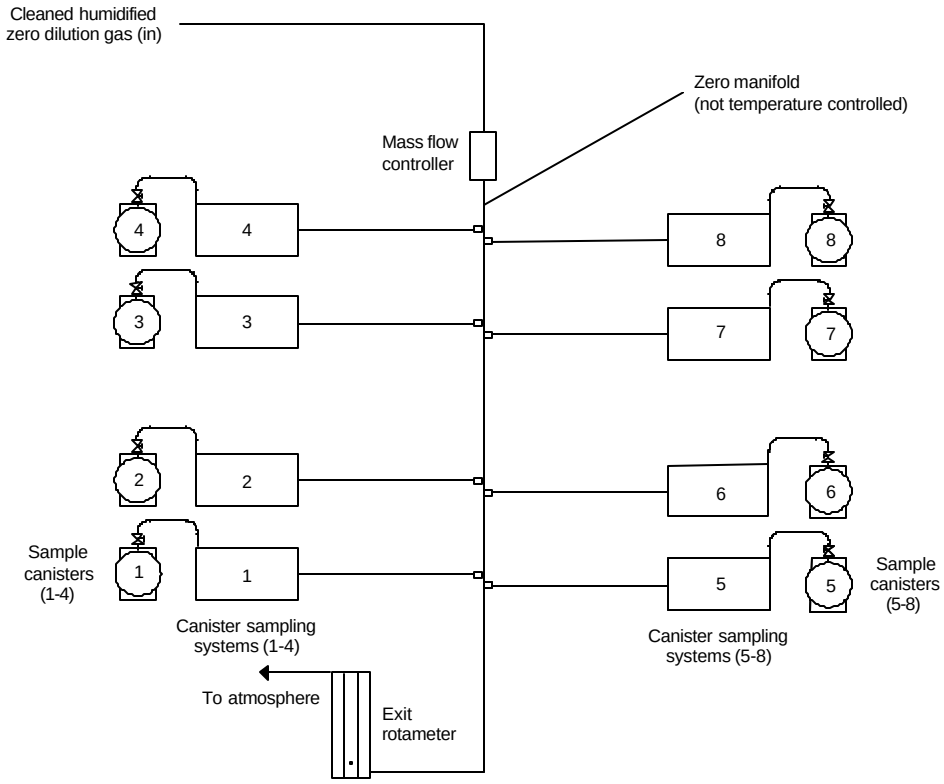


Figure 2-13. Dedicated Manifold for Zero Gas Certification

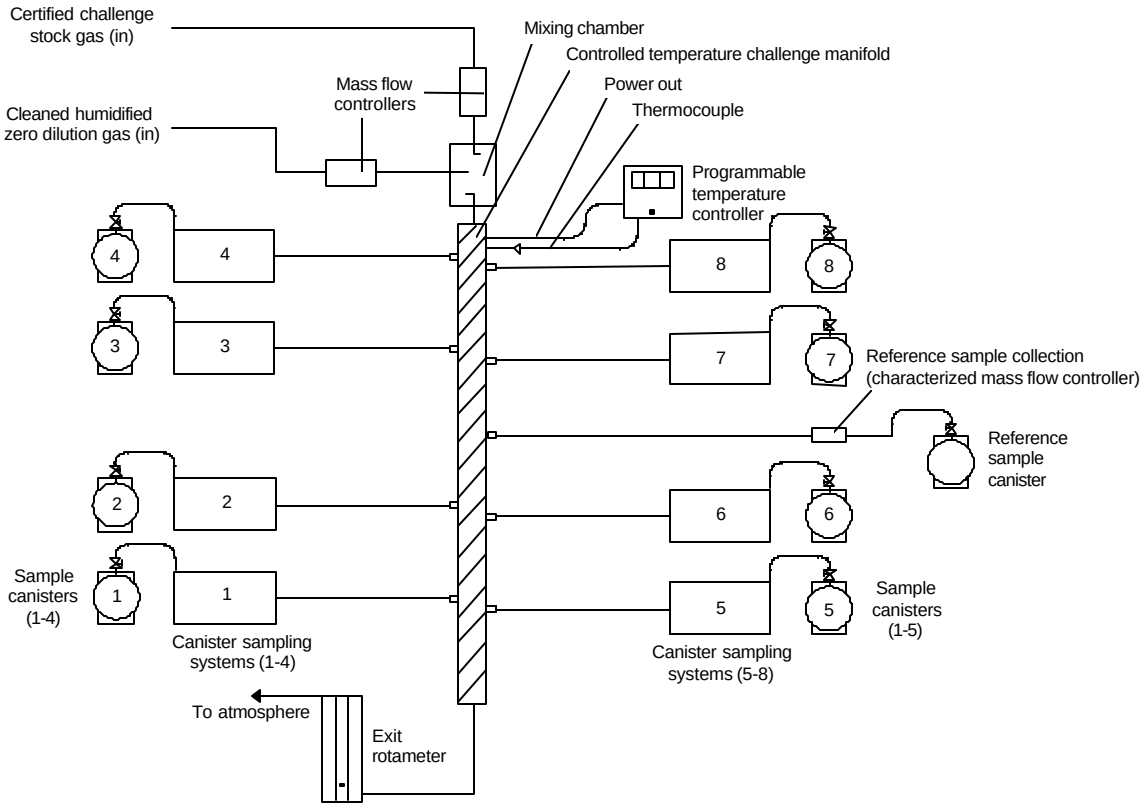


Figure 2-14. Dedicated Manifold for Challenge Gas Certification

2.5.1.7.1 Certification Equipment

The equipment required to perform canister sampling system certification is described below. The equipment listed is consistent with the systems presented in Figures 2-13 and 2-14.

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 80EC. 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 80EC.

2.5.1.7.2 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 simultaneously be 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:

$$Q_t \quad \left(Q_s \times N_1\right) + \left(Q_R \times N_2\right) \times F_1 \qquad \textbf{(2-8)}$$

where:

Q_t = Total required flow rate (mL/min)

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 = Excess flow factor = 2.0

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

Step 1

$$F_2 \quad \frac{C_1}{C_2} \qquad \textbf{(2-9)}$$

where:

F_2 = Dilution factor (for use in next equation)

C_1 = Desired challenge gas concentration (ppbv)

C_2 = Concentration of the stock cylinder (ppbv)

Step 2

$$Q_p \quad F_2 \times Q_T \qquad \textbf{(2-10)}$$

where:

Q_P = Pollutant flow rate (mL/min)

Q_T = Total required flow rate

Step 3

$$Q_D \quad Q_T - Q_P \qquad \textbf{(2-11)}$$

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 percent recoveries.

The sampling system must be challenged with a known concentration of selected analytes prior to deployment. Additional challenges at the middle and end of the sampling season are recommended. Operator/analyst judgment is critical: a challenge should be performed whenever the operation of the sampling system is questioned for any reason.

2.5.2 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., #10 ppbC 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.

2.5.2.1 Canister Cleaning 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 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 2-15 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 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.

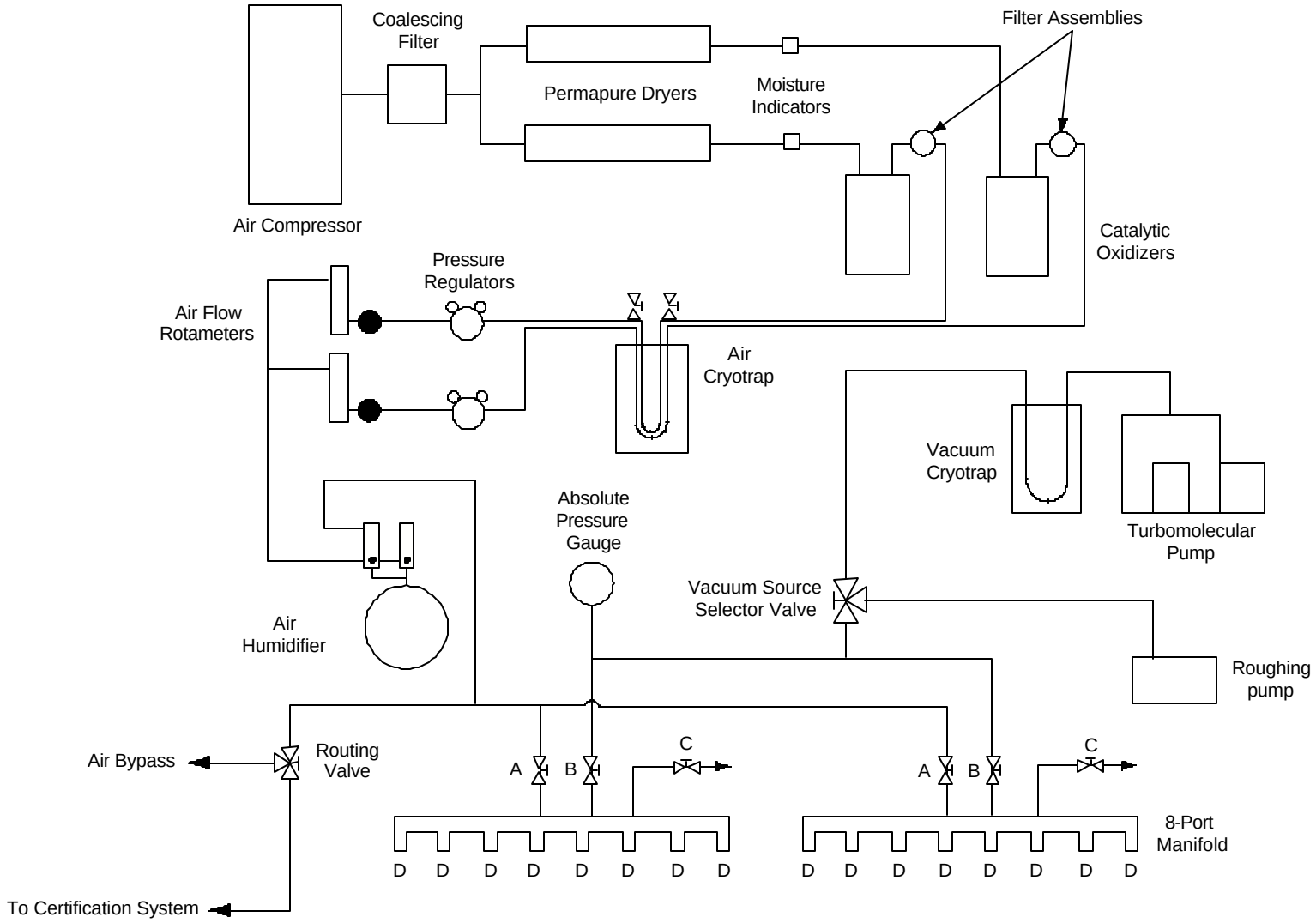
Air compressor - A shop or laboratory oil-less air compressor used to provide the air supply for the canister cleanup apparatus.

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

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

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

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.



A. Manifold Air Pressure Valve
B. Manifold Vacuum Valve
C. Manifold Pressure Release Valve
D. Manifold Port for Connecting Canisters to be Cleaned

o:/s/g/morr/3797/pams/hobson/graph5.ppt

Figure 2-15. Schematic of a Canister Cleanup System

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 2-10) 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 2-15 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%.

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 2-15 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 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 isolate 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.

2.5.2.2 Canister 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 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.

2.5.2.3 Canister 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 TNMOC 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 the PDFID technique as described in Method TO-12 (Appendix C). If this measurement meets the predetermined cleanliness criterion (i.e., #10 ppbC), 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 TNMOC concentration.

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

3. Using the PDFID technique, if the canister analysis meets the predetermined concentration criterion (i.e., #10 ppbC), 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 cleanliness criterion (i.e., #10 ppbC), 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.

2.5.2.4 Final Canister 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 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.

2.5.3 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 to minimize surface reactivity. Conditioning allows stable storage for many of the compounds of interest. Currently, there are two processes used to condition canister interior surfaces. They are the SUMMA® process and the Silcosteel® process. The SUMMA® process is a proprietary electroplating treatment that passivates the internal steel surface of the canister. The Silcosteel® process treats the internal surface by coating it with a thin layer of fused silica. SUMMA® canisters have been used extensively for the collection of VOC samples since 1983, and their use is well characterized. Silcosteel® canisters have been used since 1996 and although their use is not as well characterized as the use of SUMMA® canisters, early evaluation suggests the Silcosteel® canisters are suitable for use in ambient air sampling. Conditioned 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 2.5.1.

The presence of high levels of particulate matter can also pose problems in sampling VOCs. If a filter is used to collect particulate matter, ozone can interact with the particulate material trapped on the filter, resulting in the generation of artifacts. Also, use of a filter such as a 2 µ Teflon® filter on the inlet to the manifold or on the inlet to the monitoring system means that the filter must be changed

frequently (i.e., daily). However, if the monitoring station is near a source of particulate matter (such as industrial emissions), it may be necessary to use a filter and accept the necessity of more frequent visits to the monitoring site to change the filter.

2.5.3.1 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.

2.5.3.2 Contamination

Contamination may cause additional compounds to appear in the sample or increase the concentrations of compounds present in the ambient air. Contamination may also cause loss 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 (detection limits) 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 blank checked (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 acceptable. 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 blank checked frequently, and particularly after extended periods of storage, to ensure 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. Although the application of heat during the cleaning process can facilitate the removal of the higher-molecular-weight compounds, other potential problems may result. For example, if heat is repeatedly applied, it is difficult to maintain valve integrity. Also, the effects of heat on the SUMMA® treated surfaces have not been clearly established.

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 2.5.1.7, 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.

2.5.3.3 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. Some of the ways that the concentration of target compounds in an ambient air sample may change after sampling are:

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

A number of studies[26,27,28,29] 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 adsorptive sites on the canister's interior walls.

While many compounds have been shown to be stable in canisters, it is not known how these results extend to the variety of conditions that may be encountered during the use of canisters for PAMS. These conditions include variable quality of the canisters and their passivation process, variable moisture content or humidity in the sample air, previous history of use or residual contamination of the canister, sample pressure in the canister above or below atmospheric pressure, storage temperatures, and canister age.

Current information indicates that hydrocarbon VOCs with vapor pressures above 0.5 mm Hg at 25EC 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 limited storage stability in canisters. Recent studies in aluminum canisters have indicated that the presence of water in the sample has a great effect on the stability of polar organic compounds.[30] Results from another study confirm that the presence of water is a key factor in ensuring the stability of polar organic compounds in stainless steel canisters.[31] 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. These tests should be performed under typical conditions of use.

The potential for physical adsorption as a mechanism for loss of VOCs from the vapor phase in canisters was evaluated using the Dubinin-Radushkevich isotherm, which provides a specific relationship between the tendency for adsorption and compound or sample specific properties such as polarizability, vapor concentration, temperature, and equilibrium vapor pressure.[32] A computer-based model has been developed for predicting adsorption behavior and vapor phase losses for multicomponent systems. Solely on the basis of physicochemical properties of the compounds (i.e., independent of considerations of the properties of the surface), the model predicts displacement of the

more volatile VOCs from a canister surface by water vapor at relative humidities in the range of 1 to 20%. This prediction is generally consistent with experimental observations, but in most cases, experimental conditions (i.e., canister surface properties) are not sufficiently well characterized to permit detailed quantitative comparison with the model. The model has contributed to the following guidelines for canister sampling of VOCs:

- Relative humidity and temperature should be measured during the sampling process so that water vapor can be added to the canister prior to analysis if the relative humidity is low.
- Sample pressure in the canister should be as high as possible without causing precipitation of liquid water within the canister.
- When considering the applicability of canister sampling to new compounds, the first parameters to be evaluated should be chemical reactivity and vapor pressure of the compound.
- Since all species present in the canister participate in the competitive adsorption process, consideration of the quality of data obtained from multiple canisters at the same site should include at least semi-quantitative specification (such as total FID response) of non-target species present in the samples.

2.5.3.4 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 be withdrawn until the sample has been in the canister for at least 24 hours to allow the adsorption equilibria to stabilize.

2.5.3.5 Diluted Samples

Samples may be diluted by adding pressurized, clean air, N_2, or other gaseous diluent (Section 2.3.4.3.2). It is recommended that at least 24 hours elapse between dilution of a sample and removal of an aliquot for analysis.

2.5.3.6 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 through the bellows, evacuate the canister, check the absolute pressure, close the valve, disconnect the pressure gauge, and do not cap the valve inlet fitting. Several days later, reconnect the pressure gauge and check the pressure. 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.

2.5.4 Sample Analysis

The methodology in Section 2.5.1 describes the collection of whole air samples into SUMMA® canisters. The canisters are then sent to a central laboratory location for sample analysis. When incorporating manual methods, the user must develop procedures to perform sample analysis. Those using manual methods for sample collection may also incorporate the use of automated GC/FID systems as described in Section 2.4 for sample analysis. If a manual sample analysis system is used, it should incorporate the same basic components as discussed in the automated method which include a sample introduction system, sample conditioning system (for moisture removal), sample concentration system for sample enrichment, an optional cryo-focusing trap, a gas chromatograph which houses the appropriate analytical column(s) and FID(s), and a data acquisition and processing system. Capillary GC/FID is the recommended analytical system for PAMS but individual sites may use GC/MS or a gas chromatograph with multiple detectors (i.e., both FID and MS).

2.5.4.1 Sample Introduction

The air sample is introduced to the primary sample concentration trap of the GC system directly from a SUMMA® canister using a mass flow controller or other flow control device at a constant flow rate. Samples may also be introduced for purposes of calibration and proficiency studies directly from pressurized canisters.

2.5.4.2 Sample Conditioning

Sample moisture must be removed from the sample stream to prevent or reduce the effects of moisture on the primary concentration trap, analytical column(s), and detector(s) as described in Section 2.3.4. Moisture removal allows for analysis of larger sample volumes, which provides lower detection limits, and is crucial to the measurement of very low concentration VOCs.

Moisture may be removed from the sample stream using a Nafion® membrane sample conditioning device. Some commercially available concentration systems incorporate the use of Nafion® sample drying devices. New developments in this area using controlled temperature desorption, selective temperature condensation, hydrophobic concentration traps, etc., are currently being studied (see Section 2.3.4). The loss of polar VOCs may result from sample conditioning and significantly affect the TNMOC measurement. The user must characterize the effects of the sample conditioning method chosen on the TNMOC measurement and the target VOCs of interest. Chromatographic retention times are changed by the presence of water vapor. Also, any MS analysis is subject to response variability because of filament changes caused by the presence of water vapor. In order to characterize effects, primary calibration and/or retention time standards can be analyzed with and without the conditioning device. If a commercially available analytical system with sample conditioning is used, vendors should provide information regarding the effects of their conditioning or drying device.

Preconcentration techniques in use for sampling of atmospheric VOCs are susceptible to reactions occurring during sampling involving the organic compounds of interest and other reactive constituents of the air. The most widely recognized and significant interference results from reactions with ozone. Chemical reactions in or on the concentration media may alter the quantities of VOCs and may also contribute to the formation of artifacts which may be interpreted as atmospheric constituents. If a solid sorbent is used for preconcentration, reactive constituents of the atmosphere may also react with the solid sorbent bed to produce artifacts. In particular, unsaturated hydrocarbons such as

isoprene and monoterpenes can be depleted during cryogenic concentration in the presence of ozone.[33] In sampling trace organic gases onto solid sorbents such as Tenax® TA, unsaturated compounds such as styrene, cyclohexene, and monoterpenes were found to react with ozone during ambient sampling with loss of analyte[34,35,36,37,38,39,40,41] and formation of oxidized products.[41,42] Artifacts such as benzaldehyde, phenol, and acetophenone have been found to result from direct reaction of ozone with solid sorbents, especially Tenax® TA.[34,42,43,44,45,46,47] Reactions with oxidants can be reduced or eliminated by selectively removing the oxidant from the sample flow prior to concentration of the organic trace gases of interest. Although numerous options are available for either chemically or physically scrubbing ozone,[48] none of these options for ozone scrubbing are sufficiently or thoroughly characterized enough for VOC sampling applications to ensure that the concentrations of the trace organic compounds are not affected by use of the ozone scrubber. There is, therefore, no generally accepted ozone scrubber for VOC sampling presently in use. Ozone scrubbing options for carbonyl sampling are discussed in Section 5 of this document.

2.5.4.3 Sample Concentration

Ambient air samples are primarily concentrated using multi-bed sorbent or deactivated glass bead traps. Sampling time and flow rate are used to determine the total volume concentrated onto the primary trap. Multi-bed sorbent traps (Carbotrap® and Carbosieve®) are required to efficiently collect the complete range (C_2 through C_{12}) of VOCs for O_3 precursor monitoring.[13]

Samples are collected onto sorbent traps at sub-ambient or ambient temperatures to improve collection efficiency. Ideally, sorbent traps selectively adsorb only the trace VOCs and do not interact with the atmospheric constituents or introduce any contaminants into the system. Sorbent traps may also be designed to eliminate water vapor by using hydrophobic sorbent materials.

Sample concentration using glass bead traps, which require concentrating temperatures around -185EC, are cooled using liquid N_2, CO_2, or Ar. This process is commonly known as

cryogenic concentration or cryotrapping, and is the oldest and best known of the techniques for collecting C_2 through C_{12} VOCs. The glass beads provide surface area for collection of the VOCs at the cryogenic trapping temperature. The most prevalent system being used in the PAMS uses Peltier cooling of the concentrator to eliminate the use of liquid cryogens and make unattended automated monitoring feasible.[49]

2.5.4.4 Sample Focusing or Cryofocusing

Following sample collection and concentration, the sample is thermally desorbed either directly onto the analytical column(s) or onto a secondary cryofocusing trap. For concentrated samples that are desorbed directly onto the analytical column(s) to separate the VOCs, the analytical column is cryogenically cooled to aid in re-focusing the desorbed sample into a narrower band prior to chromatographic separation.

Concentrated samples are optionally desorbed onto a cryofocusing trap to focus the desorbed sample into a narrow "plug" for subsequent thermal desorption and injection onto the analytical column. The sample cryofocusing step is optional. Cryofocusing improves the peak separation and particularly the resolution of C_2 and C_3 hydrocarbons, and is especially helpful when the sample is desorbed from the concentration trap at low flow rates. Cryofocusing traps incorporate the use of fused silica tubing that is cooled using liquid cryogen. The fused silica tubing is wide-bore (0.32-mm I.D.) or megabore (0.53-mm I.D.) deactivated fused silica tubing that is cooled to approximately -185EC. These traps may be packed with glass beads to increase the surface area and improve the focusing of the sample band. Closed cycle coolers are available and have been used in field tests.[17,18]

2.5.4.5 Gas Chromatography

The gas chromatograph contains the analytical column(s) of choice for PAMS VOC analysis. Refer to Sections 2.3.5 and 2.3.6 for guidance on column configuration and selection. The user must

configure the GC system to meet the enhanced O_3 monitoring requirements and specifications, and must also characterize the system operation prior to use. Gas chromatographic systems may incorporate the use of single or dual-column configurations (in series or parallel) and may require sub-ambient oven temperature programs. It is important to note that implementing systems that eliminate the need for sub-ambient column oven temperatures will reduce the overall cryogen consumption of the system.

Gas chromatographic systems employ the use of a PC-based data acquisition and processing system for peak integration and quantitation. Data acquisition and processing systems are comprised of hardware and software that perform data acquisition, peak detection and integration, peak identification by retention time, post-run calculations and quantitation, calibration, peak reintegration, user program interfacing, and hard copy output. Data are automatically stored on magnetic media (e.g., hard disk or floppy diskette).

The GC acquisition and processing software is typically developed and supplied by the GC manufacturer and should contain the necessary algorithms to acquire, integrate, and identify the chromatographic peaks by retention time. The system should be capable of producing an electronic and hard copy report file that contains the information needed to identify the sample, and a listing of all peaks detected in the chromatogram. This listing should contain the peak name if the peak is a target compound. All detected target and non-target peaks should be reported with the associated concentration in ppbC, and a retention time. The listing should also contain the TNMOC and PAMHC estimates as calculated by summing the concentrations of peaks as described in Section 2.2. See Section 2.6.1 for a more detailed discussion on data processing capabilities of automated GC systems.

2.5.4.6 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. Benzene is suggested as a second primary standard to address the needs of dual-column systems that employ the use of column switching

techniques. The primary calibration standard is used to generate a per Carbon response factor for determining the concentration of each target VOC, as well as the TNMOC. It is unnecessary to determine compound specific response factors for each of the target VOCs presented in Table 2-1, because the Carbon response of the FID to these compounds is approximately linear. It is appropriate to measure each compound concentration in terms of ppbC using the relative response factor determined from the primary standard. Refer to Section 2.4.2.3 for a more detailed discussion of analytical system calibration.

2.5.5 System Operation

This section provides guidance and general operating considerations for initial system set-up, optimization of sampling parameters, and field operation for the GC system.

2.5.5.1 Initial System Set-up

During the initial set-up of the system, several parameters must be evaluated to optimize the system operating conditions. Critical parameters include, but are not limited to, the sample collection flow rate and sample integration time, sample concentration and desorption conditions, oven temperature program parameters, detector calibration, and the peak detection and integration methods used by the data acquisition and processing system. These parameters are optimized by varying the operating conditions to achieve the best resolution and detection of the target VOCs using primary calibration and retention time calibration standards.

Prior to making VOC measurements, the baseline performance of the system must be thoroughly documented. The information from the system baseline characterization is used to determine system specific target compound retention times, relative retention times, identification of co-eluting compounds and matrix effects, internal standard retention times and interferences, and detection limits.

Baseline characterization is a very important step in determining the overall quality and validity of the measurement data. See Section 2.3.7 for a discussion of pre-measurement system characterization.

The system should initially be set up and tested for conformance with the manufacturer's operational specifications. Under terms of agreement for purchase, the manufacturer should be required to provide a detailed instruction manual for system operation and be required to provide initial system setup, user training, and demonstration of adequate system performance. See System Specifications for automated GC systems in Section 2.4.5 as guidance for procurement.

2.5.5.2 Sampling Parameters

Determination of 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. The primary sampling parameters are the sample collection frequency and the sample collection or integration time.

2.5.5.3 Operation

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 maintained by a qualified operator who should perform the routine operational and critical quality control functions as specified in the SOPs. Operational parameters should be adjusted, if necessary, so that the data quality objectives are met. Primary calibration checks should be performed at least once each week or at an interval consistent with the individual site standard operating procedure. Retention time calibration checks should be performed at least once per week or at an interval consistent with the individual site standard operating procedure to provide retention time reference information for

validating compound identifications. The retention time calibration standard can also be used to track the FID response and compound recovery to determine when recalibration is necessary.

Detailed SOPs for operation of the system must be developed. The SOP should be based on information obtained during the set-up and familiarization period and the requirements of the monitoring program. Refer to QA/QC Section 2.8.3.1 for a more detailed discussion of SOP development.

2.6 Data Processing Capabilities of Automated VOC Systems and Submittal of VOC Data to the AIRS AQS Data Base

As prescribed in Section 58.45 of 40 CFR Part 58, PAMS Data Submittal, the data from VOC measurement systems is required to be submitted to EPA's Aerometric Information Retrieval System (AIRS) Air Quality Subsystem (AQS) within 6 months following the end of each quarterly reporting period. The agencies may ultimately use the data to make attainment/ nonattainment decisions, track VOC emission inventory reductions, provide input to photochemical models, prepare air quality trends, and characterize population exposure to O_3. The data that are ultimately submitted to AIRS must be uniform across all networks and consistent with enhanced O_3 monitoring requirements.

The overall approach to generating data from automated GC systems involves the same basic components (A/D converter, personal computer, acquisition and processing software, and data storage module). These basic components comprise the automated GC data acquisition and processing system. The VOC concentration data are ultimately generated in an electronic file and hard copy format specific to the data acquisition and processing system used. The information generated must finally be put in the required format for submittal to the AIRS data base.

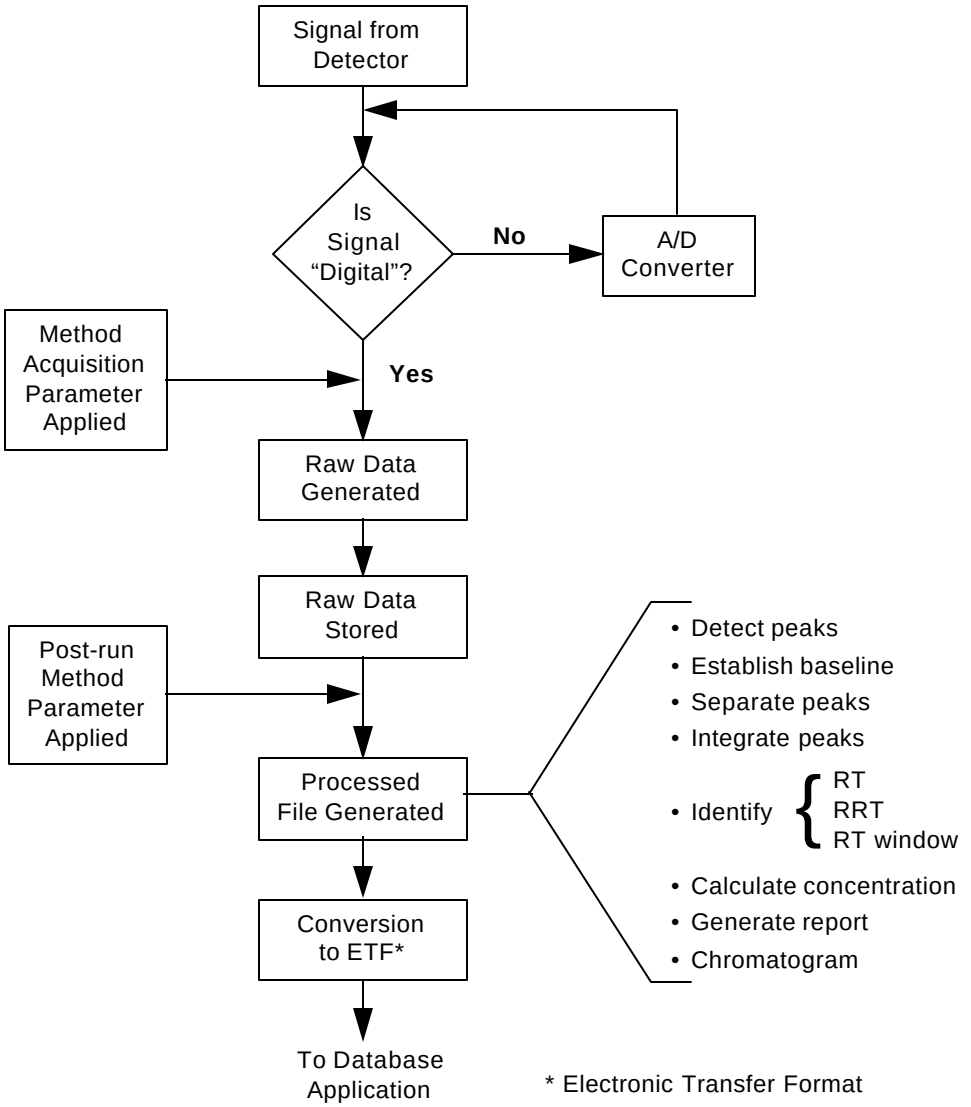
This section discusses how data acquisition and processing occurs, the data acquisition and processing capabilities of automated VOC systems and guidance on formatting and submitting the data to the AIRS data base.

2.6.1 Data Processing Capabilities of Automated VOC Measurement Systems

Automated VOC systems employ a variety of hardware and software strategies to collect and process chromatographic data. Despite these differences, their overall approach to processing data involves the same basic system components and procedures. This section provides background and important details on automated VOC data processing.

The basic components of a typical data acquisition and processing system are an analog signal generated by the chromatographic detector, an Analog/Digital (A/D) converter, a personal computer for acquiring/processing data, and a data storage module, where data are stored on magnetic media. After a sample is injected, the sample components are chromatographically separated and sent to the detector. The detector electronics respond to the amount of the analyte passing through the detector and generate an electronic signal which will be either analog or digital. Digital signals are sent directly to the next step in processing; analog signals must first be digitally converted before further processing can occur. Digitized signals are "filtered" by specified method acquisition parameters and the resulting data stored to a file in the data acquisition system.

After the analysis is complete, the post-run method parameters further refine the raw data file by applying integration algorithms and parameters, compound identification requirements, calibration response factors and data reporting format to generate a processed data file. Processed data files generally contain retention time data, peak height, peak area, and concentration data: all the elements needed to compile a data report in a specified format. The entire process from signal generation is repeated for each sample during automated operation. This report generating process is depicted in the flowchart in Figure 2-16 and discussed in greater detail in Section 2.6.1.1.



o/s/g/m/3797pams/jr-fig2.ppt

Figure 2-16. Report Generating Process

2.6.1.1 Data Acquisition and Processing

This section presents a more detailed explanation of the steps involved in data acquisition and processing.

Signal Output from Detector—An electronic signal, usually an analog voltage signal, is produced by the detector during a chromatographic analysis and is measured by the detector electrometer. The amplitude of the signal is related to the concentration of the sample. For the FID response to hydrocarbon compounds, the relationship is a direct proportion. Depending on the type of detector, the signal from the electrometer will be amplified before it is processed further. The continuously varying analog signal must be converted to discrete bits for a computer data system to process the data. These discrete bits are considered a "digital" signal. Digital signals can be transmitted directly from the output terminal to the next step in the process.

A/D Conversion—Computer systems handling data for chromatographic systems require the data to be in digitized form prior to storage. Analog-to-Digital converters, also known as A/D converters, take the continuously variable analog signal and "cut" it into discrete slices to make a digital signal for computer-based storage. These slices represent the detector response during a specific slice in time. The sum of these signals is proportional to the sample component concentration. These digital slices are the fundamental data stored for subsequent data processing.

Signal Filtering - Method Acquisition Parameters—To acquire data, the analytical system must be given a data acquisition method. This method tells the instrument how to collect the data and which data are important. The method controls the instrument by starting and stopping data collection and by controlling how frequently the data processor takes data slices, which is called the sampling rate. The peak threshold for data collection, or the minimum signal amplitude above background, is also specified. The signals collected using this set of conditions are referred to as raw data. As raw data are acquired, the data are kept in the CPU memory until acquisition is complete.

Raw Data Storage—After sample collection is complete, the raw data are written to an electronic storage module (e.g., computer disk) as a discrete data file. The raw data reside in memory (CPU) until the PC controlling data acquisition is available to receive the data. Some systems have capacity within memory to temporarily hold multiple raw data files and then to download the files to the PC storage module at specified intervals. These systems must send data to the PC before memory is exceeded or data may be lost. Once the data files are permanently stored to disk they can be backed up and archived in long term storage.

Post-run Data Interpretation/Processed File Generation—Analytical methods contain post-run instructions for interpreting raw data files. Accurate measurement of ozone precursors depends heavily on accurate and consistent chromatographic data. Analytical methods should be tailored to enhance the accuracy of output data. The term "peaks" will be used to describe the area underneath the signal curve. In this section, the basic concepts and issues that the data system must manage are presented. This information should be useful to operators setting initial conditions for post-run data processing for their particular equipment. Information presented here should also help direct corrective action when problems are identified with processed chromatographic data. Post-run routines accomplish the following tasks:

- Peak detection;
- Baseline determination;
- Peak separation and integration;
- Timed events application - controlling peak detection and integration parameters at preset times;
- Peak identification;
- Concentration calculation;
- Report production; and

C Chromatogram generation.

Peaks are detected by applying criteria for discriminating changes in signal associated with compound detection from the background signal. Certain parameters, such as minimum peak width and signal sampling rate, shape the chromatogram during acquisition by affecting the amount of detail. A higher sampling rate and smaller peak width will enhance the fine detail of the chromatogram. In contrast, detail will be lost with smaller sampling rates and greater peak widths. Since detection algorithms commonly monitor the rate of change of the signal -- looking at slope changes and the rate of slope change -- to determine the start, apex and end of a peak, the number of points defining a peak is very important for accurate detection. Some techniques, such as peak bunching, can be used to "smooth" peaks by averaging adjacent signal slices and, therefore, screening unwanted noise. Excessive bunching will also cause loss of chromatographic detail, biasing quantitation high for some compounds and completely eliminating others.

To integrate detected peaks, the data system determines how closely-eluting peaks are to be separated and draws a baseline accordingly. Well-separated peaks require simple integration treatment - either drawing a baseline from the start of one peak to the start of the next or separating peaks by adding drop lines to the baseline. For overlapping peaks, most systems have criteria based on peak proximity and size comparisons that allow reasonable quantitation. "Timed events" can be used to tailor integration schemes to a particular chromatogram or set of chromatographic conditions by changing integration parameters to be modified according to a user-defined timetable. A timed events table queues changes in integration and detection factors to enhance data accuracy. These modifications can help compensate for changes in peak characteristics, such as peak width, peak shape, and incomplete separation, resulting in more accurate and consistent data treatment.

Peak identification is based on retention time (RT) windows or retention time relative to a reference peak or internal standard.

Concentration calculations for most automated VOC systems use external standard-based quantitation. A calibration curve is generated for the primary calibration compounds and each response factor from the curve used for quantitation of the C_2 through C_{12} VOCs. For unidentified peaks, the primary response factor for propane is used to estimate concentration in ppbC.

Report Production/Chromatogram Generation—Many data systems allow great flexibility with reporting format, allowing the user to custom-build hardcopy reports. The hardcopy can be generated directly by the data system software or through a third-party data package. The information compiled in the report includes, but is not limited to, retention time, peak area, type of integration, and limits of concentration. The user can automate post-run data handling to save the processed data file in a specified electronic format to facilitate electronic data file transfer to a spreadsheet or data base.

Reprocessing Capabilities—Chromatographic data systems generally allow the user to change and re-apply data interpretation parameters to adapt them to a given set of chromatographic conditions. Frequently, changes in peak width, bunching factors, integration approach, and identification parameters are needed to compensate for changing sample conditions, flow rates, and column degradation (over time), and to generate more consistent accurate data. The data can also be reprocessed to apply different calibration response factors as needed.

Data Format Options—Data can be presented in two forms - hardcopy report or electronic data file. While hardcopy reports facilitate review, electronic data files allow the user to manipulate results to a desired format and to transfer information quickly. The electronic data formats available as part of the data system package vary from vendor to vendor. Most systems are capable of providing ASCII output files; others can produce comma-delimited files or AIA format (Analytical Instrument Association's Chromatography Data standard format), as either a routine analysis file or a result from a post-run program. This file then needs to be reformatted for submittal to AIRS as discussed in Section 2.6.2.

Telemetry—Telemetry is defined as remote interaction with the PAMS analytical system, including communication, operation, and data transfer. Telemetric capabilities may be a part of the analytical system as purchased, or these capabilities may be acquired by purchase of a commercial software package and any required associated hardware. At the very least, telemetry can be used to communicate directly with the analytical system to assess or modify the operation, as well as to transmit data files to a centrally-located host computer for further processing. Other potential telemetric capabilities may include remote operation of devices at the PAMS site, such as a standards injection system, or to perform a system malfunction auto-call should the system recognize that it has a problem.

2.6.2 AIRS AQS Data Submittal

This section provides guidance for the submittal of O_3 precursor monitoring data into the Air Quality Data Storage Subsystem of AIRS, which is a computer-based system for handling the storage and retrieval of information pertaining to airborne pollutants. AIRS AQS is administered by the U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Information Transfer and Program Integration Division (ITPID), Information Management Group. The AIRS Air Quality Subsystem (AQS) contains data submitted by state and local agencies, and EPA reporting organizations. These data correspond to the data previously handled by the SAROAD system. AIRS AQS includes descriptions of air monitoring sites and monitoring equipment, measured concentrations of air pollutants and related parameters, and calculated summary and statistical information. AIRS AQS is currently being re-engineered, but no information regarding operation of a re-engineered AIRS AQS system is presently available.

All VOC and carbonyl data collected for the enhanced O_3 monitoring network must be submitted to AIRS AQS in the form of transactions. A transaction provides the monitoring information for a particular parameter (compound) for a given day. Because the VOC target list includes over 50 compounds, over 50 line transactions are necessary to input the results from one VOC sample.

Because the carbonyl target list includes three compounds, three line transactions are necessary to input the results from one carbonyl sample. Data can be input on-line one transaction at a time or in groups.

Transactions are used to provide data and control information for updating the AIRS data base. Table 2-5 shows how the various transaction types are related.

Although transactions can be input into AIRS on-line, batch processing is recommended considering the volume of data generated to meet the minimum network monitoring requirements. Prior to submittal to AIRS, all data must be formatted to conform to the 80-character per line format as required by AIRS and saved as an ASCII file. A group of transactions (e.g., data from one week) can be saved as one file and loaded together into AIRS.

Within a transaction are fields corresponding to specific information. A field or "slot" is a column or set of columns in the 80-character input line where a specific piece of data is placed. Four general types of values are used to code the transactions: codes, dates, numeric data, and alphanumeric data. Codes must be entered exactly as they are stored in the Geo-Common Subsystem of AIRS. For example, a county code is three digits and all three digits of the code must be entered, including any leading zeros. Dates are entered in the YYMMDD format, where YY is the last two digits of the year, MM is the month number, and DD is the day of the month. Each part is two digits and any leading zeros must be included. Numeric values must be entered right-justified and do not have to include leading zeros. Alphanumeric values should be entered left-justified in the field.

Table 2-5. AIRS Transaction Types

Transaction Type	Related Transaction Records Have The Same.....
Site (A1, A2, A3, A4, A5, A6, A7)	Site-ID (state, county, site codes)
Monitor (F1, F2, F3, F4, F5)	Monitor-ID (site-ID, parameter, and POC codes)
SLAMS (M, N, P, R, S, T, U, V)	Monitor-ID, year, transaction type (any of codes M through V)
Raw Data:	
Hourly (1)	Monitor-ID, year, month, transaction type 1 AND type 4 transactions with the same monitor-ID
Daily (2)	Monitor-ID, year, month, transaction type 2 AND type 4 transactions with the same monitor-ID
Composite (3)	Monitor-ID, year, period, transaction type 3
Special:	
Minimum Detectable Value (Z)	Monitor-ID, transaction type Z
Null Value (4)	Monitor-ID, transaction type 4
Precision/Accuracy (8, 9)	Monitor-ID, year, month, transaction type

Each field occupies a specific location in the 80-character per line format. For example, the two digit code that identifies one of the 50 states, U.S. territories, or Washington, D.C., is called the State Code and is placed in columns 2-3 of the 80-character per line format. There are also international data, i.e., the code for Mexico is 80. The structure and placement of the fields in each transaction is specific and must be carefully followed.

All data collected must be entered into AIRS. Quantifiable data which are below the detection limits should be entered as the quantified value. The raw data values will be retained within

AIRS, but when any summary statistics are generated the system will automatically replace values below the detection limits with a value that is one-half the detection limit prior to performing calculations. Raw data listings will maintain the actual values. If the compound response is below the detection limit and the data are not quantifiable, a sample value of zero is entered into AIRS. This value will indicate to AIRS that the compound of interest was analyzed for but not present at a quantifiable level. If a sample is missed or invalidated for any reason, appropriate null values or validity flags are used.

Although sampling is conducted in accordance with 40 CFR Part 58 on local time, data are reported to the AIRS in local standard time.

The following sections illustrate the specific formats required for the various types of transactions.

2.6.2.1 Initial AIRS AQS Setup

A valid Time Sharing Option National Computing Center (TSO NCC) UserID and Password must be established prior to the submittal of any monitoring data into AIRS. UserIDs can be obtained by contacting the appropriate AIRS AQS Regional Coordinator. A list of the current coordinators is provided in Table 2-6.

The Air Quality (AQS) data storage processes operate on the input data transactions while they reside in a "screening file." If data are resident on a PC, the file(s) must first be transferred to a TSO dataset and then to an AIRS screening file. The screening file acts as a submittal buffer that allows entry and review of data before inclusion into AIRS. Each data storage user group of AIRS has a screening file for that organization's transactions. The records of an input transaction file are first loaded into a screening file where they remain while the authorized users examine and modify them through the AQS data storage processes. The transactions in the screening file are edited and

corrected by the user and examined by the AIRS Data Base Administrator prior to inclusion in AIRS. Screening files should exist for state agencies. When the UserID is established, a request should be made to the AIRS AQS Regional Coordinator for access to the appropriate screening file.

Table 2-6. Current AIRS AQS Regional Coordinators

Region I Ms. Wendy McDougall U.S. EPA, Region I 60 Westview Street Lexington, MA 4323 (617) 860-4323	**Region VI** Ms. Ruth Tatom U.S. EPA, Region VI 1445 Ross Avenue Dallas, TX 75202-2733 (214) 655-8355
Region II Mr. Ed Finfer U.S. EPA, Region II 290 Broadway - 20th Floor New York, NY 10007-1866 (212) 637-4244	**Region VII** Ms. Joyce Sousley U.S. EPA, Region VII 25 Funston Road Kansas City, KS 66115 (913) 551-5050
Region III Ms. Catherine Brown U.S. EPA, Region III 841 Chestnut Street Philadelphia, PA 19107 (215) 597-6149	**Region VIII** Mr. Dale Wells U.S. EPA, Region VIII (8ART-TO) 999 18th Street, Suite 500 Denver, CO 80202-2405 (303) 293-0967
Region IV Mr. Darren Palmer U.S. EPA, Region IV 345 Courtland St., NE Atlanta, GA 30365 (404) 347-3555 x4184	**Region IX** Mr. Jim Forrest U.S. EPA, Region IX 75 Hawthorne Street San Francisco, CA 94105 (415) 744-1291
Region V Mr. William Damico U.S. EPA, Region V (SQ-14J) 77 W. Jackson Boulevard Chicago, IL 60604-3590 (312) 353-8207	**Region X** Mr. Bill Puckett U.S. EPA, Region X (ES-095) 1200 6th Street Seattle, WA 98101 (206) 553-1702

Minimum detectable limit values in AIRS may be specified for each of the PAMS target compounds by the reporting agency. If no specific value is enumerated by the reporting agency, AIRS will utilize a default value defined in the Geo-Common File for the parameter, generally 0.1 ppbC.

2.6.2.2 Site and Monitor File Updates

Before any VOC or carbonyl data are submitted to AIRS AQS, transactions must be submitted to update the monitor information in AIRS. These transactions, called Type F transactions, provide information concerning the compounds of interest, the organizations involved, and the relative monitor dates. Column 1 is the transaction type code. For the Type F transactions, the entry in Column 1 is "F."

The monitor ID is placed in columns 2-16 and is comprised of the State, County, and Site Code (columns 2-10) where the sample was collected, the parameter (columns 11-15), and Parameter of Occurrence (POC) code (column 16). The POC code is used to distinguish between different monitors at the same site that are measuring the same parameter. The first monitor at the site is generally identified with POC = 1, with additional monitors at the same site measuring the same compound identified with POC = 2, etc. If a new instrument were installed to replace the original instrument used as the first monitor, that would be the same monitor and it would have POC = 1, even if the sampling method or interval were changed.

The monitor type is indicated in column 17. For PAMS Meteorological and VOC sites, the monitor type is "3," indicating other. Once the monitor information has been submitted to the AIRS AQS, the Regional Coordinator should be contacted. The Regional Coordinator will then request that the network be approved as a PAMS monitor.

The date when the monitor type became effective is recorded in columns 18-23. The date is recorded in the YYMMDD format. The year, month, and day are each two digits and any leading zeros must be included.

The next 9 columns indicate the organizations associated with analysis and collection of the sample and reporting the subsequent data. Columns 24-26 are reserved for the code indicating the

analysis laboratory. Columns 27-29 indicate the collection laboratory. The reporting organization code is stored in columns 30-32. These codes can be found in the AIRS Geo-Common Subsystem and must be entered exactly as they appear in that subsystem.

The date when the reporting organization became effective is recorded in columns 33-38. The date is recorded in the YYMMDD format. The year, month, and day are each two digits and any leading zeros must be included.

The date when the sampling program began is recorded in columns 39-44. The date is recorded in the YYMMDD format. The year, month, and day are each two digits and any leading zeros must be included.

The 4-digit code indicating the urban area represented by the site is placed in columns 72-75. The urban area codes can be found in the AIRS Geo-Common Subsystem and must be entered exactly as in the subsystem.

The PAMS required sampling frequency code is placed in column 76. Table 2-7 presents possible codes for the different sampling frequency requirements.

The transaction ID is placed in column 79. For a Type F1 transaction, the ID is "1."

The action code placed in column 80 indicates the type of data base processing to be performed by this transaction. In order to insert new values into the database, "I" is placed in column 80. Should modification to existing monitor information be necessary (e.g., a change in the reporting organization, etc.), an "M" is placed in column 80. The deletion of existing monitor information is indicated with a "D" in column 80.

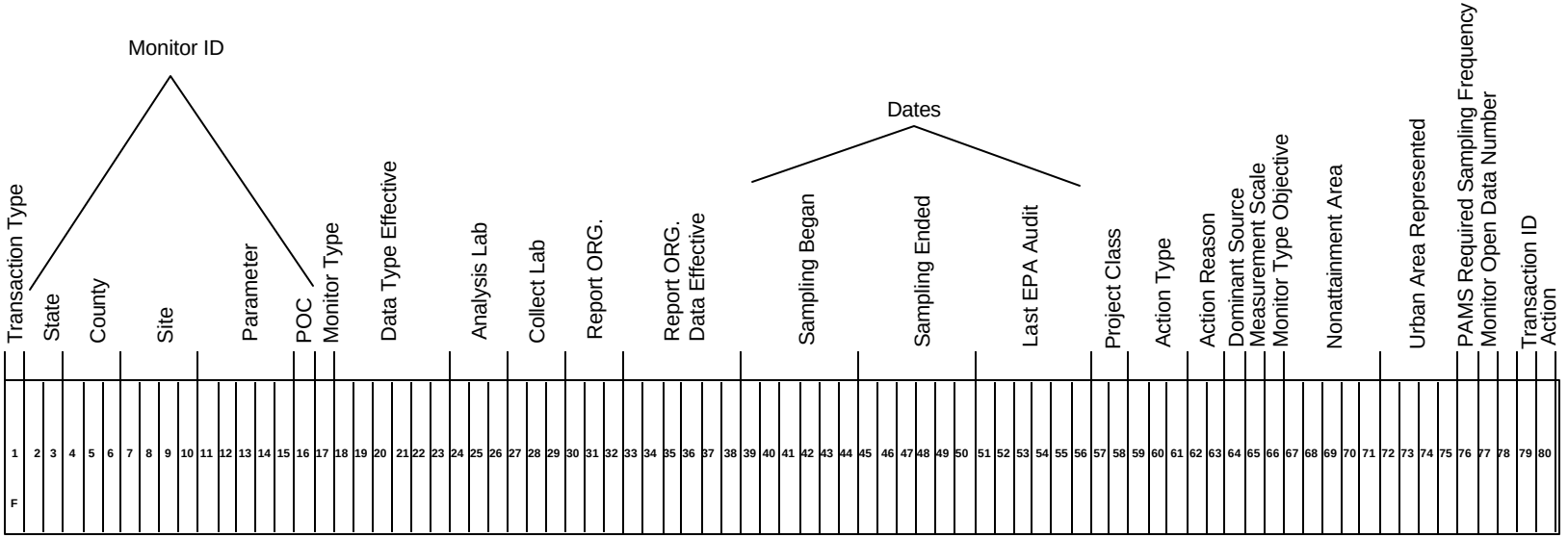
Table 2-7. AIRS Sampling Frequency Codes

Code	Sampling Frequency
A	Daily 24 1-Hr Samples - PAMS
B	Daily 8 3-Hr Samples - PAMS
C	Daily 1 3-Hr Sample - PAMS
D	Daily 1 24-Hr Sample - PAMS
E	Daily 4 6-Hr Samples - PAMS
G	Every 3rd Day 24 1-Hr Samples - PAMS
H	Every 3rd Day 8 3-Hr Samples - PAMS
I	Every 3rd Day 1 3-Hr Sample - PAMS
J	Every 3rd Day 1 24-Hr Sample - PAMS
K	Every 3rd Day 4 6-Hr Samples - PAMS
L	Every 3rd Day 4 3-Hr Samples - PAMS
M	Every 6th Day 24 1-Hr Samples - PAMS
N	Every 6th Day 8 3-Hr Samples - PAMS
O	Every 6th Day 1 3-Hr Sample - PAMS
P	Every 6th Day 1 24-Hr Sample - PAMS

One Type F1 transaction is necessary for each monitor. Unique Type F1 transactions need to be submitted only once prior to the submittal of monitoring data. Should any of the information change, the Type F1 transactions must be modified reflecting the changes. If Type F1 transactions have already been submitted and no modifications are necessary, it is not necessary to submit Type F1 transactions again before the raw data are submitted.

Figure 2-17 shows the column placement of each of the fields for a Type F1 transaction. The “F” in column 1 (transaction type) and the “1” in column 79 (transaction ID) denote the Type F1

transaction. Below the figure is an example Type F1 transaction. For this example, site 25-009-2006 (columns 2-10) began monitoring for isoprene (indicated by 43243 in



o:/s/g/morr/3797/pams/hobson/graph2.ppt

Figure 2-17. Column Placement for a Type F1 Transaction

columns 11-15) on June 1, 1994 (indicated by 940601 in columns 18-23). The state agency (001) analyzed and collected the samples, and reported the results. This site was in the Boston urban area (as indicated by 1120 in columns 72-75). The required sampling frequency was one 24-hour sample every sixth day (indicated by P in column 76). Because isoprene previously had not been monitored at this site, this transaction was inserted into AIRS (indicated by "I" in column 80). Had it been necessary to modify information, a "M" would have been placed in column 80. It is important to note the column placement of the codes in the transaction file. For example, because it is not required to input a dominant source, column 64 is left blank. The second transaction indicates that the same site began monitoring for formaldehyde (parameter 43502) on June 1, 1994, as well. Many of the necessary codes are provided in subsequent sections of this document. These and other codes can also be found in the Geo-Common Subsystem of AIRS.

In addition to Type F1 transactions, comments need to be added to the site information to identify the configuration of the sampling/analysis equipment used. Comments can be added to the site cards by submitting Type A6 (or A7) cards. Type A6 transactions add a comment to the Line 1 comment line, whereas the Type A7 transactions add a comment to the Line 2 comment line. If a comment does not appear on Line 1, submit a Type A6 transaction. If a comment currently appears on Line 1 and no comment appears on Line 2, submit a Type A7 transaction. If comments appear on both lines, submit either transaction where the comment includes the original comment plus the comment concerning the configuration of the sampling/ analysis equipment. If additional comment space is needed, the Line 2 comment may be used as a continuation of Line 1. A list of possible configuration comments appears in Table 2-8. Because of the limited space within the comment lines, it is important to make the comments concise yet as informative as possible. Choose the combinations of codes that best reflect the configuration of the sampling/analysis equipment.

Table 2-8. Configuration Comments for Type A6 or A7 Transactions

Monitoring	Equipment	Code	Description
VOC	GC (Choose one)	Single FID Dual FID	GC configured with one FID GC configured with two FIDs
	Dryer (Choose one)	W/Dryer W/O Dryer	Dryer is in line No dryer is used
	Concentrator (Choose one)	Sorbent Cryo	Sorbent sample concentrator Cryogenic sample concentrator
	Columns	BP1 GS-Q RTx Al_2O_3/Na_2SO_4	SGE, Inc. BP1 (0.22 mm diameter, 50 m length) J&W® GS-Q (0.53 mm diameter, 30 m length) Restek® RTx-502.2 (0.53 mm diameter, 25 m length) Hewlett Packard® Al_2O_3/Na_2SO_4 (0.32 mm diameter, 50 m length)
Carbonyl	Ozone Scrubber (Choose one)	Denuder Cartridge	KI Denuder Sep-Pak® KI Cartridge

Column 1 is the transaction type and for Type A6 (or A7) the transaction type is "A."

Columns 2-10 are the State, County, and Site Code where the sample is collected. The comment will be added to the Site File for this site.

Columns 11-78 are reserved for the site comment. If a Type A6 transaction is inserted, the comment will appear on Line 1. A Type A7 transaction will place a comment on Line 2.

Column 79 is the transaction ID. Type A6 transactions require a "6" in column 79, whereas Type A7 transactions require a "7" in column 80. If a Type A6 transaction is submitted, a comment is placed on Line 1. A comment is placed on Line 2 if a Type A7 transaction is submitted.

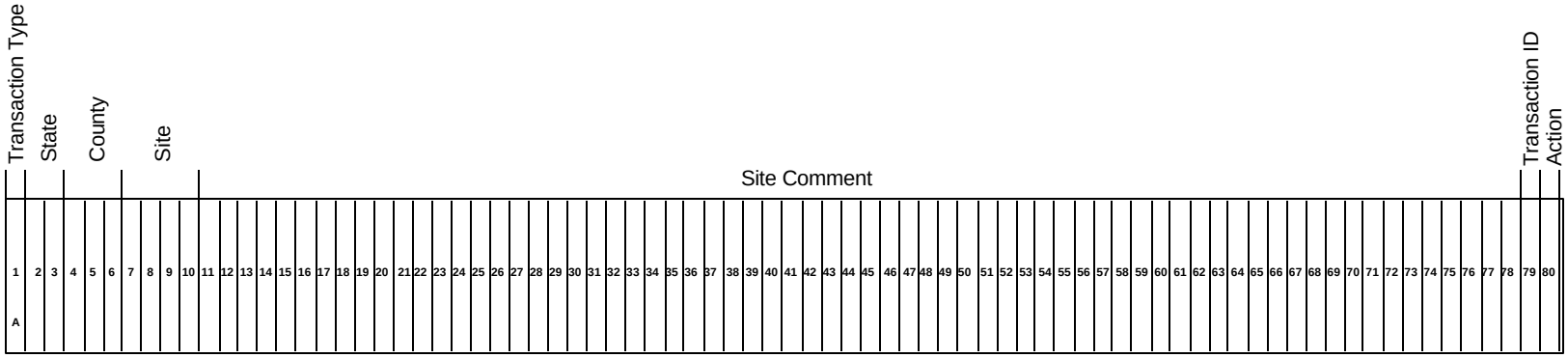
The action code placed in column 80 indicates the type of data base processing to be performed by this transaction. In order to insert a new comment into the site files, an "I" is placed in column 80. Should modifications to existing values in the site files be necessary, a "M" is placed in column 80 to indicate a modify transaction. For a modify transaction, any alteration to the current site comments will completely replace that comment. Therefore, any change will require that the entire field be re-entered. Deletions are not valid for Type A6 (or A7) transactions. To delete existing site comments, fill columns 11-78 with asterisks on a modify transaction. Be sure to fill all columns with asterisks or only asterisks will be stored in the Site File as the Site Comments.

Figure 2-18 illustrates the placement of information for a Type A6 transaction. Below the figure is an example Type A6 transaction. The Type A6 is indicated with an "A" in column 1 (transaction type) and a "6" in column 79 (transaction ID). For this example, site 25-009-2006 (Columns 2-10) has the comment PAMS MONIT-CRYO-DUAL FID BP1/RTx W/Dryer - DENUDER (Columns 11-78) inserted (column 80) as the Line 1 comment. Only one Type A6 (or A7) transaction should be created for each site.

Type F1 and A6 (or A7) files should be saved as ASCII files (multiple lines can be saved as one file). The files should then be transferred to the EPA mainframe for a subsequent loading into the screening file. Once Type F1 and A6 (or A7) transactions have been loaded, they must be edited (three edit levels). Any necessary corrections must be made and an update requested. This process is described in Section 2.6.2.4.

2.6.2.3 Raw Data Transactions

Following the update of AIRS AQS with the Type F1 and A6 (or A7) transactions, AIRS AQS will accept raw data transactions. As with the Type F1 transactions, codes have been assigned to the various fields required for the raw data transactions. Tables 2-9 and 2-10 present the AIRS codes assigned to the target VOC and carbonyl O_3 precursor compounds, respectively. Table 2-11 presents the various method codes associated with PAMS sampling and analysis.

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A250092006PAMS MONIT-CRYO-DUAL FID DB-1/RTx W/DRYER -DENUDER                  6I
```

o:/s/g/morr/3797/pams/hobson/graph1.ppt

Figure 2-18. Column Placement for a Type A6 Transaction

Table 2-9. Target Volatile Organic Compounds

AIRS Parameter Code	Target Compound Name	AIRS Parameter Code	Target Compound Name
43203	Ethylene	43249	3-Methylhexane
43206	Acetylene	43250	2,2,4-Trimethylpentane (isooctane)
43202	Ethane	43232	*n*-Heptane
43205	Propylene	43261	Methylcyclohexane
43204	Propane	43252	2,3,4-Trimethylpentane
43214	Isobutane	45202	Toluene
43280	1-Butene	43960	2-Methylheptane
43212	*n*-Butane	43253	3-Methylheptane
43216	*trans*-2-Butene	43233	*n*-Octane
43217	*cis*-2-Butene	45203	Ethylbenzene
43221	Isopentane	45109	*m/p*-Xylene
43224	1-Pentene	45220	Styrene
43220	*n*-Pentane	45204	*o*-Xylene
43243	Isoprene (2-methyl-1,3-butadiene)	43235	*n*-Nonane
43226	*trans*-2-Pentene	45210	Isopropylbenzene (cumene)
43227	*cis*-2-Pentene	45209	*n*-Propylbenzene
43244	2,2-Dimethylbutane	45212	*m*-Ethyltoluene (1-ethyl-3-methylbenzene)
43242	Cyclopentane	45213	*p*-Ethyltoluene (1-ethyl-4-methylbenzene)
43284	2,3-Dimethylbutane	45207	1,3,5-Trimethylbenzene
43285	2-Methylpentane	45211	*o*-Ethyltoluene (1-ethyl-2-methylbenzene)
43230	3-Methylpentane	45208	1,2,4-Trimethylbenzene
43245	1-Hexene*	43238	*n*-Decane
43231	*n*-Hexane	45225	1,2,3-Trimethylbenzene
43262	Methylcyclopentane	45218	*m*-Diethylbenzene
43247	2,4-Dimethylpentane	45219	*p*-Diethylbenzene
45201	Benzene	43954	*n*-Undecane
43248	Cyclohexane	43141	*n*-Dodecane*
43263	2-Methylhexane	43102	TNMOC**
43291	2,3-Dimethylpentane	43000	PAMHC***

* These compounds have been added as calibration and retention time standards primarily for the purpose of retention time verification. They can be quantitated at the discretion of the user.

** Total Nonmethane Organic Compounds

*** PAMS Hydrocarbons

Table 2-10. Carbonyl Target List

Compound	AIRS Parameter Code	Reporting Requirement for PAMS
Formaldehyde	43502	Required
Acetaldehyde	43503	Required
Acetone	43551	Required
2,5-Dimethylbenzaldehyde	45503	Optional
Acrolein	43505	Optional
Benzaldehyde	45501	Optional
Butyr/Isobutyraldehyde	43329	Optional
Crotonaldehyde	45316	Optional
Hexanaldehyde	43517	Optional
Isovaleraldehyde	43513	Optional
Propionaldehyde	43504	Optional
Tolualdehydes	45504	Optional
Valeraldehyde	43518	Optional
Methyl ethyl ketone	43552	Optional

Table 2-11. AIRS Method Codes

Category	Analysis Method	AIRS Method Code
VOC - Automated	Chrompack International Auto-TCT Concentrator with Chrompack CP 9000 GC	124
	Entech Laboratory Automation Model 2000 Concentrator with Hewlett-Packard 5890 Series II GC	122
	Nutech Model 3550A Concentrator with Hewlett-Packard 5890 Series II GC	123
	Perkin-Elmer Corporation Model ATD-400 with Perkin-Elmer Model 8700 GC	128
	Varian Chromatography Systems Ozone Precursor System with Varian Model 3600-CX GC	129
VOC - Manual	Chrompack International GC	125
	Hewlett Packard Company GC	126
	Perkin-Elmer Corporation GC	127
	Varian Chromatography Systems GC	130
Carbonyl	Cartridges coated with DNPH on silica analysis by HPLC with KI O_3 scrubber	202

Sample frequency codes and sample interval codes are listed in Table 2-7 and Table 2-12, respectively. Units codes are listed in Table 2-13. Hourly data start hours are listed in Table 2-14. Null values are listed in Table 2-15. Other codes which may be necessary can be found in the Geo-Common Subsystem of AIRS.

There are three types of raw data transactions: hourly, daily, and composite. The hourly raw data transaction is used when the sample is collected for any period of time less than 24 hours. Hourly data are indicated with a "1" in the transaction type field (column 1). The daily raw data transaction is used when the sample is collected for at least 24 hours. A transaction type code of "2" in column 1 indicates daily data. If several samples obtained at different times are combined and analyzed as one, the composite raw data transaction is used.

Raw data transactions are generally inserted into AIRS, but modifications to or deletions of previously inserted data can also be performed. An insertion is indicated with an "I" in the action field (column 80), a "M" indicates a modification, and a "D" indicates a deletion.

Hourly Data—Hourly data are those which are collected for a period of time less than 24 hours. Because several hourly samples can be collected within a given day, AIRS allows for several results for one parameter (compound) to be input with one transaction. Figure 2-19 illustrates the format for hourly data.

Composite data are indicated with a "3" in the transaction type field and will not be used for PAMS.

The transaction type, "1," indicates hourly data and is placed in column 1. All the sample values entered on a particular type 1 transaction line apply to the same day.

Table 2-12. AIRS Interval Codes

Code	Interval
A	1 Week
B	3 Hours
C	Composite Data
D	Yearly
G	Annual Geometric Mean
M	Annual Arithmetic Mean
Q	Quarterly Arithmetic Mean
X	24-Hr Block Average
Y	3-Hr Block Average
Z	8-Hr Run Average
1	1 Hour
2	2 Hour
3	4 Hour
4	6 Hour
5	8 Hour
6	12 Hour
7	24 Hours
8	1 Month
9	3 Months

Table 2-13. AIRS Unit Codes

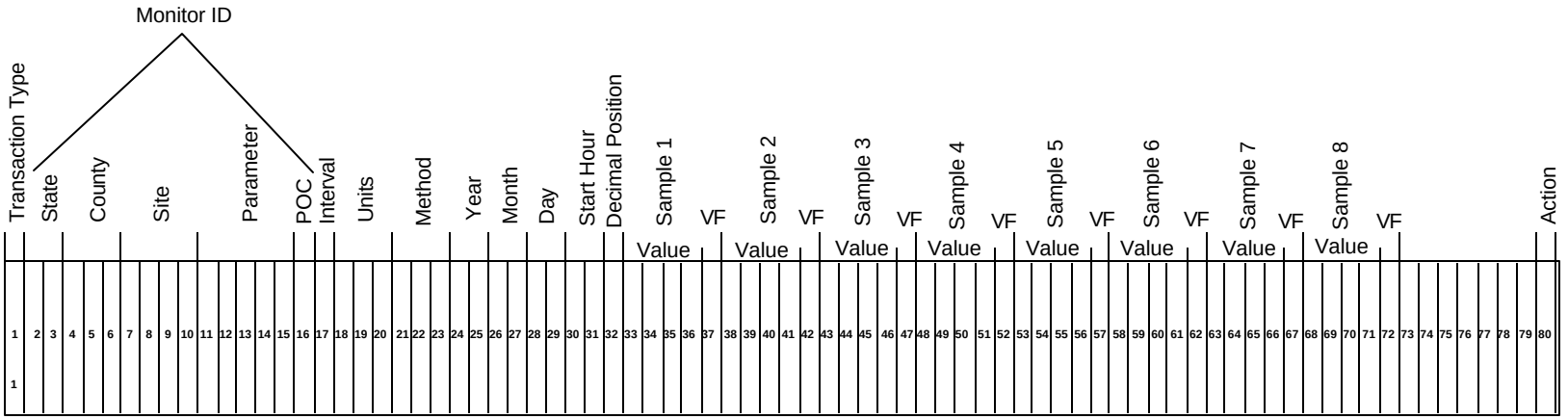
Code	Unit	Category
078	ppbC	VOC Compounds
008	ppb	Carbonyl Compounds

Table 2-14. Hourly Sample Valid Start Hour Based on the Interval

Sampling Interval	Interval Code	Start Hours
1 hour	1	00, 08, 16
2 hours	2	00, 01, 16, 17
3 hours	B	00, 01, 02
4 hours	3	00, 01, 02, 03
6 hours	4	00, 01, 02, 03, 04, 05
8 hours	5	00, 01, 02, 03, 04, 05, 06, 07
12 hours	6	00, 01, 02, 03, 04, 05, 06, 07, 08, 09, 10, 11

Table 2-15. Null Values

Value	Reason
9967	Sample Pressure Out of Limits
9968	Technician Unavailable
9969	Construction/Repairs in Area
9970	Shelter Storm Damage
9971	Shelter Temperature Outside Limits
9972	Scheduled but NOT Collected
9973	Sample Time Out of Limits
9974	Sample Flow Rate Out of Limits
9975	Insufficient Data (Can't Calculate)
9976	Filter Damage
9977	Filter Leak
9978	Voided by Operator
9979	Miscellaneous Void
9980	Machine Malfunction
9981	Bad Weather
9982	Vandalism
9983	Collection Error
9984	Lab Error
9985	Poor Quality Assurance Results
9986	Calibration
9987	Monitoring Waived
9988	Power Failure (POWR)
9989	Wildlife Damage
9990	Precision Check (PREC)
9991	QC Control Points (Zero/Span)
9992	QC Audit (Audit)
9993	Maintenance/Routine Repairs
9994	Unable to Reach Site
9995	Multipoint Calibration
9996	Auto Calibration
9997	Building/Site Repair
9998	Precision/Zero/Span

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12500920064350 21B008102940707002 280  333  516  549  716  799  658  489       I
```

o:/s/g/morr/3797/pams/hobson/graph3.ppt

Figure 2-19. Column Placement for an Hourly Data Transaction

The monitor ID is placed in columns 2-16 and is comprised of the State, County, and Site Code (columns 2-10) where the sample was collected, the parameter (columns 11-15), and Parameter of Occurrence (POC) code (column 16). The POC code is used to distinguish between different monitors at the same site that measure the same parameter. The first monitor at the site is generally identified with POC = 1, with additional monitors at the same site measuring the same compound identified with POC = 2, etc. If a new instrument were installed to replace the original instrument used as the first monitor, that would be the same monitor and it would have POC = 1, even if the sampling method or interval were changed.

Column 17 is reserved for the sampling interval code. Table 2-12 gives several interval codes which may be used. It should be noted that the interval codes must represent a non-composite sampling interval of less than 24 hours. Because there can be as many as eight sample values per transaction, the temporal scope of a given type 1 transaction varies considerably depending on the sampling interval. With some intervals, a single transaction holds all the sample values for a day, while multiple transactions are needed with other intervals. For example, only four slots of one transaction are used to report the four 6-hour observations for a day, while all eight slots of three transactions are needed to report the eight 1-hour observations for a day.

The units code is placed in columns 18-20 and indicates the dimensional system in which the parameter measurement is expressed. Table 2-13 presents several units codes.

Columns 21-23 indicate the method used to sample and analyze the parameter. A method code is valid if it exists in combination with parameter, interval, and units in the AIRS Geo-Common File. Several method codes are summarized in Table 2-11. Choose the method code that describes the analytical system used. Special notes describing the analytical system should be made using Type A6 (or A7) transactions.

The date of the sample is placed in columns 24-29 in the YYMMDD format. The year, month, and day are each two digits and any leading zeros must be included.

The start hour code is placed in columns 30-31. AIRS data base time is standard time. This code indicates the beginning hour of the sampling period for the first sample value "slot" on the transaction, given in standard time at the location of the monitoring site. The first hour of a day, 00, begins at midnight, and the last hour, 23, begins at 11:00 p.m. The hour of a sample value is determined by its position on the transaction (which "slot" it occupies). The first slot is for the hour specified in the start hour field (columns 30-31) of the transaction. The second slot is for the start hour plus the sampling interval, the third slot is for the start hour plus twice the sampling interval, and so on. In general;

Hour of a slot (start hour) + [(slot number 1) * (hours in sampling interval)]

Table 2-14 presents valid start hours for hourly data based on the interval.

Column 32 is the decimal point (DP) indicator. Because sample values are entered as integers, this code is used to indicate the number of digits to the right of the decimal point in the sample value fields. The following equation can be used to determine the correct DP for the data:

Sample Concentration 10^{DP} Sample Value entered into AIRS as an Integer

The DP applies to all sample value fields on the transaction. If the sample values require different DPs, use multiple transactions to code the compatible DP and sample values.

Columns 33-72 are reserved for eight sample values. These fields contain the actual numeric values of the hourly data. There are eight "slots" for eight observations for the sample date. These slots are in columns 33-36, 38-41, 43-46, 48-51, 53-56, 58-61, 63-66, and 68-71. The slot into which an observation is placed depends on the hour associated with the observation, the sampling

interval (in column 17), and start hour (in columns 30-31). For the day's observation, the following relationship holds:

$$\text{SLOT\#} \quad 1 + \frac{(\text{Hour} \quad \text{Start Hour})}{\text{NH}}$$

where:

Hour is the hour associated with the observation;

Start Hour is the start hour of the observations for that day (columns 30-31); and

NH is the number of hours between observations.

When inserting a transaction, there must not be a value in the data base for the date and hour corresponding to the slot used. In the sample value "slot" enter a true observation of a parameter value. Leave blank any occurrence of the sample value for an hour when you do not wish to report a true observation. Numeric integer values (no decimal points) that represent true observations must be entered right justified in the fields. Leading zeros are not required, but recommended. The sample value and the decimal point indicator together indicate the compound concentration reported in the units indicated by the unit code.

Following each sample value field is a field for the validity flag. The validity flag is used to indicate the reason for an abnormal observation. The presence of a validity flag with an observation indicates that the observation is due to an "exceptional event" or its abnormal value has been checked and found to be valid. The use of any validity flag (except "V") must be approved by state or EPA regional personnel. If an observation results from an exceptional event (e.g., volcano, forest fire, disaster clean-up, etc.), place a valid validity flag in column 37, 42, 47, 52, 57, 62, 67, and/or 72. A valid validity flag is one that exists in the AIRS Geo-Common File for this parameter. If a validity flag is not necessary, the validity flag field and/or fields should be left blank.

The action code placed in column 80 indicates the type of data base processing to be performed by this transaction. In order to insert new values into the raw data files, an "I" is placed in column 80. Should modifications to existing values in the raw data files be necessary, a "M" is placed in column 80. The deletion of existing values from the raw data files is indicated with a "D" in column 80.

A protocol has been established to explain "missing data" should there be an instance where data have not been collected. If there is a instance where data should have been collected, but were not, the DP indicator (column 32) should be left blank. This procedure indicates to AIRS that the value entered in the sample value field is a code explaining why the data are missing. A list of approved null value codes appears in Table 2-15. Always use the most appropriate null value code. When a reason for a null value exists that is not listed, use the miscellaneous void code: Number 9979.

An example of an hourly transaction appears in Figure 2-16. In the first transaction line, site 25-009-2006 is submitting data for benzene (parameter 45201) for the primary sample (POC =1). The samples were collected for three hours (interval = B). The results are presented in ppbC (units = 078) for a Varian GC (method = 129). The sample was collected July 7, 1994 (columns 24-29). Because the start hour is 00 (columns 30-31), the three hour samples were collected beginning at midnight, 3:00 a.m., 6:00 a.m., 9:00 a.m., noon, 3:00 p.m., 6:00 p.m., and 9:00 p.m. local standard time. The results are presented so that a decimal point appears two places to the left of the indicated value (column 32). The sample collected at midnight (columns 33-36) has a value of 3.98 ppbC whereas the sample collected at 3:00 p.m. (columns 58-61) has a value of 23.45 ppbC. This transaction summarizes the data collected for one compound (benzene) for one day. Similar transactions would be necessary for each of the over 50 compounds on the VOC target list for this date.

The second line is the transaction for formaldehyde. Site 25-009-2006 is submitting data for formaldehyde (parameter 43502) for the primary sample (POC=1). The samples were collected for

three hours (interval = B). The results are presented in ppbv (units = 008) for cartridges coated with DNPH on silica using a potassium iodide ozone scrubber (method = 202). The sample was collected July 7, 1994 (columns 24-29). Because the start hour is 00 (columns 30-31), the three hour samples were collected beginning at midnight, 3:00 a.m., 6:00 a.m., 9:00 a.m., noon, 3:00 p.m., 6:00 p.m., and 9:00 p.m. local standard time. The results are presented so that a decimal point appears two places to the left of the indicated value. The sample collected at 3:00 a.m. (columns 38-41) has a value of 3.33 ppbv whereas the sample collected at 9:00 p.m. (columns 68-71) has a value of 4.89 ppbv. This transaction summarizes the formaldehyde data collected for one day. Similar transactions would be necessary for each of the three compounds on the carbonyl target list for this date.

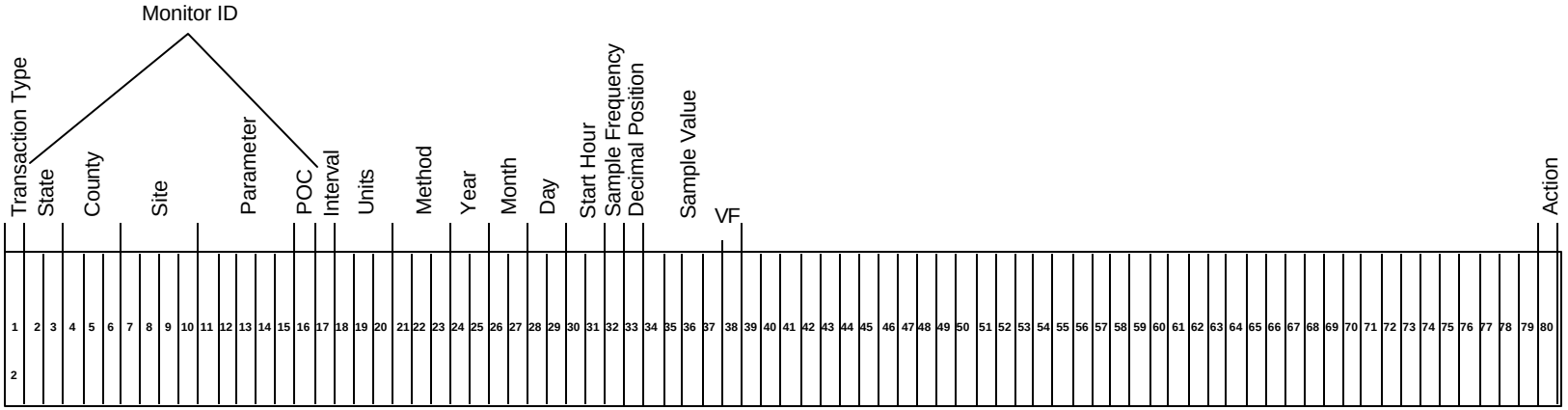
Daily Data—Daily data are those which are collected for a period of at least 24 hours or more. These data are called transaction Type 2 and are indicated with a "2" in column 1 of the transaction. The column placement for daily data is presented in Figure 2-20.

The monitor ID is placed in columns 2-16 and is comprised of the State, County, and Site Code (columns 2-10) where the sample was collected, the parameter (columns 11-15), and Parameter of Occurrence (POC) code (column 16). The POC code is used to distinguish between different monitors at the same site that are measuring the same parameter. The first monitor at the site is generally identified with POC = 1, with additional monitors at the same site measuring the same compound identified with POC = 2. If a new instrument were installed to replace the original instrument used as the first monitor, that would be the same monitor and it would have POC = 1, even if the sampling method or interval were changed.

Column 17 is reserved for the sampling interval code. Table 2-12 gives several interval codes which may be used. It should be noted that the interval codes must represent a non-composite sampling interval of at least 24 hours.

The units code is placed in columns 18-20 and indicates the dimensional system in which the parameter measurement is expressed. Table 2-13 presents several units codes.

Columns 21-23 indicate the method used to sample and analyze the parameter. A method code is valid if it exists in combination with parameter, interval, and units in the AIRS Geo-Common File. Several method codes are summarized in Table 2-11. Choose the method code that describes the analytical system used. Special notes about the analytical system should be made using Type A6 (or A7) transactions.

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12345678901234567890123456789012345678901234567890123456789012345678901234567890

22500920064520117078129940707 00P21864                                        I
22500920064350217008102940707 00P2 280                                        I
```

o:/s/g/morr/3797/pams/hobson/graph4.ppt

Figure 2-20. Column Placement for a Daily Data Transaction

The date of the sample is placed in columns 24-29 in the YYMMDD format. The year, month, and day are each two digits and any leading zeros must be included.

The start hour code is placed in columns 30-31. This entry indicates the beginning hour of the sampling period, given in standard time at the location of the monitoring site. The first hour of a day, 00, begins at midnight, and the last hour, 23, begins at 11:00 p.m.

Sampling intervals of 24 hours or more should be reported on the day in which the majority of the sampling occurred. Therefore, a 24-hour sample taken from midnight (00:00) to midnight (24:00) local daylight time on June 5, would be reported with a start time of (00:00) on June 5 rather than 23:00 on June 4.

The sample frequency code is placed in column 32 and indicates how much time elapses between observations. This code is expressed in terms compatible with the associated Interval Code. Table 2-7 presents sample frequency codes.

Column 33 is the decimal point (DP) indicator. Because sample values are entered as integers, this code is used to indicate the number of digits to the right of the decimal point in the sample value fields. The following equation can be used to determine the correct DP for the data:

$$\text{Sample Concentration} \quad 10^{DP} \quad \text{Sample Value entered into AIRS as an Integer}$$

The sample value is placed in columns 34-37. The integer value represents the true observation and is entered right justified. Leading zeros are optional.

The validity flag is placed in column 38 and is used to give the reason for an abnormal observation. The presence of a validity flag with an observation indicates that the observation is due to an “exceptional event” or its abnormal value was checked and found to be valid. The use of any

validity flag (except "V") must be approved by state or EPA regional personnel. If a validity flag is not necessary, the validity flag field should be left blank.

The action code placed in column 80 indicates the type of data base processing to be performed by this transaction. In order to insert new values into the raw data files, an "I" is placed in column 80. Should modifications to existing values in the raw data files be needed, an "M" is placed in column 80. The deletion of existing values from the raw data files is indicated with a "D" in column 80.

A protocol has been established to explain "missing data" should there be an instance where data have not been collected. If there is a instance where data should have been collected, but were not, the DP indicator (column 32) should be left blank. This blank column indicates to AIRS that the value entered in the sample value field is a code explaining why the data are missing. A list of approved null value codes appears in Table 2-14.

An example of a daily transaction appears in Figure 2-20. In the first transaction line, site 25-009-2006 is submitting data for benzene (parameter 45201) for the primary sample (POC =1). The sample was collected for 24 hours (Interval = 7). The results are presented in ppbC (units = 078) for a Varian GC (method = 129). The sample was collected July 7, 1994 (columns 24-29). The sample collection began at midnight (Start Hour = 00). The sample was collected on the PAMS schedule of one 24-hour sample every 6 days (Sample Frequency = P). The results are presented such that a decimal point appears two places to the left of the indicated value (column 33). The sample value is 18.64 ppbC (columns 34-37). This transaction summarizes the data collected for one compound (benzene) for one day. Similar transactions would be necessary for each of the over 50 compounds on the VOC list for this date.

The second line is the example transaction for formaldehyde. In this transaction, site 25-009-2006 is submitting data for formaldehyde (parameter 43502) for the primary sample (POC = 1). The sample was collected for 24 hours (interval = 7). The results are presented in ppbv (units = 008)

for cartridges coated with DNPH on silica (method = 102). The sample was collected July 7, 1994 (columns 24-29). The sample collection began at midnight local standard time (Start Hour = 00). The sample was collected on the schedule of one 24-hour sample every 6 days (Sample Frequency = P). The results are presented so that a decimal point appears two places to the left of the indicated value (column 33). The sample value is 2.80 ppbv (columns 34-37). This transaction summarizes the data collected for one compound (formaldehyde) for one day. Similar transactions would be necessary for the three carbonyl compounds for this date.

2.6.2.4 Submitting Data

Once the raw data have been formatted in accordance with the required fixed block 80-character per line formats, the process of submitting data to AIRS can begin. For batch processing, groups of transactions should be saved as ASCII files which are then loaded onto the EPA mainframe. However, the transactions must still be placed in the screening file.

Once the raw data ASCII files have been loaded onto the EPA mainframe, work within the AIRS system can begin. After accessing AIRS, entering AQS, and selecting the screening file, a four step process begins to submit the data to AIRS AQS. The process begins by choosing Submit from the AQS Menu. The submenu should then include, among others, choices for LOAD, EDIT, CORRECT, and SUBMIT.

The LOAD Process–Placing the Data in the Screening File—LOAD is a batch process which is initiated from the Air Quality "Submit" menu. The transaction records are read from the TSO dataset specified by the user and written into the user's screening file. A printed report is generated that summarizes the processing performed in terms of the number of transaction records by type or category. Suppression of the printed report can be achieved by selecting "N" for Print.

The EDIT Process–Validating the Data—EDIT is a batch process which is initiated from the Air Quality "Submit" menu. Transaction records in the user's screening file are examined and edit/validation checks are applied. The purpose is to ensure that only "valid" data get into the data base. A printed report is generated that lists each record that failed the edit checks and the reason(s) why it failed. Suppression of the printed report can be achieved by selecting "N" for Print.

There are three (3) levels of edit/validation checks. Level 1 determines whether the individual fields of a record have appropriate values (e.g., is the city code valid?). Level 2 checks the relationship among the fields or records. Duplicate transaction records would result in a Level 2 error. Level 3 statistically tests for anomalies in the data and checks for relationships among the transaction records and the AIRS Data Base. All transaction data must pass this 3-level editing system prior to admittance into the AIRS Data Base.

The CORRECT Process–Correcting the Data—Air Quality transaction records in the user's screening file may be modified in order to correct edit/validation errors identified by the EDIT process or to correct some other problem known to the user. CORRECT does not generate a printed report.

The CORRECT process allows one to "browse" in the screening file to view its contents, and to modify, delete, or add transaction records. A particular record or group of records may be selected for display on the user's terminal screen. As each record is displayed, the user may leave the data fields intact, alter the contents of the data fields, or delete the record. The user may also set (or clear) an indicator that causes the record to be excluded temporarily from EDIT and UPDATE processing, while retaining it in the file. The same kinds of operations may also be applied to groups of records using "global" commands that specify the identities (keys) of the records to be affected and the actions to be applied. New transaction records may also be inserted into the screening file. Level-1 edit checks are applied to inserted and modified records and any errors are indicated on the user's screen. Edit checks are not applied to each record modified by a global command, but to the

command itself. Any records that have passed Level-2 or Level-3 edit checks and are interdependent with a record affected by CORRECT processing will be reset to Level-1.

The NOTIFY Process–Requesting to Add Data to AIRS AQS—Once all records have passed all three edit checks, the AIRS Data Base Administrator should be notified of the impending AIRS AQS data by selecting NOTIFY from the submenu. NOTIFYing the AIRS Data Base Administrator locks the screening file and prevents further use of it until the AIRS Data Base Administrator releases it. The AIRS Data Base Administrator and the appropriate NAMS/PAMS Coordinators review the data. The data are then added to the AIRS data base.

Should there be any suspect data, the AIRS Data Base Administrator may elect not to add the data to AIRS, but instead leave the data in the user's screening file and request the user to double-check the transaction. Upon inspection, should there be an error in the transaction, the user should CORRECT the error, EDIT check/validate the data, and NOTIFY the AIRS Data Base Administrator of the impending AIRS AQS data. If the data are valid, the user may want to indicate that the data have been validated by placing a validity flag of "V" to indicate that the data are indeed valid. The transaction should then proceed through the EDIT checks/validations and after successful completion of the EDIT checks, the user should NOTIFY the AIRS Data Base Administrator of the data.

2.7 Validating Data from Automated VOC Systems

Although manual sampling methods may be used, automated GC techniques are currently the most practical and cost effective way to comply with the rigorous speciated VOC sampling frequency required for PAMS. Measuring VOCs in the atmosphere on a daily and hourly basis using these systems produces extremely large and complex data sets. Managing, processing, and validating the data requires technical expertise and an intensive effort to obtain reliable and consistent data for the timely input into the AIRS AQS data base. The AIRS data base is used as the national repository for PAMS data and can be used to assist State and local agencies in determining if the program objectives

and Data Quality Objectives (DQOs) described in the PAMS Implementation Manual[25] are met. Data submitted to AIRS by all agencies must be consistent with the PAMS monitoring DQOs and of adequate quality to meet Clean Air Act Title I objectives.

PAMS data use is discussed elsewhere in this document, but it is pertinent to the data validation process to reiterate the discussion. The data will allow the state and local agencies to develop, evaluate, and refine new O_3 control strategies; determine NAAQS attainment or non-attainment for O_3; track VOCs and NO_x emissions inventory reductions; provide photochemical prediction model input; evaluate photochemical prediction model performance; analyze ambient air quality trends; and characterize population exposure to VOCs and O_3. Data from VOC measurement systems must be submitted to AIRS within six months following the end of each quarterly reporting period.

Validating the measurement data can be as complex as the gas chromatographic techniques and methods used to collect them. The evaluation of the quality and reliability of the data from GC analyses is often referred to as the data validation process. The EPA defines data validation as a systematic process consisting of data editing, screening, checking, auditing, verification, certification, and review, for comparing a body of data to an established set of criteria to provide assurance that the data are adequate for their intended use.[50] Data validation is an element of quality assurance and includes evaluation of the data quality and reliability and assurance that the data are consistent with program data quality objectives.

Data validation is the final and most critical part of the process used to generate PAMS data. The data must be validated and reviewed to ensure the overall quality of the measurement prior to inclusion in the AIRS AQS data base. Data validation is used in conjunction with program objectives, DQOs, and QA/QC to remove inconsistencies in the data set and improve data quality. The key aspects of a complete data validation process are the pre-measurement chromatographic system verification, development of QC procedures and measurement quality objectives; and validation

of the data prior to AIRS AQS data base entry. Although the data validation process is embodied in the last of these aspects, all are of critical importance to the overall process. Prior to the development of systematic data validation procedures, pre-measurement system validation and QA/QC measurements for establishing the DQOs must be completed. QA/QC procedures pertain to the techniques applied prior to obtaining data, such as calibration checks, system blanks and external audits. Guidance for pre-measurement validation and QA/QC is given in Sections 2.3.7 and 2.8. This process is necessary to set the stage for ensuring the overall quality of the monitoring network data.

2.7.1 Data Validation Approach

This guidance provides procedures for implementing a systematic data validation process for those responsible for validating PAMS VOC data. Data validation in the context of this guidance refers to the procedures performed after the data are collected. Pre-measurement chromatographic system verification, QA/QC procedures and measurement quality objectives are established prior to collection of the data to minimize the amount of faulty data generated.

Data validation is performed as a last step before the data are submitted to AIRS and is a screening process to prevent additional unacceptable or questionable data from being submitted to AIRS. Timely data validation is required to more easily resolve data issues and unusual events and take the necessary corrective actions to minimize the generation of additional faulty data.

This data validation approach has been selected with respect to the PAMS DQOs and data use; volume and type of data generated; anticipated computational and graphical capabilities of the state and local agencies; and nature of the expected errors. Four categories have previously been identified[51] for validating air monitoring data:

- Routine checks made during the initial processing and generation of the data, including proper data result file identification, review of unusual events, review of

chromatography result reports, performance checks of the data processing system, and deterministic relationships.

- Tests for internal consistency to identify values in the data set which appear atypical when compared to values of the whole data set.
- Comparing the current data set with historical data to verify consistency over time.
- Tests for parallel consistency with data sets from the same population (region, period of time, air mass, etc.) to identify systematic bias.

The data validation guidance presented here for VOC encompasses mainly routine checks, tests for internal consistency, and historical data comparisons. Additional checks for parallel consistency, which incorporate statistical evaluations, may be considered for data validation and are only briefly discussed in this document. A flow chart of data validation activities is given in Figure 2-21.

2.7.1.1 Routine Procedures

Routine validation checks during the processing of the data include verification of proper data file identification information, chromatography result report file review, identification of unusual events, deterministic relationship checks, and performance checks of the automated data processing systems. These routine checks should be done frequently (i.e., daily or weekly) to parcel the data into manageable segments. The checks must be timely in order to address issues before the amount of faulty or unusable data generated becomes too large, thereby significantly affecting the data completeness.

Computerized data acquisition systems are used to collect the chromatographic information from the analog output of the GC systems as discussed in Section 2.6. The resulting chromatographic data files must be clearly and correctly identified, including the correct acquisition time and date, sampling location, sample name or type, processing and calibration methods, and file naming conventions. Examples of errors that may occur include: incorrect sampling locations, especially if methods are copied from one site location to another; incorrect date and time stamp due to daylight

savings time change; or a sample name that indicates a normal sample when in fact a calibration or blank check sample has been analyzed. Since these errors are mostly due to human error, an individual other than the person originally generating the data should review the information.

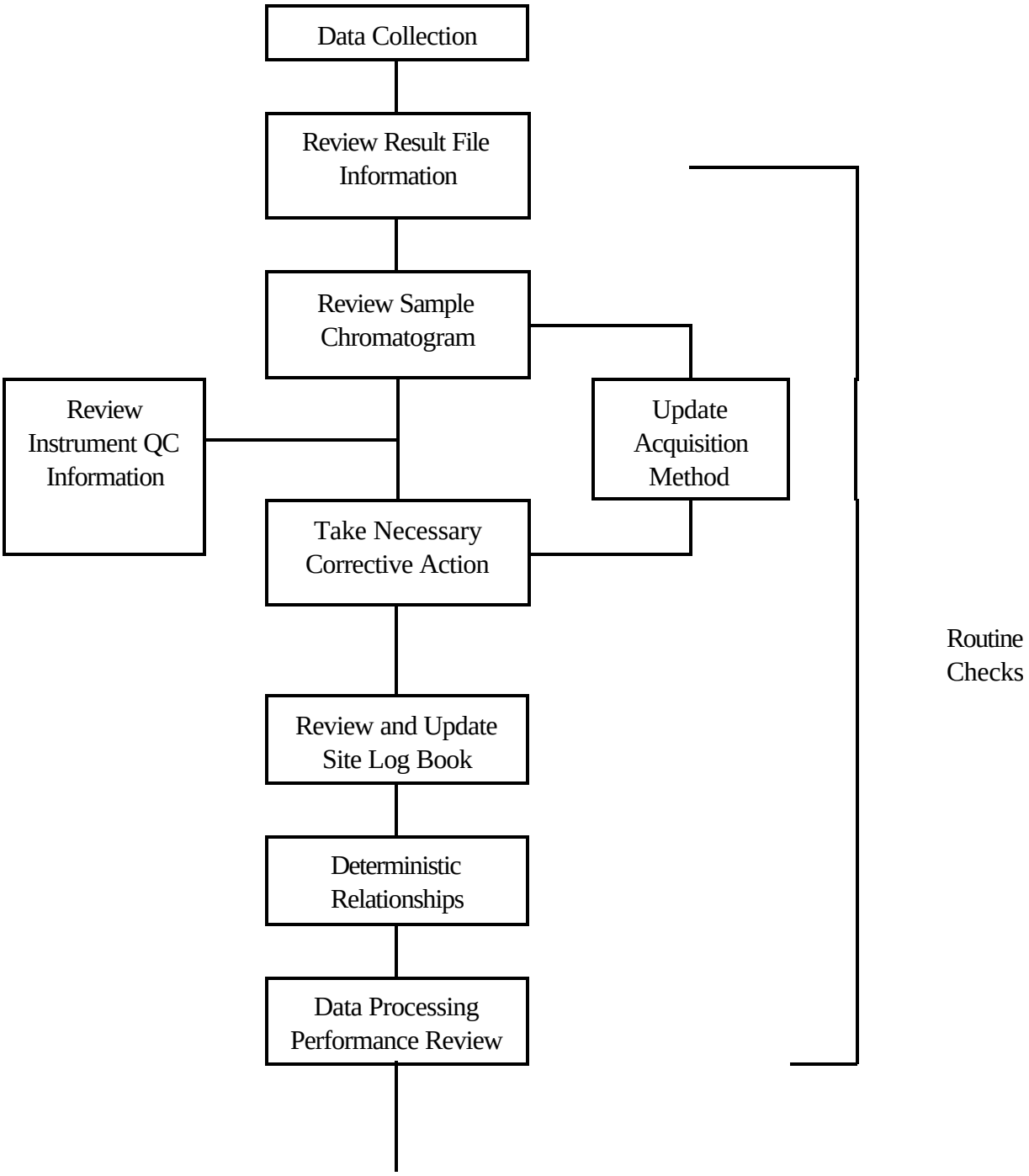

Figure 2-21. Flow of Data Validation Activities

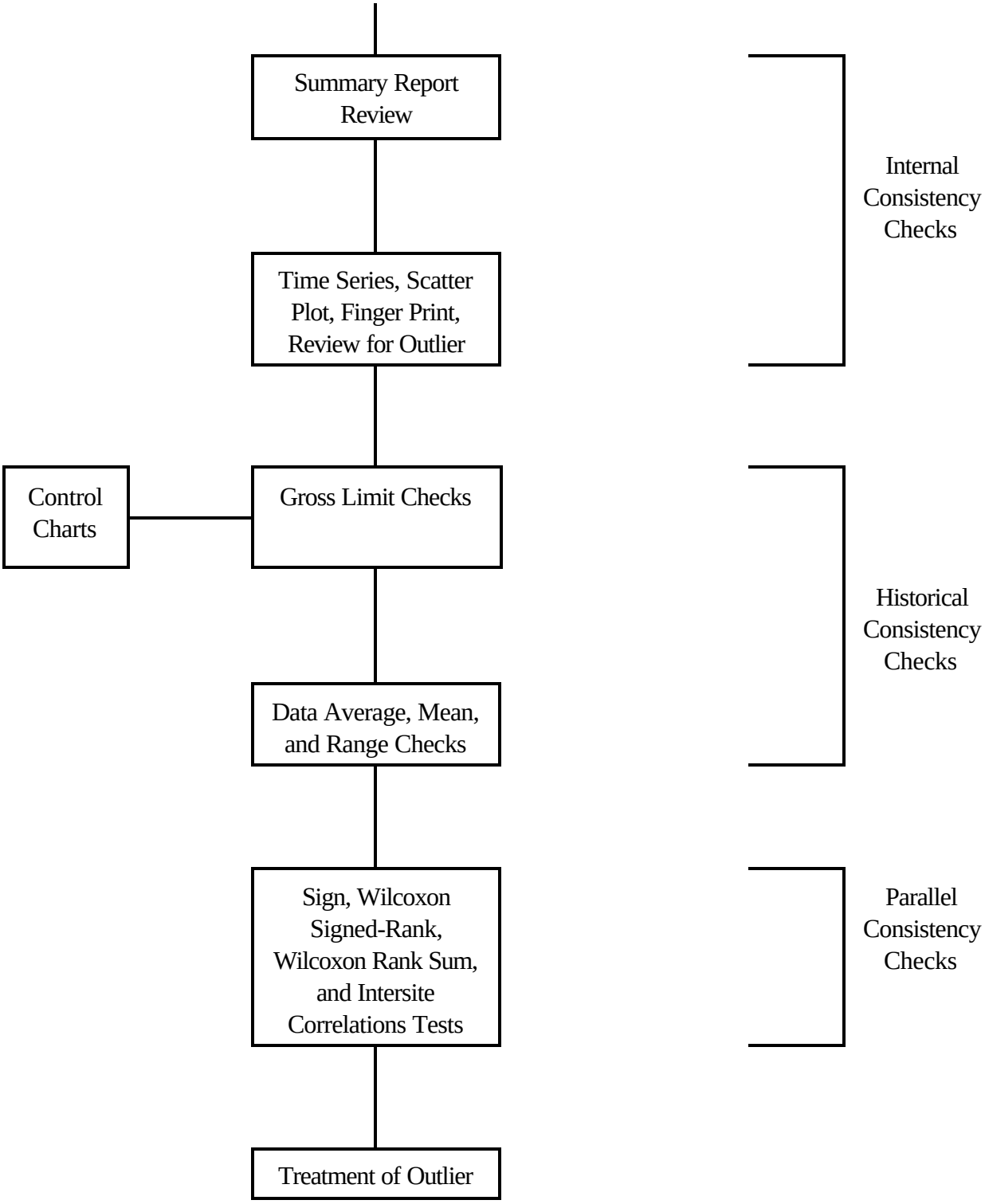

Figure 2-21. Continued

Due to the large volume of data generated from PAMS monitoring, close scrutiny of all chromatograms and result reports is not practical. For example, a system making continuous, hourly measurements of 56 target compounds can produce over 1,300 measurements per day. However, all chromatograms should go through a cursory review by the station operator to determine if the quality of the chromatography (i.e., appearance of the chromatogram, the peak shape, peak resolution, peak integration, retention times, and baseline) is acceptable. This level of review can be done quickly by an experienced chromatographer and will also determine if the chromatographic system is performing properly. Comparison of the chromatogram to reference or historical information, such as calibration and typical sample chromatograms, can simplify this process. Chromatograms are also reviewed to determine if there are any gross errors present and whether chromatographic abnormalities, such as electronic spikes, contamination, or levels of target analytes above the electrometer or calibration ranges, exist. If the chromatography is acceptable, the chromatogram can then be further processed by the data reduction and/or peak identification software as chosen by the user.

The cursory review of chromatograms may include the following determinations:

- The signal from the FID or baseline is normal and the signal output is positive (on-scale);
- Chromatographic peaks are present, integrated correctly, and the peak-shape is sharp;
- The peak resolution or separation is acceptable based on historical instrument performance;
- All components have been eluted from the analytical column as indicated by a flat or normal baseline at the end of a run; and
- No chromatographic abnormalities exist, such as large contamination or non-target co-eluting compounds, and electronic spikes.

The result reports must also go through a more in depth review, in conjunction with the chromatogram, to ensure that the key reference or internal standard compounds are identified correctly

and the resulting target peak retention times have not shifted. The results reports generated by the automated GC system are subsequently reviewed and compared to calibration or standard analyses information from the pre-measurement system verification discussed in Section 2.3.7. This review is used to ensure that correct peak assignments or identifications are made and that the resulting concentrations are correct. The information is also reviewed to determine whether the information used to make the peak identifications (i.e., retention times, relative retention times, retention indices, etc.) requires updating. The need for updating peak identification information in the acquisition method is indicated by the frequency of missed or inaccurate peak identifications automatically made by the GC system. Typically, a minimum of 10% of the data are processed through this level of review. The minimum percentage of the chromatograms generated daily are selected by the station operator for review. Chromatograms generated at the beginning and the end of an analysis day to bracket sample analyses are selected. It can then be presumed that the data generated between bracketed result files and chromatograms are acceptable and also accurate.

Routine review of the analytical instrument calibration is imperative for the ultimate quality and usefulness of the data generated. As a QC function, the station operator must review this calibration information on a regular basis to ensure that quality objectives are met and the system is operating properly during the measurement process. If the GC system calibration has gone awry and QC sample results do not agree with the specified quality objectives, the data should be appropriately qualified to indicate any impact on the analytical results. If "real-time" (same day) calibration review is implemented, quality issues can be identified and corrective actions, such as repeat analyses and instrument maintenance, can be performed prior to continuing data collection. If post analysis calibration information review is performed, the previously generated sample data should be flagged to clearly qualify any uncertainty in the results.

An on-site logbook should be maintained to record information relative to instrument repair and maintenance (replacing the cold trap) and unusual events (mowing the lawn, power outages, or repairing the sampling shelter roof) that could explain variations or excursions in the data. This

information could be critical in the explanation of missing data files, high sample concentrations, or used to reject outliers.

Deterministic relationships where two or more related parameters can be routinely checked ensure that measured values of an individual parameter do not exceed that of an aggregate parameter. The aggregate parameter must include the individual parameter. Also, relationships or ratios between two source-related compounds can be compared in order to identify errors. For example, if the total unidentified VOCs measured are greater than an established empirical percentage of the total NMOC measurement at that site, a large number of target peaks were misidentified. A total unidentified VOC value that comprises more than 30% of the total NMOC may indicate that retention times have shifted and target peak identifications are incorrect. The concentration of benzene can be compared to acetylene or toluene (all present in automobile exhaust) by developing scatter plots or calculating the ratios and comparing this information to empirical relationships determined at a specific site. The example in Figure 2-22[52] shows a scatter plot of benzene and toluene that incorrectly includes calibration information in the data set, as demonstrated by the data points around the concentration of 30 ppbC at the top part of the graph. Most of the ambient air data points in this scatter plot fall below 8 ppbC for benzene. Again, these relationships are site specific and empirical relationships must be established.

Performance checks of the automated data processing system and supplemental procedures developed to handle the data, including telemetry, should be implemented. All agencies should develop data flow diagrams to indicate the steps taken to process the data following collection, including data formatting, transmission, and processing or formatting for AIRS. The data are reviewed for inconsistencies, missing data files, or nonsensical information. Any computerized programs put in place to manipulate data should be validated at a minimum using methods for checking errors such as developing a standard set of test output parameters, processing the test data set, and comparing the results to the reference. Information regarding complex procedures required for testing and validating computer systems can also be obtained from NIST.

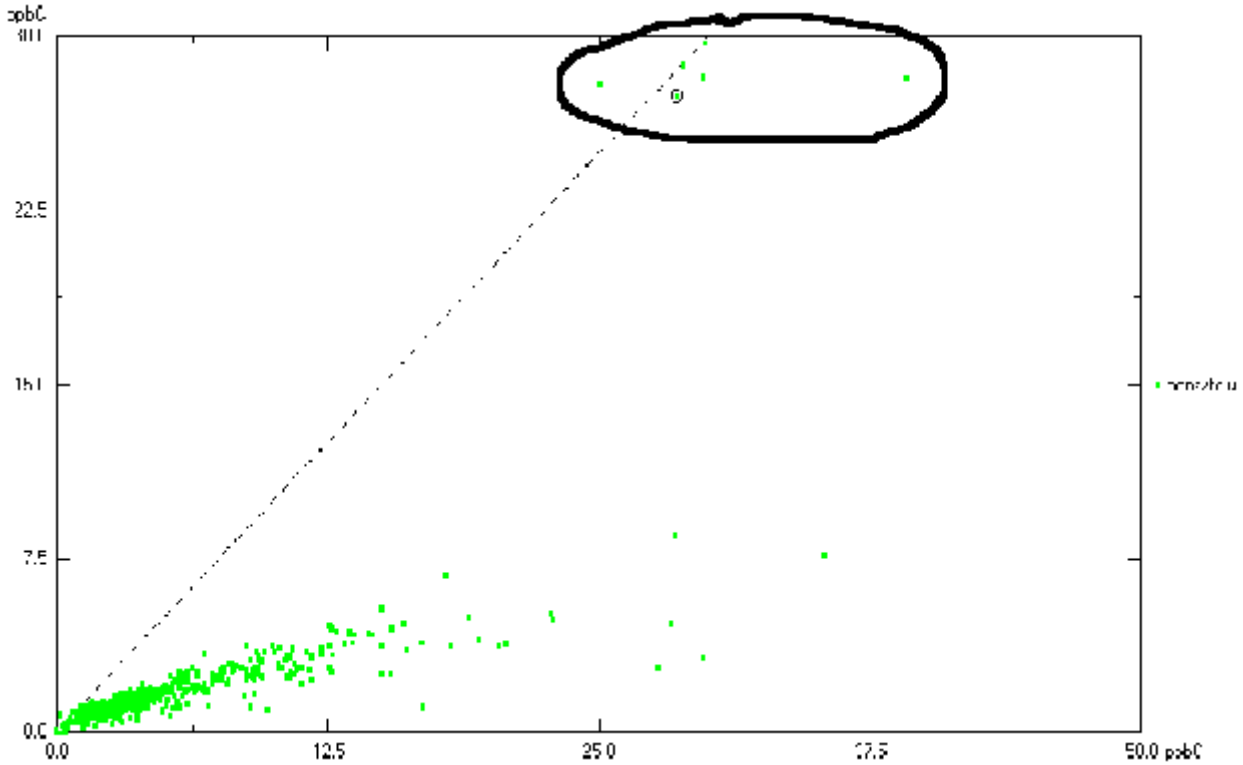

Figure 2-22. Appearance of Calibration Data at East Hartford, CT, in June 1995. Example scatter plot showing calibration data of about 30 ppbC. Data are level 0, preliminary data, CT DEP.

Main, H.H., P.T. Roberts, and M.E. Korc. Analysis of PAMS and NARSTO-Northeast Data - Supporting Evaluation and Design of Ozone Control Strategies: A Workshop. Report and presentation prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC. Presented at U.S. Environmental Protection Agency, Research Triangle Park, NC. STI-94551/94581-1551-WD1, EPA WA-5-95 and WA-8-95, December 1995.

Any software or calculation spreadsheet programs (Excel® or QuattroPro®) implemented by the user must also be verified for accuracy. Errors in spreadsheets can occur during spreadsheet or program development in the continued course of the program. Implementing a verification check of the calculations in these spreadsheets and programs can help to avoid errors in the data generated. Verification checks are accomplished by using the spreadsheet or program to calculate results for a previously known data set. A more complete test of the user developed program would include testing at the minimum and maximum expected input values. If the expected result is not obtained the program may be in error and the appropriate corrective action should be taken.

2.7.1.2 Tests for Internal Consistency

Data review for internal consistency identifies values in the data set which appear atypical when compared to values of the whole data set. Tests for internal consistency include the identification of outliers and extreme differences in adjacent values that require further investigation. A number of statistical tests can be used for internal consistency checks and determining outliers. Graphical and visual presentation of the data, such as review of summary report file information, scatter plots, time-series, or fingerprints can also be used for consistency checks.

Manual data review for internal consistency is impractical for the volume of continuous gas chromatographic data generated by PAMS. The user should consider implementing a commercially available peak processing or identification software package as an alternative to manual review. Software packages, such as MetaChrom™ (Meta Four Software, Inc.) and VOCDat (developed by Sonoma Technology, Inc., under sponsorship by EPRI[53]) have been designed to review large and complex data sets for consistency.

Summary report file information, scatter plots, time-series, fingerprints, and control charts can be generated using the Perkin-Elmer Turbochrom® Summary Report option, spreadsheet software (Excel®, QuattroPro®, or Lotus®), or the VOCDat software developed for NARSTO-NE by Sonoma

Technology, Inc. VOCDat provides a useful graphical interface for generating time-series plots, fingerprint plots, and control charts for VOC data generated by Perkin-Elmer Turbochrom® data systems.

Qualitative comparison review for internal consistency may by done by generating a data base or summary report file or "flat-file" of the concentration and peak identification results generated over time. A typical summary file can contain a large number of measurements for the target PAMS compounds: a system making continuous, hourly measurements of 56 target compounds can produce over 1,300 measurements per day. The summary files can be reduced into manageable segments for visual review. This information can assist the user in identifying system problems, target compound misidentifications, system contamination, outliers, or missed information. Qualitative comparison review of the final concentration results and peak identifications is valuable in checking for outliers or inconsistencies in peak identification, retention times, calculations, and results. The information can also be globally reviewed for clear changes in trends.

For example, the Peak Summary Option of the Perkin-Elmer Turbochrom® software can easily be used to summarize the concentration and retention time results as shown in Figure 2-23. This file can be generated weekly and the information reviewed to identify abrupt changes in concentration or retention time, and the presence of ubiquitous compounds measured at the site. A criterion for retention time shifts may also be established based on the percent relative standard deviation (%RSD) information obtained for the site to pinpoint misidentification of target peaks.

When data are reviewed for internal consistency, dealing with values that fall below the established detection limits for the system is at the discretion of the reviewer. For example, concentration values below the detection limit may not be subject to data validation due to the inherent uncertainty of these data. An action limit of 3 times the detection limit or a concentration value (i.e., 5 ppbC) may be used.

*********SUMMARY REPORT**********

		ETHANE			ETHYLENE			PROPANE			HEXANE		
File	Time of	Ret.	Area	Conc.	Ret.	Area	Conc.	Ret.	Area	Conc.	Ret.	Area	Conc.
b152001	01:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.26	4336	2.50
b152002	02:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.25	4873	2.81
b152003	03:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.27	4789	2.76
b152004	04:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.26	5232	3.02
b152005	05:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.26	5977	3.45
b152006	06:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.26	6774	3.91
b152007	07:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.25	9423	5.44
b152008	08:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.25	13032	7.52
b152009	09:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.27	6930	4.00
b152010	10:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.27	2423	1.40
b152011	11:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.28	2655	1.53
b152012	12:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.28	2440	1.41
b152013	01:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.27	930	0.54
b152014	02:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	1429	624	0.36
b152015	03:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.28	620	0.36
b152016	04:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.28	535	0.31
b152017	05:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.27	991	0.57
b152018	06:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.28	994	0.57
b152019	07:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.28	2154	1.24
b152020	08:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.29	1736	1.00
b152021	09:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.29	1174	0.68
b152022	10:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.31	970	0.56
b152023	11:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.30	844	0.49
b152024	12:42	----------	----------	----------	----------	----------	----------	----------	----------	----------	14.30	906	0.52
p152001	01:42	8.37	12417	7.25	9.22	11100	6.48	11.60	18984	11.08	----------	----------	----------
p152002	02:42	8.37	13944	8.14	9.22	11113	6.48	11.60	23687	13.82	----------	----------	----------
p152003	03:42	8.37	14162	8.26	9.22	10356	6.04	11.60	22974	13.41	----------	----------	----------
p152004	04:42	8.37	15815	9.23	9.22	12174	7.10	11.60	26559	15.50	----------	----------	----------
p152005	05:42	8.38	17284	10.09	9.22	13219	7.71	11.60	28519	16.64	----------	----------	----------
p152006	06:	8.38	21046	12.28	9.22	17568	10.25	11.60	32186	18.78	----------	----------	----------
p152007	07:42	8.37	25884	15.10	9.23	20883	12.19	11.60	40227	23.47	----------	----------	----------
p152008	08:42	8.37	42656	24.89	9.22	28060	16.37	11.59	65558	38.25	----------	----------	----------
p152009	09:42	8.38	23186	13.53	9.25	14600	8.52	11.61	32459	18.94	----------	----------	----------

Figure 2-23. Example PE Turbochrom® Summary Report

*********SUMMARY REPORT (Continued)**********

		ETHANE			ETHYLENE			PROPANE			HEXANE		
File	Time of	Ret.	Area	Conc.	Ret.	Area	Conc.	Ret.	Area	Conc.	Ret.	Area	Conc.
p152010	10:42	8.38	11453	6.68	9.26	6846	3.99	11.61	15163	8.85	----------	----------	----------
p152011	11:42	8.38	10410	6.07	9.24	5129	2.99	11.62	12338	7.20	----------	----------	----------
p152012	12:42	8.38	12713	7.42	9.24	4591	2.68	11.60	23293	13.59	----------	----------	----------
p152013	01:42	8.39	7639	4.46	9.25	1636	0.95	11.60	8271	4.83	----------	----------	----------
p152014	02:42	8.38	5728	3.34	9.26	796	0.46	11.60	3063	1.79	----------	----------	----------
p152015	03:42	8.39	5820	3.40	9.24	1269	0.74	11.61	3161	1.84	----------	----------	----------
p152016	04:42	8.38	5877	3.43	9.24	1417	0.83	11.61	3919	2.29	----------	----------	----------
p152017	05:42	8.38	5551	3.24	9.24	1417	0.83	11.61	7688	4.49	----------	----------	----------
p152018	06:42	8.38	5811	3.39	9.21	1242	0.72	11.60	4021	2.35	----------	----------	----------
p152019	07:42	8.38	6652	3.88	9.22	4785	2.79	11.59	5855	3.42	----------	----------	----------
p152020	08:42	8.39	7521	4.39	9.26	3769	2.20	11.62	5476	3.20	----------	----------	----------
p152021	09:42	8.39	8675	5.06	9.23	1806	1.05	11.61	4968	2.90	----------	----------	----------
p152022	10:42	8.38	9052	5.28	9.23	2324	1.36	11.60	4917	2.87	----------	----------	----------
p152023	11:42	8.38	8392	4.90	9.24	2735	1.60	11.61	7198	4.20	----------	----------	----------
b152024	12:42	8.37	8699	5.08	9.23	2950	1.72	11.60	6452	3.76	----------	----------	----------
Avgs		8.38	12766	7.45	9.23	7574	4.42	11.60	16956	9.89	14.28	3390	1.96
%RSD		0.08	67	67.07	0.14	96	95.83	0.06	90	90.23	0.11	95	95.20

Figure 2-23. Continued

The Turbochrom® Peak Summary Report may also be generated as an ASCII file for import into Excel® or other spreadsheet software. The ASCII summary data base file can be loaded or imported directly into spreadsheet software for further data processing or manipulation. Once the data base file is loaded into the spreadsheet software, graphical representations of the continuous measurements can easily be generated. Generation of diurnal graphs of hourly site measurement information can be very useful in clearly identifying trends and determining if the potential for outliers exists in the data base.

The VOCDat software[53] can generate graphical presentations of the data in the form of time series plots, scatter plots, and fingerprint plots for internal consistency determinations. Time series plots as shown in Figure 2-24[53] can be used to inspect each target compound, groups of target compounds, and total NMOC. This information allows the identification of outliers, increased single-hour concentrations, possible missed peak identifications, and extended periods of unusually high or low concentrations. Experienced PAMS personnel frequently look for unusual "jumps" in the time series plot between successive hourly data or departures from expected diurnal or seasonal patterns. Figure 2-24[53] shows two items that warrant further investigation: first, the unusually high concentration of 62 ppbC for propane compared to the other data points for the period which are all below 20 ppbC; and second, missing data for two periods (8/24 and 8/28). Review of the site log would be important in this case to determine if downtime occurred or instrument maintenance was performed.

The time series plot in Figure 2-25[54] shows an example of misidentification of a paraffin for an unidentified VOC, indicated on the plot by the abrupt decrease in paraffin concentration with concurrent increase in the unidentified VOC concentration. The time series plot in Figure 2-26[54] shows system contamination of the selected components that decreased in concentration, or were cleared out of the system over a period of five days.

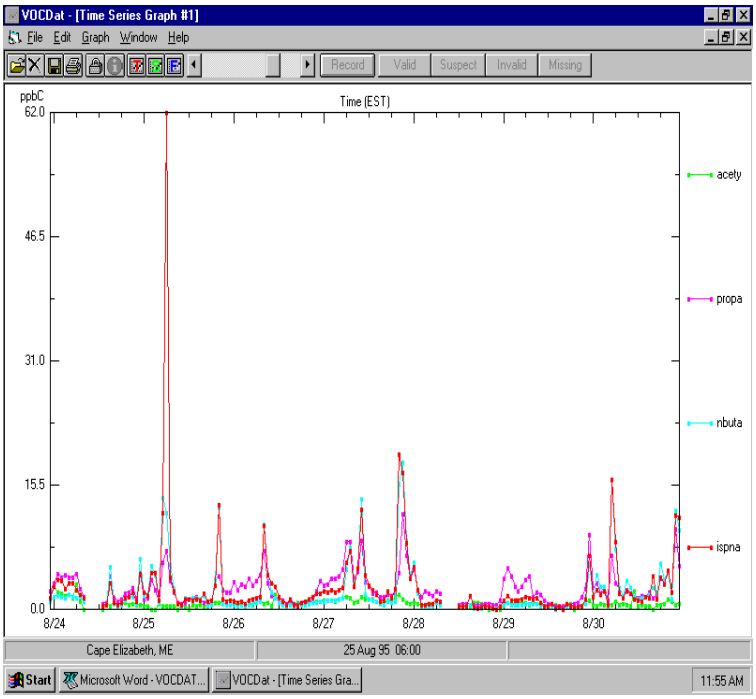

Figure 2-24. Time Series Plot

Main, H.H., P.T. Roberts, J.D. Prouty, and M.E. Korc. *Software for Display, Quality Control, and Analysis of Cont VOC Data.* Report prepared for Electric Power Research Institute, Palo Alto, CA by Sonoma Technology, Inc., S Rosa, CA. STI-996142-1594, EPRI Research Project No. WO9108-01, June 1996.

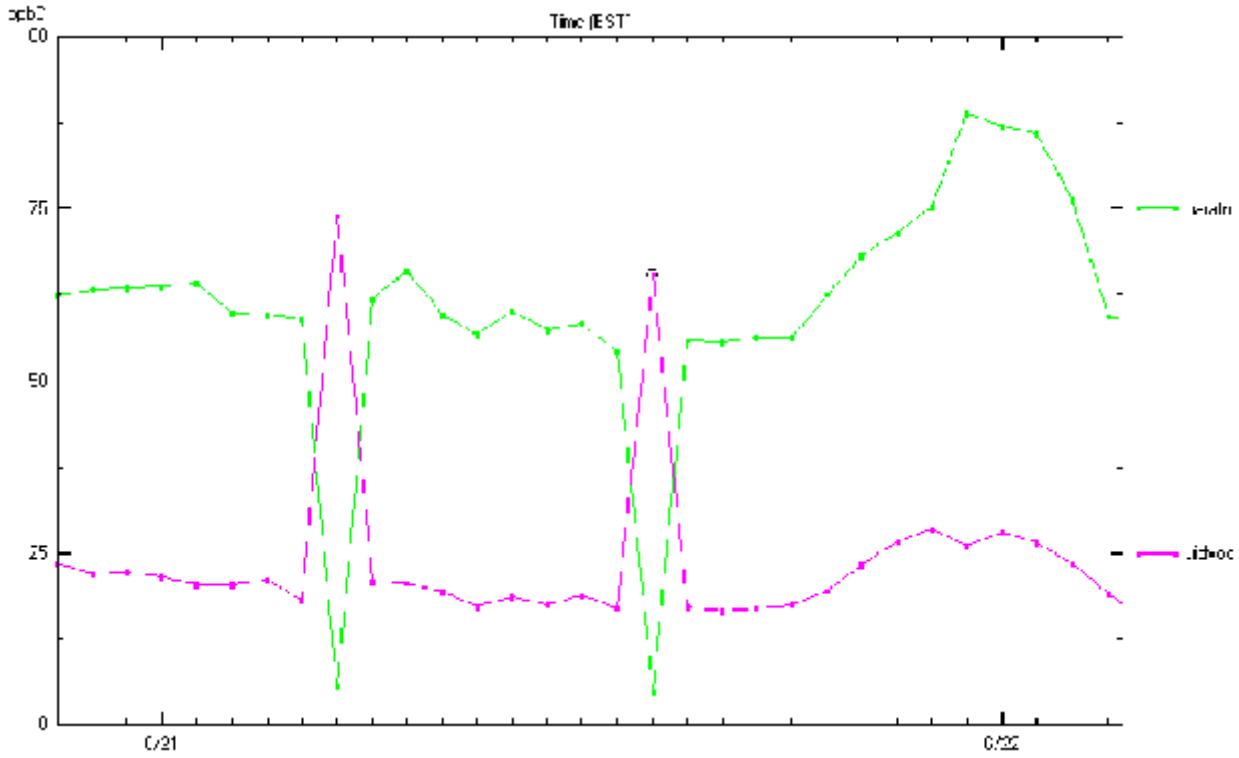

Figure 2-25. Time Series Plot of Several Species Groups at Stafford, CT, in 1994. Example of misidentification of a paraffin for an unidentified peak.

Main, H.H., P.T. Roberts, and L.R. Chinkin. PAMS Data Analysis Workshop: Illustrating the Use of PAMS Data to Ozone Control Programs. Report and presentation prepared for U.S. Environmental Protection Agency, Resea Triangle Park, NC. Presented at *California Air Resources Board and EPA Region IX,* Sacramento, CA. STI-9971 WD7. May 1997.

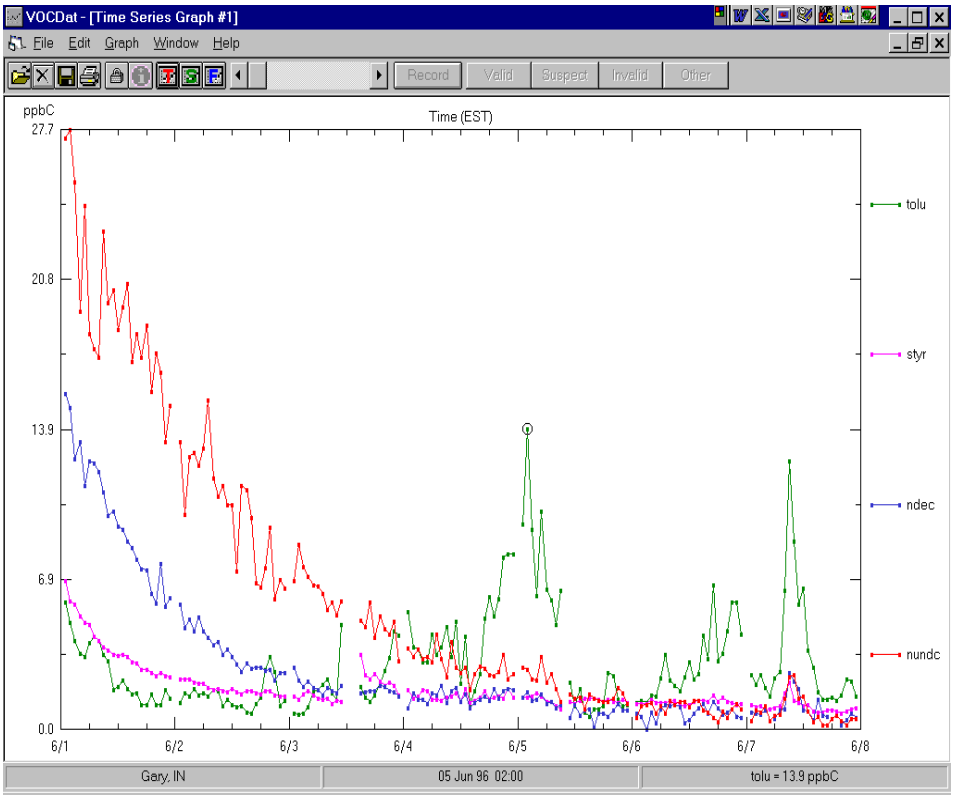

Figure 2-26. Time Series Example of System Contamination

Main, H.H., Roberts, P.T., and Chinkin, L.R. PAMS Data Analysis Workshop: Illustrating the Use of PAMS Data f Ozone Control Programs. Report and presentation prepared for U.S. Environmental Protection Agency, Resea Triangle Park, NC. Presented at *California Air Resources Board and EPA Region IX,* Sacramento, CA. STI-9971(WD7. May 1997.

A scatter plot (shown in Figure 2-27[54]) can be used to compare pairs of target compounds or target groups to identify outliers and excursions in the data such as the improper inclusion of calibration data in the data set (discussed previously). The figure shows a comparison of 2-methylheptane to toluene. The relationships between two species show a "cone" of data rather than the two distinct lines observed in the figure. In this example, the toluene peak was misidentified as 2-methylheptane over a period of several days.

A fingerprint plot shown in Figure 2-28[52] allows further inspection of samples previously flagged for more detailed review. The fingerprint plot shows the compound concentration for each compound for a single hour. The fingerprints can quickly be scanned, hour-by-hour to allow the observation of diurnal changes and inspection of hours surrounding suspect data to identify additional effects. The time series plot in Figure 2-29[52] clearly illustrates calibration data mistakenly included in the data set. In this case, the calibration gas contained about 25 ppbC of the PAMS target compounds.

Whatever methodology is used, the qualitative comparison review of summarized measurement data can be a useful tool in verifying the internal consistency and overall accuracy of the data generated from automated GC systems.

2.7.1.3 Historical Data Comparisons

Testing or comparing data for historical consistency uses many of the graphical techniques discussed in Section 2.7.1.2 to compare the data set with previous data compiled from the monitoring location. Pattern and successive value tests, parameter relationship tests, and control charts may also be used.[51] Gross limit checks are used to detect data that are unlikely and considered impossible. Upper and lower limits are established based on historical data from the site. These limits are specific to the monitoring site and should consider parameters and instrument characteristics. Values representing pollutant behavior outside the specified limits are flagged for further investigation. Limits

on the individual concentration, difference in adjacent concentration or retention time values, difference or percent difference between both adjacent

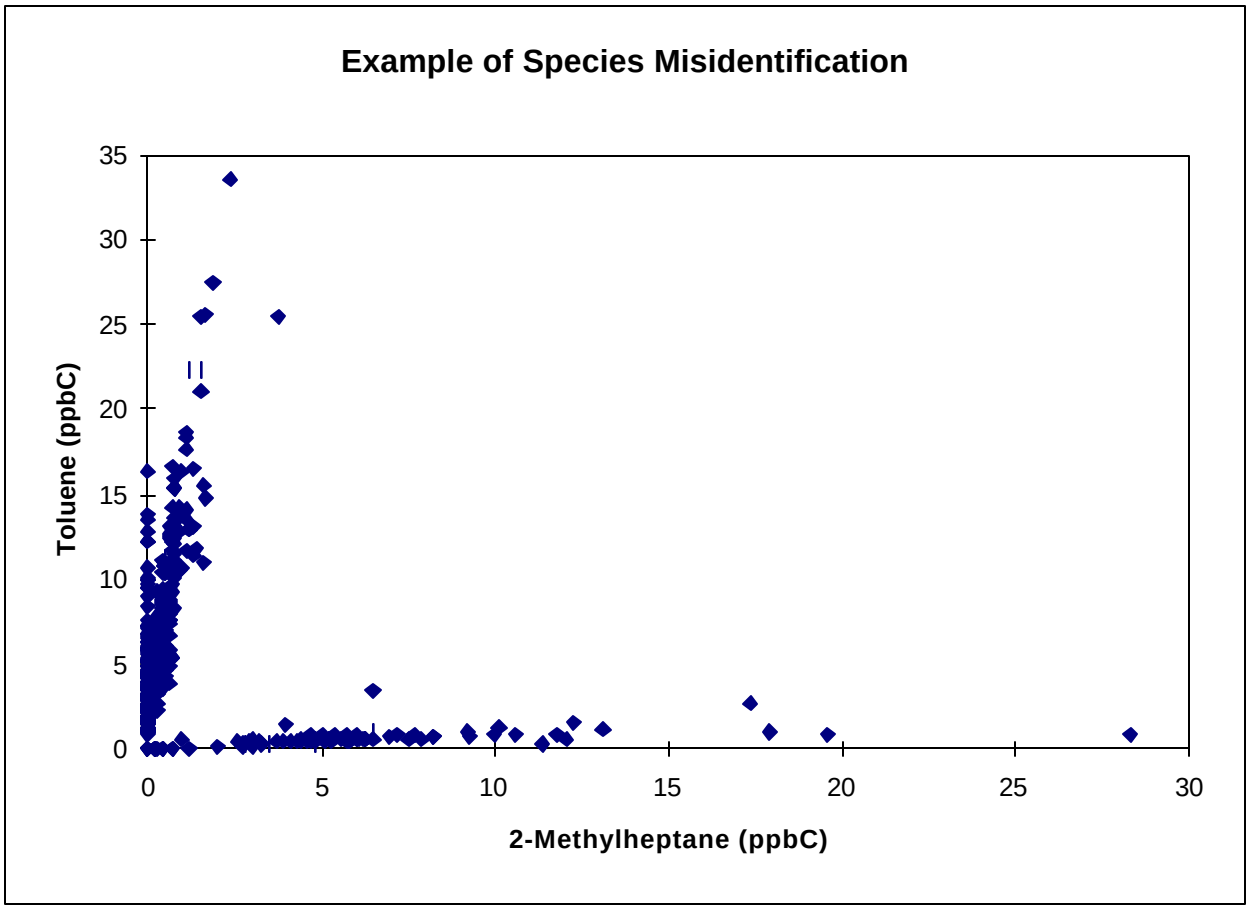

Figure 2-27. Example of Misidentification Using a Scatter Plot. Typically, data points would be present in the region of the plot between the two extreme edges.

Main, H.H., Roberts, P.T., and Chinkin, L.R. PAMS Data Analysis Workshop: Illustrating the Use of PAMS Data to Support Ozone Control Programs. Report and presentation prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC. Presented at *California Air Resources Board and EPA Region IX,* Sacramento, CA. STI-997100-1719-WD7. May 1997.

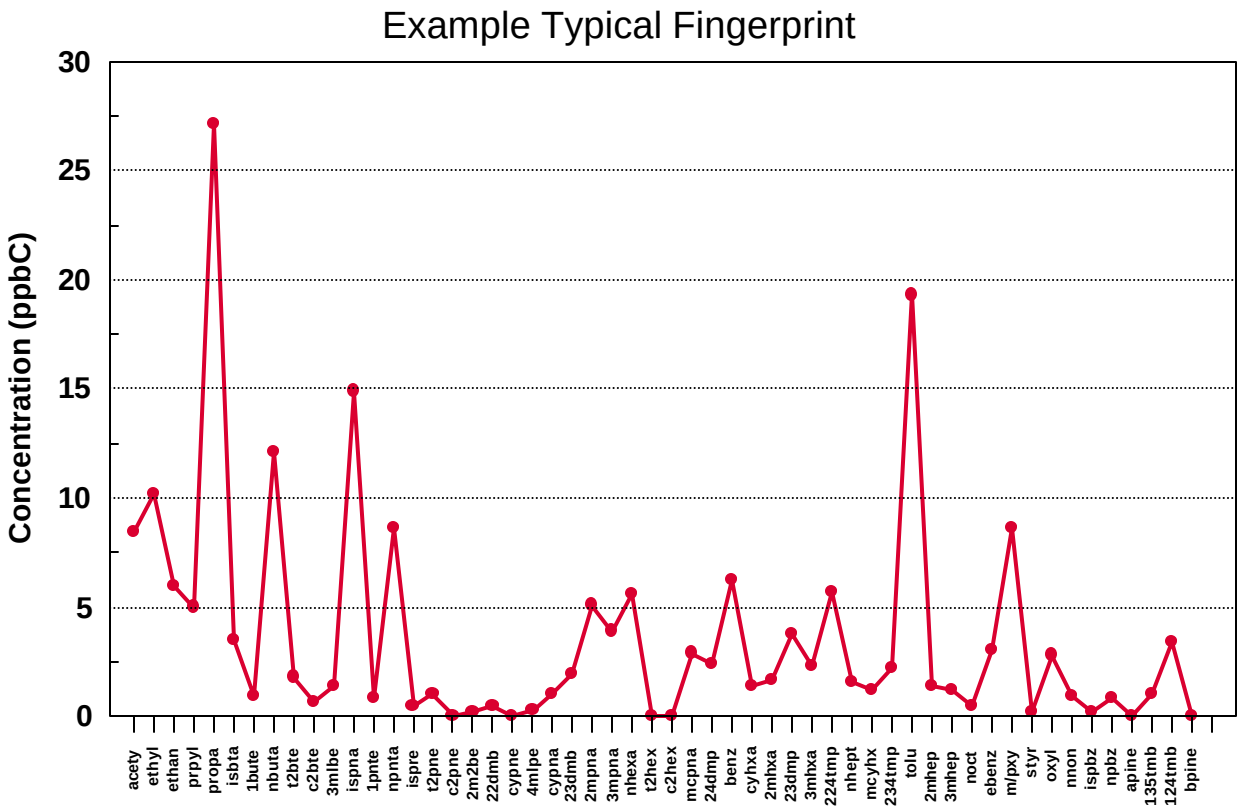

Figure 2-28. Example of a Typical "Fingerprint" Observed at a PAMS Site

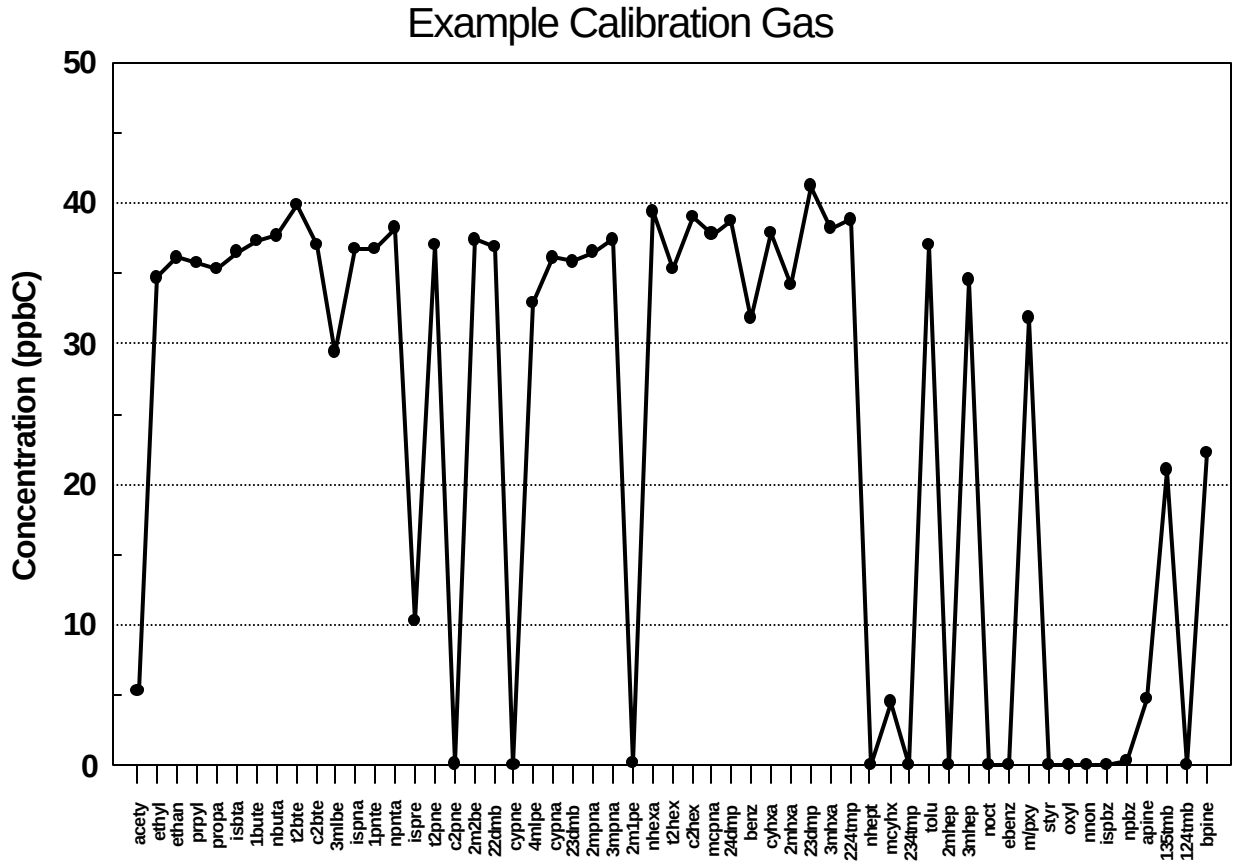

Figure 2-29. Example of Calibration Gas "Fingerprint" Observed in Data Submitted to AIRS

Main, H.H., P.T. Roberts, and M.E. Korc. Analysis of PAMS and NARSTO-Northeast Data - Supporting Evaluation and Design of Ozone Control Strategies: A Workshop. Report and presentation prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC. Presented at U.S. Environmental Protection Agency, Research Triangle Park, NC. STI-94551/94581-1551-WD1, EPA WA-5-95 and WA-8-95, December 1995.

values, and the average of four consecutive values are comparisons that may be considered. Supplemental statistical tests can be used to identify data sets which have mean or range values that are inconsistent with previous data sets.

2.7.1.4 Parallel Consistency Checks to Identify Systematic Bias

Tests to check for consistency with parallel data sets from the same population (region, period of time, air mass, etc.) are used to identify systematic bias. Systematic bias is determined by checking for the difference in average value or overall distribution values. The sign test, Wilcoxon signed-rank test, Wilcoxon rank sum test, and intersite correlation test are recommended for testing two parallel data sets.[49] The first three tests are nonparametric and consequently can be used for nonnormal data sets which frequently occur in air quality data.

2.7.2 Treatment of Outliers

Outliers may result from errors in the processing of a data set, instrument problems, and calibration errors. Once an outlier has been identified using any of the approaches identified above, treatment of the outlier must be decided. The outlier should not be arbitrarily dropped from the data set. Outliers that are found to be errors should be corrected, if possible. If the correct value cannot be obtained, the value may be appropriately flagged and excluded from the data set. Alternatively, if the suspect data are retained in the data set the necessary qualifying information in the form of a "flag" must be included with the value. There should be an explanation that warrants the exclusion or replacement of data along with documentation reflecting the action taken. If no explanation is available, the outlier should not be excluded.

The data point may be real. Data should only be excluded by the reporting agency when the values are verified as not representative of ambient data, such as calibration runs, instrument malfunction,

contamination, etc. Verification should include site or operator log book, laboratory notes, etc. Later data analysts may then choose to use the outlier or not, depending upon their analyses.

2.8 Quality Control and Quality Assurance for VOC Measurements

Data submitted to AIRS by all agencies will ultimately be used by the agencies to develop, evaluate, and refine new O_3 control strategies; determine NAAQS attainment or non-attainment for O_3; track VOCs and NO_x emissions inventory reductions; provide photochemical prediction model input; evaluate photochemical prediction model performance; analyze ambient air quality trends; and characterize population exposure to VOCs and O_3. Data from VOC measurement systems must be submitted to the Aerometric Information Retrieval System (AIRS) within six months following the end of each quarterly reporting period, and the data must be consistent with enhanced O_3 monitoring regulations and of sufficient quality to meet Clean Air Act Title I objectives.

The quality of the data submitted to the AIRS data base must be consistent across all agencies. Because a significant investment of time and assets is expended to generate measurement data, a quality control/quality assurance (QC/QA) program should be developed to ensure that the data collection is consistent and that data quality objectives (DQOs) for the measurement program are met. The quality program for VOC measurements, similar to programs for other air monitoring efforts, incorporates quality control and quality assurance. These two systems work together to achieve the goal of continuing quality in measurement efforts.

Quality assurance and quality control have been defined and interpreted in different ways. Some sources differentiate between the two terms by stating that quality control is "the operational techniques and the activities which sustain a quality of product or service (in this case, good quality data) that meets the needs; also the use of such techniques and activities," whereas quality assurance is "all those planned or systematic actions necessary to provide adequate confidence that a product or service will satisfy given needs."[55]

Quality control may also be considered "internal quality control;" mainly, routine checks included in normal internal procedures; for example, periodic calibrations and system blanks, duplicate checks, and split samples. Quality assurance may also be viewed as "external quality control," those activities that are performed on a more occasional basis, usually by a person outside of the normal routine operations; for example, on-site system surveys, independent performance audits, interlaboratory comparisons, and periodic evaluation of internal quality control data.[56]

EPA's Quality Assurance Handbook[56] uses the term quality assurance collectively to include both quality assurance and quality control. A description of the elements necessary for a PAMS QA program are found in 40 CFR Part 58, Appendix A "Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS)." Existing SIP stations are SLAMS; National Air Monitoring Stations (NAMS) and PAMS are considered a subset of SLAMS. Appendix A specifies the minimum QA requirements applicable to SLAMS air monitoring data submitted to EPA. States are encouraged to develop and maintain QA programs more extensive than the required minimum. The references found at the end of this document are also found in the 40 CFR Part 58, Appendix A for reference purposes in preparing quality assurance program documents.

This section is divided into three parts: DQOs, QC, and QA. Section 2.8.1 discusses the development of data quality objectives. Section 2.8.2 deals with the systematic activities of a QC program and Section 2.8.3 presents those assessment activities that are part of a QA system. The QC/QA procedures discussed in the following sections are the minimum and must be tailored and expanded for each PAMS monitoring network as appropriate. A clearly written QC/QA plan and associated SOPs must be developed for each network.

2.8.1 Data Quality Objectives

Data quality objectives are defined in the PAMS Implementation Manual[25] as "statements that relate the quality of environmental measurements to the level of uncertainty that decision-makers

are willing to accept for results derived from the data." The development of DQOs starts with the monitoring program objectives and goals. In order to develop DQOs for each program objective, it is first necessary to narrow each program objective to one or more specific monitoring or data objectives.

Specific and often different program objectives are associated with each specific PAMS network. The overall network should supply information sufficient to develop, evaluate, and refine new O_3 control strategies; determine NAAQS attainment or non-attainment for O_3; track VOCs and NO_x emissions inventory reductions; provide photochemical prediction model input; evaluate photochemical prediction model performance; analyze ambient air quality trends; and characterize population exposure to VOCs and O_3. The program objectives are discussed in detail in the PAMS Implementation Manual[25] and are classified into six general categories given below:

Category 1 Responsible and cost-effective control strategies;

Category 2 Photochemical modeling support;

Category 3 Reconciliation of emissions inventories;

Category 4 Ozone and precursor trends;

Category 5 Attainment and non-attainment decisions; and

Category 6 Population exposure analyses.

The DQOs must quantify the measurement variability in order for the risk in decision-making to be adequately assessed. This quantification of variability can only occur if there exists a base level of experience in use of the technologies and /or methods outlined for the program. In the case of PAMS, until its implementation in 1993 there had never been a program of this scope, with these goals and program objectives. Data compiled from the 1990 Atlanta Study[57] and other studies of this type provided the information for initial development of the PAMS DQOs.

It is important to note that all possible uses of the PAMS data are not known; therefore, every practical attempt should be made to improve data quality beyond that necessary to satisfy the

DQOs specified for PAMS. The DQOs are considered preliminary and are expected to be revised as improvements are made to the monitoring and statistical methods; as changes and/or additions are made in the program objectives or in the data use; and/or as results of the monitoring indicate a need. The PAMS DQOs are discussed in detail in the PAMS Implementation Manual[25] and highlighted below in relationship to each monitoring program objective category :

DQO 1.1 The data for any given pollutant measured at a PAMS site must be able to show the presence of a diurnal pattern, if a pattern exists, with an 80% confidence level.

DQO 1.2 The data for any given pollutant measured at a PAMS site must be able to show a change in the diurnal pattern, if a change exists, with an 80% confidence level.

DQO 2.1 The speciated VOC, ozone, NO_x and meteorological data must satisfy the regulations, including monitor siting, operation, and data quality criteria.

DQO 3.1 The monitoring data for total VOC concentrations collected at a Type 2 site must be able to demonstrate a 3% annual trend (upward or downward) over a 5-year monitoring period, if a trend exists, with an 80% confidence level.

DQO 3.2 The speciated VOC monitoring data collected at a Type 2 site, when composited into categories, must be able to demonstrate a 20% change (upward or downward) in the seasonal average between two consecutive years, if it exists, with an 80% confidence level.

DQO 3.3 The speciated VOC data collected at a Type 2 site must be able to detect ratios between key species that are indicative of specific sources. If the ratio between the emissions of two species is N:1, the compounds must be measured so that this ratio can be estimated to within ±50% with an 80% confidence level.

DQO 4.1 The composite monitoring data for a given MSA, CMSA for ozone, NO_x, and speciated VOC must be able to demonstrate a yearly downward trend with an 80% confidence level until an area achieves attainment.

DQO 5.1 The ozone (and NO_2 where appropriate) monitoring data must satisfy the criteria specified in the NAMS and SLAMS monitoring regulations, including monitor siting, operation, and data quality criteria.

DQO 6.1 The speciated VOC monitoring data must be able to provide annual average concentration data at Type 2 sites within ±50%, with a confidence level of 80%.

DQO 7.1 Meteorological data should be of sufficiently high quality that the relationship between ozone and wind speed, direction, and solar radiation can be determined. This level of quality can be shown if a functional relationship of ozone to meteorology explains a definite percentage of the ozone variation. Wind direction measurements must be of sufficient quality to develop a wind field for use in trajectory analysis.

The set of DQOs presented above assumes that the physical location of the site remains the same for the entire five-year period under consideration and that the area external to the site does not change in such a way that the appropriateness as a Type 2 site is impacted. Should either of these conditions occur, the DQOs must be modified to reflect the change in site conditions.

To meet the overall PAMS monitoring program DQOs above, specific quality objectives for VOC measurements are expressed in terms of sensitivity (detection limit), accuracy, precision, and completeness. The measurement quality objectives should not require more than the sampling and analytical procedures can provide, nor should they be based solely on the performance capability of the measurement system and methodology. The procedures used to assess the DQOs should be specified so that QC and QA procedures can be assembled to determine DQO attainment. If DQOs are not routinely met, a rapid resolution of the problem is required. Possible resolutions include redefinition of the DQO, repair/replacement of instrumentation, and/or modification of the methodology and procedures.

Detection limits reflect the smallest measured concentration of a compound that can be measured with a known degree of certainty and should be based on empirical data from the sampling and analytical system used for VOC measurements. The limit of detection is defined in the Federal Register[58] as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. Definitions for the detection limit should be related to the standard deviation of the measured values at or near zero concentration of the analyte.[59] Detection limit information should not be used to screen air measurement results. All results, even at

concentrations below the estimated detection limit, should be reported. More information is gained when a result is reported even if the data are somewhat imprecise.

Method detection limits (MDLs) for PAMS are estimated using 40 CFR, Part 136, Appendix B.[60] Replicate analyses are performed at least seven times at very low ppbC concentrations (within a factor of five times the estimated method detection limit). The standard deviation of the concentration for the replicate samples is related to the Student's t-value at the 99% confidence level with a standard deviation estimate having n-1 degrees of freedom. The detection limit is calculated by multiplying the standard deviation by the appropriate Student's t-value. (Appropriate values for six, seven, and eight replicates are 3.365, 3.143, and 2.998, respectively.) Specific MDLs are developed for each measurement method at the start of a season by performing a detection limit study. The estimated detection limit for specific target VOCs is 3 ppbC or better.

Accuracy is the relative closeness of a measurement to a known reference value. The assessment of accuracy includes both accuracy and precision and is usually expressed as bias or percent bias:

$$\% \text{ Bias} \quad \frac{\text{Measured Value - True Value}}{\text{True Value}} \times 100 \qquad \textbf{(2-12)}$$

Bias is thus a signed value: i.e., the bias may be positive or negative.

Accuracy can also be expressed as percent difference, relative percent difference, percent recovery, and percentage deviation. Estimates of bias require the analysis of a reference material or standard of known or established concentration. Reference standards are submitted in canisters as “blind” audits by an internal or external laboratory. A “blind” audit usually refers to a sample that has been submitted to the audited laboratory and identified as an audit sample of unknown concentration. The reference value for an accuracy standard should be a certified reference material (CRM) or traceable to a standard reference material such as a NIST Standard Reference Material (SRM).

Accuracy should be determined for as many target VOCs as practical based on individual testing needs consistent with the standard operating procedure at the individual PAMS site. Federal regulations require State and Local air monitoring agencies to perform annual accuracy checks. In the absence of specified objectives, the absolute accuracy should be within ±25% of the reference value.

Precision refers to the agreement among a group of experimental measurements made under identical conditions. The most commonly used estimate of precision for environmental measurements is standard deviation, or the square root of the variance. The sample standard deviation (typically used for less than 30 observations) is calculated as follows:

$$s = \sqrt{\frac{\sum_i (Y_i - \overline{Y})^2}{n - 1}}$$

where:

$\overline{Y}$ = means of all observations

Y_i = i^{th} value of observations

n = degrees of freedom

To make a comparison of two values (i.e., duplicates or replicates), Relative Percent Difference (PRD) is a more meaningful statistic than RSD, since the number of values is only two.

$$RPD \quad \frac{V_2 - V_1}{V_1} \times 100$$

Where:

V_2 = second determination

V_1 = first determination

Other measures of precision include relative standard deviation, coefficient of variation, percent difference, range, and relative range. Precision is an inverse relationship, i.e., the smaller the measure of precision, the better the agreement among measurements. For manual canister sampling approaches, two different evaluations of precision can be made: the repeated analyses of duplicate canister samples, which provide an assessment of the total method precision including elements of imprecision in both the sampling and analytical procedures; and/or replicate analysis of a single canister sample, which provides only analytical precision. Use of these two precision estimates is valuable in determining the source of imprecision in the measurement effort.

Since automated GC systems employ "real-time" sample collection and measurement techniques, estimates of precision require repeat measurements of single or collocated SUMMA® canister samples that have been collected using an external sampling device. A replicate sample is a sample that has been divided into two or more portions, at some step in the measurement process. Collocated samples are individual samples collected so they are equally representative of the variable(s) of interest at a given point in space and time. Information gathered from collocated sample results allows for estimation of sampling precision. Repeated analyses of collocated, or duplicate, samples permits estimation of the sampling and analytical precision. Precision estimates should therefore represent the variability of the entire measurement system. Collocated samples are recommended, when possible, for assessing sampling and analytical precision.

Another measure of precision involves intra-laboratory and inter-laboratory precision. Collocated samples that are processed and analyzed by the same organization provide intra-laboratory precision information for the entire measurement process. Collocated samples that are processed and analyzed by different organizations provide inter-laboratory precision information for the measurement process. A sample exchange program that involves both inter-laboratory or intra-laboratory precision gives important information concerning inconsistencies that may exist. Interpretation of these data must

be based on clear understanding and knowledge of how the data were obtained. Differences in the methodologies (i.e., detection limits, analytical column, calibration procedures, etc.) used to analyze the exchange sample must be clarified in order to interpret and resolve any inconsistencies in the results. Precision for inter- and intra-laboratory exchange samples is calculated in the same manner as precision for replicate analyses. In the absence of specified DQOs, objectives for precision should be determined from the QA program, pre-measurement system verification, and historical information for the target compounds of interest. In the absence of specified objectives, values for precision are considered acceptable if they fall within ±25% RPD. This 25% target applies to both automated methodology and manual sampling (duplicate prepared canisters or replicate analysis of a single canister).

When evaluating the precision of VOC measurements, states or agencies must consider each individual target compound because precision will be compound-dependent with an influence of physical and chemical properties (such as vapor pressure and reactivity). In reviewing species data pairs (primary and duplicate samples), the number of non-detects in both samples will probably be significant. In these "non-detect pairs," the RPD will not be useful. Instead these pairs can be said to have a qualitative precision. Data pairs where the compound is detected in both samples can be evaluated for relative percent difference, with a goal of ±25%. In the evaluation of the data, it should be noted that there will be a large range of concentrations and that compounds with an average concentration near the method detection limit will probably exceed the goal of 25%.

Specific requirements for precision and accuracy of automated and manual methods are contained in Sections 3.1 through 3.4 of Appendix A, 40 CFR 58. The calculations used for precision and accuracy data quality assessments are given in Section 5 of 40 CFR 58, Appendix A.

Completeness is the percentage of valid data reported compared to the total number of attempted field samples, minus blanks, standards, and scheduled audit analyses. Completeness is determined after the data validation process is complete, and after precision and accuracy are

determined and evaluated against the quality objectives. The objective for completeness is 85% and is determined on an annual basis.

2.8.2 Quality Control

General QC guidance can be found in the EPA QA Handbook.[56] Quality control for measurement programs covers topics from preventive maintenance to corrective actions. Four areas of particular importance to VOC measurements described in this section are sample collection, sample handling and custody, sample analysis, and data documentation and archiving.

2.8.2.1 Sample Collection

Quality Control for sample collection should address: certification of the sample collection system, calibration of the system components, field acquisition of duplicate samples, and preventive maintenance efforts. A table of QC objectives for sample collection is given in Table 2-16. Technical information pertaining to manual multiple-event and single-event VOC sample collection systems is presented in Section 2.5. Similar information pertaining to automated GC systems is presented in Section 2.4.

Table 2-16. QC Objectives for VOC Sample Collection

Assessment	QC Procedure	Frequency	Acceptance Criteria	Corrective Action
Sampling System Carry-over	Challenge with target compounds	Annual	80-120% recovery for target compounds, overall compound recovery of 85-115%	1) Additional system purge with humid zero air 2) Repeat challenge
Sampling System Background or Contamination	Humid zero air blank	Annual	2 ppbC or the MDL, whichever is less for target species or # 10 ppbC TNMOC	1) Additional system purge with humid zero air 2) Repeat zero air collection
Accuracy of Collection Period	Elapsed time meter or timing device check On/off timer check	6 Months Quarterly	Gain or loss in time # 2 minutes per 24-hour period	Adjust or replace the timing device Adjust or replace timer
Sampling Integration Period	Flow control check	Weekly	Measured transfer standard flow within 10% of indicated flow	Adjust or replace flow control device
Sampling System Pressure/Vacuum Measuring Device Accuracy	Pressure/vacuum gauge or electronic sensor check	Annual	# 10% difference between field and lab measured canister pressure	1) Adjust for differences in pressure/vacuum measurement technology 2) Repeat check
Duplicate Sample Correction Precision	Comparison of duplicate canister sample results	10% of field samples	Agreement within ±25% RPD.	1) Perform sampling system PM 2) Repeat duplicate sample collection 3) Check analytical system precision 4) Check canisters for leaks.

2.8.2.1.1 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 procedure is described in Section 2.5.1.7, Canister Sampling System Certification. Collection system certification should be conducted prior to and after each PAMS season or at the start and end of each calendar year. 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%.

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 criterion of 3 ppbC or less for any individual target compound is required if speciation analysis of the blank sample is performed, and a total NMOC concentration criterion of 10 ppbC or less is also required.

2.8.2.1.2 Calibration of Manual Sampling System Components

A QC check for the timing device in most manual sample collection systems is described in the Quality Assurance Handbook.[56] Every six months the elapsed-time meter should be checked against a timepiece of known accuracy. If the meter shows any signs of temperature-dependence, it should be checked on site during each season of the year. A gain or loss greater than 2 min/24-hour period warrants adjustment or replacement of the indicator.

The on/off timer should be calibrated and adjusted quarterly by using a calibrated elapsed-time meter as the reference. Specific procedures for QC of the elapsed-time meter and on-off timer calibration checks are provided in Section 2.2.2 of the Quality Assurance Handbook.[56]

The accurate and consistent control of flow into the sample canister is required to ensure that the sample collected is time-integrated. To check the sample collection flow rate, a flow meter (e.g., calibrated transfer standard) is installed at the inlet to the manual collection system and the system activated. The flow rate measured by the transfer standard should agree within ±10% of the flow rate indicated by the flow control device housed in the sample collection system. This check should be performed annually or as needed based on performance. The ability of the collection system to consistently perform an accurate time-integration can be assessed indirectly by making a control chart of the sample pressure collected over each sampling event. If the collection flow rate and sample collection period are not varied, the total pressure of samples collected should not differ by more than ±10%, assuming that the canisters all start with the same initial vacuum.

The vacuum/pressure measuring devices (e.g., gauges or electronic sensors) used in the manual sample collection systems must be checked for accuracy. To perform this check, a series of comparisons between a primary pressure measuring standard and the sample collection system device should be conducted prior to installation and then annually. The comparisons should cover the range of the device operation at increments representing 10% of the total range. Ensuring the accuracy of the pressure measuring device also allows the sample canister to be assessed for leaks. The final sample pressure in a canister as measured in the field should be within 10% of that measured when the canister is received for analysis at the laboratory. Note that differences in pressure may occur due to temperature and barometric pressure changes, and differences in the accuracy of the pressure measurement technology used.

2.8.2.1.3 Collection of Field Duplicate Samples

Field duplicate samples should be collected at a scheduled frequency of at least 10% (or at the frequency specified by the site standard operating procedure) and are used to estimate the precision of the manual sample collection method. Most commercially available manual sample collection systems allow for collection of duplicate samples. Care should be taken to ensure that the duplicate samples represent the same parcel of air over the same sample integration period.

Automated sample collection and analysis configurations have the same general QC requirements for sample collection as manual systems. All of the QC checks for automated systems should be done at the field station. Because true duplicates cannot be collected and analyzed with an automated GC system, precision is estimated using repeated analyses of the target VOCs at ambient concentrations. A humidified canister standard or sample is typically used as the source instead of the sample manifold. This check is actually a measure of analytical precision (replicate analysis of a single canister rather than duplicate analysis of multiple canisters). Replicate results should agree within 25% RPD.

2.8.2.1.4 Preventive Maintenance

Preventive maintenance is an important part of the overall QC program for both manual and automated sample collection systems. Maintenance items are generally specified by each sample collection system manufacturer in the operating manual. These items may include any moving parts such as valves or pumps. Most manual sample collection systems have an in-line particulate filter which needs to be replaced on a regular basis. The location and physical conditions of the sample collection system may dictate other maintenance activities that are necessary to reduce the effects of heat, dust, corrosion or other concerns.

Any maintenance activity that involves the disassembly of hardware and replacement of parts should be viewed as a potential change to the performance of the system. Replacement of major sample collection system components (e.g., a flow control device) may warrant recertification of the sample collection system. Duplicate analysis of multiple component calibration standard samples can be used to assess whether changing a major component has affected the performance of the collection system. If the duplicate analysis results compare within the quality objectives for the program, the sample collection system does not require recertification. If duplicates do not meet the quality objectives, then the sample collection system should undergo full challenge and blank recertification. Repeated analyses of a multiple component calibration standard for the automated GC should also be conducted and reviewed to check for shifts in retention time or changes in response factors that may be caused by a maintenance activity.

Quality Control activities should be thoroughly documented in a log book dedicated to the monitoring site. In addition to the technical details of the site maintenance activity, the time, date, sample collection system or instrument ID, and monitoring site ID should be recorded.

2.8.2.2 Sample Handling and Custody

The QC procedures for canister preparation are vital to manual sample collection and calibration standard preparation because all of these activities rely on leak-free uncontaminated canisters. All canisters prepared for field use should initially be checked for leaks by pressurizing the canister with zero air to a known measured pressure. Gross leaks are located by coating critical canister surfaces considered to have leak potential (e.g.,valves and fittings) with a leak detection solution. More subtle leaks are indicated by pressure changes in the canister over time. All canisters should be cleaned and checked for contamination and certified clean to 10 ppbC TNMOC. Canister cleaning procedures are described Section 2.5.2.

Sample documentation includes chain-of-custody for canister samples and proper sample identification and labeling. A chain-of-custody protocol should be developed so that at any point between the canister's initial cleaning and its disposition after analysis the sample custodian can identify and track the status of the canister. A unique identification is required for each canister at each point in the sampling event. The canister should have a permanently assigned serial number and, after the sample is collected, a unique sample identification number. A tag or label should be attached to the canister so that it can easily be identified. The chain-of-custody form should always accompany the canister and provide the means for each person responsible for custody to relinquish the canister to the next person handling that canister. For example, the laboratory technician who provides the cleaned canister to the field technician should initiate the chain-of-custody form and sign the canister over to the field technician. After the sample is taken, the field technician returns the canister to the laboratory, with the appropriate custody forms indicating the shipper and destination. The final completed form, upon receipt at the laboratory, is signed by the sample custodian. This record allows the history of each sample to be reconstructed if a problem arises with the analytical results.

A communication protocol should be established between the field sampling personnel and the analytical laboratory personnel to ensure that sample canisters arrive at the monitoring locations ahead of the scheduled sampling date. Sufficient numbers of canisters should be available to collect all required samples, including any blank or duplicate samples that may be scheduled. The communication protocol should include how to return the sample canister to the laboratory after collection.

For automated GCs, sample documentation can be accomplished using instrument specific data collection software. Each chromatogram should have a header that uniquely identifies the sample (e.g., filename and sample ID) as well as notation of the analysis conditions and column(s) used. Good maintenance records are very important for automated GCs due to the large volume of data produced. An injection or sample collection logbook should be maintained to provide a history for each analysis so that any questions about results can be resolved.

A standardized approach should be followed for identifying samples, blanks, calibration runs, audits, and other analyses. All samples collected and analyzed with an automated GC should have a unique file name designated to identify the site, instrument used to collect the sample, and the sampling date and time. A data system should automatically append a character(s) to the end of the electronic storage file which corresponds to the order in which the sample was analyzed. The user is typically limited to eight characters.

Electronic copies of all original and reprocessed files should be maintained to provide a record of any and all changes made to the data. The original raw data files should never be changed and should contain, if possible, a file name extension (such as .RAW) to differentiate them from other files. The .RAW files should be archived with any processed data files. Data processing can be checked at a later date.

2.8.2.3 Sample Analysis

Several steps are taken to ensure that the analytical system is in control, and these steps apply to GC operations whether the sample is collected using an automated or a manual method. A summary of these quality objectives is shown in Table 2-17. These objectives are the minimum QC procedures pertaining to VOC analyses. States are strongly encouraged to develop more detailed, site-specific SOPs.

During the initial analytical system set-up a multiple point calibration check using propane and/or benzene is performed, and retention time windows are determined using the retention time standard for each target compound. Calibration is the single most important operation in the measurement process. Calibration is the process of establishing the relationship between the output of a measurement process and a known input. For routine operation, the retention time calibration check samples are analyzed to demonstrate that the retention times for each target VOC are within the established window, to monitor the detector response drift, and verify the target compound recoveries.

Results outside of the expected retention time window or detector response range may indicate the need for maintenance, adjustment or recalibration of the analytical system before further sample analysis. A humidified zero air blank should be analyzed after the highest level calibration standard to assess analytical system carry-over of any target analytes.

Table 2-17. Continued

Table 2-17. VOC QC Procedures

Assessment	QC Procedure	Frequency	Acceptance Criteria	Corrective Action
System Background and Carry-over	System Blank Analysis, Humidified Zero Air	Weekly, following retention time/calibration check and after multiple-point calibration curve	20 ppbC total, both analytical columns, or 10 ppbC per column	1) Repeat analysis 2) Check system for leaks 3) Clean system with wet air 4) Condition sample trap
Calibration	Multiple Point Calibration (3 points minimum). Propane/benzene bracketing the expected sample concentration	Prior to analysis at start of season and when system maintenance is performed	Correlation Coefficient $ 0.995	1) Repeat individual sample analysis 2) Repeat linearity check 3) Prepare new calibration standards and repeat
Quantitative and Qualitative Performance	Retention Time/Calibration check using mid-point of calibration curve	Weekly	RF within 10% RPD of calibration curve average RF RT within ± 0.1 minutes of target % recovery for targets 80-120%	1) Repeat check 2) Repeat calibration curve
Qualitative Performance	Canister cleaning certification	All canisters prior to use	# 10 ppbC total	Reclean canister and reanalyze
Detection Limit	40 CFR 136 Part B	Prior to analysis at start of season	2 ppbC or better, specific target peaks selected	N/A

Table 2-17. Continued

Assessment	QC Procedure	Frequency	Acceptance Criteria	Corrective Action
Precision	Replicate sample analysis, manual or automated	10% of samples	Within ± 25% RPD for target concentrations > 5 times the MDL	Repeat sample analysis
Accuracy	Performance evaluation or NPAP sample analysis	Prior to start of season, and monthly during monitoring season	20% absolute bias	Repeat sample analysis

After the system is optimized as described in Section 2.4.3.1, analytical system blanks are analyzed to verify that the analytical system contributes no more than the maximum specified background level of a total 20 ppbC (10 ppbC per analytical column) to the analytical results. System blanks are typically run with each analysis batch (or at a specific time of day for continuous GCs but not the same time every day to avoid loss of data for the same time period for the entire season), and usually in a predetermined order, such as the first or last analyses in a batch, after a calibration check standard, etc. The hour chosen for system blank analysis on automated systems should be varied so the data from the same hour are not consistently lost. Each blank must be humidified to ensure that the analytical system responds similarly to ambient samples.

A calibration control standard or calibration curve should be analyzed to assess qualitative and quantitative performance of the sampling system. Sample analyses should not be attempted until the results demonstrate performance within the program's acceptance criteria. This type of control sample should also be analyzed with each batch (or at various times of day for automated GC) and in a predetermined order, usually before the analytical system blank. Again, the analysis hour should be varied for automated GC systems. A calibration check sample is analyzed at least weekly to verify calibration control.

An additional QC check of retention time windows for all target analytes should be performed on both manual and automated GC systems using a retention time standard. This standard should be used at program start up and weekly or as needed thereafter to provide a comprehensive check of retention time windows and peak identifications for all target VOCs. The retention times should not vary by more than 0.1 minutes. The results from repetitive analysis of this standard can indicate trends in quantitative performance of the GC. If independent verification of the vendor supplied cylinder can be performed, then the cylinder can also be used as the quantitative QC check discussed in the preceding paragraph.

The QC check standard may also be used to measure percent recovery for the target compounds. Compound recovery can be used to verify sample trapping and transfer efficiency. At a minimum, one target compound representing each carbon group should be checked for recovery between 80 and 120%.

Replicate analyses are valuable in providing a means to estimate analytical precision. From these data, control charts may be generated and simple statistical analyses performed on the analytical results for each compound to estimate precision. The calculations are typically made in units of relative percent difference or relative standard deviation (percent coefficient of variation). Variability in the measurement data will be higher at low concentrations, which is also the range in which most ambient VOC data are measured. For these reasons, precision measurements are made at ambient concentrations, even though variability (imprecision) increases as the detection limit is approached. Manual sampling systems provide sufficient sample in each canister to perform replicate analyses. Repeated analysis should be performed on 10% of the samples to determine if the analytical precision is within ±25% RPD for compounds greater than 5 times the MDL.

To determine precision for automated GC systems, analysis of a humidified gas standard or typical field sample is required. The sample is composed of target compounds at ambient concentrations in humid air. A control check sample from a gas cylinder or a diluted aliquot in a SUMMA® canister can be used for this purpose.

2.8.2.4 Data Documentation and Archives

Data documentation protocols are vital for reporting results in a consistent manner and for providing an audit trail. Identification of samples must be consistent throughout the documentation process. Logbooks should be maintained for each system in the laboratory, including logs for calibration standard, instrument run logs, and maintenance logs. Good laboratory practices should be followed for logbook entries, including the use of indelible ink, corrections made only by single line

strikeout (initialed and dated), and identification of authorship for each entry. These logbooks should be periodically peer reviewed by one person and evidence of the review should be written in the logbooks.

Electronic logbooks may be used if certain precautions are taken. A prime concern for QC of data documentation files is the ability to recover data in the event of equipment failure. Logbooks may be kept in electronic format if desired, but a protocol specific to the use and backup of electronic log entries must be established. All software and data files used in recording and archiving raw data should be backed up so that an equipment hardware failure or tampering does not destroy the logbook information. Once entered, electronic logbook files should have file attributes set to "Read Only." Bound hard copy indices of each electronic notebook should also be maintained. Index entries should include file name, date of entry, author's name and subject.

Logbooks can be kept in electronic form for calibrations, computer access (recording logins), computer boot logs, etc. Among the advantages of using electronic logs is the capability for remote access to the information contained in the logbook. An automated GC system can be designed to allow personnel remote access to all monitoring data, including all supporting documentation.

As part of a QC program, the data should periodically be reviewed to look for anomalies in the data. Examples of items that should be examined in the periodic QC or validation of data include the following:

- Missing data;
- Consistency of identification of target compound between standards and samples;
- Concentrations of compounds within expected ranges and variances according to weather conditions, traffic patterns, etc.;
- Identification of target compounds in the retention time check standard;

- Response factors from the primary calibration check standard within acceptable limits; and

- Compounds detected in the blank within acceptable levels.

A complete discussion on data validation is found in Section 2.7.

Data validation cannot practically be performed on 100% of the compound identifications and concentrations. The analyst should be responsible for cursory review of all chromatograms, primarily for anomalies. The analyst should also review a small percentage of the files in depth to confirm peak identifications and look for changes in methods that could affect automated data processing. The key element to this activity is consistency to ensure that the same peak is identified the same way to the extent allowable by the automated software in a batch reprocess mode. Exploratory data processing software packages like MetaChrom® and VOCDat® may be used to validate the data in more depth.

The processed results from raw data should be stored in a different directory on the computer system. Reprocessed files should be compressed into storage files and given a unique file name. The compressed file name may be used to designate that the automated software files have been reprocessed and the level of reprocessing.

2.8.3 Quality Assurance

The procedures and activities associated with QC need periodic independent review and assessment to ensure that the data meet the quality expectations of the program. This independent review or auditing function should be done by an independent source with no daily involvement in the operation of the sampling or analysis systems. In addition, independent review should be done on DQOs and SOPs to ensure that the quality goals of the agency are reflected by the QC program. After

SOPs and the QC program are put into place, the QA function provides review of their adequacy and implementation in meeting the DQOs of the monitoring program.

2.8.3.1 Development of Standard Operating Procedures

An SOP is written so that procedures may be performed consistently by everyone involved in the monitoring program. The decision of whether an SOP is needed for a particular procedure is made by answering two questions:

- Does the procedure significantly affect data quality?
- Is the procedure repetitive or routine?

If the answer to both questions is yes, an SOP is needed.

Few routine laboratory or field projects can be described completely in just one SOP; several may be needed. In general, an SOP for each of several smaller segments should be written instead of one large SOP for an entire operation.

At a minimum, written SOPs to support the VOC monitoring effort should be prepared for the following activities:

- Sample collection;
- Sample analysis;
- Sample canister handling;
- SUMMA® canister preparation and blanking;
- Data handling;
- Sample identification and labeling requirements; and

- Automated or manual data reporting.

Table 2-18 shows the suggested format for an SOP, including examples of items that should be included in each section. The examples shown are only a few of the many that may be

Table 2-18. Format for Standard Operating Procedures

A. Technical Sections		
	Section	**Typical Examples**
1.	Scope and Application	Overview outlining purpose, range, sensitivity, acceptance criteria
2.	Summary of Method	Overview describing sampling criteria and analytical methods, method and instrumentation detection limits, reasons for deviations from *Federal Register* methods
3.	Definitions	All acronyms, abbreviations, specialized terms
4.	Interferences	Sources of contamination
5.	Personnel Requirements	Educational level and training of intended SOP users, number of operators required
6.	Facilities Requirements	Mobile analytical laboratory, air conditioning, type of electricity
7.	Safety Precautions	Special handling procedures; i.e., handling compressed gases, hazard warnings, placed immediately before relevant part of text
8.	Apparatus	Larger items such as a meteorological tower, audit device, gas chromatograph
9.	Reagents/Materials	*All* chemicals used, including distilled or deionized water; grades of reagents and materials
10.	Samples/Sampling Procedures	Sample preparation, collection, storage, transport, and data sheets
11.	Calibration/Standardization	Preparation of standards and calibration curves, frequency, and schedule
12.	Analysis Procedures	Standard and custom-tailored methods for all target analytes
13.	Calculations	Data reduction, validation, and statistical treatment, including confidence levels and outliers
14.	Data Reporting	Selection criteria, format, equations, units
15.	Corrective Action	Criteria for initiation; individuals responsible
16.	Method Precision and Accuracy	Tabular or narrative summary of DQOs
B. Quality Control/Quality Assurance Sections		
	Section	**Typical Examples**
1.	QC Checks	Precision, accuracy, reproducibility, blanks, replicates, criteria, and frequency summarized in tables
2.	QC/QA Controls	Audits, notebook checks, control charts and graphs; actions to be taken when QC data approaches or exceeds QC limits
C. Reference Section		
Standard reference methods, reports, SOPs, journal articles; avoid citing unpublished documents		

covered. The SOP must be comprehensive and cover every step of the procedure in detail. The author of a SOP tends to be extremely familiar with the material and may omit "obvious" information. The written SOP should be reviewed extensively and executed by persons not intimately familiar with the procedure to evaluate the completeness of the instructions presented in the SOP. Once the DQOs have been established and SOPs are in place, QA measures can be planned and implemented to ensure that DQOs are met. In the remainder of this section, program audits are described that guide QA for sample collection, analysis, and reporting. Additional guidance for development of a VOC monitoring QA program are discussed in the EPA QA Handbook,[56] and this information should be used in conjunction with the guidance presented here.

2.8.3.2 QA Program Guidance

The QA program plan and activities should be developed to catalog and assess the data quality requirements of the program. The QA plan ensures that procedures are being implemented correctly and that all of the QC and SOP requirements are being followed to collect, analyze, and report samples that meet agency DQOs. The QA plan also provides guidance for regular assessment of the quality program for the monitoring network. An integral part of the QA program is a regular series of audits. The QA plan should provide guidance for audits, performed by an independent person or group to formally evaluate if systems are in place and being followed in order to meet the DQOs. The QA program should be a cooperative effort between independent auditors and program auditees so that quality issues can be identified and, if necessary, appropriate corrective actions implemented.

2.8.3.2.1 Audit Types

Three audit types are described in the following sections: technical systems audits, performance audits, and data quality audits. These audits are used to determine whether data quality

objectives are being met. An audit may also uncover additional findings useful in improving the monitoring program.

As defined in the QA Handbook (Volume II)[61] the **Technical Systems Audit** is a systematic, qualitative on-site review of the adequacy of the facilities, equipment, training, record keeping, validation, reporting, sampling, analysis, and QC/QA procedures. This type of audit should be used throughout the VOC monitoring program to ensure that the QA/QC program elements are in place and being followed. Systems audits are normally done immediately before, or shortly after, measurement systems are operational and should be repeated on a regularly scheduled basis, at least annually.

Technical systems audits should cover areas specific to VOC monitoring networks, including sampling system certification, QC check procedures, and record keeping. Sampling system certification critical to the success of a VOC monitoring program is often overlooked. Sampling system QC checks should be reviewed to determine if proper blank and challenge gas tests have been performed on the sampling systems before they are used to collect samples. Checks for leaks in sampling systems and canisters, vacuum/pressure gauge calibration, and flow meter testing should be reviewed to confirm that the QC procedures were implemented and systems are ready for use. Vacuum and pressure measurement checks should be audited with a NIST-traceable high resolution gauge. Changes in canister pressure can then be corrected for barometric pressure differences and final corrected canister pressures can be reviewed to identify leaking canisters.

The technical systems audit investigates the specific elements of the measurement system to ensure that established procedures are followed. With an emphasis on improving the program, the technical systems audit evaluates the documentation and paper trail of a particular site to show that the VOC monitoring is conducted according to the QA/QC program elements. An audit of this type is conducted by an auditor familiar with VOC monitoring and the required types of record keeping used in a VOC program. The auditor uses QA/QC guidance documents such as this document as well as

the site-specific SOPs to evaluate the site's measurement system. A specific checklist of required elements is prepared and used as a guide for the auditor's review. Significant deficiencies are noted and discussed at the time of the audit and any additional deficiencies are noted and resolved by the generation of a list of corrective actions to be taken by the site. Additional suggestions for improvement are made by the audit team and delivered as part of their systems audit report.

A Performance Evaluation Audit is a quantitative evaluation of the measurement system and includes all associated data collection and analysis procedures. A Performance Evaluation Audit involves the analysis of a reference material of known value. For both manual and automated VOC sampling systems, the audit sample is usually a canister or compressed gas cylinder containing humidified air with VOC target analytes at known concentrations. Performance evaluation audits should be conducted on a regular basis specific to the program, at least once per season.

The EPA initiated a national performance audit program (NPAP) which applies to the VOC, carbonyl, O_3, and NO_2 measurement systems used at PAMS monitoring stations. This program mirrors the present EPA national performance audit program for SLAMS criteria pollutants. Agencies collecting data in the PAMS monitoring network are required to participate in the national audit program. The audit program uses performance evaluation samples which were field tested by the EPA in 1993-1994. The EPA has established limits for acceptable performance on each type of Performance Evaluation sample based on a statistical analysis of the results obtained from pilot tests.

The VOC and Performance Evaluation samples were pilot tested through a series of proficiency tests. The VOC samples consist of 1.5 L compressed gas cylinders containing 10 to 50 of the target VOC compounds. Participants in the audit program receive the Performance Evaluation samples, determine the concentrations and report the results to the EPA. The EPA compares the reported results to the expected results and issues a report to all participants.

A Data Quality Audit exhaustively evaluates the information generated from data collection through reporting. Procedures that are evaluated include raw data recording and transfer, calculations and equations, documentation of data handling, reporting and completeness, comparability, and discussion of QC indicators such as precision, accuracy, and representativeness. A Data Quality Audit for PAMS should include an audit of the data entered into the AIRS. Data Quality Audits should be conducted routinely on various components of the data generation system, and a comprehensive Data Quality Audit should be combined with Technical Systems Audits once the program is generating data on a regular basis.

The QA/QC Procedures outlined in the above sections serve as a guide to the process of ensuring that the VOC measurements are conducted properly. Collection of data and the subsequent submission of the data to the AIRS data base must be consistent across all agencies. The defined sections of DQOs: Sample collection, certification, calibration, duplicates, maintenance, sample handling and custody, and sample analysis are a necessary framework and starting point for site-specific SOPs. Coupled with the documentation of the data, the technical and system audit program provides a regular evaluation of the system, data collection, and analysis process. The QA/QC program in this document establishes the program elements which are necessary for the successful operation of a VOC measurements analytical program.

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Section 3.0
Determination Of Total Nonmethane Organic Compounds Using Method TO-12

Qualitative and quantitative determinations of individual VOCs and measurement of total NMOC using the GC based methodology described in Section 2.0 requires instrumentation that is expensive, complex, and difficult to operate and maintain. Method TO-12[1] provides a similar measurement of total NMOC, but does not provide information on the individual VOCs comprising the total. Method TO-12 is part of the "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air," and is presented in Appendix C. Method TO-12 involves a simple preconcentration procedure with subsequent direct flame ionization detection and provides accurate and sensitive 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.

Although Method TO-12 is not directly applicable to PAMS, the method is included here because:

- Method TO-12 is a viable, practical, and effective method of post clean-up determinations of canister cleanliness;
- Method TO-12 can be used for ambient total NMOC measurements as input into O_3 predictive models that do not require speciated VOC information; and
- Used in combination with the manual (canister) methodology described in Section 2.5 or in an automated form, Method TO-12 can be applied (i.e., with the approval of the EPA Administrator) as a viable alternative monitoring approach to the automated methodology described in Section 2.4.

Total NMOC data, resulting from measurements made using Method TO-12, should be entered into the AIRS data base. These NMOC data are entered under Parameter Code 43102. The abbreviation for parameter code 43102 is "TNMOC." The Method Code is 012. Method

Code 012 describes the sum of data gathered by preconcentrated direct flame ionization detection PDFID). PDFID is the TO-12 EPA-approved method which includes not only the sum of C_2-C_{12} data, but also any compounds larger than C_{12} that are detected.

3.1 References

1. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Compendium Method TO-12. *Method for the Determination of Non-Methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID).* EPA-600/4-89/017. Research Triangle Park, NC: U.S. Environmental Protection Agency. 1988.

Section 4.0

Methodology for Measuring Oxides of Nitrogen And Total Reactive Oxides of Nitrogen in Ambient Air

Measurement of ambient concentrations of nitric oxide (NO) and nitrogen dioxide (NO_2) is a requirement of the 40 CFR Part 58, Subpart E,[1] enhanced O_3 network monitoring program. The NO and NO_2 measurements are used to better characterize the nature and extent of the O_3 problem, track oxides of nitrogen emission inventory reductions, assess air quality trends, and make attainment/nonattainment decisions. Information on measuring NO and NO_2, including method and equipment descriptions, is presented in Section 4.1.

Although not specifically required under 40 CFR Part 58, Subpart E, measurement of total reactive oxides of nitrogen (NO_y) is strongly encouraged by the EPA. Measurements of NO_y constitute a valuable adjunct to current NO and NO_2 monitoring because the individual species comprising NO_y include not only NO and NO_2 but also other organic nitroxyl compounds that have recently been shown to play a significant role in the photochemical O_3 formation process. Information on measuring NO_y, including measurement principle and procedures and equipment descriptions, is presented in Section 4.2.

4.1 Oxides of Nitrogen

Oxides of nitrogen, defined here as the sum of the concentrations of NO and NO_2 at the same point in time, are principal precursors to the formation of O_3. The Urban Airshed Model (UAM), another type of mathematical O_3 prediction model, requires NO and NO_2, total NMOC, and speciated VOC concentrations as inputs.

4.1.1 Measurement Principle

NO and NO_2 are typically measured using a chemiluminescence instrument. The principle of operation of this instrumentation is based on the gas-phase reaction of NO and O_3. This reaction produces a characteristic near infrared luminescence with an intensity that is linearly proportional to the concentration of NO present. Specifically,

$$(NO + O_3) \rightarrow (NO_2 + O_2 + h_v) \qquad \textbf{(4-1)}$$

where:

h_v = emitted photon energy (function of Planck's constant and the frequency of radiation)

Prior to measurement, nitrogen dioxide is converted into NO using a molybdenum (Mo) reducing surface heated to 325°C. Specifically,

$$(NO_2 + Mo) \rightarrow (NO + MoO_3) \qquad \textbf{(4-2)}$$

where:

Mo = molybdenum chemical reductant

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

To determine the concentration of NO, the sample gas is blended with O_3 in a reaction chamber causing the reaction to occur. The chemiluminescence that results from the reaction is monitored by an optically filtered high-sensitivity photomultiplier. The optical filter and photomultiplier respond to light in a narrow-wavelength band unique to the NO and O_3 reaction. The electronic signal produced in the photomultiplier is proportional to the NO concentration.

To determine the concentration of NO_x (i.e., NO + NO_2), the sample gas is routed through an NO_2-to-NO chemical reductant converter and the NO_2 converted to NO+O_2. The

$NO+O_2$ is blended with O_3. The chemiluminescent response is proportional to the concentration of NO_x entering the converter. The NO_2 determinations are not the result of direct measurement. The concentration of NO_2 is calculated as the difference between a measured NO_x value and a measured NO value representing the same point in time. There are basically two types of NO_2-to-NO converters; the chemical reductant converter and the photolytic converter. The chemical reductant converter uses a reducing agent such as molybdenum or gold/carbon monoxide to convert NO_2 to NO. The photolytic converter uses high energy light to perform the conversion.

Instruments using chemical reductant conversion permit accurate measurement of NO, NO_2, and NO_x as long as there are no other nitroxyl compounds present in the sampled atmosphere. Peroxyacetyl nitrate (PAN) and nitric acid (HNO_3) are primary interferents to the accurate measurement of NO_2 when a chemical reductant converter is used. Chemical reductant converters may partially or completely convert PAN, HNO_3, and/or other nitroxyl compounds to NO. The conversion of compounds other than NO_2 causes artificially high values for NO_2. The least biased measurements are typically early morning measurements in urban areas where NO and/or NO_2 concentrations are high and concentrations of PAN, HNO_3, and/or other nitroxyl compounds are low. The potential for biasing the NO_2 measurement due to the chemical reductant conversion of PAN, HNO_3, and/or other nitroxyl compounds is greatest in urban areas during late afternoon because the ambient concentration of NO is negligible (i.e., at or below the detection limit of most conventional instruments) and PAN and HNO_3 and/or nitroxyl compounds other than NO and NO_2 comprise a significant percentage of the total airborne nitroxyl compounds. Therefore, the conversion of the interfering compounds has a greater biasing effect yielding values that are more closely related to NO_y (i.e., organic nitroxyl compounds including NO and NO_2) than to NO_x. Although the potential for measurement bias exists, measurements of NO and NO_2 are required under 40 CFR Part 58, Subpart E using EPA approved instrumentation.

The photolytic converter uses high energy light (i.e., wavelengths from 300 to 430 nanometers) to specifically convert NO_2 to $NO+O_2$. The $NO+O_2$ are then mixed with O_3 and

measured by a chemiluminescence detector. Although the photolytic converter specifically converts NO_2 to NO, it is not 100% efficient and must be calibrated regularly to determine and quantify conversion efficiency. Because the photolytic converter converts only NO_2 to NO, bias caused by the partial or complete conversion of other nitroxyl compounds is not experienced. The photolytic converter is not as well developed as the chemical reductant converter and is therefore more expensive to purchase, operate, and maintain.

4.1.2 Method and Equipment Description

Instrumentation approved or designated as reference or equivalent methods for measuring ambient concentrations of NO_2 are listed in 40 CFR Part 53.[2] Subject to any limitations specified in the applicable designation, each instrument is acceptable for use in enhanced O_3 monitoring networks, unless the applicable designation is subsequently canceled. Instruments designated as reference methods for NO_2 are also approved for measuring NO. The detailed procedure for measuring ambient concentrations of NO_2 using approved instrumentation is contained in 40 CFR Part 50, Subpart C, Appendix F.[3]

Figure 4-1 presents the flow schematic of a typical NO-NO_2 instrument (i.e., the Thermo Environmental Instruments, Inc., Model 42, Designated Reference Method Number RFNA-1289-074). Sample enters the instrument through a flow control capillary. A solenoid valve routes the sample either through the converter (i.e., NO_2 measurement mode) or around the converter (i.e., NO measurement mode). When the sample flow is routed through the converter, the chemiluminescence measured in the reaction chamber represents the concentration of NO + NO_2 and any other oxides of nitrogen compounds that are converted. When the sample flow is routed around the converter, only NO is measured. The concentration of NO_2 is calculated automatically by a microprocessor in the instrument as the difference between a measured NO_x value and a measured NO value for the sample point in time.

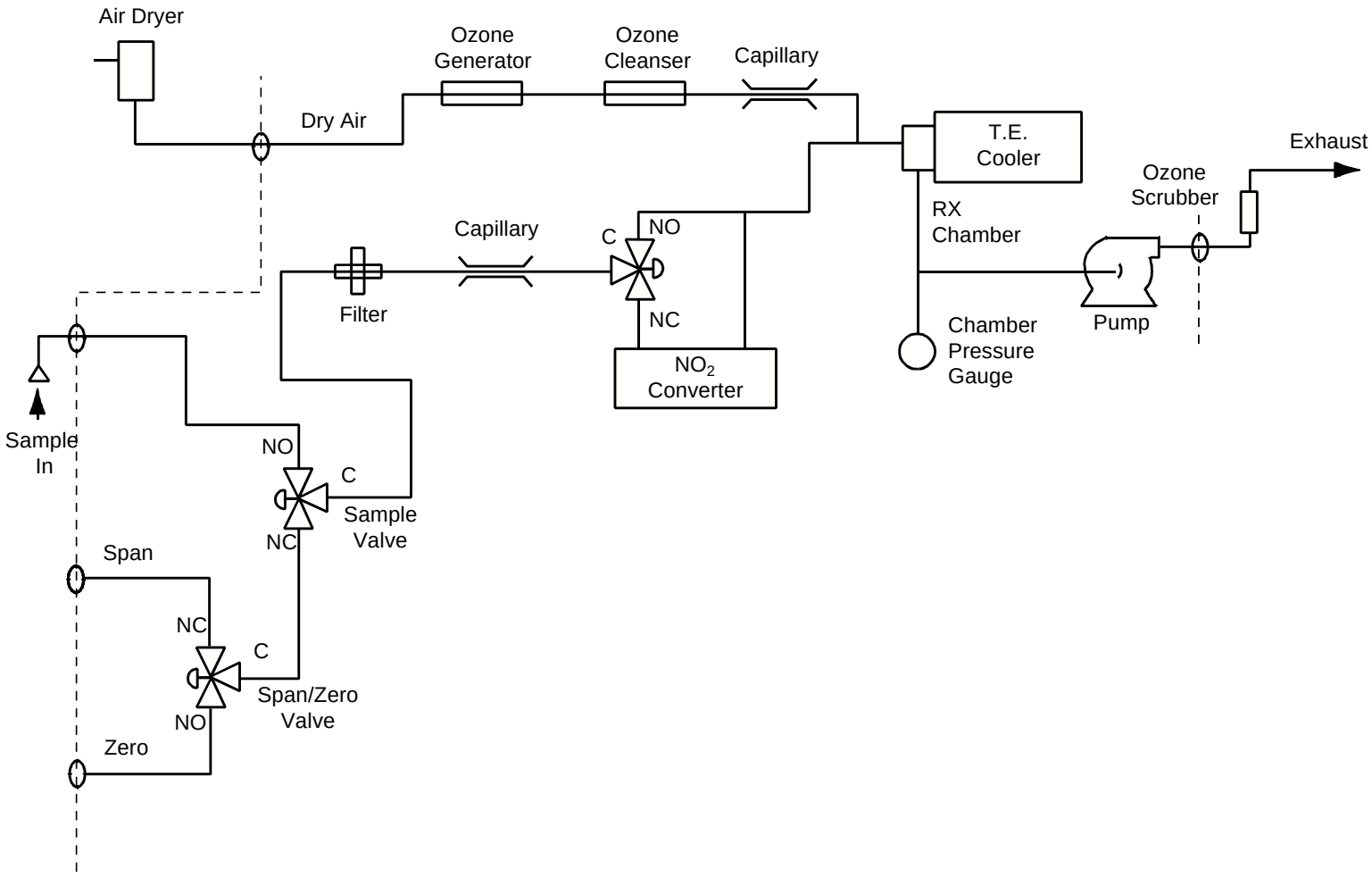

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Figure 4-1. Flow Schematic of a Typical NO-NO_2 Instrument

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 specifically defined. This group contains all of the nitroxyl compounds that react in the troposphere to any significant extent and, therefore, contribute to the photochemical formation of O_3.

Identified NO_y constituents include:

- NO;
- NO_2;
- nitrogen trioxide, N_2O_3;
- nitrogen pentoxide, N_2O_5;
- nitrous acid, HNO_2;
- HNO_3;
- peroxynitrate;
- PAN;
- other organic nitrates; and
- other aerosol nitrates.

In typical urban environments the principal NO_y compounds are NO, NO_2, PAN, and HNO_3. Measurements of NO_y are a valuable metric serving multiple purposes. Speciated measurements of NO_y compounds provide valuable information relevant to understanding photochemical cycles and evaluating the behavior of chemical mechanisms applied in O_3 prediction models. Because NO_y is a conservative determination of all nitrogen emissions releases, excluding losses due to deposited nitrogen, NO_y should be an excellent indicator of NO and NO_2 emissions trends. However, speciated NO_y measurements (i.e., analyzing separately for each NO_y compound) on a

routine basis are presently impractical because they require that the user know the identity of all the compounds to be measured and that appropriate individual methods can be applied.

One of the more important uses of NO_y data is predicting tropospheric O_3 and assessing the importance of NO and NO_2 and VOC levels to O_3 production and control. Observational based models (OBMs) assess the age of air masses to evaluate control strategies. Generally, air masses that contain predominantly "fresh" NO emissions are more likely to be hydrocarbon-deficient and require VOCs to produce O_3. Air masses that contain nitroxyl compounds are aged and are NO_x deficient, requiring NO_x for maximum O_3 production. In either case, it is critical to know NO, NO_2 and NO_y levels to decide the best regional control strategy for O_3.

Since the measurement of individual reactive nitroxyl compounds is technically difficult, time consuming, and expensive, it is currently impractical to require routine monitors of these species at PAMS stations. However, a practical instrument based total NO_y measurement procedure has been developed. This total NO_y measurement principle and procedure is presented in Section 4.3. Measuring total NO_y is not required by 40 CFR, Part 58, Subpart E.[1] However, for the reasons discussed above, it is strongly encouraged by the EPA as part of enhanced O_3 monitoring programs.

4.3 Measurement of Total Reactive Oxides of Nitrogen in the Atmosphere (Gas Phase Chemiluminescence) - Measurement principle and Procedures

The measurement principle and procedures addresses the need to measure total NO_y in a practical, standardized manner. The total NO_y measurement principle and procedures is based on reconfiguration and operation of a commercially available NO_y instrument (i.e., the Thermo Environmental Instruments, Inc., Model 42s)—the only NO_y instrument commercially available at the time of preparation of this guidance. Although the total NO_y measurement principle and procedures are based on this specific instrument, the approach is sufficiently generic to be used

with other similar equipment. Any instruments used to measure NO_y must have the sensitivity to measure the low concentrations typically encountered during late afternoon periods and also be able to measure the high concentrations encountered during early morning periods. Automatic range change capabilities will probably be required to accommodate the wide range of NO_y concentrations experienced in a typical urban atmosphere. The total NO_y measurement principle and procedures are structured according to Federal Register format and includes the same topics and level of detail as the EPA NO_2 instrumental method. The EPA recognizes that NO_y measurement is an emerging technology. As advances in the technology are made, the NO_y instrumental method will be updated.

Applicability of the measurement of total NO_y is presented in Section 4.3.1 and the operational principle of measurement is presented in Section 4.3.2. Information on modification and final configuration of the NO_y instrument is presented in Section 4.3.3. Calibration procedures, including generation of calibration curves and determination of converter efficiency, are found in Section 4.3.4.

4.3.1 Applicability

The total NO_y measurement principle and procedures are applicable to the measurement of ambient concentrations of NO and NO_y as part of PAMS networks. The data obtained using these procedures are intended for use in mathematical models that predict tropospheric O_3 trends.

4.3.2 Principle of Measurement

Ambient NO and NO_y concentrations are determined by photometrically measuring the light intensity at wavelengths greater than 600 nanometers from the chemiluminescent reaction of NO with O_3.[4,5,6] This principle is identical to that used for the measurement of NO and NO_2.

To measure NO_y, sample air is passed through a probe-mounted chemical reductant converter and the nitroxyl compounds present are reduced to NO.[7,8,9,10,11] NO, which commonly exists in ambient air, passes through the converter unchanged. The NO resulting from the reduction of these nitroxyl compounds, plus any native NO, is reacted with O_3 and the resulting chemiluminescent light is measured as the total NO_y concentration.

To measure NO separately and specifically, sample air is by-passed around the chemical reductant converter so that no reduction of the other nitroxyl compounds[10] to NO occurs. The NO (i.e., native NO only) is reacted with O_3 and the resulting chemiluminescent light is measured as the NO concentration.

It should be noted that field and laboratory studies have been conducted to compare various NO_y measurement techniques.[11,12] Application of the total NO_y measurement principle and procedures using a heated chemical reductant surface is supported by these studies. However, qualifiers do apply.

4.3.3 Measurement Apparatus

The NO_y instrument presented in these procedures is based on the design of an approved NO_2 instrument. Details on the differences between the configuration of the NO_y instrument and the EPA-approved NO_2 instrument are presented below.

4.3.3.1 Configuration

The configuration of the NO_y instrument is very similar to that of the EPA-approved NO_2 instrument. The primary differences between the configurations are the locations of the converter, particulate filter(s), flow control capillary, and the 3-way solenoid valve used for mode control. Differences between the NO_y instrument configuration and the EPA-approved NO_2 instrument configuration can be better understood by comparing the NO_y instrument flow

schematic presented in Figure 4-2 to the flow schematic of the approved NO_2 instrument presented in Figure 4-1.

The NO_y instrument uses a heated molybdenum chemical reductant converter that also serves as the sample probe inlet to the instrument. The converter is positioned at a program specific height above ground level within the range of 3 to 15 meters as required for enhanced O_3 monitoring programs. Because the converter serves as the sample probe inlet, conversion of PAN, HNO_3, and other nitroxyl compounds to NO is maximized because the surface area, and consequently surface adsorption of these compounds that typically occurs prior to reaching the converter, is minimized. It is critical to the performance and longevity of the reductant material that it not be overheated. The converter operating temperature is actively controlled at 325°C (±20°C). Separate sample transfer lines are used for the NO_y and NO channels, and another separate transfer line is used to deliver calibration and converter efficiency assessment standards to the sample inlet.

The EPA-approved NO_2 instrument incorporates a particulate filter that is located prior to the flow control capillary and the chemical reductant converter. In the NO_y instrument configuration, the particulate filter is located after the chemical reductant converter in the NO_y sample transfer line to further minimize surface area and consequently surface adsorption of nitroxyl compounds in the sample air. Because the NO channel uses a separate sample transfer line, a second separate particulate filter is installed.

The EPA-approved NO_2 instrument uses a 3-way solenoid valve (i.e., mode control valve), located prior to the chemical reductant converter, to route sample gas through or around the chemical reductant converter depending on whether the instrument is in the NO or NO_2 mode. In the NO_y instrument configuration, the mode control valve performs the same function but is located after the chemical reductant converter to reduce surface area and surface effects.

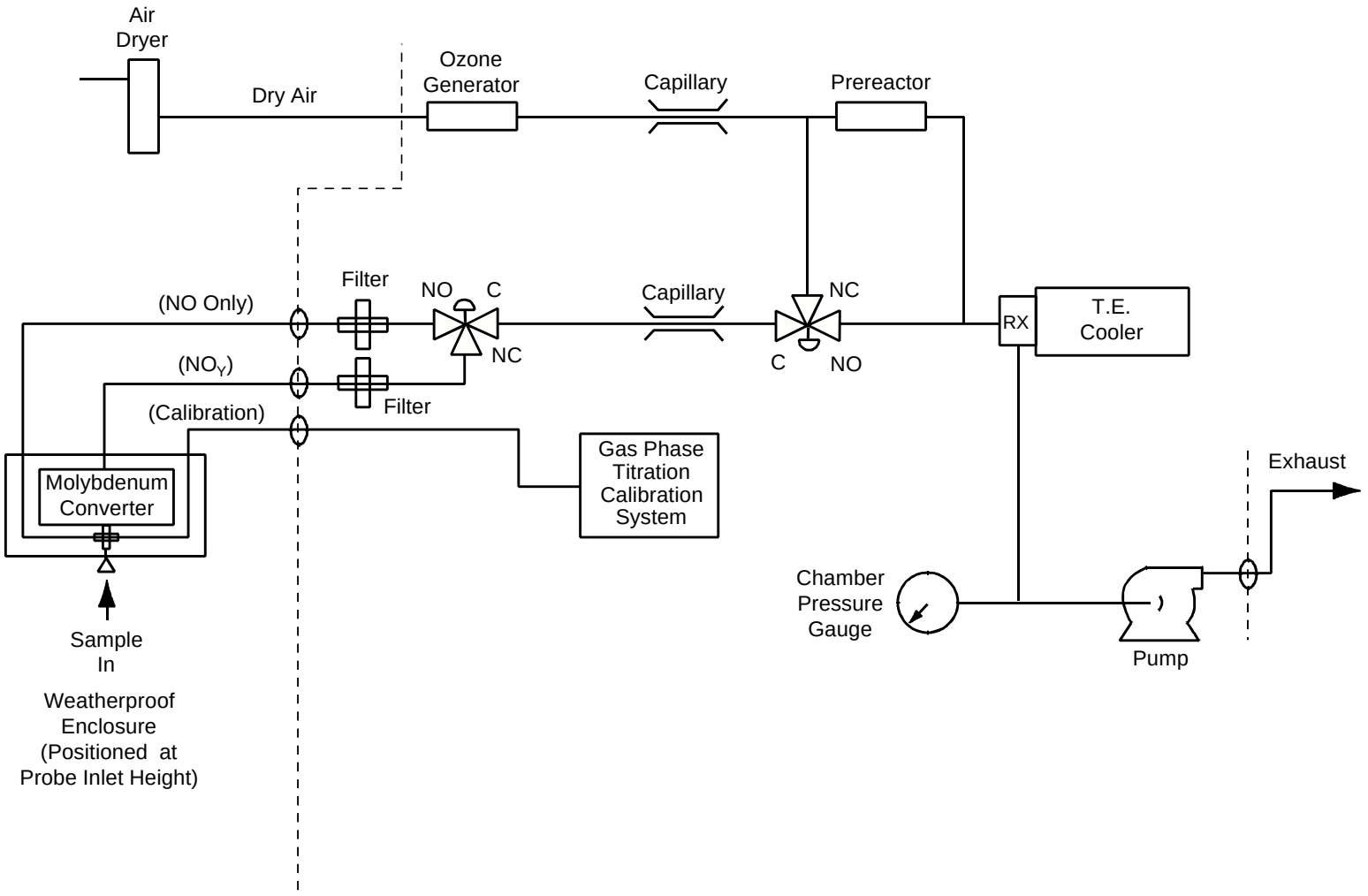

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Figure 4-2. Flow Schematic of the Reconfigured NO_y Instrument for PAMS Application

The EPA approved NO_2 instrument incorporates a glass capillary to control the sample air flow rate through the instrument. The capillary is located prior to the mode control valve and chemical reductant converter. In the NO_y instrument configuration, the flow control capillary is located after the chemical reductant converter and mode control valve. Positioning the capillary after the mode control valve allows the flow rate through the separate NO and NO_y sample transfer lines to be controlled equally using only one flow control device.

4.3.3.2 Reconfiguration

The reconfiguration of the commercially available NO_x instrument into the NO_y instrument applicable to PAMS requires modification of elements of the plumbing (i.e., the flow pattern) and electronics (i.e., the converter temperature control system) of the instrument. Modifications to the sampling station must also be made to accommodate the PAMS NO_y instrument configuration. General information on these modifications is presented below. Specific details on modifications must be obtained from individual manufacturers.

Note: Refer as needed to Figure 4-2 and the instrument manual supplied by the manufacturer while performing the modifications. All modifications should be made in strict accordance with applicable ordinances (e.g., OSHA Regulations, electrical codes, zoning requirements, etc.).

4.3.3.2.1 Shelter

Attach an open-bottomed weatherproof enclosure (i.e., unpainted aluminum or stainless steel), sized (i.e., approximately 12 in. high, 6 in. wide, and 7 in. deep) to accommodate the converter assembly to a 4 ft. long sampling tower mast. Attach the mast with enclosure to the sampling tower at the sample probe inlet height specified in the monitoring program requirements. Attach one end of a length of 1-1/2 in. O.D. flexible conduit to the weatherproof enclosure. Route the flexible conduit along the mast, down the tower, and into the shelter, securing as required to provide adequate support.

4.3.3.2.2 Plumbing

The following modifications are performed outside the instrument chassis:

(a) Remove the converter assembly from the chassis of the instrument and mount it in the weatherproof enclosure so that the inlet of the converter faces down toward the open bottom of the enclosure. Connect a 3/8 in. "Cross" fitting to the inlet of the converter using ancillary fittings as required to insure proper mating.

(b) Extend a length of uniquely identified 1/4 in. O.D. thick wall Teflon® tubing through the flexible conduit from the shelter into the weatherproof enclosure. Connect this uniquely identified Teflon® tube to the outlet of the converter to serve as the NO_y sample transfer line.

(c) Extend a length of uniquely identified 1/4 in. O.D. thick wall Teflon® tubing through the flexible conduit from the shelter into the weatherproof enclosure. Connect this uniquely identified Teflon® tube to one of the side ports of the 3/8 in. "Cross" fitting using ancillary fittings as required to insure proper mating to serve as the NO sample transfer line.

(d) Extend a length of uniquely identified 3/8 in. O.D. thick wall Teflon® tubing through the flexible conduit from the shelter into the weatherproof enclosure. Connect this uniquely identified Teflon® tube to the remaining side port of the "Cross" fitting to serve as the calibration and converter efficiency assessment standards transfer line. Connect the end of the Teflon® tube located in the shelter to the outlet of the calibration system (refer to Section 4.3.4.1).

Note: The bottom port of the "Cross" fitting is left open. This open port serves as the sample air inlet during monitoring and as the excess calibration standard gas vent during calibration.

The following modifications are performed inside of the instrument chassis:

(a) Remove and replumb the flow rate control capillary so that it is connected to the common port (C) of the mode control solenoid valve.

(b) Remove and replumb the particulate filter assembly so that the outlet of the particulate filter assembly is connected to the normally closed port (NC) of the mode control solenoid valve. Attach the appropriate Teflon® tube leading from the sampling probe to the inlet of the particulate filter assembly.

(c) Plumb a second particulate filter assembly so that the outlet of the particulate filter assembly is connected to the normally open port (NO) of the mode control solenoid valve. Attach the appropriate Teflon® tube leading from the sampling probe to the inlet of the particulate filter assembly.

4.3.3.2.3 Electronics

The following modifications are performed outside of the instrument chassis:

(a) Extend a length of thermocouple wire (i.e., type K - Chromel/Alumel, 16 gauge solid core, twisted pair with stainless steel overbraiding) through the flexible conduit from the shelter into the weatherproof enclosure. Connect the thermocouple wire to the thermocouple located in the converter. Ensure that the chromel wires are mated and that the alumel wires are mated.

(b) Extend a length of power wire (i.e., two conductors with ground, 14 gauge solid core copper, rated for outdoor use) through the flexible conduit from the shelter into the weatherproof enclosure. Connect the two conductors of the power wire to the heater located in the converter. Connect the ground wire directly to the weatherproof enclosure using a screw and nut.

The following modifications are performed inside of the instrument chassis:

(a) Connect the thermocouple wire (i.e., end located in the shelter) to the converter temperature control board. Ensure that the chromel and alumel wires are attached to the correct terminals (refer to the manufacturer's instrument manual).

(b) Connect the power wire (i.e., end located in the shelter) to the converter temperature control board. Ensure that the two conductors of the power wire are attached to the correct terminals (refer to the manufacturer's instrument manual). Connect the ground wire directly to the chassis ground of the instrument.

4.3.4 Calibration

Calibration of NO_y instruments is accomplished by gas phase titration (GPT) of an NO standard with O_3. Major equipment/components required are a stable O_3 generator, a chemiluminescence NO_y instrument with strip chart recorder(s), and an NO concentration standard. The principle of this calibration technique is based upon the rapid gas phase reaction between NO and O_3 to produce stoichiometric quantities of NO_2 in accordance with the following equation:[13]

$$(NO + O_3) \rightarrow (NO_2 + O_2) \qquad \textbf{(4-3)}$$

When the NO concentration is known, the concentration of NO_2 can be determined. Ozone is added to excess NO in a dynamic calibration system, and the NO channel of the chemiluminescence NO_y instrument is used as an indicator of changes in NO concentration. Upon the addition of O_3, the decrease in NO concentration observed on the calibrated NO channel is equivalent to the concentration of NO_2 produced. The amount of NO_2 generated may be varied by adding variable amounts of O_3 from a stable uncalibrated O_3 generator.[14]

Note: Because the principle, apparatus, and procedures used to calibrate the NO_y instrument are consistent with calibration of NO_x and NO_y instruments, it should be possible to calibrate both types of instruments simultaneously. However, the large quantity of calibration gas required may render simultaneous calibration of NO_x and NO_y instruments impractical.

4.3.4.1 Apparatus

Figure 4-3 presents a schematic of a typical GPT calibration system and shows the suggested configuration of the components listed below. All connections between components in the calibration system downstream from the O_3 generator should be constructed of glass, Teflon®, or other nonreactive material.

4.3.4.1.1 Air Flow Controllers

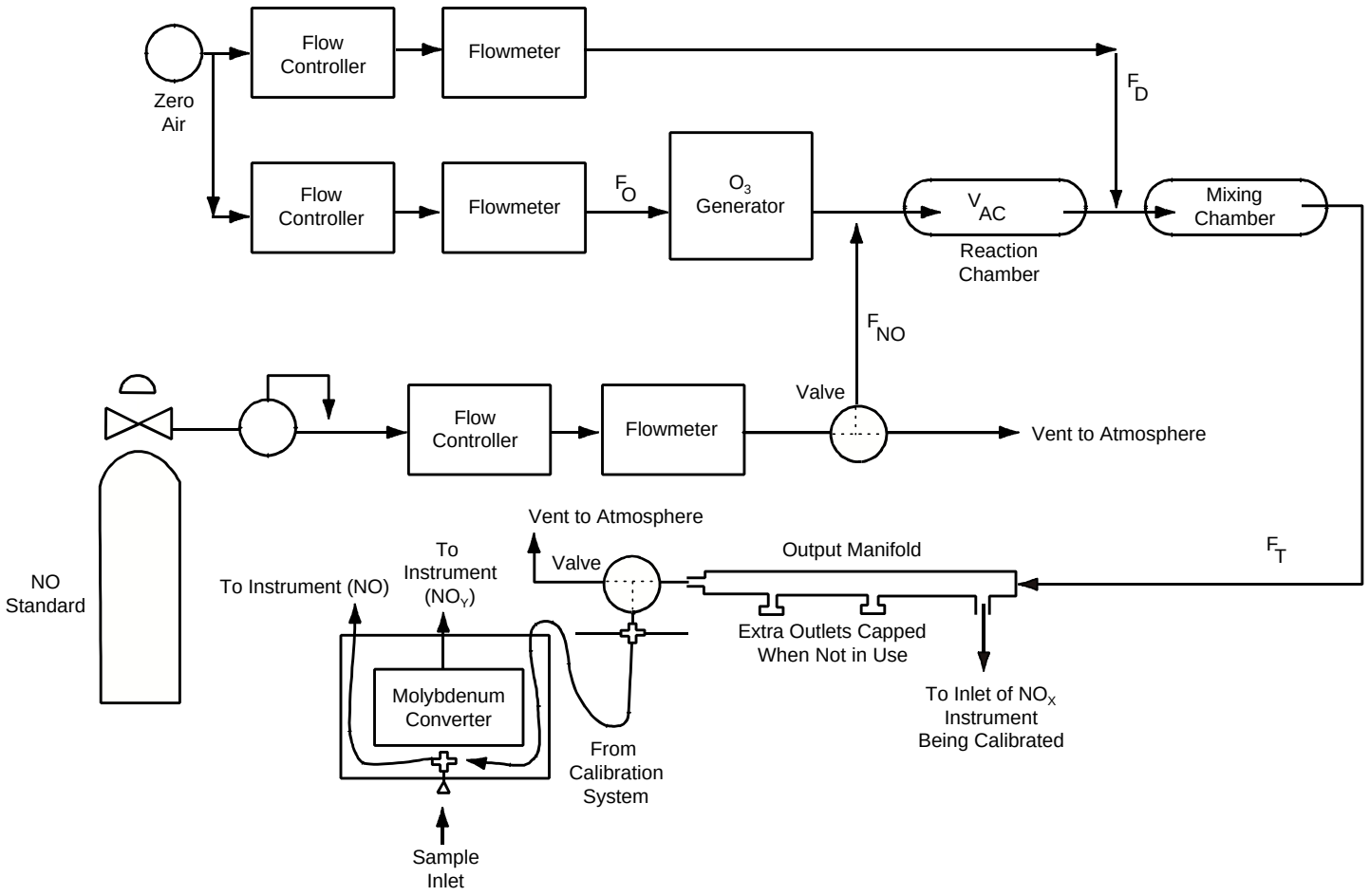
Devices capable of maintaining constant air flows within ±2% of the required flow rate.

4.3.4.1.2 NO Flow Controller

A device capable of maintaining constant NO flows within ±2% of the required flow rate. Component parts in contact with the NO should be made of a nonreactive material.

4.3.4.1.3 Air Flowmeters

Calibrated flowmeters capable of measuring and monitoring air flow rates with an accuracy of ±2% of the measured flow rate.



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F_D = flow of diluent gas
F_O = flow of ozonated gas
F_{NO} = flow of NO
F_T = total flow

Figure 4-3. Flow Schematic of a Typical Gas Phase Titration Calibration System

4.3.4.1.4 NO Flowmeter

A calibrated flowmeter capable of measuring and monitoring NO flow rates with an accuracy of ±2% of the measured flow rate. Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.

4.3.4.1.5 Pressure Regulator For Standard NO Cylinder

The regulator must have a stainless steel diaphragm and internal parts and a suitable delivery pressure.

4.3.4.1.6 Ozone Generator

The generator must be capable of generating sufficient and stable levels of O_3 for reaction with NO to generate NO_2 concentrations in the range required. Ozone generators of the electric discharge type may produce NO and NO_2 and are not recommended. Photolytic O_3 generators are recommended.

4.3.4.1.7 Valve

A valve used to divert the NO flow when zero air is required at the manifold. The valve should be constructed of glass, Teflon®, or other nonreactive material.

4.3.4.1.8 Reaction Chamber

A chamber, constructed of glass, Teflon®, or other nonreactive material, for the quantitative reaction of O_3 with excess NO. The chamber should be of sufficient volume such that the residence time meets the requirements specified in Section 4.3.4.3. For practical reasons, residence time should be less than 2 minutes.

4.3.4.1.9 Mixing Chamber

A chamber constructed of glass, Teflon®, or other nonreactive material and designed to provide thorough mixing of reaction products and diluent air. The residence time is not critical when the dynamic parameter specification given in Section 4.3.4.3 is met.

4.3.4.1.10 Output Manifold

The output manifold should be constructed of glass, Teflon®, or other non-reactive material and should be of sufficient diameter to ensure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to ensure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

4.3.4.1.11 Valve

A valve used to isolate the calibration line (i.e., Teflon® line used to deliver standard gases to the NO_y instrument sample inlet during calibration) when the instrument is monitoring. The valve must be sized to ensure atmospheric pressure at the manifold and should be constructed of glass, Teflon®, or other nonreactive material.

4.3.4.2 Reagents

4.3.4.2.1 NO Concentration Standard

Gas cylinder standard containing 50 to 100 ppm NO in N_2 with less than 1 ppm NO_2. This standard must be traceable to a National Institute of Standards and Testing (NIST) NO in N_2 Standard Reference Material (SRM 1683 or SRM 1684), an NBS NO_2 Standard Reference Material (SRM 1629), or an NBS/ EPA-approved commercially available Certified Reference Material (CRM).[15] A recommended protocol[16] for certifying NO gas cylinders against either a NO SRM or CRM is given in Section 2.0.7 of the reference. Procedures[17] for certifying a NO gas

cylinder against a NIST NO_2 SRM and for determining the amount of NO_2 impurity in a NO cylinder are presented in the reference.

4.3.4.2.2 Zero Air

Zero air is free of contaminants that are detectable on the NO/NO_y analyzer or that react with either NO, O_3, or NO_2 in the gas phase titration. A procedure for generating zero air is given in the reference.[14]

4.3.4.3 Dynamic Parameter Specification

1. The O_3 generator air flow rate (F_0) and NO flow rate (F_{NO}) (see Figure 4-3) must be adjusted such that the following relationship holds:

$$P_R = [NO]_{RC} \times t_R = 2.75 \text{ ppm} - \text{minutes} \quad \textbf{(4-4)}$$

$$[NO]_{RC} = [NO]_{STD} \left(\frac{F_{NO}}{F_o + F_{NO}} \right) \quad \textbf{(4-5)}$$

$$t_R = \frac{V_{RC}}{F_o + F_{NO}} \prec 2 \text{ minutes} \quad \textbf{(4-6)}$$

where:

P_R = dynamic parameter specification, determined empirically, to ensure complete reaction of the available O_3, ppm-minute

$[NO]_{RC}$ = NO concentration in the reaction chamber, ppm

t_R = residence time of the reactant gases in the reaction chamber, minute

$[NO]_{STD}$ = concentration of the undiluted NO standard, ppm

F_{NO} = NO flow rate, scm^3/min

F_O = O_3 generator air flow rate, scm^3/min

V_{RC} = volume of the reaction chamber, scm^3

2. The flow conditions to be used in the GPT system are determined by the following procedure:

   (a) Determine the total flow required at the output manifold (F_T=analyzer demand plus 50% excess). If a conventional NO_x instrument is being calibrated simultaneously with the NO_y instrument, F_T must reflect the demand of both.

   (b) Establish $[NO]_{OUT}$ as the highest NO concentration (ppm) which will be required at the output manifold. $[NO]_{OUT}$ should be approximately equivalent to 90% of the upper range limit (URL) of the NO_2 concentration range to be covered.

   (c) Determine F_{NO} as follows:

$$F_{NO} = \frac{[NO]_{OUT} \times F_t}{[NO]_{STD}} \qquad \textbf{(4-7)}$$

   (d) Select a convenient or available reaction chamber volume. Initially, a trial V_{RC} may be selected to be in the range of approximately 200 to 500 scm^3.

   (e) Compute F_O as follows:

$$F_O = \sqrt{\frac{[NO]_{STD} \times F_{NO} \times V_{RC}}{2.75}} - F_{NO} \qquad \textbf{(4-8)}$$

(f) Compute t_R as follows:

$$t_R = \frac{V_{RC}}{F_O + F_{NO}} \quad \textbf{(4-9)}$$

Verify that $t_R < 2$ minutes. If not, select a reaction chamber with a smaller V_{RC}.

(g) Compute the diluent air flow rate as follows:

$$F_D = F_T - F_O - F_{NO} \quad \textbf{(4-10)}$$

where:

F_{NO} = NO flow rate, scm^3/min

$[NO]_{OUT}$ = the highest NO concentration (ppm) that will be required at the output manifold

F_T = analyzer demand plus 50% excess

$[NO]_{STD}$ = concentration of the undiluted NO standard, ppm

F_O = O_3 generator air flow rate, scm^3/min

V_{RC} = volume of the reaction chamber, scm^3

t_R = residence time of the reactant gases in the reaction chamber, minute

F_D = diluent air flow rate, scm^3/min

(h) If F_O turns out to be impractical for the desired system, select a reaction chamber having a different V_{RC} and recompute F_O and F_D.

Note: A dynamic parameter lower than 2.75 ppm-minutes may be used if it can be determined empirically that quantitative reaction of O_3 with NO occurs. A procedure for making this determination as well as a more detailed discussion of

the above requirements and other related considerations is included in the reference.[14]

4.3.4.4 Calibration Procedure

The calibration procedure is presented below.

1. Assemble a dynamic calibration system configured like the one shown in Figure 4-3.

2. Ensure that all flowmeters are calibrated under the conditions of use against a primary standard (i.e., bubble flow meter or wet-test meter). All volumetric flow rates should be corrected to 25°C and 760 mm Hg.

3. Precautions must be taken to remove O_2 and other contaminants from the NO pressure regulator and delivery system prior to the start of calibration to avoid any conversion of the standard NO to NO_2. Failure to do so can cause significant errors in calibration. This problem may be minimized by (1) carefully evacuating the regulator after the regulator has been connected to the cylinder and before opening the cylinder valve; (2) thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; and (3) not removing the regulator from the cylinder between calibrations. If the regulator is removed, steps 1 and 2 should be repeated.

4. Select the operating range of the NO/NO_y instrument to be calibrated. In order to obtain maximum precision and accuracy, the NO and NO_y channels of the instrument should be set to the same range.

5. Connect the recorder output cable(s) of the NO/NO_y instrument to the input terminals of the strip chart recorder(s). All adjustments to the instrument should

be performed based on the appropriate strip chart readings. **References to instrument responses in the procedures given below refer to recorder responses.**

6. Determine the GPT flow conditions required to meet the dynamic parameter specification as indicated in Section 4.3.4.3.

7. Adjust the diluent air and O_3 generator air flows to obtain the flows determined in Section 4.3.4.3, step 2. The total air flow must exceed the total demand of the instrument(s) connected to the output manifold to ensure that no back diffusion of ambient air occurs. Allow the instrument to sample zero air until stable NO and NO_y responses are obtained. After the responses have stabilized, adjust the instrument zero control(s). Record the stable zero air responses as ZNO and ZNO_y.

Note: Some instruments may have separate zero controls for NO and NO_y, while still others may have only one zero control common to both channels. Offsetting the instrument zero adjustments to +5% of scale is recommended to facilitate observing negative zero drift.

8. Prepare the NO and NO_y calibration curves as follows:

   (a) Adjustment of NO span control. Adjust the NO flow from the standard NO cylinder to generate a NO concentration of approximately 80% of the URL of the NO range. The exact NO concentration is calculated from:

$$[NO]_{OUT} = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_O + F_D} \qquad \textbf{(4-11)}$$

where:

$[NO]_{OUT}$ = the highest NO concentration (ppm) that will be required at the output manifold

F_{NO} = NO flow rate, scm^3/min

$[NO]_{STD}$ = concentration of the undiluted NO standard, ppm

F_O = O_3 generator air flow rate, scm^3/min

F_D = diluent air flow rate, scm^3/min

Sample this NO concentration until the NO and NO_y responses have stabilized. Adjust the NO span control to obtain a recorder response (percent scale) as indicated below:

$$\text{Recorder Response} = \left(\frac{[NO]_{OUT}}{URL} \times 100 \right) + ZNO \qquad \textbf{(4-12)}$$

where:

$[NO]_{OUT}$ = diluted NO concentration at the output manifold, ppm

URL = nominal upper range limit of the NO channel, ppm

ZNO = stable zero air response for NO, percent scale

Note: Some instruments may have separate span controls for NO and NO_y, while still others may have only one span control common to both channels. When only one span control is available, the span adjustment is made on the NO channel of the instrument.

If substantial adjustment of the NO span control is required, it may be necessary to recheck the zero and span adjustments by repeating Section 4.3.4.4, step 7 and step 8(a). Record the NO concentration and the instrument's NO response.

(b) Adjustment of NO_y span control. When adjusting the instrument's NO_y span control, the presence of any NO_2 impurity in the standard NO cylinder must be taken into account. The exact NO_y concentration is calculated from:

$$[NO_y]_{OUT} = \frac{F_{NO}\ ([NO]_{STD} + [NO_2]_{IMP})}{F_{NO} + F_O + F_D} \qquad \textbf{(4-13)}$$

where:

$[NO_y]_{OUT}$ = diluted NO_y concentration at the output manifold, ppm

F_{NO} = NO flow rate, scm^3/min

$[NO]_{STD}$ = concentration of the undiluted NO standard, ppm

$[NO_2]_{IMP}$ = concentration of NO_2 impurity in the standard NO cylinder, ppm

F_O = O_3 generator air flow rate, scm^3/min

F_D = diluent air flow rate, scm^3/min

Adjust the NO_y span control to obtain a recorder response (percent scale) as indicated below: where:

$$\left(\frac{[NO_y]_{OUT}}{URL} \text{ x } 100 \right) + ZNO_x \qquad \textbf{(4-14)}$$

$[NO_y]_{OUT}$ = diluted NO_y concentration at the output manifold, ppm

URL = nominal upper range limit of the NO channel, ppm

ZNO_y = stable zero air response for NO_y, percent scale

Note: If the instrument has only one span control, the span adjustment is made on the NO channel and no further adjustment is made for NO_y. If

substantial adjustment of the NO_y span control is required, it may be necessary to recheck the zero and span adjustments by repeating Section 4.3.4.4, step 7 and step 8(a). Record the NO_y concentration and the instrument's NO_y response.

(c) Generate several additional concentrations (at least five evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing F_{NO} or increasing F_D. For each concentration generated, calculate the exact NO and NO_y concentrations using Equations 4-11 and 4-13, respectively. Record the instrument's NO and NO_y responses for each concentration. Plot the instrument responses versus the respective calculated NO and NO_y concentrations and plot the NO and NO_y calibration curves and calculate the linear regression. For subsequent calibrations where linearity can be assumed, these curves may be checked with a two-point calibration consisting of a zero air point and NO and NO_y concentrations of approximately 80% of the URL.

9. Preparation of NO_2 Converter Efficiency Assessment Standards.

(a) Assuming the NO_y zero has been properly adjusted while sampling zero air as described in Section 4.3.4.4, step 7, adjust F_O and F_D as determined in Section 4.3.4.3, step 2. Adjust F_{NO} to generate a NO concentration near 90% of the URL of the NO range. Sample this NO concentration until the NO and NO_y responses have stabilized. Using the NO calibration curve obtained in Section 4.3.4.4, step 8, measure and record the NO concentration as $[NO]_{orig}$. Using the NO_y calibration curve obtained in Section 4.3.4.4, step 8, measure and record the NO_y concentration as $[NO_y]_{orig}$.

(b) Adjust the O_3 generator to generate sufficient O_3 to produce a decrease in the NO concentration equivalent to approximately 80% of the URL of the NO_2

range. The decrease must not exceed 90% of the NO concentration determined in Section 4.3.4.4, step 9(a). After the instrument responses have stabilized, record the resultant NO and NO_y concentrations as $[NO]_{rem}$ and $[NO_y]_{rem}$.

(c) Calculate the resulting NO_2 concentration from:

$$[NO_2]_{OUT} = \left([NO]_{orig} - [NO]_{rem}\right) + \left(\frac{F_{NO}\ ([NO_2]_{IMP})}{F_{NO} + F_O + F_D} \right) \qquad \textbf{(4-15)}$$

where:

$[NO_2]_{OUT}$ = diluted NO_2 concentration at the output manifold, ppm

$[NO]_{orig}$ = original NO concentration, prior to addition of O_3, ppm

$[NO]_{rem}$ = NO concentration remaining after addition of O_3, ppm

F_{NO} = NO flow rate, scm^3/min

$[NO_2]_{IMP}$ = concentration of NO_2 impurity in the standard NO cylinder, ppm

F_O = O_3 generator air flow rate, scm^3/min

F_D = diluent air flow rate, scm^3/min

(d) Maintaining the same F_{NO}, F_O, and F_D as in Section 4.3.4.4, step 9(a), adjust the ozone generator to obtain several other concentrations of NO_2 over the NO_y range (at least five evenly spaced points across the remaining scale are suggested). Calculate each NO_2 concentration using Equation 4-15 and record the corresponding instrument NO_y responses.

4.3.4.5 Determination of Converter Efficiency

For each NO_2 concentration generated (see Section 4.3.4.4, step 9), calculate the concentration of NO_2 converted from:

$$[NO_2]_{CONV} = [NO_2]_{OUT} - ([NO_y]_{orig} - [NO_y]_{rem}) \quad \textbf{(4-16)}$$

where:

$[NO_2]_{CONV}$ = concentration of NO_2 converted, ppm

$[NO_2]_{OUT}$ = diluted NO_2 concentration at the output manifold, ppm

$[NO_y]_{orig}$ = original NO_y concentration prior to addition of O_3, ppm

$[NO_y]_{rem}$ = NO_x concentration remaining after addition of O_3, ppm

Plot $[NO_2]_{CONV}$ (y-axis) versus $[NO_2]_{OUT}$ (x-axis) and plot the converter efficiency curve and calculate the linear regression. The slope of the curve times 100 is the average converter efficiency (EC). The EC must be greater than 96%; if it is less than 96%, replace or service the converter.

4.3.4.6 Frequency of Calibration

The frequency of calibration, as well as the number of points necessary to establish the calibration curve and the frequency of other performance checks, will vary from one instrument to another. The user's quality control program should provide guidelines for initial establishment of these variables and for subsequent verification and alteration as operational experience is accumulated. Manufacturers of instruments should include in their instruction/operation manuals information and guidance as to these variables and on other matters of operation, calibration, and quality control.

4.3.4.7 Analyzer Challenge

The instrument must be challenged annually, at the start of the sampling season. Additional challenges, at the beginning, middle, and end of the sampling season, are suggested. The optimum challenge would consist of a mixture of representative NO_y compounds, but there is presently no comprehensive commercial mixture covering a broad range of the compounds of potential interest available to be used as a challenge gas. To assess general instrument performance, the instrument should be challenged with NO, since this is the gas used for calibration. Additionally, the system should be assessed for its ability to measure other NO_y constituents by challenging the instrument with other candidate analytes such as 50 ppm *n*-propyl nitrite or nitric acid.

4.4 Nitric Acid Measurement

The NO_y measurement instrument described above can be obtained from the vendor in a modified configuration that allows for the separate measurement of total NO_y and nitric acid. This configuration is called the Model 42CW. The Model 42CW cycles between two separate converters. One of the converters has a nylon filter located at the inlet. Ambient nitric acid is absorbed by the nylon filter. The nitric acid concentration is determined as the difference between unfiltered total NO_y value and the value determined for the filtered channel.

4.5 References

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Section 5.0

Methodology for Determining Carbonyl Compounds in Ambient Air

Determination of ambient concentrations of carbonyl compounds is a requirement of 40 CFR Part 58,[1] Subpart E, enhanced O_3 network monitoring programs. Carbonyl compounds have been shown to contribute to the formation of photochemical O_3. Formaldehyde, acetaldehyde, and acetone are specifically required target compounds for PAMS; however, other carbonyl compounds may be added to the target list consistent with individual program objectives. The methodology used to accomplish carbonyl compounds monitoring is Compendium Method TO-11A.[2] Method TO-11A, presented in Appendix D, provides sensitive and accurate measurements of carbonyl compounds and involves sample collection and analysis procedures. In this method, a cartridge(s) containing a solid sorbent is used to capture the target compounds. Information on solid sorbents used is presented in Section 4.4 of Method TO-11A. Ozone has been identified as an interferent in the measurement of carbonyl compounds when using Method TO-11A. To eliminate this interference, removal or scrubbing of O_3 from the sample air stream is mandatory. Section 5.1 presents information on O_3 scrubbers. Sample analysis is accomplished using high performance liquid chromatography (HPLC) with ultraviolet/visible detection.

Under 40 CFR Part 58,[1] Subpart E, States are required to obtain 3-hour and 24-hour integrated measurements of carbonyl compounds at specified collection frequencies based on individual enhanced O_3 monitoring 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 and minimum network monitoring requirements for carbonyl compounds are presented in Table 5-1. *(Note: This section is intended to be independent of other sections. Figures, tables, and text from other sections are repeated as required.)* The sample collection frequencies necessitate the use of an automated multiple-event sample collection approach. Section 5.2 presents information on multiple-event sample collection

Table 5-1 . PAMS Minimum Monitoring Network Requirements

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

[1]Whichever area is larger.

[2]Frequency Requirements Are As Follows:

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

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

C = Eight 3-hour samples on the 5 peak O_3 days plus each previous day, eight 3-hour samples every sixth day and one additional 24-hour sample every sixth day during the monitoring period.

D = Eight 3-hour samples every third day during the monitoring period.

E = Eight 3-hour samples on the 5 peak O_3 days plus each previous day and eight 3-hour samples every sixth day during the monitoring period.

F = Eight 3-hour samples on the 5 peak O_3 days plus each previous day, eight 3-hour samples every sixthe day and one additional 24-hour sample every sixth day during the monitoring period.

Table 5-1 . PAMS Minimum Monitoring Network Requirements (Continued)

The minimum sampling frequency requirements for speciated VOC monitoring are prescribed in 40 CFR Part 58, Subpart E, Appendix D - Network Design for State and Local Air Monitoring Stations (SLAMS), National Air Monitoring Stations (NAMS), and Photochemical Assessment Monitoring Stations (PAMS). Section 4.3 - Monitoring Period requires, at a minimum, that O_3 precursor monitoring be conducted annually throughout the months of June, July, and August when peak O_3 values are expected. Section 4.4 - Minimum Monitoring Network Requirements specifies the minimum required number and type of monitoring sites and sampling frequency requirements based on the population of the affected MSA/CMSA or nonattainment area, whichever is larger. The minimum speciated VOC sampling frequency requirements are summarized by site type below:

- Site Type 1 - Eight 3-hour samples every third day and one additional 24-hour sample every sixth day during the monitoring period; or eight 3-hour samples on the 5 peak O_3 days plus each previous day and eight 3-hour samples and one 24-hour sample every sixth day, during the monitoring period.

- Site Type 2 - (population less than 500,000) - Same as Site Type 1.

- Site Type 2 - (population greater than 500,000) - Eight 3-hour samples every day during the monitoring period and one additional 24-hour sample every sixth day year around.

- Site Type 3 - (population greater than 500,000) - Same as Site Type 1.

- Site Type 4 - (population more than 2,000,000) - Same as Site Type 1.

Samples collected should represent a time-integrated average for the required sampling period. It is important to understand that the 3-hour sample integration period is a maximum requirement in the sense that samples can be collected more frequently at shorter sampling intervals (i.e., three 1-hour periods) but not less frequently for longer sampling intervals.

systems, including a generic equipment description and operating procedure and recommended specifications applicable to evaluation and procurement.

5.1 Ozone Scrubbers

The EPA has determined through laboratory tests that O_3 present in ambient air interferes with the measurement of carbonyl compounds when using Method TO-11A. Ozone can interfere with carbonyl analyses in three ways:

- The ozone reacts with the 2,4-dinitrophenylhydrazine (DNPH) on the cartridge, making the DNPH unavailable for derivatizing carbonyl compounds;
- The ozone also degrades the carbonyl derivatives formed on the cartridge during sampling; and
- If the analytical separation is insufficient, the DNPH degradation products can coelute with target carbonyl derivatives.

The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Carbonyl compound losses have been estimated to be as great as 48% on days when the ambient O_3 concentration reaches 120 ppbv. Eliminating this measurement interference problem by removing or scrubbing O_3 from the sample air stream prior to collection of the carbonyl compounds is a mandatory facet of carbonyl compounds sample collection for enhanced O_3 monitoring programs. Two types of O_3 scrubbers, the Denuder O_3 scrubber and the Cartridge O_3 scrubber, have been developed. Both the Denuder and Cartridge O_3 scrubbers use potassium iodide (KI) as the scrubbing agent. Scrubbing is based on the reaction of O_3 with KI, specifically:

$$O_3 + 2I^- + H_2O \rightarrow I_2 + O_2 + 2OH^- \qquad \textbf{(5-1)}$$

where:

O_3	=	ozone (ambient)
H_2O	=	water (ambient)
I^-	=	the iodide ion from potassium iodide forming molecular iodine (I_2), oxygen (O_2), and the hydroxide ion (OH^-)

Both O_3 scrubber designs effectively remove O_3 at sample collection flow rates up to 1 L/minute and have sufficient scrubbing capacity to meet the needs of carbonyl compounds measurement for enhanced O_3 monitoring programs.

This section presents details of the two types of O_3 scrubber equipment and recommended procedures for their use.

5.1.1 Denuder Ozone Scrubber

The Denuder O_3 Scrubber is a copper tube coated internally with a saturated solution of KI. The tube is coiled and housed in a temperature controlled chamber that is heated to, and maintained at, 66°C during sample collection. Heating prevents condensation from occurring in the tube during sampling. The scrubber is connected to the inlet of the sample collection system. Sample air is extracted from a sample probe and distribution manifold (see Section 5.2.3) and pulled through the scrubber by an oilless vacuum pump. Ozone in the sample air is converted (i.e., scrubbed) by the chemical reaction previously described in Section 5.1.

The Denuder O_3 Scrubber is reusable. The copper tube should be recoated with a saturated solution of KI after each six months of use. The Denuder O_3 Scrubber prepared as described in TO-11A has been found to effectively remove ozone from the air stream for up to 100,000 ppb-hours. Thus, the scrubber will last for six months of 24-hour sampling on every sixth day when sampling air with an average ozone concentration of 120 ppbv. To recoat the

denuder, fill the copper tube with a saturated solution of KI in water. Allow the solution to remain in contact with the tube for a few minutes. Then, drain the tube. Dry the tube by blowing a stream of clean air or nitrogen through the tube for about one hour.

An alternative to using a KI coated copper tube is to use a modified Dasibi ozone scrubber device. Replace the manganese dioxide coated screens with 15 KI coated copper or stainless steel screens assembled in a cartridge holder. Wash the screens in pure water in a sonic bath. Dry the screens. Then, coat the screens by dipping them into a saturated KI solution in water. Air dry the KI coated screens. This procedure deposits about 4 mmoles or about 700 mg of KI over a sandwich of 15 two-inch diameter screens. Assemble the coated screens in the Dasibi encasement with a fiberglass filter at each end. Close and seal the encasement including the O-rings with the screws. Based on this removal capacity, this scrubber will last approximately 300 days when sampling air with an average ozone concentration of 120 ppbv at a rate of 1 L/min.

5.1.1.1 Denuder Ozone Scrubber Equipment

Figure 5-1 presents a cross-sectional view of the Denuder O_3 Scrubber. The scrubber is comprised of the following components:

Copper tubing - A 3 foot length of 1/4-inch O.D. copper tubing, coiled into a spiral approximately 2 inches in diameter. Used as the body of the O_3 scrubber.

Potassium iodide - The inside surface of the copper coil is coated with a saturated solution of ACS Reagent Grade KI. Used to provide the O_3 scrubbing mechanism.

Cord heater - A 2 foot long cord heater, rated at approximately 80 watts, wrapped around the outside of the copper coil. Used to provide heat to prevent condensation of water or organic compounds from occurring within the coil.

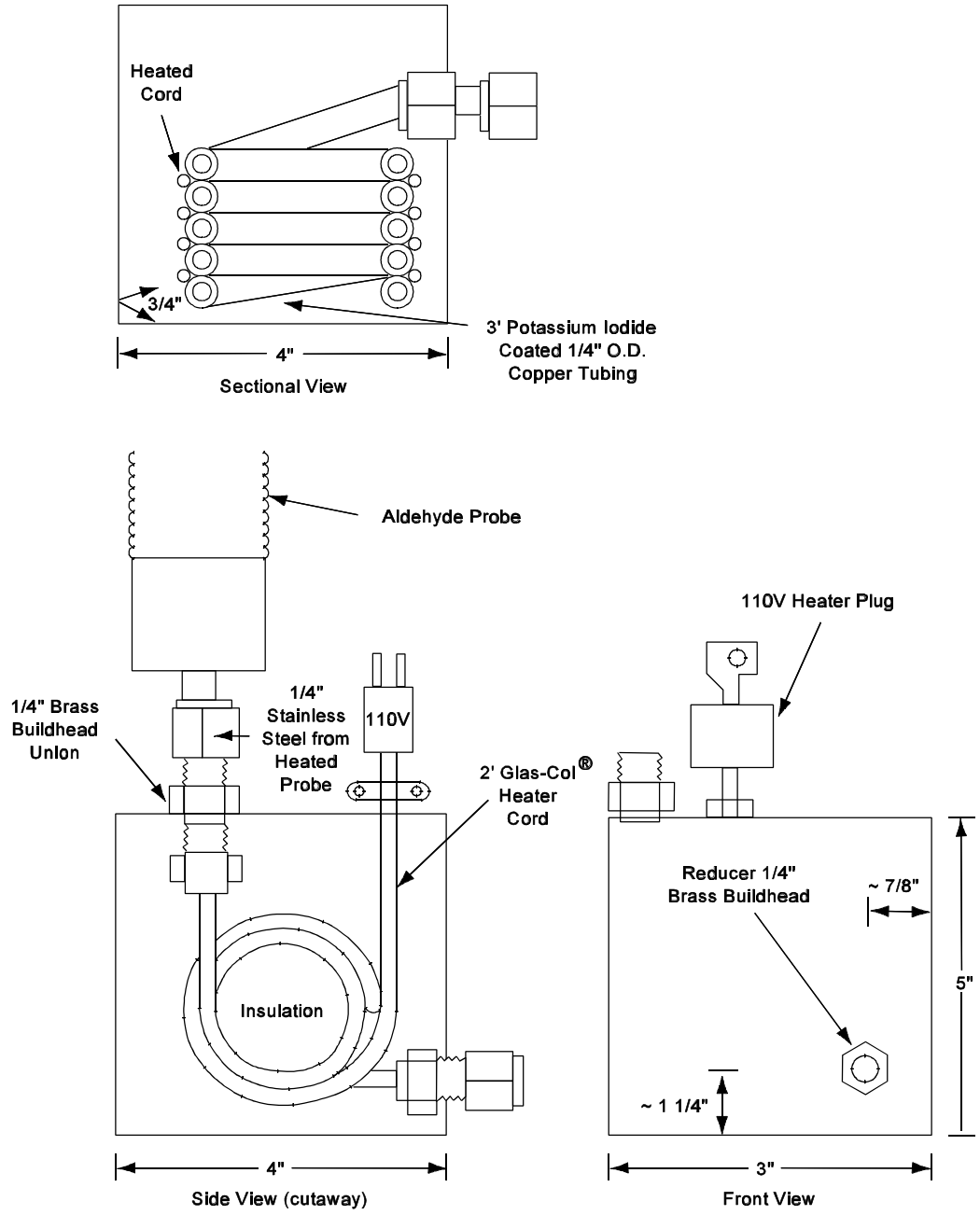

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Figure 5-1. Cross-Sectional View of the Denuder O_3 Scrubber

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

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

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

Chassis box - Conveniently sized aluminum enclosure. Used to contain the fittings, coated copper tube, heater, and thermocouple.

5.1.1.2 Denuder Ozone Scrubber Operational Procedure

Recommended procedural steps for operation of the Denuder O_3 Scrubber are as follows:

(1) Connect the inlet of the Denuder O_3 scrubber to the sample probe and distribution manifold (see Figure 5-1).

(2) Connect the outlet of the Denuder O_3 scrubber to the sample collection system inlet.

(3) Set the temperature controller to maintain the scrubber at 66°C.

(4) Conduct sampling in accordance with the recommended procedures for operating multiple-event sample collection systems as described in Section 5.2.2 and/or Method TO-11A sampling procedures as described in Section 5.11 (see Appendix D).

5.1.2 Cartridge Ozone Scrubber

The Cartridge O_3 Scrubber is a standard Sep-Pak® Plus cartridge (i.e., identical in size and shape to the precoated DNPH Silica Sep-Pak® cartridge) filled with approximately 1 gram of ACS Reagent Grade KI. The scrubber is positioned at the inlet of the sample collection system. Sample air is extracted from the sample probe and distribution manifold (see Figure 5-1) and

pulled through the O_3 scrubber by an oilless vacuum pump. Ozone in the sample air is converted (i.e., scrubbed) by the chemical reaction previously described in Section 5.1.

The Cartridge O_3 Scrubber is commercially available (i.e., Waters Corporation) and is disposable. The theoretical removal capacity of the scrubber, based on 100% consumption of KI, is 200 mg of O_3. Based on experience in the field, the cartridge O_3 scrubber should be replaced every three weeks.

5.1.2.1 Cartridge Ozone Scrubber Equipment

Figure 5-2 presents a cross-sectional view of the Cartridge O_3 Scrubber. The scrubber is comprised of the following components:

Cartridge housing - A two-part plastic vessel with an O.D. of approximately ½ inches and an overall length of approximately 1-5/8 inches. One of the parts has a female Luer style connector that serves as the scrubber inlet. The other part has a male Luer style connector that serves as the scrubber outlet. Used to contain the scrubber media.

Potassium iodide - The scrubber medium is granular ACS Reagent Grade KI. Used to provide the ozone scrubbing mechanism.

Inlet and outlet filters - Polyethylene fritted filters located inside the cartridge housing at the inlet and outlet ends. Used to retain the scrubber media inside the cartridge housing during sampling.

Compression ring - An aluminum ring sized to fit around the outside of the two cartridge housing parts and seal them through compression. Used to provide a secure leak-free seal between the two cartridge housing parts.

5.1.2.2 Cartridge Ozone Scrubber Operational Procedure

Recommended procedural steps for operation of the Cartridge O_3 Scrubber are as follows:

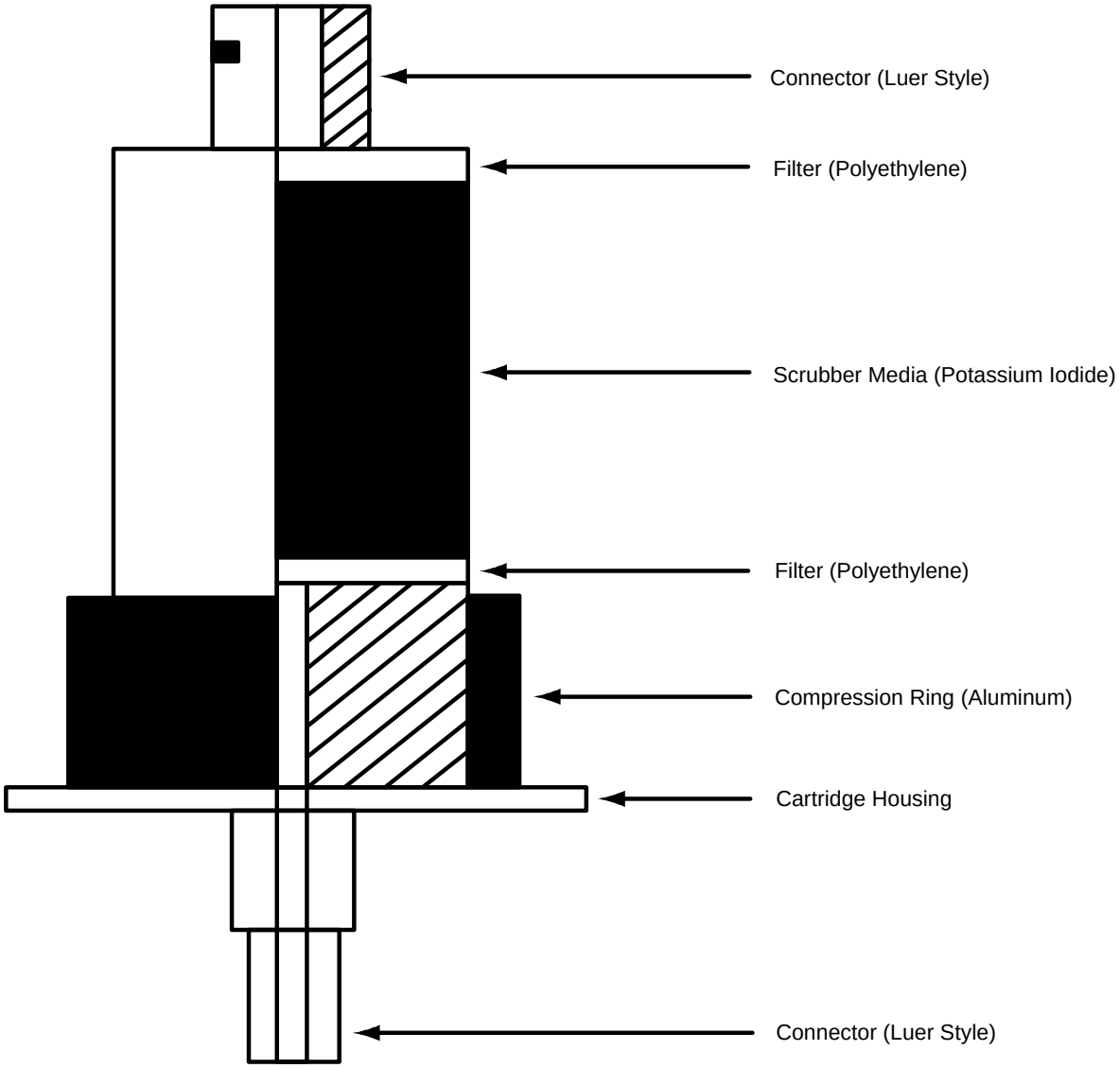

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Figure 5-2. Cross-Section View of the Cartridge O_3 Scrubber

1. Connect the inlet of the Cartridge O_3 scrubber to the sample probe and distribution manifold (see Section 2.4.1.1).

2. Connect the outlet of the Cartridge O_3 scrubber to the sample collection system inlet.

3. Ensure that a leak-free connection is obtained.

4. Conduct sampling in accordance with the recommended procedures for operating multiple-event sample collection systems as described in Section 5.2.2 and/or Method TO-11A sampling procedures as described in Section 5.10 of Method TO-11A (See Appendix D). **Note: Heating of the cartridge ozone scrubbers to 35°C may be advisable under certain circumstances to prevent condensation of water.**

5.2 Multiple-event Sample Collection Systems

The use of solid sorbent cartridge sample collection systems to satisfy the sample collection frequencies specified in Table 5-1 necessitates the use of multiple-event sample collection systems. Multiple-event collection systems should be capable of unattended operation in order to allow for multiple sample collection in a practical, non-labor intensive manner. Multiple-event sampling systems are manufactured commercially or can be custom manufactured by the user for a specific application. Several multiple-event sampling systems are commercially available.

The following sections generally describe multiple-event sampling equipment, procedures, and specifications. Also, recommended system specifications applicable to the evaluation and procurement of multiple-event sampling systems are presented.

5.2.1 Multiple-event Collection System Equipment

A typical multiple-event sampling system configuration is presented in Figure 5-3. The multiple-event cartridge sampling system is comprised of the following primary components:

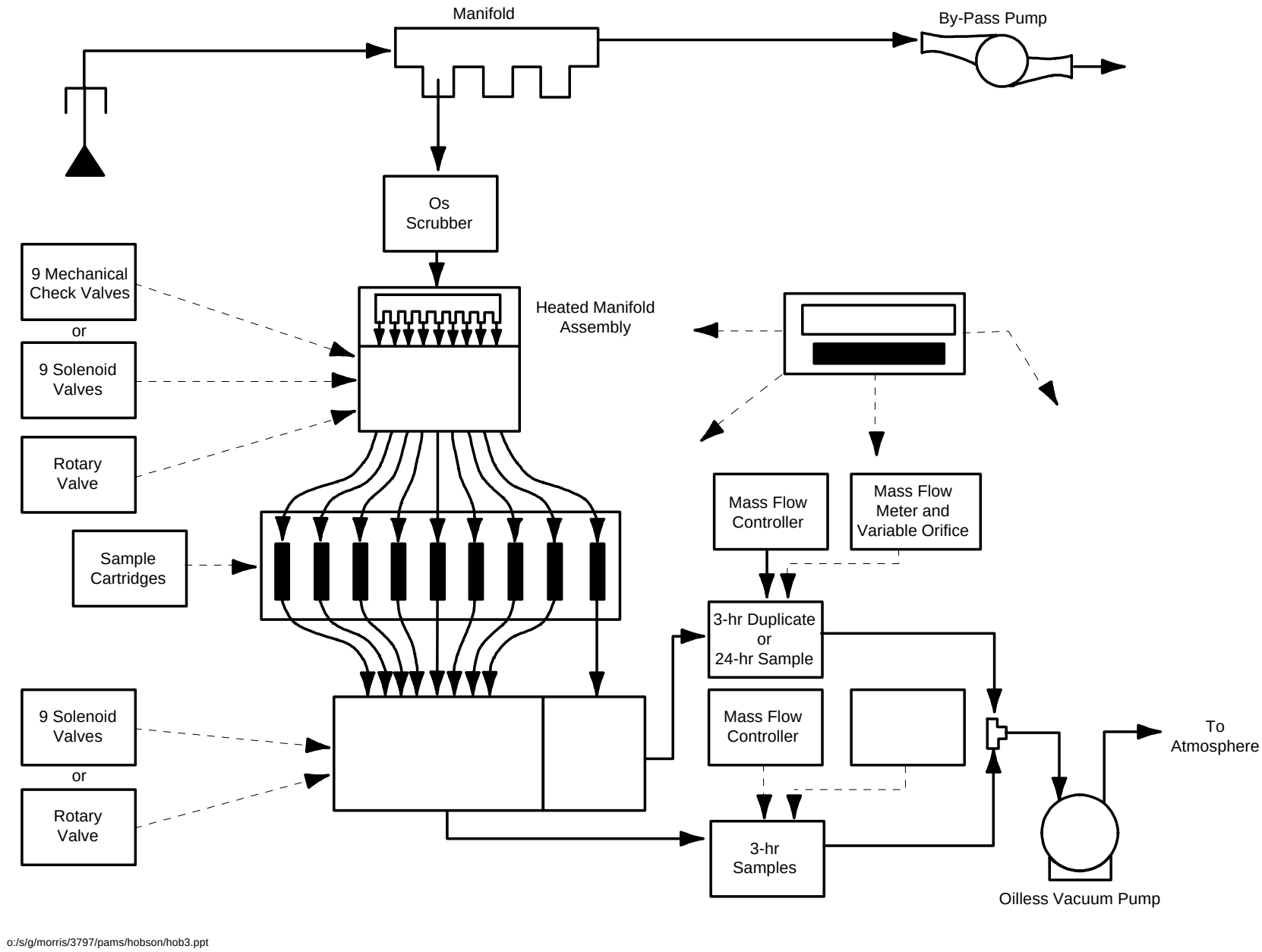


Figure 5-3. Schematic of a Typical Multiple-Event Carbonyl Cartridge Sampling System

Inlet probe and manifold assembly - Constructed of glass (see Figure 5-1) or stainless steel. Used as a conduit to extract sample air from the atmosphere at the required sampling height and distribute it for collection.

By-pass pump - A single- or double-headed diaphragm pump, or a caged rotary blower. Used to continuously draw sample air through the inlet probe and manifold assembly at a rate in excess of the sampling system total uptake. All excess sample air is exhausted back to the atmosphere.

Sample pump - An oilless vacuum pump, capable of achieving an inlet pressure of -25 inches Hg continually. Used to extract sample air from the manifold assembly and pull it through the sample cartridges during collection.

Sample inlet line - Chromatographic-grade stainless steel tubing. Used to connect the sampler to the manifold assembly. This line should be kept as short as possible.

Ozone scrubber - A Denuder or Cartridge type of O_3 scrubber. Used to remove ambient O_3 from the sample air stream prior to exposure to the sample cartridge.

Sample cartridges - A plastic housing containing silica gel or C18 solid sorbent (see Section 4.4 of Method TO-11A in Appendix D) coated with DNPH. Used to contain the collected sample for transportation and analysis.

Adjustable orifice and mass flow meter assembly, or electronic mass flow controller - An indicating flow control device(s). Used to maintain a constant flow rate (± 10%) over a specific sampling period under conditions of changing temperature (20-40°C) and humidity (0-100% relative).

Microprocessor - An event control and data acquisition device. Used to allow unattended operation (i.e., activation and deactivation of each sampling event) of the collection system, and to record sampling event specific process data (i.e., start and end times, elapsed times, collection flow rates, etc.).

Check valves, solenoid valves, or a multi-port rotary valve - Eight stainless steel check valves, eight solenoid valves with electric-pulse-operated or low temperature coils, stainless steel bodies, and Viton® plunger seats and o-rings, or 1 multi-port stainless steel body rotary valve with Viton® o-rings. Used to provide access to or isolation of the inlet side of the sample cartridges.

Solenoid valves or a multi-port rotary valve - Eight solenoid valves with electric-pulse-operated or low temperature coils, stainless steel bodies, and Viton® plunger seat and o-rings, or 1 multi-port stainless steel body rotary valve with Viton® o-rings. Used to provide access to or isolation of the outlet side of the sample cartridges.

Tubing and fittings (Stainless steel or Teflon®) - Hardware for isolation and interconnection of components. Used to complete system interconnections. All stainless steel tubing in contact with the sample prior to analysis should be chromatographic grade stainless steel and all fittings should be 316 grade stainless steel. Note that if the manifold is heated, stainless steel tubing should be used because of the potential of off-gassing of the tubing.

Note: Elapsed-time indicators installed in-line with sample pumps can provide backup documentation that all samples ran for 180 minutes and can indicate that a malfunction occurred with the programmable timers or that power was interrupted.

5.2.2 Multiple-event Sampling Procedures

Samples are collected on individual solid sorbent sample cartridges using a single pump and one or more flow control devices. An oil-less vacuum pump draws ambient air from the sampling probe and manifold assembly through the sample cartridge at a constant flow rate during each specific sampling event.

A flow control device(s) is used to maintain a constant sample flow rate through each sample cartridge over each specific sampling period. The flow rate used is a function of the desired total volume of ambient air sampled and the specified sampling period. The flow rate is calculated as follows:

$$F = \frac{V \times 1000}{T \times 60} \qquad \textbf{(5-2)}$$

where:

F	=	flow rate (milliliters/minute)
V	=	desired total volume of ambient air sampled (liters)
1000	=	milliliters in a liter
T	=	sample period (hours)

60 = minutes in an hour

For example, if the desired total volume of ambient air to be sampled is 168 L over each individual 3-hour cartridge collection episode, the flow rate specific to each cartridge collection episode is calculated as follows:

$$F = \frac{168 \times 1000}{3 \times 60} = 933 \text{ milliliters/minute} \quad \textbf{(5-3)}$$

During operation, the microprocessor control device is programmed to activate and deactivate the components of the sample collection system, consistent with the beginning and end of each individual sample collection period.

Cartridge sampling systems can collect sample from a shared sample probe and manifold assembly as described in Section 5.2.3 or from a dedicated stainless steel sample probe, manifold assembly, and by-pass pump. If a dedicated probe, manifold assembly, and by-pass pump are used, a separate timer device should be incorporated to start the by-pass pump several hours prior to the first sampling event of a multiple-event collection period to flush and condition the probe and manifold assembly components. The connecting lines between the manifold assembly and the sampling system should be kept as short as possible to minimize the system residence time.

The flow rate through each sample cartridge should remain relatively constant over the entire collection period of each sampling event. Each adjustable orifice and mass flow meter assembly, or mass flow controller, used as a flow control device should be calibrated against a primary flow measurement standard (i.e., a bubble flow meter, etc.). Calibrations should include multiple points of comparison (i.e., indicated flow versus measured flow), across the entire range of the flow control device at increments reflecting 10% of the range. Calibration curves are generated from these comparisons and are used to set actual desired flow rates based on the flow

rates indicated by the flow control devices. Calibration of the flow control devices should be repeated periodically according to program specific QA/QC schedules as developed by the user.

Generic steps for operating a typical multiple-event sample collection system are as follows:

1. Set the sampling system to the desired sample collection flow rate(s) (i.e., referencing the corresponding calibration curve(s) and considering the desired total volume of ambient air to be sampled and the sampling period for each sampling event).

2. Program the microprocessor event control system to start and stop sample collection consistent with program specific collection frequency requirements.

3. Attach all sample cartridges to the sampling system.

4. Record the start and end time of each collection event and the corresponding flow rate onto the sampling field data sheet and calculate an average flow rate. The microprocessor event control and data acquisition system should automatically store these data for each collection event. The final total volume of ambient air sampled should be close to the desired total volume.

5. Remove each sample cartridge (i.e., one at a time), cap both ends, and attach an identifier to each (i.e., again, one at a time to avoid mislabeling). Sample event number, sample type, location, collection date, should be recorded on the field data sheet.

6. Place cartridges in tightly enclosed transport containers and transport the samples and corresponding information to the central laboratory for preparation and analysis.

5.2.3 Sample Probe and Manifold

A sample probe and manifold assembly should be used to provide a representative air sample for collection and subsequent analysis. Sample probe and manifold assemblies are commercially available or can be custom fabricated.

The sample probe is constructed of glass that is approximately 1 inch in outside diameter (O.D.). The inlet of the sample probe is configured with an inverted funnel, approximately 4 inches O.D. The sample manifold is constructed of glass, approximately 1 and ½ inches O.D. The manifold has ports used for sample distribution. The number of ports located on the manifold must be equal to or greater than the total number of monitoring systems that sample will be delivered to. The port nearest to the inlet of the manifold should be reserved for VOC sampling; the second port or any other port may be used for carbonyl sampling.

Teflon® bushings are used to connect sample lines to the manifold. Because the manifold and ports are constructed of glass, care must be taken to not place excessive stress on the assembly to avoid breakage. For VOC sampling, the sample lines should be constructed of 1/8 inch O.D. stainless steel tubing. The 1/8 inch tubing is flexible and will accommodate the flow rates typically associated with VOC sample collection. The sample lines should be kept as short as possible to reduce sample transfer time. For carbonyl sampling, the sample lines should be constructed of 1/4 inch O.D. stainless steel tubing; the scrubber and the carbonyl sample cartridge holder assembly should be positioned as close to the manifold as possible.

A blower and bleed adapter are located at the exit end of the sample manifold. The blower is used to pull sample air through the probe and manifold and the bleed adapter is used to control the rate at which the sample air is pulled through the manifold. An excess of sample air is 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 of outside ambient air. Sample air flow through the sample probe and manifold should be at least two times greater than the total air flow being removed for collection and analysis by all systems on the manifold.

The vertical placement of the sample probe and inlet funnel should be at a height of 3 to 15 meters above ground level. Because the O_3 monitoring requirements involve multiple-pollutant measurements, this range serves as a practical compromise for probe position. In addition, the probe inlet should be positioned more than 1 meter, both vertically and horizontally, away from the housing 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 any obstacle should be a 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 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 degree clearance is required. More specific details of probe positioning are presented in the "Enhanced Ozone Monitoring Network Design and Siting Criteria Guideline Document."[3] The glass probe should be reinforced or supported along the straight vertical axis of the assembly. Typically this support is provided by routing the probe shaft through a rigid section of metal or plastic tubing that is secured to the housing structure.

The manifold can be positioned in either a horizontal or vertical configuration. Figure 5-4 presents the manifold assembly in the vertical configuration. Figure 5-5 presents the manifold assembly in the horizontal configuration. If the horizontal configuration is used, the sample ports must point upward so that material that may be present in the manifold will not be transferred into the sample lines.

With continuous use the sample probe and manifold can accumulate deposits of particulate material and other potential contaminants. The sample probe and manifold should be cleaned to remove these materials. The recommended frequency for cleaning is quarterly. To clean the assembly, disconnect the sample lines and blower from the manifold. The sample lines and blower are not cleaned. For safety, electric power to the blower should be terminated until the cleaning process is completed. Disassemble the individual components by disconnecting the probe, manifold, collection bottle, and coupling devices from each other. The individual components should then be cleaned using heated high purity distilled water and a long handled bottle brush. The components should then be rinsed with the distilled water and allowed to dry completely before reassembling. If required, mild glass cleaner or detergent can be used to clean particularly dirty components. However, care should be taken to select cleaners and detergents that are advertised to have low organic compound content and the number of rinses performed should be increased to ensure that all associated residues are removed.

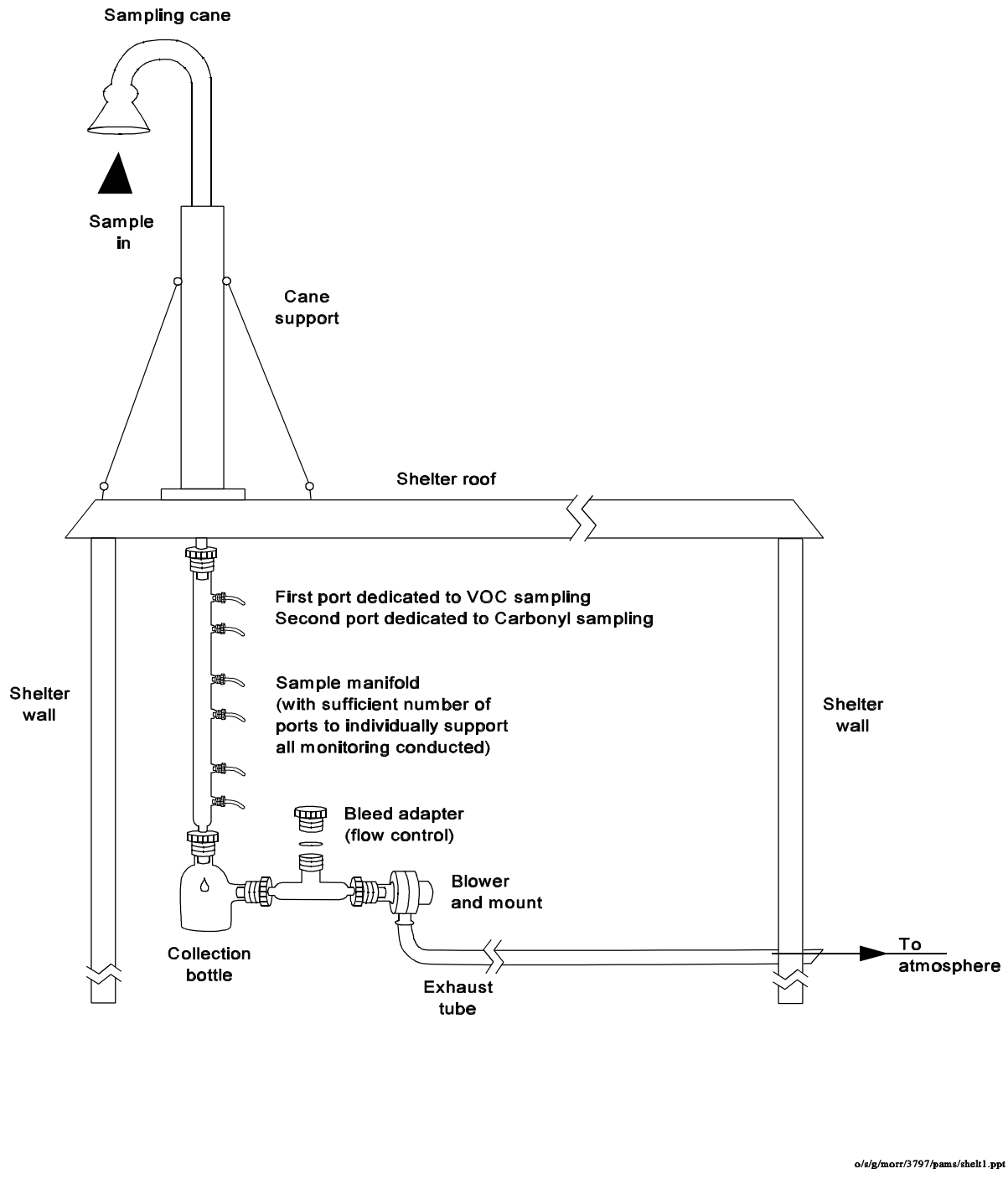
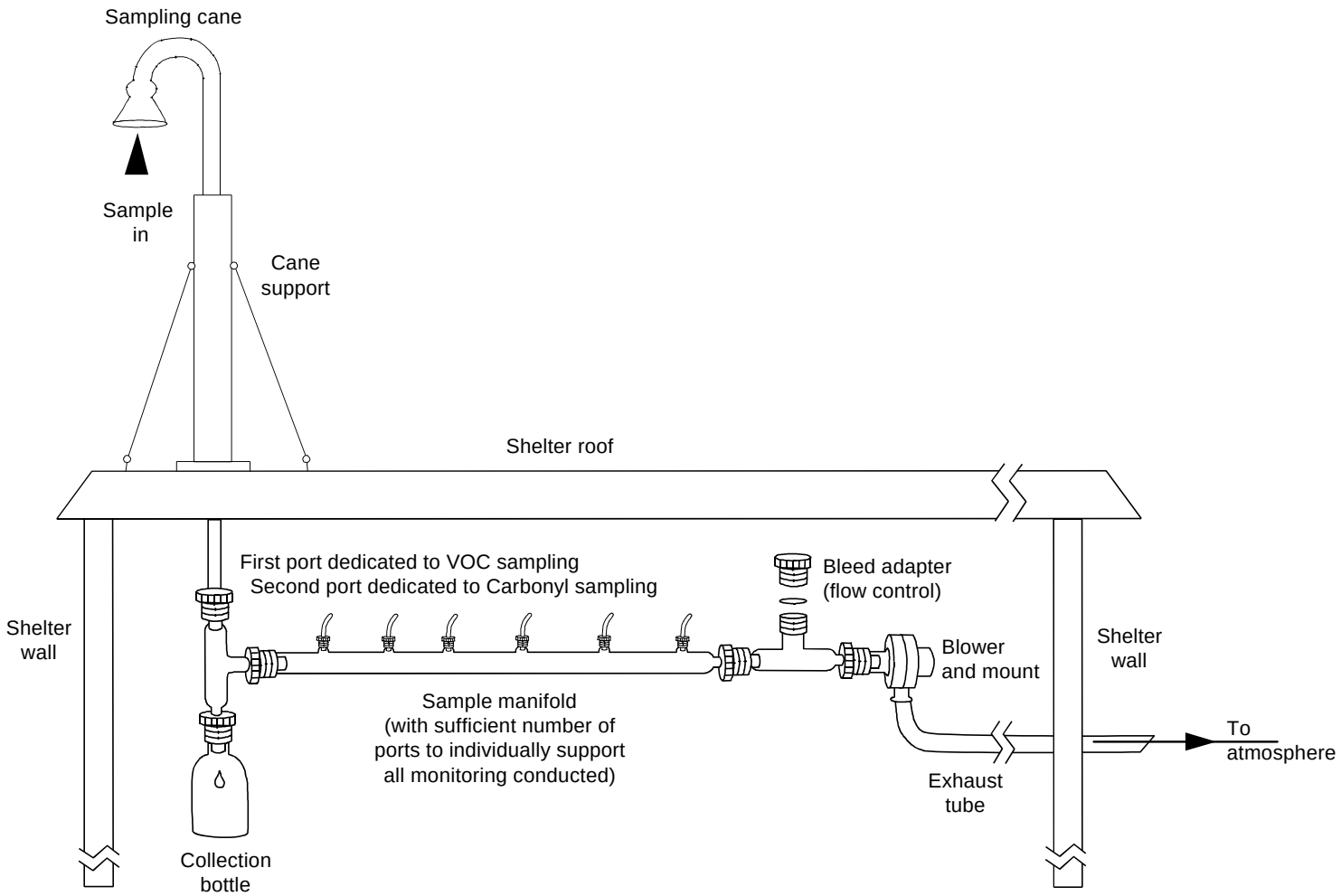


Figure 5-4. Vertical Configuration



o/s/g/morr/3797/pams/shelt2.ppt

Figure 5-5. Horizontal Configuration

5.2.4 Multiple-event System Specifications

The use of sample cartridges to practically address the sampling frequency and schedule for carbonyl compounds specified in Table 5-1 requires the use of multiple-event cartridge sampling systems. The use of a single-event system to collect eight back-to-back 3-hour cartridge samples would require that an operator be physically present on site to manually complete the activities associated with the start and stop of each sampling event.

To ensure that a multiple-event sample collection system will meet the user's program needs, system specifications and other pertinent general considerations should be presented to, and addressed by, the candidate vendor(s) prior to procurement. Primary system specifications are presented below. However, additional system specifications and considerations may be added at the discretion of the user.

- An in-depth, detailed manual covering all aspects of the sample collection system (i.e., operation, maintenance, etc.) must be provided by the vendor.
- The overall size of the sampling system should be kept as compact as possible. The sampling systems are usually installed into existing sampling site shelters where many other parameters (i.e., criteria pollutants concentrations, meteorological conditions, etc.) are also measured. Each of the other parameters requires separate instrumentation and consequently the shelters can become very crowded.
- The sample collection system should meet all applicable electrical and safety codes, operate on standard 110 Vac power, and incorporate a main power fuse or circuit breaker. Specific potential electrical hazards and/or other safety considerations should be detailed in a supplied user's manual.
- The overall configuration, and components comprising that configuration, should allow for simple operation, maintenance, and service of the sample collection system. Materials used in the construction of components of the sample collection system should exhibit nonbiasing characteristics. The components themselves should generally conform to the descriptions presented in Section 5.2.1. All surfaces that come in direct contact with sampled air should be constructed of glass, stainless steel, or Viton®.

- To avoid cross-contamination, the sample collection system must have provisions to isolate the inlet and outlet of each sample cartridge when that cartridge is not collecting sample.

- The sampling system must incorporate or provide for removal of O_3, consistent with the O_3 scrubber designs detailed in Section 5.1.

- Ideally, the sampling system should be able to accommodate the most intensive sample collection event frequency presented in Figure 5-6 on an automated unattended basis, and simultaneously accommodate a duplicate collection for one of the 3-hour sampling events as recommended for quality control purposes. These requirements mean that the sampling system should have the capability to collect the following during any given 24-hour period:

  - Eight 3-hour cartridge samples;

  - One 3-hour duplicate cartridge sample, collected concurrently with one of the eight 3-hour cartridge samples; and

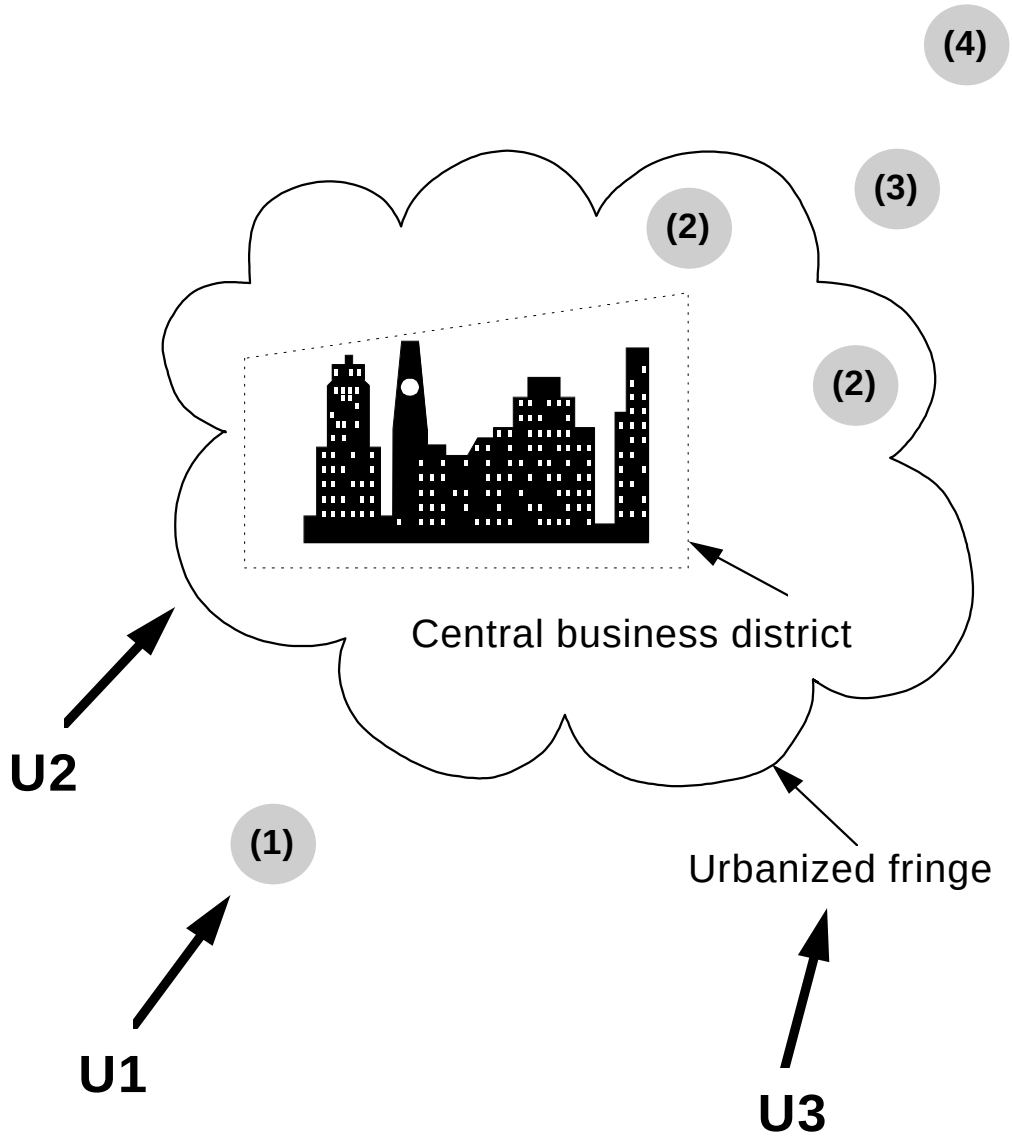
  - One 24-hour cartridge sample, collected concurrently with the eight 3-hour cartridge samples, but <u>not</u> concurrent with a duplicate 3-hour cartridge sample.

  It is imperative that the sample collection system have the collection capabilities detailed above. If not, a second sampling system would be required to address the 24-hour sample collection, and consequently more overall labor and space would be needed to fully address the network monitoring requirements.

  The ability of the sampling system to perform sample collections as presented above would require the operator to visit the site only twice during the 24-hour period being characterized; once to install sample cartridges prior to sampling and once to remove sample cartridges containing the collected samples. Each 24-hour period is scheduled to begin at 12:00 A.M. (i.e., midnight) and end at 11:59 P.M. of the day being characterized. The sampling system must be able to automatically address these periods (i.e., must be able to start and stop at the specified times without requiring an operator to go to the site and manually actuate the system).

- The sampling system should incorporate a microprocessor event control and data acquisition device. At a minimum this microprocessor should be able to be programmed to control the start and stop times of every collection event within a given 24-hour sampling duration. The microprocessor should also be able to simultaneously collect and store all the sample collection process data pertaining to each sampling event as follows:

Isolated Area Network Design



Note:
U1 and U2 represent the first and second most predominant high ozone day morning wind direction.
U3 represents the high ozone day afternoon wind direction.

o:s/g/morr/3797/pams/isolated.ppt

(1), (2), (3), and (4) are different types of PAMS sites (See Table 5-1).

Figure 5-6. Isolated Area Network Design

- Start and stop times for each sample collection; and

- Beginning and ending collection flow rates for each cartridge collection.

The microprocessor should incorporate a battery backup system to address power failure situations. Incorporation of a battery backup system should result in fewer invalidated sample collections and a higher sample collection completion rate. The battery backup system would ensure that all programmed control activities and collection process data would be retained for a predetermined interval should standard power to the system be interrupted. Retaining the programmed control activities would allow sampling to resume automatically at the next programmed event time when standard power is once again established to the sampling system. Retaining the collection process data obtained for samples collected prior to the termination of standard power would allow these samples to be qualified as valid or invalid based on sampling start and stop times and initial and flow rates. Although not absolutely necessary, the incorporation of a miniature printer that would allow for a report style listing of all sample collection process data would be advantageous.

- Expedient and responsive vendor support should be a mandatory requirement and primary consideration when procuring a multiple-event cartridge sampling system. The user should specify that the vendor will maintain an adequate supply of replacement parts and a staff of qualified service technicians to ensure that the absolute minimum number of sample collection events are missed should a sample collection system failure occur. The user should specify that the vendor guarantee that parts/components be delivered to the sampling site within two working days of order placement. The user should also specify that a sample collection system delivered to the vendor for repair be serviced and returned to the user within seven working days.

The manufacturer of a carbonyl sampling device and experience at some of the PAMS sites indicate that the carbonyl sampler should not be located inside a shelter but outside to alleviate the possibility of off-gassing from the shelter interfering with the samples. The sampling methodology itself does not specify the location of the sampler. The wisdom of locating the carbonyl sampler outside rather than inside a shelter would depend upon the composition of the shelter and the security of the sampler if it is located in an outside area.

5.3 Process Blanks

To ensure data quality and obtain quantitative carbonyl compound concentrations, the collection of blanks is necessary. For the purposes of PAMS, there are three types of blanks used to ensure data quality: certification blanks, field blanks, and trip blanks. The guidance given here should be considered a minimum and users are encouraged to build upon this guidance as necessary.

- **Certification blanks** consist of a minimum of three laboratory blank cartridges that are eluted with acetonitrile and analyzed to verify the acceptability of a specific cartridge lot from a commercial vendor. Certification blanks are analyzed for each specific lot used for sampling. The mean mass plus 3 standard deviations ($\bar{x}$ + 3s) for the group of three laboratory blanks is used to assess acceptability.

- **Field blanks** are blank cartridges which are sent to the field, connected to the sampling system and treated identically to the samples except that no air is drawn through the cartridge. Field blanks are used to assess the background carbonyl levels for cartridges used during the ambient sample collection process.

- **Trip blanks** are blank cartridges of the same lot that are sent to the field, stored, and returned to the laboratory with the sample cartridges. Trip blanks are optional and may be used to resolve contamination problems determined from the field blanks. Trip blanks can be used to determine whether the contamination occurred during the sampling process or during the shipping and storage process.

5.3.1 Blank Criteria

The acceptance criteria for blanks are discussed below. The criteria for certification are considered conservative; most certification blank results will be well below these criteria. If the mean mass plus 3 standard deviations ($\bar{x} \pm 3s$) for the group of three laboratory blanks meets the criteria, then no further certification or laboratory blanks are required for a particular lot. If large differences are observed for the 3 laboratory blank samples, additional laboratory blanks should be analyzed to obtain values for the mean and standard deviation. For the certification blanks to be acceptable, the following criteria should be met:

- Formaldehyde: <0.15 g/cartridge*
- Acetaldehyde: <0.10 g/cartridge
- Acetone: <0.30 g/cartridge
- Other aldehydes or ketones, concentration (per individual component): <0.10 µg/cartridge.

* The equivalent formaldehyde concentration in ppbv as taken from Table 3 in EPA Compendium Method TO-11A (see Appendix D) is 0.679 ppbv for a 180 L sample volume.

Using good techniques and collection systems (not mixing lots or vendors), field blanks should consistently be at levels that are less than 2 times the average measured laboratory blank value for a specific lot. The laboratory blank is a cartridge blank used for lot certification that has never been shipped to the field. If field blanks do not meet these criteria, corrective action is required. Sites that are unable to achieve these levels for field blanks must determine the source of contamination. An assessment of the air in the sampling shelter may also provide useful information in the determination of sources for field blank and sample contamination.

As a minimum, a sampling system blank sample should be collected at least on an annual basis before initiation of sampling. Collection of a pre- and post-sampling blank is strongly recommended to aid in the qualification of data. If the sampler is subjected to only a single blank audit, a failure to meet QA/QC limits will leave open the question of whether the previous year's data should be flagged or not. It is possible for a sampler to become contaminated (or appear to become contaminated) during the down season, in which case there would be no reason to invalidate the data from the previous year. Pre- and post-season audits remove the ambiguity. Collect a sampler blank using carbonyl-free air when possible. Generate carbonyl free air by purging air through acidic DNPH solution in a bubbling device or DNPH-coated cartridge. Alternatively, measure the carbonyl content of the air using a DNPH-coated cartridge and subtract the carbonyl content in the air from that in the sampler blank. Before collecting the sampler blank, flush the system using the same procedures as used for collecting a sample.

5.3.2 Frequency of Collection

At least one field blank, or the square root of the field sample size, whichever is larger, should be collected and analyzed with each sample lot collected at the site. The square root of the sample size is used to result in more field blanks for a smaller sample size and fewer field blanks for a larger sample size. For example, if 100 field samples will be taken at the site, then 10 field blank samples (the square root of 100) are collected and analyzed. If multiple lots are used, ensure that each lot has the necessary number of associated field blanks. Certification blanks are not included in the number of field blanks. Certification blanks are analyzed in addition to field blanks to verify acceptability of a specific cartridge lot from the vendor. At a minimum, three laboratory blanks from each lot are used for certification. Table 5-2 gives an example collection schedule for a field samples from a single lot.

Table 5-2. Example Schedule for the Collection of Blanks

Field Sample Size	Lab Blanks for Lot Certification	Field Blanks (square root of the sample size)
50	3	7
100	3	10
200	3	16

Since field blank samples may not be collected on every sampling day, the issue of maintaining consistency in the overall data treatment using blank subtraction is a challenge. For PAMS blank subtraction must be performed using the average field blank mass obtained for each field sample lot. Using the information in Table 5-2 as an example, for a sample size of 100, the average mass for the 10 field blank samples is subtracted from each of the 100 samples. Again, it is important that cartridge lot be tracked and the appropriate number of field blanks be collected and subtracted from the samples for each lot used.

5.4 Breakthrough Analysis

Method TO-11A requires the use of a back-up cartridge during the first sampling event. If less than 10% of the analyte is collected on the back-up cartridge, then back-up cartridges are only required for 10% of the field samples. If more than 10% of the analyte is collected on the back-up cartridge, then use back-up cartridges for all sampling events. Breakthrough is more likely to occur when sampling at high flow rates, when sampling very dry or very humid air, when sampling air containing high levels of oxides, and when sampling air containing high levels of carbonyl compounds. Perform breakthrough analyses on the 24-hour sample or on the duplicate 3-hour sample. Be careful in determining the flow rate because two cartridges installed in series create a higher pressure drop, decreasing the sampling rate. If breakthrough occurs, minimize the breakthrough by replacing the ozone scrubber more frequently, sampling at a lower flow rate, using larger capacity cartridges, or heating the cartridges slightly to prevent moisture condensation when sampling very humid air.

5.5 Collection of Collocated Samples

A collocated sample is collected from one manifold by two independent sampling devices in the same sampling period. Collect collocated samples as indicated in Table 5-2. Analyze the collocated samples in replicate. The replicate analyses should agree to within ±10% and the means of the replicate analyses for the collocated samples should agree to within ±20%. If the collocated samples do not agree to within ±20% and the replicate analyses are within ±10%, check the samples to ensure that they are truly collocated and check the sample flow rates to ensure that the sampler is working correctly. Also verify that the sampler is not leaking by performing a leak check as described in Section 10.2 of TO-11A (see Appendix D).

5.6 Quality Assurance and Quality Control

General quality assurance and quality control requirements are provided in Section 13.6 of Method TO-11A (see Appendix D). Each laboratory should develop SOPs for the sampling

and analysis of carbonyls and should develop criteria for sampling and analysis that are specific to the laboratory. Table 5-3 provides the quality assurance and quality control procedures consistent with Method TO-11A.

5.7 General Cartridge Handling Guidelines

Unintentional exposure of the DNPH cartridges and eluted samples to aldehyde and ketone sources can result in contamination of the samples, creating a positive bias in the collected data. Various aldehydes and ketones are ubiquitous in the environment. For example, biological processes can produce formaldehyde, acetone, and acetaldehyde on peoples' skin and in peoples' breath. Wear polyethylene gloves at all times when handling the DNPH cartridges during sampling collection and analysis. In addition, laboratory air often holds high concentrations of acetone (and sometimes formaldehyde). Measure background levels of carbonyls in the laboratory air using a DNPH cartridge and sample pump. If high background levels are present, handle the cartridges in a nitrogen-purged glove box or under a purge of carbonyl free air. Labeling inks, adhesives, and packing containers are all additional sources of contamination. Avoid packing cartridges in old newspapers, writing directly on the cartridges with ink, or placing adhesive labels directly on the cartridges. Additionally, DNPH is light sensitive. Always protect the cartridges from direct sunlight.

Table 5-3. Quality Assurance and Quality Control Criteria

Parameter	Frequency	Limits	Corrective Action
Flow calibration	Each sampling event, pre- and post-checks	±10%	Mark sample as suspect
Mass flow meter calibration factor	Every quarter	1.0 ± 0.1	Repair mass flow meter
Leak check	Each sampling event, pre- and post-checks	No air flow	Check for leaks
Sampler blank	Pre- and post-seasons	> MDL	Clean sampler, qualify data if required
Collocated samples	10% of field samples	±20%	Mark sample as suspect
Back-up cartridges	10% of field samples	10% of total on back-up cartridge	Use back-up cartridges for all samples
Trip blanks	10% of field samples	<0.15 µg formaldehyde/cartridge	Blank correct data
Field blanks	10% of field samples	<0.15 µg formaldehyde/cartridge	Blank correct data
Spiked cartridges	10% of field samples	80 to 120% recovery	Flag data
Multi-point calibration	Every 6 months	0.999	Recalibrate
Continuing calibration standard	Every analytical run	±10%	Recalibrate
Method detection limits	Annually or after each instrument change	<0.1 ppbv for 180 L sample volume	Modify instrument as needed
Replicate injections	10% of samples	±10%	Reanalyze samples
Performance evaluation sample	Before and after samples	±15%	Reanalyze samples

5.8 References

1. U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40, Part 58. Ambient Air Quality Surveillance, Final Rule Federal Register, Vol. 58, No. 28, February 12, 1993.

2. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Compendium Method TO-11A. *Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)*. EPA-625/R-96/010b. Cincinnati, OH: U.S. Environmental Protection Agency, 1997.

3. Grassick, D. and R. Jongleux. *Enhanced Ozone Monitoring Network—Design and Siting Criteria Guideline Document*. Contract No. 68-D0-0125. Research Triangle Park, NC: U.S. Environmental Protection Agency, 1991.

Section 6.0

Guidance for PAMS Meteorological Monitoring

6.1 Background

Title 40 Part 58 of the Code of Federal Regulations[1] required the States to establish a network of Photochemical Assessment Monitoring Stations (PAMS) in ozone nonattainment areas which were classified as serious, severe, or extreme. The regulation states that each PAMS program must include provisions for enhanced monitoring of ozone, the precursors to ozone, and both surface and upper-air meteorological conditions. Although the PAMS rule establishes a requirement for meteorological monitoring, it does not provide specifics; e.g., a list of the meteorological variables to be monitored. Discussions to develop such a list took place in the Spring of 1994. Recommendations based on these discussions were issued in April 1994[2] and incorporated in an early draft of this document. The list of variables has since been revised to reflect input from the review of this and subsequent drafts. Currently, the list of meteorological variables includes: wind direction, wind speed, temperature, humidity, atmospheric pressure, precipitation, solar radiation, UV radiation, and mixing height. Table 6-1 provides an overview of the requirements for monitoring these variables.

The remainder of this section is organized as follows: Section 6.2 describes the PAMS site types as established by the PAMS rule. Section 6.3 provides material on the application of PAMS meteorological data. Sections 6.4 and 6.5 provide details related to measurement of surface and upper-air meteorological variables, respectively. Section 6.6 provides a list of references.

Users are referred to the “Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements”[3] for recommended procedures for quality assurance and audit activities. The procedures provided in “On-Site Meteorological Program

Table 6-1. Overview of PAMS Meteorological Monitoring Requirements

QUESTION	ANSWER
Where to monitor?	All serious, severe, and extreme ozone nonattainment areas
How many sites?	2 to 5 surface sites per network plus one upper-air site
When to monitor?	Routine continuous monitoring during the PAMS monitoring season (3 months per year minimum)
How long?	Until the area is redesignated as attainment for ozone
What variables?	Wind Direction[a] Wind Speed[a] Air Temperature[a] Humidity[a] Solar Radiation[b] Ultraviolet Radiation[b] Barometric Pressure[b] Precipitation[b,c]
What interval?	Surface measurements should be continuous and should be reported hourly. Upper-air measurements (profiles of wind and temperature) should be made at least 4 times per day.
What levels?	Surface measurements should be made at 2 meters (temperature and humidity) or 10 meters (wind direction and wind speed). Other surface measurements are nominally made at about 2 meters.

[a] A required measurement for all PAMS sites.
[b] A required measurement for at least one site per PAMS area.
[c] Precipitation data from other sources (National Weather Service or others) are acceptable on a case-by-case basis.

Guidance for Regulatory Modeling Applications"[4] should be followed for processing of meteorological measurements.

6.2 PAMS Site Types

The PAMS requirements were designed to provide as much information as practicable on the roles of ozone precursors, pollutant transport, and local meteorology in the photochemical process. Specific provisions of the Rule require the establishment and operation of four monitoring sites in each PAMS area; each of the sites has specific data quality objectives (DQOs). The four sites are as follows:

Site #1 - **Upwind and background characterization site**. These sites are established to characterize upwind background and transported ozone and its precursor concentrations entering the area and will identify those areas which are subjected to overwhelming incoming transport of ozone. The #1 Sites are located in the predominant morning wind direction from the local area of maximum precursor emissions and at a distance sufficient to obtain urban scale measurements. Typically, these sites will be located near the upwind edge of the photochemical grid model domain.

Site #2 - **Maximum ozone precursor emissions impact site.** These sites are established to monitor the magnitude and type of precursor emissions in the area where maximum precursor emissions representative of the Metropolitan Statistical Area (MSA)/Consolidated Metropolitan Statistical Area (CMSA) are expected to impact and are suited for the monitoring of urban air toxic pollutants. The #2 Sites are located immediately downwind (using the same morning wind direction as for locating Site #1) of the area of maximum precursor emissions and are typically placed near the downwind boundary of the central business district (CBD) or primary area of precursor emissions mix to obtain neighborhood scale measurements. Additionally, **a second #2 Site may be required** depending on the size of the area, and it should be placed in the second-most predominant morning wind direction.

Site #3 - **Maximum ozone concentration site.** These sites are intended to monitor maximum ozone concentrations occurring downwind from the area of maximum precursor emissions. Locations for #3 Sites should be chosen so that urban scale measurements are obtained. Typically, these sites are located 10 to 30 miles from the fringe of the urban area.

Site #4 - **Extreme downwind monitoring site.** These sites are established to characterize the extreme downwind transported ozone and its precursor concentrations exiting the area and will identify those areas which are

potentially contributing to overwhelming ozone transport into other areas. The #4 Sites are located in the predominant afternoon downwind direction from the local area of maximum precursor emissions at a distance sufficient to obtain urban scale measurements. Typically, these sites will be located near the downwind edge of the photochemical grid model domain.

6.3 Applications of PAMS Meteorological Data

Meteorology is a critical element in the formation, transport, and ultimate disposition of both ozone and its precursors. Consequently, meteorological data are essential to the development and evaluation of ozone control strategies. Other types of evaluations which depend on meteorological data include photochemical modeling, receptor modeling, emissions tracking, and trends analysis. Other application areas associated with the PAMS meteorological measurements are indicated in Table 6-2. Examples of applications can be found in the Draft Guidelines for Quality Assurance and Management of PAMS Upper-Air Meteorological Data.[5]

Table 6-2. Application of the PAMS Meteorological Data

Variable	Photochemical Modeling	Diagnostic Analysis	Receptor Modeling
Wind Direction[a]	✓	✓	✓
Wind Speed[a]	✓	✓	✓
Air Temperature[a]	✓	✓	
Humidity[a]	✓	✓	
Pressure[b]	✓	✓	
Precipitation[b]		✓	✓
Solar Radiation[b]	✓	✓	
UV Radiation[b]	✓	✓	

[a] To be measured at multiple sites in each PAMS area.
[b] To be measured at one representative site in each PAMS area.

6.4 Surface Meteorological Monitoring

A minimum level of surface meteorological monitoring is required for each PAMS site regardless of the site type (see Section 6.2). The minimum level includes measurements of wind direction, wind speed, ambient temperature, and humidity (e.g., dew point or relative humidity). In addition, measurements of solar radiation, ultraviolet radiation, barometric pressure, and precipitation are required for at least one site in each PAMS network.

6.4.1 Siting and Exposure

The selection of an appropriate site for the surface meteorological measurements depends on the intended use of the data; i.e., the Data Quality Objectives (DQOs). Ideally, for general application, the site should be located in a level open area away from the influence of obstructions such as buildings or trees. The area surrounding the site should have uniform surface characteristics.[6,7,8] Although it may be desirable to collocate the surface meteorological measurements with the ambient air quality measurements, collocation of the two functions may not be possible at all PAMS sites without violating one or more of the above criteria. Siting and exposure requirements specific to each of the PAMS surface meteorological variables are discussed in subsequent sections.

Surface meteorological measurements in urban areas, where compliance with siting and exposure criteria may be precluded by the close proximity of buildings and other structures, present special difficulties. In such cases, the individual involved in the site selection needs to assess the likelihood that the data which may be collected at a given location will conform to the DQOs. In all cases, the specific site characteristics should be well documented. This documentation of the specific site characteristics is especially important in areas where surface characteristics and/or terrain are not uniform and whenever standard exposure and siting criteria cannot be met.

6.4.2 Specifications

System specifications for the surface measurements are given in Table 6-3. The recommended sampling interval of the meteorological sensors by the data acquisition system is 10 seconds. Data for all variables should be processed to obtain one hour averages. The data acquisition system clock should have an accuracy of ±1 minute per week.

Table 6-3. System Specifications for Surface Meteorological Measurements[a]

Variable	Range	Accuracy	Resolution	Time/Distance Constants
Wind Speed	0.5 to 50 m/s	±0.2 m/s + 5%	0.1 m/s	5 m (63% response)
Wind Direction	0 to 360 deg.	±5 deg.	1 deg.	5 m (50% recovery)
Air Temperature	-20 to 40 °C	±0.5 °C	0.1 °C	60 s (63% response)
Dew Point	-30 to +30°C	±1.5°C	0.1°C	30 minutes
Relative Humidity	0 to 100 %RH	±3 %RH	0.5 %RH	60 s (63% response)
Solar Radiation	0 to 1200 W m^{-2}	±5%	10 W m^{-2}	60 s (99% response)
UV Radiation	0 to 12 W m^{-2}	±5%	0.01 W m^{-2}	60 s (99% response)
Barometric Pressure	800 to 1100 hPa	±3 hPa	0.5 hPa	60 s (63% response)
Precipitation	0 to 30 mm/hr	±10%	0.25 mm	60 s (63% response)

[a]Quality assurance guidance for auditing these values is provided in *Quality Assurance Handbook for Air Pollution Measurement Systems. Volume IV - Meteorological Measurements.* EPA/600/R-94/038d. U.S. Environmental Protection Agency, 1995.

6.4.3 Wind Speed and Wind Direction

Wind speed and direction are essential to the evaluation of transport and dispersion processes of all atmospheric pollutants. Wind speed is typically measured with a cup or propeller anemometer; wind direction is typically measured with a wind vane.

The standard height for surface layer wind measurements is 10 m above ground level.[3,7,9] The location of the site for the wind measurements should ensure that the horizontal distance to obstructions (e.g., buildings, trees, etc.) is at least ten times the height of the obstruction.[9] In urban areas, where the "ten times" criterion may not be met, one should provide a protocol for invalidating the measurements for the problem directions. Evans and Lee[10] provide a discussion of the validity of 10-meter wind data in an urban setting where the average obstruction height is of the same order as the wind measurement height.

An open lattice tower is the recommended structure for monitoring of meteorological variables at the 10-meter level. In the case of wind measurements, certain precautions are necessary to ensure that the measurements are not significantly affected by turbulence in the immediate wake of the meteorological tower. To avoid such tower effects, the wind sensor should be mounted on a mast a distance at least one tower width above the top of the tower, or if the tower is higher than 10 m, on a boom projecting horizontally from the tower. In the latter case, the boom should extend a distance at least twice the diameter/diagonal of the tower from the nearest point on the tower. The boom should project into the direction which provides the least distortion for the most important wind direction (i.e., into the prevailing wind).

There are several types of open lattice towers: Fixed, tilt-over, and telescopic. A fixed tower is usually assembled as a one-piece structure from several smaller sections. This type of tower must be sturdy enough so that it can be climbed safely to install and service the instruments. Tilt-over towers are also one-piece structures, but are hinged at ground level. This type of tower has the advantage of allowing the instruments to be serviced at the ground. Telescopic 10 m towers are usually composed of three sections, each approximately 4 m in length. The top section is the smallest in diameter and fits inside the middle section which, in turn, fits inside the base section. The tower can be extended to a height of 10 m by use of a hand crank located at the lowest section. The top of the tower can be lowered to a height of about 4 m providing easy access to the wind sensors. Telescopic and tilt-over towers are not generally recommended for heights above 10 m. Regardless of which type of tower is used, the structure should be sufficiently rigid and properly guyed to ensure that the instruments maintain a fixed

orientation at all times. Instrumentation for monitoring wind speed and direction should never be mounted on or near solid structures such as buildings, stacks, water storage tanks, cooling towers, etc., because all such structures create significant distortions in the flow field.

A sensor with a high accuracy at low wind speeds and a low starting threshold is recommended for PAMS applications. Light weight materials (e.g., molded plastic or polystyrene foam) should be employed for cups and propeller blades to achieve a starting threshold (lowest speed at which a rotating anemometer starts and continues to turn and produce a measurable signal when mounted in its normal position) of ≤ 0.5 m s^{-1}. Wind vanes or tail fins should also be constructed from light weight materials. The starting threshold (lowest speed at which a vane will turn to within 5^{o} of the true wind direction from an initial displacement of 10^{o}) should be ≤ 0.5 m s^{-1}. Overshoot must be $\leq 25\%$ and the damping ratio should lie between 0.4 and 0.7. The above information is summarized in Table 6-3.

6.4.4 Temperature

Temperature affects photochemical reaction rates and consequently, is an essential variable for PAMS applications. Sensors used for monitoring ambient temperature include: wire bobbins, thermocouples, and thermistors. Platinum resistance temperature detectors (RTD) are among the more popular sensors used in ambient monitoring; these sensors provide accurate measurements and maintain a stable calibration over a wide temperature range.

The standard height for surface layer ambient temperature measurements is 2 meters above ground level.[7] If a tower is used, the temperature sensor should be mounted on a boom which extends at least one tower width/diameter from the tower. The measurement should be made over a uniform plot of open, level ground at least 9 m in diameter. The surface should be covered with non-irrigated or un-watered short grass or, in areas which lack a vegetation cover, natural earth. Concrete, asphalt, and oil-soaked surfaces and other similar surfaces should be avoided to the extent possible. The sensor should be at least 30 m from any paved area. Other areas to avoid include large industrial heat sources, roof tops, steep slopes, hollows, high

vegetation, swamps, snow drifts, standing water, and air exhausts. The distance to obstructions for accurate temperature measurements should be at least four times the obstruction height. In urban areas, one should be especially conscious of and avoid extraneous energy sources (e.g., tunnels and subway entrances, roof tops, etc.).

Temperature measurements should be accurate to ±0.5°C over a range of -20 to +40°C with a resolution of 0.1°C. The time constant (63.2%) should be ≤ 60 seconds. Solar heating is usually the greatest source of error and, consequently, adequate shielding is needed to provide a representative ambient air temperature measurement. Ideally, the radiation shield should block the sensor from view of the sun, sky, ground, and surrounding objects. The shield should reflect all incident radiation and not reradiate any of that energy towards the sensor. The best type of shield is one which provides forced aspiration at a rate of at least 3 m s^{-1} over a radiation range of -100 to +1100 W m^{-2}. Errors in temperature should not exceed ±0.25°C when a sensor is placed inside a forced aspiration radiation shield. The sensor must also be protected from precipitation and condensation, otherwise evaporative effects and other forms of radiational heating or cooling will lead to a depressed temperature measurement (i.e., wet bulb temperature). Temperatures may also be reported to AIRS AQS in °F, but metric is the preferred and recommended system of units for meteorological measurements.

6.4.5 Atmospheric Humidity

Measurements of atmospheric humidity are essential to understanding chemical reactions involving ozone precursors and water vapor. Measures of atmospheric humidity include vapor pressure, dew point temperature, specific humidity, absolute humidity, and relative humidity. There are several ways to measure the water vapor content of the atmosphere. The classical measurement methods can be classified in terms of six scientific principles; examples are provided in Table 6-4.

The standard height for humidity measurements is 2 m above ground level. The humidity sensor should be installed using the same siting criteria as used for temperature. If possible, the

Table 6-4. Principles of Humidity Measurement[a]

Principle	Instrument/Method
Reduction of temperature by evaporation	psychrometer
Dimensional changes due to absorption of moisture, based on hygroscopic properties of materials	hygrometers with sensors of hair, wood, natural and synthetic fibers
Chemical or electrical changes due to absorption or adsorption	electric hygrometers such as the Dunmore Cell; lithium, carbon, and aluminum oxide stirps; capacitance film
Formation of dew or frost by artificial cooling	cooled mirror surfaces
Diffusion of moisture through porous membranes	diffusion hygrometers
Adsorption spectra of water vapor	infrared and UV absorption; Lyman-alpha radiation hygrometers

[a]Middleton, W.E.K. and A.F. Spillhaus, *Meteorological Instruments*, University of Toronto Press (1953).

humidity sensor should be housed in the same aspirated radiation shield as the temperature sensor. The humidity sensor should be protected from contaminants such as salt, hydrocarbons, and other particulates. The best protection is the use of a porous membrane filter which allows the passage of ambient air and water vapor while keeping out particulate matter.

6.4.6 Solar Radiation

Solar radiation refers to the electromagnetic energy in the solar spectrum (0.10 to 4.0 µm wavelength). The latter is commonly classified as ultraviolet (0.10 to 0.40 µm), visible light (0.40 to 0.73 µm), and near-infrared (0.73 to 4.0 µm) radiation. About 97% of the solar radiation reaching the earth's outer atmosphere lies between 0.29 and 3.0 µm.[7] A portion of this energy penetrates through the atmosphere and is either absorbed or reflected at the earth's surface. The rest of the solar radiation is scattered and/or absorbed in the atmosphere before reaching the surface. Solar radiation measurements are used in heat flux calculations, for estimating atmospheric stability, and in modeling photochemical reactions.

Energy fluxes in the spectrum of solar radiation are measured using a pyranometer. These instruments are configured to measure what is referred to as global solar radiation; i.e., direct plus diffuse (scattered) solar radiation. The sensing element of the typical pyranometer is protected by a clear glass dome to prevent entry of energy (wavelengths) outside the solar spectrum (i.e., long-wave radiation). The glass domes used on typical pyranometers are transparent to wavelengths in the range of 0.28 to 2.8 µm.

Solar radiation measurements should be taken in a location with an unrestricted view of the sky in all directions. In general, locations should be avoided where there are obstructions that could cast a shadow or reflect light on the sensor; light colored walls or artificial sources of radiation should also be avoided. The horizon as viewed from the pyranometer should not exceed 5 degrees. Sensor height is not critical for pyranometers; consequently, tall platforms or roof tops are typical locations. Regardless of where the pyranometer is sited, it is important to ensure that the level of instrument is maintained,[11] and that the glass dome is cleaned as necessary. To facilitate leveling, the pyranometers should be equipped with an attached circular spirit level.

Manufacturer's specifications should match the requirements of the World Meteorological Organization[7] for either a secondary standard or first class pyranometer (see Table 6-5) especially if the measurements are to be used for estimating heat flux. Photovoltaic pyranometers (which usually fall under second class pyranometers) may be used for PAMS applications on a case-by-case basis. The cost of photovoltaic sensors is significantly less than that of thermocouple-type sensors; however, their spectral response is limited to the visible spectrum.

6.4.7 Ultraviolet Radiation

Ultraviolet (UV) radiation may be divided into three sub-ranges: UV-A (0.315 to 0.400 µm), UV-B (0.280 - 0.315 µm), and UV-C (0.100 - 0.280 µm). Due to absorption by stratospheric ozone, the UV radiation reaching the surface of the earth consists primarily of wavelengths longer than 0.28 µm (UV-A and UV-B ranges). The most important

Table 6-5. Classification[7] of Pyranometers[a]

Characteristic	Units	Secondary Standard	First Class	Second Class
Resolution	W m^{-2}	±1	±5	±10
Stability	%FS $year^{-1}$	±1	±2	±5
Cosine Response	%	< ±3	< ±7	< ±15
Azimuth Response	%	< ±3	< ±5	< ±10
Temperature Response	%	±1	±2	±5
Nonlinearity	%FS	±0.5	±2	±5
Spectral Sensitivity	%	±2	±5	±10
Response Time (99%)	seconds	< 25	< 60	< 240

[a]Quality Assurance guidance for auditing these parameters is provided in *Quality Assurance Handbook for Air Pollution Measurement Systems. Volume IV - Meteorological Measurements.* EPA/600/R-94/038d. U.S. Environmental Protection Agency, 1995.

photochemically active chemical species at these wavelengths are ozone, nitrogen dioxide, and formaldehyde. All three of these chemical species are important in the formation of ozone. Pyranometers with a spectral response covering both the UV-A and UV-B (0.280 to 0.400 m) ranges are recommended for PAMS applications. The same siting criteria used for "all wave" global solar radiation measurements apply.

6.4.8 Barometric Pressure

Barometric pressure (station pressure) is used in the calculation of fundamental thermodynamic quantities (e.g., air density). The type of sensor used to measure pressure is called a pressure transducer. There are numerous commercially available pressure transducers which meet the specifications in Table 6-3. Ideally, the pressure sensor should be located in a ventilated shelter about 2 m above ground level. The height of the station above mean sea level

and the height of the pressure sensor above ground level should be documented. If needed, the pressure can then be adjusted to a standard height.

If the pressure sensor is placed indoors, accommodations should be made to vent the pressure port to the outside environment. One end of a tube should be attached to the sensor's pressure port and the other end vented to the outside of the trailer or shelter so that pressurization due to the air conditioning or heating system is avoided. The wind can often cause dynamical changes of pressure in a room where a sensor is placed. These fluctuations may be on the order of 2 to 3 hPa when strong or gusty winds prevail.

6.4.9 Precipitation

Precipitation should be measured with a recording rain gauge such as a tipping bucket or weighing bucket. The rain gauge should be located on level ground in an open area. Obstructions should not be closer than two to four times their height from the instrument. The area around the rain gauge should be covered with natural vegetation. The mouth of the rain gauge should be level and should be as low as possible while still precluding in-splashing from the ground (30 cm above ground level is the recommended minimum height). A wind shield/wind screen (such as an Alter-type wind shield,[3] consisting of a ring with approximately 32 free-swinging separate metal leaves) should be employed to minimize the effects of high wind speeds.

6.5 Upper-Air Meteorological Monitoring

The design of the upper-air monitoring program will depend upon region specific factors such that the optimal design for a given PAMS region is expected to be some combination of remote sensing and conventional atmospheric soundings - in special cases, the upper-air monitoring plan may be augmented with data from aircraft and/or tall towers. Data from existing sources, e.g., the National Weather Service (NWS) upper-air network, should be considered and integrated with the PAMS monitoring plan.

Remote sensing systems (e.g., doppler SODAR) provide continuous measurements of wind speed and wind direction as a function of height. These data are needed to provide wind data with the necessary temporal and vertical resolution to evaluate changes in transport flow fields coincident with the evolution of the convective boundary layer. Such evaluations will aid in the diagnosis of conditions associated with extreme ozone concentrations. Remote sensing platforms for use in obtaining these data are discussed in Section 6.3.5.

Conventional atmospheric soundings obtained using rawinsondes or their equivalent are needed to provide atmospheric profiles with the necessary vertical resolution for estimating the mixing height (see Section 6.3.6) and for use in initializing the photochemical grid models used for evaluating ozone control strategies. Such soundings should extend to the top of the CBL or 1000 meters, whichever is greater, and should include measurements of wind speed, wind direction, temperature, and humidity. Four soundings per day are needed to adequately characterize the development of the atmospheric boundary layer. These soundings should be acquired just prior to sunrise when the atmospheric boundary layer is usually the most stable; in mid-morning when the growth of the boundary layer is most rapid; during mid-afternoon when surface temperatures are maximum; and in late-afternoon when the boundary layer depth is largest. Soundings obtained from a NWS upper-air station may be used to fulfill part of this requirement depending on the time of the sounding and the location of the NWS site. Rawinsondes for use in obtaining these data are discussed in Section 3.4.

The information presented in Sections 6.3.2 (Aircraft), 6.3.3 (Tall Towers), 6.3.4 (Balloon Systems), and 6.3.5 (Ground-Based Remote Sensors) provides background for use in designing an upper air monitoring plan for PAMS. The capabilities of the various platforms for upper-air meteorological monitoring (towers, balloon systems, and remote sensors) are compared in Table 6-6.

Table 6-6. Capabilities and Limitations of Meteorological Measurement Systems for Vertical Profiling of the Lower Atmosphere

Typical Maximum Height/Range (meters agl)[a]

	Measurement System						
Variable	Tower	SODAR	Mini-SODAR	RADAR	RADAR with RASS	Radio-sonde	Tether-sonde
Wind Speed	100[b]	600	300	2-3 km	2-3 km	>10 km	1000
Wind Direction	100[b]	600	300	2-3 km	2-3 km	>10 km	1000
Wind Sigmas[c]	100[b]	600	300	2-3 km	2-3 km	[d]	[d]
Relative Humidity	100[b]	[d]	[d]	[d]	[d]	>10 km	1000
Temperature	100[b]	[d]	[d]	[d]	1.2 km	>10 km	1000

Typical Minimum Height (meters agl)[a]

	Measurement System						
Variable	Tower	SODAR	Mini-SODAR	RADAR	RADAR with RASS	Radio-sonde	Tether-sonde
Wind Speed	10	50	10	100	100	10	10
Wind Direction	10	50	10	100	100	10	10
Wind Sigmas[c]	10	50	10	100	100	[d]	[d]
Relative Humidity	2	[d]	[d]	[d]	[d]	10	10
Temperature	2	[d]	[d]	[d]	100	10	10

Typical Resolution (meters)

	Measurement System						
Variable	Tower	SODAR	Mini-SODAR	RADAR	RADAR with RASS	Radio-sonde	Tether-sonde
Wind Speed	2-10	25	10	60-100	60-100	5-10	10
Wind Direction	2-10	25	10	60-100	60-100	5-10	10
Wind Sigmas[c]	2-10	25	10	60-100	60-100	[d]	[d]
Relative Humidity	2-10	[d]	[d]	[d]	[d]	5-10	10
Temperature	2-10	[d]	[d]	[d]	60-100	5-10	10

[a] Meters above ground level
[b] Typically meteorological towers do not exceed 100 m. However, radio and TV towers may exceed 600 m.
[c] The standard deviation of horizontal and vertical wind components.
[d] No capability for this variable

6.5.1 Siting and Exposure

The upper-air measurements are intended for more macro-scale application[3] than are the surface meteorological measurements. Consequently, the location of the upper-air site need not be associated with any particular PAMS surface site. Factors that should be considered in selecting a site for the upper-air monitoring include whether the upper-air measurements for the proposed location are likely to provide the necessary data to characterize the meteorological conditions associated with high ozone concentrations, and the extent to which data for the proposed location may augment an existing upper-air network. Near lake shores and in coastal areas, where land/sea/lake breeze circulations may play a significant role in ozone formation and transport, additional upper-air monitoring sites may be needed; this consideration would also apply to areas located in complex terrain. All of the above are necessary components of the DQOs for an upper-air monitoring plan.

6.5.2 Aircraft

Aircraft (both airplanes and helicopters) are a prime example of a mobile observation station. They are capable of traversing large horizontal and vertical distances in a relatively short period of time. An aircraft platform equipped with meteorological instrumentation can provide detailed atmospheric observations over large areas. Traditionally, aircraft are used for episodic field studies which often require extensive data sets for model evaluation. Lenschow[12] provides an excellent overview of aircraft measurements in boundary layer applications. While an aircraft can provide detailed atmospheric observations over large areas, the total sampling time per flight (typically 6 to 8 hours) is relatively short because of fuel considerations. Aircraft may also be subject to Federal Aviation Administration (FAA) restrictions on flight paths over urban areas. In addition, the operating cost for this type of platform is extremely expensive.

6.5.3 Tall Towers

In some instances it may be possible to use existing towers which may be located in PAMS areas to acquire vertical profiles of atmospheric boundary layer data. Radio and television transmission towers, which may be as tall as 600 m, can be equipped with in situ meteorological sensors at many levels. An advantage to using a tower is the ability to run an unattended data acquisition system. Also, data can normally be collected under all weather conditions. However, the main disadvantage of using a tower is the inability to determine the mixed layer height during most of the day. When moderate to strong convective conditions exist, the mixed layer height easily exceeds that of the tallest towers. Another disadvantage is the potentially high cost of maintenance, especially during instances when the instrumentation needs to be accessed for adjustments or repairs.

6.5.4 Balloon Systems

Balloon based systems include rawinsonde (sometimes called radiosonde) and tethersonde systems. The rawinsonde consists of a helium filled balloon, an instrument package, a radio transmitter, and a tracking device. The instrument package includes sensors for measuring atmospheric temperature, relative humidity, and barometric pressure. Data from ground-based radar, which is used to track the balloon, are processed to determine wind speed and direction. The height of the instrument package is determined by the ascent rate of the balloon. Typical specifications for the sensors used in rawinsondes are given in Table 6-7.

Table 6-7. Manufacturers' Specifications for Sensors Used in Rawinsondes

Sensor	Range	Accuracy	Resolution
Pressure	1080 to 3 mb	±0.5 mb	0.1 mb
Temperature	-90 to +60 °C	±0.2 °C	0.1 °C
Relative Humidity	5 to 100% RH		

Unlike surface measurements, there is no equivalent to system accuracy for upper-air meteorological measurements from rawinsondes. Consequently, to assess the quality of rawinsonde measurements, the NWS uses a special statistical parameter called the "functional precision," defined as the root-mean-square (rms) difference between measurements made by identical instruments at as nearly as possible the same time and same point in the atmosphere.[13] The functional precision of NWS radiosonde measurements is given in Table 6-8.

Table 6-8. Functional Precision of Rawinsonde Measurements[13]

Variable	Functional Precision
Wind Speed[a]	±3.1 m/s
Wind Direction[a]	±18 deg [≤ 3.1 m/s] ±14 deg [5.1 m/s] ± 9 deg [10.3 m/s] ± 6 deg [15.4 m/s] ± 5 deg [20.6 m/s]
Temperature[b]	±0.6°C
Dew Point Depression[b]	±3.3°C
Height[b]	±24 m

[a] at the same height
[b] at the same pressure

A tethersonde system is comprised of a tethered balloon with one or more instrument packages attached to the tether. The instrument package includes a radio transmitter and sensors to measure atmospheric temperature, relative humidity, barometric pressure, wind speed, and wind direction. Data are telemetered to the ground by radio or by conductors incorporated within the tethering cable. Tethersondes are capable of providing data up to about 1000 m in good conditions. Use of a tethersonde is limited by wind speed; they can only be used reliably in light to moderate wind conditions (5 m/s at the surface to 15 m/s aloft). Tethered balloons are also considered a hazard to aviation and thus are subject to FAA regulations. A permit is required to operate such a system.

6.5.5 Ground-Based Remote Sensors

Ground-based remote sensors have become effective tools for acquiring upper-air information and have played an increasingly important role in atmospheric boundary layer studies. There are two basic types of remote sensing systems used to acquire three-component wind velocity profiles: Radar (radio detection and ranging) and sodar (sound detection and ranging). Radars (also called wind profilers) transmit an electromagnetic signal (~ 915 MHZ) into the atmosphere in a predetermined beam width which is controlled by the configuration of the transmitting antenna. Sodars (also called acoustic sounders) transmit an acoustic signal (~ 2 to 5 KHz) into the atmosphere in a predetermined beam width which is also controlled by the transmitting antenna. The radar has a range of approximately 150 to 3000 m with a resolution of 60 to 100 m. The sodar has a range of about 50 to 1500 m with a resolution of about 25 to 50 m.

Both systems transmit their respective signals in pulses. Each pulse is both reflected and absorbed by the atmosphere as it propagates upwards. The vertical range of each pulse is determined by how high it can go before the signal becomes so weak that the energy reflected back to the antenna can no longer be detected. As long as the reflected pulses can be discerned from background noise, meaningful wind velocities can be obtained by comparing the doppler shift of the return signal to that of the output signal. A positive or negative doppler shift indicates whether the radial wind velocity is moving towards or away from the transmitting antenna. The attenuation of a transmitted pulse is a function of signal type, signal power, signal frequency, and atmospheric conditions. Radar signal reflection depends primarily on the presence of an index of refraction gradient in the atmosphere which varies with temperature and humidity. Sodar signal reflection depends primarily on the presence of small scale atmospheric turbulence. The reflected signals received by either a radar or sodar are processed in a system computer by signal conditioning algorithms.

In order to obtain a profile of the three-component wind velocity (U, V, W), one vertical beam and two tilted beams are needed. The two tilted beams are usually between 15^{o} and 30^{o}

from the vertical. These two beams are also at right angles to each other in azimuth. For example, one tilted beam may be oriented towards the north while the second tilted beam points east. Each antenna transmits a pulse and then listens for the reflected signal in succession. After all three antennas perform this function, enough information is available to convert the radial velocities into horizontal and vertical wind velocities by using simple trigonometric relationships.

There are two types of antenna configurations for radars and sodars: Monostatic and phased array. Monostatic systems consist of three individual transmit/receive antennas. Phased array consist of a single antenna array which can electronically steer the beam in the required directions. Vertical panels (also known as clutter fences) are usually placed around the antennas. This placement effectively acts to block out any stray side-lobe echoes from contaminating the return signal of a radar. For sodars, these panels cut down on the side-lobe noise which may be a nuisance to nearby residents and also prevents any background noise which may contaminate the return signal.

A RASS (radio acoustic sounding system) utilizes a combination of electromagnetic and acoustic pulses to derive a virtual air temperature profile. A RASS usually consists of several acoustic antennas placed around a radar system. The antennas transmit a sweep of acoustic frequencies vertically into the atmosphere. As the sound pulses rise, the speed of the acoustic wave varies according to the virtual air temperature. Concurrently, a radar beam is emitted vertically into the atmosphere. The radar beam will most strongly reflect off the sound wave fronts created by the acoustic pulses. The virtual air temperature is computed from the speed of sound which is measured by the reflected radar energy. The typical range of a RASS is approximately 150 to 1500 m with a resolution of 60 to 100 m.

Unlike in situ sensors which measure by direct contact, remote sensors do not disturb the atmosphere. Another fundamental difference is that remote sensors measure a volume of air rather than a fixed point in space. The thickness of the volume is a function of the pulse length and frequency used. The width of the volume is a function of beam spread and altitude. Siting

of these profilers is sometimes a difficult task. Artificial and natural objects located near the sensors can potentially interfere with the transmission and return signals, thereby contaminating the wind velocity data.

Since sodars utilize sound transmission and reception to determine the overlying wind field, a clear return signal with a sharply defined atmospheric peak frequency is required. Thus, consideration of background noise may put limitations on where a sodar can be located. External noise sources can be classified as active or passive, and as broad-band (random frequency) or narrow-band (fixed frequency). General background noise is considered active and is broad-band. If loud enough, it can cause the sodar software to reject data because it can not find a peak or because the signal-to-noise ratio is too low. The net effect is to lower the effective sampling rate due to the loss of many transmission pulses. A qualitative survey should be conducted to identify any potential noise sources. A quantitative noise survey may be necessary to determine if noise levels are within the instrument's minimum requirements.

Examples of active, broad-band noise sources include highways, industrial facilities, power plants, and heavy machinery. Some of these noise sources have a pronounced diurnal, weekly, or even seasonal pattern. A noise survey should at least cover diurnal and weekly patterns. Examination of land-use patterns and other sources of information may be necessary to determine if any seasonal activities may present problems.

Examples of active, fixed-frequency noise sources include rotating fans, a back-up beeper on a piece of heavy equipment, birds, and insects. If these noise sources have a frequency component in the sodar operating range, they may be misinterpreted as good data by the sodar. Some of these sources can be identified during the site selection process. One approach to reducing the problem of fixed frequency noise sources is to use a coded pulse, i.e., the transmit pulse has more than one peak frequency. A return pulse would not be identified as data unless peak frequencies were found in the return signal the same distance apart as the transmit frequencies.

Passive noise sources are objects either on or above the ground (e.g., tall towers, power transmission lines, buildings, trees) that can reflect a transmitted pulse back to the sodar antenna. While most of the acoustic energy is focused in a narrow beam, side-lobes do exist and are a particular concern when antenna enclosures have degraded substantially. Side-lobes reflecting off stationary objects and returning at the same frequency as the transmit pulse may be interpreted by the sodar as a valid atmospheric return with a speed of zero. It is not possible to predict precisely which objects may be a problem. Anything in the same general direction in which the antenna is pointing and higher than 5 to 10 m may be a potential reflector. It is therefore important to construct an "obstacle vista diagram" prior to sodar installation that identifies the direction and height of potential reflectors in relation to the sodar. This diagram can be used after some data have been collected to assess whether or not reflections are of concern at some sodar height ranges. Note that reflections from an object at distance X from an antenna will show up at height $X\cos(\alpha)$, where α is the tilt angle of the antenna from the vertical.

The radar, sodar, and RASS antennas should be aligned and tilted carefully as small errors in orientation or tilt angle can produce unwanted biases in the data. True North should also be established for antenna alignment. Installation of the antennas should not be permanent since problems are very likely to arise in siting the profilers in relation to the tower and other objects that may be in the area. One final consideration is the effect of the instrument on its surroundings. The sound pulse from a sodar and RASS is quite audible and could become a nuisance to residents who might happen to live near the installation site. This audible pulse should be a consideration in the siting process because of the potential irritation to nearby residents.

6.5.6 Estimation of Mixing Height

In addition to the directly measured meteorological variables, estimates are also required of the depth of the mixed layer (i.e., mixing height). The mixing height is a derived variable indicating the depth through which vertical mixing of pollutants occurs. Reliable estimates of the mixing height are essential to dispersion modeling in support of PAMS.

The EPA recommended method for estimating mixing height requires measurements of the vertical temperature profile.[14,15] In this method, the afternoon mixing height is calculated as the height above the ground of the intersection of the dry adiabatic extension of the maximum surface temperature with the 12 z morning temperature profile. This concept of a mixing layer in which the lapse rate is roughly dry adiabatic is well founded on general theoretical principles and on operational use in regulatory dispersion modeling over the last two decades. Comparisons of mixing height estimates based on the Holzworth method with several other techniques indicate that all methods perform similarly in estimating the maximum afternoon mixing depth.[16,17] The Holzworth method is normally preferred because of its simplicity.

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APPENDIX A

Method TO-15

Determination of Volatile Organic Compounds (VOCs) in Air Collected-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)

EPA/625/R-96/010b

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-15

Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

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Method TO-15
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METHOD TO-15

Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

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METHOD TO-15

Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

1. Scope

1.1 This method documents sampling and analytical procedures for the measurement of subsets of the 97 volatile organic compounds (VOCs) that are included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. VOCs are defined here as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25°C and 760 mm Hg. Table 1 is the list of the target VOCs along with their CAS number, boiling point, vapor pressure and an indication of their membership in both the list of VOCs covered by Compendium Method TO-14A (1) and the list of VOCs in EPA's Contract Laboratory Program (CLP) document entitled: *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites (2)*.

Many of these compounds have been tested for stability in concentration when stored in specially-prepared canisters (see Section 8) under conditions typical of those encountered in routine ambient air analysis. The stability of these compounds under all possible conditions is not known. However, a model to predict compound losses due to physical adsorption of VOCs on canister walls and to dissolution of VOCs in water condensed in the canisters has been developed (3). Losses due to physical adsorption require only the establishment of equilibrium between the condensed and gas phases and are generally considered short term losses, (i.e., losses occurring over minutes to hours). Losses due to chemical reactions of the VOCs with cocollected ozone or other gas phase species also account for some short term losses. Chemical reactions between VOCs and substances inside the canister are generally assumed to cause the gradual decrease of concentration over time (i.e., long term losses over days to weeks). Loss mechanisms such as aqueous hydrolysis and biological degradation (4) also exist. No models are currently known to be available to estimate and characterize all these potential losses, although a number of experimental observations are referenced in Section 8. Some of the VOCs listed in Title III have short atmospheric lifetimes and may not be present except near sources.

1.2 This method applies to ambient concentrations of VOCs above 0.5 ppbv and typically requires VOC enrichment by concentrating up to one liter of a sample volume. The VOC concentration range for ambient air in many cases includes the concentration at which continuous exposure over a lifetime is estimated to constitute a 10^{-6} or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at 10^{-6} risk concentrations, the total risk may be significantly greater.

1.3 This method applies under most conditions encountered in sampling of ambient air into canisters. However, the composition of a gas mixture in a canister, under unique or unusual conditions, will change so that the sample is known not to be a true representation of the ambient air from which it was taken. For example, low humidity conditions in the sample may lead to losses of certain VOCs on the canister walls, losses that would not happen if the humidity were higher. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water-soluble compounds. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence an absolute storage stability cannot be assigned to a specific gas. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs can be recovered from canisters near their original concentrations after storage times of up to thirty days (see Section 8).

1.4 Use of the Compendium Method TO-15 for many of the VOCs listed in Table 1 is likely to present two difficulties: (1) what calibration standard to use for establishing a basis for testing and quantitation, and (2) how to obtain an audit standard. In certain cases a chemical similarity exists between a thoroughly tested compound and others on the Title III list. In this case, what works for one is likely to work for the other in terms of making standards. However, this is not always the case and some compound standards will be troublesome. The reader is referred to the Section 9.2 on standards for guidance. Calibration of compounds such as formaldehyde, diazomethane, and many of the others represents a challenge.

1.5 Compendium Method TO-15 should be considered for use when a subset of the 97 Title III VOCs constitute the target list. Typical situations involve ambient air testing associated with the permitting procedures for emission sources. In this case sampling and analysis of VOCs is performed to determine the impact of dispersing source emissions in the surrounding areas. Other important applications are prevalence and trend monitoring for hazardous VOCs in urban areas and risk assessments downwind of industrialized or source-impacted areas.

1.6 Solid adsorbents can be used in lieu of canisters for sampling of VOCs, provided the solid adsorbent packings, usually multisorbent packings in metal or glass tubes, can meet the performance criteria specified in Compendium Method TO-17 which specifically addresses the use of multisorbent packings. The two sample collection techniques are different but become the same upon movement of the sample from the collection medium (canister or multisorbent tubes) onto the sample concentrator. Sample collection directly from the atmosphere by automated gas chromatographs can be used in lieu of collection in canisters or on solid adsorbents.

2. Summary of Method

2.1 The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister. Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

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

2.3 Upon receipt at the laboratory, the canister tag data is recorded and the canister is stored until analysis. Storage times of up to thirty days have been demonstrated for many of the VOCs (5).

2.4 To analyze the sample, a known volume of sample is directed from the canister through a solid multisorbent concentrator. A portion of the water vapor in the sample breaks through the concentrator during sampling, to a degree depending on the multisorbent composition, duration of sampling, and other factors. Water content of the sample can be further reduced by dry purging the concentrator with helium while retaining target compounds. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on a reduced

temperature trap or small volume multisorbent trap. The sample is then released by thermal desorption and carried onto a gas chromatographic column for separation.

As a simple alternative to the multisorbent/dry purge water management technique, the amount of water vapor in the sample can be reduced below any threshold for affecting the proper operation of the analytical system by reducing the sample size. For example, a small sample can be concentrated on a cold trap and released directly to the gas chromatographic column. The reduction in sample volume may require an enhancement of detector sensitivity.

Other water management approaches are also acceptable as long as their use does not compromise the attainment of the performance criteria listed in Section 11. A listing of some commercial water management systems is provided in Appendix A. One of the alternative ways to dry the sample is to separate VOCs from condensate on a low temperature trap by heating and purging the trap.

2.5 The analytical strategy for Compendium Method TO-15 involves using a high resolution gas chromatograph (GC) coupled to a mass spectrometer. If the mass spectrometer is a linear quadrupole system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN mode) or by monitoring select ion monitoring mode (SIM) of compounds on the target list. If the mass spectrometer is based on a standard ion trap design, only a scanning mode is used (note however, that the Selected Ion Storage (SIS) mode for the ion trap has features of the SIM mode). Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound. This establishes the compound concentration that exists in the sample.

Mass spectrometry is considered a more definitive identification technique than single specific detectors such as flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), or a multidetector arrangement of these (see discussion in Compendium Method TO-14A). The use of both gas chromatographic retention time and the generally unique mass fragmentation patterns reduce the chances for misidentification. If the technique is supported by a comprehensive mass spectral database and a knowledgeable operator, then the correct identification and quantification of VOCs is further enhanced.

3. Significance

3.1 Compendium Method TO-15 is significant in that it extends the Compendium Method TO-14A description for using canister-based sampling and gas chromatographic analysis in the following ways:

- Compendium Method TO-15 incorporates a multisorbent/dry purge technique or equivalent (see Appendix A) for water management thereby addressing a more extensive set of compounds (the VOCs mentioned in Title III of the CAAA of 1990) than addressed by Compendium Method TO-14A. Compendium Method TO-14A approach to water management alters the structure or reduces the sample stream concentration of some VOCs, especially water-soluble VOCs.

- Compendium Method TO-15 uses the GC/MS technique as the only means to identify and quantitate target compounds. The GC/MS approach provides a more scientifically-defensible detection scheme which is generally more desirable than the use of single or even multiple specific detectors.
- In addition, Compendium Method TO-15 establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent sampling and analytical equipment. There are several new and viable commercial approaches for water management as noted in Appendix A of this method on which to base a VOC monitoring technique as well as other approaches to sampling (i.e., autoGCs and solid adsorbents) that are often used. This method lists performance criteria that these alternatives must meet to be acceptable alternatives for monitoring ambient VOCs.
- Finally, Compendium Method TO-15 includes enhanced provisions for inherent quality control. The method uses internal analytical standards and frequent verification of analytical system performance to assure control of the analytical system. This more formal and better documented approach to quality control guarantees a higher percentage of good data.

3.2 With these features, Compendium Method TO-15 is a more general yet better defined method for VOCs than Compendium Method TO-14A. As such, the method can be applied with a higher confidence to reduce the uncertainty in risk assessments in environments where the hazardous volatile gases listed in the Title III of the Clean Air Act Amendments of 1990 are being monitored. An emphasis on risk assessments for human health and effects on the ecology is a current goal for the U.S. EPA.

4. Applicable Documents

4.1 ASTM Standards

- **Method D1356** *Definitions of Terms Relating to Atmospheric Sampling and Analysis*.
- **Method E260** *Recommended Practice for General Gas Chromatography Procedures*.
- **Method E355** *Practice for Gas Chromatography Terms and Relationships.*
- **Method D5466** *Standard Test Method of Determination of Volatile Organic Compounds in Atmospheres (Canister Sampling Methodology).*

4.2 EPA Documents

- *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II,* U. S. Environmental Protection Agency, EPA-600/R-94-038b, May 1994.
- *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air,* U. S. Environmental Protection Agency, EPA-600/4-83-027, June 1983.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-14, Second Supplement,* U. S. Environmental Protection Agency, EPA-600/4-89-018, March 1989.
- *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites,* U. S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C., Draft Report, June 1990.
- *Clean Air Act Amendments of 1990,* U. S. Congress, Washington, D.C., November 1990.

5. Definitions

[Note: Definitions used in this document and any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, E260, and E355. Aside from the definitions given below, all pertinent abbreviations and symbols are defined within this document at point of use.]

5.1 Gauge Pressure—pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or psi. Zero gauge pressure is equal to atmospheric (barometric) pressure.

5.2 Absolute Pressure—pressure measured with reference to absolute zero pressure, usually expressed in units of kPa, or psi.

5.3 Cryogen—a refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Typical cryogens are liquid nitrogen (bp -195.8°C), liquid argon (bp -185.7°C), and liquid CO_2 (bp -79.5°C).

5.4 Dynamic Calibration—calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system from a manifold through which the gas standards are flowing.

5.5 Dynamic Dilution—means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with humidified zero air in a manifold so that a flowing stream of calibration mixture is available at the inlet of the analytical system.

5.6 MS-SCAN—mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

5.7 MS-SIM—mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

5.8 Qualitative Accuracy—the degree of measurement accuracy required to correctly identify compounds with an analytical system.

5.9 Quantitative Accuracy—the degree of measurement accuracy required to correctly measure the concentration of an identified compound with an analytical system with known uncertainty.

5.10 Replicate Precision—precision determined from two canisters filled from the same air mass over the same time period and determined as the absolute difference between the analyses of canisters divided by their sum and expressed as a percentage (see Section 11 for performance criteria for replicate precision).

5.11 Duplicate Precision—precision determined from the analysis of two samples taken from the same canister. The duplicate precision is determined as the absolute difference between the canister analyses divided by their sum and expressed as a percentage (see Section 11 for performance criteria for duplicate precision).

5.12 Audit Accuracy—the difference between the analysis of a sample provided in an audit canister and the nominal value as determined by the audit authority, divided by the audit value and expressed as a percentage (see Section 11 for performance criteria for audit accuracy).

6. Interferences and Contamination

6.1 Very volatile compounds, such as chloromethane and vinyl chloride can display peak broadening and co-elution with other species if the compounds are not delivered to the GC column in a small volume of carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing trap or at the head of the gas chromatographic column, mitigates this problem.

6.2 Interferences in canister samples may result from improper use or from contamination of: (1) the canisters due to poor manufacturing practices, (2) the canister cleaning apparatus, and (3) the sampling or analytical system. Attention to the following details will help to minimize the possibility of contamination of canisters.

6.2.1 Canisters should be manufactured using high quality welding and cleaning techniques, and new canisters should be filled with humidified zero air and then analyzed, after "aging" for 24 hours, to determine cleanliness. The cleaning apparatus, sampling system, and analytical system should be assembled of clean, high quality components and each system should be shown to be free of contamination.

6.2.2 Canisters should be stored in a contaminant-free location and should be capped tightly during shipment to prevent leakage and minimize any compromise of the sample.

6.2.3 Impurities in the calibration dilution gas (if applicable) and carrier gas, organic compounds out-gassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with Buna-N rubber components must be avoided.

6.2.4 Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses. Whenever a high concentration (>25 ppbv of a trace species) sample is encountered, it should be followed by an analysis of humid zero air to check for carry-over contamination.

6.2.5 In cases when solid sorbents are used to concentrate the sample prior to analysis, the sorbents should be tested to identify artifact formation (see Compendium Method TO-17 for more information on artifacts).

7. Apparatus and Reagents

[Note: Compendium Method To-14A list more specific requirements for sampling and analysis apparatus which may be of help in identifying options. The listings below are generic.]

7.1 Sampling Apparatus

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

7.1.1 Subatmospheric Pressure (see Figure 1, without metal bellows type pump).

7.1.1.1 Sampling Inlet Line. Stainless steel tubing to connect the sampler to the sample inlet.

7.1.1.2 Sample Canister. Leak-free stainless steel pressure vessels of desired volume (e.g., 6 L), with valve and specially prepared interior surfaces (see Appendix B for a listing of known manufacturers/resellers of canisters).

7.1.1.3 Stainless Steel Vacuum/Pressure Gauges. Two types are required, one capable of measuring vacuum (–100 to 0 kPa or 0 to - 30 in Hg) and pressure (0–206 kPa or 0–30 psig) in the sampling system and a second type (for checking the vacuum of canisters during cleaning) capable of measuring at 0.05 mm Hg (see Appendix B) within 20%. Gauges should be tested clean and leak tight.

7.1.1.4 Electronic Mass Flow Controller. Capable of maintaining a constant flow rate (± 10%) over a sampling period of up to 24 hours and under conditions of changing temperature (20–40°C) and humidity.

7.1.1.5 Particulate Matter Filter. 2-μm sintered stainless steel in-line filter.

7.1.1.6 Electronic Timer. For unattended sample collection.

7.1.1.7 Solenoid Valve. Electrically-operated, bi-stable solenoid valve with Viton® seat and O-rings. A Skinner Magnelatch valve is used for purposes of illustration in the text (see Figure 2).

7.1.1.8 Chromatographic Grade Stainless Steel Tubing and Fittings. For interconnections. All such materials in contact with sample, analyte, and support gases prior to analysis should be chromatographic grade stainless steel or equivalent.

7.1.1.9 Thermostatically Controlled Heater. To maintain above ambient temperature inside insulated sampler enclosure.

7.1.1.10 Heater Thermostat. Automatically regulates heater temperature.

7.1.1.11 Fan. For cooling sampling system.

7.1.1.12 Fan Thermostat. Automatically regulates fan operation.

7.1.1.13 Maximum-Minimum Thermometer. Records highest and lowest temperatures during sampling period.

7.1.1.14 Stainless Steel Shut-off Valve. Leak free, for vacuum/pressure gauge.

7.1.1.15 Auxiliary Vacuum Pump. Continuously draws air through the inlet manifold at 10 L/min. or higher flow rate. Sample is extracted from the manifold at a lower rate, and excess air is exhausted.

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

7.1.1.16 Elapsed Time Meter. Measures duration of sampling.

7.1.1.17 Optional Fixed Orifice, Capillary, or Adjustable Micrometering Valve. May be used in lieu of the electronic flow controller for grab samples or short duration time-integrated samples. Usually appropriate only in situations where screening samples are taken to assess future sampling activity.

7.1.2 Pressurized (see Figure 1 with metal bellows type pump and Figure 3).

7.1.2.1 Sample Pump. Stainless steel, metal bellows type, capable of 2 atmospheres output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds.

[Note: An alternative sampling system has been developed by Dr. R. Rasmussen, The Oregon Graduate Institute of Science and Technology, 20000 N.W. Walker Rd., Beaverton, Oregon 97006, 503-690-1077, and is illustrated in Figure 3. This flow system uses, in order, a pump, a mechanical flow regulator, and a mechanical compensation flow restrictive device. In this configuration the pump is purged with a large sample flow, thereby eliminating the need for an auxiliary vacuum pump to flush the sample inlet.]

7.1.2.2 Other Supporting Materials. All other components of the pressurized sampling system are similar to components discussed in Sections 7.1.1.1 through 7.1.1.17.

7.2 Analytical Apparatus

7.2.1 Sampling/Concentrator System (many commercial alternatives are available).

7.2.1.1 Electronic Mass Flow Controllers. Used to maintain constant flow (for purge gas, carrier gas and sample gas) and to provide an analog output to monitor flow anomalies.

7.2.1.2 Vacuum Pump. General purpose laboratory pump, capable of reducing the downstream pressure of the flow controller to provide the pressure differential necessary to maintain controlled flow rates of sample air.

7.2.1.3 Stainless Steel Tubing and Stainless Steel Fittings. Coated with fused silica to minimize active adsorption sites.

7.2.1.4 Stainless Steel Cylinder Pressure Regulators. Standard, two-stage cylinder regulators with pressure gauges.

7.2.1.5 Gas Purifiers. Used to remove organic impurities and moisture from gas streams.

7.2.1.6 Six-port Gas Chromatographic Valve. For routing sample and carrier gas flows.

7.2.1.7 Multisorbent Concentrator. Solid adsorbent packing with various retentive properties for adsorbing trace gases are commercially available from several sources. The packing contains more than one type of adsorbent packed in series.

7.2.1.7.1A pre-packed adsorbent trap (Supelco 2-0321) containing 200 mg Carbopack B (60/80 mesh) and 50 mg Carbosieve S-III (60/80 mesh) has been found to retain VOCs and allow some water vapor to pass through (6). The addition of a dry purging step allows for further water removal from the adsorbent trap. The steps constituting the dry purge technique that are normally used with multisorbent traps are illustrated in Figure 4. The optimum trapping and dry purging procedure for the Supelco trap consists of a sample volume of 320 mL and a dry nitrogen purge of 1300 mL. Sample trapping and drying is carried out at 25°C. The trap is back-flushed with helium and heated to 220°C to transfer material onto the GC column. A trap bake-out at 260°C for 5 minutes is conducted after each run.

7.2.1.7.2 An example of the effectiveness of dry purging is shown in Figure 5. The multisorbent used in this case is Tenax/Ambersorb 340/Charcoal (7). Approximately 20% of the initial water content in the sample remains after sampling 500 mL of air. The detector response to water vapor (hydrogen atoms detected by atomic emission detection) is plotted versus purge gas volume. Additional water reduction by a factor of 8 is indicated at temperatures of 45°C or higher. Still further water reduction is possible using a two-stage concentration/dryer system.

7.2.1.8 Cryogenic Concentrator. Complete units are commercially available from several vendor sources. The characteristics of the latest concentrators include a rapid, "ballistic" heating of the concentrator to release any trapped VOCs into a small carrier gas volume. This facilitates the separation of compounds on the gas chromatographic column.

7.2.2 Gas Chromatographic/Mass Spectrometric (GC/MS) System.

7.2.2.1 Gas Chromatograph. The gas chromatographic (GC) system must be capable of temperature programming. The column oven can be cooled to subambient temperature (e.g., -50°C) at the start of the gas

chromatographic run to effect a resolution of the very volatile organic compounds. In other designs, the rate of release of compounds from the focusing trap in a two stage system obviates the need for retrapping of compounds on the column. The system must include or be interfaced to a concentrator and have all required accessories including analytical columns and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with Buna-N rubber components must not be used.

7.2.2.2 Chromatographic Columns. 100% methyl silicone or 5% phenyl, 95% methyl silicone fused silica capillary columns of 0.25- to 0.53-mm I.D. of varying lengths are recommended for separation of many of the possible subsets of target compounds involving nonpolar compounds. However, considering the diversity of the target list, the choice is left to the operator subject to the performance standards given in Section 11.

7.2.2.3 Mass Spectrometer. Either a linear quadrupole or ion trap mass spectrometer can be used as long as it is capable of scanning from 35 to 300 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 50 ng or less of p-bromofluorobenzene (BFB) is analyzed.

7.2.2.3.1Linear Quadrupole Technology. A simplified diagram of the heart of the quadrupole mass spectrometer is shown in Figure 6. The quadrupole consists of a parallel set of four rod electrodes mounted in a square configuration. The field within the analyzer is created by coupling opposite pairs of rods together and applying radiofrequency (RF) and direct current (DC) potentials between the pairs of rods. Ions created in the ion source from the reaction of column eluates with electrons from the electron source are moved through the parallel array of rods under the influence of the generated field. Ions which are successfully transmitted through the quadrupole are said to possess stable trajectories and are subsequently recorded with the detection system. When the DC potential is zero, a wide band of m/z values is transmitted through the quadrupole. This "RF only" mode is referred to as the "total-ion" mode. In this mode, the quadrupole acts as a strong focusing lens analogous to a high pass filter. The amplitude of the RF determines the low mass cutoff. A mass spectrum is generated by scanning the DC and RF voltages using a fixed DC/RF ratio and a constant drive frequency or by scanning the frequency and holding the DC and RF constant. With the quadrupole system only 0.1 to 0.2 percent of the ions formed in the ion source actually reach the detector.

7.2.2.3.2Ion Trap Technology. An ion-trap mass spectrometer consists of a chamber formed between two metal surfaces in the shape of a hyperboloid of one sheet (ring electrode) and a hyperboloid of two sheets (the two end-cap electrodes). Ions are created within the chamber by electron impact from an electron beam admitted through a small aperture in one of the end caps. Radio frequency (RF) (and sometimes direct current voltage offsets) are applied between the ring electrode and the two end-cap electrodes establishing a quadrupole electric field. This field is uncoupled in three directions so that ion motion can be considered independently in each direction; the force acting upon an ion increases with the displacement of the ion from the center of the field but the direction of the force depends on the instantaneous voltage applied to the ring electrode. A restoring force along one coordinate (such as the distance, r, from the ion-trap's axis of radial symmetry) will exist concurrently with a repelling force along another coordinate (such as the distance, z, along the ion traps axis), and if the field were static the ions would eventually strike an electrode. However, in an RF field the force along each coordinate alternates direction so that a stable trajectory may be possible in which the ions do not strike a surface. In practice, ions of appropriate mass-to-charge ratios may be trapped within the device for periods of milliseconds to hours. A diagram of a typical ion trap is illustrated in Figure 7. Analysis of stored ions is performed by increasing the RF voltage, which makes the ions successively unstable. The effect of the RF voltage on the ring electrode is to "squeeze" the ions in the xy plane so that they move along the z axis. Half the ions are lost to the top cap (held at ground potential); the

remaining ions exit the lower end cap to be detected by the electron multiplier. As the energy applied to the ring electrode is increased, the ions are collected in order of increasing mass to produce a conventional mass spectrum. With the ion trap, approximately 50 percent of the generated ions are detected. As a result, a significant increase in sensitivity can be achieved when compared to a full scan linear quadrupole system.

7.2.2.4 GC/MS Interface. Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points for each of the analytes of interest and can be used to achieve all acceptable performance criteria may be used. Gas chromatograph to mass spectrometer interfaces constructed of all-glass, glass-lined, or fused silica-lined materials are recommended. Glass and fused silica should be deactivated.

7.2.2.5 Data System. The computer system that is interfaced to the mass spectrometer must allow the continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as a Selected Ion Current Profile (SICP). Software must also be available that allows integrating the abundance in any SICP between specified time or scan number limits. Also, software must be available that allows for the comparison of sample spectra with reference library spectra. The National Institute of Standards and Technology (NIST) or Wiley Libraries or equivalent are recommended as reference libraries.

7.2.2.6 Off-line Data Storage Device. Device must be capable of rapid recording and retrieval of data and must be suitable for long-term, off-line data storage.

7.3 Calibration System and Manifold Apparatus (see Figure 8)

7.3.1 Calibration Manifold. Stainless steel, glass, or high purity quartz manifold, (e.g.,1.25-cm I.D. x 66-cm) with sampling ports and internal baffles for flow disturbance to ensure proper mixing. The manifold should be heated to ~50°C.

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

7.3.3 Electronic Mass Flow Controllers. One 0 to 5 L/min unit and one or more 0 to 100 mL/min units for air, depending on number of cylinders in use for calibration.

7.3.4 Teflon Filter(s). 47-mm Teflon® filter for particulate collection.

7.4 Reagents

7.4.1 Neat Materials or Manufacturer-Certified Solutions/Mixtures. Best source (see Section 9).

7.4.2 Helium and Air. Ultra-high purity grade in gas cylinders. He is used as carrier gas in the GC.

7.4.3 Liquid Nitrogen or Liquid Carbon Dioxide. Used to cool secondary trap.

7.4.4 Deionized Water. High performance liquid chromatography (HPLC) grade, ultra-high purity (for humidifier).

8. Collection of Samples in Canisters

8.1 Introduction

8.1.1 Canister samplers, sampling procedures, and canister cleaning procedures have not changed very much from the description given in the original Compendium Method TO-14. Much of the material in this

section is therefore simply a restatement of the material given in Compendium Method TO-14, repeated here in order to have all the relevant information in one place.

8.1.2 Recent notable additions to the canister technology has been in the application of canister-based systems for example, to microenvironmental monitoring (8), the capture of breath samples (9), and sector sampling to identify emission sources of VOCs (10).

8.1.3 EPA has also sponsored the development of a mathematical model to predict the storage stability of arbitrary mixtures of trace gases in humidified air (3), and the investigation of the SilcoSteel™ process of coating the canister interior with a film of fused silica to reduce surface activity (11). A recent summary of storage stability data for VOCs in canisters is given in the open literature (5).

8.2 Sampling System Description

8.2.1 Subatmospheric Pressure Sampling [see Figure 1 (without metal bellows type pump)].

8.2.1.1 In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.05 mm Hg (see Appendix C for discussion of evacuation pressure). When the canister is opened to the atmosphere containing the VOCs to be sampled, the differential pressure causes the sample to flow into the canister. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-weighted-average (TWA) samples (duration of 1-24 hours) taken through a flow-restrictive inlet (e.g., mass flow controller, critical orifice).

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

8.2.2 Pressurized Sampling [see Figure 1 (with metal bellows type pump)].

8.2.2.1 Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. The sample is collected in a canister using a pump and flow control arrangement to achieve a typical 101-202 kPa (15-30 psig) final canister pressure. For example, a 6-liter evacuated canister can be filled at 10 mL/min for 24 hours to achieve a final pressure of 144 kPa (21 psig).

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

8.2.3 All Samplers.

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

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

where:

F = flow rate, mL/min.

P = final canister pressure, atmospheres absolute. P is approximately equal to

$$\frac{\text{kPa gauge}}{101.2} + 1$$

V = volume of the canister, mL.
T = sample period, hours.

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

$$F = \frac{2 \text{ x } 6000}{24 \text{ x } 60} = 8.3 \text{ mL/min}$$

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

8.2.3.3 The use of the Skinner Magnelatch valve (see Figure 2) avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve that would have to be energized during the entire sample period. The temperature rise in the valve could cause outgassing of organic compounds from the Viton® valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained either with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods, or with a conventional mechanical timer and a special pulse circuit. A simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer is illustrated in Figure 2(a). However, with this simple circuit, the valve may operate unreliably during brief power interruptions or if the timer is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 2(b).

8.2.3.4 The connecting lines between the sample inlet and the canister should be as short as possible to minimize their volume. The flow rate into the canister should remain relatively constant over the entire sampling period.

8.2.3.5 As an option, a second electronic timer may be used to start the auxiliary pump several hours prior to the sampling period to flush and condition the inlet line.

8.2.3.6 Prior to field use, each sampling system must pass a humid zero air certification (see Section 8.4.3). All plumbing should be checked carefully for leaks. The canisters must also pass a humid zero air certification before use (see Section 8.4.1).

8.3 Sampling Procedure

8.3.1 The sample canister should be cleaned and tested according to the procedure in Section 8.4.1.

8.3.2 A sample collection system is assembled as shown in Figures 1 and 3 and must be cleaned according to the procedure outlined in Sections 8.4.2 and 8.4.4.

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

8.3.3 Prior to locating the sampling system, the user may want to perform "screening analyses" using a portable GC system, as outlined in Appendix B of Compendium Method TO-14A, to determine potential volatile organics present and potential "hot spots." The information gathered from the portable GC screening analysis would be used in developing a monitoring protocol, which includes the sampling system location, based upon the "screening analysis" results.

8.3.4 After "screening analysis," the sampling system is located. Temperatures of ambient air and sampler box interior are recorded on the canister sampling field test data sheet (FTDS), as documented in Figure 9.

[Note: The following discussion is related to Figure 1]

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

[Note: For a subatmospheric sampler, a flow meter and practice canister are needed. For the pump-driven system, the practice canister is not needed, as the flow can be measured at the outlet of the system.]

A certified mass flow meter is attached to the inlet line of the manifold, just in front of the filter. The canister is opened. The sampler is turned on and the reading of the certified mass flow meter is compared to the sampler mass flow controller. The values should agree within ±10%. If not, the sampler mass flow meter needs to be recalibrated or there is a leak in the system. This should be investigated and corrected.

[Note: Mass flow meter readings may drift. Check the zero reading carefully and add or subtract the zero reading when reading or adjusting the sampler flow rate to compensate for any zero drift.]

After 2 minutes, the desired canister flow rate is adjusted to the proper value (as indicated by the certified mass flow meter) by the sampler flow control unit controller (e.g., 3.5 mL/min for 24 hr, 7.0 mL/min for 12 hr). Record final flow under "CANISTER FLOW RATE" on the FTDS.

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

[Note: Whenever the sampler is turned off, wait at least 30 seconds to turn the sampler back on.]

8.3.7 The "practice" canister and certified mass flow meter are disconnected and a clean certified (see Section 8.4.1) canister is attached to the system.

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

8.3.9 Pressure/vacuum in the canister is recorded on the canister FTDS (see Figure 9) as indicated by the sampler vacuum/pressure gauge.

8.3.10 The vacuum/pressure gauge valve is closed and the maximum-minimum thermometer is reset to current temperature. Time of day and elapsed time meter readings are recorded on the canister FTDS.

8.3.11 The electronic timer is set to start and stop the sampling period at the appropriate times. Sampling starts and stops by the programmed electronic timer.

8.3.12 After the desired sampling period, the maximum, minimum, current interior temperature and current ambient temperature are recorded on the FTDS. The current reading from the flow controller is recorded.

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

[Note: For a subatmospheric sampling system, if the canister is at atmospheric pressure when the field final pressure check is performed, the sampling period may be suspect. This information should be noted on the sampling field data sheet.]

Time of day and elapsed time meter readings are also recorded.

8.3.14 The canister valve is closed. The sampling line is disconnected from the canister and the canister is removed from the system. For a subatmospheric system, a certified mass flow meter is once again connected to the inlet manifold in front of the in-line filter and a "practice" canister is attached to the Magnelatch valve of the sampling system. The final flow rate is recorded on the canister FTDS (see Figure 9).

[Note: For a pressurized system, the final flow may be measured directly.]

The sampler is turned off.

8.3.15 An identification tag is attached to the canister. Canister serial number, sample number, location, and date, as a minimum, are recorded on the tag. The canister is routinely transported back to the analytical laboratory with other canisters in a canister shipping case.

8.4 Cleaning and Certification Program

8.4.1 Canister Cleaning and Certification.

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

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

[Note: The canister cleaning system in Figure 10 can be used for this task.]

The initial pressure is measured, the canister valve is closed, and the final pressure is checked after 24 hours. If acceptable, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period.

8.4.1.3 A canister cleaning system may be assembled as illustrated in Figure 10. Cryogen is added to both the vacuum pump and zero air supply traps. The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The vacuum pump is started and the vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) are evacuated to <0.05 mm Hg (see Appendix B) for at least 1 hour.

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

Air released/evacuated from canisters should be diverted to a fume hood.

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

8.4.1.5 The zero air shut-off valve is closed and the canister(s) is allowed to vent down to atmospheric pressure through the vent shut-off valve. The vent shut-off valve is closed. Repeat Sections 8.4.1.3 through 8.4.1.5 two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

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

8.4.1.7 The canister is reattached to the cleaning manifold and is then reevacuated to <0.05 mm Hg (see Appendix B) and remains in this condition until used. The canister valve is closed. The canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting. The canister is now ready for collection of an air sample. An identification tag is attached to the inlet of each canister for field notes and chain-of-custody purposes. An alternative to evacuating the canister at this point is to store the canisters and reevacuate them just prior to the next use.

8.4.1.8 As an option to the humid zero air cleaning procedures, the canisters are heated in an isothermal oven not to exceed 100°C during evacuation of the canister to ensure that higher molecular weight compounds are not retained on the walls of the canister.

[Note: For sampling more complex VOC mixtures the canisters should be heated to higher temperatures during the cleaning procedure although a special high temperature valve would be needed].

Once heated, the canisters are evacuated to <0.05 mm Hg (see Appendix B) and maintained there for 1 hour. At the end of the heated/evacuated cycle, the canisters are pressurized with humid zero air and analyzed by a GC/MS system after a minimum of 12 hrs of "aging." Any canister that has not tested clean (less than 0.2 ppbv each of targeted compounds) should not be used. Once tested clean, the canisters are reevacuated to <0.05 mm Hg (see Appendix B) and remain in the evacuated state until used. As noted in Section 8.4.1.7, reevacuation can occur just prior to the next use.

8.4.2 Cleaning Sampling System Components.

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

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

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

8.4.3 Zero Air Certification.

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

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

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

8.4.3.3 The humid zero gas stream passes through the calibration manifold, through the sampling system (without an evacuated canister) to the water management system/VOC preconcentrator of an analytical system.

[Note: The exit of the sampling system (without the canister) replaces the canister in Figure 11.]

After the sample volume (e.g., 500 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed and refocussed on a cold trap. This trap is heated and the VOCs are thermally desorbed

onto the head of the capillary column. The VOCs are refocussed prior to gas chromatographic separation. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC/MS (see Section 10) system. The analytical system should not detect greater than 0.2 ppbv of any targeted VOCs in order for the sampling system to pass the humid zero air certification test. Chromatograms (using an FID) of a certified sampler and contaminated sampler are illustrated in Figures 12(a) and 12(b), respectively. If the sampler passes the humid zero air test, it is then tested with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling (e.g., 0.5 to 2 ppbv) as outlined in Section 8.4.4.

8.4.4 Sampler System Certification with Humid Calibration Gas Standards from a Dynamic Calibration System

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

8.4.4.2 Verify that the calibration system is clean (less than 0.2 ppbv of any target compounds) by sampling a humidified gas stream, *without* gas calibration standards, with a previously certified clean canister (see Section 8.1).

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

8.4.4.4 For generating the humidified calibration standards, the calibration gas cylinder(s) containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs is attached to the calibration system as illustrated in Figure 8. The gas cylinders are opened and the gas mixtures are passed through 0 to 10 mL/min certified mass flow controllers to generate ppb levels of calibration standards.

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

8.4.4.6 Sample the dynamic calibration gas stream with the sampling system.

8.4.4.7 Concurrent with the sampling system operation, realtime monitoring of the calibration gas stream is accomplished by the on-line GC/MS analytical system [Figure 8(a)] to provide reference concentrations of generated VOCs.

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

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

8.4.5 Sampler System Certification without Compressed Gas Cylinder Standards.

8.4.5.1 Not all the gases on the Title III list are available/compatible with compressed gas standards. In these cases sampler certification must be approached by different means.

8.4.5.2 Definitive guidance is not currently available in these cases; however, Section 9.2 lists several ways to generate gas standards. In general, Compendium Method TO-14A compounds (see Table 1) are available commercially as compressed gas standards.

9. GC/MS Analysis of Volatiles from Canisters

9.1 Introduction

9.1.1 The analysis of canister samples is accomplished with a GC/MS system. Fused silica capillary columns are used to achieve high temporal resolution of target compounds. Linear quadrupole or ion trap mass spectrometers are employed for compound detection. The heart of the system is composed of the sample inlet concentrating device that is needed to increase sample loading into a detectable range. Two

examples of concentrating systems are discussed. Other approaches are acceptable as long as they are compatible with achieving the system performance criteria given in Section 11.

9.1.2 With the first technique, a whole air sample from the canister is passed through a multisorbent packing (including single adsorbent packings) contained within a metal or glass tube maintained at or above the surrounding air temperature. Depending on the water retention properties of the packing, some or most of the water vapor passes completely through the trap during sampling. Additional drying of the sample is accomplished after the sample concentration is completed by forward purging the trap with clean, dry helium or another inert gas (air is not used). The sample is then thermally desorbed from the packing and backflushed from the trap onto a gas chromatographic column. In some systems a "refocusing" trap is placed between the primary trap and the gas chromatographic column. The specific system design downstream of the primary trap depends on technical factors such as the rate of thermal desorption and sampled volume, but the objective in most cases is to enhance chromatographic resolution of the individual sample components before detection on a mass spectrometer.

9.1.3 Sample drying strategies depend on the target list of compounds. For some target compound lists, the multisorbent packing of the concentrator can be selected from hydrophobic adsorbents which allow a high percentage of water vapor in the sample to pass through the concentrator during sampling and without significant loss of the target compounds. However, if very volatile organic compounds are on the target list, the adsorbents required for their retention may also strongly retain water vapor and a more lengthy dry purge is necessary prior to analysis.

9.1.4 With the second technique, a whole air sample is passed through a concentrator where the VOCs are condensed on a reduced temperature surface (cold trap). Subsequently, the condensed gases are thermally desorbed and backflushed from the trap with an inert gas onto a gas chromatographic column. This concentration technique is similar to that discussed in Compendium Method TO-14, although a membrane dryer is not used. The sample size is reduced in volume to limit the amount of water vapor that is also collected (100 mL or less may be necessary). The attendant reduction in sensitivity is offset by enhancing the sensitivity of detection, for example by using an ion trap detector.

9.2 Preparation of Standards

9.2.1 Introduction.

9.2.1.1 When available, standard mixtures of target gases in high pressure cylinders must be certified traceable to a NIST Standard Reference Material (SRM) or to a NIST/EPA approved Certified Reference Material (CRM). Manufacturer's certificates of analysis must be retained to track the expiration date.

9.2.1.2 The neat standards that are used for making trace gas standards must be of high purity; generally a purity of 98 percent or better is commercially available.

9.2.1.3 Cylinder(s) containing approximately 10 ppmv of each of the target compounds are typically used as primary stock standards. The components may be purchased in one cylinder or in separate cylinders depending on compatibility of the compounds and the pressure of the mixture in the cylinder. Refer to manufacturer's specifications for guidance on purchasing and mixing VOCs in gas cylinders.

9.2.2 Preparing Working Standards.

9.2.2.1 Instrument Performance Check Standard. Prepare a standard solution of BFB in humidified zero air at a concentration which will allow collection of 50 ng of BFB or less under the optimized concentration parameters.

9.2.2.2 Calibration Standards. Prepare five working calibration standards in humidified zero air at a concentration which will allow collection at the 2, 5, 10, 20, and 50 ppbv level for each component under the optimized concentration parameters.

9.2.2.3 Internal Standard Spiking Mixture. Prepare an internal spiking mixture containing bromochloromethane, chlorobenzene-d_5, and 1,4-difluorobenzene at 10 ppmv each in humidified zero air to be added to the sample or calibration standard. 500 µL of this mixture spiked into 500 mL of sample will result in a concentration of 10 ppbv. The internal standard is introduced into the trap during the collection time for all calibration, blank, and sample analyses using the apparatus shown in Figure 13 or by equivalent means. The volume of internal standard spiking mixture added for each analysis must be the same from run to run.

9.2.3 Standard Preparation by Dynamic Dilution Technique.

9.2.3.1 Standards may be prepared by dynamic dilution of the gaseous contents of a cylinder(s) containing the gas calibration stock standards with humidified zero air using mass flow controllers and a calibration manifold. The working standard may be delivered from the manifold to a clean, evacuated canister using a pump and mass flow controller.

9.2.3.2 Alternatively, the analytical system may be calibrated by sampling directly from the manifold if the flow rates are optimized to provide the desired amount of calibration standards. However, the use of the canister as a reservoir prior to introduction into the concentration system resembles the procedure normally used to collect samples and is preferred. Flow rates of the dilution air and cylinder standards (all expressed in the same units) are measured using a bubble meter or calibrated electronic flow measuring device, and the concentrations of target compounds in the manifold are then calculated using the dilution ratio and the original concentration of each compound.

$$\text{Manifold Conc.} = \frac{(\text{Original Conc.})\ (\text{Std. Gas Flowrate})}{(\text{Air Flowrate}) + (\text{Std. Gas Flowrate})}$$

9.2.3.3 Consider the example of 1 mL/min flow of 10 ppmv standard diluted with 1,000 mL/min of humid air provides a nominal 10 ppbv mixture, as calculated below:

$$\text{Manifold Conc.} = \frac{(10\ \text{ppm})(1\ \text{mL/min})(1000\ \text{ppb/1 ppm})}{(1000\ \text{mL/min}) + (1\ \text{mL/min})} = 10\ \text{ppb}$$

9.2.4 Standard Preparation by Static Dilution Bottle Technique

[Note: Standards may be prepared in canisters by spiking the canister with a mixture of components prepared in a static dilution bottle (12). This technique is used specifically for liquid standards.]

9.2.4.1 The volume of a clean 2-liter round-bottom flask, modified with a threaded glass neck to accept a Mininert septum cap, is determined by weighing the amount of water required to completely fill up the flask. Assuming a density for the water of 1 g/mL, the weight of the water in grams is taken as the volume of the flask in milliliters.

9.2.4.2 The flask is flushed with helium by attaching a tubing into the glass neck to deliver the helium. After a few minutes, the tubing is removed and the glass neck is immediately closed with a Mininert septum cap.

9.2.4.3 The flask is placed in a 60°C oven and allowed to equilibrate at that temperature for about 15 minutes. Predetermined aliquots of liquid standards are injected into the flask making sure to keep the flask temperature constant at 60°C.

9.2.4.4 The contents are allowed to equilibrate in the oven for at least 30 minutes. To avoid condensation, syringes must be preheated in the oven at the same temperature prior to withdrawal of aliquots to avoid condensation.

9.2.4.5 Sample aliquots may then be taken for introduction into the analytical system or for further dilution. An aliquot or aliquots totaling greater than 1 percent of the flask volume should be avoided.

9.2.4.6 Standards prepared by this method are stable for one week. The septum must be replaced with each freshly prepared standard.

9.2.4.7 The concentration of each component in the flask is calculated using the following equation:

$$\text{Concentration, mg/L} = \frac{(V_a)(d)}{V_f}$$

where: V_a = Volume of liquid neat standard injected into the flask, µL.
d = Density of the liquid neat standard, mg/µL.
V_f = Volume of the flask, L.

9.2.4.8 To obtain concentrations in ppbv, the equation given in Section 9.2.5.7 can be used.

[Note: In the preparation of standards by this technique, the analyst should make sure that the volume of neat standard injected into the flask does not result in an overpressure due to the higher partial pressure produced by the standard compared to the vapor pressure in the flask. Precautions should also be taken to avoid a significant decrease in pressure inside the flask after withdrawal of aliquot(s).]

9.2.5 Standard Preparation Procedure in High Pressure Cylinders

[Note: Standards may be prepared in high pressure cylinders (13). A modified summary of the procedure is provided below.]

9.2.5.1 The standard compounds are obtained as gases or neat liquids (greater than 98 percent purity).

9.2.5.2 An aluminum cylinder is flushed with high-purity nitrogen gas and then evacuated to better than 25 in. Hg.

9.2.5.3 Predetermined amounts of each neat standard compound are measured using a microliter or gastight syringe and injected into the cylinder. The cylinder is equipped with a heated injection port and nitrogen flow to facilitate sample transfer.

9.2.5.4 The cylinder is pressurized to 1000 psig with zero nitrogen.

[Note: User should read all SOPs associated with generating standards in high pressure cylinders. Follow all safety requirements to minimize danger from high pressure cylinders.]

9.2.5.5 The contents of the cylinder are allowed to equilibrate (~24 hrs) prior to withdrawal of aliquots into the GC system.

9.2.5.6 If the neat standard is a gas, the cylinder concentration is determined using the following equation:

$$\text{Concentration, ppbv} = \frac{\text{Volume}_{\text{standard}}}{\text{Volume}_{\text{dilution gas}}} \times 10^9$$

[Note: Both values must be expressed in the same units.]

9.2.5.7 If the neat standard is a liquid, the gaseous concentration can be determined using the following equations:

$$V = \frac{nRT}{P}$$

and:

$$n = \frac{(mL)(d)}{MW}$$

where:
V = Volume of injected compound at EPA standard temperature (25°C) and pressure (760 mm Hg), L.
n = Moles.
R = Gas constant, 0.08206 L-atm/mole °K.
T = 273°K (standard temperature).
P = 1 standard pressure, 760 mm Hg (1 atm).
mL = Volume of liquid injected, mL.
d = Density of the neat standard, gm/mL.
MW = Molecular weight of the neat standard expressed, gm/gm-mole.

The volume of injected compound is divided by the cylinder volume at STP and then multiplied by 10^9 to obtain the component concentration in ppb units.

9.2.6 Standard Preparation by Water Methods.

[Note: Standards may be prepared by a water purge and trap method (14) and summarized as follows].

9.2.6.1 A previously cleaned and evacuated canister is pressurized to 760 mm Hg absolute (1 atm) with zero grade air.

9.2.6.2 The air gauge is removed from the canister and the sparging vessel is connected to the canister with the short length of 1/16 in. stainless steel tubing.

[Note: Extra effort should be made to minimize possible areas of dead volume to maximize transfer of analytes from the water to the canister.]

9.2.6.3 A measured amount of the stock standard solution and the internal standard solution is spiked into 5 mL of water.

9.2.6.4 This water is transferred into the sparge vessel and purged with nitrogen for 10 mins at 100 mL/min. The sparging vessel is maintained at 40°C.

9.2.6.5 At the end of 10 mins, the sparge vessel is removed and the air gauge is re-installed, to further pressurize the canister with pure nitrogen to 1500 mm Hg absolute pressure (approximately 29 psia).

9.2.6.6 The canister is allowed to equilibrate overnight before use.

9.2.6.7 A schematic of this approach is shown in Figure 14.

9.2.7 Preparation of Standards by Permeation Tubes.

9.2.7.1 Permeation tubes can be used to provide standard concentration of a trace gas or gases. The permeation of the gas can occur from inside a permeation tube containing the trace species of interest to an

air stream outside. Permeation can also occur from outside a permeable membrane tube to an air stream passing through the tube (e.g., a tube of permeable material immersed in a liquid).

9.2.7.2 The permeation system is usually held at a constant temperature to generate a constant concentration of trace gas. Commercial suppliers provide systems for generation and dilution of over 250 compounds. Some commercial suppliers of permeation tube equipment are listed in Appendix D.

9.2.8 Storage of Standards.

9.2.8.1 Working standards prepared in canisters may be stored for thirty days in an atmosphere free of potential contaminants.

9.2.8.2 It is imperative that a storage logbook be kept to document storage time.

10. GC/MS Operating Conditions

10.1 Preconcentrator

The following are typical cryogenic and adsorbent preconcentrator analytical conditions which, however, depend on the specific combination of solid sorbent and must be selected carefully by the operator. The reader is referred to Tables 1 and 2 of Compendium Method TO-17 for guidance on selection of sorbents. An example of a system using a solid adsorbent preconcentrator with a cryofocusing trap is discussed in the literature (15). Oven temperature programming starts above ambient.

10.1.1 Sample Collection Conditions

Cryogenic Trap		**Adsorbent Trap**	
Set point	-150°C	Set point	27°C
Sample volume	- up to 100 mL	Sample volume	- up to 1,000 mL
Carrier gas purge flow	- none	Carrier gas purge flow	- selectable

[Note: The analyst should optimize the flow rate, duration of sampling, and absolute sample volume to be used. Other preconcentration systems may be used provided performance standards (see Section 11) are realized.]

10.1.2 Desorption Conditions

Cryogenic Trap		**Adsorbent Trap**	
Desorb Temperature	120°C	Desorb Temperature	Variable
Desorb Flow Rate	~ 3 mL/min He	Desorb Flow Rate	~3 mL/min He
Desorb Time	<60 sec	Desorb Time	<60 sec

The adsorbent trap conditions depend on the specific solid adsorbents chosen (see manufacturers' specifications).

10.1.3 Trap Reconditioning Conditions.

Cryogenic Trap		**Adsorbent Trap**	
Initial bakeout	120°C (24 hrs)	Initial bakeout	
Variable (24 hrs)			
After each run	120°C (5 min)	After each run	Variable (5 min)

10.2 GC/MS System

10.2.1 Optimize GC conditions for compound separation and sensitivity. Baseline separation of benzene and carbon tetrachloride on a 100% methyl polysiloxane stationary phase is an indication of acceptable chromatographic performance.

10.2.2 The following are the recommended gas chromatographic analytical conditions when using a 50-meter by 0.3-mm I.D., 1 µm film thickness fused silica column with refocusing on the column.

Item	**Condition**	
Carrier Gas:	Helium	
Flow Rate:	Generally 1-3 mL/min as recommended by manufacturer	
Temperature Program:	Initial Temperature:	-50°C
	Initial Hold Time:	2 min
	Ramp Rate:	8° C/min
	Final Temperature:	200°C
	Final Hold Time:	Until all target compounds elute.

10.2.3 The following are the recommended mass spectrometer conditions:

Item	**Condition**
Electron Energy:	70 Volts (nominal)
Mass Range:	35-300 amu [the choice of 35 amu excludes the detection of some target compounds such as methanol and formaldehyde, and the quantitation of others such as ethylene oxide, ethyl carbamate, etc. (see Table 2). Lowering the mass range and using special programming features available on modern gas chromatographs will be necessary in these cases, but are not considered here.
Scan Time:	To give at least 10 scans per peak, not to exceed 1 second per scan].

A schematic for a typical GC/MS analytical system is illustrated in Figure 15.

10.3 Analytical Sequence

10.3.1 Introduction. The recommended GC/MS analytical sequence for samples during each 24-hour time period is as follows:

- Perform instrument performance check using bromofluorobenzene (BFB).
- Initiate multi-point calibration or daily calibration checks.

- Perform a laboratory method blank.
- Complete this sequence for analysis of ≤20 field samples.

10.4 Instrument Performance Check

10.4.1 Summary. It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. The GC/MS system is set up according to the manufacturer's specifications, and the mass calibration and resolution of the GC/MS system are then verified by the analysis of the instrument performance check standard, bromofluorobenzene (BFB).

10.4.2 Frequency. Prior to the analyses of any samples, blanks, or calibration standards, the Laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard containing BFB. The instrument performance check solution must be analyzed initially and once per 24-hour time period of operation.

The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or daily calibration check criteria) begins at the injection of the BFB which the laboratory records as documentation of a compliance tune.

10.4.3 Procedure. The analysis of the instrument performance check standard is performed by trapping 50 ng of BFB under the optimized preconcentration parameters. The BFB is introduced from a cylinder into the GC/MS via a sample loop valve injection system similar to that shown in Figure 13.

The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is conducted using a single scan prior to the elution of BFB.

10.4.4 Technical Acceptance Criteria. Prior to the analysis of any samples, blanks, or calibration standards, the analyst must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard as specified in Table 3.

10.4.5 Corrective Action. If the BFB acceptance criteria are not met, the MS must be retuned. It may be necessary to clean the ion source, or quadrupoles, or take other necessary actions to achieve the acceptance criteria.

10.4.6 Documentation. Results of the BFB tuning are to be recorded and maintained as part of the instrumentation log.

10.5 Initial Calibration

10.5.1 Summary. Prior to the analysis of samples and blanks but after the instrument performance check standard criteria have been met, each GC/MS system must be calibrated at five concentrations that span the monitoring range of interest in an initial calibration sequence to determine instrument sensitivity and the linearity of GC/MS response for the target compounds. For example, the range of interest may be 2 to 20 ppbv, in which case the five concentrations would be 1, 2, 5, 10 and 25 ppbv.

One of the calibration points from the initial calibration curve must be at the same concentration as the daily calibration standard (e.g., 10 ppbv).

10.5.2 Frequency. Each GC/MS system must be recalibrated following corrective action (e.g., ion source cleaning or repair, column replacement, etc.) which may change or affect the initial calibration criteria or if the daily calibration acceptance criteria have not been met.

If time remains in the 24-hour time period after meeting the acceptance criteria for the initial calibration, samples may be analyzed.

If time does not remain in the 24-hour period after meeting the acceptance criteria for the initial calibration, a new analytical sequence shall commence with the analysis of the instrument performance check standard followed by analysis of a daily calibration standard.

10.5.3 Procedure. Verify that the GC/MS system meets the instrument performance criteria in Section 10.4.

The GC must be operated using temperature and flow rate parameters equivalent to those in Section 10.2.2. Calibrate the preconcentration-GC/MS system by drawing the standard into the system. Use one of the standards preparation techniques described under Section 9.2 or equivalent.

A minimum of five concentration levels are needed to determine the instrument sensitivity and linearity. One of the calibration levels should be near the detection level for the compounds of interest. The calibration range should be chosen so that linear results are obtained as defined in Sections 10.5.1 and 10.5.5.

Quantitation ions for the target compounds are shown in Table 2. The primary ion should be used unless interferences are present, in which case a secondary ion is used.

10.5.4 Calculations.

[Note: In the following calculations, an internal standard approach is used to calculate response factors. The area response used is that of the primary quantitation ion unless otherwise stated.]

10.5.4.1 Relative Response Factor (RRF). Calculate the relative response factors for each target compound relative to the appropriate internal standard (i.e., standard with the nearest retention time) using the following equation:

$$RRF = \frac{A_x C_{is}}{A_{is} C_x}$$

where: RRF = Relative response factor.
A_x = Area of the primary ion for the compound to be measured, counts.
A_{is} = Area of the primary ion for the internal standard, counts.
C_{is} = Concentration of internal standard spiking mixture, ppbv.
C_x = Concentration of the compound in the calibration standard, ppbv.

[Note: The equation above is valid under the condition that the volume of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume of field and QC sample introduced into the trap is the same for each analysis. C_{is} and C_x must be in the same units.]

10.5.4.2 Mean Relative Response Factor. Calculate the mean RRF for each compound by averaging the values obtained at the five concentrations using the following equation:

$$\overline{RRF} = \sum_{i=1}^{n} \frac{x_i}{n}$$

where: $\overline{RRF}$ = Mean relative response factor.

x_i = RRF of the compound at concentration i.

n = Number of concentration values, in this case 5.

10.5.4.3 Percent Relative Standard Deviation (%RSD). Using the RRFs from the initial calibration, calculate the %RSD for all target compounds using the following equations:

$$\%RSD = \frac{SD_{RRF}}{\overline{RRF}} \times 100$$

and

$$SD_{RRF} = \sqrt{\sum_{i=1}^{N} \frac{(RRF_i - \overline{RRF})^2}{N - 1}}$$

where: SD_{RRF} = Standard deviation of initial response factors (per compound).

RRF_i = Relative response factor at a concentration level i.

$\overline{RRF}$ = Mean of initial relative response factors (per compound).

10.5.4.4 Relative Retention Times (RRT). Calculate the RRTs for each target compound over the initial calibration range using the following equation:

$$RRT = \frac{RT_c}{RT_{is}}$$

where: RT_c = Retention time of the target compound, seconds

RT_{is} = Retention time of the internal standard, seconds.

10.5.4.5 Mean of the Relative Retention Times ($\overline{RRT}$). Calculate the mean of the relative retention times ($\overline{RRT}$) for each analyte target compound over the initial calibration range using the following equation:

$$\overline{RRT} = \sum_{i=1}^{n} \frac{RRT}{n}$$

where: $\overline{RRT}$ = Mean relative retention time for the target compound for each initial calibration standard.

RRT = Relative retention time for the target compound at each calibration level.

10.5.4.6 Tabulate Primary Ion Area Response (Y) for Internal Standard. Tabulate the area response (Y) of the primary ions (see Table 2) and the corresponding concentration for each compound and internal standard.

10.5.4.7 Mean Area Response ($\overline{Y}$) for Internal Standard. Calculate the mean area response ($\overline{Y}$) for each internal standard compound over the initial calibration range using the following equation:

$$\overline{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$

where: $\overline{Y}$ = Mean area response.

Y = Area response for the primary quantitation ion for the internal standard for each initial calibration standard.

10.5.4.8 Mean Retention Times ($\overline{RT}$). Calculate the mean of the retention times ($\overline{RT}$) for each internal standard over the initial calibration range using the following equation:

$$\overline{RT} = \sum_{i=1}^{n} \frac{RT_i}{n}$$

where: $\overline{RT}$ = Mean retention time, seconds

RT = Retention time for the internal standard for each initial calibration standard, seconds.

10.5.5 Technical Acceptance Criteria for the Initial Calibration.

10.5.5.1 The calculated %RSD for the RRF for each compound in the calibration table must be less than 30% with at most two exceptions up to a limit of 40%.

10.5.5.2 The RRT for each target compound at each calibration level must be withiin 0.06 RRT units of the mean RRT for the compound.

10.5.5.3 The area response Y of at each calibration level must be within 40% of the mean area response $\overline{Y}$ over the initial calibration range for each internal standard.

10.5.5.4 The retention time shift for each of the internal standards at each calibration level must be within 20 s of the mean retention time over the initial calibration range for each internal standard.

10.5.6 Corrective Action.

10.5.6.1 Criteria. If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the initial calibration technical acceptance criteria.

10.5.6.2 Schedule. Initial calibration acceptance criteria *must* be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed.

10.6 Daily Calibration

10.6.1 Summary. Prior to the analysis of samples and blanks but after tuning criteria have been met, the initial calibration of each GC/MS system must be routinely checked by analyzing a daily calibration standard to ensure that the instrument continues to remain under control. The daily calibration standard, which is the nominal 10 ppbv level calibration standard, should contain all the target compounds.

10.6.2 Frequency. A check of the calibration curve must be performed once every 24 hours on a GC/MS system that has met the tuning criteria. The daily calibration sequence starts with the injection of the BFB. If the BFB analysis meets the ion abundance criteria for BFB, then a daily calibration standard may be analyzed.

10.6.3 Procedure. The mid-level calibration standard (10 ppbv) is analyzed in a GC/MS system that has met the tuning and mass calibration criteria following the same procedure in Section 10.5.

10.6.4 Calculations. Perform the following calculations.

[Note: As indicated earlier, the area response of the primary quantitation ion is used unless otherwise stated.]

10.6.4.1 Relative Response Factor (RRF). Calculate a relative response factor (RRF) for each target compound using the equation in Section 10.5.4.1.

10.6.4.2 Percent Difference (%D). Calculate the percent difference in the RRF of the daily RRF (24-hour) compared to the mean RRF in the most recent initial calibration. Calculate the %D for each target compound using the following equation:

$$\%D = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

where: RRF_c = RRF of the compound in the continuing calibration standard.

$\overline{RRF_i}$ = Mean RRF of the compound in the most recent initial calibration.

10.6.5 Technical Acceptance Criteria. The daily calibration standard must be analyzed at the concentration level and frequency described in this Section 10.6 and on a GC/MS system meeting the BFB instrument performance check criteria (see Section 10.4).

The %D for each target compound in a daily calibration sequence must be within ±30 percent in order to proceed with the analysis of samples and blanks. A control chart showing %D values should be maintained.

10.6.6 Corrective Action. If the daily calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the daily calibration technical acceptance criteria.

Daily calibration acceptance criteria must be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed. If the % D criteria are not met, it will be necessary to rerun the daily calibration sample.

10.7 Blank Analyses

10.7.1 Summary. To monitor for possible laboratory contamination, laboratory method blanks are analyzed at least once in a 24-hour analytical sequence. All steps in the analytical procedure are performed on the blank using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis.

A laboratory method blank (LMB) is an unused, certified canister that has not left the laboratory. The blank canister is pressurized with humidified, ultra-pure zero air and carried through the same analytical procedure as a field sample. The injected aliquot of the blank must contain the same amount of internal standards that are added to each sample.

10.7.2 Frequency. The laboratory method blank must be analyzed after the calibration standard(s) and before any samples are analyzed.

Whenever a high concentration sample is encountered (i.e., outside the calibration range), a blank analysis should be performed immediately after the sample is completed to check for carryover effects.

10.7.3 Procedure. Fill a cleaned and evacuated canister with humidified zero air (RH >20 percent, at 25°C). Pressurize the contents to 2 atm.

The blank sample should be analyzed using the same procedure outlined under Section 10.8.

10.7.4 Calculations. The blanks are analyzed similar to a field sample and the equations in Section 10.5.4 apply.

10.7.5 Technical Acceptance Criteria. A blank canister should be analyzed daily.

The area response for each internal standard (IS) in the blank must be within ±40 percent of the mean area response of the IS in the most recent valid calibration.

The retention time for each of the internal standards must be within ±0.33 minutes between the blank and the most recent valid calibration.

The blank should not contain any target analyte at a concentration greater than its quantitation level (three times the MDL as defined in Section 11.2) and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte.

10.7.6 Corrective Action. If the blanks do not meet the technical acceptance criteria, the analyst should consider the analytical system to be out of control. It is the responsibility of the analyst to ensure that contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures need to be taken and documented before further sample analysis proceeds.

If an analyte in the blank is found to be out of control (i.e., contaminated) and the analyte is also found in associated samples, those sample results should be "flagged" as possibly contaminated.

10.8 Sample Analysis

10.8.1 Summary. An aliquot of the air sample from a canister (e.g., 500 mL) is preconcentrated and analyzed by GC/MS under conditions stated in Sections 10.1 and 10.2. If using the multisorbent/dry purge approach, adjust the dry purge volume to reduce water effects in the analytical system to manageable levels.

[Note: The analyst should be aware that pressurized samples of high humidity samples will contain condensed water. As a result, the humidity of the sample released from the canister during analysis will vary in humidity, being lower at the higher canister pressures and increasing in humidity as the canister pressures decreases. Storage integrity of water soluble compounds may also be affected.]

10.8.2 Frequency. If time remains in the 24-hour period in which an initial calibration is performed, samples may be analyzed without analysis of a daily calibration standard.

If time does not remain in the 24-hour period since the injection of the instrument performance check standard in which an initial calibration is performed, both the instrument performance check standard and the daily calibration standard should be analyzed before sample analysis may begin.

10.8.3 Procedure for Instrumental Analysis. Perform the following procedure for analysis.

10.8.3.1 All canister samples should be at temperature equilibrium with the laboratory.

10.8.3.2 Check and adjust the mass flow controllers to provide correct flow rates for the system.

10.8.3.3 Connect the sample canister to the inlet of the GC/MS analytical system, as shown in Figure 15 [Figure 16 shows an alternate two stage concentrator using multisorbent traps followed by a trap cooled by a closed cycle cooler (15)]. The desired sample flow is established through the six-port chromatographic valve and the preconcentrator to the downstream flow controller. The absolute volume of sample being pulled through the trap must be consistent from run to run.

10.8.3.4 Heat/cool the GC oven and cryogenic or adsorbent trap to their set points. Assuming a six-port value is being used, as soon as the trap reaches its lower set point, the six-port chromatographic valve is cycled to the trap position to begin sample collection. Utilize the sample collection time which has been optimized by the analyst.

10.8.3.5 Use the arrangement shown in Figure 13, (i.e., a gastight syringe or some alternate method) introduce an internal standard during the sample collection period. Add sufficient internal standard equivalent to 10 ppbv in the sample. For example, a 0.5 mL volume of a mixture of internal standard compounds, each at 10 ppmv concentration, added to a sample volume of 500 mL, will result in 10 ppbv of each internal standard in the sample.

10.8.3.6 After the sample and internal standards are preconcentrated on the trap, the GC sampling valve is cycled to the inject position and the trap is swept with helium and heated. Assuming a focusing trap is being used, the trapped analytes are thermally desorbed onto a focusing trap and then onto the head of the capillary column and are separated on the column using the GC oven temperature program. The canister valve is closed and the canister is disconnected from the mass flow controller and capped. The trap is maintained at elevated temperature until the beginning of the next analysis.

10.8.3.7 Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak should be acquired. Scanning also allows identification of unknown compounds in the sample through searching of library spectra.

10.8.3.8 Each analytical run must be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound.

10.8.3.9 Secondary ion quantitation is allowed only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the laboratory record book.

10.8.4 Calculations. The equation below is used for calculating concentrations.

$$C_x = \frac{A_x C_{is} DF}{A_{is} RRF}$$

where:
- C_x = Compound concentration, ppbv.
- A_x = Area of the characteristic ion for the compound to be measured, counts.
- A_{is} = Area of the characteristic ion for the specific internal standard, counts.
- C_{is} = Concentration of the internal standard spiking mixture, ppbv.
- RRF = Relative response factor from the analysis of the continuing calibration standard or the mid level standard of the initial calibration.
- DF = Dilution factor calculated as described in section 2. If no dilution is performed, DF = 1.

[Note: The equation above is valid under the condition that the volume (~500 µL) of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume (~500 mL) of field and QC sample introduced into the trap is the same for each analysis.]

10.8.5 Technical Acceptance Criteria.

[Note: If the most recent valid calibration is an initial calibration, internal standard area responses and RTs in the sample are evaluated against the corresponding internal standard area responses and RTs in the mid level standard (10 ppbv) of the initial calibration.]

10.8.5.1 The field sample must be analyzed on a GC/MS system meeting the BFB tuning, initial calibration, and continuing calibration technical acceptance criteria at the frequency described in Sections 10.4, 10.5 and 10.6.

10.8.5.2 The field samples must be analyzed along with a laboratory method blank that met the blank technical acceptance criteria.

10.8.5.3 All of the target analyte peaks should be within the initial calibration range.

10.8.5.4 The retention time for each internal standard must be within ±0.33 minutes of the retention time of the internal standard in the most recent valid calibration.

10.8.6 Corrective Action. If the on-column concentration of any compound in any sample exceeds the initial calibration range, an aliquot of the original sample must be diluted and reanalyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

- Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.
- The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.
- Do not submit data for more than two analyses, i.e., the original sample and one dilution, or, if the screening procedure was employed, the most concentrated dilution analyzed and one further dilution.

[Note: Analysis involving dilution should be reported with a dilution factor and nature of the dilution gas.]

10.8.6.1 Internal standard responses and retention times must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 20 sec from the latest daily (24-hour) calibration standard (or mean retention time over the initial calibration range), the GC/MS system must be inspected for malfunctions, and corrections made as required.

10.8.6.2 If the area response for any internal standard changes by more than ±40 percent between the sample and the most recent valid calibration, the GC/MS system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

10.8.6.3 If, after reanalysis, the area responses or the RTs for all internal standards are inside the control limits, then the problem with the first analysis is considered to have been within the control of the Laboratory. Therefore, submit only data from the analysis with SICPs within the limits. This is considered the initial analysis and should be reported as such on all data deliverables.

11. Requirements for Demonstrating Method Acceptability for VOC Analysis from Canisters

11.1 Introduction

11.1.1 There are three performance criteria which must be met for a system to qualify under Compendium Method TO-15. These criteria are: the method detection limit of ≤0.5 ppbv, replicate precision within 25 percent, and audit accuracy within 30 percent for concentrations normally expected in contaminated ambient air (0.5 to 25 ppbv).

11.1.2 Either SIM or SCAN modes of operation can be used to achieve these criteria, and the choice of mode will depend on the number of target compounds, the decision of whether or not to determine tentatively identified compounds along with other VOCs on the target list, as well as on the analytical system characteristics.

11.1.3 Specific criteria for each Title III compound on the target compound list must be met by the analytical system. These criteria were established by examining summary data from EPA's Toxics Air Monitoring System Network and the Urban Air Toxics Monitoring Program network. Details for the determination of each of the criteria follow.

11.2 Method Detection Limit

11.2.1 The procedure chosen to define the method detection limit is that given in the *Code of Federal Regulations* (40 CFR 136 Appendix B).

11.2.2 The method detection limit is defined for each system by making seven replicate measurements of the compound of interest at a concentration near (within a factor of five) the expected detection limit, computing the standard deviation for the seven replicate concentrations, and multiplying this value by 3.14 (i.e., the Student's t value for 99 percent confidence for seven values). Employing this approach, the detection limits given in Table 4 were obtained for some of the VOCs of interest.

11.3 Replicate Precision

11.3.1 The measure of replicate precision used for this program is the absolute value of the difference between replicate measurements of the sample divided by the average value and expressed as a percentage as follows:

$$\text{percent difference} = \frac{|x_1 - x_2|}{\bar{x}} \times 100$$

where:
x_1 = First measurement value.
x_2 = Second measurement value.
$\bar{x}$ = Average of the two values.

11.3.2 There are several factors which may affect the precision of the measurement. The nature of the compound of interest itself such as molecular weight, water solubility, polarizability, etc., each have some effect on the precision, for a given sampling and analytical system. For example, styrene, which is classified as a polar VOC, generally shows slightly poorer precision than the bulk of nonpolar VOCs. A primary influence on precision is the concentration level of the compound of interest in the sample, i.e., the precision degrades as the concentration approaches the detection limit. A conservative measure was obtained from replicate analysis of "real world" canister samples from the TAMS and UATMP networks. These data are

summarized in Table 5 and suggest that a replicate precision value of 25 percent can be achieved for each of the target compounds.

11.4 Audit Accuracy

11.4.1 A measure of analytical accuracy is the degree of agreement with audit standards. Audit accuracy is defined as the difference between the nominal concentration of the audit compound and the measured value divided by the audit value and expressed as a percentage, as illustrated in the following equation:

$$\text{Audit Accuracy, \%} = \frac{\text{Spiked Value} - \text{Observed Value}}{\text{Spiked Value}} \times 100$$

11.4.2 Audit accuracy results for TAMS and UATMP analyses are summarized in Table 6 and were used to form the basis for a selection of 30 percent as the performance criterion for audit accuracy.

12. References

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APPENDIX A.

LISTING OF SOME COMMERCIAL WATER MANAGEMENT SYSTEMS USED WITH AUTOGC SYSTEMS

Tekmar Dohrman Company
7143 East Kemper Road
Post Office Box 429576
Cincinnati, Ohio 45242-9576
(513) 247-7000
(513) 247-7050 (Fax)
(800) 543-4461
[Moisture control module]

Entech Laboratory Automation
950 Enchanted Way No. 101
Simi Valley, California 93065
(805) 527-5939
(805) 527-5687 (Fax)
[Microscale Purge and Trap]

Dynatherm Analytical Instruments
Post Office Box 159
Kelton, Pennsylvania 19346
(215) 869-8702
(215) 869-3885 (Fax)
[Thermal Desorption System]

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380
(818) 787-4275 (Fax)
[Multi-adsorbent trap/dry purge]

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(770) 319-9999
(770) 319-0336 (Fax)
(800) 241-6898
[Controlled Desorption Trap]

Varian Chromatography System
2700 Mitchell Drive
Walnut Creek, California 94898
(510) 945-2196
(510) 945-2335 (FAX)
[Variable Temperature Adsorption Trap]

APPENDIX B.

COMMENT ON CANISTER CLEANING PROCEDURES

The canister cleaning procedures given in Section 8.4 require that canister pressure be reduced to <0.05mm Hg before the cleaning process is complete. Depending on the vacuum system design (diameter of connecting tubing, valve restrictions, etc.) and the placement of the vacuum gauge, the achievement of this value may take several hours. In any case, the pressure gauge should be placed near the canisters to determine pressure. The objective of requiring a low pressure evacuation during canister cleaning is to reduce contaminants. If canisters can be routinely certified (<0.2 ppbv for target compounds) while using a higher vacuum, then this criteria can be relaxed. However, the ultimate vacuum achieved during cleaning should always be <0.2mm Hg.

Canister cleaning as described in Section 8.4 and illustrated in Figure 10 requires components with special features. The vacuum gauge shown in Figure 10 must be capable of measuring 0.05mm Hg with less than a 20% error. The vacuum pump used for evacuating the canister must be noncontaminating while being capable of achieving the 0.05 mm Hg vacuum as monitored near the canisters. Thermoelectric vacuum gauges and turbomolecular drag pumps are typically being used for these two components.

An alternate to achieving the canister certification requirement of <0.2 ppbv for all target compounds is the criteria used in Compendium Method TO-12 that the total carbon count be <10ppbC. This check is less expensive and typically more exacting than the current certification requirement and can be used if proven to be equivalent to the original requirement. This equivalency must be established by comparing the total nonmethane organic carbon (TNMOC) expressed in ppbC to the requirement that individual target compounds be <0.2 ppbv for a series of analytical runs.

APPENDIX C.

LISTING OF COMMERCIAL MANUFACTURERS AND RE-SUPPLIERS OF SPECIALLY-PREPARED CANISTERS

BRC/Rasmussen
17010 NW Skyline Blvd.
Portland, Oregon 97321
(503) 621-1435

Meriter
1790 Potrero Drive
San Jose, CA 95124
(408) 265-6482

Restek Corporation
110 Benner Circle
Bellefonte, PA 16823-8812
(814) 353-1300
(800) 356-1688

Scientific Instrumentation Specialists
P.O. Box 8941
815 Courtney Street
Moscow, ID 83843
(208) 882-3860

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(404) 319-9999
(800) 241-6898

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380

APPENDIX D.

LISTING OF COMMERCIAL SUPPLIERS OF PERMEATION TUBES AND SYSTEMS

Kin-Tek
504 Laurel St.
Lamarque, Texas 77568
(409) 938-3627
(800) 326-3627

Vici Metronics, Inc.
2991 Corvin Drive
Santa Clara, CA 95051
(408) 737-0550

Analytical Instrument Development, Inc.
Rt. 41 and Newark Rd.
Avondale, PA 19311
(215) 268-3181

Ecology Board, Inc.
9257 Independence Ave.
Chatsworth, CA 91311
(213) 882-6795

Tracor, Inc.
6500 Tracor Land
Austin, TX
(512) 926-2800

Metronics Associates, Inc.
3201 Porter Drive
Standford Industrial Park
Palo Alto, CA 94304
(415) 493-5632

TABLE 1. VOLATILE ORGANIC COMPOUNDS ON THE TITLE III CLEAN AIR AMENDMENT LIST--MEMBERSHIP IN COMPENDIUM METHOD TO-14A LIST AND THE SOW-CLP LIST OF VOCs

Compound	CAS No.	BP (°C)[1]	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Methyl chloride (chloromethane); CH3Cl	74-87-3	-23.7	3.8×10^3	50.5	X	X
Carbonyl sulfide; COS	463-58-1	-50.0	3.7×10^3	60.1		
Vinyl chloride (chloroethene); C2H3Cl	75-01-4	-14.0	3.2×10^3	62.5	X	X
Diazomethane; CH2N2	334-88-3	-23.0	2.8×10^3	42.1		
Formaldehyde; CH2O	50-00-0	-19.5	2.7×10^3	30		
1,3-Butadiene; C4H6	106-99-0	-4.5	2.0×10^3	54		X
Methyl bromide (bromomethane); CH3Br	74-83-9	3.6	1.8×10^3	94.9	X	X
Phosgene; CCl2O	75-44-5	8.2	1.2×10^3	99		
Vinyl bromide (bromoethene); C2H3Br	593-60-2	15.8	l.l x 10^3	107		
Ethylene oxide; C2H4O	75-21-8	10.7	1.1×10^3	44		
Ethyl chloride (chloroethane); C2H5Cl	75-00-3	12.5	1.0×10^3	64.5	X	X
Acetaldehyde (ethanal); C2H4O	75-07-0	21.0	952	44		
Vinylidene chloride (1,1-dichloroethylene); C2H2Cl2	75-35-4	31.7	500	97	X	X
Propylene oxide; C3H6O	75-56-9	34.2	445	58		
Methyl iodide (iodomethane); CH3I	74-88-4	42.4	400	141.9		
Methylene chloride; CH2Cl2	75-09-2	40.0	349	84.9	X	X
Methyl isocyanate; C2H3NO	624-83-9	59.6	348	57.1		
Allyl chloride (3-chloropropene); C3H5Cl	107-05-1	44.5	340	76.5	X	X
Carbon disulfide; CS2	75-15-0	46.5	260	76		
Methyl ter-butyl ether; C5H12O	1634-04-4	55.2	249	86		
Propionaldehyde; C2H5CHO	123-38-6	49.0	235	58.1		
Ethylidene dichloride (1,1-dichloroethane); C2H4Cl2	75-34-3	57.0	230	99	X	
Chloroprene (2-chloro-1,3-butadiene); C4H5Cl	126-99-8	59.4	226	88.5		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)[1]	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Acrolein (2-propenal); C3H4O	107-02-8	52.5	220	56		X
1,2-Epoxybutane (1,2-butylene oxide); C4H8O	106-88-7	63.0	163	72		
Chloroform; CHCl3	67-66-3	61.2	160	119	X	X
Ethyleneimine (aziridine); C2H5N	151-56-4	56	160.0	43		
1,1-Dimethylhydrazine; C2H8N2	57-14-7	63	157.0	60.0		
Hexane; C6H14	110-54-3	69.0	120	86.2	X	
1,2-Propyleneimine (2-methylaziridine); C3H7N	75-55-8	66.0	112	57.1		
Acrylonitrile (2-propenenitrile); C3H3N	107-13-1	77.3	100	53	X	
Methyl chloroform (1,1,1-trichloroethane); C2H3Cl3	71-55-6	74.1	100	133.4	X	X
Methanol; CH4O	67-56-1	65.0	92.0	32		X
Carbon tetrachloride; CCl4	56-23-5	76.7	90.0	153.8	X	X
Vinyl acetate; C4H6O2	108-05-4	72.2	83.0	86		X
Methyl ethyl ketone (2-butanone); C4H8O	78-93-3	79.6	77.5	72		X
Benzene; C6H6	71-43-2	80.1	76.0	78	X	X
Acetonitrile (cyanomethane); C2H3N	75-05-8	82	74.0	41.0		X
Ethylene dichloride (1,2-dichloroethane); C2H4Cl2	107-06-2	83.5	61.5	99	X	X
Triethylamine; C6H15N	121-44-8	89.5	54.0	101.2		
Methylhydrazine; CH6N2	60-34-4	87. 8	49.6	46.1		
Propylene dichloride (1,2-dichloropropane); C3H6Cl2	78-87-5	97.0	42.0	113	X	X
2,2,4-Trimethyl pentane C8H18	540-84-l	99.2	40.6	114		
1,4-Dioxane (1,4-Diethylene oxide); C4H8O2	123-91-1	101	37.0	88		
Bis(chloromethyl) ether; C2H4Cl2O	542-88-1	104	30.0	115		
Ethyl acrylate; C5H8O2	140-88-5	100	29.3	100		
Methyl methacrylate-C5H8O2	80-62-6	101	28.0	100.1		
1,3-Dichloropropene; C3H4Cl2 (cis)	542-75-6	112	27.8	111	X	X
Toluene; C7H8	108-88-3	111	22.0	92	X	X

TABLE 1. (continued)

Compound	CAS No.	BP (°C)[1]	v.p. (mmgHg)[1]	MW[1]	TO-14A	CLP-SOW
Tetrachloroethylene; C2Cl4	127-18-4	121	14.0	165.8	X	X
Epichlorohydrin (1-chloro-2,3-epoxy propane); C3H5ClO	106-89-8	117	12.0	92.5		
Ethylene dibromide (1,2-dibromoethane); C2H4Br2	106-93-4	132	11.0	187.9	X	X
N-Nitroso-N-methylurea; C2H5N3O2	684-93-5	124	10.0	103		
2-Nitropropane; C3H7NO2	79-46-9	120	10.0	89		
Chlorobenzene; C6H5Cl	108-90-7	132	8.8	112.6	X	X
Ethylbenzene; C8H10	100-41-4	136	7.0	106	X	X
Xylenes (isomer & mixtures); C8H10	1330-20-7	142	6.7	106.2	X	X
Styrene; C8H8	100-42-5	145	6.6	104	X	X
p-Xylene; C8H10	106-42-3	138	6.5	106.2	X	X
m-Xylene; C8H10	108-38-3	139	6.0	106.2	X	X
Methyl isobutyl ketone (hexone); C6H12O	108-10-1	117	6.0	100.2		
Bromoform (tribromomethane); CHBr3	75-25-2	149	5.6	252.8		
l,l,2,2-Tetrachloroethane; C2H2Cl4	79-34-5	146	5.0	167.9	X	X
o-Xylene; C8H10	95-47-6	144	5.0	106.2	X	X
Dimethylcarbamyl chloride; C3H6ClNO	79-44-7	166	4.9	107.6		
N-Nitrosodimethylamine; C2H6N2O	62-75-9	152	3.7	74		
Beta-Propiolactone; C3H4O2	57-57-8	Decomposes at 162	3.4	72		
Cumene (isopropylbenzene); C9Hl2	98-82-8	153	3.2	120		
Acrylic acid; C3H4O2	79-10-7	141	3.2	72		
N,N-Dimethylformamide; C3H7NO	68-12-2	153	2.7	73		
1,3-Propane sultone; C3H6O3S	1120-71-4	180/30 mm	2.0	122.1		
Acetophenone; C8H8O	98-86-2	202	1.0	120		
Dimethyl sulfate; C2H6O4S	77-78-l	188	l.0	126.1		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)[1]	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Bis(2-Chloroethyl)ether; C4H8Cl2O	111-44-4	178	0.71	143		
Chloroacetic acid; C2H3ClO2	79-11-8	189	0.69	94.5		
Aniline (aminobenzene); C6H7N	62-53-3	184	0.67	93		
1,4-Dichlorobenzene (p-); C6H4Cl2	106-46-7	173	0.60	147	X	X
Ethyl carbamate (urethane); C3H7NO2	51-79-6	183	0.54	89		
Acrylamide; C3H5NO	79-06-1	125/25 mm	0.53	71		
N,N-Dimethylaniline; C8H11N	121-69-7	192	0.50	121		
Hexachloroethane; C2Cl6	67-72-1	Sublimes at 186	0.40	236.7		
Hexachlorobutadiene; C4Cl6	87-68-3	2l5	0.40	260.8	X	X
Isophorone; C9H14O	78-59-1	215	0.38	138.2		
N-Nitrosomorpholine; C4H8N2O2	59-89-2	225	0.32	116.1		
Styrene oxide; C8H8O	96-09-3	194	0.30	120.2		
Diethyl sulfate; C4H10O4S	64-67-5	208	0.29	154		
Cresylic acid (cresol isomer mixture)	1319-77-3	202	0.26	108		
o-Cresol; C7H8O	95-48-7	191	0.24	108		
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	240	0.22	110		
Phenol; C6H6O	108-95-2	182	0.20	94		
1,2,4-Trichlorobenzene; C6H3Cl3	120-82-1	213	0.18	181.5	X	X
Nitrobenzene; C6H5NO2	98-95-3	211	0.15	123		

[1]Vapor pressure (v.p.), boiling point (BP) and molecular weight (MW) data from:
(a) D. L. Jones and J. bursey, "Simultaneous Control of PM-10 and Hazardous Air Pollutants II: Rationale for Selection of Hazardous Air Pollutants as Potential Particulate Matter," Report EPA-452/R-93/013, U. S. Environmental Protection Agency, Research Triangle Park, NC. October 1992;
(b) R. C. Weber, P. A. Parker, and M. Bowser. Vapor Pressure Distribution of Selected Organic Chemicals, Report EPA-600/2-81-021, U. S. Environmental Protection Agency, Cincinnati, OH, February 1981; and
(c) R. C. Weast, ed., "CRC Handbook of Chemistry and Physics," 59th edition, CRC Press, Boca Raton, 1979.

TABLE 2. CHARACTERISTIC MASSES (M/Z) USED FOR QUANTIFYING THE TITLE III CLEAN AIR ACT AMENDMENT COMPOUNDS

Compound	CAS No.	Primary Ion	Secondary Ion
Methyl chloride (chloromethane); CH3Cl	74-87-3	50	52
Carbonyl sulfide; COS	463-S8-1	60	62
Vinyl chloride (chloroethene); C2H3Cl	7S-01-4	62	64
Diazomethane; CH2N2	334-88-3	42	41
Formaldehyde; CH20	50-00-0	29	30
1,3-Butadiene; C4H6	106-99-0	39	54
Methyl bromide (bromomethane); CH3Br	74-83-9	94	96
Phosgene; CCl2O	75-44-5	63	65
Vinyl bromide (bromoe hene); C2H3Br	593-60-2	106	108
Ethylene oxide; C2H4O	75-21-8	29	44
Ethyl chloride (chloroethane); C2H5Cl	75-00-3	64	66
Acetaldehyde (ethanal); C2H4O	75-07-0	44	29, 43
Vinylidene chloride (1,1-dichloroethylene); C2H2Cl2	75-35-4	61	96
Propylene oxide; C3H6O	75-56-9	58	57
Methyl iodide (iodomethane); CH3I	74-88-4	142	127
Methylene chloride; CH2Cl2	75-09-2	49	84, 86
Methyl isocyanate; C2H3N0	624-83-9	57	56
Allyl chloride (3-chloropropene); C3H5Cl	107-05-1	76	41, 78
Carbon disulfide; CS2	75-15-0	76	44, 78
Methyl ter-butyl ether; C5H12O	1634-04-4	73	41, 53
Propionaldehyde; C2H5CHO	123-38-6	58	29, 57
Ethylidene dichloride (1,1-dichloroethane); C2H4Cl2	75-34-3	63	65, 27
Chloroprene (2-chloro-1,3-butadiene); C4H5Cl	126-99-8	88	53, 90
Chloromethyl methyl ether; C2H5ClO	107-30-2	45	29, 49
Acrolein (2-propenal); C3H4O	107-02-8	56	55
1,2-Epoxybutane (1,2-butylene oxide); C4H8O	106-88-7	42	41, 72
Chloroform; CHCl3	67-66-3	83	85, 47
Ethyleneimine (aziridine); C2H5N	151-56-4	42	43
1,1-Dimethylhydrazine; C2H8N2	57-14-7	60	45, 59
Hexane; C6H14	110-54-3	57	41, 43
1,2-Propyleneimine (2-methylazindine); C3H7N	75-55-8	56	57, 42
Acrylonitrile (2-propenenitrile); C3H3N	107-13-1	53	52
Methyl chloroform (1,1,1 trichloroethane); C2H3Cl3	71-55-6	97	99, 61
Methanol; CH4O	67-56-1	31	29
Carbon tetrachloride; CCl4	56-23-5	117	119
Vinyl acetate; C4H6O2	108-05-4	43	86
Methyl ethyl ketone (2-butanone); C4H8O	78-93-3	43	72
Benzene; C6H6	71-43-2	78	77, 50
Acetonitrile (cyanomethane); C2H3N	75-05-8	41	40

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Ethylene dichloride (1,2-dichloroethane); C2H4Cl2	107-06-2	62	64, 27
Triethylamine; C6H15N	121-44-8	86	58, 101
Methylhydrazine; CH6N2	60-34-4	46	31, 45
Propylene dichloride (1,2-dichloropropane); C3H6Cl2	78-87-5	63	41, 62
2,2,4-Trimethyl pentane; C8H18	540-84-1	57	41, 56
1,4-Dioxane (1,4 Diethylene oxide); C4H8O2	123-91-1	88	58
Bis(chloromethyl) ether; C2H4Cl2O	542-88-1	79	49, 81
Ethyl acrylate; C5H8O2	140-88-5	55	73
Methyl methacrylate; C5H8O2	80-62-6	41	69, 100
1,3-Dichlompropene; C3H4Cl2 (cis)	542-75-6	75	39, 77
Toluene; C7H8	108-88-3	91	92
Trichloethylene; C2HCl3	79-01-6	130	132, 95
1,1,2-Trichloroethane; C2H3Cl3	79-00-5	97	83, 61
Tetrachloroethylene; C2Cl4	127-18-4	166	164, 131
Epichlorohydrin (l-chloro-2,3-epoxy propane); C3H5ClO	106-89-8	57	49, 62
Ethylene dibromide (1,2-dibromoethane); C2H4Br2	106-93-4	107	109
N-Nitrso-N-methylurea; C2H5N3O2	684-93-5	60	44, 103
2-Nitropropane; C3H7NO2	79-46-9	43	41
Chlorobenzene; C6H5Cl	108-90-7	112	77, 114
Ethylbenzene; C8H10	100-41-4	91	106
Xylenes (isomer & mixtures); C8H10	1330-20-7	91	106
Styrene; C8H8	100-42-5	104	78, 103
p-Xylene; C8H10	106-42-3	91	106
m-Xylene; C8H10	108-38-3	91	106
Methyl isobutyl ketone (hexone); C6H12O	108-10-1	43	58, 100
Bromoform (tribromomethane); CHBr3	75-25-2	173	171, 175
1,1,2,2-Tetrachloroethane; C2H2Cl4	79-34-5	83	85
o-Xylene; C8H10	95-47-6	91	106
Dimethylcarbamyl chloride; C3H6ClNO	79-44-7	72	107
N-Nitrosodimethylamine; C2H6N2O	62-75-9	74	42
Beta-Propiolactone; C3H4O2	57-57-8	42	43
Cumene (isopropylbenzene); C9H12	98-82-8	105	120
Acrylic acid; C3H4O2	79-10-7	72	45, 55
N,N-Dimethylformamide; C3H7NO	68-12-2	73	42, 44
1,3-Propane sultone; C3H6O3S	1120-71-4	58	65, 122
Acetophenone; C8H8O	98-86-2	105	77, 120
Dimethyl sulfate; C2H6O4S	77-78-1	95	66, 96
Benzyl chloride (a-chlorotoluene); C7H7Cl	100-44-7	91	126
1,2-Dibromo-3-chloropropane; C3H5Br2Cl	96-12-8	57	155, 157
Bis(2-Chloroethyl)ether; C4H8Cl2O	111-44-4	93	63, 95
Chloroacetic acid; C2H3ClO2	79-11-8	50	45, 60

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Aniline (aminobenzene); C6H7N	62-53-3	93	66
1,4-Dichlorobenzene (p-); C6H4Cl2	106-46-7	146	148, 111
Ethyl carbamate (urethane); C3H7NO2	51-79-6	31	44, 62
Acrylamide; C3H5NO	79-06-1	44	55, 71
N,N-Dimethylaniline; C8H11N	121-69-7	120	77, 121
Hexachloroethane; C2Cl6	67-72-1	201	199, 203
Hexachlorobutadiene; C4Cl6	87-68-3	225	227, 223
Isophorone; C9H14O	78-59-1	82	138
N-Nitrosomorpholine; C4H8N2O2	59-89-2	56	86, 116
Styrene oxide; C8H8O	96-09-3	91	120
Diethyl sulfate; C4H10O4S	64-67-5	45	59, 139
Cresylic acid (cresol isomer mixture)	1319-77-3		
o-Cresol; C7H8O	95-48-7	108	107
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	110	64
Phenol; C6H6O	108-95-2	94	66
1,2,4-Trichlorobenzene; C6H3Cl3	120-82-1	180	182, 184
Nitrobenzene; C6H5NO2	98-95-3	77	51, 123

TABLE 3. REQUIRED BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria[1]
50	8.0 to 40.0 Percent of m/e 95
75	30.0 to 66.0 Percent of m/e 95
95	Base Peak, 100 Percent Relative Abundance
96	5.0 to 9.0 Percent of m/e 95 (See note)
173	Less than 2.0 Percent of m/e 174
174	50.0 to 120.0 Percent of m/e 95
175	4.0 to 9.0 Percent of m/e 174
176	93.0 to 101.0 Percent of m/e 174
177	5.0 to 9.0 Percent of m/e 176

[1]All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

TABLE 4. METHOD DETECTION LIMITS (MDL)[1]

TO-14A List	Lab #1, SCAN	Lab #2, SIM
Benzene	0.34	0.29
Benzyl Chloride	--	--
Carbon tetrachloride	0.42	0.15
Chlorobenzene	0.34	0.02
Chloroform	0.25	0.07
1,3-Dichlorobenzene	0.36	0.07
1,2-Dibromoethane	--	0.05
1,4-Dichlorobenzene	0.70	0.12
1,2-Dichlorobenzene	0.44	--
1,1-Dichloroethane	0.27	0.05
1,2-Dichloroethane	0.24	--
1,1-Dichloroethene	--	0.22
cis-1,2-Dichloroethene	--	0.06
Methylene chloride	1.38	0.84
1,2-Dichloropropane	0.21	--
cis-1,3-Dichloropropene	0.36	--
trans-1,3-Dichloropropene	0.22	--
Ethylbenzene	0.27	0.05
Chloroethane	0.19	--
Trichlorofluoromethane	--	--
1,1,2-Trichloro-1,2,2-trifluoroethane		--
1,2-Dichloro-1,1,2,2-tetrafluoroethane	--	--
Dichlorodifluoromethane	--	--
Hexachlorobutadiene	--	--
Bromomethane	0.53	--
Chloromethane	0.40	--
Styrene	1.64	0.06
1,1,2,2-Tetrachloroethane	0.28	0.09
Tetrachloroethene	0.75	0.10
Toluene	0.99	0.20
1,2,4-Trichlorobenzene	--	--
1,1,1-Trichloroethane	0.62	0.21
1,1,2-Trichloroethane	0.50	--
Trichloroethene	0.45	0.07
1,2,4-Trimethylbenzene	--	--
1,3,5-Trimethylbenzene	--	--
Vinyl Chloride	0.33	0.48
m,p-Xylene	0.76	0.08
o-Xylene	0.57	0.28

[1]Method Detection Limits (MDLs) are defined as the product of the standard deviation of seven replicate analyses and the student's "t" test value for 99% confidence. For Lab #2, the MDLs represent an average over four studies. MDLs are for MS/SCAN for Lab #1 and for MS/SIM for Lab #2.

TABLE 5. SUMMARY OF EPA DATA ON REPLICATE PRECISION (RP)

FROM EPA NETWORK OPERATIONS[1]

Monitoring Compound Identification	EPA's Urban Air Toxics Monitoring Program (UATMP)			EPA's Toxics Air Monitoring Stations (TAMS)		
	%RP	#	ppbv	%RP	#	ppbv
Dichlorodifluoromethane	--		--	13.9	47	0.9
Methylene chloride	16.3	07	4.3	19.4	47	0.6
1,2-Dichloroethane	36.2	31	1.6	--	--	--
1,1,1-Trichloroethane	14.1	44	1.0	10.6	47	2.0
Benzene	12.3	56	1.6	4.4	47	1.5
Trichloroethene	12.8	08	1.3	--	--	--
Toluene	14.7	76	3.1	3.4	47	3.1
Tetrachloroethene	36.2	12	0.8	--	--	--
Chlorobenzene	20.3	21	0.9	--	--	--
Ethylbenzene	14.6	32	0.7	5.4	47	0.5
m-Xylene	14.7	75	4.0	5.3	47	1.5
Styrene	22.8	59[2]	1.1	8.7	47	0.2[2]
o-Xylene	--		--	6.0	47	0.5
p-Xylene	--					
1,3-Dichlorobenzene	49.1	06	0.6	--	--	--
1,4-Dichlorobenzene	14.7	14	6.5	--	--	--

[1]Denotes the number of replicate or duplicate analysis used to generate the statistic. The replicate precision is defined as the mean ratio of absolute difference to the average value.
[2]Styrene and o-xylene coelute from the GC column used in UATMP. For the TAMS entries, both values were below detection limits for 18 of 47 replicates and were not included in the calculation.

TABLE 6. AUDIT ACCURACY (AA) VALUES[1] FOR SELECTED COMPENDIUM METHOD TO-14A COMPOUNDS

Selected Compounds From TO-14A List	FY-88 TAMS AA(%), N=30	FY-88 UATMP AA(%), N=3
Vinyl chloride	4.6	17.9
Bromomethane	--	6.4
Trichlorofluoromethane	6.4	--
Methylene chloride	8.6	31.4
Chloroform	--	4.2
1,2-Dichloroethane	6.8	11.4
1,1,1-Trichloroethane	18.6	11.3
Benzene	10.3	10.1
Carbon tetrachloride	12.4	9.4
1,2-Dichloropropane	--	6.2
Trichloroethene	8.8	5.2
Toluene	8.3	12.5
Tetrachloroethene	6.2	--
Chlorobenzene	10.5	11.7
Ethylbenzene	12.4	12.4
o-Xylene	16.2	21.2

[1]Audit accuracy is defined as the relative difference between the audit measurement result and its nominal value divided by the nominal value. N denotes the number of audits averaged to obtain the audit accuracy value. Information is not available for other TO-14A compounds because they were not present in the audit materials.

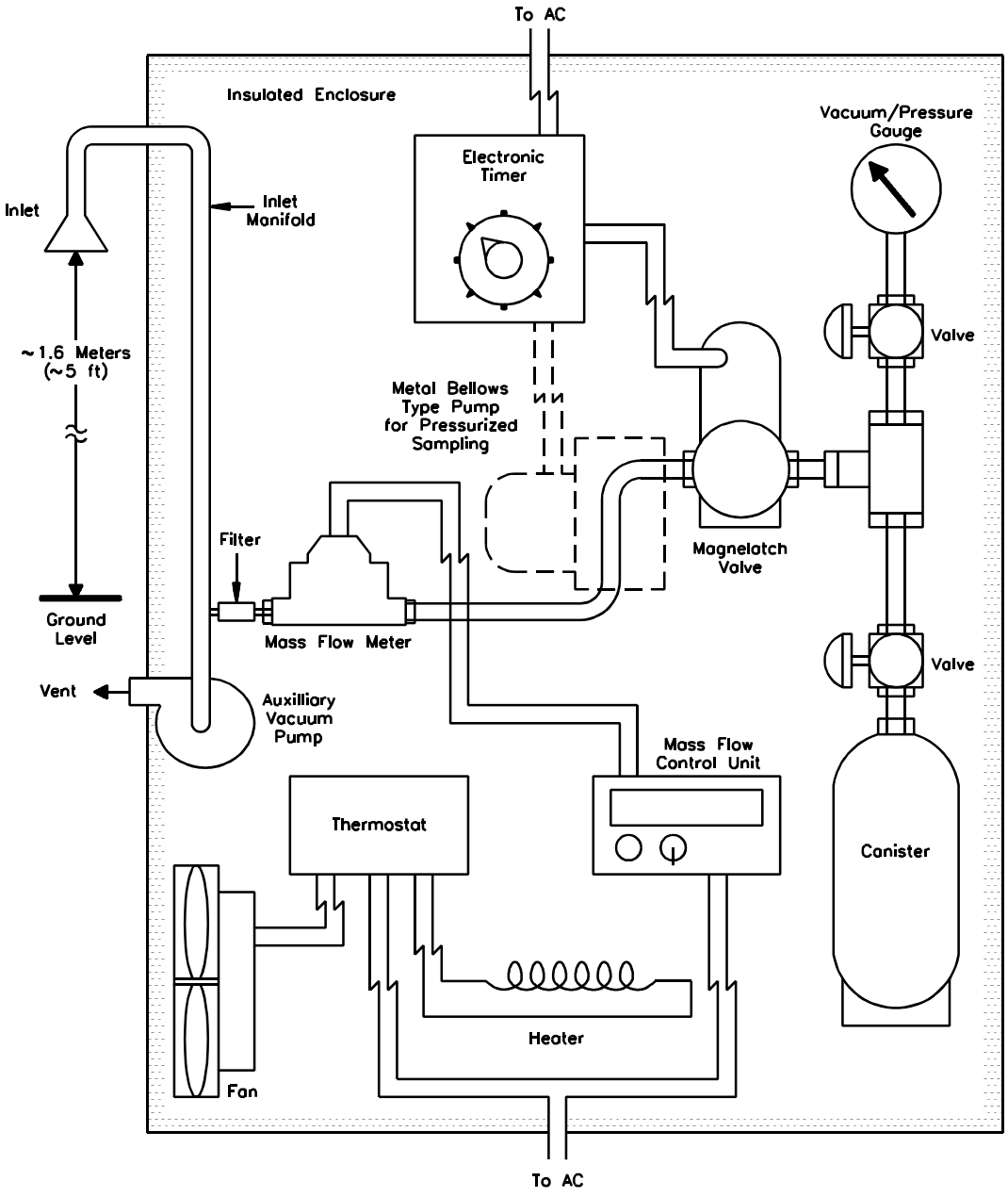
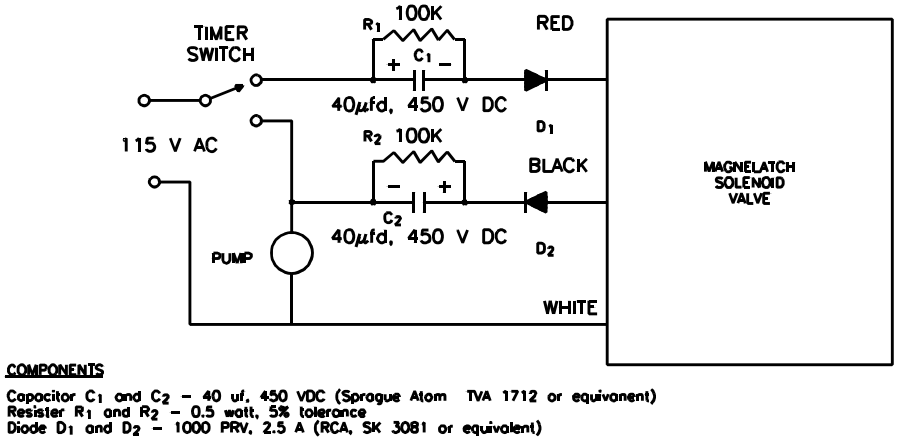


FIGURE 2. SAMPLER CONFIGURATION FOR SUBATMOSPHERIC

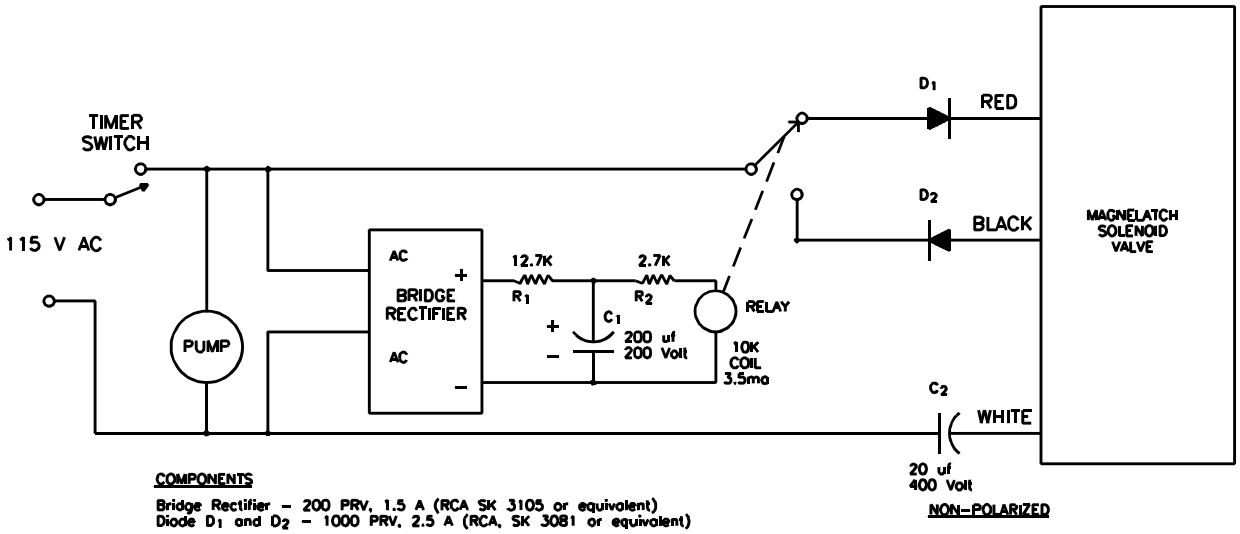
Figure 1. Sampler configuration for subatmospheric pressure or pressurized canister sampling.



COMPONENTS

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

(a). Simple Circuit for Operating Magnelatch Valve



COMPONENTS

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

(b). Improved Circuit Designed to Handle Power Interruptions

FIGURE 9. ELECTRICAL PULSE CIRCUITS FOR DRIVING

Figure 2. Electrical pulse circuits for driving Skinner magnelatch solenoid valve with mechanical timer.

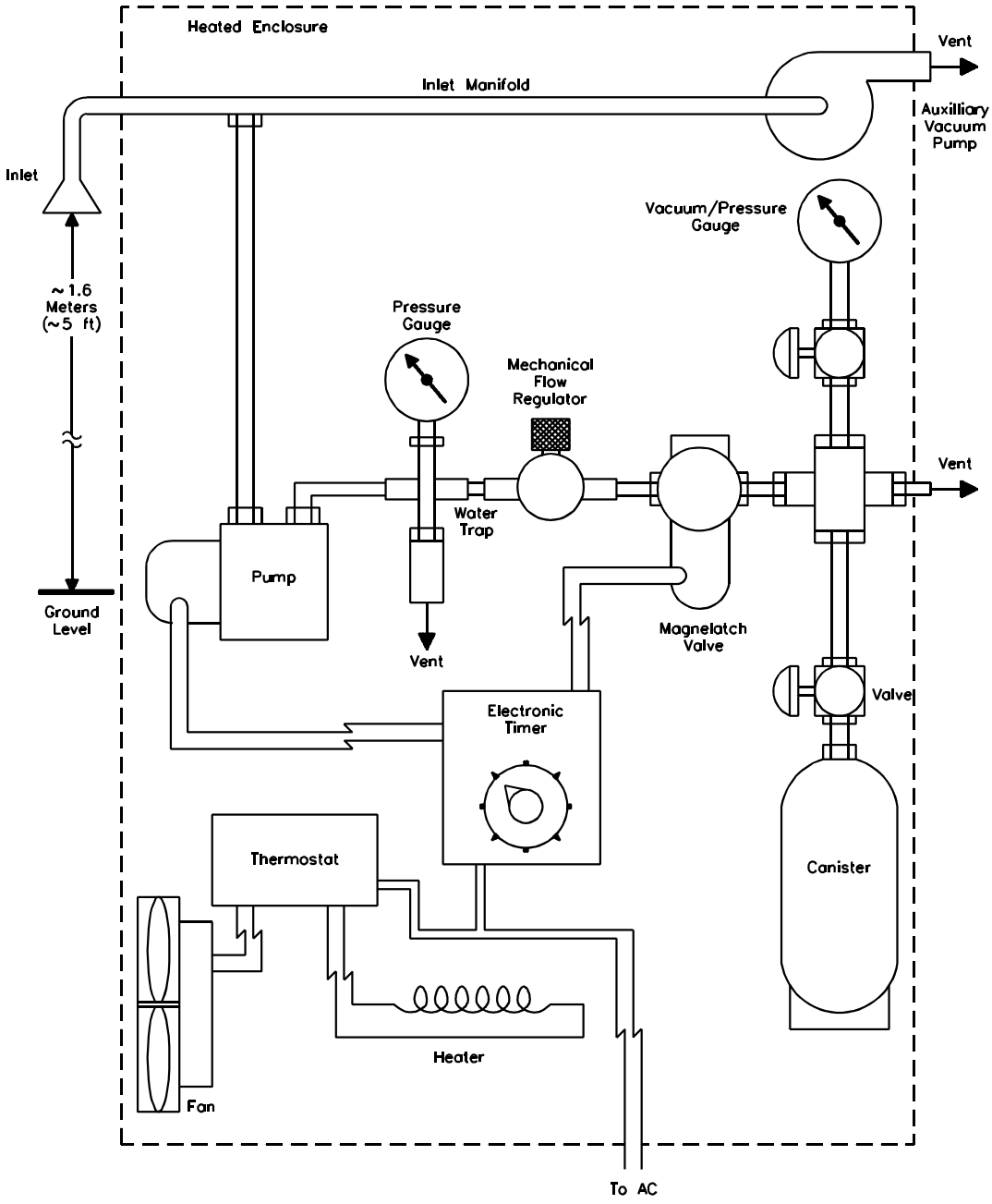


FIGURE 3. ALTERNATIVE SAMPLER CONFIGURATION FOR
Figure 3. Alternative sampler configuration for pressurized canister sampling.

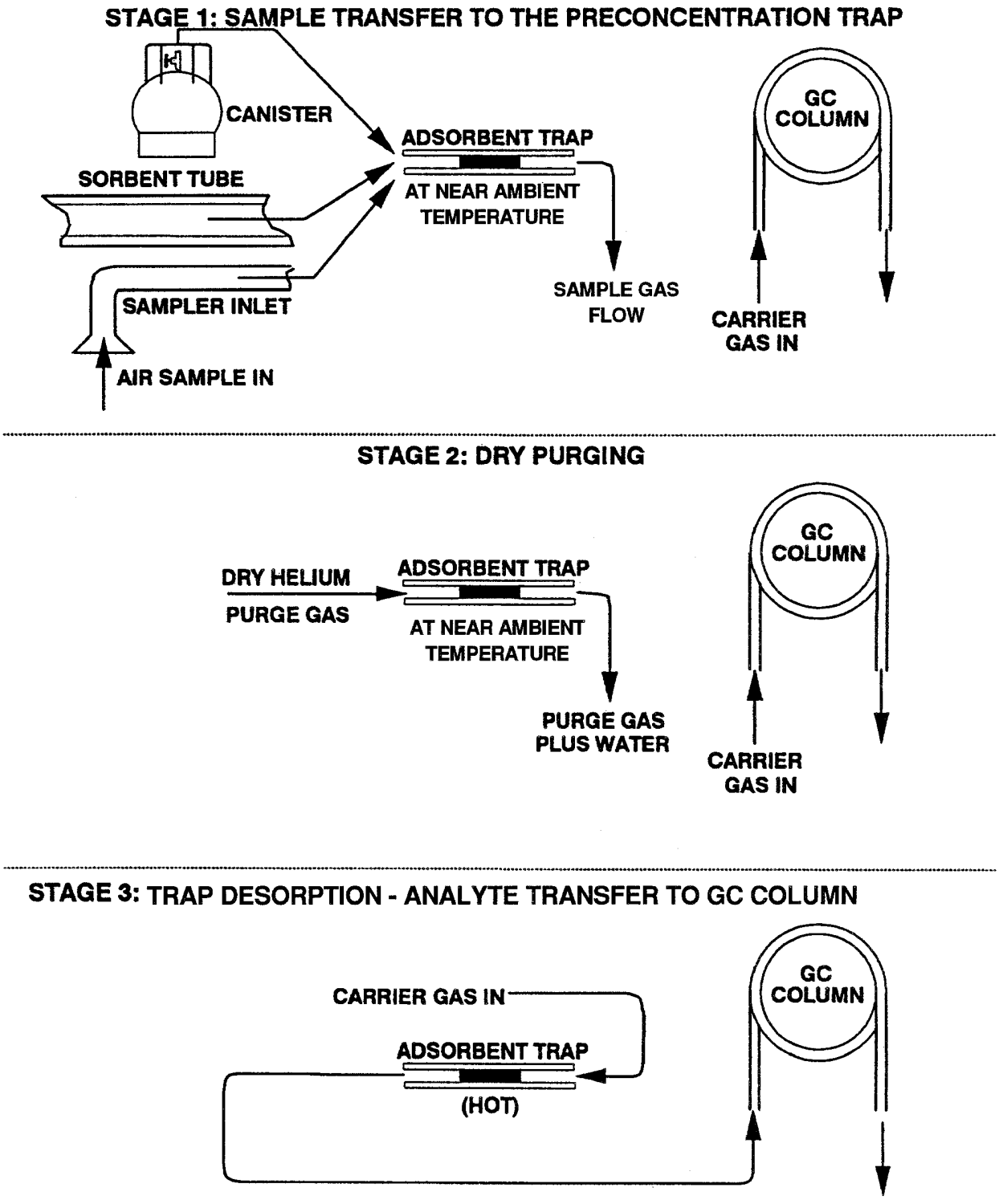


Figure 4. Illustration of three stages of dry purging of adsorbent trap.

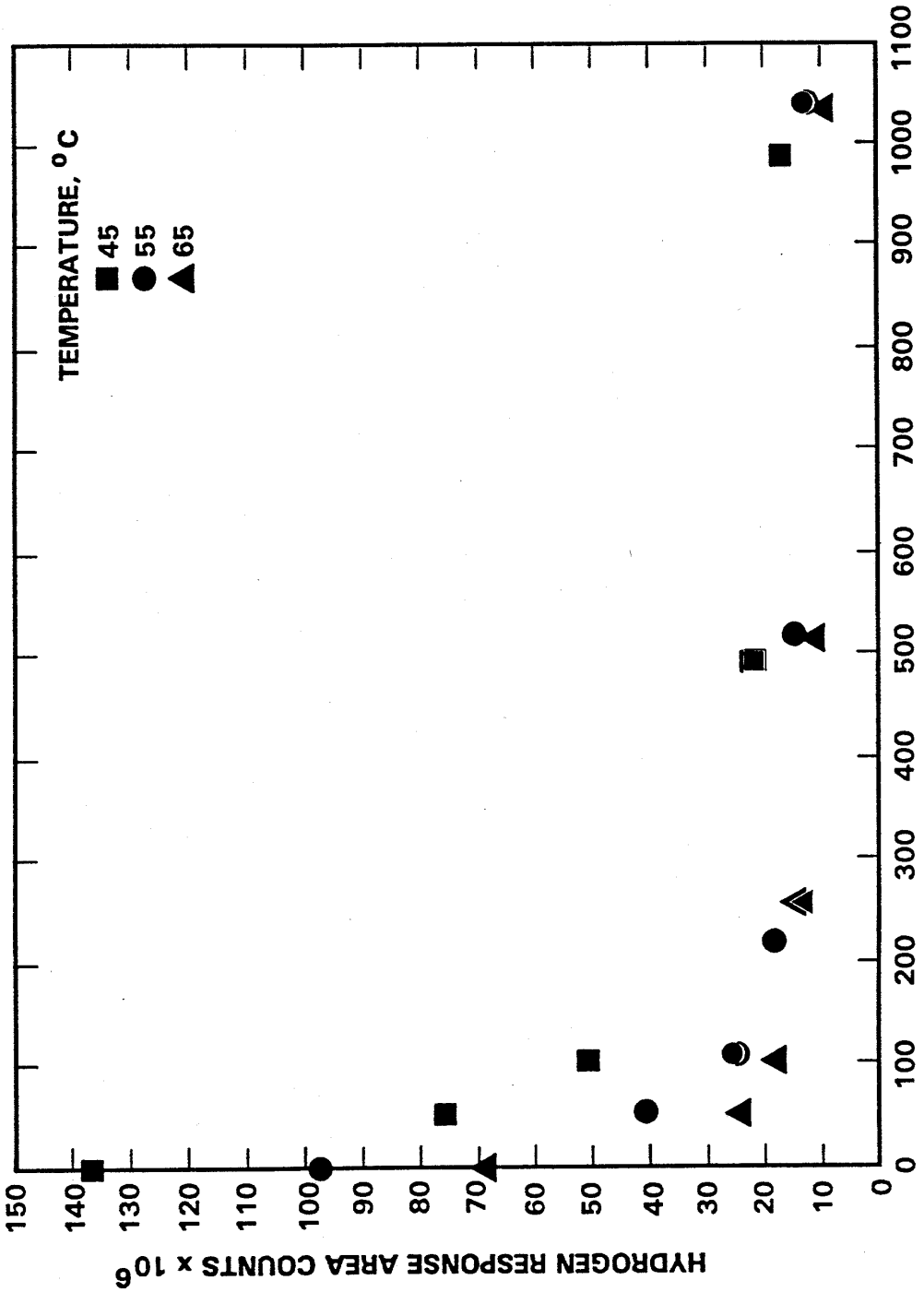


Figure 5. Residual water vapor on VOC concentrator vs. dry He purge volume.

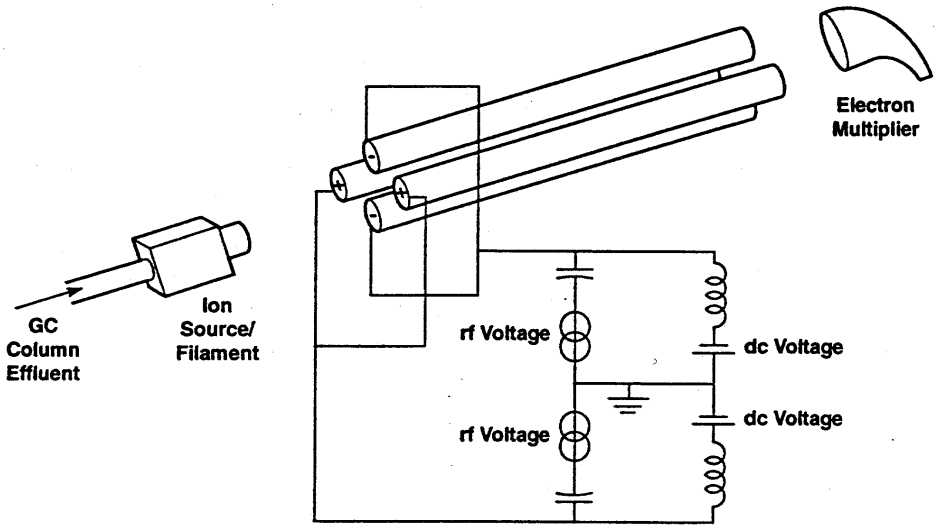


Figure 6. Simplified diagram of a quadrupole mass spectrometer.

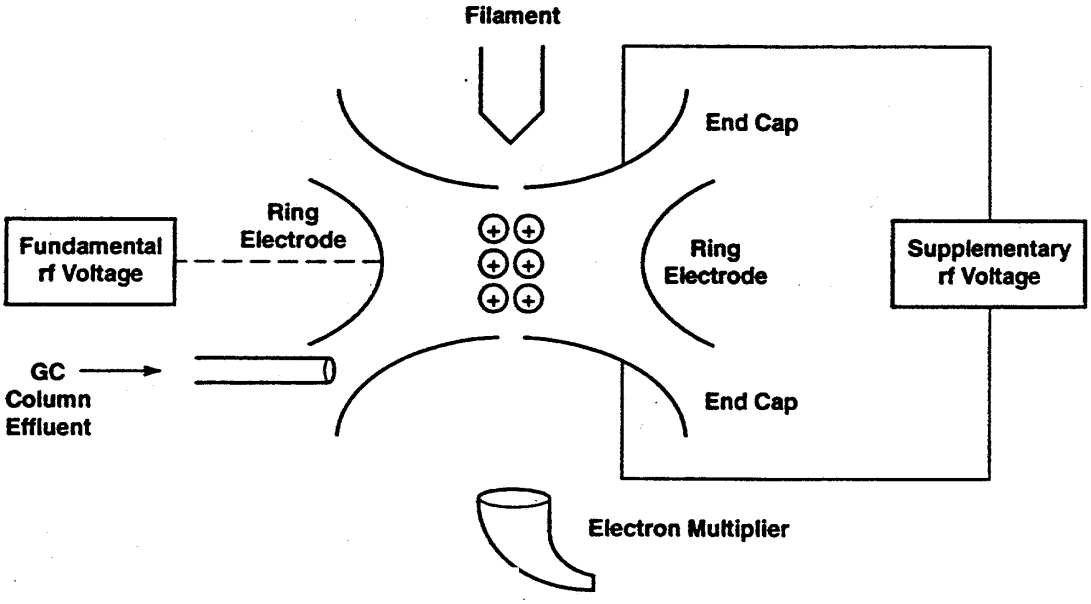


Figure 7. Simplified diagram of an ion trap mass spectrometer.

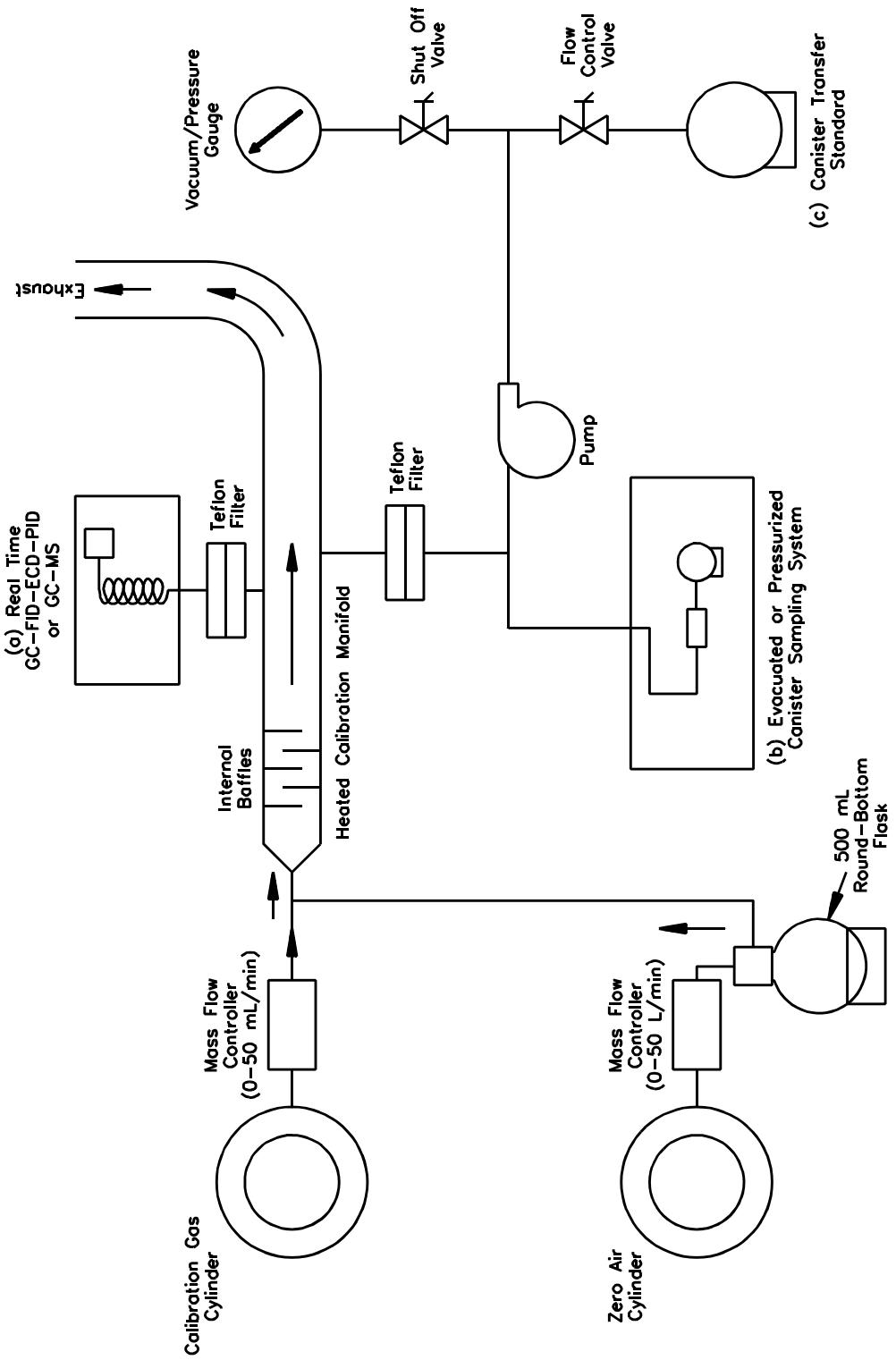


Figure 8. Schematic diagram of calibration system and manifold for (a) analytical system calibration, (b) testing canister sampling system and (c) preparing canister transfer standards.

COMPENDIUM METHOD TO-15
CANISTER SAMPLING FIELD TEST DATA SHEET

A.GENERAL INFORMATION

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

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

B. SAMPLING INFORMATION

	TEMPERATURE				PRESSURE	
	INTERIOR	AMBIENT	MAXIMUM	MINIMUM	CANISTER PRESSURE	
START						
STOP						

	SAMPLING TIMES		FLOW RATES		
	LOCAL TIME	ELAPSED TIME METER READING	MANIFOLD FLOW RATE	CANISTER FLOW RATE	FLOW CONTROLLER READOUT
START					
STOP					

SAMPLING SYSTEM CERTIFICATION DATE: _____
QUARTERLY RECERTIFICATION DATE: _____

C. LABORATORY INFORMATION

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

_____
SIGNATURE/TITLE

Figure 9. Canister sampling field test data sheet (FTDS).

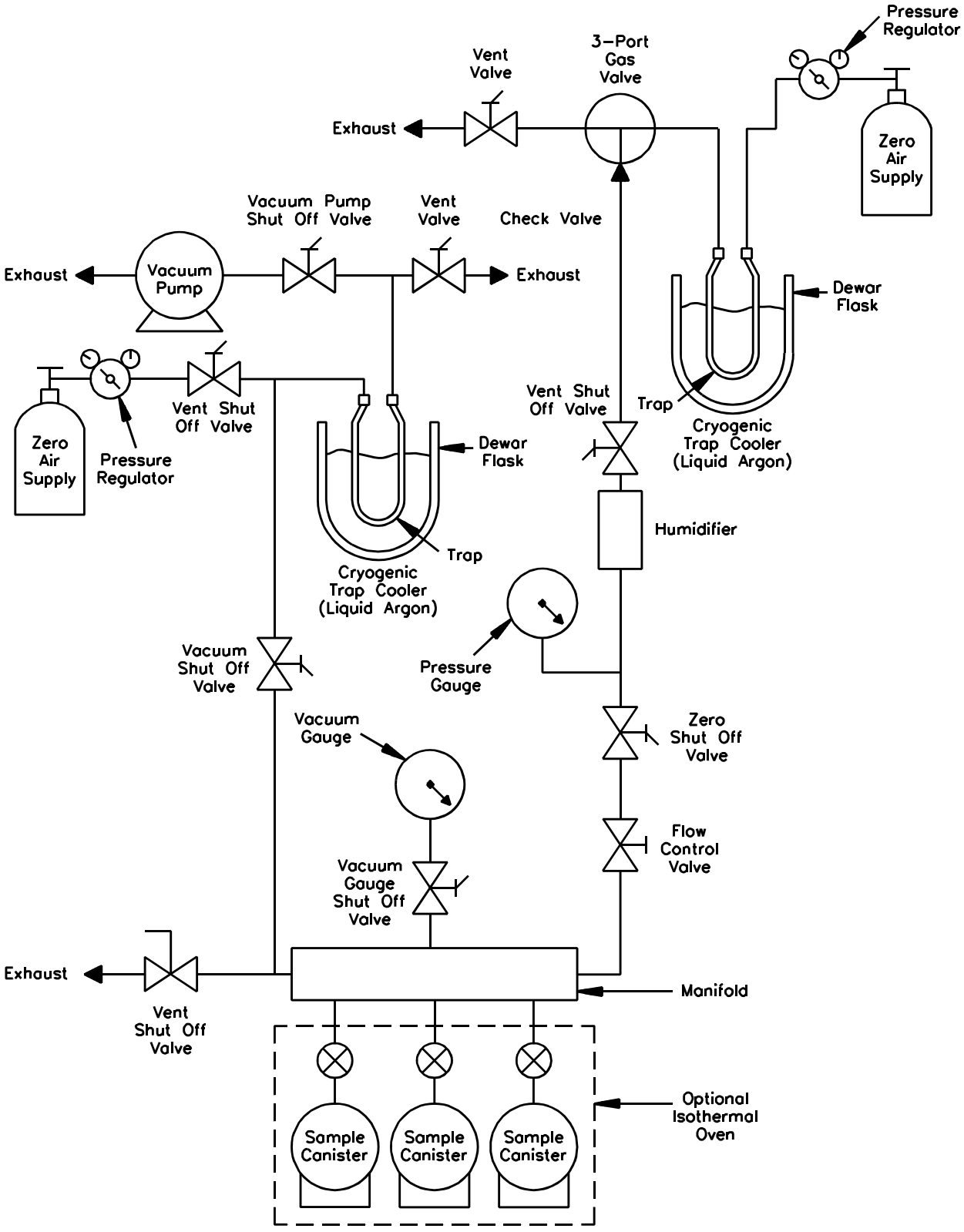


Figure 10. Canister cleaning system.

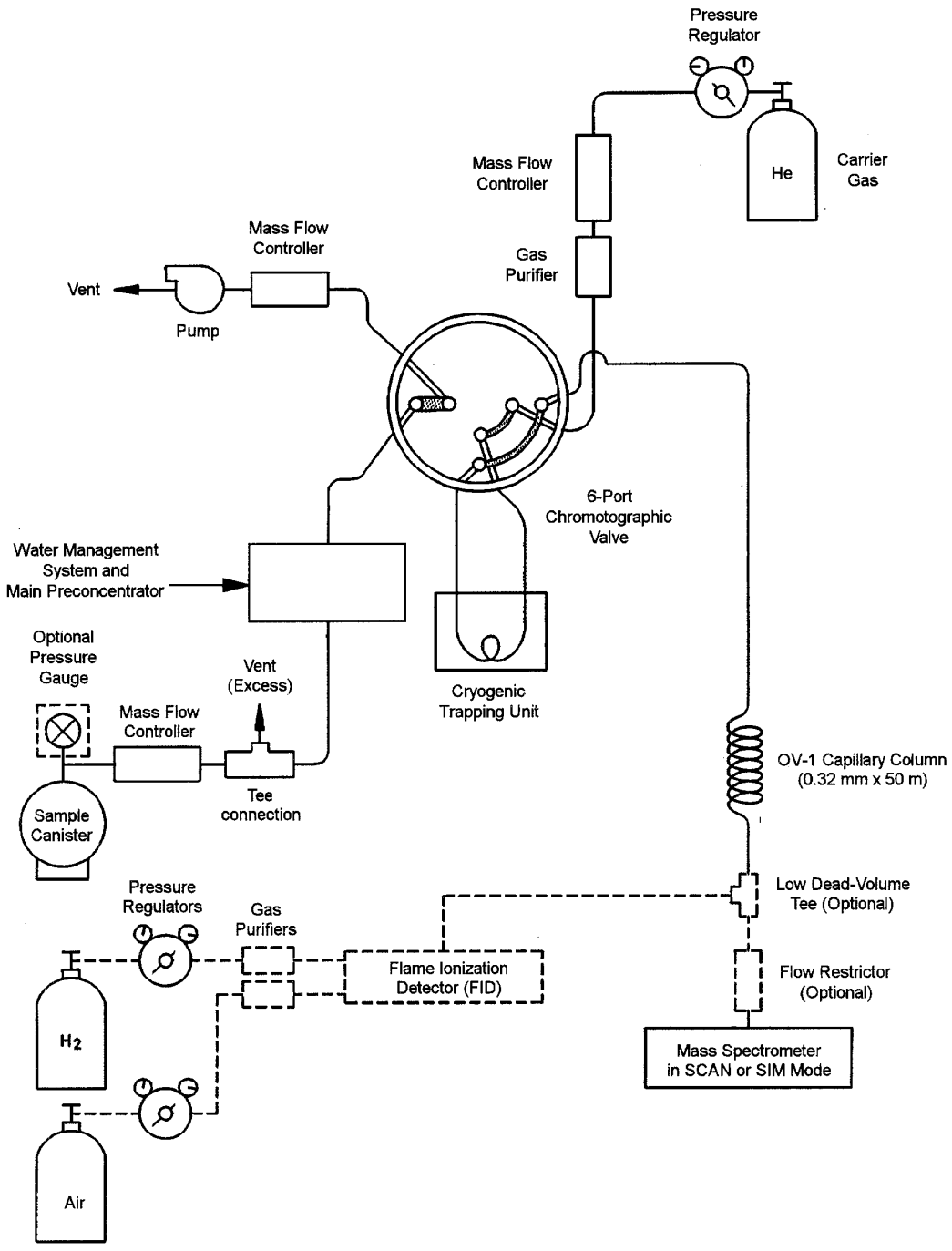
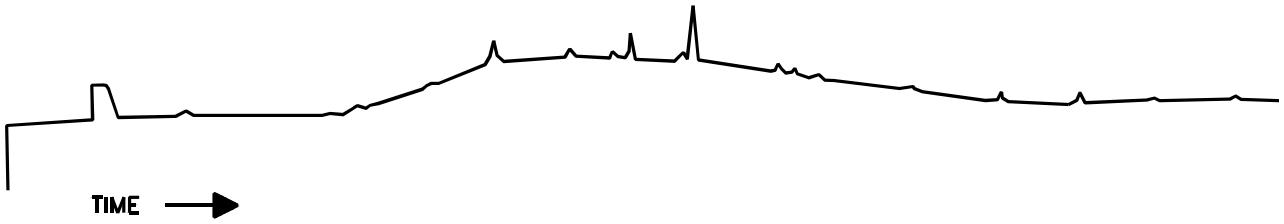
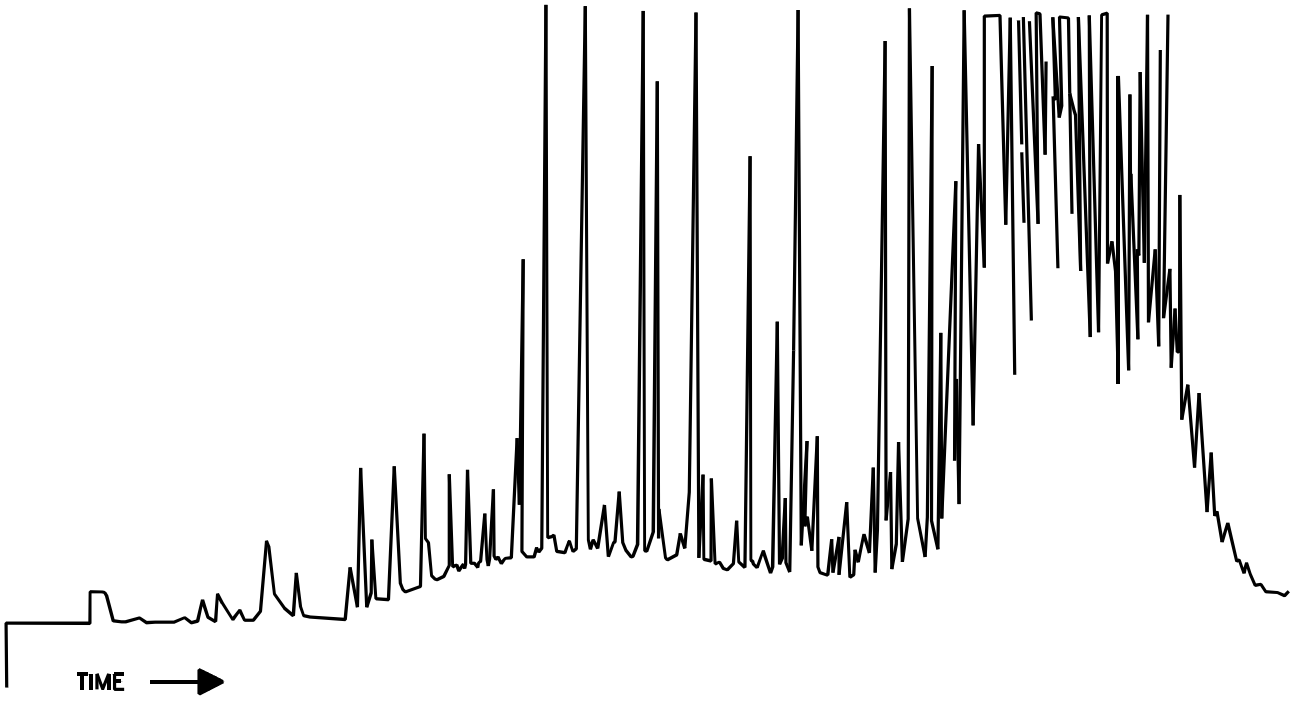


Figure 1 h 6-port



(a). Certified Sampler



(b). Contaminated Sampler

Figure 12. Example of humid zero air test results for a clean sample canister (a) and a contaminated sample canister (b).

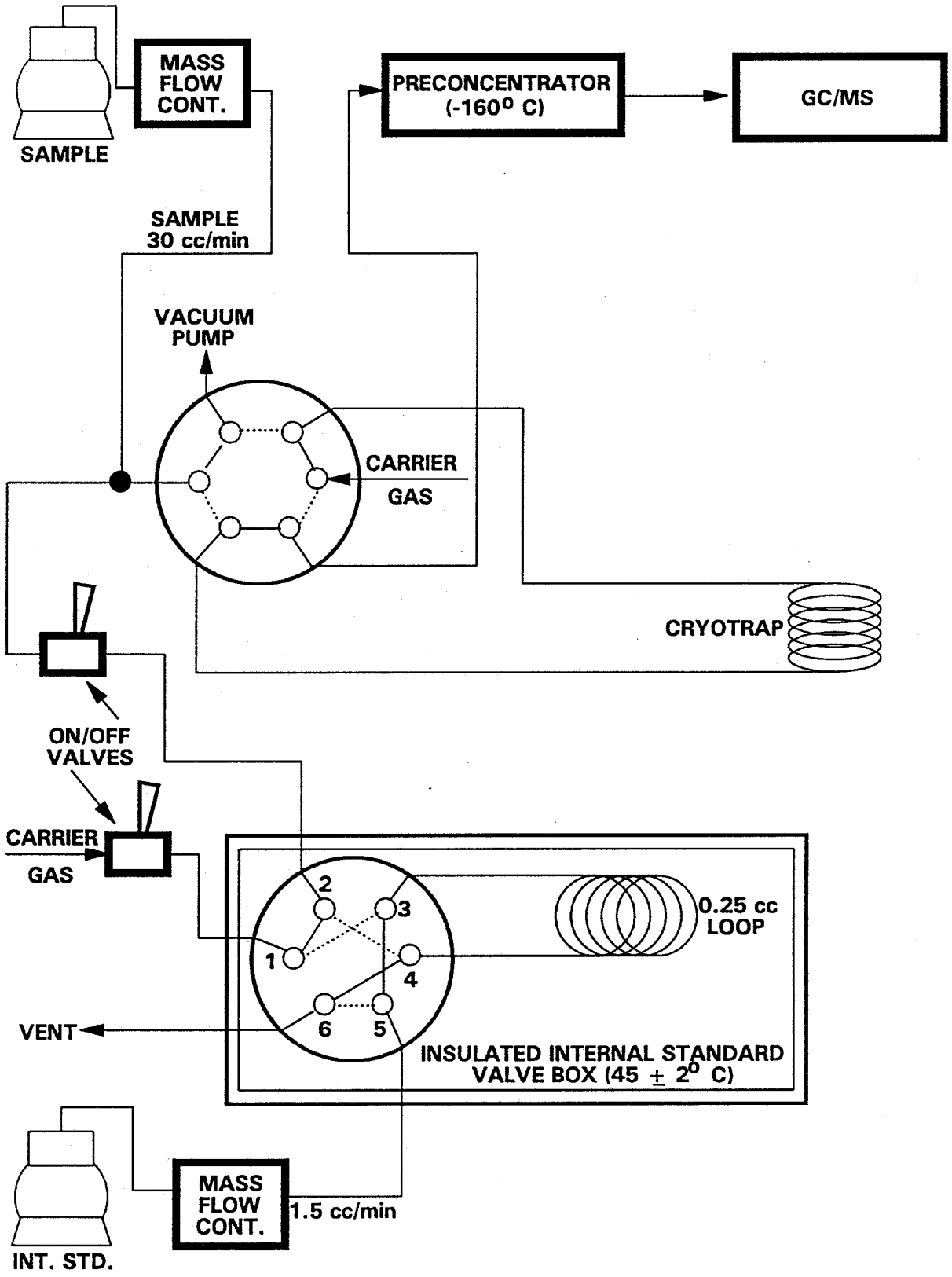


Figure 13. Diagram of design for internal standard addition.

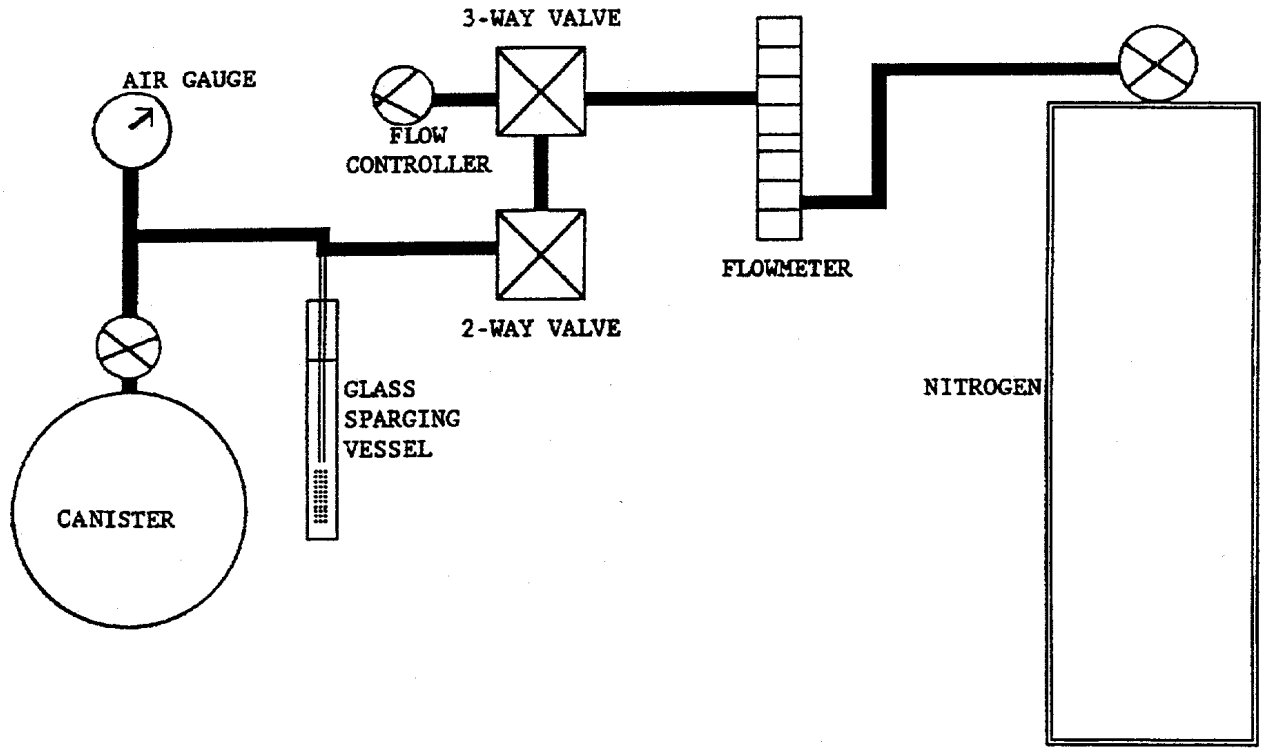


Figure 14. Water method of standard preparation in canisters.

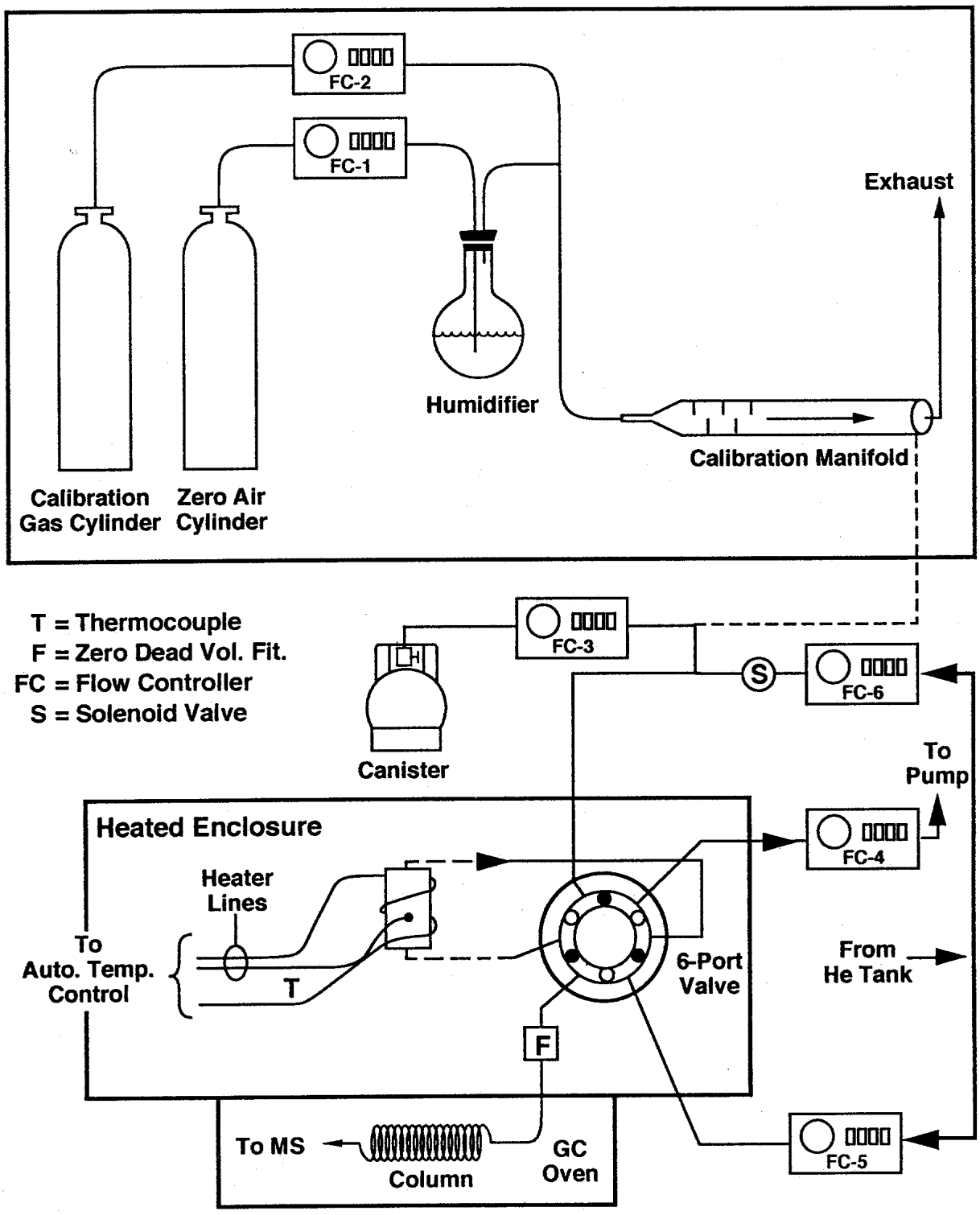
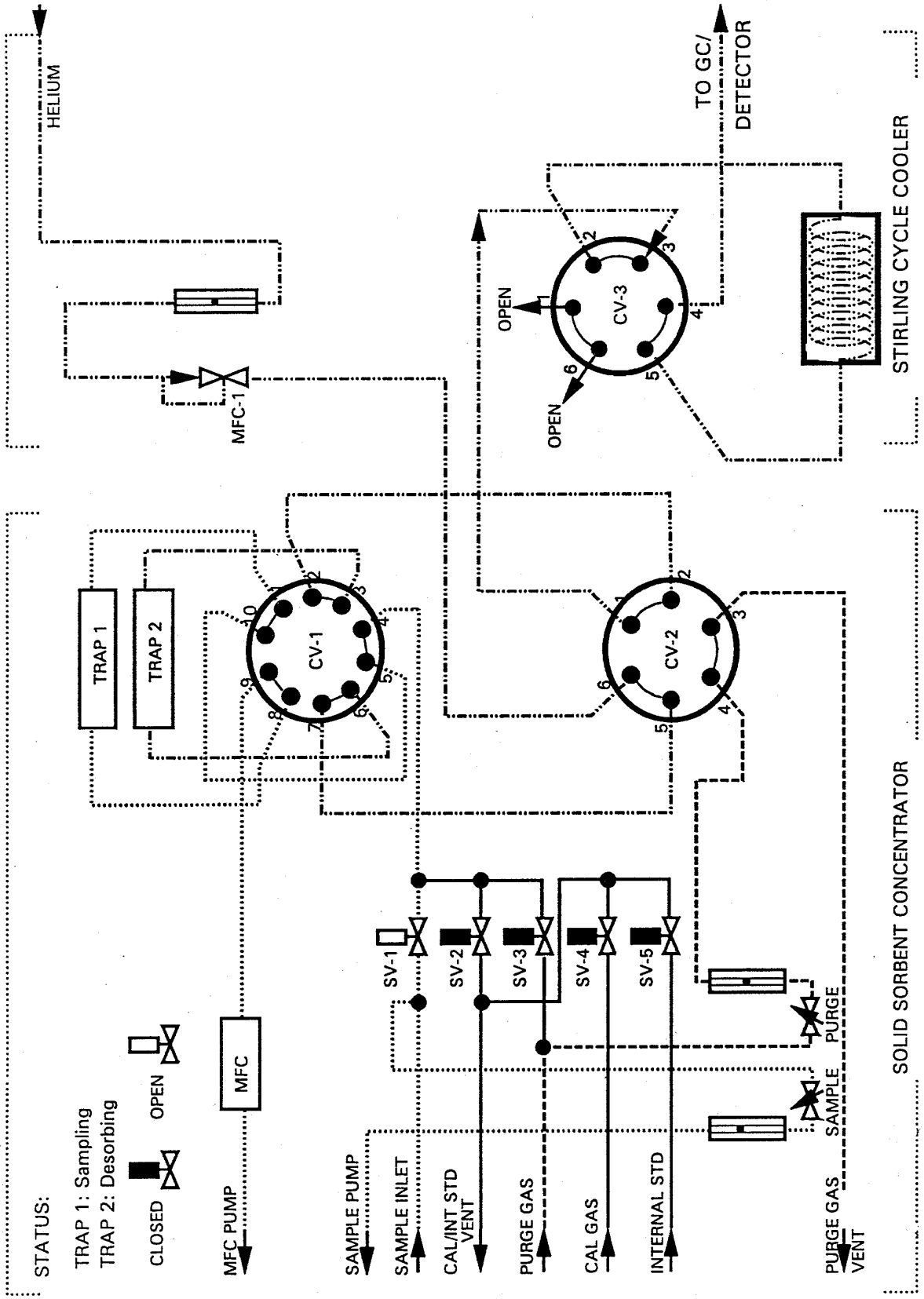


Figure 15. Diagram of the GC/MS analytical system.


HELIUM
MFC-1
TO GC/
DETECTOR
STIRLING CYCLE COOLER
OPEN
CV-3
OPEN
TRAP 1
TRAP 2
CV-1
CV-2
SOLID SORBENT CONCENTRATOR
SV-1
SV-2
SV-3
SV-4
SV-5
PURGE
SAMPLE
STATUS:
TRAP 1: Sampling
TRAP 2: Desorbing
OPEN
CLOSED
MFC
MFC PUMP
SAMPLE PUMP
SAMPLE INLET
CAL/INT STD
VENT
PURGE GAS
CAL GAS
INTERNAL STD
PURGE GAS
VENT

APPENDIX B

Humidity

Appendix B

Humidity[1]

Dalton's Law of partial pressures and the hypothesis that water vapor equilibrium above a canister surface is identical to that established above liquid water can be used to predict the variation of the percent relative humidity (%RH) of air released from canisters used in ambient air sampling, typically 6L canisters pressurized with 18L of air. During sampling, water vapor partial pressure increases as air enters the canister. When (and if) the water vapor partial pressure exceeds its saturation vapor pressure, the rate of water vapor condensation on the canister walls equals its sampling rate into the canister. Under constant temperature conditions, the %RH of air subsequently released from the canister can be calculated. This development shows that the air released from the canister is initially less humid than the original sample, if the ambient %RH >33% RH and increases as air is released from the canister according to the relationship:

$$\%RH = 100\% \frac{6\ L}{V_s} \text{ for } V_s > V_r$$

where:

V_s = Residual air volume in canister;

V_r = The residual air volume at which water is predicted to be completely removed (using the assumptions) from the canister wall.

For $V_s < V_r$, the %RH is constant and equal to its value at V_r. V_r is shown to depend on the %RH of the ambient air sample. Experimental values are shown to agree reasonably well

[1]McClenny, W.A., S.M. Schmidt, and K.G. Kronmiller. "Variation of the Relative Humidity of Air Released from Canisters After Ambient Sampling." In *Proceedings of the Measurement of Toxic and Related Air Pollutants International Symposium*, Research Triangle Park, NC, 1997.

with predictions. However, experimental values were systematically lower than predicted especially when ambient air with mid-range %RH was sampled. The difference appears to be related to the mass of water vapor condensed on the sampling apparatus upstream of the canister. Near V_r, some effects due to strongly adsorbed water vapor may also be present.

Note: The results of mathematical prediction of the %RH of air released from a canister are summarized below and graphical information is provided to allow predictions to be made for a variety of situations.

Three ranges of %RH of the ambient air that is initially sampled into the canister are conveniently treated:

- 0%RH $\leq$ original ambient %RH $\leq$ 33.3%RH

  No condensation occurs and (neglecting any adsorbed water vapor) the relative humidity of air released from the canister should be constant at its original ambient air value although in practice some water vapor will be adsorbed on the canister wall.

- 33.3%RH < original ambient %RH < 70%RH

  Locate the ambient sample %RH on the abscissa (the value of 60%RH was chosen in Figure B-1 as an example) and the point of intersection of this value with the curve A.

  Identify the value of canister volume on the ordinate scale corresponding to the point of intersection (8L in the example). This value is the volume V_r at which all condensed water vapor on the canister walls has been evaporated during the process of releasing the sample air from the canister.

  Use V_r to locate a point of intersection on curve B. This point $V_r = V_s$ divides the curve B into two sections, (1) $V_s \leq V_r$ and (2) $V_s \geq V_r$.

  Note: In general (for any ambient %RH), as the sample is released from the canister (at any stage having a volume V_s remaining in the canister), the curve B indicates the %RH (on the abscissa scale) of the released sample air over the range 18L $\leq V_s \leq$ 6L.

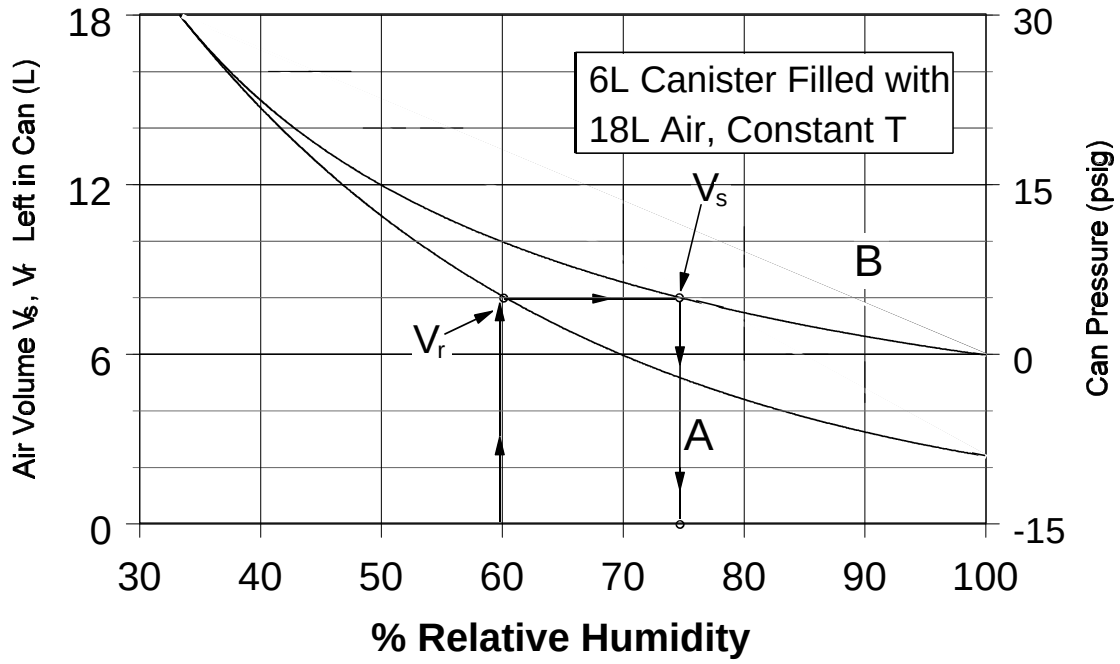


Figure B-1. **A** - Original %RH of the sample air vs the remaining sample volume, V_r, in the canister when all condensed water is evaporated; **B** - residual sample volume, V_s vs %RH of air released from canister.

For the example, for $V_s \leq 8L$, since all condensed water in the canister will have been evaporated, the mixture of water vapor and air will be constant and the %RH of the remaining sample air will be released at its value at $V_s = 8L$. In the example this value if 74%RH.

For $V_s \geq V_r$, the abscissa value (obtained with curve B) corresponding to V_s indicates the predicted %RH value of released air. In the example, this applies for any remaining sample volume between 18L and 8L.

Figure B-2 shows the modification of Figure B-1 (curve B) to predict the %RH of released sample air for the example (when the %RH of the ambient air sample was 60%). To do this locate the ordinate value corresponding to the volume V_s remaining in the canister [between 18L (30psig) and 6L (15psig)] and read the abscissa value of %RH for the point of intersection of V_s and the curve.

- 70%RH ≤ original ambient %RH ≤ 100%RH

  Refer to Figure B-1 and note from curve A that $V_r \leq 6L$ which is equivalent to stating that some condensed water is always on the canister wall for $18L \leq V_s \leq 6L$. The %RH of released air is determined by using curve B in Figure B-1 to find the value of %RH corresponding to any residual volume V_s over the entire range of values of $V_s \geq 6L$.

Results of Experimental Determination of the %RH of Sample Air Released from Pressurized Canisters—Figures B-3 and B-4 show the %RH of air released from canisters initially pressurized to 18L when 34%, 61% and 90%RH (23 ± 3ºC) ambient air samples were made available to the sampling manifold. The predicted values are shown for comparison. Some of the difference between experimental and predicted values appears to be due to condensation of water vapor on the sampling apparatus. This condensation causes a systematic displacement of the entire set of experimental points such as seen in Figure B-4.

The curves in Figure B-4 correspond to a 61% Relative Humidity value for ambient air and involve both water vapor condensation followed by evaporation of available water from the canister wall as the sample air is released. Two experimental approaches (Can 1 and Can 2) are shown. The two differ as the sample value remaining approaches V_r. The Can 2 values show the general features of the predicted characteristic. However, the value of V_r (constant % Relative Humidity) occurs at a higher value (58% Relative Humidity) than predicted (76%), probably due

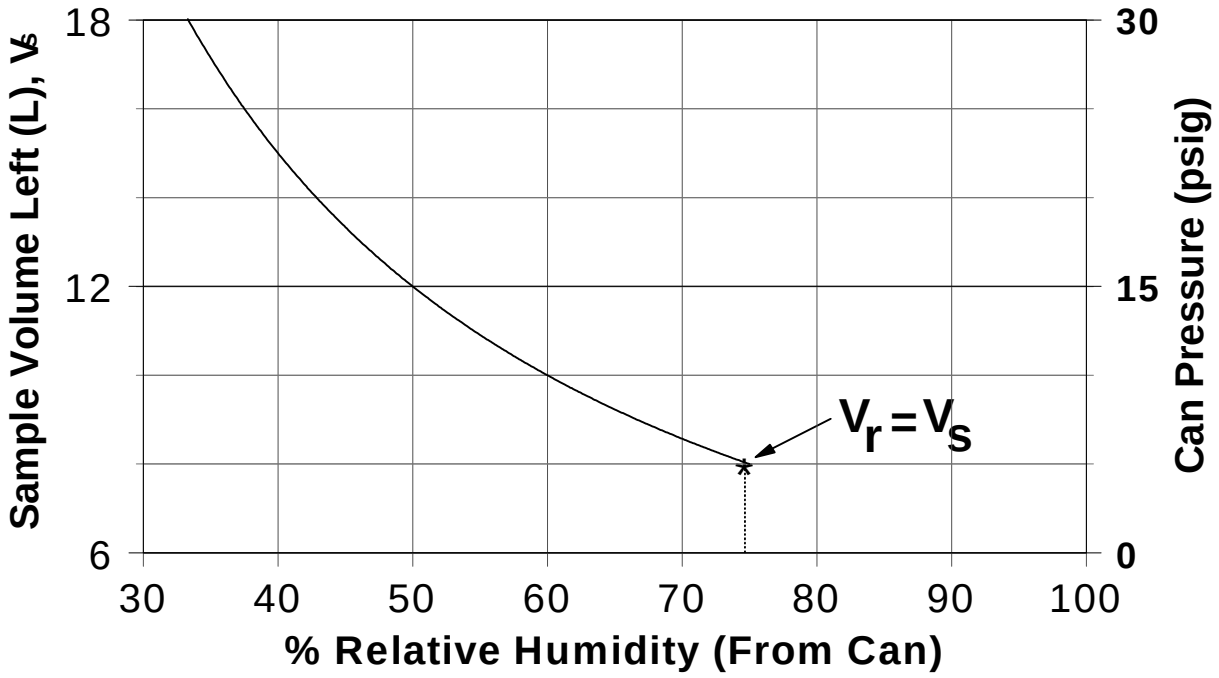


Figure B-2. Residual Sample Volume, V_S Versus %RH of Air Released From Canister

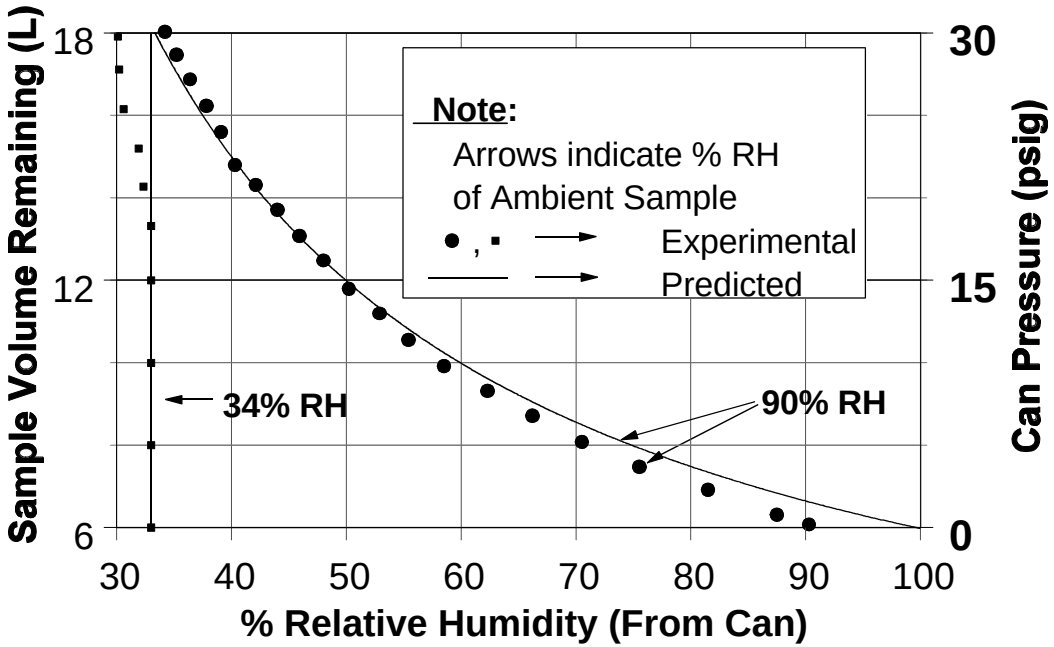


Figure B-3. Comparison of Predicted and Experimental %RH Values of Released Air Versus Volume of Sample Remaining in Canister; 34% RH and 90% RH Ambient Air Sample

B-6

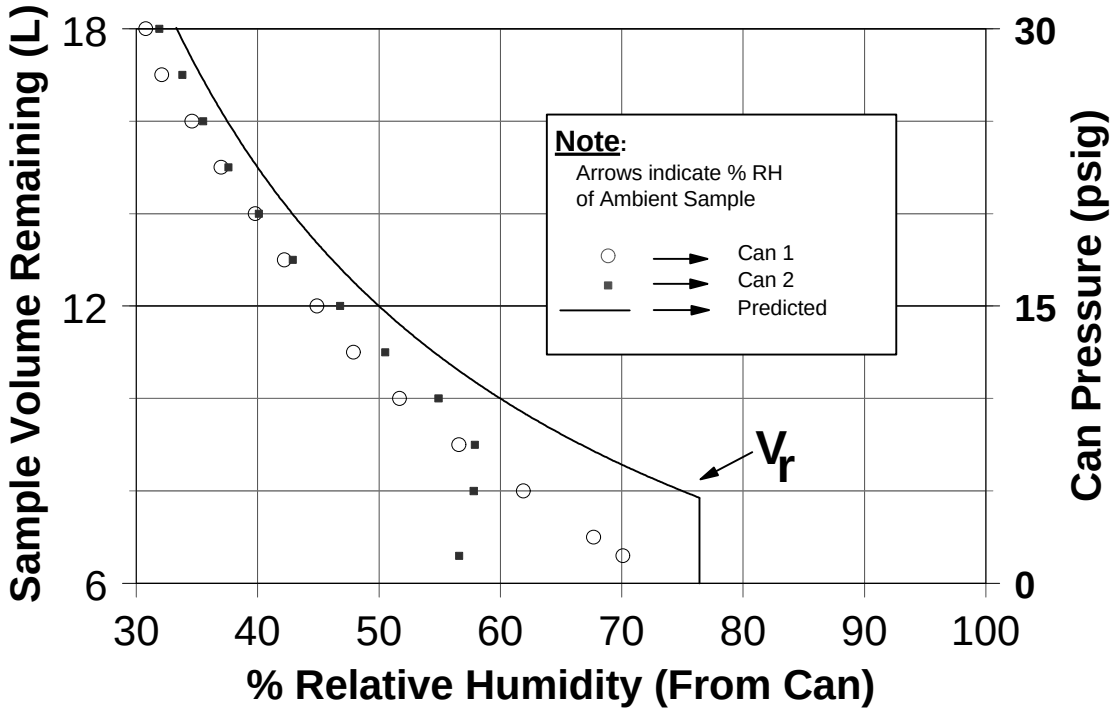


Figure B-4. Comparison of Predicted and Experimental %RH Values of Released Air Versus Volume of Sample Remaining in Canister; 61% RH Ambient Air Sample

to the condensation of water vapor on the inlet lines during sampling. Can 1 shows a monotonically increasing value of % Relative Humidity as residual canister volume decreases. Recent experimental work indicates that different canisters exhibit different behaviors near V_r. Additional experimental work is being carried out to investigate whether these differences may be related to the condition of the interior surface of the canister.

Adjustments must be made to the predicted values when ambient conditions of temperature change appreciably between sampling and release of air. Obviously, more or less water is condensed in the canister when the ambient temperature at which the canister is held becomes lower or higher than the temperature at which the sample was taken. Consideration should also be given to the mass of water in the canister since the condensation of water in the canister for the same %RH but different temperatures may lead to droplets with various surface to volume ratios. Another factor that could make a difference in the response profile of %RH versus canister pressure is the manner in which water is introduced into the canister. Water added to synthetic samples for humidification by using a certain number of µL probably has a different surface distribution in the canister than humidified samples introduced directly from the ambient air.

APPENDIX C

Method TO-12

Method for the Determination of Non-Methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID)

METHOD TO-12

METHOD FOR THE DETERMINATION OF NON-METHANE ORGANIC COMPOUNDS (NMOC) IN AMBIENT AIR USING CRYOGENIC PRECONCENTRATION AND DIRECT FLAME IONIZATION DETECTION (PDFID)

1. Scope

1.1 In recent years, the relationship between ambient concentrations of precursor organic compounds and subsequent downwind concentrations of ozone 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 compliance with applicable ambient air quality standards for ozone (1,2).

1.2 The more elaborate theoretical models generally require detailed organic species data obtained by multicomponent gas chromatography (3). The Empirical Kinetic Modeling Approach (EKMA), however, requires only the total non-methane organic compound (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.

1.3 Method TO1, "Method for The Determination of Volatile Organic Compounds in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS)", employs collection of certain volatile organic compounds on Tenax® GC with subsequent analysis of thermal desorption/cryogenic preconcentration and GC/MS identification. This method (TO12) combines the same type of cryogenic concentration techniques used in Method TO1 for high sensitivity with the simple flame ionization detector (FID) of the GC for total NMOC measurements, without the GC columns and complex procedures necessary for species separation.

1.4 In a flame ionization detector, 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 nearly a universal detector. However, the detector response varies with the species of [functional group in] the organic compound in an oxygen atmosphere. Because this method employs a helium or argon carrier gas, the detector response is nearly one for all compounds. Thus,

the historical short-coming of the FID involving varying detector response to different organic functional groups is minimized.

1.5 The method can be used either for direct, in situ ambient measurements or (more commonly) for analysis of 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 to prepare State Implementation Plans (SIPs) for ozone control to achieve compliance with the National Ambient Air Quality Standards (NAAQS) for ozone. 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 the 6 a.m. to 9 a.m. average NMOC concentration. 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. This method has incorporated both sampling approaches.

2. Applicable Documents

2.1 ASTM Standards

D1356 - Definition of Terms Related to Atmospheric Sampling and Analysis

E260 - Recommended Practice for General Gas Chromatography Procedures

E355 - Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

U. S. Environmental Protection Agency Technical Assistance Documents (4,5)

Laboratory and Ambient Air Studies (6-10)

3. Summary of Method

3.1 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.

3.2 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 -186°C with liquid argon. The cryogenic trap simultaneously collects and concentrates the NMOC (either via condensation or adsorption) 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 must be precisely repeatable between the calibration and the analytical phases.

3.3 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 restablizes, the cryogen is removed and the temperature of the trap is raised to approximately 90°C.

3.4 The organic compounds previously collected in the trap revolatilize due to 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 with known concentrations of propane.

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

3.6 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.

4. Significance

4.1 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. Achieving and maintaining compliance with the NAAQS for ozone thus depends largely on control of ambient levels of NMOC.

4.2 The NMOC concentrations typically found at urban sites may range up to 5-7 ppmC or higher. 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 ppm.

4.3 Conventional methods that depend on gas chromatography and qualitative and quantitative species evaluation are excessively difficult and expensive to operate and maintain when speciated measurements are not needed. The method described here involves a

simple, cryogenic preconcentration procedure with subsequent, direct, flame ionization detection. The method is sensitive and provides accurate measurements of ambient NMOC concentrations where speciated data are not required as applicable to the EKMA.

5. Definitions

[Note: Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D1356 and E355. All abbreviations and symbols are defined within this document at point of use.]

5.1 Absolute pressure - Pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as pounds-force per square inch absolute (psia).

5.2 Cryogen - A substance used to obtain very low trap temperatures in the NMOC analysis system. Typical cryogens are liquid argon (bp-185.7) and liquid oxygen (bp-183.0).

5.3 Dynamic calibration - Calibration of an analytical system with pollutant concentrations that are generated in a dynamic, flowing system, such as by quantitative, flow-rate dilution of a high concentration gas standard with zero gas.

5.4 EKMA - Empirical Kinetics Modeling Approach; an empirical model that attempts to relate morning ambient concentrations of non-methane organic compounds (NMOC) and NO_x with subsequent peak, downwind ambient ozone concentrations; used by pollution control agencies to estimate the degree of hydrocarbon emission reduction needed to achieve compliance with national ambient air quality standards for ozone.

5.5 Gauge pressure - Pressure measured with reference to atmospheric pressure (as opposed to absolute pressure). Zero gauge pressure (0 psig) is equal to atmospheric pressure, or 14.7 psia (101 kPa).

5.6 In situ - In place; In situ measurements are obtained by direct, on-the-spot analysis, as opposed to subsequent, remote analysis of a collected sample.

5.7 Integrated sample - A sample obtained uniformly over a specified time period and representative of the average levels of pollutants during the time period.

5.8 NMOC - Nonmethane organic compounds; total organic compounds as measured by a flame ionization detector, excluding methane.

5.9 ppmC - Concentration unit of parts per million carbon; for a specific compound, ppmC is equivalent to parts per million by volume (ppmv) multiplied by the number of carbon atoms in the compound.

5.10 Sampling - The process of withdrawing or isolating a representative portion of an ambient atmosphere, with or without the simultaneous isolation of selected components for subsequent analysis.

6. Interferences

6.1 In field and laboratory evaluation, water 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 adjusted baseline used for calculating the area of the NMOC peak(s).

6.2 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.

7. Apparatus

7.1 Direct Air Sampling (Figure 1)

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

7.1.2 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.

7.2 Remote Sample Collection in Pressurized Canisters (Figure 2)

7.2.1 Sample canister(s) - stainless steel, Summa®-polished vessel(s) of 4-6 L capacity (Scientific Instrumentation Specialists, Inc., P.O. Box 8941, Moscow, ID 83843), used for automatic collection of 3-hour integrated field air samples. Each canister should have a unique identification number stamped on its frame.

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

7.2.3 Pressure gauge - 0-30 psig (0-240 kPa).

7.2.4 Solenoid valve - special electrically-operated, bistable solenoid valve (Skinner Magnelatch Valve, New Britain, CT), to control sample flow to the canister with negligible temperature rise (Figure 3). The use of the Skinner Magnelatch valve avoids any substantial temperature rise that would occur with a conventional,

normally closed solenoid valve, which would have to be energized during the entire sample period. This temperature rise in the valve could cause outgasing of organics from the Viton valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods or with a conventional mechanical timer and a special pulse circuit. Figure 3[a] illustrates a simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer. However, with this simple circuit, the valve may operate unpredictably during brief power interruptions or if the time is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 3[b].

7.2.5 Stainless steel orifice (or short capillary) - capable of maintaining a substantially constant flow over the sampling period (see Figure 4).

7.2.6 Particulate matter filter - 2 micron stainless steel sintered in-line type (see Figure 4).

7.2.7 Timer - used for unattended sample collection. Capable of controlling pump(s) and solenoid valve.

7.3 Sample Canister Cleaning (Figure 5)

7.3.1 Vacuum pump - capable of evacuating sample canister(s) to an absolute pressure of <5 mm Hg.

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

7.3.3 Shut off valve(s) - seven required.

7.3.4 Vacuum gauge - capable of measuring vacuum in the manifold to an absolute pressure of 5 mm Hg or less.

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

7.3.6 Pressure gauge - 0-50 psig (0-345 kPa), to monitor zero air pressure.

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

7.3.8 Humidifier - water bubbler or other system capable of providing moisture to the zero air supply.

7.4 Analytical System (Figure 1)

7.4.1 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 to obtain an adequate FID response while maintaining as stable a flame as possible throughout all phases of the analytical cycle.

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

7.4.3 Electronic integrator - capable of integrating the area of one or more FID response peaks and calculating peak area corrected for baseline drift. If a separate integrator and chart recorder are used, care must be exercised to be sure 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.

Note: The FID (7.4.1), chart recorder (7.4.2), integrator (7.4.3), valve heater (7.4.5), and a trap heating system are conveniently provided by a standard laboratory chromatograph and associated integrator. EPA has adapted two such systems for the PDFID method: a Hewlett-Packard model 5880 (Hewlett-Packard Corp., Avondale, PA) and a Shimadzu model GC8APF (Shimadzu Scientific Instruments Inc., Columbia, MD; see Reference 5). Other similar systems may also be applicable.

7.4.4 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 6. 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 (7.4.9), 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 on and off the trap and also to facilitate heating of the trap (see 7.4.13).

7.4.5 Six-port chromatographic valve - Seiscor Model VIII (Seismograph Service Corp., Tulsa, OK), Valco Model 9110 (Valco Instruments Co., Houston, TX), or equivalent. The 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.

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

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

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

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

7.4.10 Absolute pressure gauge - 0-450 mm Hg, (2 mm Hg [scale divisions indicating units]), to monitor repeatable volumes of sample air through cryogenic trap (Wallace and Tiernan, Model 61C-ID-0410, 25 Main Street, Belleville, NJ).

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

7.4.12 Gas purifiers - gas scrubbers containing Drierite® or silica gel and 5A molecular sieve to remove moisture

and organic impurities in the helium, air, and hydrogen gas flows (Alltech Associates, Deerfield, IL). Note: Check purity of gas purifiers prior to use by passing zero-air through the unit and analyzing according to Section 11.4. Gas purifiers are clean if produce [contain] less than 0.02 ppmC hydrocarbons.

7.4.13 Trap heating system - chromatographic oven, hot water, or other means to heat the trap to 80° to 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, 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.

7.4.14 Toggle shut-off valves (2) - leak free, for vacuum valve and sample valve.

7.4.15 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.

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

7.4.17 Rotameter - to verify vent flow.

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

7.4.19 Chromatographic-grade stainless steel tubing (Alltech Applied Science, 2051 Waukegan Road, Deerfield, IL, 60015, (312) 948-8600) and stainless steel plumbing fittings - for interconnections. All such materials in contact with the sample, analyte, or support gases prior to analysis should be stainless steel or other inert metal. Do not use plastic or Teflon® tubing or fittings.

7.5 Commercially Available PDFID System (5)

7.5.1 A convenient and cost-effective modular PDFID system suitable for use with a conventional laboratory chromatograph is commercially available (NuTech Corporation, Model 8548, 2806 Cheek Road, Durham, NC, 27704, (919) 682-0402).

7.5.2 This modular system contains almost all of the apparatus items needed to convert the chromatograph into a PDFID analytical system and has been designed to be readily available and easy to assemble.

8. Reagents and Materials

8.1 Gas cylinders of helium and hydrogen - ultrahigh purity grade.

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

8.3 Propane calibration standard - cylinder containing 1-100 ppm (3-300 ppmC) propane in air. The cylinder assay should be traceable to a National Bureau of Standards (NBS) Standard Reference Material (SRM) or to a NBS/EPA-approved Certified Reference Material (CRM).

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

8.5 Liquid cryogen - liquid argon (bp -185.7°C) or liquid oxygen, (bp -183°C) may be used as the cryogen. Experiments have shown no differences in trapping efficiency between liquid argon and liquid oxygen. However, appropriate safety precautions must be taken if liquid oxygen is used. Liquid nitrogen (bp -195°C) should not be used because it causes condensation of oxygen and methane in the trap.

9. Direct Sampling

9.1 For direct ambient air sampling, the cryogenic trapping system draws the air sample directly from a pump-ventilated distribution manifold or sample line (see Figure 1). 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.

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

10. Sample Collection in Pressurized Canister(s)

For integrated pressurized canister sampling, ambient air is sampled by a metal bellows pump through a critical orifice (to maintain constant flow), and pressurized into a clean, evacuated, Summa®-polished sample canister. The critical orifice size is chosen so that the canister is pressurized to approximately one atmosphere above ambient pressure, at a

constant flow rate over the desired sample period. Two canisters are connected in parallel for duplicate samples. The canister(s) are then returned to the laboratory for analysis, using the PDFID analytical system. Collection of ambient air samples in pressurized canisters provides the following advantages:

- Convenient integration of ambient samples over a specific time period
- Capability of remote sampling with subsequent central laboratory analysis
- Ability to ship and store samples, if necessary
- Unattended sample collection
- Analysis of samples from multiple sites with one analytical system
- Collection of replicate samples for assessment of measurement precision

With canister sampling, however, great care must be exercised in selecting, cleaning, and handling the sample canister(s) and sampling apparatus to avoid losses or contamination of the samples.

10.1 Canister Cleanup and Preparation

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

10.1.2 Leak test all canisters by pressurizing them to approximately 30 psig [200 kPa (gauge)] with zero air. The use of the canister cleaning system (see Figure 5) may be adequate for this task. Measure the final pressure - close the canister valve, then check the pressure after 24 hours. If leak tight, the pressure should not vary more than $\pm$ 2 psig over the 24-hour period. Note leak check result on sampling data sheet, Figure 7.

10.1.3 Assemble a canister cleaning system, as illustrated in Figure 5. Add cryogen to both the vacuum pump and zero air supply traps. Connect the canister(s) to the manifold. Open the vent shut off valve and the canister valve(s) to release any remaining pressure in the canister. Now close the vent shut off valve and open the vacuum shut off valve. Start the vacuum pump and evacuate the canister(s) to $\leq$ 5.0 mm Hg (for at least one hour). [Note: On a daily basis or more often if necessary, blow-out the cryogenic traps with zero air to remove any trapped water from previous canister cleaning cycles.]

10.1.4 Close the vacuum and vacuum gauge shut off valves and open the zero air shut off valve to pressurize the

canister(s) with moist zero air to approximately 30 psig [200 kPa (gauge)]. If a zero gas generator systems is used, the flow rate may need to be limited to maintain the zero air quality.

10.1.5 Close the zero shut off valve and allow canister(s) to vent down to atmospheric pressure through the vent shut off valve. Close the vent shut off valve. Repeat steps 10.1.3 through 10.1.5 two additional times for a total of three (3) evacuation/ pressurization cycles for each set of canisters.

10.1.6 As a "blank" check of the canister(s) and cleanup procedure, analyze the final zero-air fill of 100% of the canisters until the cleanup system and canisters are proven reliable. The check can then be reduced to a lower percentage of canisters. Any canister that does not test clean (compared to direct analysis of humidified zero air of less than 0.02 ppmC) should not be utilized.

10.1.7 The canister is then re-evacuated to $\leq$ 5.0 mm Hg, using the canister cleaning system, and remains in this condition until use. Close the canister valve, remove the canister from the canister cleaning system and cap canister connection with a stainless steel fitting. The canister is now ready for collection of an air sample. Attach an identification tag to the neck of each canister for field notes and chain-of-custody purposes.

10.2 Collection of Integrated Whole-Air Samples

10.2.1 Assemble the sampling apparatus as shown in Figure 2. The connecting lines between the sample pump and the canister(s) should be as short as possible to minimize their volume. A second canister is used when a duplicate sample is desired for quality assurance (QA) purposes (see Section 12.2.4). The small auxiliary vacuum pump purges the inlet manifold or lines with a flow of several L/min to minimize the sample residence time. The larger metal bellows pump takes a small portion of this sample to fill and pressurize the sample canister(s). Both pumps should be shock-mounted to minimize vibration. Prior to field use, each sampling system should be leak tested. The

outlet side of the metal bellows pump can be checked for leaks by attaching the 0-30 psig pressure gauge to the canister(s) inlet via connecting tubing and pressurizing to 2 atmospheres or approximately 29.4 psig. If pump and connecting lines are leak free pressure should remain at ±2 psig for 15 minutes. To check the inlet side, plug the sample inlet and insure that there is no flow at the outlet of the pump.

10.2.2 Calculate the flow rate needed so that the canister(s) are pressurized to approximately one atmosphere above ambient pressure (2 atmospheres absolute pressure) over the desired sample period, utilizing the following equation:

$$F = \frac{(P)(V)(N)}{(T)(60)}$$

where:

F = flow rate (cm^3/min)
P = final canister pressure (atmospheres absolute)
= (Pg/Pa) + 1
V = volume of the canister (cm^3)
N = number of canisters connected together for simultaneous sample collection
T = sample period (hours)
Pg = gauge pressure in canister, psig (kPa)
Pa = standard atmospheric pressure, 14.7 psig (101 kPa)

For example, if one 6-L canister is to be filled to 2 atmospheres absolute pressure (14.7 psig) in 3 hours, the flow rate would be calculated as follows:

$$F = \frac{2 \text{ x } 6000 \text{ x } 1}{3 \text{ x } 60} = 67 \text{ cm}^3/\text{min}$$

10.2.3 Select a critical orifice or hypodermic needle suitable to maintain a substantially constant flow at the calculated flow rate into the canister(s) over the desired sample period. A 30-gauge hypodermic needle,

2.5 cm long, provides a flow of approximately 65 cm^3/min with the Metal Bellows Model MBV-151 pump (see Figure 4). Such a needle will maintain approximately constant flow up to a canister pressure of about 10 psig (71 kPa), after which the flow drops with increasing pressure. At 14.7 psig (2 atmospheres absolute pressure), the flow is about 10% below the original flow.

10.2.4 Assemble the 2.0 micron stainless steel in-line particulate filter and position it in front of the critical orifice. A suggested filter-hypodermic needle assembly can be fabricated as illustrated in Figure 4.

10.2.5 Check the sampling system for contamination by filling two evacuated, cleaned canister(s) (See Section 10.1) with humidified zero air through the sampling system. Analyze the canisters according to Section 11.4. The sampling system is free of contamination if the canisters contain less than 0.02 ppmC hydrocarbons, similar to that of humidified zero air.

10.2.6 During the system contamination check procedure, check the critical orifice flow rate on the sampling system to insure that sample flow rate remains relatively constant ($\pm$10%) up to about 2 atmospheres absolute pressure (101 kpa). Note: A drop in the flow rate may occur near the end of the sampling period as the canister pressure approaches two atmospheres.

10.2.7 Reassemble the sampling system. If the inlet sample line is longer than 3 meters, install an auxiliary pump to ventilate the sample line, as illustrated in Figure 2.

10.2.8 Verify that the timer, pump(s) and solenoid valve are connected and operating properly.

10.2.9 Verify that the timer is correctly set for the desired sample period, and that the solenoid valve is closed.

10.2.10 Connect a cleaned, evacuated canister(s) (Section 10.1) to the non-contaminated sampling system, by way of the solenoid valve, for sample collection.

10.2.11 Make sure the solenoid valve is closed. Open the canister valve(s). Temporarily connect a small rotameter to the sample inlet to verify that there is

no flow. Note: Flow detection would indicate a leaking (or open) solenoid valve. Remove the rotameter after leak detection procedure.

10.2.12 Fill out the necessary information on the Field Data Sheet (Figure 7).

10.2.13 Set the automatic timer to start and stop the pump or pumps to open and close the solenoid valve at the appropriate time for the intended sample period. Sampling will begin at the pre-determined time.

10.2.14 After the sample period, close the canister valve(s) and disconnect the canister(s) from the sampling system. Connect a pressure gauge to the canister(s) and briefly open and close the canister valve. Note the canister pressure on the Field Data Sheet (see Figure 7). The canister pressure should be approximately 2 atmospheres absolute [1 atmosphere or 101 kPa (gauge)]. Note: If the canister pressure is not approximately 2 atmospheres absolute (14.7 psig), determine and correct the cause before next sample. Re-cap canister valve.

10.2.15 Fill out the identification tag on the sample canister(s) and complete the Field Data Sheet as necessary. Note any activities or special conditions in the area (rain, smoke, etc.) that may affect the sample contents on the sampling data sheet.

10.2.16 Return the canister(s) to the analytical system for analysis.

11. Sample Analysis

11.1 Analytical System Leak Check

11.1.1 Before sample analysis, the analytical system is assembled (see Figure 1) and leak checked.

11.1.2 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 psig at the vacuum valve outlet.

11.1.3 Attach a valve and a zero air supply to the sample inlet port. Pressurize the system to about 50 psig (350 kPa) and close the valve.

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

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

11.1.6 The analytical system leak check procedure needs to be performed during the system checkout, during a series of analysis or if leaks are suspected. This should be part of the user-prepared SOP manual (see Section 12.1).

11.2 Sample Volume Determination

11.2.1 The vacuum reservoir and absolute pressure gauge are used to meter a precisely repeatable volume of sample air through the cryogenically-cooled trap, as follows: With the sample valve closed and the vacuum valve open, the reservoir is first evacuated with the vacuum pump to a predetermined pressure (e.g., 100 mm Hg). Then the vacuum valve is closed and the sample valve is opened to allow sample air to be drawn through the cryogenic trap and into the evacuated reservoir until a second predetermined reservoir pressure is reached (e.g., 300 mm Hg). The (fixed) volume of air thus sampled is determined by the pressure rise in the vacuum reservoir (difference between the predetermined pressures) as measured by the absolute pressure gauge (see Section 12.2.1).

11.2.2 The sample volume can be calculated by:

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

where:

V_s = volume of air sampled (standard cm^3)

$)P$ = pressure difference measured by gauge (mm Hg)

V_r = volume of vacuum reservoir (cm^3) usually 1 L

P_s = standard pressure (760 mm Hg)

For example, with a vacuum reservoir of 1000 cm^3 and a pressure change of 200 mm Hg (100 to 300 mm Hg), the volume

sampled would be 263 cm^3. [Note: Typical sample volume using this procedure is between 200-300 cm^3.]

11.2.3 The sample volume determination need only be performed once during the system check-out and shall be part of the user-prepared SOP Manual (see Section 12.1).

11.3 Analytical System Dynamic Calibration

11.3.1 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. This should be carried out initially and periodically thereafter [may be done only once during a series of analyses]. This should be part of the user-prepared SOP Manual (See Section 12.1). The calibration should be verified with two or three-point calibration checks (including zero) each day the analytical system is used to analyze samples.

11.3.2 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 (see Section 8.3). Dilution flow rates must be measured accurately, and the combined gas stream must be mixed thoroughly for successful calibration of the analyzer. Calibration standards should be sampled directly from a vented manifold or tee. Note: Remember that a propane NMOC concentration in ppmC is three times the volumetric concentration in ppm.

11.3.3 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. Note: Modern GC integrators may provide automatic ranging such 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 (see Section 12.1).

11.3.4 Analyze each calibration standard three times according to the procedure in Section 11.4. 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 cm^3/minute; helium carrier, 30 cm^3/minute; burner air, 400 cm^3/minute.

11.3.5 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 to define the calibration curve adequately.

11.4 Analysis Procedure

11.4.1 Insure the analytical system has been assembled properly, leaked checked, and properly calibrated through a dynamic standard calibration. Light the FID detector and allow to stabilize.

11.4.2 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 re-volatilized NMOC from the trap into the FID. A single-stage auxiliary regulator between the cylinder and the analyzer may not be necessary, but is recommended to regulate the helium pressure better than the multistage cylinder regulator. When an auxiliary regulator is used, the secondary stage of the two-stage regulator must be set at a pressure higher than the pressure setting of the single-stage

regulator. Also check the FID hydrogen and burner air flow rates (see 11.3.4).

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

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

11.4.5 Open the sample valve and adjust the sample flow rate needle valve for an appropriate trap flow of 50-100 cm^3/min. Note: The flow will be lower later, when the trap is cold.

11.4.6 Check the sample canister pressure before attaching it to the analytical system and record on Field Data Sheet (see Figure 7). Connect the sample canister or direct sample inlet to the six-port valve, as shown in Figure 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 assures 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 hence the vent flow rate will be higher) when the trap is cold.

11.4.7 Close the sample valve and open the vacuum valve (if not already open) 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 [with both valves open, the pressure reading won't change] to flush and condition the inlet lines.

11.4.8 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.

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

11.4.10 Submerge the trap in the cryogen. Allow a few minutes for the trap to cool completely (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 beaded portion of the trap.

11.4.11 Open the sample valve and observe the increasing pressure on the pressure gauge. When it reaches the specific predetermined pressure (typically 300 mm Hg) representative of the desired sample volume (Section 11.2), close the sample valve.

11.4.12 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. Note: This insures that organics do not bleed from the trap and are counted as part of the NMOC peak(s).

11.4.13 Switch the 6-port valve to the inject position, keeping the cryogenic liquid on the trap until the methane and upset peaks have diminished (10-20 seconds). Now close the canister valve to conserve the remaining sample in the canister.

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

11.4.15 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°. Heating the trap volatilizes the concentrated NMOC such that the FID produces integrated peaks. A uniform trap temperature rise rate (above 0°C) helps to 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°/minute; final temperature, 90°C.

11.4.16 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.

11.4.17 Continue the integration (generally, in the range of 1-2 minutes is adequate) only long enough to include all of the organic compound peaks and to establish the end point FID baseline, as illustrated in Figure 8. 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 (see Figure 8) so that the calculated operational baseline effectively compensates for the water-shifted baseline. Electronic integrators either do this automatically or they should be programmed to make this 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 insure all water has been removed to prevent buildup of water in the trap. Therefore, be sure that the 6-port valve remains in the inject position until all moisture has purged from the trap (3 minutes or longer).

11.4.18 Use the dynamic calibration curve (see Section 11.3) to convert the integrated peak area reading into concentration units (ppmC). Note that the NMOC peak shape may not be precisely reproducible due to variations in heating the trap, but the total NMOC peak area should be reproducible.

11.4.19 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 $\pm$ 5% relative standard deviation (RSD), additional analyses should be made to identify inaccurate measurements and produce a more accurate average (see also Section 12.2).

12. 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.

12.1 Standard Operating Procedures (SOPs)

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

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

12.2 Method Sensitivity, Accuracy, Precision and Linearity

12.2.1 The sensitivity and precision of the method is 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 cm^3. Sample volumes below about 100-150 cm^3 may cause increased measurement variability due to dead volume in lines and valves. For most typical ambient NMOC

concentrations, sample volumes in the range of 200-400 cm^3 appear to be appropriate. If a response peak obtained with a 400 cm^3 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, hence the sample volume, is repeatable within 1%. A 1000 cm^3 vacuum reservoir and a pressure change of 200 mm Hg, measured with the specified pressure gauge, have provided a sampling precision of $\pm$ 1.31 cm^3. A smaller volume reservoir may be used with a greater pressure change to accommodate absolute pressure gauges with lower resolution, and vice versa.

12.2.2 Some FID detector 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 use, as discussed in Section 12.2.1.

12.2.3 System linearity has been documented (6) from 0 to 10,000 ppbC.

12.2.4 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.

12.2.5 Simultaneous collection of duplicate samples decreases the possibility of lost measurement data from samples lost due to leakage or contamination in either of the canisters. Two (or more) canisters can be filled simultaneously by connecting them in parallel (see Figure 2(a)) and selecting an appropriate flow rate to accommodate the number of canisters (Section 10.2.2). Duplicate (or replicate) samples also allow assessment of measurement precision based on the differences between duplicate samples (or the standard deviations among replicate samples).

13. Method Modification

13.1 Sample Metering System

13.1.1 Although the vacuum reservoir and absolute pressure gauge technique for metering the sample volume during analysis is efficient and convenient, other techniques should work also.

13.1.2 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.

13.2 FID Detector System

13.2.1 A variety of FID detector systems should be adaptable to the method.

13.2.2 The specific flow rates and necessary modifications for the helium carrier for any alternative FID instrument should be evaluated prior to use as apart of the user-prepared SOP manual.

13.3 Range

13.3.1 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.

13.3.2 Any attempt to increase sensitivity should be evaluated as part of the user-prepared SOP manual.

13.4 Sub-Atmospheric Pressure Canister Sampling

13.4.1 Collection and analysis of canister air samples at sub-atmospheric pressure is also possible with minor modifications to the sampling and analytical procedures.

13.4.2 Method TO-14, "Integrated Canister Sampling for Selective Organics: Pressurized and Sub-atmospheric Collection Mechanism," addresses sub-atmospheric pressure canister sampling. Additional information can be found in the literature (11-17).

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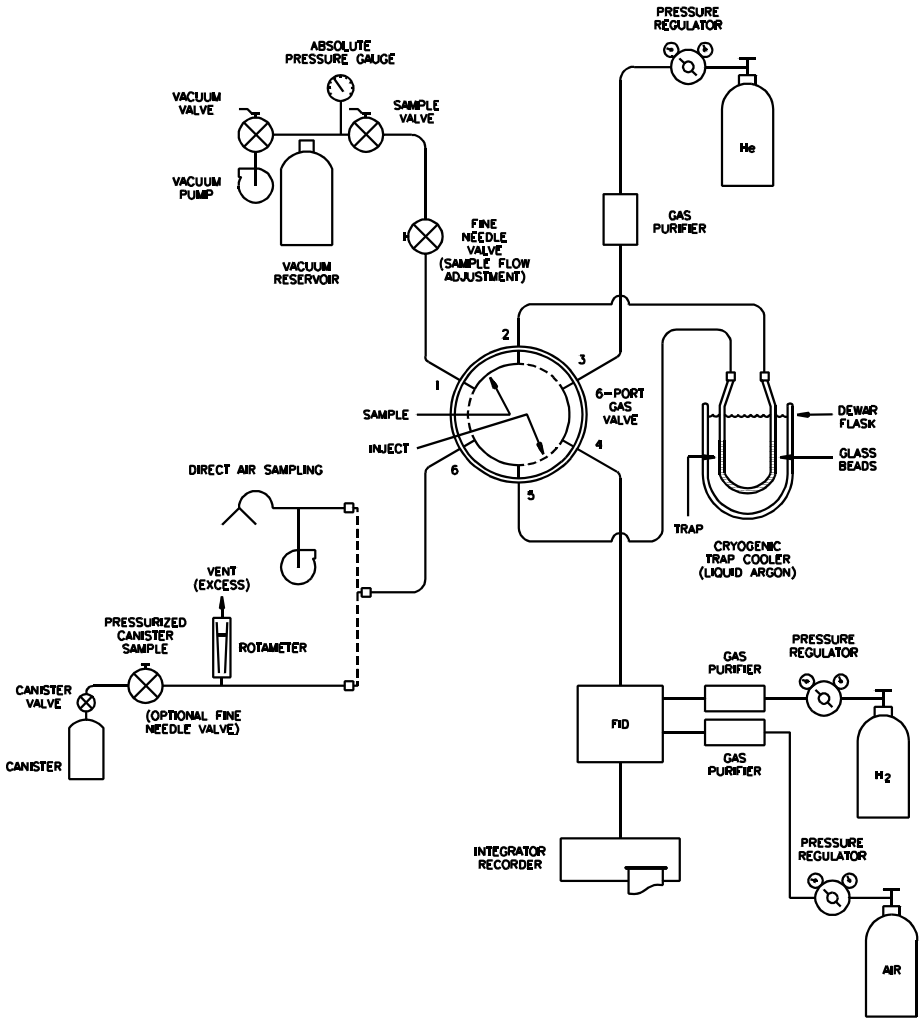


FIGURE 1. SCHEMATIC OF ANALYTICAL SYSTEM FOR NMOC–TWO SAMPLING MODES

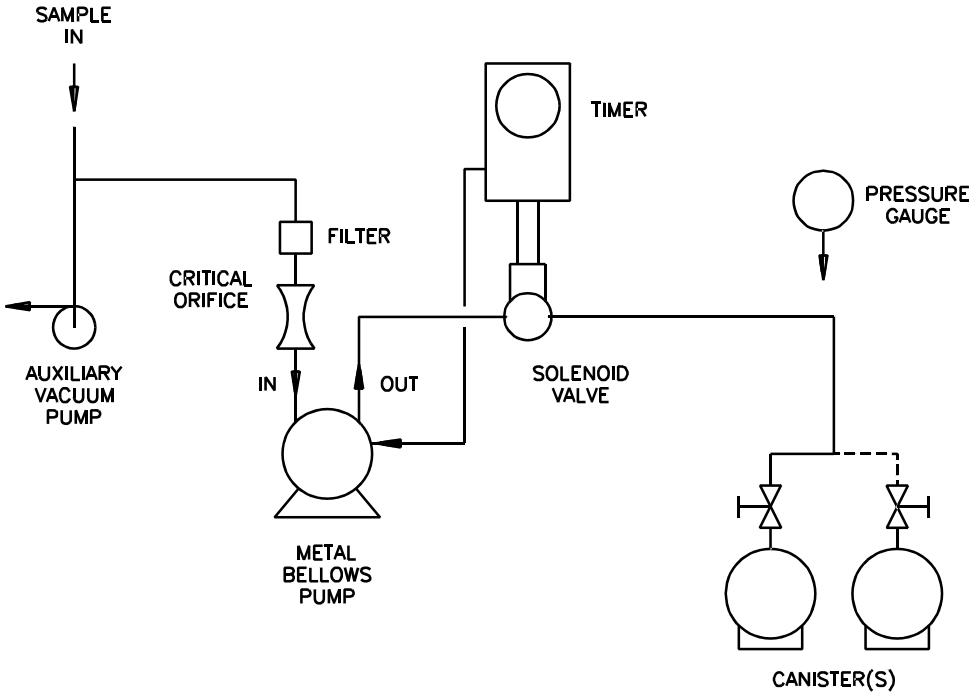
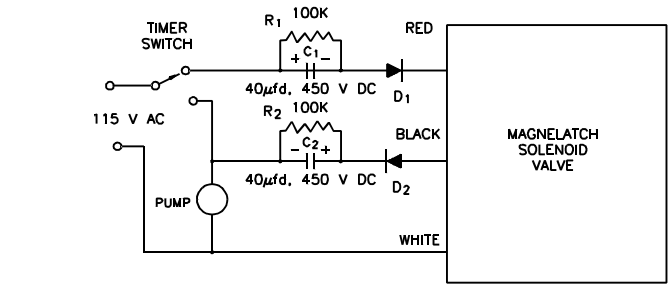


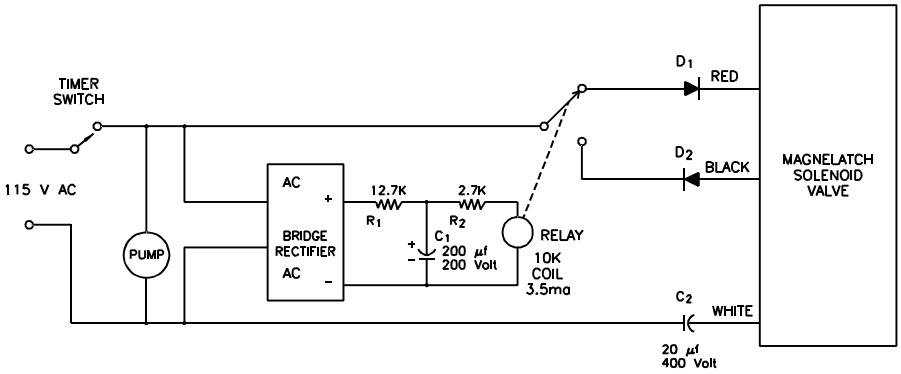
FIGURE 2. SAMPLE SYSTEM FOR AUTOMATIC COLLECTION
OF 3-HOUR INTEGRATED AIR SAMPLES



COMPONENTS

Capacitor C_1 and C_2 – 40 μf, 450 VDC (Sprague Atom® TVA 1712 or equivalent)
Register R_1 and R_2 – 0.5 watt, 5% tolerance
Diode D_1 and D_2 – 1000 PRV, 2.5 A (RCA, SK 3001 or equivalent)

FIGURE 3[a]. SIMPLE CIRCUIT FOR OPERATING MAGNELATCH VALVE



COMPONENTS

Bridge Rectifier – 200 PRV, 1.5 A (RCA, SK 3105 or equivalent)
Diode D_1 and D_2 – 1000 PRV, 2.5 A (RCA, SK 3061 or equivalent)
Capacitor C_1 – 200 μf, 250 VDC (Sprague Atom® TVA 1528 or equivalent)
Capacitor C_2 – 20 μf, 400 VDC Non-Polarized (Sprague Atom® TVAN 1552 or equivalent)
Relay – 10,000 ohm coil, 3.5 ma (AMF Potter and Brumfield, KCP 5, or equivalent)
Resister R_1 and R_2 – 0.5 watt, 5% tolerance

FIGURE 3[b]. IMPROVED CIRCUIT DESIGNED TO HANDLE POWER INTERRUPTIONS

FIGURE 3. ELECTRICAL PULSE CIRCUITS FOR DRIVING SKINNER MAGNELATCH SOLENOID VALVE WITH A MECHANICAL TIMER

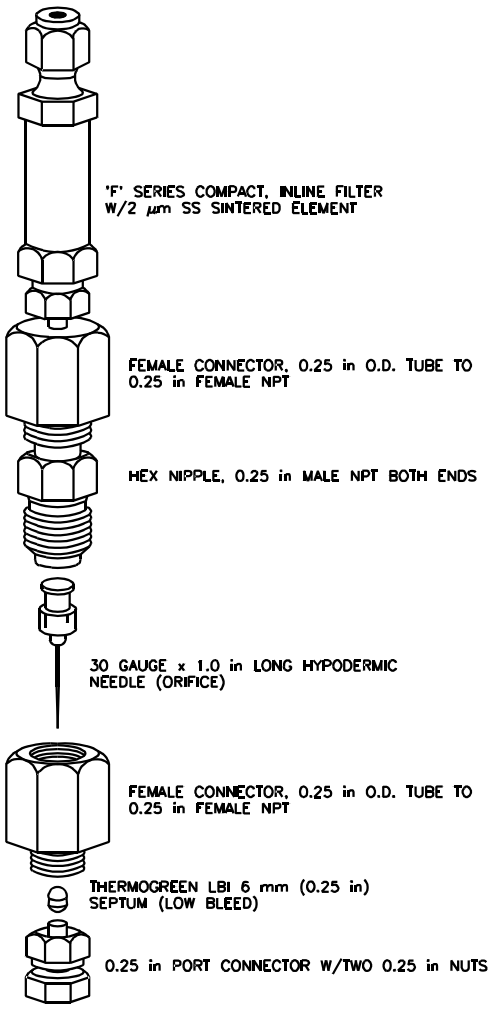


FIGURE 4. FILTER AND HYPODERMIC NEEDLE ASSEMBLY FOR SAMPLE INLET FLOW CONTROL

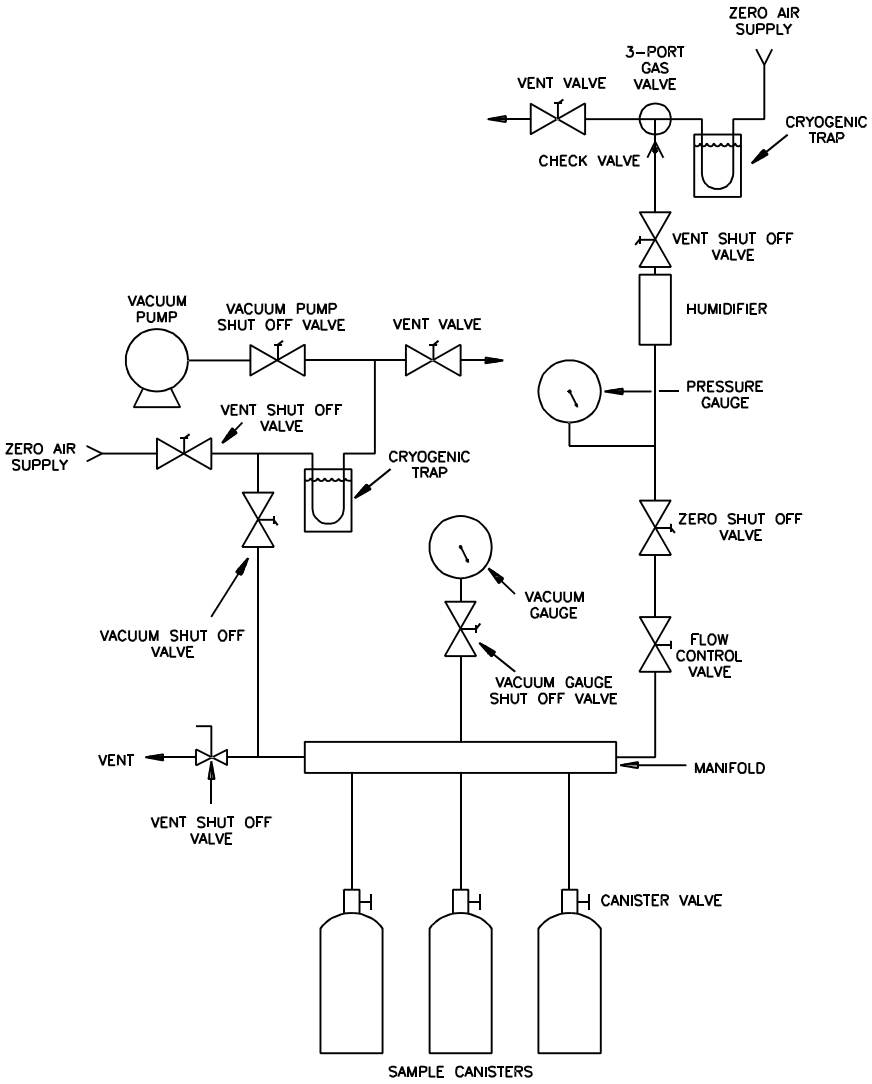


FIGURE 5. CANISTER CLEANING SYSTEM

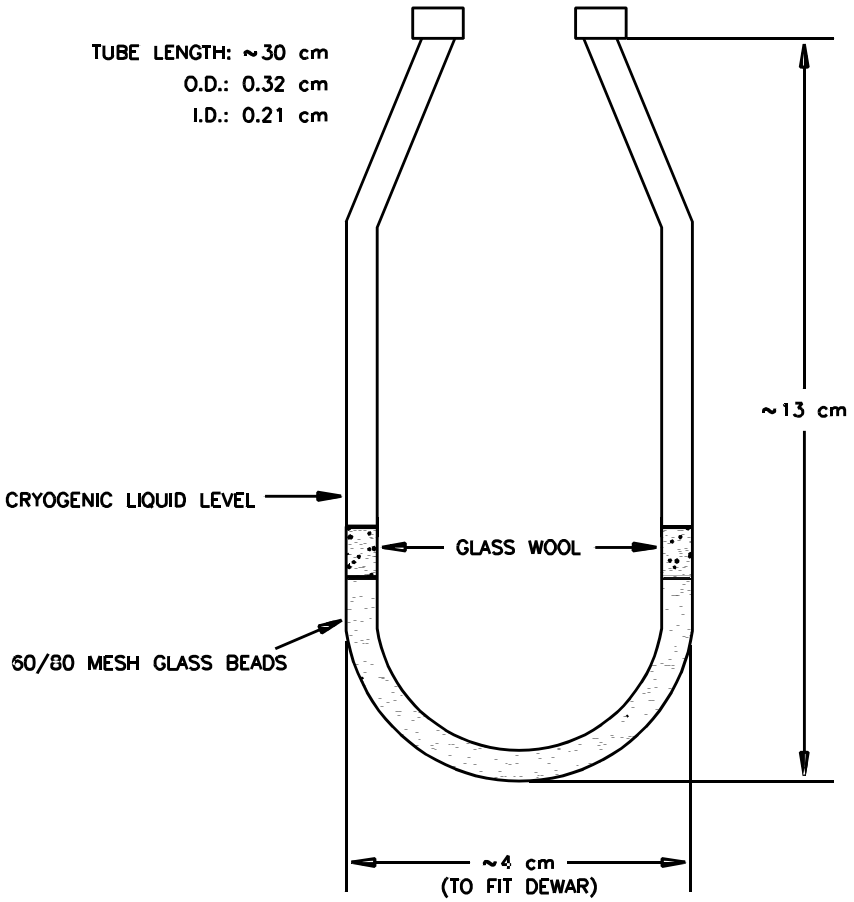


FIGURE 6. CRYOGENIC SAMPLE TRAP DIMENSIONS

PRESSURIZED CANISTER SAMPLING DATA SHEET

GENERAL INFORMATION:

PROJECT:_____ OPERATOR:_____
SITE:_____ ORIFICE IDENTIFICATION:_____
LOCATION:_____ FLOW RATE:_____
MONITOR STATION NUMBER:_____ CALIBRATED BY:_____
PUMP SERIAL NUMBER:_____ LEAK CHECK _____ _____
Pass Fail

FIELD DATA:

Date	Canister Serial Number	Sample Number	Sample Time		Average Atmospheric Conditions			Canister pressure Final, Laboratory		Comments
			Start	Stop	Temperature	Pressure	Relative Humidity			

_____ _____ _____
Date Title Signature

FIGURE 7. EXAMPLE SAMPLING DATA SHEET

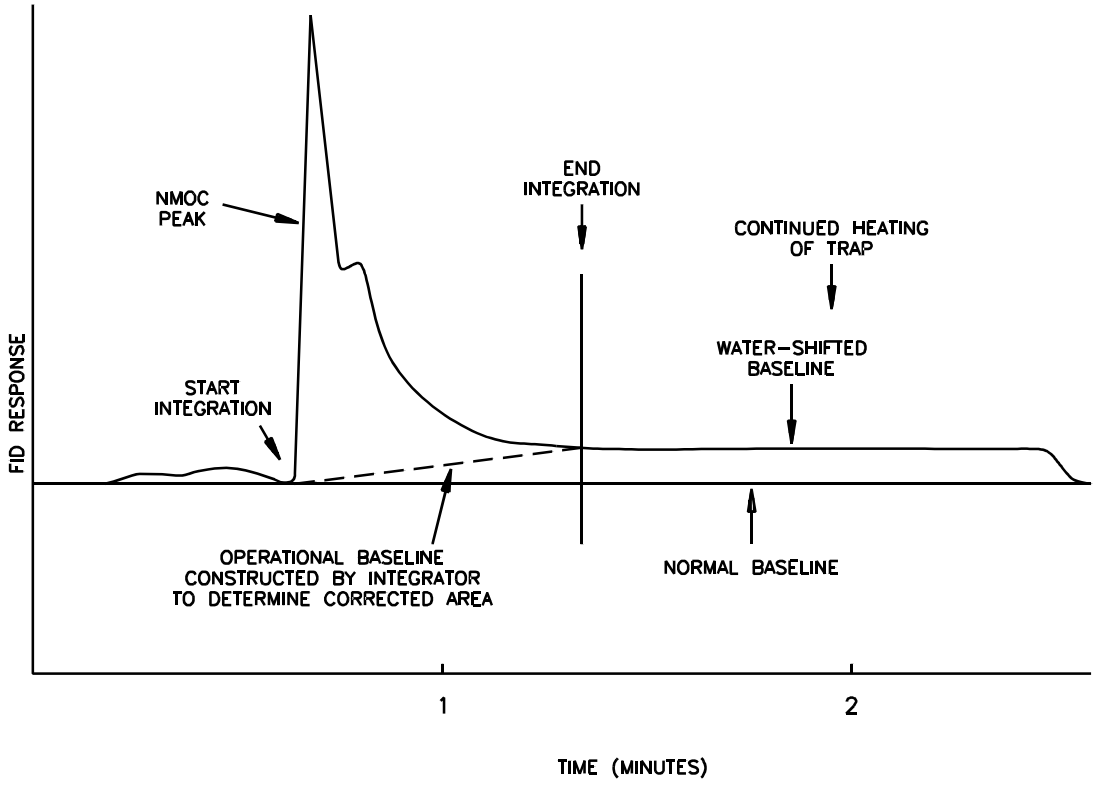


FIGURE 8. CONSTRUCTION OF OPERATIONAL BASELINE AND CORRESPONDING CORRECTION OF PEAK AREA

APPENDIX D

Compendium Method TO-11A

Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]

EPA/625/R-96/010b

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-11A

Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

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Method TO-11A
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Method TO-11 was originally published in March of 1989 as one of a series of peer reviewed methods in the second supplement to *"Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,"* EPA 600/4-89-018. In an effort to keep these methods consistent with current technology, Method TO-11 has been revised and updated as Method TO-11A in this Compendium to incorporate new or improved sampling and analytical technologies.

This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

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DISCLAIMER

This Compendium has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Method TO-11A

Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]

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METHOD TO-11A

Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]

1. Scope

1.1 This document describes a method for the determination of formaldehyde and other carbonyl compounds (aldehydes and ketones) in ambient air utilizing a coated-solid adsorbent followed by high performance liquid chromatographic detection. Formaldehyde has been found to be a major promoter in the formation of photochemical ozone. In particular, short term exposure to formaldehyde and other specific aldehydes (acetaldehyde, acrolein, crotonaldehyde) is known to cause irritation of the eyes, skin, and mucous membranes of the upper respiratory tract**.**

1.2 Over the last several years, numerous methods have been developed for the sampling and analysis of carbonyl compounds. Because of the role which formaldehyde plays in photochemistry, most of the more recent methods were designed to quantitate formaldehyde specifically. Early methods centered around wet chemical technology involving a bubbler or impinger containing a reactive reagent (1). In some cases the reactive reagent produced a color in the presence of formaldehyde. Examples of the more commonly used reagents were: 3-methyl-2-benzothiazolone hydrazone (MBTH), sodium sulfite, 4-hexylresorcinol, water, sodium tetrachloromercurate, and chromatropic acid. These reagents demonstrated high collection efficiency (>95%), provided fairly stable non-volatile products and minimized formation of undesirable by-products. Indeed, as part of U. S. Environmental Protection Agency's (EPA's) effort to quantitate atmospheric concentrations of formaldehyde, the National Air Sampling Network utilized the impinger technique for several years containing chromatrophic acid specifically for formaldehyde. However, impinger sampling had numerous weaknesses which eventually lead to its demise. They were**:**

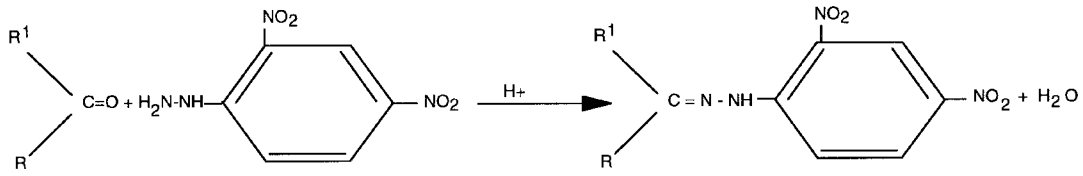
- Labor intense.
- Used acidic/hazardous reagents.
- Lacked sensitivity.
- Prone to interferences.
- Poor reproducibility at ambient concentration levels.

As EPA's interest focused upon formaldehyde and it's sources, the development of passive personal sampling devices (PSDs) developed (2). These devices were mainly used by industrial hygienists to assess the efforts of respiratory exposure for formaldehyde on workers. However, because of the design and flow rate limitation, they require long exposures (up to 7 days) to the atmosphere to meet traditional bubbler technique sensitivities. Consequently, the passive PSD had limited application to ambient monitoring.

To address the need for a monitoring method to sample carbonyl compounds in the air at sensitivities needed to reach health-base detection limits (10^{-6} risk level), a combination of wet chemistry and solid adsorbent methodology was developed (3-6). Activating or wetting the surface of an adsorbent with a chemical specific for reacting with carbonyl compounds allowed greater volumes of air to be sampled, thus enabling better sensitivity in the methodology. Various chemicals and adsorbents combinations have been utilized with various levels of success. The most commonly used technique is based on reacting airborne carbonyls with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated on an adsorbent cartridge followed by separation and analysis of the hydrazone derivative by high performance liquid chromatography (HPLC) with ultraviolet (UV) detection.

1.3 Historically, Compendium Method TO-5, "*Method For the Determination of Aldehydes and Ketones in Ambient Air Using High Performance Liquid Chromatography (HPLC)*" was used to quantitate formaldehyde

in ambient air. This method involved drawing ambient air through a midget impinger sampling train containing 10 mL of 2N HCl/0.05% 2,4-DNPH reagent. Formaldehyde (and other aldehydes and ketones) readily formed a stable derivative with the DNPH reagent, and the DNPH derivative is analyzed for aldehydes and ketones utilizing HPLC. Compendium Method T0-11 modifies the sampling procedures outlined in Method TO-5 by introducing a coated adsorbent. Compendium Method TO-11 is based on the specific reaction of organic carbonyl compounds (aldehydes and ketones) with DNPH-coated silica gel cartridges in the presence of a strong acid, as a catalyst, to form a stable color hydrazone derivative according to the following reaction**:**



CARBONYL GROUP (ALDEHYDES AND KETONES) | 2,4-DINITROPHENYLHYDRAZINE (DNHP) | STABLE COLOR HYDRAZONE DERIVATIVE | WATER

where R and R[1] are organic alkyl or aromatic group (ketones) or either substituent is a hydrogen (aldehydes). The reaction proceeds by nucleophilic addition to the carbonyl followed by 1,2-elimination of water to form the 2,4-diphenylhydrazone derivative. The determination of formaldehyde from the DNPH-formaldehyde derivative is similar to Method TO-5 in incorporating HPLC as the analytical methodology.

1.4 Due to recent requirements in atmospheric carbonyl monitoring, EPA has determined a need to update the present methodology found in Compendium Method TO-11. The revised Compendium Method TO-11A, as published here, includes**:**

- Guidance on collocated sampling.
- Addition of ozone denuder or scrubber to reduce interferences.
- Sampler design update to allow heated-inlet and sequential sampling.
- Update HPLC procedure for column alternatives.
- Use of commercially prepared low pressure drop DNPH-coated cartridges.

The target compound for this method is formaldehyde; however, at least 14 other carbonyl compounds can be detected and quantified.

1.5 The sampling method gives a time-weighted average (TWA) sample. It can be used for long-term (1-24 hr) sampling of ambient air where the concentration of formaldehyde is generally in the low ppb (v/v) or for short-term (5-60 min) sampling of source-impacted atmospheres where the concentration of formaldehyde could reach the ppm (v/v) levels.

1.6 The method instructs the user to purchase commercially pre-coated DNPH cartridges. The method still includes the instructions of Compendium Method TO-11 for the preparation of DNPH-coated cartridges. However due to the tedious preparation and clean room requirements, the method recommends the purchase of pre-coated DNPH cartridges that are now commercially available from at least three major suppliers. Different from previous cartridges identified in Compendium Method TO-11, the pressure drop across the newer low-pressure drop cartridges are less than 37 inches of water at a sampling flow of up to 2.0

liters/minute, allowing compatibility with pumps used in personal sampling equipment. These pre-coated commercial cartridges have generally lower and more consistent background (7) concentration of carbonyls than cartridges prepared under normal chemical laboratory environment, as specified in the original Compendium Method TO-11.

1.7 The commercially-prepared pre-coated cartridges are used as received and are discarded after use. The collected and uncollected cartridges are stored in culture tubes with polypropylene caps and placed in cold storage when not in use.

1.8 This method may involve hazardous materials, operations, and equipments. This method does not purport to address all the safety problems associated with its use. It is the responsibility of whoever uses this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Applicable Documents

2.1 ASTM Standards

- D1193 *Specification for Reagent Water*
- D1356 *Terminology Relating to Atmospheric Sampling and Analysis*
- D3195 *Practice for Rotameter Calibration*
- D3631 *Method for Measuring Surface Atmospheric Pressure*
- D5197 *Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)*
- E177 *Practice for Use of the Terms Precision and Bias in ASTM Test Methods*
- E682 *Practice for Liquid Chromatography Terms and Relationships*

2.2 Other Documents

- *Technical Assistance Document for Sampling and Analysis Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA-600/4-83-027, June 1983.
- *Quality Assurance Handbook for Air Pollution Measurement Systems*, U. S. Environmental Protection Agency, EPA-600/R-94-D38b, May 1994.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-11, Second Supplement*, U. S. Environmental Protection Agency, EPA-600/4-89-018, March 1989.

2.3 Other Documents

- Existing Procedures (8-10).
- Ambient Air Studies (11-15).

3. Summary of Method

3.1 A known volume of ambient air is drawn through a prepacked cartridge coated with acidified DNPH at a sampling rate of 100-2000 mL/min for an appropriate period of time. Sampling rate and time are dependent upon carbonyl concentration in the test atmosphere.

3.2 After sampling, the sample cartridges and field blanks are individually capped and placed in shipping tubes with polypropylene caps. Sample identifying tags and labels are then attached to the capped tubes. The capped tubes are then placed in a polypropylene shipping container cooled to subambient temperature (~4°C), and returned to the laboratory for analysis. Alternatively, the sample vials can be placed in a thermally-insulated 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 with 5 mL of acetonitrile from a plastic syringe reservoir to a graduated test tube or a 5 mL volumetric flask.

3.3 The eluate is then diluted to a known volume and refrigerated until analysis.

3.4 For determining formaldehyde, the DNPH-formaldehyde derivative can be determined using isocratic reverse phase HPLC with an ultraviolet (UV) absorption detector operated at 360 nm. To determine formaldehyde and 14 other carbonyls, the HPLC system is operated in the linear gradient program mode.

3.5 For quantitative evaluation of formaldehyde and other carbonyl compounds, a cartridge blank is likewise desorbed and analyzed.

3.6 Formaldehyde and other carbonyl compounds in the sample are identified and quantified by comparison of their retention times and peak heights or peak areas with those of standard solutions. Typically, C_1-C_7 carbonyl compounds, including benzaldehyde, are measured effectively to less than 0.5 ppbv.

4. Significance

4.1 Formaldehyde is a major compound in the formation of photochemical ozone (16). Short term exposure to formaldehyde and other specific aldehydes (acetaldehyde, acrolein, crotonaldehyde) is known to cause irritation of the eyes, skin, and mucous membranes of the upper respiratory tract (19). Animal studies indicate that high concentrations can injure the lungs and other organs of the body (19). In polluted atmospheres, formaldehyde may contribute to eye irritation and unpleasant odors that are common annoyances.

4.2 Over the last several years, carbonyl compounds including low molecular weight aldehydes and ketones have received increased attention in the regulatory community. This is due in part to their effects on humans and animals as primary irritation of the mucous membranes of the eyes, the upper respiratory tract, and the skin. Animal studies indicate that high concentrations of carbonyl compounds, especially formaldehyde, can injure the lungs, may contribute to eye irritation and effect other organs of the body. Aldehydes, either directly of indirectly, may also cause injury to plants. Sources of carbonyl compounds into the atmosphere range from natural occurrences to secondary formation through atmospheric photochemical reactions. Consequently, carbonyl compounds are both primary (directly emitted) and secondary (formed in the atmosphere) air pollutants (19).

4.2.1 Natural Occurrence. Natural sources of carbonyls do not appear to be important contributors to air pollution. Acetaldehyde is found in apples and as a by-product of alcoholic fermentation process. Other lower molecular weight aliphatic aldehydes are not found in significant quantities in natural products. Olefinic and aromatic aldehydes are present in some of the essential oils in fruits and plants. These include citronella, in rose oil; citral, in oil of lemongrass; benzaldehyde, in oil of bitter almonds; and cinnamaldehyde, in oil of cinnamon.

4.2.2 Production Sources. Aldehydes are commercially manufactured by various processes, depending on the particular aldehyde. In general, they are prepared via oxidation reactions of hydrocarbons, hydroformulation of alkenes, dehydrogenation of alcohols, and addition reactions between aldehydes and other

compounds. Formaldehyde is manufactured from the oxidation of methanol as illustrated in the following equation:

$$CH_3OH \xrightarrow{[cat.]} CH_2O + H_2$$

Formaldehyde and other aldehyde production in the United States has shown a substantial growth over the last several years. This is due, in part, to their use in a wide variety of industries, such as the chemical, rubber, tanning, paper, perfume, and food industries. The major use is as an intermediate in the synthesis of organic compounds, including, alcohols, carboxylic acids, dyes, and medicinals.

4.2.3 Mobile Combustion Sources. A major source of carbonyl compounds in the atmosphere may be attributed to motor vehicle emissions. In particular, formaldehyde is the major carbonyl in automobile exhaust, accounting for 50-70 percent of the total carbonyl burden to the atmosphere (19). Furthermore, motor vehicles emit reactive hydrocarbons that undergo photochemical oxidation to produce formaldehyde and other carbonyls in the atmosphere.

4.3 Secondary Pollutant. As a secondary pollutant (formed in the atmosphere), carbonyls are formed by very complex photo-oxidation mechanism involving volatile organic compounds (VOCs) with nitrogen oxide (20,21). Both anthropogenic and biogenic (e.g., isoprene) hydrocarbons leads to *in situ* formation of carbonyls, especially formaldehyde compounds. Aldehydes are both primary pollutants and secondary products of atmospheric photochemistry.

The complete photo-oxidation mechanism is indeed complex and not well understood. However, a brief discussion is warranted (22). When VOCs and oxides of nitrogen (NO_x) are in the atmosphere and are irradiated with sunlight, their equilibrium in the photostationary state is changed. The photostationary state is defined by the equilibrium between nitrogen dioxide (NO_2), nitrous oxide (NO) and ozone (O_3). This equilibrium is theoretically maintained until VOCs are introduced. Various reactions occur to produce OH radicals. The VOCs react with the OH radicals and produce RO_2 radicals that oxidizes NO to NO_2, destroying the photostationary state. Carbonyls react with OH to produce RO_2 radicals. Likewise carbonyls, particularly formaldehyde in sunlight, are sources of the OH radicals.

The results of these processes lead to the following:

- Accumulation of ozone.
- Oxidation of hydrocarbons (HCs) to aldehydes and ketones which lead to the continued production of $HO_2\cdot$ and $OH\cdot$ radicals, the real driving force in photochemistry smog.

Consequently, the determination of formaldehyde and other carbonyl compounds in the atmosphere is of interest because of their importance as precursors in the production of photochemical smog, as photochemical reaction products and as major source of free radicals in the atmosphere.

4.4 Historically, DNPH impinger techniques have been widely used to determine atmospheric carbonyls. However, due to the limitation of applying this technique to remote locations, the solid adsorbent methodology has become a convenient alternative to impinger sampling. A number of solid adsorbents have been used over the years to support the DNPH coating. They are: glass beads, glass fiber filters, silica gel, Chromosorb® P, Florisil®, Carbopack® B, XAD-2, and C18. Several of these adsorbents are available commercially as pre-packed cartridges. The commercially available cartridges provide convenience of use, reproducibility and low formaldehyde blanks. Two of the more widely used pre-packed adsorbents are silica gel and C18.

4.4.1 Silica Gel. Silica gel is a regenerative adsorbent, consisting of amorphous silica (SiO_2) with surface OH groups, making it a polar material and enhancing surface absorption. DNPH-coated silica gel cartridges

have been used by numerous investigators since 1980 for sampling formaldehyde in ambient air. Tejada (3,4) evaluated several adsorbents, including C18, Florsil, silanized glass wool, and silica gel as possible supports for the DNPH coating. Results indicated that silica gel provided the best support with minimum interferences. The studies did document that olefinic aldehydes such as acrolein and crotonaldehyde degraded partially and formed unknown species. For stable carbonyls such as formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde, and acetone, correlation with an DNPH-impinger technique was excellent. However, further studies by Arnts and Tejada identified a severe loss of carbonyl-DNPH derivative due to the reaction of atmospheric ozone on DNPH-coated silica gel cartridges while sampling ambient air. This bias was eliminated when sampling continued with the application of an ozone scrubber system (KI denuder) preceding the cartridge.

4.4.2 C18 Cartridge. C18 is an octadecylsilane bonded silica substrate which is non-polar, hydrophobic, and relatively inert, whose surface has been passivated with non-polar paraffinic groups. Because of these qualities, C18 has been used historically as an adsorbent trap for trace organics in environmental aqueous samples through hydrophobic interactions. The adsorbed trace organic molecules are then eluted from the adsorbent with various organic solvents. In early 1990, C18 was used in an ambient air study as the support for DNPH. While C18 showed promising results (23), it's use today as the support for DNPH is limited.

4.5 Both adsorbents have historically performed adequately as the support for the DNPH coating. The comparison between silica gel and C18 as the adsorbent for the DNPH is illustrated in Table 1. The user is encouraged to review the weaknesses and strengths outlined in Table 1 for using silica gel or C18 as the adsorbent for the DNPH coating.

5. Definitions

[Note: Definitions used in this document and any user-prepared Standard Operating Procedures (SOPs) should be consistent with those used in ASTM D1356. All abbreviations and symbols are defined within this document at the point of first use.]

5.1 C18— C18 is an octadecylsilane bonded silica substrate, which is non-polar, hydrophobic, and relatively inert.

5.2 HPLC— high performance liquid chromatography.

5.3 Method Detection Limit (MDL)— the minimum concentration of an analyte that can be reported with 95% confidence that the value is above zero, based on a standard deviation of at least seven repetitive measurements of the analyte in the matrix of concern at a concentration near the low standard.

5.4 Photochemical Reaction— any chemical reaction that is initiated as a result of absorption of light.

5.5 Photochemical Smog— air pollution resulting from photochemical reactions.

5.6 ppbv— a unit of measure of the concentration of gases in air expressed as parts of the gas per billion (10^9) parts of the air-gas mixture, normally both by volume.

5.7 ppmv— a unit of measure of the concentration of gases in air expressed as parts of the gas per million (10^6) parts of the air-gas mixture, normally both by volume**.**

5.8 Silica Gel—silica gel is a regenerative adsorbent consisting of amorphous silica (SiO_2) with OH surface groups making it a polar material and enhancing surface reactions.

5.9 Denuder— A device designed to remove gases from an air sampling stream by the process of molecular diffusion to a collecting surface.

5.10 Certification Blank— certification blank is defined as the mean value of the cartridge blank plus three standard deviations. For Compendium Method TO-11A, the Certification Blank should be less than 0.15 µg/cartridge for formaldehyde.

5.11 Cartridge Blank— cartridge blank is the measured value of the carbonyl compounds on an unsampled, DNPH-coated cartridge. This is the value used in the calculations delineated in section 12.

5.12 Scrubber— to remove a specific gas from the air stream by passing through a pack bed.

6. Extended Methodology and Common Interferences

6.1 This procedure has been written specifically for the sampling and analysis of formaldehyde. Other carbonyl compounds found in ambient air are also observed in the HPLC analysis. Resolution of these compounds depend upon column and mobile phase conditions during HPLC analysis. Organic compounds that have the same retention time and significant absorbance at 360 nm as the DNPH derivative of formaldehyde will interfere. Such interferences (24) can often be overcome by altering the separation conditions (e.g., using alternative HPLC columns or mobile phase compositions). In addition, other aldehydes and ketones can be detected with a modification of the basic procedure. In particular, chromatographic conditions can be optimized to separate acetone and propionaldehyde and 12 other higher molecular weight aldehydes and ketones (within an analysis time of about one hour), as identified below, by utilizing one or two Zorbax ODS columns in series under a linear gradient program:

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

The linear gradient program varies the mobile phase composition periodically to achieve maximum resolution of the C-3, C-4, and benzaldehyde region of the chromatogram.

6.2 Formaldehyde may be a contamination of the DNPH reagent. If user- prepared cartridges are employed, the DNPH must be purified by multiple recrystallizations in UV grade carbonyl-free 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 carbonyl-free acetonitrile until use. Impurity levels of carbonyl compounds in the DNPH are determined by HPLC prior to use and should be less than the Certification Blank value of 0.15 μg/cartridge**.**

6.3 The purity of acetonitrile is an important consideration in the determination of allowable formaldehyde blank concentration in the reagent. Background concentrations of formaldehyde in acetonitrile will be quantitatively converted to the hydrazone, adding a positive bias to the ambient air formaldehyde concentration. Within the project quality control procedures, the formaldehyde in the acetonitrile reagent should be checked on a regular basis (see Section 9.1).

6.4 Ozone at high concentrations has been shown to interfere negatively by reacting with both the DNPH and its carbonyl derivatives (hydrazones) on the cartridge (25,26). The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Significant negative interference from ozone was observed even at concentrations of formaldehyde and ozone typical of clean ambient air (i.e., 2 and 40 ppb, respectively).

6.5 Exposure of the DNPH-coated sampling cartridges to direct sunlight may produce artifacts and should be avoided.

6.6 The presence of ozone in the sample stream is readily inferred from the appearance of new compounds with retention times different from the other carbonyl hydrazone compounds.

6.7 The most direct solution to the ozone interference is to remove the ozone before the sample stream reaches the coated cartridge. This process entails constructing an ozone denuder (9) or scrubber and placing it in front of the cartridge. The denuder can be constructed of 1 m of 0.64-cm outside diameter (O.D.) by 0.46-cm inside diameter (I.D.) copper tubing, that is filled with a saturated solution of KI, allowed to stand for a few minutes, drained and dried with a stream of clean air or nitrogen for about 1 h. The capacity of the ozone denuder as described is about 100,000 ppb-hour of ozone. Packed-bed granular potassium iodide (KI) scrubbers can also be used in place of the denuder and are commercially available. Very little work has been done on long term usage of a denuder or KI scrubber to remove ozone from the ambient air gas stream. The ozone removal devices should be replaced periodically (e.g., monthly) in the sample train to maintain the integrity of the data generated.

6.8 Test aldehydes or carbonyls (formaldehyde, acetaldehyde, acrolein, propionaldehyde, benzaldehyde, and p-tolualdehyde) that were dynamically spiked into an ambient sample air stream passed through the KI denuder with practically no losses (7). Similar tests were also performed for formaldehyde (26).

6.9 Ozone scrubbers (cartridge filled with granular KI) are also available from suppliers of pre-coated DNPH cartridges. These scrubbers are optimized when the ambient air contains a minimum of 15% relative humidity.

7. Apparatus

7.1 Isocratic HPLC. System consisting of a mobile phase reservoir a high pressure pump; an injection valve (automatic sampler with an optional 25-µL loop injector); a Zorbax ODS (DuPont Instruments, Wilmington, DE) reverse phase (RP) column, or equivalent (25-cm x 4.6-mm ID); a variable wavelength UV detector operating at 360 nm; and a data system, as illustrated in Figure 1.

[Note: Most commercial HPLC analytical systems will be adequate for this application.]

7.2 Cartridge sampler. Prepacked, pre-coated cartridge (see Figure 2), commercially available or coated *in situ* with DNPH according to Section 9.

[Note: This method was developed using the Waters Sep-Pak cartridge, coated in situ with DNPH on silica gel by the users, as delineated in the original Compendium Method TO-11 as a guideline. EPA has experience in use of this cartridge during various field monitoring programs over the last several years. Other manufacturer's cartridges should work as well. However, modifications to these procedures may be necessary if another commercially available cartridge is selected.]

Major suppliers of pre-coated cartridges are:

- Supelco, Supelco Park, Bellefonte, PA 16823-0048, (800) 247-6628.
- SKC Inc., 334 Valley View Road, Eighty Four, PA 15330-9614, (800) 752-8472.
- Millipore/Waters Chromatography, P.O. Box 9162, Marlborough, MA 01752-9748, (800) 252-4752.
- Atmospheric Analysis and Consulting (AAC) Inc., 4572 Telephone Rd., Suite 920, Ventura, CA 93003, (805) 650-1642.

[Note: The SKC cartridge (see Figure 2) is an example of a dual bed tube. The glass cartridge contains a front bed of 300 mg DNPH-coated silica gel with the back bed of 150 mg DNPH-coated silica gel. Air flow through the tube should be from front to back bed, as indicated by the arrows enscribed on the cartridge. The dual bed tube cartridge may be used in atmospheres containing carbonyl concentrations in excess of the American Conference of Government Industrial Hygienists (ACGIH) 8-hour exposure limit, where breakthrough of carbonyls on the adsorbent might occur. If used in routine ambient air monitoring applications, the tube is recovered as one unit, as specified in Section 11.2.]

If commercially prepared DNPH-coated cartridges are purchased, ensure that a *"Certification Blank for Formaldehyde"* is provided for the specific batch of which that cartridge is a member. For a commercial cartridge to be acceptable, the following criteria must be met:

- Formaldehyde concentration: <0.15 µg/cartridge.

If the enhanced carbonyl analysis is being performed, the following Certification Blank criteria must also be met:

- Speciated carbonyl concentration:
  - Acetaldehyde: <0.10 µg/cartridge
  - Acetone: <0.30 µg/cartridge
  - Other: <0.10 µg/cartridge

Typical physical and chemical characteristics of commercial cartridge adsorbents are listed in Table 2 and illustrated in Figure 2.

7.3 Sampling system. the DNPH-cartridge approach is capable of accurately and precisely sampling 100-2000 mL/min of ambient air. The monitoring of carbonyl compounds has recently been enhanced by the promulgation of new ambient air quality surveillance regulations outlined in Title 40, Part 58. These regulations require States to establish additional air monitoring stations as part of their existing State Implementation Plan (SIP) monitoring network as part of EPA's Photochemical Assessment Monitoring Stations (PAMS) to include provisions for enhanced (1) monitoring of ozone and oxides of nitrogen (NO_x), (2) monitoring of volatile organic compounds (VOCs), (3) monitoring of meteorological parameters, and (4) monitoring selected carbonyl compounds (formaldehyde, acetone, and acetaldehyde). Specifically, monitoring for carbonyl involves:

- 8, 3 h sequential samples starting at midnight.
- 1, 24 h time-integrated "reality check" sample.

Consequently, the sampler must be able to accommodate numerous regulatory and practical needs. Practical needs would include:

- Ability to sequence two cartridges in series for breakthrough volume confirmation for a 24-hour sampling event.
- Ability to collocate with any of the 8, 3 h samples.

Traditionally, three sampling approaches have been used to monitor carbonyl compounds in the ambient air. They are:

- Manual single-port carbonyl sampler.
- Programmable single-port carbonyl sampler.
- Automated multi-port sampler.

Components of the single-port carbonyl sampler, for both manual and semi-automatic, are illustrated in Figure 3. Components usually include a heated manifold/sample inlet, a denuder/cartridge assembly, a flow meter, a vacuum gauge/pump, a timer and a power supply. In operation, ambient air is drawn through the denuder/cartridge assembly with a vacuum pump at a fixed flow rate between 0.1 to 2 Lpm. The vacuum gauge is used to measure the net vacuum in the system for all flow-rate corrections. Controlling the system is usually a 7-day, 14-event timer to coordinate sampling events to allow a sample to be extracted continuously or intermittently over a period of time. Finally, an elapsed-time counter is employed to measure the actual time the sampling took place. This is particularly suitable for unattended sampling when power fails for short periods.

The automated multi-port sampler is especially designed to collect numerous short-term (2 to 3 hours) sample sequentially over a 24 hour, 7 day a week, nighttime and weekend monitoring period. This arrangement allows for the sampling of short periods where the objectives of the project are to identify progress of atmospheric reactions involving carbonyls. As illustrated in Figure 4, components of the fully automated multi-port carbonyl sampler includes a heated inlet, ozone denuder (or scrubber) inlet manifold assembly, inlet check valves, DNPH multi-port cartridge assembly, exhaust manifold, mass flow controller and sample pump. The multi-port sampler automatically switches between sampling ports at preselected times, as programmed by the user. Typically, a sequential air sampler contains a microprocessor timer/controller that provides precise control over each sampling event. The microprocessor allows the user to program individual start date and time, sample duration, and delays between samples. The timer also allows activation of the flow system prior (approximately 10 min) to sequencing to allow purging of the sampler inlet with fresh sample. Finally, the automated sequential sampler can be operated from an external signal, such as an ozone monitor, so that sampling starts above certain preset ozone levels or via a modem. As a final option, various manufacturers provide wind sensor instrumentation (wind speed and direction) which is connected to the automated sequential sampler so that sampling begins when the wind is from a preset direction and speed.

Major suppliers of commercially available carbonyl samplers are:

- Supelco, Supelco Park, Bellefonte, PA 16823-0048, (800) 247-6628.
- SKC Inc., 334 Valley View Road, Eighty Four, PA 15330-9614, (800) 752-8472.
- Millipore/Waters Chromatography, P.O. Box 9162, Marlborough, MA 01752-9748, (800) 252-4752.
- XonTech, Inc. 6862 Hayvenhurst Avenue, Van Nuys, CA 91406, (818) 787-7380.
- ATEC Atmospheric Technology, P.O. Box 8062, Calabasas, CA 91372-8062, (310) 457-2671.
- Atmospheric Analysis and Consulting (AAC) Inc., 4572 Telephone Road, Suite 920, Ventura, CA 93003, (805) 650-1642.
- Scientific Instrumentation Specialists, P.O. Box 8941, Moscow, ID, (209) 882-3860.

7.4 Stopwatch.

7.5 Polypropylene shipping container (see Figure 5) with polyethylene-air bubble padding. To hold sample cartridges.

7.6 Thermometer. To record ambient temperature.

7.7 Barometer (optional).

7.8 Volumetric flasks. Various sizes, 5-2000 mL**.**

7.9 Pipets. Various sizes, 1-50 mL.

7.10 Erlenmeyer flask, 1 L. For preparing HPLC mobile phase.

7.11 Graduated cylinder, 1 L. For preparing HPLC mobile phase.

7.12 Syringe, 100-250 μL. For HPLC injection, with capacity at least four times the loop value.

7.13 Sample vials.

7.14 Melting point apparatus (optional).

7.15 Rotameters.

7.16 Calibrated syringes.

7.17 Soap bubble meter or wet test meter.

7.18 Mass flow meters and mass flow controllers. For metering/setting air flow rate through sample cartridge of 100-2000 mL/min.

[Note: The mass flow controllers are necessary because cartridges may develop a high pressure drop and at maximum flow rates, the cartridge behaves like a "critical orifice." Recent studies have shown that critical flow orifices may be used for 24-hour sampling periods at a maximum rate of 2 L/min for atmospheres not heavily loaded with particulates without any problems.]

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

7.20 Cartridge drying manifold. With multiple standard male Luer® connectors.

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

7.22 Syringe rack. Made of an aluminum plate (0.16 cm x 36 cm x 53 cm) with adjustable legs on four corners. A matrix (5 cm x 9 cm) of circular holes of diameter slightly larger than the diameter of the 10-mL syringes was symmetrically drilled from the center of the plate to enable batch processing of 45 cartridges for cleaning, coating, and/or sample elution.

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

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

7.25 Culture tubes (20 mm x 125 mm) with polypropylene screw caps. Used to transport coated cartridges for field applications (see Figure 5), Fisher Scientific, Pittsburgh, PA, or equivalent.

7.26 Polyethylene gloves. Used to handle cartridges, best source.

7.27 Dry test meter.

7.28 User-prepared copper tubing for ozone scrubber (see Figure 6a). A 36 inch length of ¼-inch O.D. copper tubing is used as the body of the ozone scrubber. The tubing should be coiled into a spiral approximately 2 inches in O.D. EPA has considerable field experience with the use of this denuder.

[Note: Ozone scrubbers (cartridge filled with granular KI) are also available from suppliers of pre-coated DNPH cartridges, as illustrated in Figure 6(b).]

7.29 Cord heater and Variac. A 24 inch long cord heater, rated at approximately 80 watts, wrapped around the outside of the copper coil denuder, controlled by a Variac, to provide heat (~50°C) to prevent condensation of water or organic compounds from occurring within the coil.

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

8. Reagents and Materials

[Note: Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available; Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of ASTM Specifications D 1193.]

8.1 2,4-Dinitrophenylhydrazine (DNPH). Aldrich Chemical or J.T. Baker, reagent grade or equivalent. Recrystallize at least twice with UV grade acetonitrile before use.

8.2 DNPH coated cartridges. DNPH coated cartridge systems are available from several commercial suppliers.

8.3 High purity acetonitrile. UV grade, Burdick and Jackson "distilled-in-glass," or equivalent. The formaldehyde concentration in the acetonitrile should be <1.5 ng/mL. It is imperative (mandatory) that the user establish the purity of the acetonitrile before use (see Section 9.1).

8.4 Deionized-distilled water. Charcoal filtered**.**

8.5 Perchloric acid. Analytical grade, best source, 60%, specific gravity 1.51**.**

8.6 Ortho-phosphoric acid. Analytical grade, best source, 36.5-38%, specific gravity 1.19**.**

8.7 Formaldehyde. Analytical grade, best source, 37% solution (w/w).

8.8 Aldehydes and ketones, analytical grade, best source. Used for preparation of DNPH derivative standards (optional).

8.9 Carbonyl hydrazones. Formaldehyde and other carbonyl hydrazones are available for use as standards from commercial sources at various levels of purity.

8.10 Ethanol or methanol. Analytical grade, best source.

8.11 Nitrogen. High purity grade, best source.

8.12 Charcoal. Granular, best source.

8.13 Helium. High purity grade, best source.

8.14 Potassium Iodide. Analytical grade, best source. Used for coating inside of copper tubing of denuder system to remove ozone interference.

9. Preparation of Reagents and Cartridges

9.1 Purity of the Acetonitrile

9.1.1 The purity of acetonitrile is an important consideration in the determination of the formaldehyde blank concentration. Formaldehyde in the reagent will be quantitatively converted to the hydrazone and measured as part of the blank. The contribution to the blank from the reagent is dependent on the formaldehyde concentration in the reagent and the amount of the reagent used for extraction. Some examples will illustrate these considerations.

Example A

- Silica gel DNPH cartridge has a blank level of 60 ng.
- Cartridge is eluted with 5-mL of acetonitrile reagent containing a formaldehyde of 3 ng/mL.
- Analyst measures a blank level of 75 ng of which 80% comes from the cartridge and 20% comes from the reagent.

Example B

- Silica gel DNPH cartridge has a blank level of 30 ng.
- Cartridge is eluted with 5 mL of acetonitrile reagent containing a formaldehyde of 6 ng/mL.
- Analyst measures a blank level of 60 ng of which 50% comes from the cartridge and 50% comes from the reagent.

9.1.2 As a quality control procedure, the formaldehyde in the acetonitrile reagent should be checked on a regular basis. This can be done by mixing known proportions of the acetonitrile reagent and a DNPH solution having a measured formaldehyde blank. (The extract from a blank cartridge can serve as the DNPH solution.) After analyzing the resultant solution, a mass balance is performed on the observed formaldehyde level and the contribution from the DNPH reagent as shown in the following example.

- 1 mL of a DNPH solution containing 2.1 ng/mL of formaldehyde (as carbonyl) is mixed with 9 mL of acetonitrile reagent containing as unknown formaldehyde blank. The analyst measures a resultant solution concentration of 1.55 ng of formaldehyde. This data can be used to calculate the formaldehyde in the reagent:

$$\text{HCHO ng/mL} = \frac{(1.55\text{ng/mL} \times 10\text{ml} - 2.1\text{ng/mL} \times 1\text{mL})}{9\text{mL}} = 1.49\text{ng/mL}$$

The formaldehyde contribution to the cartridge blank should be as low as possible but certainly less than 20% of the total measured blank. Using a cartridge blank level of 30 ng/cartridge, the formaldehyde concentration in the reagent would have to be less than 1.5 ng/mL (i.e., 50 n*M*) to give a blank level less than 20% of the measured blank.

9.2 Purification of 2,4-Dinitrophenylhydrazine (DNPH)

[Note: This procedure should be performed under a properly ventilated hood, as inhalation of acetonitrile can result in nose and throat irritation. Various health effects are resultant from the inhalation of acetonitrile. At 500 ppm in air, brief inhalation has produced nose and throat irritation. At 160 ppm, inhalation for 4 hours has caused flushing of the face (2 hour delay after exposure) and bronchial tightness (5 hour delay). Heavier exposures have produced systemic effects with symptoms ranging from headache, nausea, and lassitude to vomiting, chest or abdominal pain, respiratory depression, extreme weakness, stupor, convulsions and death (dependent upon concentration and time).]

[Note: Purified DNPH, suitable for preparing cartridges, can be purchased commercially.]

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

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

9.2.3 Maintain the solution at this temperature (40-60°C) until 95% of solvent has evaporated.

9.2.4 Decant solution to waste, and rinse crystals twice with three times their apparent volume of acetonitrile.

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

9.2.6 Repeat rinsing process as described in Section 9.2.4.

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

[Note: An acid is necessary to catalyze the reaction of the carbonyls with DNPH. Most strong inorganic acids such as hydrochloric, sulfuric, phosphoric, or perchloric acids will do the job. Perchloric or phosphoric acids are the preferred catalyst for using acetonitrile solution of DNPH as the absorbing solution. The DNPH derivatives do not precipitate from solution as readily as when hydrochloric or phosphoric acids are used as the catalyst. This is an ideal situation for an HPLC analytical finish as this minimizes sample handling. For most ambient air sampling, precipitation is not a problem because the carbonyl concentration is generally in the ppb range.]

9.2.8 An impurity level of <0.15 μg/cartridge of formaldehyde in DNPH-coated cartridge is acceptable (based on the Certification Blank section 5.10). An acceptable impurity level for an intended sampling application may be defined as the mass of the analyte (e.g., DNPH-formaldehyde derivative) in a unit volume of the reagent solution equivalent to less than one tenth (0.1) the mass of the corresponding analyte from a volume of an air sample when the carbonyl (e.g., formaldehyde) is collected as DNPH derivative in an equal unit volume of the reagent solution. An impurity level unacceptable for a typical 10 L sample volume may be acceptable if sample volume is increased to 100 L. If the impurity level is not acceptable for intended sampling application, repeat recrystallization.

9.2.9 If the impurity level is not satisfactory, pipet off the solution to waste, then add 25 mL of acetonitrile to the purified crystals. Repeat rinsing with 20 mL portions of acetonitrile until a satisfactorily low impurity level in the supernatant is confirmed by HPLC analysis.

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

9.2.11 Maintain only a minimum volume of saturated solution adequate for day to day operation. This will minimize wastage 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.

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

9.3 Preparation of DNPH-Formaldehyde Derivative

[Note: Purified crystals or solutions of DNPH-derivatives can be purchased commercially.]

9.3.1 To a portion of the recrystallized DNPH, add sufficient 2N HCl to obtain an approximately saturated solution. Add to this solution formaldehyde (other aldehydes or ketones may be used if their detection is desirable), in molar excess of the DNPH. Allow it to dry in air.

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

9.3.3 Check the purity of the DNPH-formaldehyde derivative by melting point determination or HPLC analysis. The DNPH-formaldehyde derivative should melt at 167°C ± 1°C. If the impurity level is not acceptable, recrystallize the derivative in ethanol. Repeat purity check and recrystallization as necessary until acceptable level of purity (e.g., 99%) is achieved.

9.3.4 DNPH derivatives of formaldehyde and other carbonyls suitable for use as standards are commercially available both in the form of pure crystals and as individual or mixed stock solutions in acetonitrile.

9.4 Preparation of DNPH-Formaldehyde Standards

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

9.4.2 Prepare a working calibration standard mix from serial dilution of the standard stock solution. The concentration of the DNPH-formaldehyde compound in the standard mix solutions should be adjusted to reflect relative distribution in a real sample.

[Note: Individual stock solutions of approximately 100 mg/L are prepared by dissolving 10 mg of the solid derivative in 100 mL of acetonitrile. The individual solution is used to prepare calibration standards containing the derivative of interest at concentrations of 0.5-20 μg/mL, which spans the concentration of interest for most ambient air work.]

9.4.3 Store all standard solutions in a refrigerator. They should be stable at least one month.

9.4.4 DNPH-formaldehyde standards can also be purchased from various commercial suppliers. If purchased, ensure that a "*Certification of Concentration*" is provided.

9.5 Preparation of DNPH-Coated Cartridges

[Note: This procedure 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 carbonyl free acetonitrile. Contact of reagents with laboratory air must be minimized. Polyethylene gloves must be worn when handling the cartridges. If the user wishes to purchase commercially prepared DNPH-coated cartridges, they are available from various vendors. If commercial prepared DNPH-coated cartridges are purchased, ensure that a "Certification Blank for Formaldehyde" is provided for the specific batch of which that cartridge is a member. For a commercial cartridge to be acceptable, the following criteria must be met:

- *Formaldehyde concentration: <0.15 µg/cartridge.*

If the enhanced carbonyl analysis is being performed, the following Certification Blank criteria must also be met:

- *Speciated carbonyl concentration:*
  - *Acetaldehyde: <0.10 µg/cartridge*
  - *Acetone: <0.30 µg/cartridge*
  - *Other: <0.10 µg/cartridge*

One who is not experienced in the preparation of DNPH-coated cartridge is strongly advised to use certified commercially available cartridges.]

9.5.1 DNPH Coating Solution

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

9.5.1.2 Acidify with 1.0 mL of ortho-phosphoric acid (H_3PO_4).

[Note: The atmosphere above the acidified solution should preferably be filtered through a DNPH-coated 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.]

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

9.5.1.4 Dispense an aliquot solution to a sample vial, and check the impurity level of the acidified solution by HPLC according to Section 9.2.

9.5.1.5 The impurity level should be less than the Certification Blank of <0.15 μg/cartridge for formaldehyde, similar to that in the DNPH coating solution.

9.5.2 Coating of Cartridges

9.5.2.1 Open the pre-packed cartridge package, connect the short end to a 10-mL syringe, and place it in a syringe rack (see Figure 7).

[Note: Prepare as many cartridges (~100) and syringes as possible.]

9.5.2.2 Using a positive displacement repetitive pipet, add 10 mL of acetonitrile to each of the syringes (see Figure 7).

9.5.2.3 Let liquid drain to waste by gravity.

[Note: Remove any air bubbles that may be trapped between the syringe and the silica cartridge by displacing them with the acetonitrile in the syringe.]

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

9.5.2.5 Once the effluent flow at the outlet of the cartridge has stopped, dispense 7 mL of the DNPH coating reagent into each of the syringes (see Figure 7).

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

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

9.5.2.8 Assemble a drying manifold with a scrubber or "guard cartridge" connected to each of the ports (see Figure 7). These "guard cartridges" are DNPH-coated and serve to remove any trace of formaldehyde in the nitrogen gas supply.

9.5.2.9 Insert cartridge connectors (flared at both ends, 0.64 by 2.5-cm outside diameter TFE-fluorocarbon FEP tubing with inside diameter slightly smaller than the outside diameter of the cartridge port) onto the long end of the scrubber cartridges.

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

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

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

9.5.2.13 Stop the flow of nitrogen after 15 minutes, wipe the cartridge exterior free of rinsed acetonitrile and remove the dried cartridge.

9.5.2.14 Plug both ends of the coated cartridge with standard polypropylene Luer® male plugs, place the plugged cartridge in a shipping tube with polypropylene screw caps.

9.5.2.15 Put a serial number and a lot number label on each of the individual shipping tubes.

9.5.2.16 Store shipping tubes containing the DNPH-coated cartridges in a refrigerator at 4°C until use.

[Note: Plugged cartridges may also be placed in screw-capped glass culture tubes and placed in a refrigerator until use. Cartridges will maintain their integrity for up to 90 days stored in refrigerated, capped shipping tubes.]

9.5.2.17 Take a minimum of 3 blank cartridges from the cartridge batch and analyze for formaldehyde, as delineated in Section 11. The batch of user-prepared DNPH-coated cartridges is acceptable if the following criteria are met:

- Formaldehyde Certification Blank: <0.15 µg/cartridge.

If the enhanced carbonyl analysis is being performed, the following certification criteria must also be met:

- Speciated carbonyl concentration:
  - Acetaldehyde: <0.10 µg/cartridge
  - Acetone: <0.30 µg/cartridge
  - Other: <0.10 µg/cartridge

9.5.2.18 If analysis meets the above criteria, provide documentation with all cartridges associated with that batch involving *"Certification Blank for Formaldehyde."* This certificate must be part of the project records.

9.5.2.19 If the cartridge results are close to, but above the Certification Blank, run a few more blank cartridges to check background level.

9.5.2.20 If analysis indicates failure of the cartridge, then *all* cartridges in that batch are unacceptable. Prepare a new batch of cartridges according to Section 9.5 until certification is achieved.

9.5.2.21 Store all certified cartridges in a refrigerator at 4°C until use.

9.5.2.22 Before transport, remove the shipping container (or screw-capped glass culture tubes) containing the adsorbent tubes from the refrigerator and place culture tubes in a friction-top metal can containing 1-2 inches of charcoal for shipment to sampling location. Alternately, acidified DNPH-coated filters can be used in place of charcoal filters to remove impurity carbonyl compounds in the air.

9.5.2.23 As an alternative to friction-top cans for transporting sample cartridges, the coated cartridges could be shipped in their individual glass containers (see Figure 5a). A batch of coated cartridges may also be packed in a polypropylene shipping container for shipment to the field (see Figure 5b). The container should be padded with clean tissue paper or polyethylene-air bubble padding. **Do not use polyurethane foam or newspaper as padding material**.

9.5.2.24 The cartridges should be immediately stored in a refrigerator or freezer (<4°C) upon arrival in the field.

9.6 Equivalent Formaldehyde Cartridge Concentration

9.6.1 One can calculate the equivalent formaldehyde background concentration (ppbv) contributed from a commercial or user-prepared DNPH-coated cartridge following exposure to formaldehyde-free air.

9.6.2 The equivalent formaldehyde background concentration includes the contribution of formaldehyde from both the acetonitrile and the cartridge.

9.6.3 Knowing the equivalent background concentration, as determined by the user (see Section 9.5.2) or supplied by the commercial supplier (see *Note*, Section 9.5), of formaldehyde in the cartridge (ng/cartridge), the formaldehyde background concentration contributed by the DNPH-coated cartridge (thus the method minimum detection limits) can be related to the total sample volume, as identified in Table 3.

9.6.4 For example, if the averaged background formaldehyde concentration supplied by the manufacturer is 70 ng/cartridge, then that cartridge can add 0.95 ppbv of equivalent formaldehyde, to the final ambient air concentration value, as delineated in Table 3 for a total air volume of 60 L.

9.6.5 The user should use DNPH-coated cartridges with the lowest background concentration to improve accuracy and detection limits.

10. Sampling Procedure

10.1 The sampling system is assembled and should be similar to that shown in Figures 3 and 4.

[Note: Figures 3 and 4 illustrate different tube/pump configurations. The tester should ensure that the pump is capable of constant flow rate throughout the sampling period.]

It is recommended that the sampling system employ a heated inlet (~50°C) coupled to an ozone denuder or scrubber to minimize water and ozone interference associated with the DNPH-coated adsorbent tube. Historically, the coated cartridges have been used as direct probes and traps for sampling ambient air when the ambient temperature was above freezing.

[Note: As illustrated in Figure 8, the ozone denuder has been effective for up to 80 hours without breakthrough at ozone levels of approximately 700 ppb. Other studies have evaluated both denuders and scrubbers at ozone concentrations between 125 and 200ppbv and found they have effectively removed ozone from the air stream for up to 100,000 ppb-hours; however, moisture was required (~10% RH) in the gas stream (26). The user should evaluate the length of time of the application of the denuder or scrubber to his field work. Caution should be utilized when using these devices for extensive periods of time at high humidity (>65%). Regarding the 24 hour samples, special caution shoud be taken while sampling nighttime periods when relative humidities approaching 100% are frequently encountered. It is recommended that routine schedule of ozone removal device replacement should be implemented as part of the sampling program.]

[Note: For sampling ambient air below freezing, a short length (30-60 cm) of heated (50-60°F) stainless steel tubing must be added to condition the air sample prior to collection on the DNPH-coated cartridges.]

10.2 Before sample collection, the system must be checked for leaks. Plug the inlet of the system 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.

10.3 Air flow through the DNPH-adsorbent cartridge may change during sampling as airborne particles deposit on the front of the cartridge. The flow change could be significant when sampling particulate-laden atmospheres. Particle concentrations greater than 50 ug/m^3 are likely to represent a problem. For unattended or extended sampling periods, a mass flow controller is highly recommended to maintain constant flow. The mass flow controller should be set at least 20% below the maximum air flow through the cartridge.

10.4 The entire assembly (including a "test" sampling cartridge) is installed and the flow rate checked at a value near the desired sampling rate. In general, flow rates of 1,000-2,000 mL/min should be employed. The total sample volume should be selected to ensure that the collected formaldehyde concentration exceeds the background formaldehyde DNPH-cartridge concentration, as illustrated in Table 3. The total moles of carbonyl in the volume of air sampled should not exceed that of the DNPH concentration (i.e., 2 mg cartridge). In general, a safe estimate of the sample size should be 75% of the DNPH loading of the cartridge.

[Note: If the user suspects that there will be breakthrough of a DNPH-coated cartridge during the sampling event, a backup cartridge should be used during the first sampling event. One would analyze the back-up cartridge for formaldehyde. If the back-up cartridge concentration exceeds 10% of the formaldehyde concentration on the front cartridge, then continue to use back-up cartridges in the monitoring program. However, if formaldehyde is not detected above the average blank level in the back-up cartridge after the first sampling event, then one can continue to use only one cartridge under normal representative conditions.]

[Note: The SKC tube is a dual bed configuration, allowing one to analyze the back bed (see Figure 2) for quantifying breakthrough.]

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.

[Note: ASTM Method D3686 describes an appropriate calibration scheme that does not require a sealed flow system downstream of the pump.]

10.5 The operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. A dry gas meter may be included in the system to measure total sample volume and to compare against the in-line mass flow controller. Some commerical systems use flow monitors with data loggers to make these measurements.

10.6 Before sampling, flush the inlet (denuder/manifold, etc.) for approximately 15 min at the established flow rate to condition the system. 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.

10.7 Using polyethylene gloves, remove the DNPH-coated cartridge from the shipping container and connect it to the sampling system with a Luer® adapter fitting. Most commercially available cartridges are bidirectional. However, review manufacturer suggestions for orientation of the cartridge to the inlet of the sampler.

[Note: If using the SKC dual bed tube, ensure the ambient air is pulled through the tube in the direction enscribed on the tube by an arrow.]

Record the following parameters on Compendium Method TO-11A field test data sheet (FTDS), as illustrated in Figure 9: 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 dry gas meter pump identification numbers.

10.8 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 tandem cartridges.

10.9 The sampler is operated for the desired period, with periodic recording of the variables listed in Figure 9.

10.10 If the ambient air temperature during sampling is below 15°C, a heated inlet probe is recommended. However, no pronounced effect of relative humidity (between 25% - 90%) has been observed for sampling under various weather conditions--cold, wet, and dry winter months and hot and humid summer months. However, a negative bias has been observed when the relative humidity is <25%. At high humidity, the possibility of condensation must be guarded against, especially when sampling is an air conditioned trailer.

10.11 At the end of the sampling period, the parameters discussed in Section 10.7 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 10%, the sample should be marked as suspect.

10.12 Immediately after sampling, remove the cartridge (using polyethylene gloves) from the sampling system, cap with Luer® end plugs, and place it back in the original labeled glass shipping container or culture tube. Cap, seal with TFE-fluorocarbon tape, and place it in appropriate padding. Refrigerate at 4°C until analysis. Refrigeration period prior to analysis should not exceed 2 weeks. If a longer storage period is expected, the cartridge should be extracted with 5 mL of acetonitrile (see Section 11.2.4 and 11.2.5) and the eluant placed in a vial for long term storage.

[Note: If samples are to be shipped to a central laboratory for analysis, the duration of the non-refrigerated period should be kept to a minimum, preferably less than two days.]

10.13 If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate must be calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots Q_N}{N}$$

where:

Q_A = average flow rate, L/min.
$Q_1, Q_2 \ldots Q_N$ = flow rates determined at beginning, end, and intermediate points during sampling, L/min.
N = number of points averaged.

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

$$V_m = (T_2 - T_1) \times Q_A$$

where:

V_m = total volume sampled at measured temperature and pressure, L.
T_2 = stop time, minutes.
T_1 = start time, minutes.
$T_2 - T_1$ = total sampling time, minutes.
Q_A = average flow rate, L/min.

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

$$V_s = V_m \times \frac{\overline{P_A}}{760} \times \frac{298}{273 + \overline{T}_A}$$

where:

V_s = total sample volume at 25°C and 760 mm Hg pressure, L.
V_m = total sample volume at measured temperature and pressure, L.
$\overline{P_A}$ = average ambient pressure, mm Hg.
$\overline{T_A}$ = average ambient temperature, °C.

11. Sample Analysis

11.1 Sample Preparation

11.1.1 The samples (trip blank, field blank and field samples) are returned to the laboratory in a shipping container and stored in a refrigerator at (<4°C) until analysis. Alternatively, the samples may also be stored alone in their individual containers.

11.1.2 The time between sampling and extraction should not exceed 2 weeks. Since background levels may change during storage, always compare field samples to those associates with field and trip to a blank samples, stored under the same conditions.

11.2 Sample Extraction

[Note: Beware of unintentional exposure of samplers and eluted samples to aldehyde and ketone sources. Laboratory air often holds high concentrations of acetone. Labeling inks, adhesives, and packaging containers (including vials with plastic caps) are all possible sources on contamination.]

[Note: Contamination is most likely to occur during sample extraction. Before eluting derivatives, clean all glassware by rinsing with acetonitrile, then heating in a 60°C vacuum oven for at least 30 minutes. Eluting the samples in a nitrogen-purged glove bag further reduces the risk of contamination.

The acetonitrile used to elute the DNPH derivatives is a typical source of contamination. Formaldehyde-free acetonitrile used to elute samples should be used only for this purpose, and stored in a carbonyl free environment. A concentrations of 10 µg/L of any aldehyde or ketone in the acetonitrile adds 0.05 µg of that carbonyl to sampler blank values if using 5 mL extraction volumes.]

11.2.1 Remove the sample cartridge from the labeled shipping tube or container. Connect the sample cartridge to a clean syringe.(Some commerical cartridges do not require the addition of a syringe for elution.)

[Note: The liquid flow during desorption should be in the reverse direction of air flow during sample collection.]

11.2.2 Place the sample cartridge syringe in the syringe rack (see Figure 7).

[Note: If the two beds in the SKC tube are being recovered separately for breakthrough studies, break the tube and place the beds in separate vials. Proceed with recovery, as specified in Section 11.2.3 through Section 11.2.6.]

11.2.3 Backflush the cartridge (gravity feed) by passing 5 mL of acetonitrile from the syringe through the cartridge to a 5-mL volumetric flask. The backflush elution approach may add particulate particles also collected on the cartridge to the acetonitrile solution which can cause sample valve failure and increase column back pressure. To minimize this, frontflush the cartridge contents with the acetonitrile reagent rather than blackflush. The use of 5mL of acetonitrile is sufficient for quantitative cartridge sample elution in either mode.

[Note: A dry cartridge has an acetonitrile holdup volume of about 0.3 mL. The eluant flow may stop before the acetonitrile in the syringe is completely drained into the cartridge because of air trapped between the cartridge filter and the syringe Luer® tip. If this happens, displace the trapped air with the acetonitrile in the syringe using a long-tip disposable Pasteur pipet.]

11.2.4 Dilute to the 5-mL mark with acetonitrile. Label the flask with sample identification. Store in refrigerated conditions until the sample is analyzed by HPLC. Pipet two aliquots into sample vials with TFE-

fluorocarbon-lined septa. Analyze the first aliquot for the derivative carbonyls by HPLC. Store the second aliquot in the refrigerator until the results of the analysis of the first aliquot are complete and validated. The second aliquot can be used for confirmatory analysis, if necessary.

11.2.5 Sample eluates are stable at 4°C for up to one month.

11.3 HPLC Analysis

11.3.1 The HPLC system is assembled and calibrated as described in Section 11.4. The operating parameters are as follows when formaldehyde is the only carbonyl of interest:

Column:	Zorbax ODS (4.6-mm ID 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. Thirteen minutes for formaldehyde with two Zorbax ODS columns.
Sample Injection Volume:	25 µL.

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

11.3.2 The HPLC mobile phase is prepared by mixing 600 mL of acetonitrile and 400 mL of water. This mixture is filtered through a 0.22-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 (350 kPa) or short length (15-30 cm) of 0.25-mm (0.01 inch) ID Teflon® tubing should be placed after the detector to eliminate further mobile phase outgassing.

11.3.3 The mobile phase is placed in the HPLC solvent reservoir and the pump is set at a flow rate of 1.0 mL/min and allowed to pump for 20-30 minutes before the first 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. The isocratic flow of 60% acetonitrile/40% water is adequate for the analysis of formaldehyde; however, sufficient time between air sample analyses is required to assure that all other carbonyl compounds are eluted from the HPLC column prior to the next sample. The gradient flow approach ,mentioned later (see Section 14.3) is properly programmed to elute other carbonyl compounds.

11.3.4 A 100-µL aliquot of the sample is drawn into a clean HPLC injection syringe. The sample injection loop (25-µL) is loaded and an injection is made. The data system, if available, is activated simultaneously with the injection. If a strip chart recorder is used, mark the point of injection on the chart paper.

11.3.5 After approximately one minute, the injection valve is returned to the "load" position and the syringe and valve are rinsed or flushed with acetonitrile/water mixture in preparation for the next sample analysis.

[Note: The flush/rinse solvent should not pass through the sample loop during flushing.]

The loop is cleaned while the valve is in the "load" mode.

11.3.6 After elution of the DNPH-formaldehyde derivative (see Figure 10), data acquisition is terminated and the component concentrations are calculated as described in Section 12.

11.3.7 After a stable baseline is achieved, the system can be used for further sample analyses as described above. Be sure to examine the chromatogram closely to ensure that background DNPH-formaldehyde derivative peaks are not on the solvent slope of the DNPH peak.

[Note: After several cartridge analyses, background buildup on the column may be removed by flushing with several column volumes of 100% acetonitrile.]

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

11.3.9 If the retention time is not duplicated (±10%), 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. If retention time is not reproducing, the problem may be associated with the HPLC flow system. A control chart is recommended to evaluate retention time changes.

[Note: The chromatographic conditions described here have been optimized for the detection of formaldehyde. Analysts are advised to experiment with their HPLC system to optimize chromatographic conditions for their particular analytical needs. If a solvent change is necessary, always recalibrate before running samples.]

11.4 HPLC Calibration

11.4.1 Calibration standards can be prepared by the user in acetonitrile from the solid DNPH-formaldehyde derivative or liquid standards can be purchased from various manufacturers. From the solid compound, individual stock solutions of 100 ug/mL are prepared by dissolving 10 mg of solid derivative in 100 mL of acetronitrile. Since the MW of HCHO-hydrazone is 210 g/mol, and the MW of HCHO is 30 g/mol, the stock solution concentration converts to 14.3 ug/mL as formaldehyde (30/210 x 100mg/mL). The solid compound is weighed using a 5-place analytical balance and liquid dilutions are made with volumetric glassware. Stock solutions obtained from commercial suppliers generally range from 1 to 50 ug/mL as the carbonyl compound. These stock solutions are typically provided in 1 mL ampules.

11.4.2 Using the stock solution, working calibration standards are produced. To generate the highest concentration working standard, use a pipette to quantitatively transfer 1.00 ml of the stock solution to a 25 mL volumetric flask. For example, using a 14.3 ug/mL stock solution produces a working standard solution of 570 ng/mL (14300 ng/mL x 1/25). The high concentration working standard diluted serially, using 1 to 5 mL pipettes and volumetric flasks, can produce working standards ranging between 28.5 and 570 ng/mL.

11.4.3 Each calibration standard (at least five levels) is analyzed three times and area response is tabulated against mass concentration injected (see Figure 11). All calibration runs are performed as described for sample analyses in Section 11.3. The results are used to prepare a calibration curve, as illustrated in Figure 12. The slope of the calibration curve gives the response factor, RF. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (mass concentration versus area response) is obtained. The intercept of the calibration curve should pass through the origin. If it does not, check your reagents and standard solutions preparation procedure for possible contamination. If the calibration curve does not pass through the origin, the equation for the calibration curve should include the intercept.

11.4.4 Once linear response has been documented, a concentration standard near the anticipated levels of each carbonyl component, but at least 10 times the detection limit, should be chosen for daily calibration. The day to day response for the various components should be within 10% of the calibration value. If greater variability is observed, prepare a fresh calibration check standard. If the variability using a freshly prepared calibration check standard is greater than 15% , a new calibration curve must be developed from fresh standards. A plot of the daily values on a Quality Control Chart (day versus concentration) is helpful to check for long term drift of the concentration value.

11.4.5 The response for each component in the daily calibration standard is used to calculate a response factor according to the following equation shown for formaldehyde:

$$RF_{HCHO} = \frac{(P - P_o)}{C_{HCHO}}$$

where:

RF_{HCHO} = response factor for formaldehyde given as area counts per ng/mL.
C_{HCHO} = concentration of analyte in the calibration standard in units of ng/mL.
P = peak area counts for the formaldehyde standard.
P_o = calibration curve intercept; in most cases this is zero.

11.4.2 The RF for each carbonyl compound is determined in the same way as that given for formaldehyde. The concentration of HCHO and other carbonyl compounds is determined with the calibration curves for each component in the analyzed sample. Example calculation for HCHO is given in section 12.

12. Calculations

Determination of the carbonyl compound air concentration requires three steps: (1) determination of the average blank and the standard deviation of the blank; (2) determination of the collected carbonyl compound mass of the cartridge; (3) calculation of the carbonyl compound air concentration. The following discusion provides these steps for formaldehyde.

12.1 Blank Determination

Since the blank level for any arbitary cartridge is unknown, an average value for the blank is used in the calculation. As noted earlier, the average blank value is determined for each lot of cartridges. For a given lot size, N, a minimum of $\sqrt{N}$ cartridge blanks (rounded to the next whole number) should be analyzed; i.e., for a lot size of 200, a minimum of $\sqrt{200}$ or 14 cartridge blanks should be analyzed. A minimum of 3 of these blanks are used for the Certification Blank, and the remaining 11 are used for field blanks. The mass of HCHO on each cartridge is determined by multiplying the observed peak area for blank cartridge solution by the acetonotrile extract volume (typically 5 mL) and dividing by the response factor as provided in the following equation:

$$M_{BL-HCHO_i} = \frac{P_{BL-HCHO_i} \times V_E}{RF_{HCHO}}$$

where:

$M_{BL-HCHOi}$ = the blank HCHO mass for cartridge , i.
RF_{HCHO} = HCHO response factor calculated in Section 11.4.5.
$P_{BL-HCHOi}$ = area counts for HCHO in blank sample extract.
V_E = extract volume in mL (usually 5 mL).

Once all blank cartridges have been measured, the average blank value is determined by the following equation:

$$\overline{M}_{BL-HCHO} = \frac{1}{N} \times \sum_{N}^{i=1} M_{BL-HCHO_i}$$

where:

$\overline{M}_{BL-HCHO}$ = the average HCHO mass for all cartridges.
$M_{BL-HCHOi}$ = blank HCHO mass for cartridge, i.
N = the number of blank cartridges.

[Note: Measurement of cartridge blanks should be destributed over the period that this particular cartridge lot is used for ambient air sampling. It is recommended that a trend plot of blank results be constructed to evaluate background carbonyl results over the period of cartridge lot utilization in the sampling program. If significant drifting is observed, blank average values should be segmented to be more representative of carbonyl background.]

12.2 Carbonyl Analyte Mass

The calculation equation for the mass of the collected carbonyl compound mass for an individual cartridge is the as that for the cartrigde blanks. The gross measured carbonyl mass is determined with an equation analogous to that given in section 12.1. The equation for formaldehyde is given as**:**

$$M_{SA_i} = \frac{P_{SA_i} \times V_E}{RF_{HCHO}}$$

where:

M_{SAi} = gross HCHO mass for cartridge, i.
P_{SAi} = HCHO peak area counts for cartridge, i.
RF_{HCHO} = the response factor for HCHO.
V_E = acetonitrile extract volume in mL (typically 5 mL).

The net HCHO mass for an individual cartridge is determined by substracting the average blank value from the gross HCHO mass obtained for sample i, and is given as:

$$M_{HCHO_i} = M_{SA_i} - \overline{M}_{BL-HCHO}$$

12.3 Carbonyl Compound Concentration

The sample air concentration for carbonyl compounds cannot be determined directly from the mass measurement and requires conversion to units of volume. The conversion calculation for HCHO is determined using the ideal gas law and is given by the following equation:

$$V_{HCHO_i} = \frac{M_{HCHO_i}}{MW} \times (R \times T_{AMB}) \times \frac{760}{P_{AMB}}$$

where:

V_{HCHOi} = gas volume of HCHO on cartridge, i.
M_{HCHOi} = mass of HCHO on cartridge, i.
MW = molecular weight of HCHO, 30.03 g/mole.
R = gas constant, 0.082 L-atm/mol-deg.
T_{AMB} = ambient air temperature in degrees Kelvin, 273 + T (C^o).
P_{AMB} = ambient air pressure in torr.

For an ambient air temperature of 25°C and a pressure of 760 torr, the ideal law equation reduces to:

$$V_{HCHO_i} = 1.2276 \times M_{HCHO_i}$$

In this equation, the HCHO mass in ng is converted to a volume in nL. The volume of air that was passed through the cartridge was measured by either a mass flow controller or dry test meter calibrated at a known temperature and pressure. To determine HCHO concentration in the units of ppbv, apply the following equation:

$$C_{HCHO}\text{ppbv} = \frac{V_{HCHO_i}}{V_{AIR}}$$

where:

V_{HCHOi} = volume of formaldehyde in nL
V_{AIR} = volume of sample air through the cartridge

13. Performance Criterial and Quality Assurance

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

13.1 Standard Operating Procedures (SOPs).

13.1.1 Users should generate SOPs describing the following activities in their laboratory: (1) assembly, calibration, and operation of the sampling system, with make and model of equipment used; (2) preparation, purification, storage, and handling of sampling reagent and samples; (3) assembly, calibration, and operation of the HPLC system, with make and model of equipment used; and (4) all aspects of data recording and processing including lists of computer hardware and software used.

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

13.2 HPLC System Performance

13.2.1 The general appearance of the HPLC system should be similar to that illustrated in Figure 1.

13.2.2 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54 \left(\frac{t_r}{W_{1/2}} \right)^2$$

where:

N = column efficiency, theoretical plates.
t_r = retention time of analyte, seconds.
$W_{1/2}$ = width of component peak at half height, seconds.

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

13.2.3 Precision of response for replicate HPLC injections should be ±10% or less, day to day, for analyte calibration standards at 150 ng/mL or greater levels (as the carbonyl compound). At 75 ng/mL levels and below, precision of replicate analyses could vary up to 25%. Precision of retention times should be ±7% on a given day.

13.3 Process Blanks

13.3.1 At least one field blank should be used for each day of field sampling, 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 minimum number of blanks is obtained for a given cartridge lot used for field samples. The field blank is treated identically to the samples except that no air is drawn through the cartridge. The performance criteria described in Section 9.2 should be met for field blanks. It is also desirable to analyze trip and laboratory blank cartridges as well, to distinguish between possible field and lab contamination.

[Note: Remember to use the field blank value for each cartridge lot when calculating concentration. Do not mix cartridge lots in the blank value determinations]

13.4 Method Precision and Accuracy

13.4.1 At least 50% of the sampling events should include a collocated sample. A collocated sample is defined as a second sampling port off the common sampling manifold. If more than five samples are collected per sampling event, a collocated sample should be collected for each sampling event. Precision for the collocated samples should be ±20% or better. EPA historical data has demonstrated effectiveness in reaching ±20%, as illustrated in Figure 13.

13.4.2 Precision for replicate HPLC injections should be ±10% or better, day to day, for calibration standards.

13.4.3 Cartridges spiked with analytes of interest can be used in round-robin studies to intercompare several laboratories performing carbonyl analyses. The spiked samples are prepared in the laboratory by spiking a blank cartridge with a solution of derivatized carbonyls in acetonitrile. The laboratory preparing the spike samples should analyze at a minimum 3 of the prepared spiked samples to evaluate the consistency of prepared samples.

13.4.4 Before initial use of the method, each laboratory should generate triplicate spiked samples at a minimum of three concentration levels, bracketing the range of interest for each compound. Triplicate nonspiked samples must also be processed. Spike recoveries of >80 ±10% and blank levels should be achieved.

13.4.5 For ambient air sampling, an ozone denuder must be used as part of the sampling system. As discussed in Section 6.4, ozone effects the ultimate method precision and accuracy by reacting with its carbonyl derivative (hydrazones) on the cartridge. To illustrate this point, Figure 14 documents the concentration of formaldehyde captured on collocated DNPH-cartridges, one with a denuder (see Figure 14a) and the other without a denuder (see Figure 14b). The formaldehyde peak is considerably higher with use of an ozone denuder.

13.5 Method Detection Limits

13.5.1 Determine method detection limits using the procedures in 40 CFR Part 136B. Prepare a low level standard of the carbonyl derivatives at a concentration within two to five times the estimated method detection limit. Inject the standard into the analytical system seven times.

13.5.2 Calculate the measured concentration using the calibration curve.

13.5.3 Determine the standard deviation for the seven analyses and use the standard deviation to calculate the detection limit as described in 40 CFR Part 136B.

13.6 General QA/QC Requirements

13.6.1 General QA/QC requirements associated with the performance of Compendium Method TO-11A include:

Sampling

- Each sampling event, flow calibration with bubble meter, both pre- and post-checks.
- Mass flow meter calibration factor determined every quarter.
- Each sampling event, leak check, both pre- and post-checks.
- 10 percent of field samples collocated to help calculate method precision and evaluate biases.
- 10 percent of field samples operated with back-up cartridge to evaluate analyte breakthrough.

- Field and trip (optional) blank cartridges are included with each field sample collection program.
- Sample volumes calculated and reviewed project QA officer.

Reagents

- Coating solution prepared from concentrated stock solution immediately before each coating.
- Solution analyzed before each coating to determine acceptability (less than 0.10 µg/cartridge for each aldehyde), control chart of contaminant concentration maintained.
- Three blank cartridges per lot for immediate elution/analysis to determine Certification Blank for the carbonyl compounds.

Analysis

- Multi point calibration curve performed each six months.
- Continuing calibration standard (mid-level) analyzer every analytical run to evaluate precision, peak resolution and retention time drift.
- Method detection limits (MDLs) verified annually or after each instrument change.
- Replicate analysis of approximately 10 percent of sample eluents to evaluate precision.
- Samples quantitated against least squares calibration line.
- Performance evaluation (PE) sample acquired from independent sources analyzed prior to and after field samples.
- Random collocated samples shipped to independent laboratory for analysis and compared to in-house collocated sample.
- Testing of acetonitrile used for sample extraction for background carbonyl evaluation.

Data Acquisition

- Sample chromatograms and standards checked daily for peak shape and integration quality, resolution of carbonyls, overall sensitivity and retention time drift.
- Separate tape backups made of raw data immediately after completion of each analysis.
- Peaks in each sample checked for correct ID and integration using system software before export to ASCII file.
- Final results checked and edited by project QA officer before producing final report.
- Tape backups of final data files produced.

13.6.2 All results should be reviewed by the project QA officer, independent of the field and laboratory operations, to evaluate the overall adherence to the methodology in meeting the program data quality objectives (DQOs).

14. Detection of Other Aldehydes and Ketones

14.1 Introduction

14.1.1 The procedure outlined above has been written specifically for the sampling and analysis of formaldehyde in ambient air using an adsorbent cartridge and HPLC. Ambient air contains other aldehydes and ketones. Optimizing chromatographic conditions by using two Zorbax ODS columns in series and varying the mobile phase composition through a gradient program will enable the analysis of other aldehydes and ketones. Alternatively, other aldehydes and ketones may also be analyzed using a single C-18, reverse phase column and a ternary gradient as described by Waters or Smith, et al. (*J. Chromatography*, 483, 1989, 431-436). Thus, other aldehydes and ketones can be detected with a modification of the basic procedure.

14.1.2 In particular, chromatographic conditions can be optimized to separate acetaldehyde, acetone, propionaldehyde, and some higher molecular weight carbonyls within an analysis time of about 1 h by utilizing two Zorbax ODS columns in series, and a linear mobile phase program. Operating the HPLC in a gradient mode with one Zorbax ODS column may also provide adequate resolution and separation. Carbonyl compounds covered within the scope of this modification include:

Formaldehyde	Crotonaldehyde	
o-Tolualdehyde		
Aceteldehyde	Butyraldehyde	
m-Tolualdehyde		
Acetone	Benzaldehyde	
p-Tolualdehyde		
Propionaldehdye	Isovaleraldehyde	
Hexanaldehyde		
Valeraldehyde	2,5-Dimethylbenzaldehyde	Methyl ethyl ketone

14.1.3 The linear gradient program varies the mobile phase composition periodically to achieve maximum resolution of the C-3, C-4 and benzaldehyde region of the chromatogram. The following gradient program was found to be adequate to achieve this goal: Upon sample injection, linear gradient from 65% acetonitrile (ACN)/35% water to 55% ACN/45% water in 36 min; to 100% ACN in 20 min; 100% ACN for 5 min; reverse linear gradient from 100% ACN to 60% ACN/40% water in 1 min; maintain at 60% ACN/40% water for 15 min.

14.2 Sampling Procedures

Same as Section 10.

14.3 HPLC Analysis

14.3.1 The HPLC system is assembled and calibrated as described in Section 11. The operating parameters are as follows:

Column:	Zorbax ODS, two columns in series
Mobile Phase:	Acetonitrile/water, linear gradient
Step 1.	60-75% acetonitrile/40-25% water in 30 minutes.
Step 2.	75-100% acetonitrile/25-0% water in 20 minutes.
Step 3.	100% acetonitrile for 5 minutes.
Step 4.	60% acetonitrile/40% water reverse gradient in 1 minute.
Step 5.	60% acetonitrile/40% water, isocratic, for 15 minutes.
Detector:	Ultraviolet, operating at 360 nm
Flow Rate:	1.0 mL/min
Sample Injection Volume:	25 µL

14.3.2 The gradient program allows for optimization of chromatographic conditions to separate acetaldehyde, acetone, propionaldehyde, and other higher molecular weight aldehydes and ketones in an analysis time of about one hour.

14.3.3 The chromatographic conditions described here have been optimized for a gradient HPLC system equipped with a UV detector (variable wavelength), an automatic sampler with a 25-µL loop injector

and two DuPont Zorbax ODS columns (4.6 x 250-mm), a recorder, and an electronic integrator. Analysts are advised to experiment with their HPLC systems to optimize chromatographic conditions for their particular analytical needs. Highest chromatographic resolution and sensitivity are desirable but may not be achieved. The separation of acetaldehyde, acetone, and propionaldehyde should be a minimum goal of the optimization.

14.3.4 The carbonyl compounds in the sample are identified and quantified by comparing their retention times and area counts with those of standard DNPH derivatives. Formaldehyde, acetaldehyde, acetone, propionaldehyde, crotonaldehyde, benzaldehyde, and o-, m-, p-tolualdehydes can be identified with a high degree of confidence. The identification of butyraldehyde is less certain because it coelutes with isobutyraldehyde and is only partially resolved from methyl ethyl ketone under the stated chromatographic conditions. A typical chromatogram obtained with the gradient HPLC system for detection of other aldehydes and ketones is illustrated in Figure 15.

14.3.5 The concentrations of individual carbonyl compounds are determined as outlined in Section 12.

14.3.6 Performance criteria and quality assurance activities should meet those requirements outlined in Section 13.

15. Precision and Bias

15.1 This test method has been evaluated by round robin testing. It has also been used by two different laboratories for analysis of over 1,500 measurements of formaldehyde and other aldehydes in ambient air for EPA's Urban Air Toxics Program (UATP), conducted in 14 cities throughout the United States.

15.2 The precision of 45 replicate HPLC injections of a stock solution of formaldehyde-DNPH derivative over a 2-month period has been shown to be 0.85% relative standard deviation (RSD).

15.3 Triplicate analyses of each of twelve identical samples of exposed DNPH cartridges provided formaldehyde measurements that agreed within 10.9% RSD.

15.4 A total of 16 laboratories in the U.S., Canada, and Europe participated in a round robin test that included 250 blank DNPH-cartridges, three sets of 30 cartridges spiked at three levels with DNPH derivatives, and 13 sets of cartridges exposed to diluted automobile exhaust gas. All round robin samples were randomly distributed to the participating laboratories. A summary of the round robin results is shown in Table 4.

15.5 The absolute percent differences between collocated duplicate sample sets from the 1988 UATP program were 11.8% for formaldehyde (n=405), 14.5% for acetaldehyde (n=386), and 16.7% for acetone (n=346).

15.6 Collocated duplicate samples collected in the 1989 UATP program and analyzed by a different laboratory showed a mean RSD of 0.07, correlation coefficient of 0.98, and bias of -0.05 for formaldehyde. Corresponding values for acetaldehyde were 0.12, 0.95 and -0.54, respectively. In the 1988 UATP program, single laboratory analyses of spiked DNPH cartridges provided over the year showed an average bias of +6.2% for formaldehyde (n=14) and +13.8% for acetaldehyde (n=13).

15.7 Single laboratory analyses of 30 spiked DNPH cartridges during the 1989 UATP program showed an average bias of +1.0% (range -49 to +28%) for formaldehyde and 5.1% (range -38% to +39%) for acetaldehyde.

16. References

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TABLE 1. COMPARISON OF DNPH COATED CARTRIDGES: SILICA GEL VS. C18

Topic	Comparison	Discussion
Background	Silica gel < C18	Silica gel is purer, therefore less background contamination from acetone and formaldehyde as compared to C18.
Breakthrough	Silica gel < C18	C18 allows carbonyl compounds to breakthrough easier with longer sampling periods, thus causing bias results. C18 has a lower capacity for carbonyls in general. Loading of DNPH on C18 plays an important role in breakthrough for carbonyls.
Ozone interference	Silica gel C18	Ozone interference with silica gel is documented. Ozone interference with C18 is not clear at this time. Therefore, must use denuder with both systems.
Extraneous chromato-graphic peaks	Silica gel C18	Researchers have detected extraneous peaks in the chromatography of both C18 and silica gel when ozone is present.

TABLE 2. TYPICAL DNPH-CARTRIDGE SPECIFICATIONS

Category	Typical Specifications
Adsorbent	chromatographic grade silica or C18 coated with 2,4-dinitrophenylhydrazine (DNPH)
Particle size	150-1000 µm (60/100 mesh to 18/35 mesh)
DNPH loading[1]	0.3-0.9% (~1-3 mg/cartridge)
Bed weight[2]	approx. 350 mg
Capacity	approx. 75 µg formaldehyde, assuming a 50% consumption of DNPH
Background (per cartridge)	<0.15 µg formaldehyde <0.10 µg acetaldehyde <0.10 μg other carbonyls <0.30 µg acetone
Pressure drop	7 inches of water @ 0.5 L/min 15 inches of water @ 1.0 L/min 37 inches of water @ 2.0 L/min
Sampling temperature	10°C to 100°C
Collection efficiency	>95% for formaldehyde for sampling rates up to 2.0 L/min
Solvent hold-up volume	~1.0 mL
Tube dimensions	From ~2 inches to ~5 inches in length ~1 inch O.D. at widest point

[1]Loading is variable among commercial suppliers.
[2]The SKC tube is a dual bed cartridge with 300 mg of DNPH-coated silica gel in the front bed and 150 mg of DNPH-coated silica gel in the back bed.

TABLE 3. EQUIVALENT FORMALDEHYDE CONCENTRATION (ppbv) RELATED TO BACKGROUND FORMALDEHYDE CONCENTRATION (ng/cartridge)

Equivalent formaldehyde concentration (ppbv)		Sample volume, L			
		60	120	180	1440
Background formaldehyde cartridge concentration, ng/cartridge	70	0.950	0.475	0.317	0.040
	100	1.358	0.679	0.453	0.057
	150	2.037	1.018	0.679	0.085

TABLE 4. ROUND ROBIN TEST RESULTS[a]

Sample Type	Formaldehyde	Acetaldehyde	Propionaldehyde	Benzaldehyde
Blank cartridges:				
µg aldehyde	0.13	0.18	0.12	0.06
(% RSD)	46	70	47	44
n	33	33	23	8
Spiked[b] cartridges:				
% recovery (% RSD)				
low	89.0 (6.02)	92.6 (13.8)	108.7 (32.6)	114.7 (36.1)
medium	97.2 (3.56)	97.8 (7.98)	100.9 (13.2)	123.5 (10.4)
high	97.5 (2.15)	102.2 (6.93)	100.1 (6.77)	120.0 (8.21)
n	12	13	12	14
Exhaust samples:				
µg aldehyde	5.926	7.990	0.522	0.288
% RSD	12.6	16.54	26.4	19.4
n	31	32	32	17

[a]Sixteen participating laboratories. Statistics shown after removal of outliers.
[b]Normal spiking levels were approximately 0.5, 5 and 10 µg of aldehyde, designated as low, medium, and high in this table.

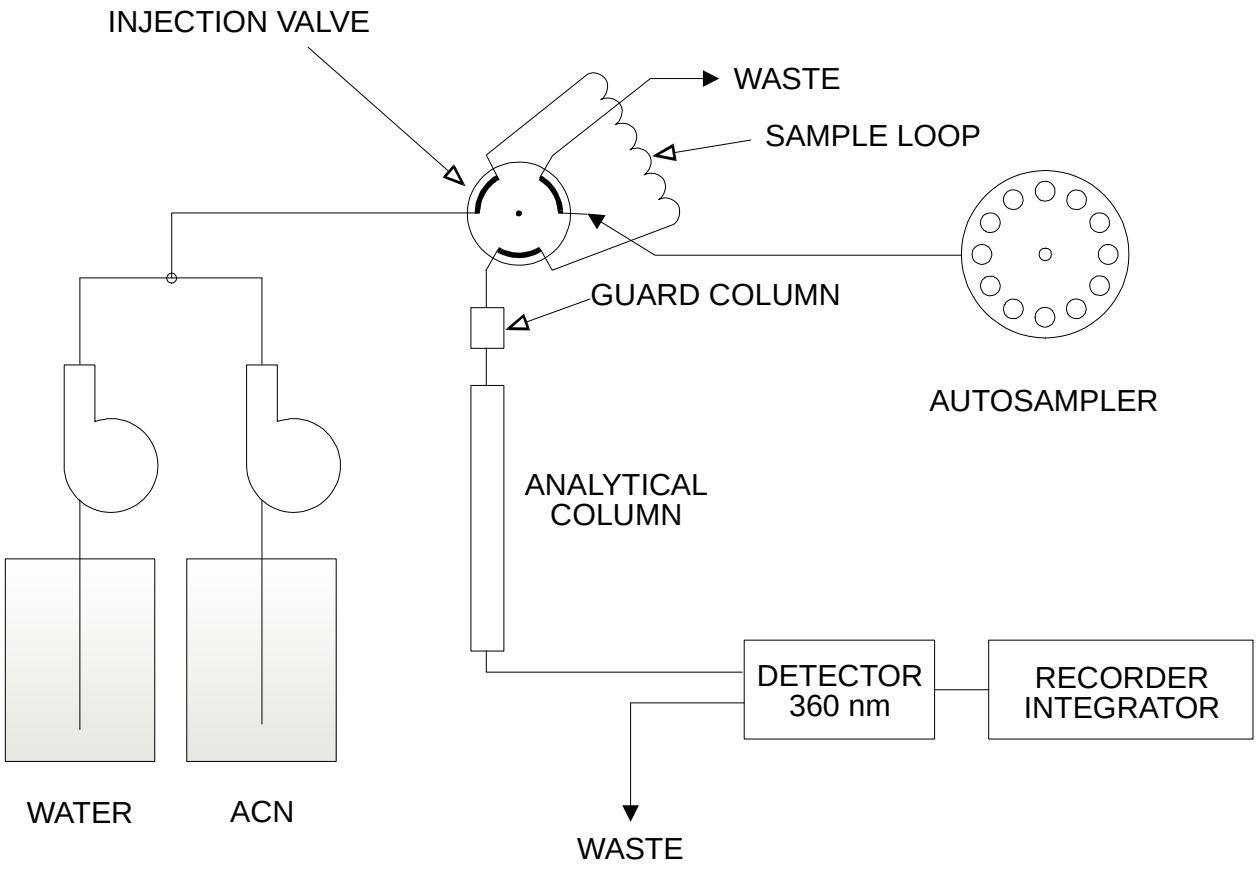


Figure 1. Basic high-performance liquid chromatographic (HPLC) system used for carbonyl analysis.

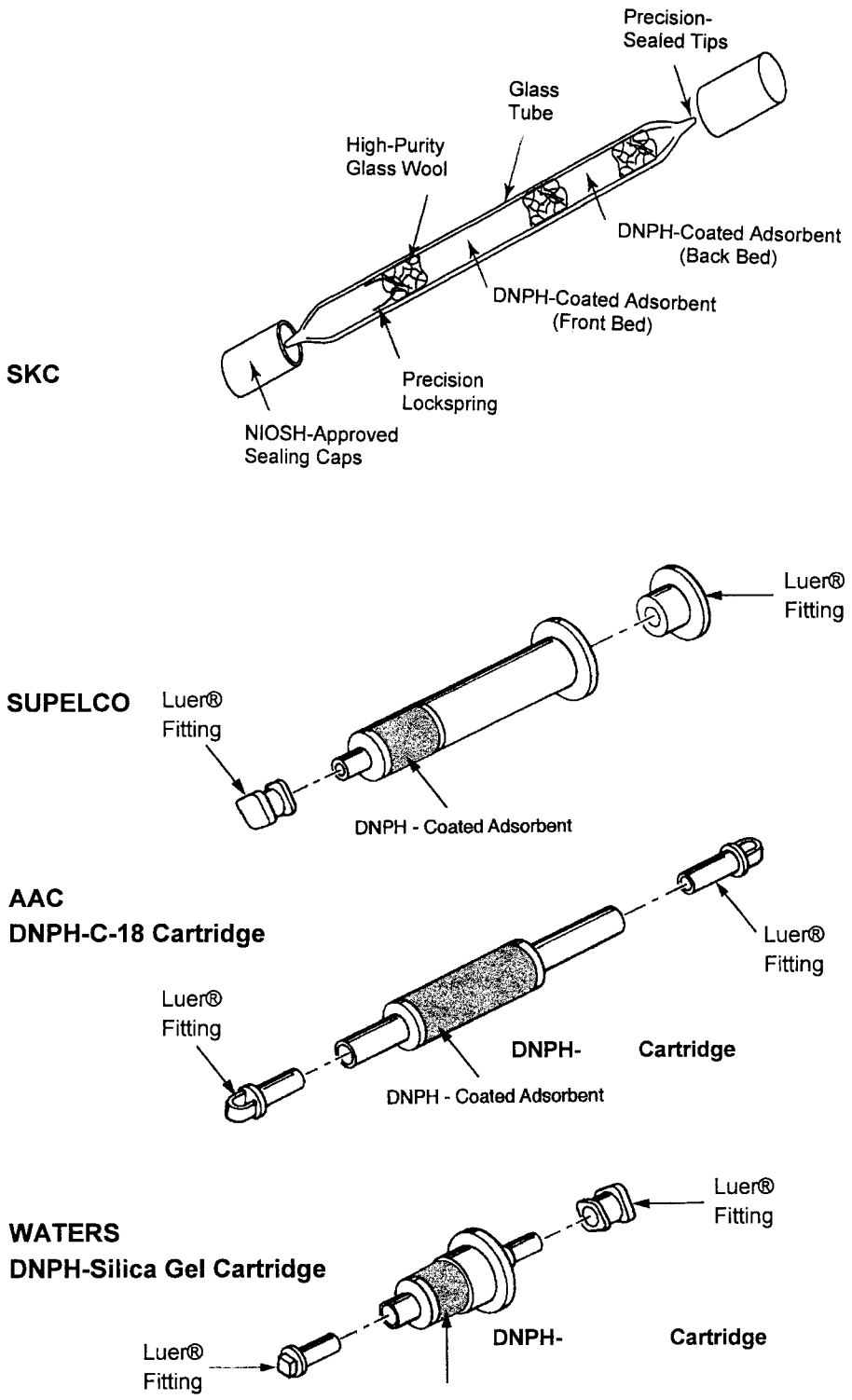


Figure 2. Example of commercially available DNPH-cartridges.

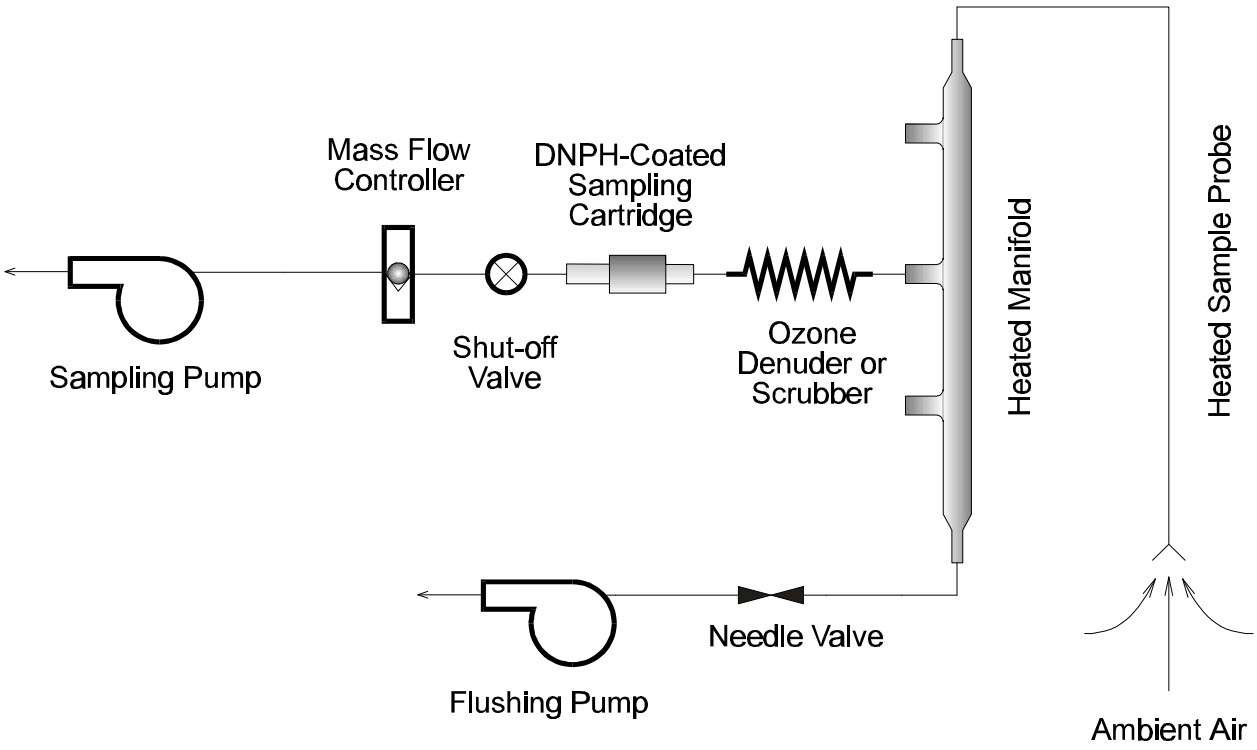


Figure 3. Example of configuration of a single-port carbonyl sampler using DNPH-coated cartridges.

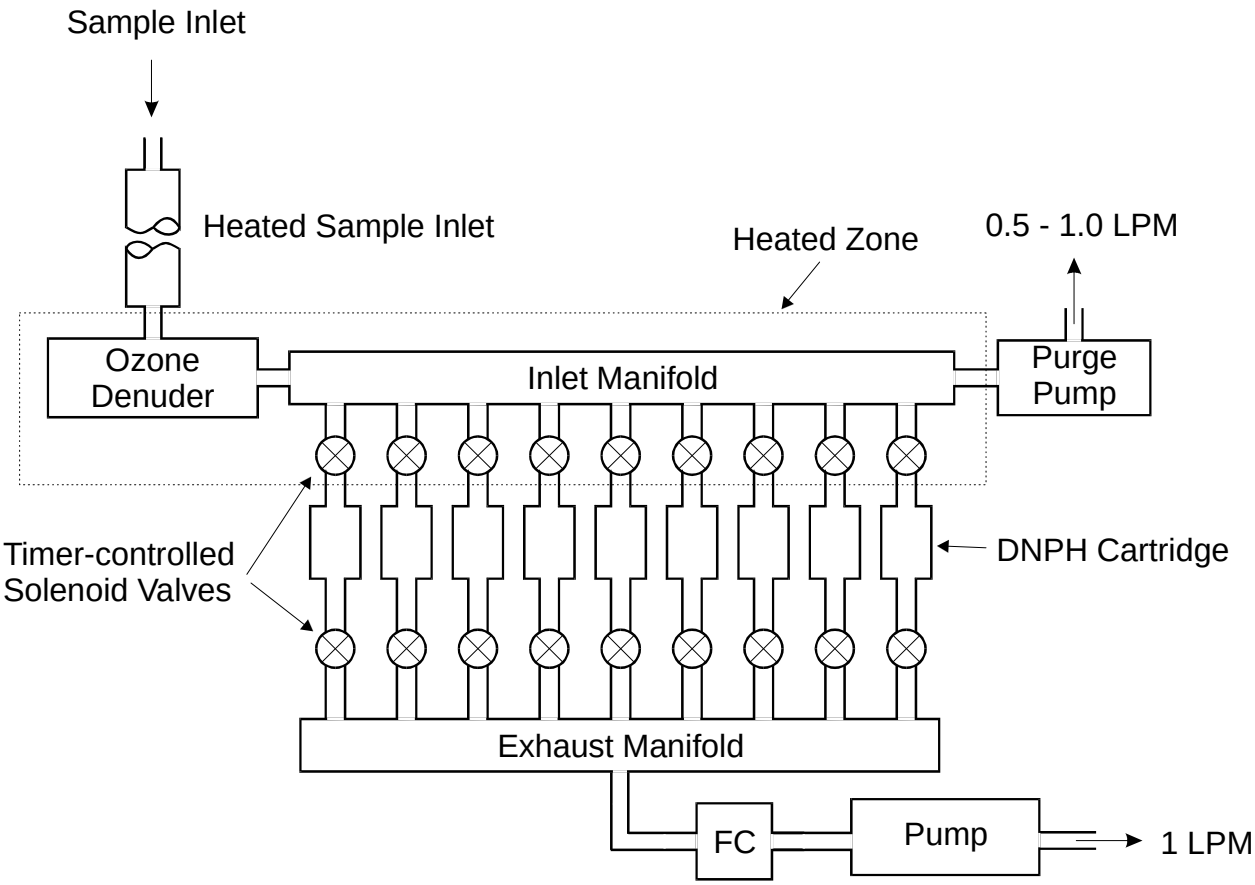


Figure 4. Example of components of an automated multi-port sampler for carbonyls monitoring using DNPH-coated cartridges.

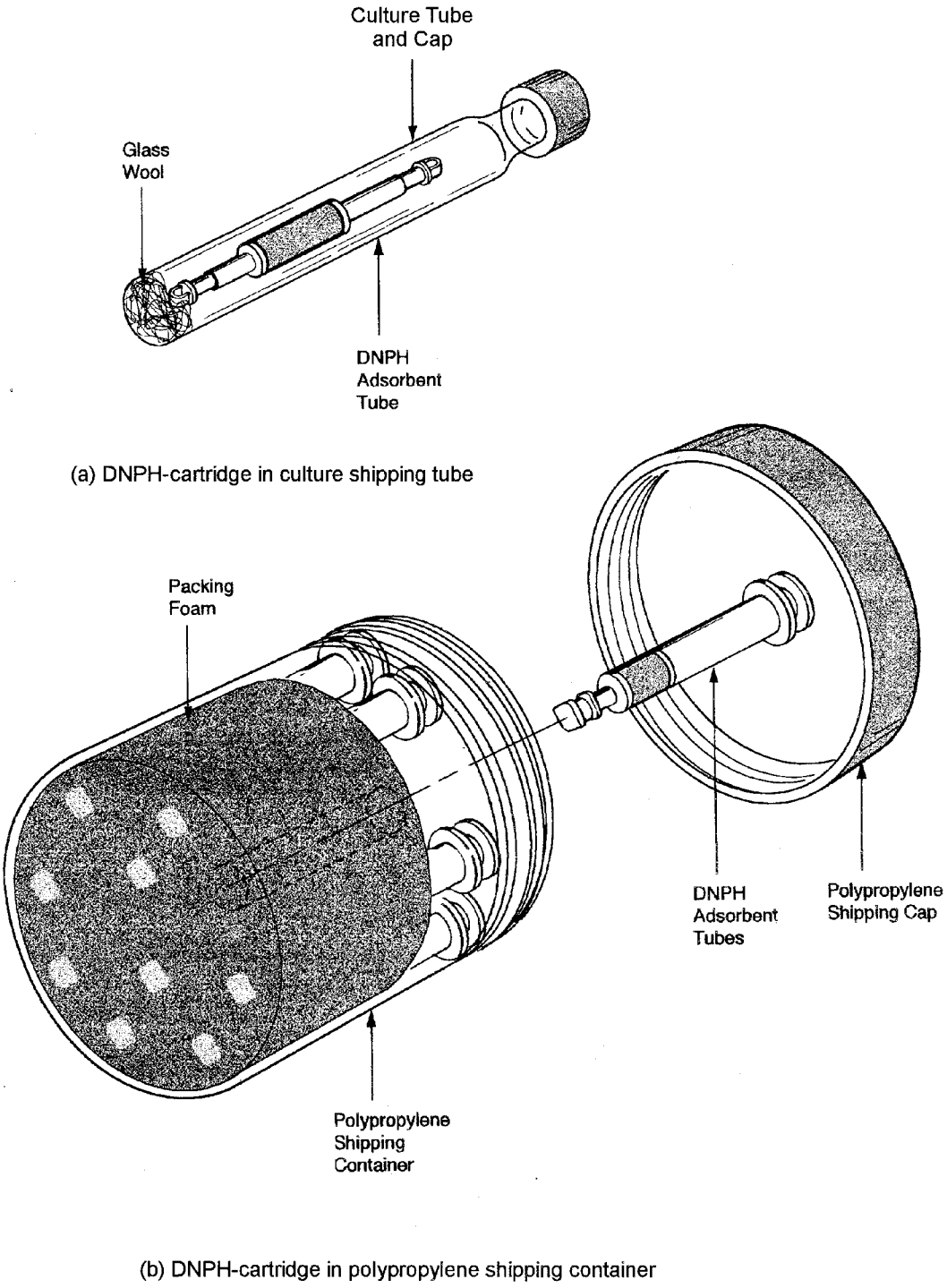
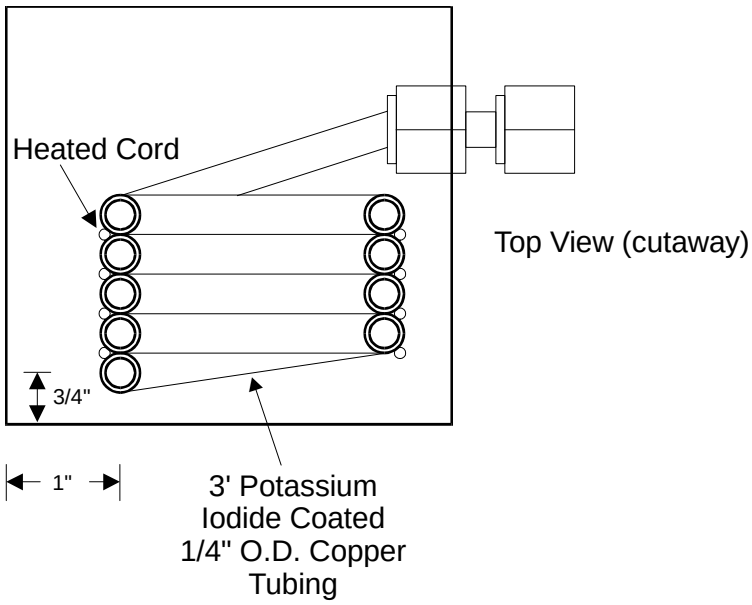
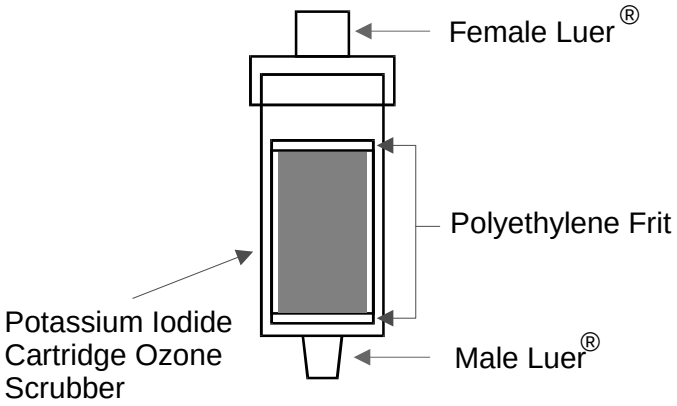


Figure 5. Example of commercially available shipping containers for DNPH cartridges.

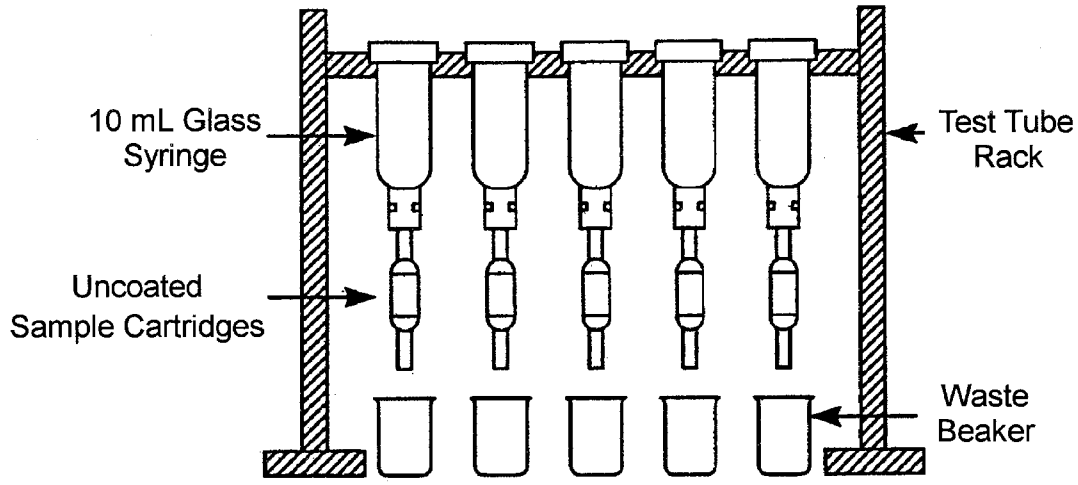


(a) Cross-sectional view of EPA's ozone denuder assembly

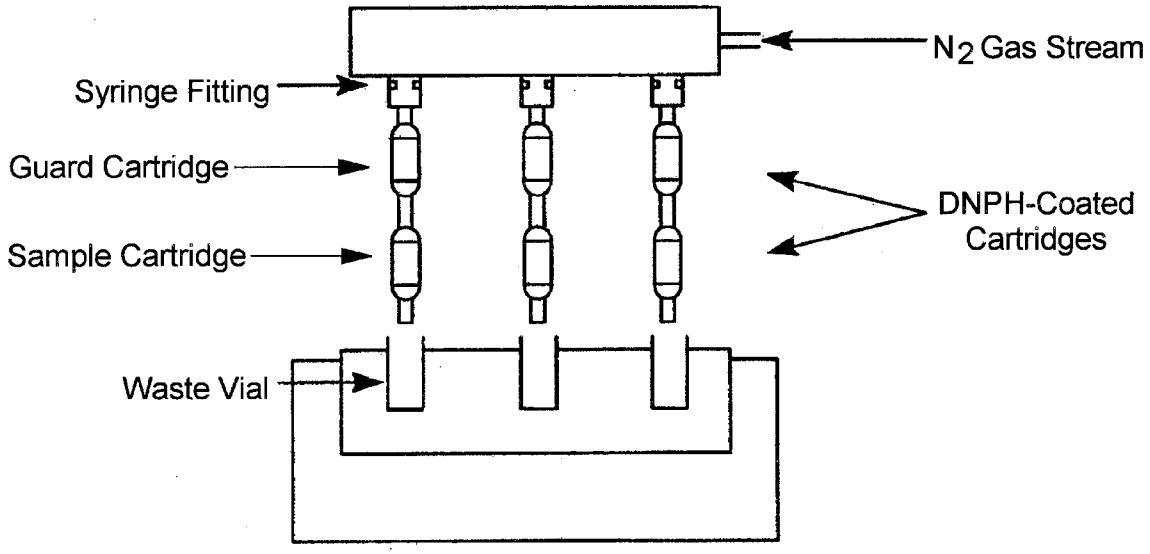


(b) Commercially available packed granular potassium iodide (KI) ozone scrubber

Figure 6. Example of (a) cross-sectional view of EPA's ozone denuder assembly, and (b) commercially available packed granular potassium iodide (KI) ozone scrubber.



(a) Rack for Coating Cartridges



(b) Rack for Drying DNPH-Coated Cartridges

Figure 7. Example of a typical syringe rack for coating (a) and drying (b) sample cartridges.

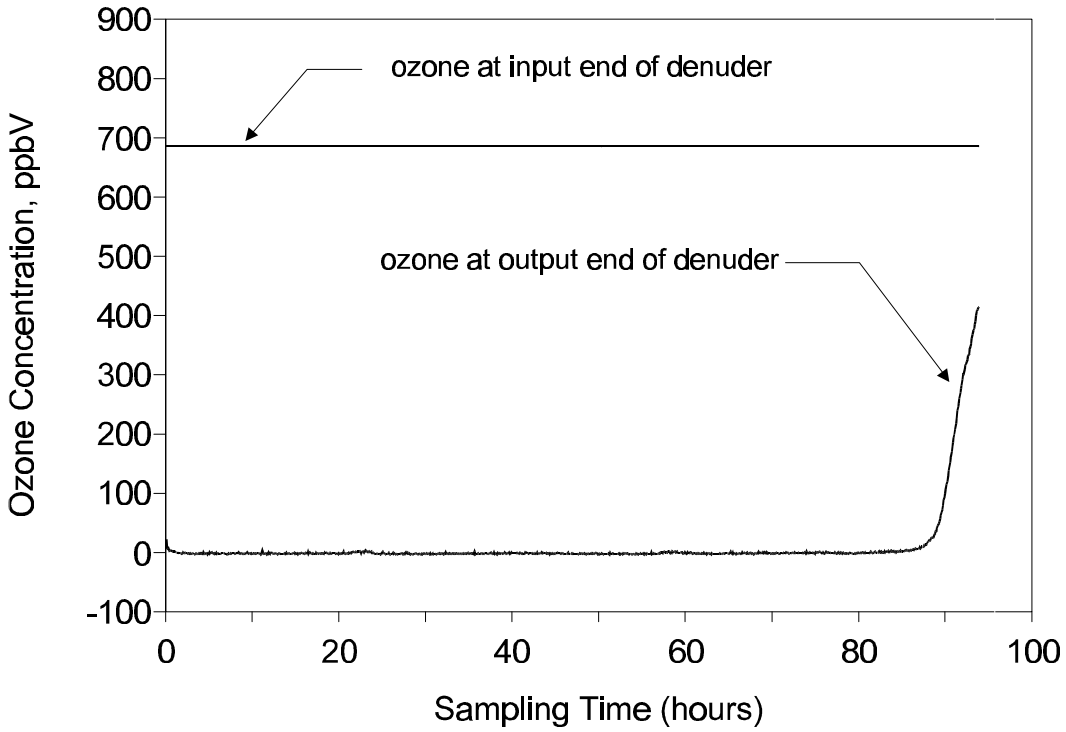


Figure 8. Example of capacity of 3' x 0.25" O.D. x 4.6-mm I.D. copper KI ozone denuder at 2 L/min flow.

COMPENDIUM METHOD TO-11A
CARBONYL SAMPLING FIELD TEST DATA SHEET
(One Sample per Data Sheet)

I. GENERAL INFORMATION

PROJECT: _____
SITE: _____
LOCATION: _____
INSTRUMENT MODEL NO.: _____
PUMP SERIAL NO.: _____

DATES(S) SAMPLED: _____
TIME PERIOD SAMPLED: _____
OPERATOR: _____
CALIBRATED BY: _____
OZONE DENUDER USE TIME (Hr): _____
HEATED INLET: _____ **YES** _____ **NO**

ADSORBENT CARTRIDGE INFORMATION:

Type: _____
Adsorbent: _____
Serial Number: _____
Sample Number: _____

II. SAMPLING DATA INFORMATION

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 gras meter, if available)

V_m = (Final - Initial) Dry Gas Meter Reading, or = _____ L
or

$$V_m = \frac{Q_1 + Q_2 + Q_3 \ldots Q_N}{N} \times \frac{1}{1000 \times (\textit{Sampling Time in Minutes})}$$ = ___ L

III. COMMENTS

_____
_____
_____

Figure 9. Example of Compendium Method TO-11A field test data sheet (FTDS).

OPERATING PARAMETERS
HPLC

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

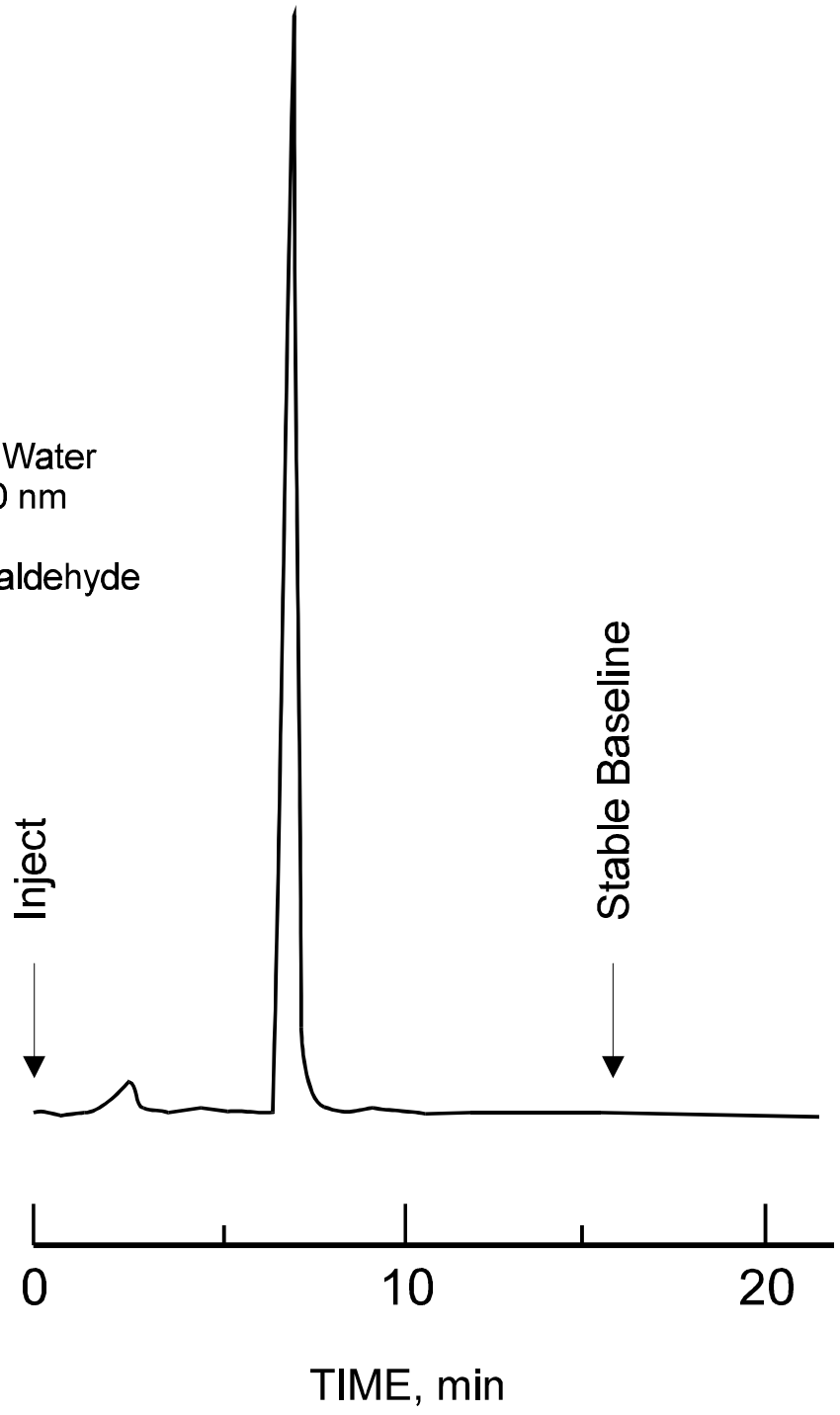


Figure 10. Example of chromatogram of DNPH-formaldehyde derivative.

OPERATING PARAMETERS HPLC

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

Peak	Conc. μg/mL	Area Counts
a	0.61	226541
b	1.23	452186
c	6.16	2257271
d	12.32	4711408
e	18.48	6053812

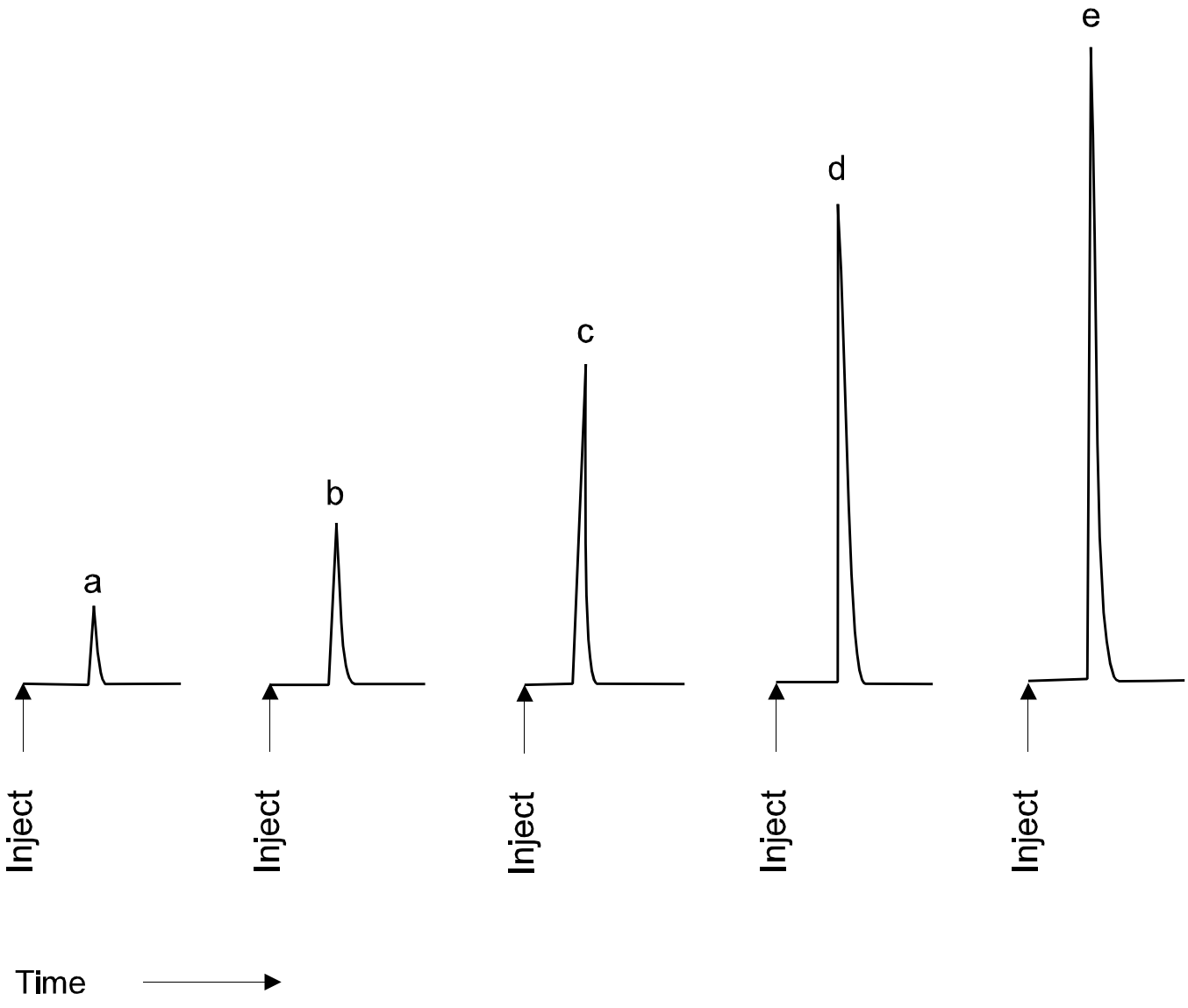


Figure 11. Example of HPLC chromatogram of varying concentration of DNPH-formaldehyde derivative.

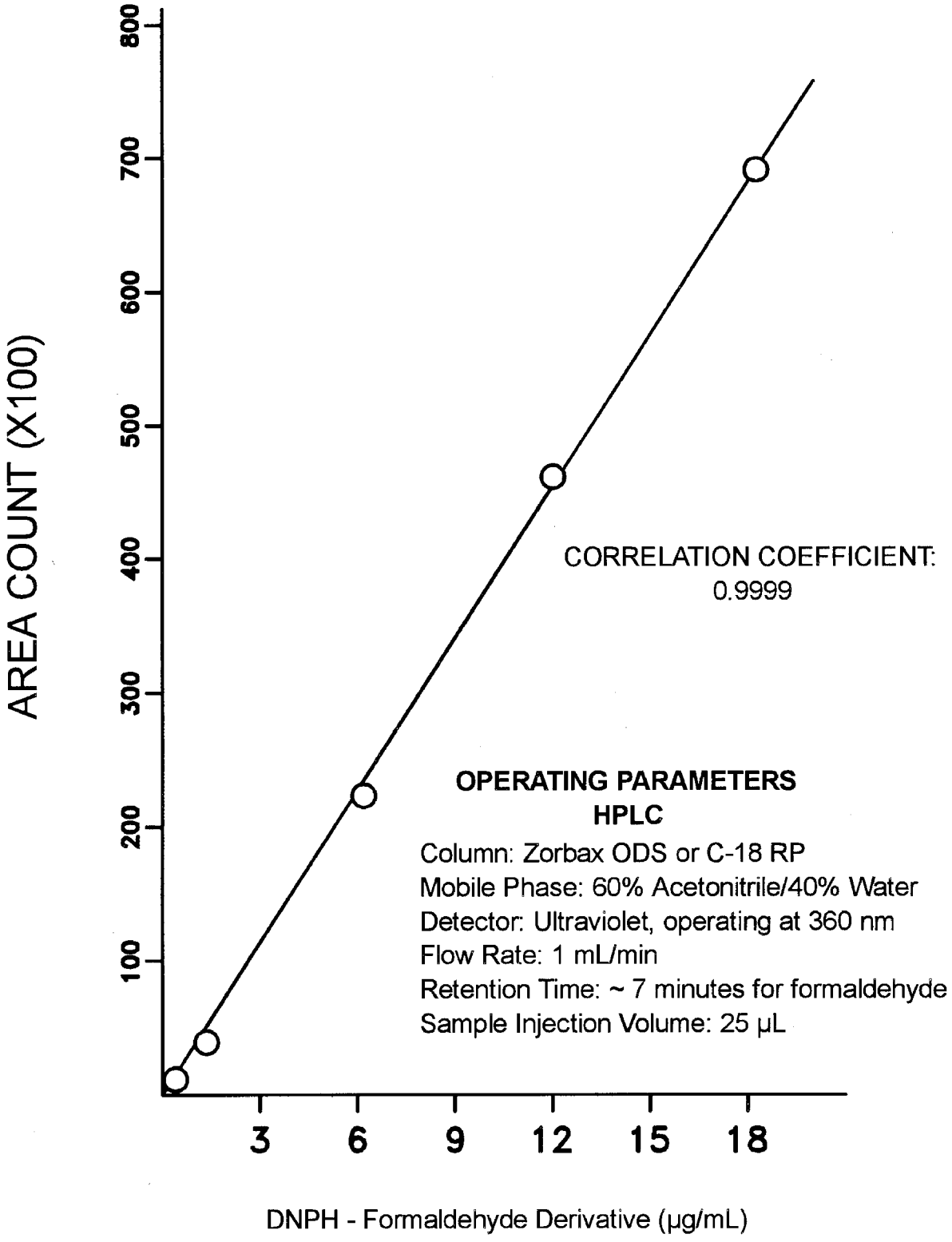


Figure 12. Example of calibration curve for formaldehyde.

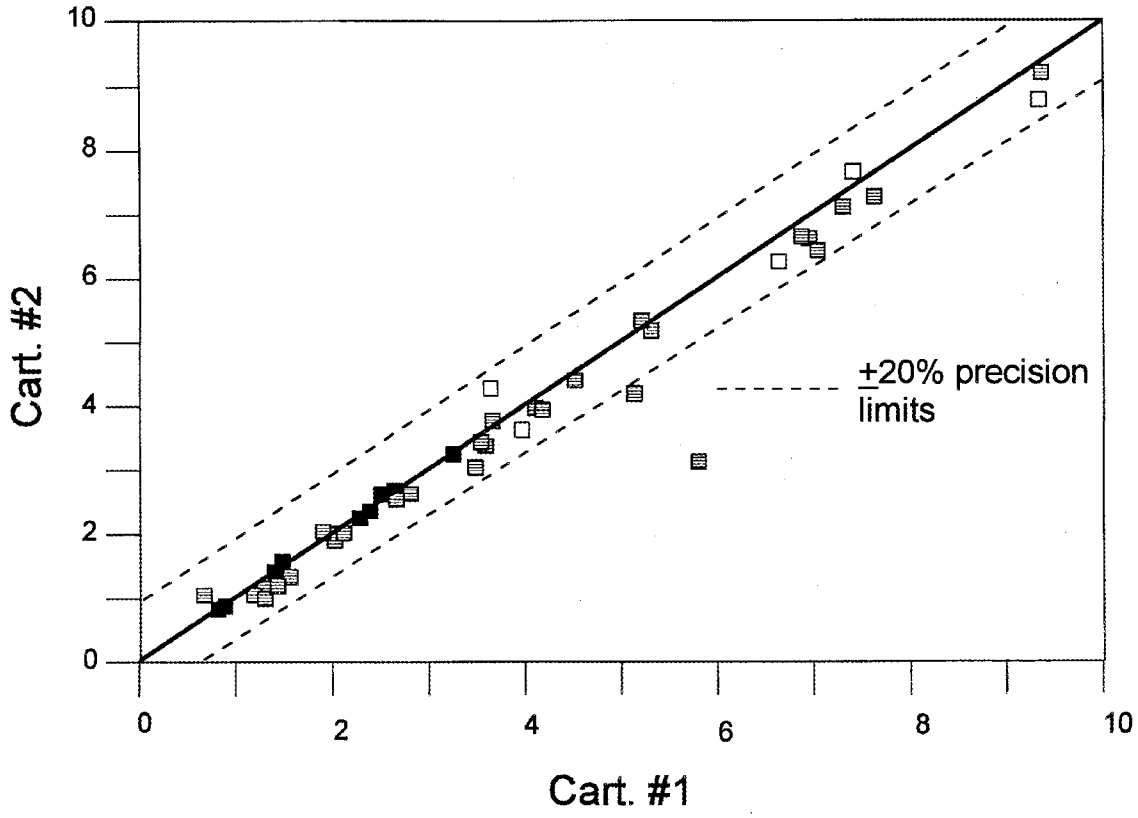


Figure 13. Historical data associated with collocated samples for formaldehyde (ppbv) in establishing 20% precision.

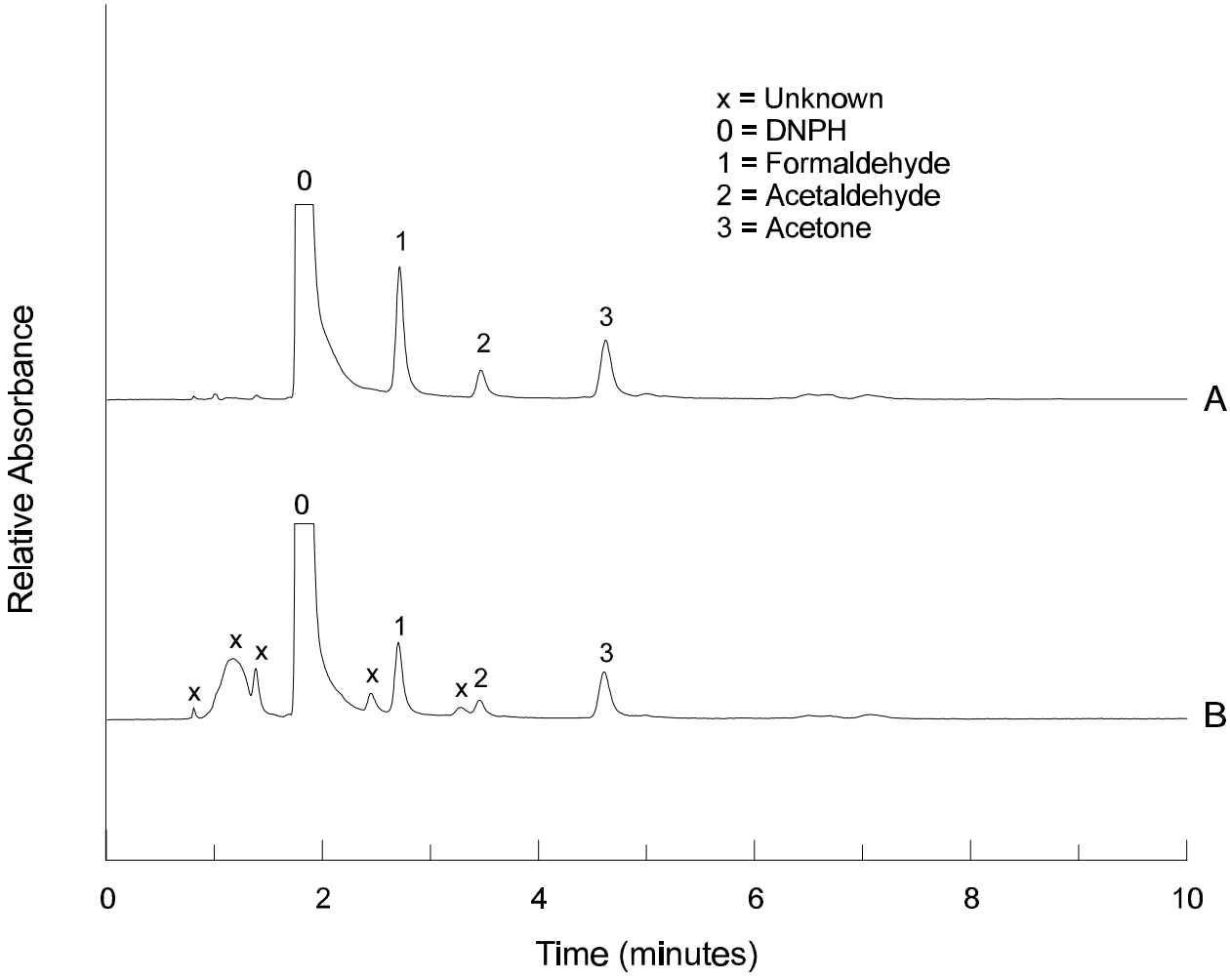
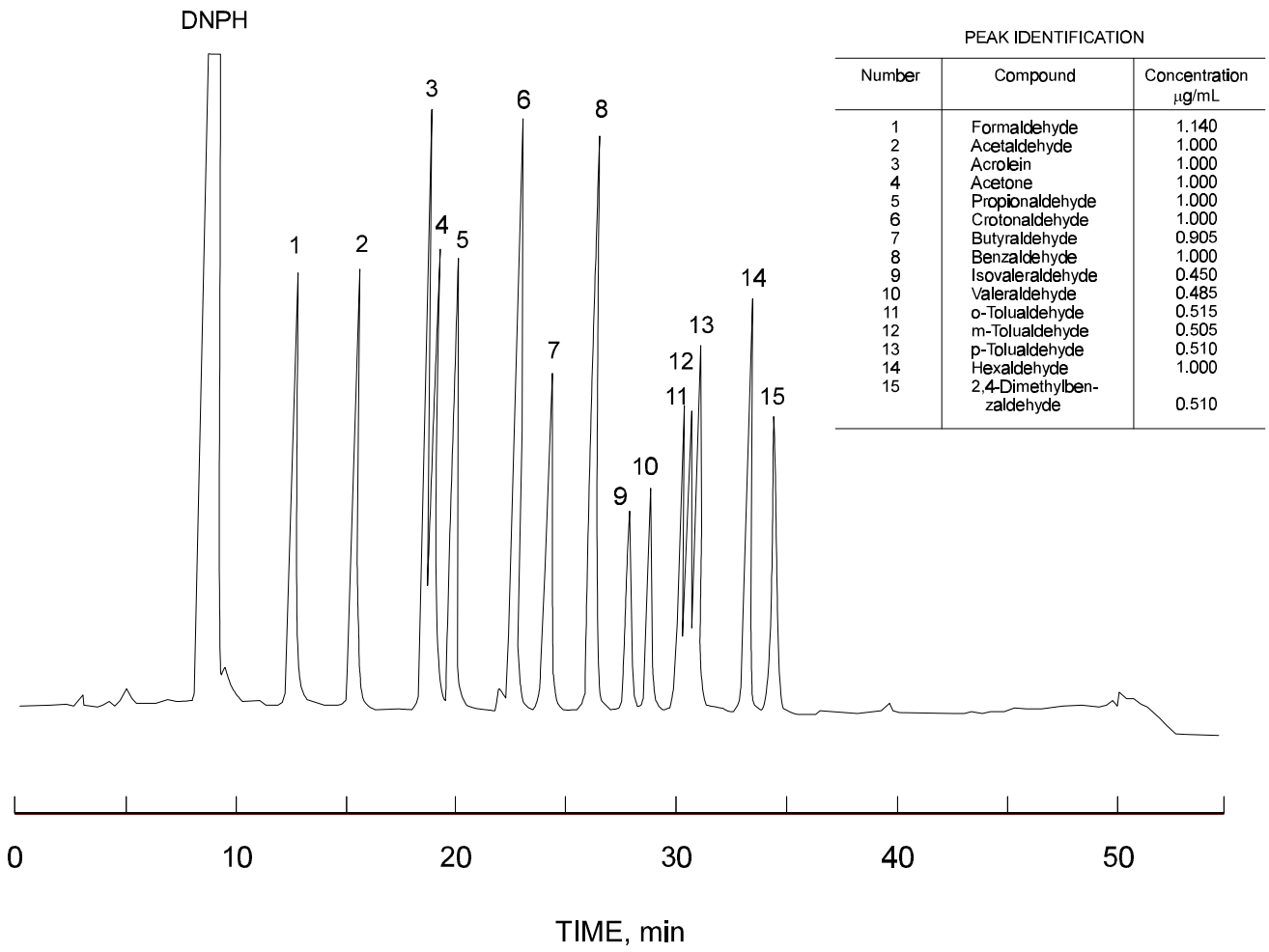


Figure 14. Example of analysis demonstrating DNPH-coated cartridges sampling air with (A) and without (B) ozone denuders, in the determination of formaldehyde.



PEAK IDENTIFICATION

Number	Compound	Concentration µg/mL
1	Formaldehyde	1.140
2	Acetaldehyde	1.000
3	Acrolein	1.000
4	Acetone	1.000
5	Propionaldehyde	1.000
6	Crotonaldehyde	1.000
7	Butyraldehyde	0.905
8	Benzaldehyde	1.000
9	Isovaleraldehyde	0.450
10	Valeraldehyde	0.485
11	o-Tolualdehyde	0.515
12	m-Tolualdehyde	0.505
13	p-Tolualdehyde	0.510
14	Hexaldehyde	1.000
15	2,4-Dimethylbenzaldehyde	0.510

Figure 15. Typical chromatogram of a linear gradient program for analyzing other aldehydes/ketones from a DNPH-coated cartridge.