Chapter 7

Ozone Precursors: Measurement Principle and Calibration Procedure

Introduction

Section 182 (c)(1) of the 1990 Clean Air Act Amendments (CAAA) required the Environmental Protection Agency (EPA) to promulgate rules for enhanced monitoring to obtain more comprehensive and representative data on ozone air pollution. The EPA has revised the ambient air quality surveillance regulations in Title 40 Part 58 of the Code of Federal Regulations 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 ozone and the need to obtain a more comprehensive air quality data base for ozone and its precursors. Analysis of the data will help the EPA understand the underlying causes of ozone pollution, devise effective controls, and measure improvement.

This chapter will focus on the measurement of ozone 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. Discussion of the methodology for measuring NO_x, as required by PAMS, and issues associated with the collection of total reactive oxides of nitrogen (NO_y) will be limited since these topics are covered in detail in Chapter 9 of this manual. Meteorological measurements provide important information on the issues associated with ozone formation and transport and will be discussed in this chapter as well as in Chapter 10 of this manual.

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). Further discussion of air monitoring networks can be found in Chapter 10 of this manual.

The EPA has prepared a guidance document on enhanced O_3 monitoring network design and siting criteria 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 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 the Technical Assistance Document for Sampling and Analysis of Ozone Precursors (EPA/600-R-98/161) for direction.

The use of approved alternative VOC measurement methodology (including new or innovative technologies) is permitted. 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.

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 7-1. 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 O3 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 Chapter 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 it is 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.

Table 7-1. PAMS Minimum Monitoring Network Requirements.

Population of MSA/CMSA[1]	**Required Site Type**	**Sampling Frequency Minimum VOCs** [2]	**Compounds Sampling Frequency Minimum Carbonyl** [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.

Target Volatile Organic Compound (VOCs) - Ozone Precursors

For the purposes of ozone precursor sampling, the term VOCs refers to gaseous aliphatic and aromatic nonmethane organic compounds that have a vapor pressure greater than 0.14 mm Hg at 25 ^{0}C, 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 7-2 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). The VOCs listed in Table 7-2 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.

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.

Table 7-2. Target Volatile Organic Compounds (VOCs)

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
42380	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
43201	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

The compounds listed in Table 7-2 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 7-2. Compounds 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 by volume (ppbv).

The target compound list in Table 7-3 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.

Table 7-3. Classification of Target VOC's

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.

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. 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.

Compendium Method TO-12, preconcentration direct flame ionization detector (PDFID) techniques described later in this chapter, 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:

(Eq. 7-1)

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

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

(Eq. 7-2)

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

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

Methodology for the Sampling and Analysis of Volatile Organic Compounds

In accordance with the provisions for the enhanced O_3 ambient monitoring network requirements specified in 40 CFR Part 58, Subpart E, this section provides a discussion of the methods for measuring volatile organic compounds (VOCs) that contribute to the formation of ozone under the right atmospheric conditions. 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

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.

Gas chromatography is a method for separating the constituents of an ambient air sample that contains VOCs. By separating the constituents they can be identified and quantified.
Prior to injecting the sample into the GC it is typically conditioned (dehumidified) and concentrated. The sample is then vaporized and injected into GC along with a carrier gas (the *mobile phase*) which delivers the sample into the column which contains the *stationary phase*. The stationary phase impedes the progress of each of the sample constituent through the column by differing amounts. If the column(s) have been properly selected complete separation (*elution*) of the sample will occur with each of the sample constituents emerging from the column at different times (described as the *retention time*). As the chemicals exit the end of the column, they are detected and identified. It is typical for the results to be presented by graphically (chromatogram) and electronically.

Two methods are presented for collecting and analyzing VOC samples: an automated method and a manual method. 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 in this manual are generic. Background information on the potential benefits and limitations of the methods are also provided.

The subsections of this section will discuss the issues of automated and manual sampling techniques and the GC/FID technique utilized to identify and quantify the collected sample. In addition, relevant QC/QA topics will be discussed.

GC/FID Analytical Methodology for the Quantification of VOCs

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.

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(s).

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. 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 first be determined for each target compound using pure components or mixtures of pure components diluted with a humidified inert gas.

Identification and Quantification Issues

Although GC/FID systems are 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.

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.

Quantitative errors can be reduced by careful attention to quality control (calibration details and system blanks), performing 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.

Sample Moisture Issues

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 temperature 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.);
- 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.

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*).

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. Detailed procedures for preparing humidified standards and for diluting standards is given in the Technical Assistance Document for Sampling and Analysis of Ozone Precursors (EPA/600-R-98/161).

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.

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. 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.

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.

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 into an evacuated SUMMA® passivated stainless steel canister or other inert container. 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.

Detailed procedures for the preparation of calibration standards are given in the Technical Assistance Document for Sampling and Analysis of Ozone Precursors (EPA/600-R-98/161).

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. 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. 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® switch have been used to accommodate these dual-column configurations.

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.

Figure 7-1 is a schematic of a GC/FID analyzer fitted with duel columns and shown in a typical configured with ancillary equipment.

Figures 7-2 and 7-3 are example chromatograms of retention time calibration standards containing the PAMS target compounds as eluted from a *PLOT* column (0.32 mm I.D., 50 m, 5 micrometer, Al_2O_3/Na_2SO_4) and a *BP1* column (0.22 mm I.D., 50 m, 1 micrometer, SGE, Incorporated). Since these columns have been successfully used by others, users should give primary consideration to these column types during their column selection process.

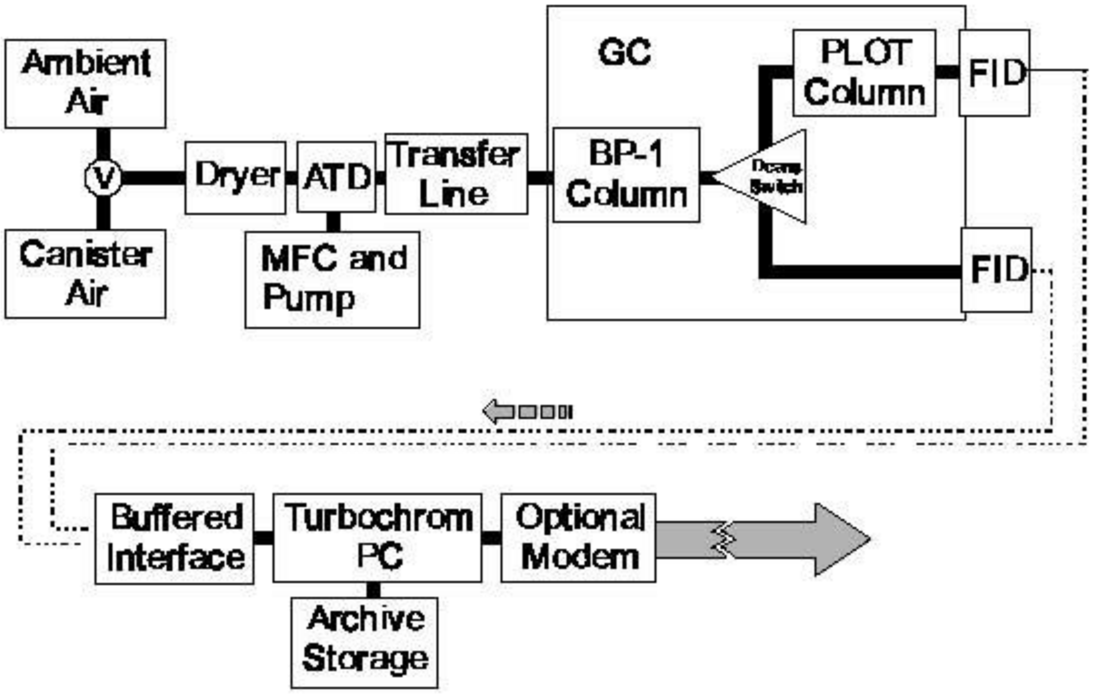
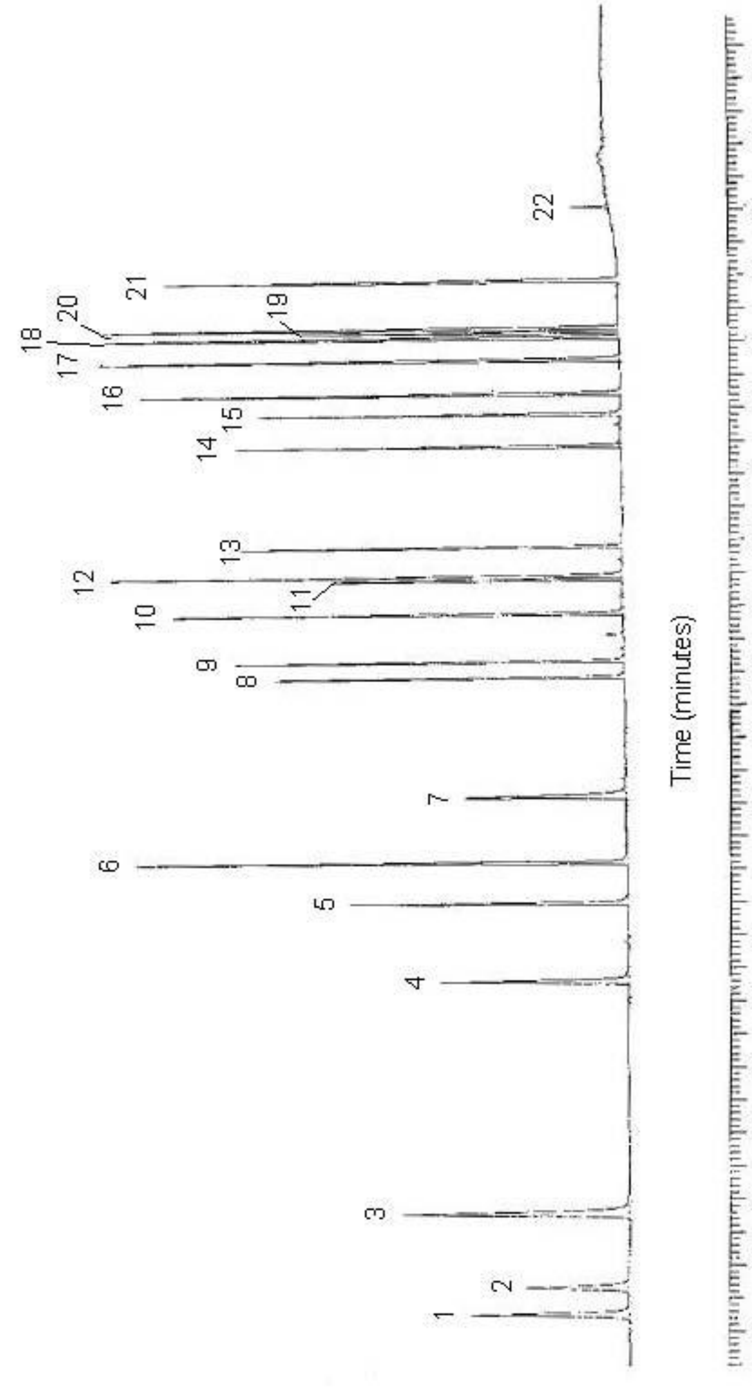


Figure 7-1. Schematic of a GC/FID analyzer fitted with duel columns and shown in a typical configured with ancillary equipment.



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

Figure 7-2. Example Chromatogram for the PAMS Target Compounds from the PLOT Analytical Column

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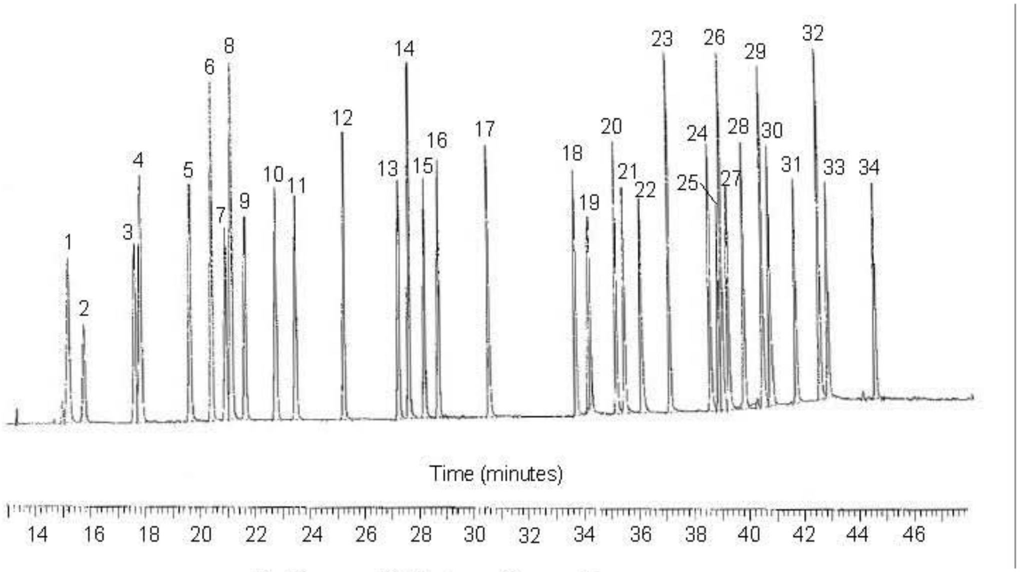


Column:	SGE, Inc. BPI, 50m x 0.22mm x 1µm
Carrier:	Helium, ~2.5ml/min
Initial Temp:	45°C, 15 minutes
Rate 1:	5°C/min.
Temp 2:	170°C
Rate 2:	15°C/min.
Final Temp:	200°C, 6 minutes

Peak #	AIRS Code	Compound Name	Peak #	AIRS Code	Compound Name
1	43231	Hexane	18	45203	Ethylbenzene
2	N/A	Unknown	19	45109	m/p-Xylene
3	43262	Methylcyclopentane	20	45220	Styrene
4	43247	2, 4-Dimethylpentane	21	45204	O-Xylene
5	45201	Benzene	22	43235	n-Nonane
6	43248	Cyclohexane	23	45210	Isopropylbenzene
7	43263	2-Methylhexane	24	45209	n-Propylbenzene
8	43291	2, 3-Dimethylpentane	25	45212	m-Ethyltoluene
9	43249	3-Methylhexane	26	45213	p-Ethyltoluene
10	43250	2, 2, 4-Trimethylpentane	27	45207	1, 3, 5-Trimethylbenzene
11	43232	n-Heptane	28	45211	o-Ethyltoluene
12	43261	Methylcyclohexane	29	45208	1, 2, 4-Trimethylbenzene
13	43252	2, 3, 4-Trimethylpentane	30	43238	n - Decane
14	45202	Toluene	31	45225	1, 2, 3-Trimethylbenzene
15	43960	2-Methylheptane	32	45218	m-Diethylbenzene
16	43253	3-Methylheptane	33	45219	p-Diethylbenzene
17	43233	n-Octane	34	43954	n-Undecane

o x/gfmom/6797/pams/compound2.ppt

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

Figure 7-3. Example Chromatogram for the PAMS Target Compounds from the BP1 Analytical

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.

Refer to the Technical Assistance Document for Sampling and Analysis of Ozone Precursors (EPA/600-R-98/161) for guidance on the procedures for pre-measurement verifications for PAMS.

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

The rigorous sampling frequency requirements of enhanced O_3 monitoring (e.g., eight 3hour 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. The discussion will focus on the generic configuration and operation of automated GC systems. The selected 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 (See Figure 7-1).

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 a subsequent section of this chapter.

The O_3 precursor compounds are collected from a sample manifold with a probe (Figure 7-4). 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 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, 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.

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). 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.

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.

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.

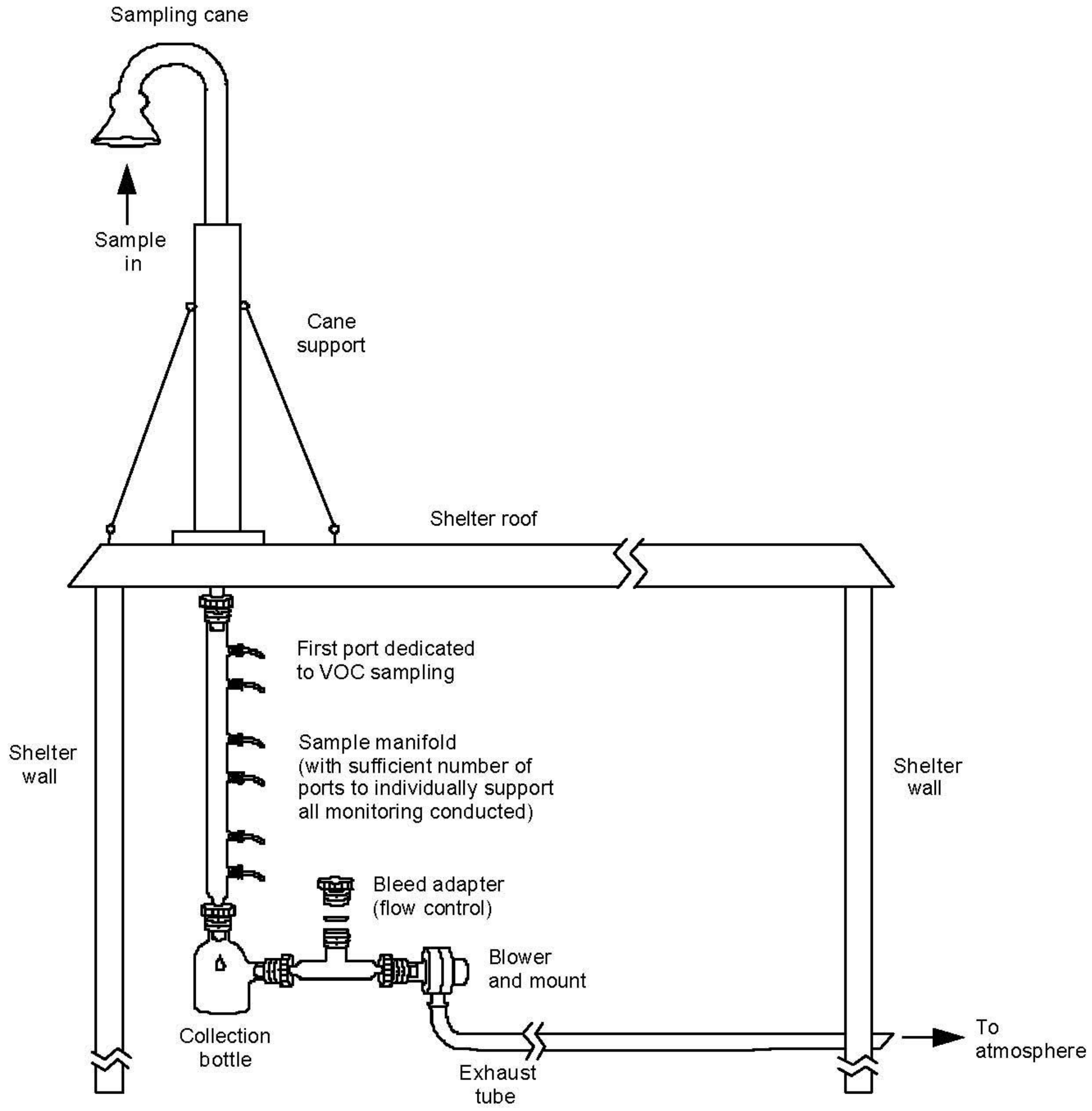


Figure 7-4. Example of a vertical configuration of a PAMS sample probe and manifold.

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. 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.

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.

Commercially available GC systems are typically configured with the appropriate analytical column(s) to separate the VOCs of interest. The user must characterize the performance of the system operation prior to use by conducting the pre-measurement system verification. 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.

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® 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 7-2 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:

(Eq. 7-3) $$C_A = RF\ (AC)$$

Where:

Ca = Concentration (ppbC)
RF = Response Factor, ppbC/area count
AC = Area Count

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:

(Eq. 7-4) $$RF = \frac{3(C_B)}{MAC}$$

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 an earlier section of this chapter. 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 (discussed in a previous section) 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.

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.

Manual Method for Collecting and Analyzing Volatile Organic Compound Ozone Precursor Samples

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. Additional discussion of sample collection methodology is provided in EPA Compendium Method TO-15.

Application of the manual methodology to the enhanced O_3 monitoring regulations requires the collection and analysis of a large number of canister samples. 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.

The following sections generally describe multiple-event and single-event canister sampling equipment, and their basic operation.

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 7-1.

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). Time-integration techniques generally involve the use of electronic and/or mechanical devices to facilitate sampling. 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.

Multiple-event Sample Collection Equipment

A typical multiple-event sample collection system configuration is presented in Figure 7-5. The multiple-event canister sample collection system is comprised of the following primary components:

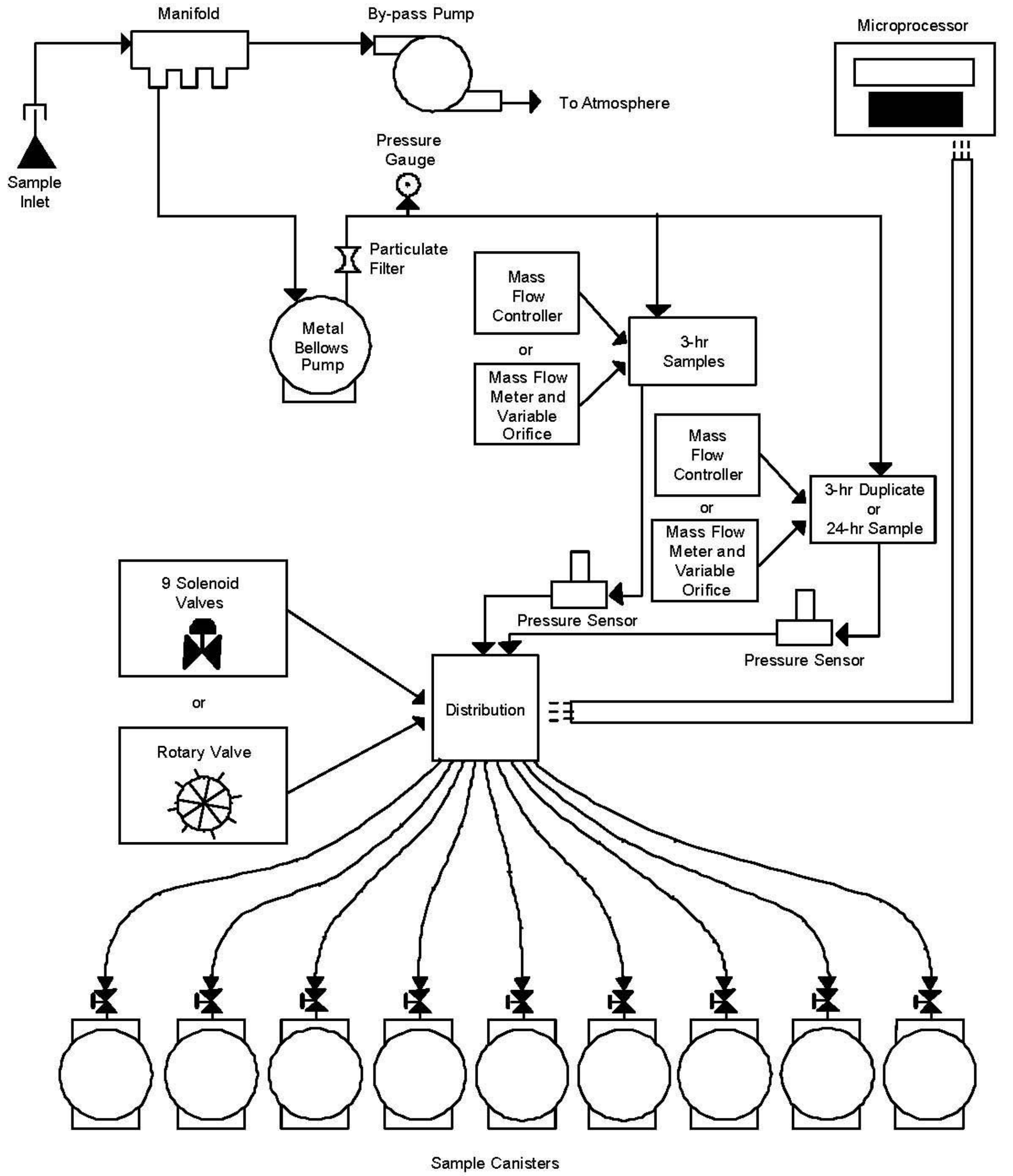


Figure 7-5. A typical Multi-event Sample Collection System.

<u>Inlet probe and manifold assembly</u> - Constructed of glass (see Figures 7-4) or stainless steel. Used as a conduit to transport sample air from the atmosphere at the required sampling height and distribute it for collection.

<u>By-pass pump</u> - 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 (20-40°C) 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.

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:

(Eq. 7-5)

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

Where:

F = flow rate (mL/min)
P = final canister pressure, atmospheres on a absolute basis
V = volume of the canister (mL) at one atmosphere
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:

(Eq. 7-6)

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

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.

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 above pertaining to canister sampling system certification). The canisters should also be determined to be clean before each use (refer to Section below 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.). Pressure sensors should be calibrated against a primary pressure measurement standard (i.e., manometer or absolute pressure gauge. 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).

Single-event Sample Collection Equipment

A typical single-event sample collection system configuration is presented in Figure 7-6.

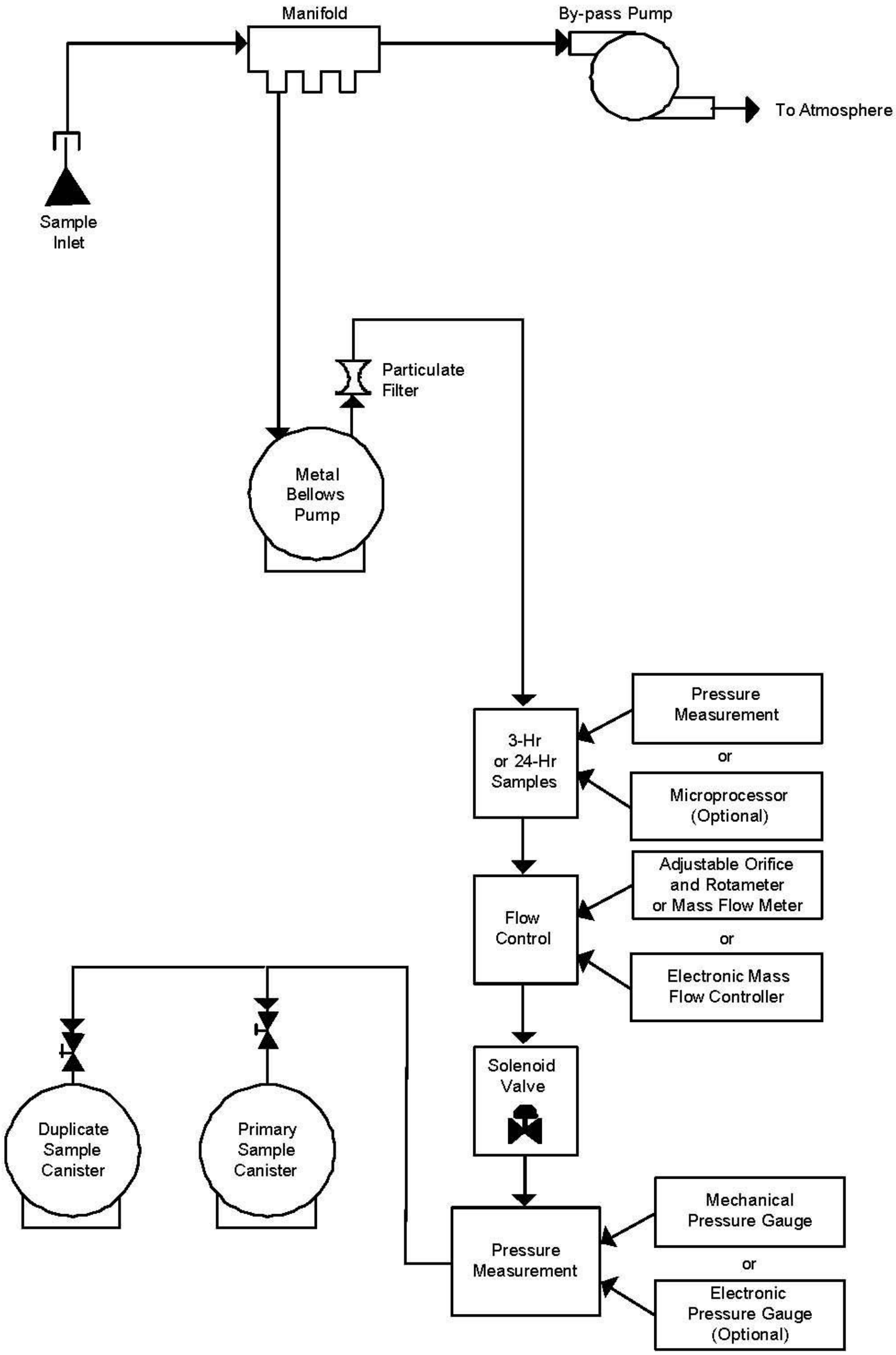


Figure 7-6. A typical Single-event Sample Collection System.

The single-event sample collection system consists of identical components to those for the multi-event sample collection system, except for the following:

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 & 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 (20-40°C) and humidity (0-100% relative).

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.

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 identical formula provided for multi-event sampling, above.

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 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 non-biasing, meaning that the sample collection system does not add to or subtract from the concentrations of the samples collected using it (refer to the Section above pertaining to canister sampling system certification). The canisters should also be determined to be clean before each use (refer to the Section below pertaining to canister cleaning).

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.

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 7-7 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.

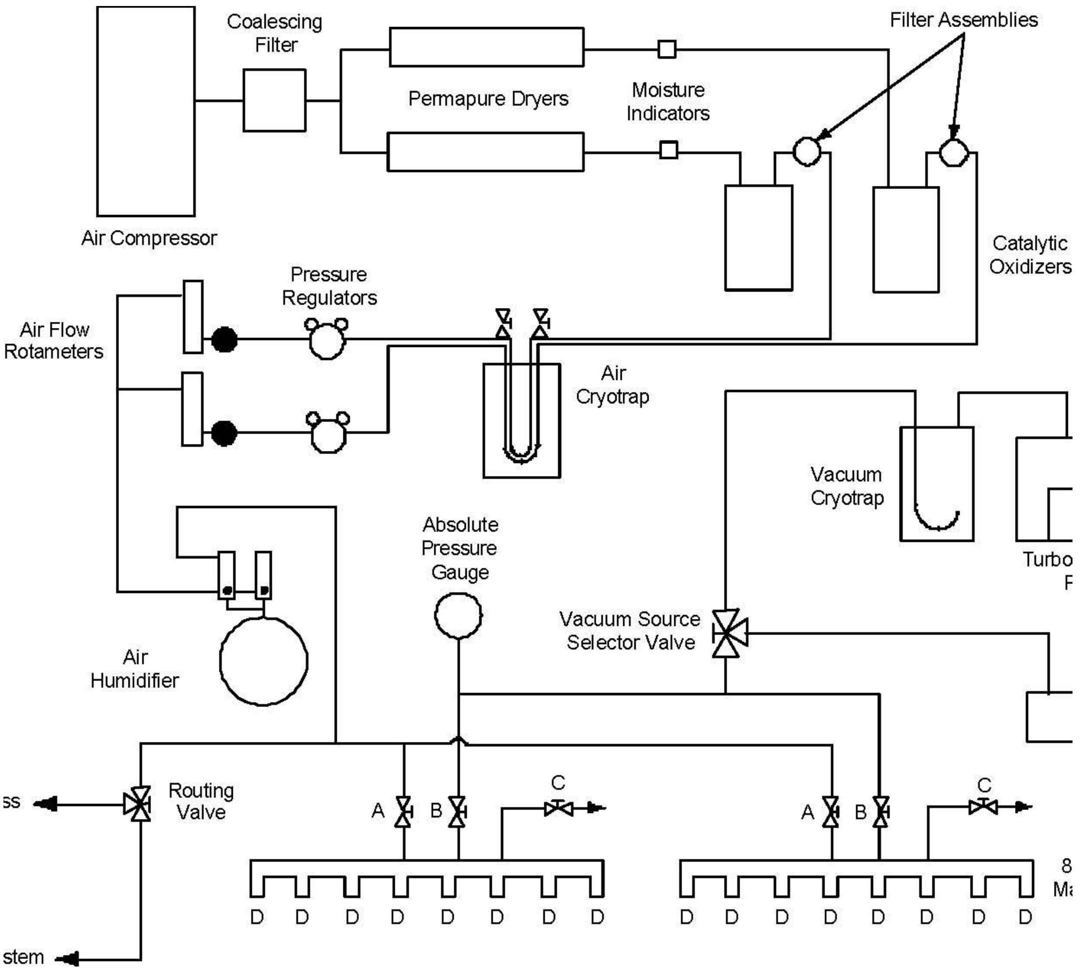


Figure 7-7. Schematic of a Canister Cleanup System.

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 7-7 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 7-7 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 multi-position 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.

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 blank sample is analyzed using the PDFID technique as described in the EPA Compendium Method TO-12. 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

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.

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, 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 re-analyses using different analytical systems for specific peak identification and confirmation.

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.

Precautions in the Use of Canisters

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.

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.

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. These systems should be certified before installation based on a canister sampling system certification protocol as described in detail in the Technical Assistance Document for Sampling and Analysis of Ozone Precursors (EPA/600-R-98/161).

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.

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 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.

Other considerations include vapor pressure of the VOC (vapor pressures above 0.5 mm Hg at 25°C store well in canisters as do halogenated hydrocarbons with similar vapor pressure properties), the canister type (aluminum or stainless steel), and presence of water (enhances the stability of polar organic compounds in stainless steel canisters).

Target analytes for which there is little stability information or for which storage stability characterization is questionable should be specifically tested for storage stability in the canisters. These tests should be performed under typical conditions of use.

There is a potential for physical adsorption as a mechanism for loss of VOCs from the vapor phase in canisters. 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.

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.

Diluted Samples

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

Canister Leakage

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

1. Faulty canister welds;
2. Leakage at the connection of the valve to the canister; and
3. 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. Over-tightening 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 over-tightening. 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.

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.

Sample Analysis

The analysis that follows the collection of whole air samples into SUMMA® canisters is identical to the procedures discussed in the Automated Sampling section. The only minor difference is that the canisters are sent to a central laboratory location for sample analysis as opposed to being analyzed on site.

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).

Quality Control and Quality Assurance for VOC Measurements

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.

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)."

General QC guidance can be found in the EPA QA Handbook. 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.

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 7-4. Technical information pertaining to manual multiple-event and single-event VOC sample collection systems automated GC systems are presented in previous Sections of this chapter.

Table 7-4. 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	Additional system purge with humid zero air 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 diff. 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.

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.

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 should be cleaned and checked for contamination and certified clean to 10 ppbC TNMOC.

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. 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.

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 7-5. 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.

Table 7-5. 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
Precision	Replicate sample analysis, manual or automated	10% of samples	Within ±25% RPD for target conc. > 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

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 previously requires instrumentation that is expensive, complex, and difficult to operate and maintain. Method TO-12 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." 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 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 earlier.

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 Method Code is 012, which 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 through C_{12} data, but also any compounds larger than C_{12} that are detected.

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, 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.

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.

Information on measuring NO and NO_2, including method and equipment descriptions, is presented in Chapter 9 of this manual.

Although not specifically required in 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.

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.

Information on measuring NO_y, including measurement principle and procedures and equipment descriptions, is presented in Chapter 9 of this manual.

Methodology for Determining Carbonyl Compounds in Ambient Air

Determination of ambient concentrations of carbonyl compounds is a requirement of 40 CFR Part 58, 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 EPA Compendium Method TO-11A. Method TO-11A 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. 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. Sample analysis is accomplished using high performance liquid chromatography (HPLC) with ultraviolet/visible detection.

Under 40 CFR Part 58, 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 7-1. The sample collection frequencies necessitate the use of an automated multiple-event sample collection approach similar to the system used for VOC sampling as discussed in the previous section of this chapter.

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:

1. The ozone reacts with the 2,4-dinitrophenylhydrazine (DNPH) on the cartridge, making the DNPH unavailable for derivatizing carbonyl compounds;
2. The ozone also degrades the carbonyl derivatives formed on the cartridge during sampling; and

3. If the analytical separation is insufficient, the DNPH degradation products can co-elute 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:

(Eq. 7-7) $$O_3 + 2I^- + \mathrm{H2O}\ \tau\ I_2 + O_2 + 2OH^-$$

where:

O_3 = ozone (ambient)
H_2O = water (ambient)
I- = the iodide ion from potassium iodide forming molecular iodine (I_2)
O_2 = oxygen (O_2)
OH^- = 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.

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 as it is for VOCs (see Figure 7-10) and pulled through the scrubber by an oil less vacuum pump. Ozone in the sample air is converted (i.e., scrubbed) by the chemical reaction previously described.

The Denuder O 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 to100,000 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.

Figure 7-8 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.
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.

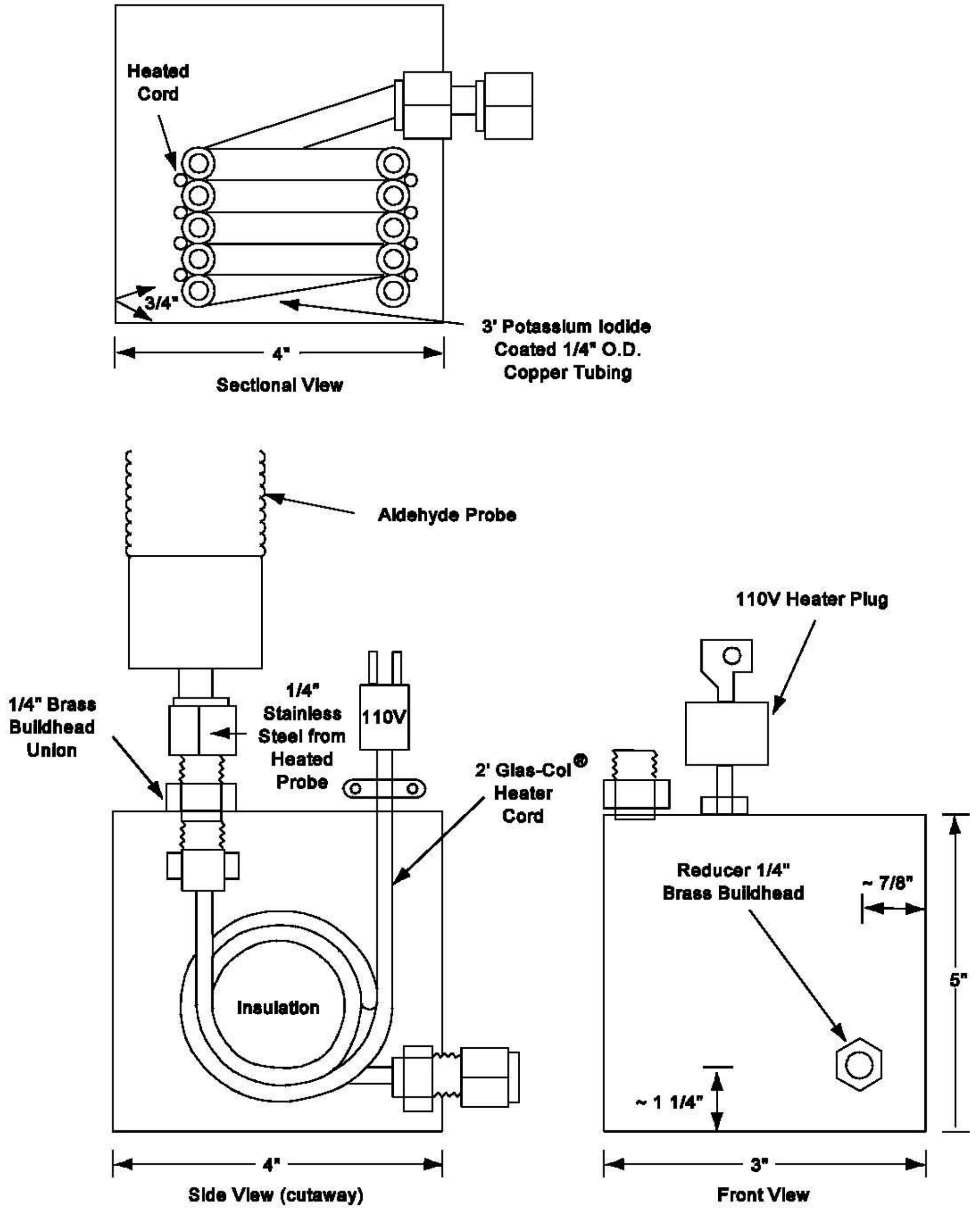


Figure 7-8. Cross-Sectional View of the Denuder O_3 Scrubber

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 7-10).
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 Method TO-11A sampling procedures.

Cartridge Ozone Scrubber

The Cartridge O 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 7-10) and pulled through the O_3 scrubber by an oil less vacuum pump. Ozone in the sample air is converted (i.e., scrubbed) by the chemical reaction previously described. 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.

Figure 7-9 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.

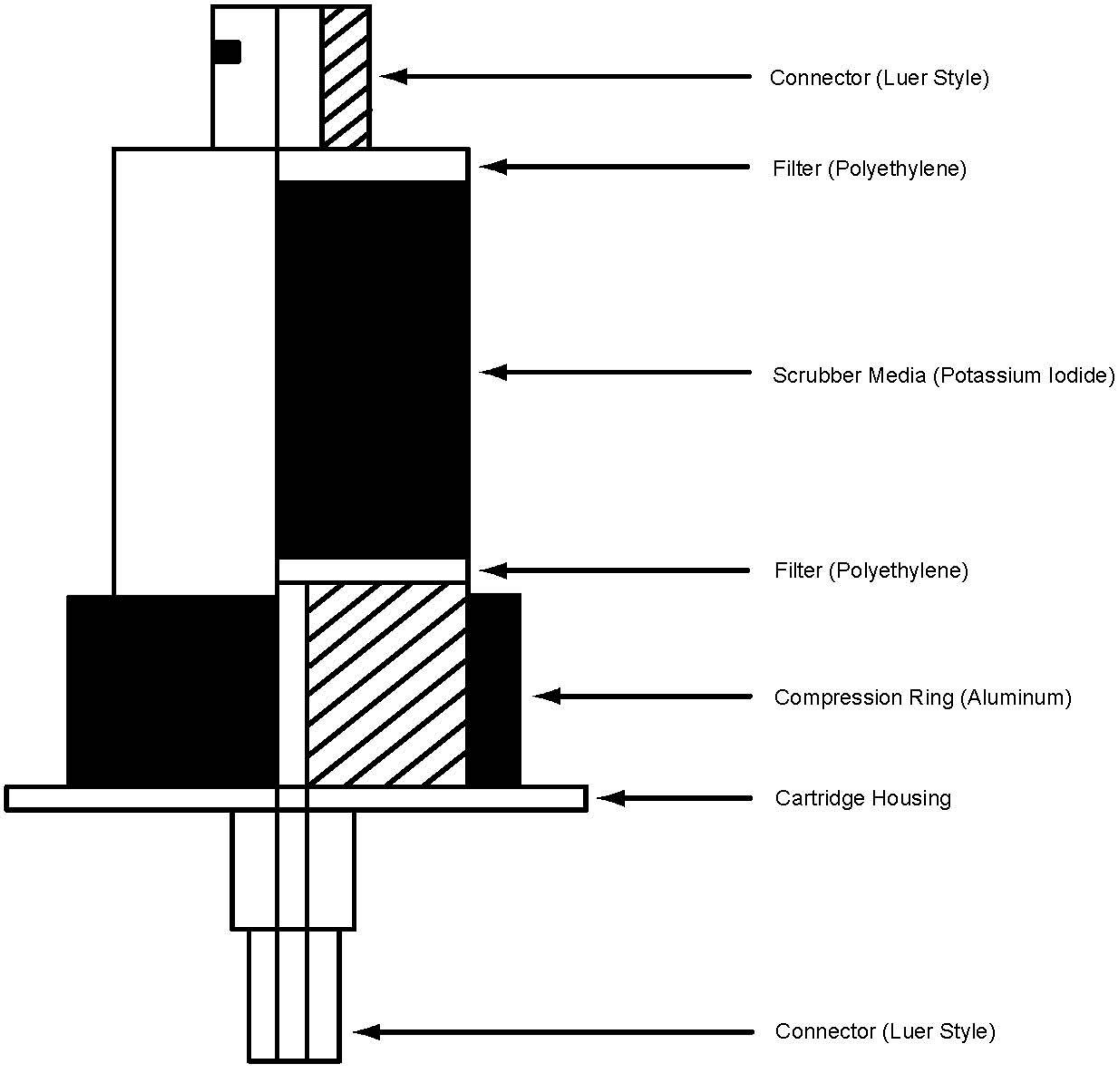


Figure 7-9. Cross-Section View of the Cartridge O Scrubber

Cartridge Ozone Scrubber Operational Procedure

Recommended procedural steps for operation of the Cartridge O_3 Scrubber are as follows:

1. Connect the inlet of the Cartridge O_3 scrubber to the sample probe and distribution manifold (see Figure 7-10).
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 Method TO-11A sampling procedures. **Note: Heating of the cartridge ozone scrubbers to 35°C may be advisable under certain circumstances to prevent condensation of water.**

Multiple-event Sample Collection Systems

The use of solid sorbent cartridge sample collection systems to satisfy the sample collection frequencies specified in Table 7-1 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.

Multiple-event Collection System Equipment

A typical multiple-event sampling system configuration is presented in Figure 7-10. The multiple-event cartridge sampling system is comprised of the following primary components:

Inlet probe and manifold assembly - Constructed of glass (see Figure 7-4) 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 oil less 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) 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.**

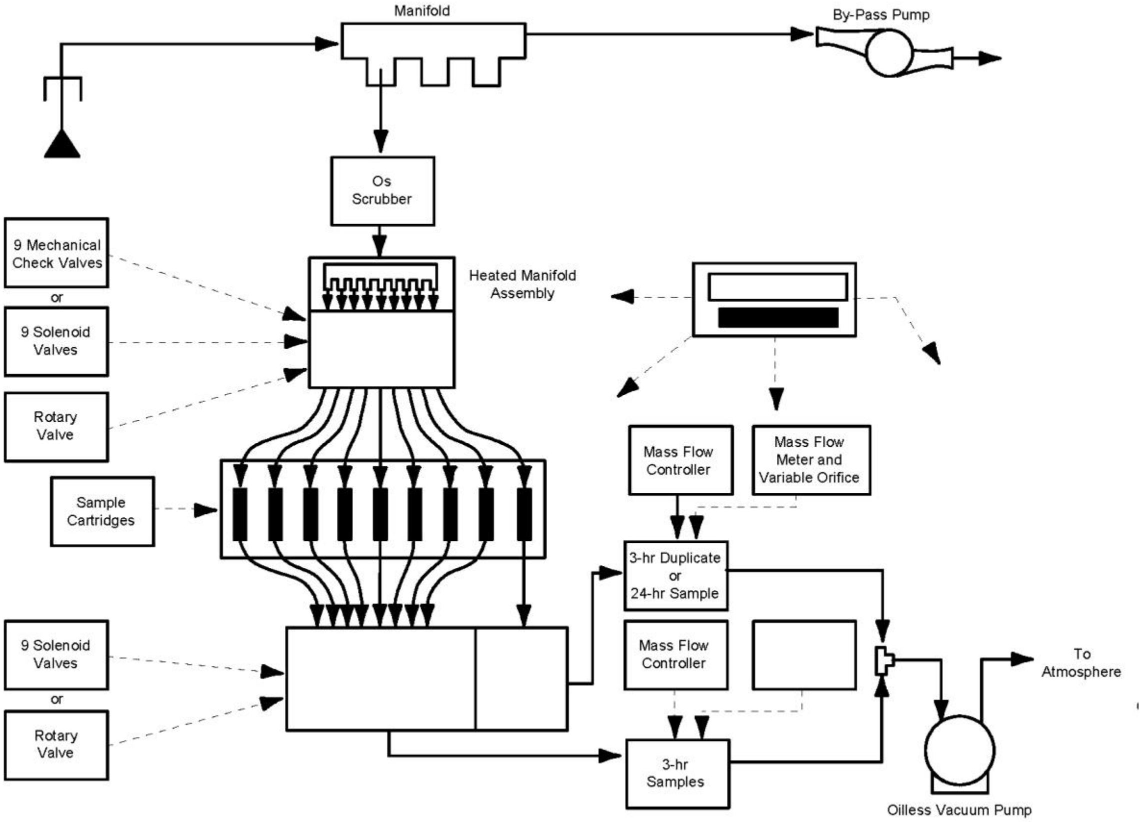


Figure 7-10. Schematic of a Typical Multiple-Event Carbonyl Cartridge Sampling System

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:

(Eq. 7-8)

$$F = \frac{V \times 1000}{T \times 60}$$

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 per 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:

$$F = \frac{168 \times 1000}{3 \times 60} = 933 \text{ milliliters/minute}$$

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 previously 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.

A sample probe and manifold assembly should be used to provide a representative air sample for collection and subsequent analysis. The specifications are identical to those of the VOC apparatus. Sample probe and manifold assemblies are commercially available or can be custom fabricated.

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*. A description of each type of blank is as follows:

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 three standard deviations (0 + 3s) for the group of three laboratory blanks are 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.

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 three standard deviations (0 ± 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 three 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 Fg/cartridge*
- Acetaldehyde: <0.10 Fg/cartridge
- Acetone: <0.30 Fg/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 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.

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.

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.

Quality Assurance and Quality Control

General quality assurance and quality control requirements are provided in Section 13.6 of Method TO-11A. 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 7-6 provides the quality assurance and quality control procedures consistent with Method TO-11A.

Table 7-6. 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

PAMS Meteorological Monitoring

The 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. Currently, the list of meteorological variables includes: wind direction, wind speed, temperature, humidity, atmospheric pressure, precipitation, solar radiation, UV radiation, and mixing height. Table 7-7 provides an overview of the requirements for monitoring these variables.

Table 7-7. 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.

Surface Meteorological Monitoring

A minimum level of surface meteorological monitoring is required for each PAMS site regardless of the site type (see Table 7-1). 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.

The selection of an appropriate site for the surface meteorological measurements depend 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. 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.

System specifications for the surface measurements are given in Table 7-8. 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 7-8. System Specifications for Surface Meteorological Measurements[a]

Variable	**Range**	**Accuracy**	**Resolution**	**Constants Time/Distance**
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.*

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.

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 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.

Table 7-9. 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

The upper-air measurements are intended for more macro-scale application3 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.

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.

Additional information for all the topics discussed in this chapter can be found in the Technical Assistance Document for Sampling and Analysis of Ozone Precursors (EPA/600-R-98/161) and the “Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements" for recommended procedures for quality assurance and audit activities. The procedures provided in "On-Site Meteorological Program Guidance for Regulatory Modeling Applications" should be followed for processing of meteorological measurements.

References

Technical Assistance Document for Sampling and Analysis of Ozone Precursors (EPA/600-R-98/161)

Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV.

Chapter 8

Carbon Monoxide Measurement Principle and Calibration Procedure

The prescribed procedure for measurement of carbon monoxide (CO) consists of a reference measurement principle and calibration procedure. Any analyzer that uses the specified measurement principle, meets the prescribed specification, and is calibrated in accordance with the specified calibration procedure may be designated a Reference Method by EPA. The measurement principle utilizes the phenomenon of molecular absorption of nondispersive infrared (NDIR) radiation. Nondispersive refers to the fact that the emissions from the infrared energy source are not dispersed into component wavelengths. A broad wavelength band of infrared emissions is used instead of employing monochromatic filters or diffraction gratings to isolate one particular wavelength (as is done in UV photometry for ozone). The calibration procedure consists of checking the analyzer's carbon monoxide response by "challenging" the analyzer with known concentrations of carbon monoxide.

While the obvious problems of widespread elevated concentrations have been largely solved for some criteria pollutants, problems related to particulate matter (PM), ozone (O_3), and toxic air pollutants remain. It is now clear that even very low air pollution levels can be associated with adverse environmental and human health effects. As a result, the use of highly sensitive commercial air pollutant monitors for the characterization of the precursor gases CO, SO_2, and total reactive oxides of nitrogen (NO_y) in a new national core monitoring network (NCore). The high sensitivity CO and SO_2 analyzers are fundamentally the same as those designated as Federal Reference and Equivalent methods (http://www.epa.gov/ttn/amtic/criteria.html), but with Precursor Gas Technical Assistance Document (TAD) modifications to improve sensitivity and accuracy or reduce interferences. The use of such precursor gas analyzers in the NCore network will still allow determination of compliance with the NAAQS, but will provide measurements at much lower detection limits than are achievable by current monitors. The implementation of high sensitivity monitoring for CO, SO_2, and NO_y in the NCore network will require installation of new analyzers at selected sites, and implementation of new monitoring, calibration, and data acquisition procedures. The purpose of Precursor Gas TAD is to provide state, local, and tribal (S/L/T) agencies with guidance on the equipment, procedures, data acquisition, and quality assurance/quality control (QA/QC) efforts needed to properly implement high sensitivity precursor gas monitoring.

In this chapter, the discussion will begin with the carbon monoxide measurement principle and calibration procedure for use with traditional ambient monitors; followed by a similar discussion as it relates to high sensitivity, precursor gas monitoring. Overtime, high sensitivity analyzers will increasingly be brought online; however, traditional analyzers will remain part of the NAAQS monitoring network for many years to come.

Measurement Principle

When certain molecular species are exposed to a broad band of infrared radiation, they have characteristic absorption peaks centered at a particular region within that band of infrared spectrum (Figure 8-1). The centers of these absorption peaks are characteristic for individual chemical compounds. Table 8-1 is a list of several gaseous pollutant compounds' band center locations. As the table indicates, CO has characteristic absorption peaks at 2.3 and 4.6 µm. Carbon monoxide concentrations are determined by using a filter which allows radiation of a fairly wide wavelength band to be emitted from the infrared energy source, while simultaneously narrowing that band to the characteristic absorption band of carbon monoxide. This band-narrowing filter is termed a "band pass" filter, due to the characteristics mentioned above. Concentrations of carbon monoxide can be measured due to the decrease in energy resulting from the absorption of some of the infrared energy. The less energy exiting a sample cell containing carbon monoxide, the higher the concentration of that gas, due to the absorption of energy by the gas molecules (i.e., infrared absorption is directly proportional to carbon monoxide concentration).

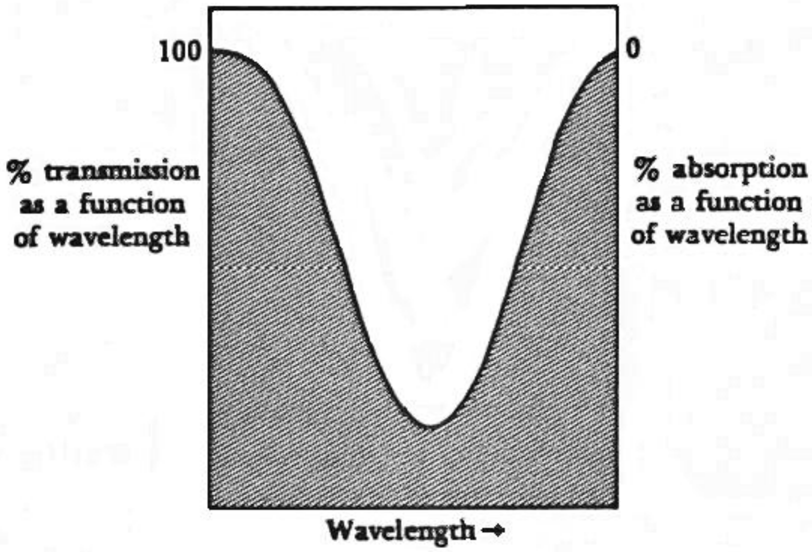


Figure 8-1. An absorption curve.

Table 8-1. Infrared band centers of some common gases.

Gas	Location of band centers (µm)	Wave number (cm^{-1})
NO	5.0 to 5.5	1800 to 2000
NO_2	5.5 to 20	500 to 1800
SO_2	8 to 14	700 to 1250
H_2O	3.1 5.0 to 5.5 7.1 to 10	1000 to 1400 1800 to 2000 3200
CO	2.3 4.6	2200 4300
CO_2	2.7 5.2 8.12	850 to 1250 1900 3700
NH_3	10.5	950
CH_4	3.3 7.7	1300 3000
Aldehyde	3.4 to 3.9	2550 to 2950

Equipment

A typical Luft-type NDIR carbon monoxide analyzer is shown in Figure 8-2. The analyzer consists of two identical infrared sources, bandpass filters, a beam chopper, a sample cell, a comparison or reference cell, a detector cell, a sample-handling system, an electronics section, and in some instruments an interference cell or filter cell for reducing interferences.

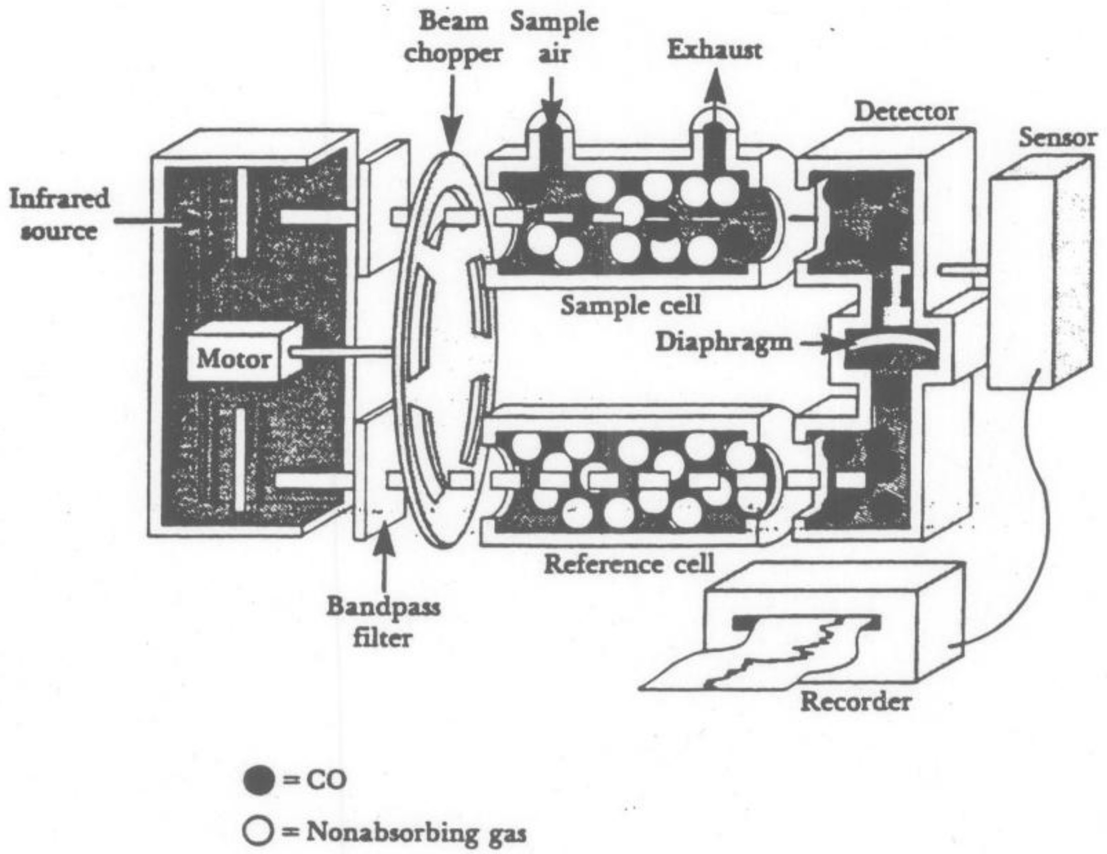


Figure 8-2. Typical Luft-type carbon monoxide NDIR analyzer.

The source for the infrared radiation used in detection usually is a heated wire. As mentioned above, this infrared emission is altered by a bandpass filter to render the radiation useful for CO analysis. The chopper is merely a rotating wheel or blade which pulses the infrared emissions. By so doing, it allows the detector to better differentiate among the infrared signal of interest and other superfluous signals, as well as permitting better amplification of the detector's output.

The two infrared rays, having identical intensities, are passed through separate reference and sample cells. The reference cell contains a nonabsorbing gas, usually dry nitrogen. Hence, the infrared ray passing through the reference cell will have no dissipation in its energy. The sample cell allows the air sample to be measured for CO content. If CO is present in the sample cell, some of the infrared energy will be absorbed. Therefore, the energy emerging from the sample cell will be less than the energy exiting the reference cell.

The detector cell consists of two compartments filled with equal concentrations of CO. These two compartments are separated by a thin metal diaphragm whose movement is detected by an induction transducer. The resultant infrared signal from the reference cell strikes one compartment of the detector cell, while the resultant infrared signal from the sample cell strikes the other side of the detector cell. The detector functions in the following manner: when a molecule of CO absorbs infrared radiation, it absorbs the energy of that radiation. This increase in energy results in the CO molecule becoming more active (it begins to vibrate and move more rapidly). This increase in molecular activity causes the CO gas to expand. However, because the gas is contained in a rigid compartment, expansion results in an increase in the pressure of the CO gas within the cell. When CO is present in the sample cell, the compartment receiving the reference signal receives more infrared energy and, subsequently, more energy is absorbed by the CO molecules contained there. This results in a higher gaseous pressure on the reference side of the detector relative to the sample side of the detector. The thin metal diaphragm naturally bends toward the area of lower pressure (the sample side), and the amount of this deflection is measured by means of the induction transducer. This signal is then amplified and used to activate the concentration readout device.

Certain gaseous molecules have the capacity to absorb energy in the same spectral region as CO. When these molecules are present in the sample gas, they cause a positive interference in the CO concentration determination. To eliminate the effects of these CO measurement interferences, certain additions or modifications can be applied to CO analyzers. These modifications are discussed in the subsequent section concerning interferences (APHA 1977).

Auxiliary sections of the instruments include the sample-handling system and the electronic section. Components of the sample-handling system usually include a flow regulator, air pump, gas manifold, moisture removal or constant humidity system, particulate matter filter, and flow meter. The electronic section incorporates an amplifier, demodulator, output filter, zero control, span control, and other controls for internal adjustments.

Calculations

Carbon monoxide analyzers generally read out directly in ppm. Before the direct concentration readout is utilized, it is necessary to calibrate the analyzer using known concentrations of gases. If it is necessary to convert CO concentrations from ppm to milligrams per cubic meter (mg/m^3), the following conversion factor can be used:

(Eq. 8-1)
$$\frac{\text{mg CO}}{\text{m}^3} = \text{ppmCO} \times 1.14$$

If the analyzer does not readout in ppm, but rather in $\frac{\text{mg CO}}{\text{m}^3}$, the following factor can be used to derive the ppm CO concentration:

(Eq. 8-2)
$$\text{ppmCO} = \frac{\text{mg CO}}{\text{m}^3} \times 0.874$$

Calibration Procedure

Calibration consists of determining the response of the instrument to various known concentrations of carbon monoxide generated from compressed gas cylinders and preparing calibration curves or tables. The analyzer is set up in its sampling mode and "zero" gas is introduced via the analyzer's sampling line into the sample cell. The zero adjustment control is set to give an instrument readout reflecting zero concentration.

The next step in calibration is the introduction of the "span gas". This gas should have a CO concentration that is approximately 80% of the instrument's operating range. The instrument's span adjustment control is set so that the instrument's output reflects the span gas concentration. At least three other concentrations of carbon monoxide covering the analyzer's operating range are then introduced to check linearity of response. CO cylinder gases may consist of CO and dry nitrogen if they are to be diluted to at least 100:1 with air when preparing calibration gases. If CO cylinder gases are to be diluted less than 100:1 when preparing calibration gases, the cylinder should consist of CO and air. If a strip chart recorder is used with the analyzer, it should be adjusted to reflect the calibration standards. A calibration curve should be prepared for each instrument calibration. A typical calibration curve for an ambient CO monitor is shown in Figure 8-3. The instrument's operating manual should be consulted for additional recommendations concerning calibration.

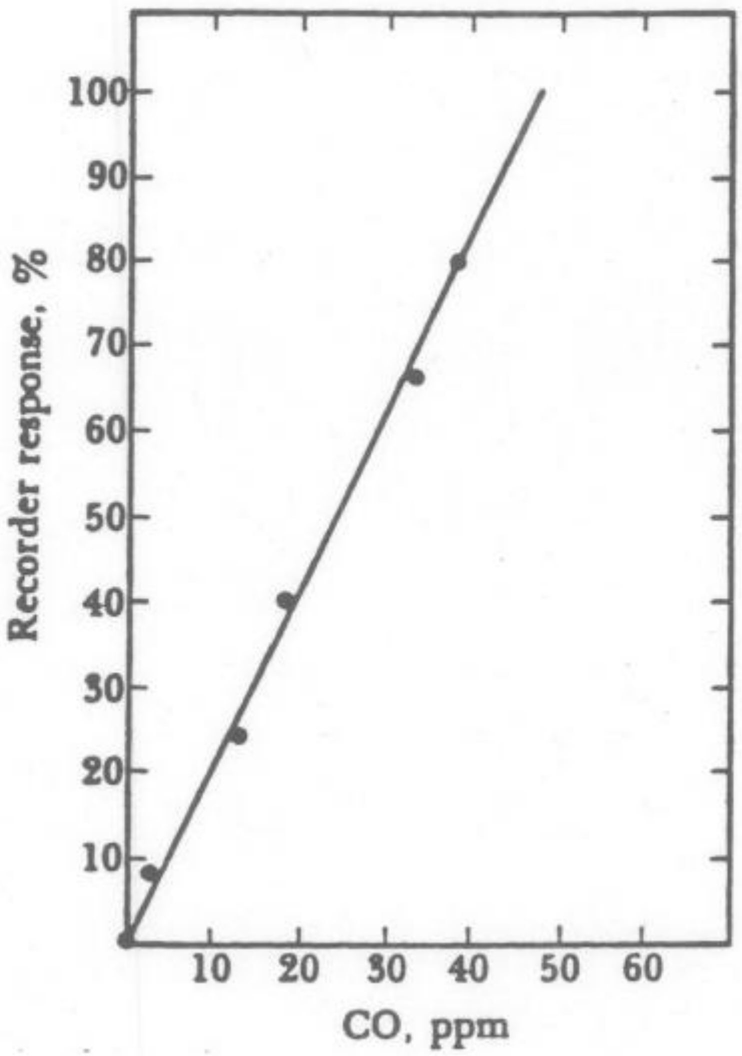


Figure 8-3. Typical calibration curve.

Reference Measurement Principle - Characteristics and Capabilities

Advantages

Nondispersive infrared analyzers have the advantage of being relatively independent of ambient temperature and flow rate changes. Also, they have short response times, and they require no chemicals or ancillary equipment (other than calibration gases).

Interferences

Interferences may arise from gases that absorb infrared radiation in wavelength bands that overlap that of carbon monoxide. Some of the possible interferences are carbon dioxide, water vapor, methane, and ethane. Carbon dioxide and water vapor pose the major interference problems due to their common occurrence in the atmosphere, and also due to the probability that their concentrations will exceed the discrimination ratio (discrimination ratio equals the concentration of interferences required to give an instrument response which is equivalent to 1 ppm of carbon monoxide).

Water Vapor

Water vapor absorbs infrared radiation to a varying degree throughout the infrared region. Its presence can be a primary, positive interference in Luft-type NDIR instruments.

Various measures may be taken to minimize moisture interference. The most obvious is a drying tube device in the sample inlet section of the analyzer. This tube is filled with silica gel or other suitable desiccants. The sample air passed over the desiccant before it enters the absorption cell. Converse to this method, the sample air is passed through a saturator maintained at a constant temperature. The saturator maintains a constant humidity level in the sample air. This constant humidity is also added to the calibration gases, thereby negating the moisture effects on concentration readings.

Refrigeration units in the sampling inlet systems are often used in commercial analyzers to maintain a constant, low humidity level. By cooling the sampled air, the moisture is condensed and, subsequently, removed from the air stream.

Moisture-eliminating devices and constant-humidity systems, when employed, should be used on all gases entering the analyzer (i.e. calibration, zero, span gases, and air samples).

Two other methods commonly employed to remove water vapor interference involve correcting the action of water vapor on the absorption phenomenon. Narrow bandpass optical filters can be used to remove those wavelengths most sensitive to water vapor from the irradiation beam. In a similar manner an "interference cell" containing water vapor and other principal interferences can be placed in line, between the infrared source, and the sample cell. The interference cell absorbs, and therefore eliminates, those wavelengths which overlap the CO absorption band. This prevents the overlapping wavelengths from reaching the detector and affecting the results. Figure 8-4 shows a diagram of an instrument that uses an interference cell.

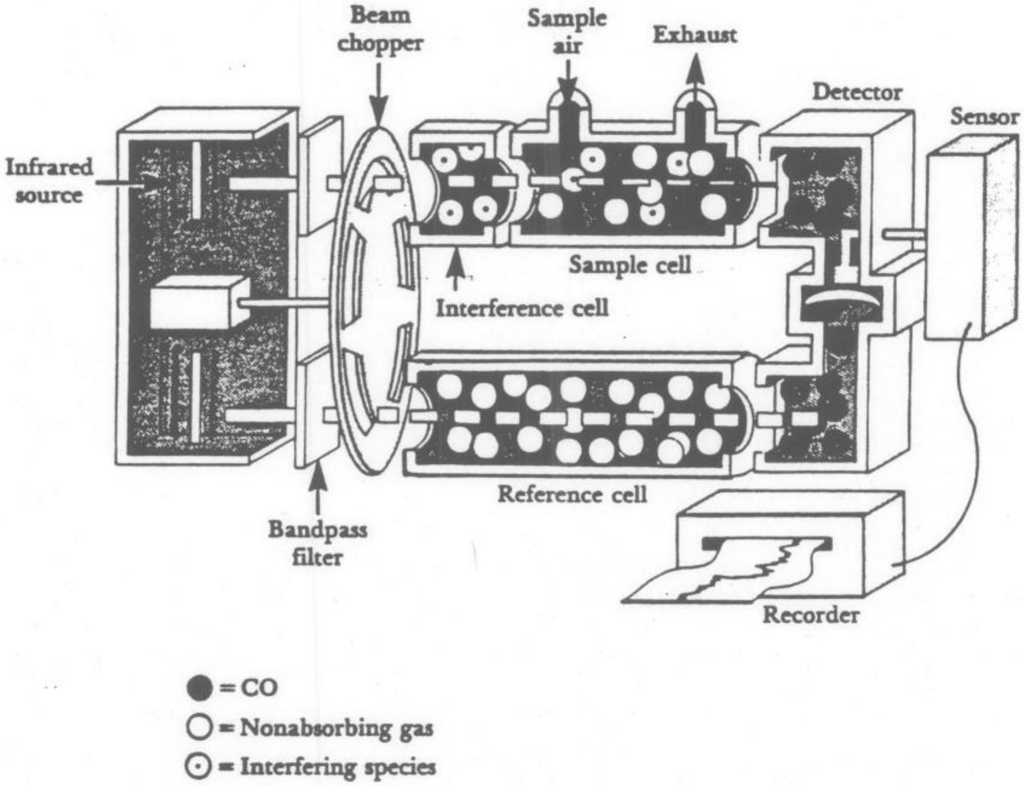


Figure 8-4. NDIR CO analyzer employing an interference cell.

Carbon Dioxide

Concentrations of carbon dioxide (CO_2) normally found in ambient air (approximately 400 ppm) do not interfere with CO measurements. However, in air grossly contaminated with combustion products, CO_2 (in excess of 1000 ppm) could result in positive interferences of 1 ppm or higher.

Measures to eliminate CO_2 interferences are essentially the same as for water vapor. The use of a narrow bandpass filter or of carbon dioxide in an interference cell is equally effective in the elimination of interference due to CO_2 as it is for water vapor interference.

Another method of alleviating the interferences, due to both CO_2 and water vapor (as well as other interferences), is negative filtering. Negative filtering employs detector cells mounted in series rather than in parallel. Figure 8-5 depicts a negative-filter NDIR analyzer. The front and rear measuring chambers are constructed so that their pressures are equal when no CO is present in the sample cell. At this “steady state” condition, the thin metal diaphragm is balanced between the two cells. As previously explained, these detector cells are filled with a concentration of CO. Negative filtering is involved with the phenomenon of carbon monoxide absorbing the majority of the infrared energy of its particular absorption band peak at the center of that peak. As the infrared beam is passed through the sample cell containing carbon monoxide, much of the energy at the center of the peak is dissipated. Therefore, the energy reaching the front detector cell is such that not much energy can be absorbed by the CO molecules there. By the time the beam reaches the rear detector cell, all of the energy at the center frequencies will be gone, so for any absorption to take place CO must absorb those frequencies found at the edges of the peak. This results in the rear detector cell being more activated than the front cell. Hence, the difference in pressures will cause the diaphragm to deflect toward the front cell. Negative filtering serves to negate interferences by narrowing, in effect, the band path to just that of CO and excluding the outlying wavelengths characteristic of the various interferences (Jahnke and Aldina 1979).

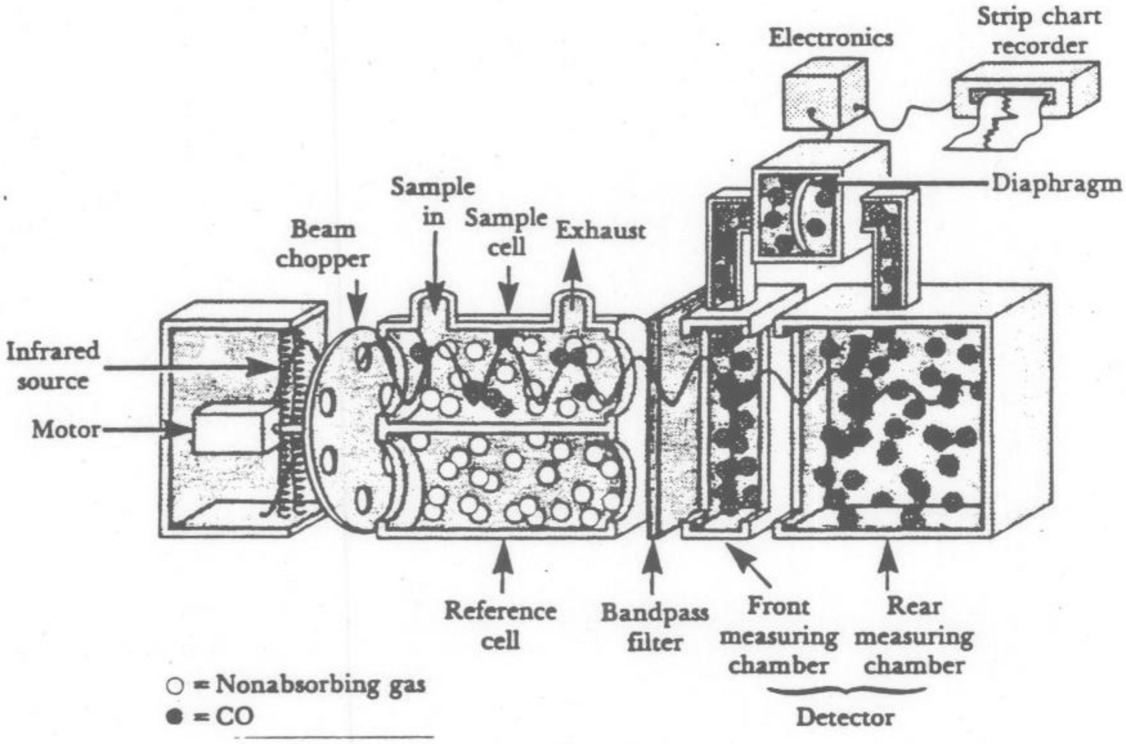


Figure 8-5. Negative-filter NDIR analyzer.

In another type of analyzer (Figure 8-6), sample air continuously flows through a reference cell as well as through a sample cell. However, before flowing through the reference cell, the sample air passes through a catalytic converter that transforms any CO present in the sample air to CO_2. Therefore, any interfering species present in the sample cell are also present in the reference cell in the same concentration, except possibly for CO_2, since any CO present in the sample air is passed converted to CO_2 before entering the reference cell. However, because of the large ratio of CO_2 to CO in ambient air, any difference between the amounts of CO_2 present in the reference cell and the sample cell is negligible. Sample air in the reference cell allows the absorption of infrared radiation by interfering species in the sample cell to be offset by interfering species in the reference cell.

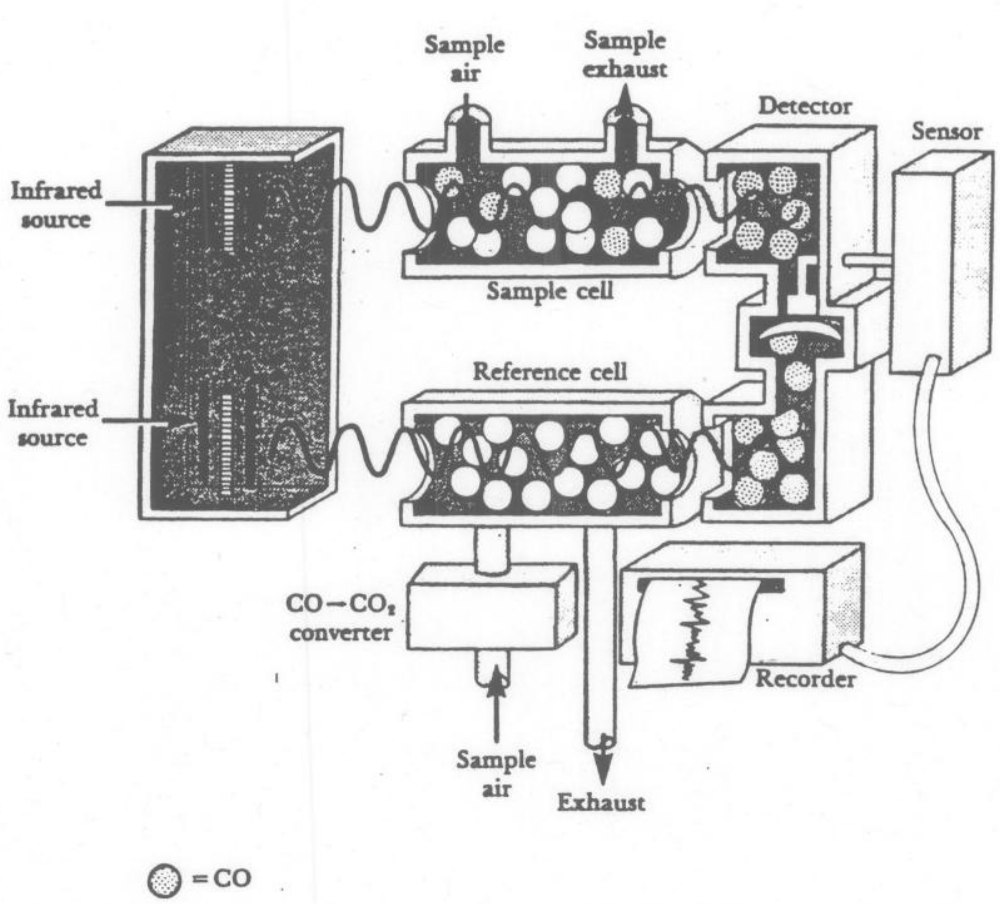


Figure 8-6. Flowing reference-cell NDIR CO analyzer.

A more recent modification, the m*icroflow* detector, is similar to the Luft detector, but employs a small orifice between the two detection chambers. Instead of differential pressure, the resulting flow is measured. A thermocouple arrangement in the orifice is used for this purpose. This detector is relatively immune to mechanical vibration, but is not as simple as the solid state type.

In an effort to develop a NDIR CO analyzer which does not have the limitations of the Luft-type NDIR analyzers, an instrument based on gas-filter correlation has been developed. In an NDIR gas-filter correlation analyzer, chopped radiation from an infrared source alternately passes through a cell filled with CO (the reference beam) and a cell filled with nitrogen that is aligned with a neutral density filter (the measure beam) before entering the analyzer's sample chamber. After leaving the sample chamber and passing through a bandpass filter, the alternating radiation beams are measured by an electronic detector to obtain the carbon monoxide concentration of the sample air (Figure 8-7).

The CO cell absorbs any radiation that can be absorbed by CO present in the sample are contained in the sample chamber. No absorption takes place in the nitrogen cell. However, after leaving the nitrogen cell, infrared radiation passes through a neutral density filter that reduces its energy to equal the remaining energy of the infrared beam that passed through the CO cell.

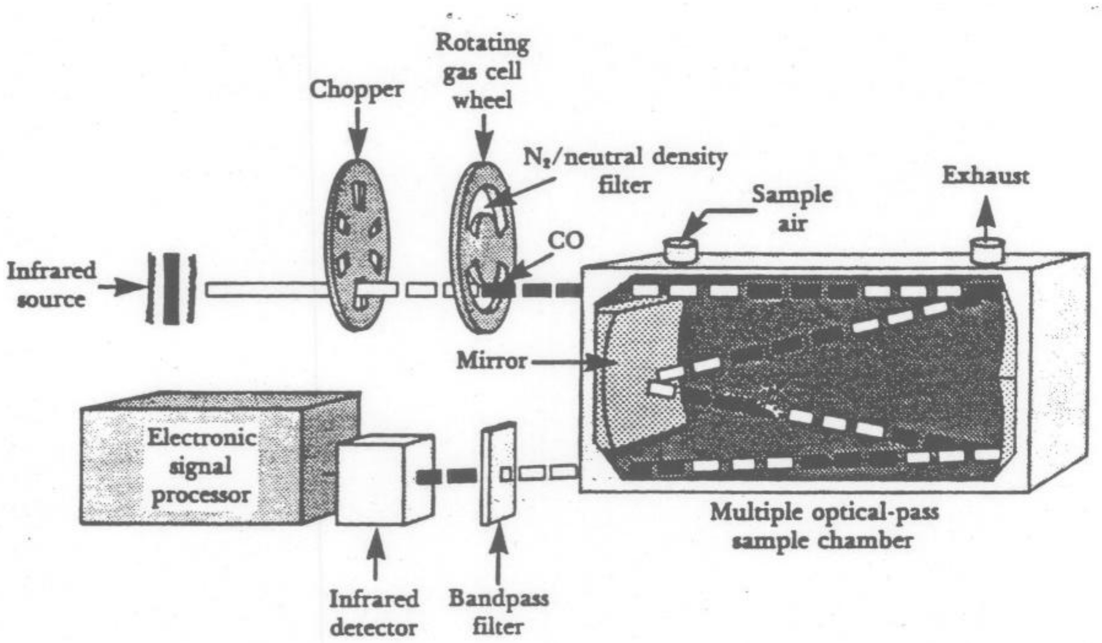


Figure 8-7. Gas-filter correlation NDIR CO analyzer.

The detector determines the CO concentration of the sample air by measuring the difference in energy of the two infrared beams. Any energy difference creates an electronic signal that is proportional to CO concentration. If no CO is present in the sample air, no absorption of the infrared beam that passed through the nitrogen cell takes place. Therefore, the energies of both beams measured by the detector will be equal, and no electronic signal related to CO concentration will be generated (Figure 8-8a). However, if CO is present in the sample air, some of the infrared radiation that passed through the nitrogen cell will be absorbed. Therefore, its energy will be less than the energy of the infrared radiation that passed through the CO cell, and an electronic signal will be generated by the detector (Figure 8-8b).

For a component of the sample air having a spectral pattern that perfectly correlates (overlaps) the spectral patter of CO, the analyzer would erroneously indicate a positive CO concentration (Figure 8-8c). Conversely, the analyzer would erroneously indicate a negative CO concentration for a sample air component having a spectral pattern that perfectly anti-correlates (does not overlap) the spectral pattern of CO (Figure 8-8d). This is caused by more infrared energy being lost from the reference beam than from the measure beam, because absorption of the reference beam takes place at higher radiation intensities than does absorption of the measure beam.

Fortunately, spectra of sample air components are usually uncorrelated (neither perfectly correlated nor perfectly anti-correlated). Components of the sample air having totally uncorrelated absorption spectra (having equal amounts of correlated and anti-correlated absorbances) absorb the same amounts of infrared radiation in both the measure and reference beams, thus producing no erroneous indication of CO concentration (Figure 8-8e). However, usually the spectra of sample air components are not totally uncorrelated, so a small CO interference could occur.

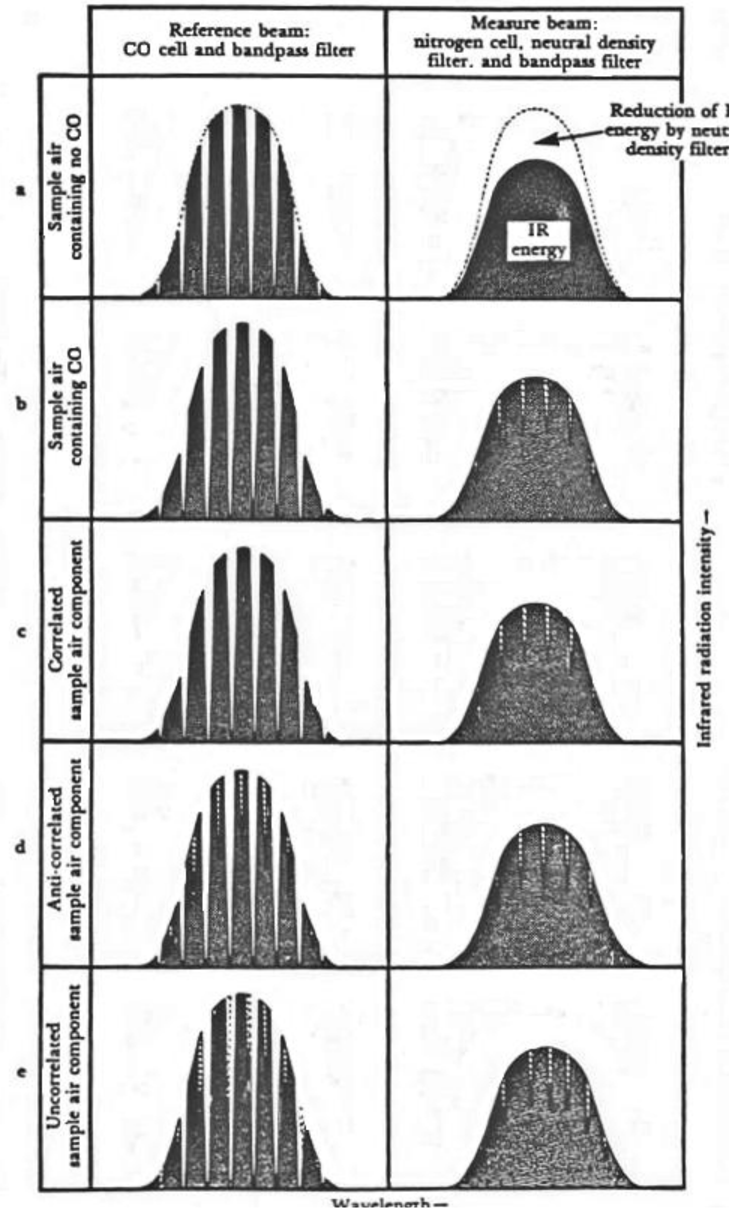


Figure 8-8. Infrared energy spectra received by the detector.

Today, FRM-designated instruments are available from several manufacturers using both Luft-type and GFC methods; however in ambient applications the GFC method is almost exclusively used.

Range and Sensitivity

The range of an acceptable instrument for use as a reference method is required to be from 0 to 50 ppm (957 mg/m^3). Ranges up to two times the required range may also be used if appropriate approval has been given by EPA. Most commercially available instruments are designed for measurements up to at least 100 ppm (114 mg/m^3).

The available range for a given type of instrument is function, principally, of analyzer design, and is determined mainly by the length of the sample cell and the operating pressure used. A decrease in either leads to an increase in range, but usually with a corresponding decrease in sensitivity.

Sensitivity in the NDIR technique is limited principally by electrical and optical noise and by performance of the signal processing components. Generally, the concentration change which will result in a change in output display is 0.5 ppm or less, when using the 0 to 100 ppm detector range. For example, the Lower Detectable Limit (LDL) for a TECO 48C CO analyzer is 0.04 ppm.

The performance specifications required for automated CO analyzers currently in use are shown in Table 8-2. A test analyzer must exhibit performance better than, or equal to, the specified values for each of specification (except for Range). For a method having more than one selectable range, one range must be that specified in Table B-1 of 40 CFR Part 53 Subpart B and shown here in Table 8-2.

Table 8-2: Performance specifications for CO automated method (Reproduced as an excerpt from Table B-1 of 40 CR Part 53 Subpart B)

Performance parameter	Units	Carbon monoxide	Definitions & test procedures
Range	ppm	0–50	Sec. 53.23(a)
Noise	ppm	0.50	Sec. 53.23(b)
Lower detectable limit	ppm	1.0	Sec. 53.23(c)
Interference equivalent			Sec. 53.23(d)
Each interferant	ppm	±1.0	
Total interferant	ppm	1.5	
Zero drift, 12 & 24 hour	ppm	±1.0	Sec. 52.23(e)
Span drift, 24 hour			Sec. 52.23(e)
20 % of upper range limit	%	±10.0	
80 % of upper range limit	%	±2.5	
Lag time	Mins.	10	Sec. 52.23(e)
Rise time	Mins.	5	Sec. 52.23(e)
Fall time	Mins.	5	Sec. 52.23(e)
Precision			Sec. 52.23(e)
20 % of upper range limit	ppm	0.5	
80 % of upper range limit	ppm	0.5	

Definitions:

Range: Nominal minimum and maximum concentrations that a method is capable of measuring.

Noise: The standard deviation about the mean of short duration deviations in output that are not caused by input concentration changes.

Lower detectable limit: The minimum pollutant concentration that produces a signal of twice the noise level.

Interference equivalent: Positive or negative response caused by a substance other than the one measured.
Zero drift: The change in response to zero pollutant concentration during continuous unadjusted operation.
Span drift: The percent change in response to an upscale pollutant concentration during continuous unadjusted operation.
Lag time: The time interval between a step change in input concentration and the first observable corresponding change in response.
Rise time: The time interval between initial response and 95% of final response.
Fall time: The time interval between initial response to a step decrease in concentration and 95% of final response.
Precision: Variation about the mean of repeated measurements of the same pollutant concentration, expressed as one standard deviation about the mean.

Problems, Precautions, Troubleshooting

Several factors affect both precision and bias. Of most concern are span drift (slow variation of the response signal yielded by the span gas) and zero drift. These factors are instrument dependent, and their combined effect should be maintained at less than 1% of span in 24 hours. If sampling is conducted without proper particulate matter filtering, the optical windows of the sample cell will accumulate dust and dirt, resulting in a gradual loss in sensitivity accompanied by zero drift.
Temperature fluctuations can cause changes in instrumental response. In many instruments a temperature controlled housing encloses the detector portion of the monitor, in order to minimize this effect. In the absence of temperature control, response may change by as much as 0.5 ppm for each degree Celsius temperature change. Refer to the instrument's operating manual to determine if temperature control is necessary.

Pressure, too, can cause changes in instrumental response. Changes in sample cell pressure can result in proportional changes in output for a given concentration of CO. Barometric pressure changes can result in span drift 1%, although it has not been customary to make corrections for this effect. However, if greater accuracy is desired, corrections for barometric pressure would be necessary. Also, if the flow rate of the sampled air varies, cell pressure might also vary due to restrictions in the sampling line. These slow changes in resistance to flow may cause span drift, and need to be corrected. Again, refer to the operating manual.

Mechanical vibration of instruments using the Luft principle is likely to cause signal noise due to the instability of the optical system or by mechanically induced motion of the detector cell's diaphragm. Manufacturers prevent this by shock mounting the detector section of the analyzer or by substituting a flow sensor for the diaphragm. For additional assurance it is advisable to place Luft-type NDIR instruments on shock-dampening material when in use. Other causes of signal noise include inadequate voltage regulation and instability of amplifier components. Such factors contribute to loss in precision. The use of a microflow detector in a Luft-type NDIR analyzer is meant to minimize the problem of vibration.

Preventative maintenance is required for NDIR monitors. As in most air sampling instruments, the moving components of the mechanical vacuum pump must be checked periodically. Also, the infrared radiation sources must be inspected regularly. Associated optics must be checked and cleaned when found to be dirty.

In time, the sample cell may require disassembly for cleaning. This will be indicated by a gradual decrease in instrument sensitivity accompanied by an increase in electronic signal "noise". The reference cell of Luft-type analyzers will almost never have to be dismantled, although the optical windows may require cleaning of the exterior surfaces periodically. Should it become necessary to disassemble a cell for any reason, the manufacturer's instructions should be followed explicitly.

On most instruments the detector is a sealed unit, and will not have to be maintained unless a failure develops. Should it become necessary to perform maintenance on the detector, the manufacturer's instructions should be followed closely. In most cases, shop repair is necessary should operational difficulties develop with the detector.

Regular checks should also be made of the electrical circuits from the detector, through the amplifier, to the data recording system.
Preventive maintenance is dependent upon the operating conditions of the instrument and is variable for each manufacturer's instrument. Suggestions on maintenance are contained in most instruments' operating manuals. Table 8-3 is intended to serve as a guide for locating and remedying problems, given an observed symptom. In addition, modern instruments are equipped with self-diagnostic to assist in identifying malfunctions or out of control conditions. Furthermore, they are also typically equipped with alarms on certain instrument systems (e.g. reaction chamber temperature, IR source voltage, flow rate, etc.) to warn the operator of a problem before it causes an out of control condition.

Quality Assurance

Procedures which are useful in maintaining adequate quality of CO data include: checks of zero drift and span drift; checks of sensitivity of the instrument response to variations in flow rate, temperature, and voltage; calibration of the flow meter and of the sample cell's pressure gauge; and moisture interference tests.

Table 8-3. Typical CO monitor problems.

Observation	Problem Cause	Remedy
1. CO level too low	1. Reference infrared source failing 2. Sample lines clogged or broken 3. Decreased pressure in reference compartment of detector 4. Vacuum pump failing 5. Amplifier failing	1. Run span gas check 2. Check with flow meter 3. Check after inspection of infrared source 4. Inspect pump 5. Completely check-out electronics
2. CO level too high	1. Sample infrared source failing 2. Sample cell optics dirty 3. Decreased pressure in sample compartment of detector	1. Run span gas check 2. Inspect and clean if necessary 3. Run span gas check after inspection of infrared source

	4. Amplifier failing	4. Completely check-out electronics system
3. Abnormal positive zero drift	1. Moisture elimination devices inoperative (if applicable) 2. Dirty optical surfaces 3. Amplifier failing	1. Re-charge silica gel; check refrigeration unit 2. Clean cells as necessary; check particulate filter 3. Check-out electronics system completely

Water Vapor Interference Check

To fully assess the effect of ambient moisture on the CO monitoring instrument and its subsequent data, it is advisable to do periodic water vapor interference checks.

The equivalent CO concentration due to moisture is measured by obtaining the instrument response from dry zero gas (introduced to the instrument bypassing the drying device); then saturating the same zero gas by passing it through a water-containing impinger prior to introduction into the instrument (the saturated gas is passed through the drying device as in normal sampling before measurement). The equivalent CO concentration is determined as the difference between the dry and saturated values (the dry value is always subtracted from the saturated value). If the equivalent CO concentration is as large as 0.5 ppm, the desiccant must be replaced.

Devices other than drying tubes may be in use on NDIR instruments. Such devices as refrigeration units, optical filters, etc., may be evaluated in the same manner as used to check the drying tube.

Table 6-4 indicates the more important aspects of a quality assurance/quality control program for CO monitoring. Included in the table are the actions required to assure that these variables are addressed in the QA/QC program.

Table 8-4. Operational parameters.

QA/QC Parameter	Actions
1. Calibration gas concentration	Measurement of control samples as part of the auditing program
2. Water vapor interference	Water vapor interference checks performed as a part of the auditing program
3. Data processing errors	Data processing checks performed as a part of the auditing program
4. Zero drift	Zero check and adjustment before each sampling period as part of routine operating procedure
5. Span drift	Span check and adjustment before each sampling period as part of routine operating procedure
6. System noise	Check of strip chart record trace for signs of noise after each sampling period as part of routine operating procedure
7. Sample cell pressure variation	Reading and recording sample cell pressure at the

	beginning and end of a sampling period as part of routine operating procedure
8. Temperature variation	Minimum-maximum thermometer placed near the analyzer, or any other temperature-indicating device, read periodically throughout the sampling period- this would usually be done as a special check.
9. Voltage variation	A.C. voltmeter measuring the voltage to the analyzer and read periodically throughout the sampling period- this would usually be done as a special check

Table 8-5, reprinted from the USEPA QA Handbook for Air Pollution Measurement Systems, Volume II, Part 1, Appendix 3 (EPA-454/R-98-004), provides recommended Measurement Quality Objectives (MQO) in support of ambient monitoring using a NDIR CO analyzer. These MQO are derived in large part from 40 CFR Part 50, 53, and 58.

In theory, if these MQOs are met, measurement uncertainty should be controlled to the levels required by the Data Quality Objectives (DQO) that in turn ensure reliable data. Tables of the most critical MQOs can be developed. Table 8-5 is an example of an MQO table for carbon monoxide.

Table 8-5: Measurement Quality Objectives - Parameter CO (Nondispersive Infrared Photometry)

Requirement	**Frequency**	**Acceptance Criteria**	**Reference**	**Information/Action**
Standard Reporting Units	All data	ppm	40 CFR, Pt 50.8	
Shelter Temp.			40 CFR, Pt. 53.20 Vol II, S 7.1 $^{1/}$	Instruments designated as reference or equivalent have been tested over this temperature range. Maintain shelter temperature above sample dewpoint. Shelter should have a 24-hour temperature recorder. Flag all data for which temperature range or fluctuations are outside acceptance criteria.
Temp. range	Daily	20 to 30 °C.		
Temp. control	Daily	< ± 2 °C		
Equipment				
CO analyzer	Purchase Specification	Reference or equivalent method	40 CFR, Pt 50, App C	
Flow controllers	“	Flow rate regulated to ± 1%	"	
Flowmeters	“	Accuracy ± 2%	“	

Detection Limit Noise	Purchase Specification	0.5 ppm	40 CFR, Pt 53.20 & 23	Instruments designated as reference or equivalent have been determined to meet these acceptance criteria.
Lower detectable level	“	1.0 ppm	“	
Completeness 8-hour average	hourly	75 % of hourly averages for the 8-hour period	40 CFR, Pt 50.8	
Compressed Gases Dilution gas (zero air)	Purchase specification	< 0.1 ppm CO	40 CFR, Pt 50, App C	Return cylinder to supplier.
Gaseous standards	Purchase specification	NIST Traceable (e.g., EPA Protocol Gas)	" EPA-600/R97/12	Carbon monoxide in nitrogen or air EPA Protocol Gases have a 36-month certification period and must be recertified to extend the certification.
Calibration Multipoint calibration (at least 5 points)	Upon receipt, adjustment, or 1/ 6 months	All points within ± 2% of full scale of best-fit straight line	Vol II, S 12.6 Vol II, MS.2.6.1	Zero gas and at least four upscale calibration points. Points outside acceptance criterion are repeated. If still outside criterion, consult manufacturers manual and invalidate data to last acceptable calibration.
Zero/span check-level 1	1/ 2 weeks	Zero drift ± 2 - 3 ppm Span drift ± 20 - 25 % Zero drift ± 1 - 1.5 ppm Span drift ± 15%	Vol II, S 12.6 " Vol II, S 12.6 "	**If calibration updated at each zero/span**, invalidate data to last acceptable check, adjust analyzer, and perform multipoint calibration. **If fixed calibration used to calculate data**, invalidate data to last acceptable check, adjust analyzer, and perform multipoint calibration.
Flowmeters	1/3 months	Accuracy ± 2 %	Vol II, App 12	Flowmeter calibration should be traceable to NIST standards.
Performance Evaluation (NPAP)	1/year at selected sites	Mean absolute difference # 15%	Vol II, S 16.3	Use information to inform reporting agency for corrective action and technical systems audits
State audits	1 /year	State requirements	Vol II, pp 15, S 3	

Precision				
Single analyzer	1/2 weeks	None		
Reporting organization	1/3 months	95% CI # ± 15%	40 CFR, Pt 58, App A EPA-600/4-83-023 Vol II, App 15, S 5	Concentration = 8 to 10 ppm. Aggregation of a quarters measured precision values.
Accuracy				
Single analyzer		None		
Reporting organization	25 % of sites quarterly (all sites yearly)	95% CI ± 20%	40 CFR, Pt 58, App A	Four concentration ranges. If failure, recalibrate and reanalyze. Repeated failure requires corrective action.

[1/] - reference refers to the QA Handbook for Air Pollution Measurement Systems, Volume II, Part 1.
S - The use of “S” refers to sections within Part 1 of Volume II.
MS – The use of “MS” refers to method-specific sections in Volume II.

Since the Ambient Air Quality Monitoring Network was established prior to the development of the DQO Process, a different technique was used to establish data quality acceptance levels. Therefore, all criteria pollutants are being reviewed in order to establish DQOs using the current DQO process.

High Sensitivity CO Analyzer – Percursor Gas Monitoring

Modifications in commercial NDIR Gas Filter Correlation (GFC) CO instruments have lowered estimated LDL values to 0.04 ppm (40 ppb). The lower detectable limit (LDL) for an ambient monitor is defined as that minimum concentration level that produces a signal of twice the baseline noise level (Code of Federal Regulations, Volume 40, Part 53.23c, or, in the shortened format used hereafter, 40 CFR 53.23c). This section describes the recommended performance criteria and the analyzer features that are recommended in order to achieve the performance criteria, and provides examples of commercial high sensitivity CO analyzers that are available for deployment at the NCore sites.

Since the high sensitivity analyzers deployed at NCore sites are intended to monitor low ambient CO concentrations, it is important that they meet a variety of performance criteria as described below. Many of these performance criteria are more stringent than those for routine CO analyzers; consequently, there are a number of recommended features that the precursor CO analyzers should have in order to achieve the performance criteria.

This section describes the recommended performance criteria and the analyzer features that are recommended in order to achieve the performance criteria.

Recommended Method Performance Criteria

The U.S. EPA has assessed the measurement quality objectives needed for high sensitivity precursor gas monitoring in NCore, relative to the long-established statistics stated in 40 CFR 58. In particular, EPA recommends that measurement quality objectives for bias and precision be based on upper confidence limits at the monitoring site level, to provide a higher probability of reaching appropriate conclusions (e.g., in comparisons to NAAQS). The intent of this recommendation is to move S/L/T agencies to a performance-based quality system i.e., allowing organizations that show tight control of precision and bias to reduce the frequency of certain QC checks, and to focus their quality system efforts where most needed.

The U.S. EPA recommends that the high sensitivity CO analyzers that are deployed at NCore sites meet a number of method performance criteria as described below. Additional details regarding these criteria can be found in USEPA Technical Assistance Document (TAD) For Precursor Gas Measurements in the NCore Multi-Pollutant Monitoring Network, Version 4 (EPA-454/R-05-003).

Precision

Precision is defined as the measure of agreement among individual measurements of the same property taken under the same conditions. Precision is assessed from checks that are performed at least once every two weeks and should be used to assess precision on a quarterly basis. It is recommended that high sensitivity CO analyzers have a 95 percent probability limit for precision of ±15 percent or less. Calculation of precision starts with the comparison of the known challenge concentration used in the precision checks to the corresponding measured concentrations reported by the analyzer.

Bias

Bias is defined as a systematic or persistent distortion of a measurement process that causes errors in one direction. Bias is assessed from the degree of agreement between a measured value and the true, expected, or accepted value. Analyzer bias is calculated using comparisons of known challenge concentrations to the corresponding measured concentrations reported by the analyzer. The challenge comparisons used to assess bias should be the same as those used to assess precision. It is recommended that high sensitivity CO analyzers have an upper bound for the average bias of ± 15 percent or less.

Representativeness

Representativeness refers to whether the data collected accurately reflect the conditions being measured. It is the data quality indicator most difficult to quantify. Unless the samples are truly representative, the other indicators are meaningless. Representativeness for monitoring of low ambient levels of CO in NCore is different than for routine monitoring, since the objectives of the monitoring are much different. Representativeness can only be assured in terms of the appropriate selection of the sampling site, proper implementation of ambient air sampling, and reasonable coverage of the sampling schedule (i.e., 24 hours per day, 7 days per week, ideally).

Completeness

Completeness is defined as the amount of data collected relative to the total expected amount. Ideally, 100 percent of the expected amount of data would always be collected; in practice, completeness will be less for many reasons, ranging from calibration time and site relocation to power outages and equipment failure. For monitoring of ambient CO concentrations in NCore, EPA requires a minimum data completeness of 75 percent. In practice typical completeness values can often approach 90 to 95 percent.

Comparability

Comparability is defined as the process of collecting data under conditions that are consistent with those used for other data sets of the same pollutant. The goal is to ensure that instruments purchased and operated by different states and local agencies produce comparable data. To promote comparability, the USEPA Technical Assistance Document (TAD) For Precursor Gas Measurements in the NCore Multi-Pollutant Monitoring Network, Version 4, (EPA-454/R-05-003) describes the recommended characteristics of high sensitivity CO analyzers and the procedures for their installation and use.

Method Detection Limit

The *method detection limit* (MDL) refers to the lowest concentration of a substance that can be reliably determined by a given procedure. The MDL is typically not provided by the vendor. Based on the objectives of the Precursor Gas Program, it is expected that most sites will be measuring pollutant concentrations at lower ranges than the typical SLAMS/NAMS network. Therefore, the ability to quantify concentrations at these lower levels will be very important. The use of a vendors advertised LDL is sufficient to make intelligent purchasing decisions; however, vendors quantify LDLs under ideal conditions and therefore one might consider this value as the best possible detection that can be achieved.

As these monitors are deployed into monitoring networks, where both environmental conditions, equipment (calibration, dilution devices, sampling lines, gaseous standards) and operator activities can vary, it is important to estimate what pollutant concentrations can truly be detected, above background noise (the potential conditions mentioned above). The site specific MDL establishes an estimate based on the routine operation (and conditions) of that instrument in the network and provides a more meaningful evaluation of data as it is aggregated across the precursor gas network. By establishing site specific MDLs, values less than the MDL can be flagged which would allow data users a more informed decision on the use of that data.

It is recommended the MDL for high sensitivity CO analyzers be established prior to putting the analyzers into service, and should be 0.080 ppm (80 ppb) or lower over an averaging time of no more than 5 minutes.

Lower Detectable Limit

The *Lower Detectable Limit* (*LDL)* is the minimum pollutant concentration that produces a signal of twice the noise level. To estimate the LDL, zero air is sampled and the noise level of the CO readings is determined according to 40 CFR 53.23(b). The vendor-specified LDL for the most sensitive range of high sensitivity CO analyzers should be 0.040 ppm (40 ppb) or lower, over an averaging time of no more than 5 minutes.

Linear Range

The *linear range* of each high sensitivity CO analyzer should extend from approximately 0.040 ppm to at least 5 ppm. Users should determine if their range should exceed 5 ppm and adjust accordingly. Note that some high sensitivity CO analyzers can operate simultaneously on a number of ranges, with each range recorded on a separate data logger channel with its own calibration curve. Although requiring slightly more effort to calibrate and maintain, recording of multiple ranges would allow capture of a wide range of CO concentrations.

Zero/Span Drift

Zero drift is defined as the change in response to zero pollutant concentration, over 12- and 24-hour periods of continuous unadjusted operation. *Span drift* is defined as the percent change in response to an upscale pollutant concentration over a 24-hour period of continuous unadjusted operation. Zero and span drift specifications should be obtained from the vendor prior to putting a high sensitivity CO analyzer into service. Such CO analyzers should have 12- and 24-hour zero drift less than 100 ppb, and should have a span drift of less than ±1 percent of the full scale measurement range of the analyzer per 24 hours. Zero tests should be performed with the internal zero engaged. It is suggested that the *zero trap* of the analyzer be initially and periodically (annually) evaluated for efficiency or if the operator suspects a problem with the zero trap. A suggested means of confirming the functionality of the zero trap is to sample calibration air spiked with 1000 to 2000 ppb CO during the zero cycle, and review results for the automatic zeroing periods. This approach tests the key components of the zeroing/drying system and should meet the vendor-specified zero drift criterion.

Recommended Analyzer Features for High Sensitivity CO Measurements

Continuous high sensitivity CO analyzers are commercially available from a number of vendors. The design of these analyzers is similar among vendors with some slight variations. A diagram of a typical high sensitivity GFC CO instrument is described in Figure 6-9. In general, analyzers contain the following systems:

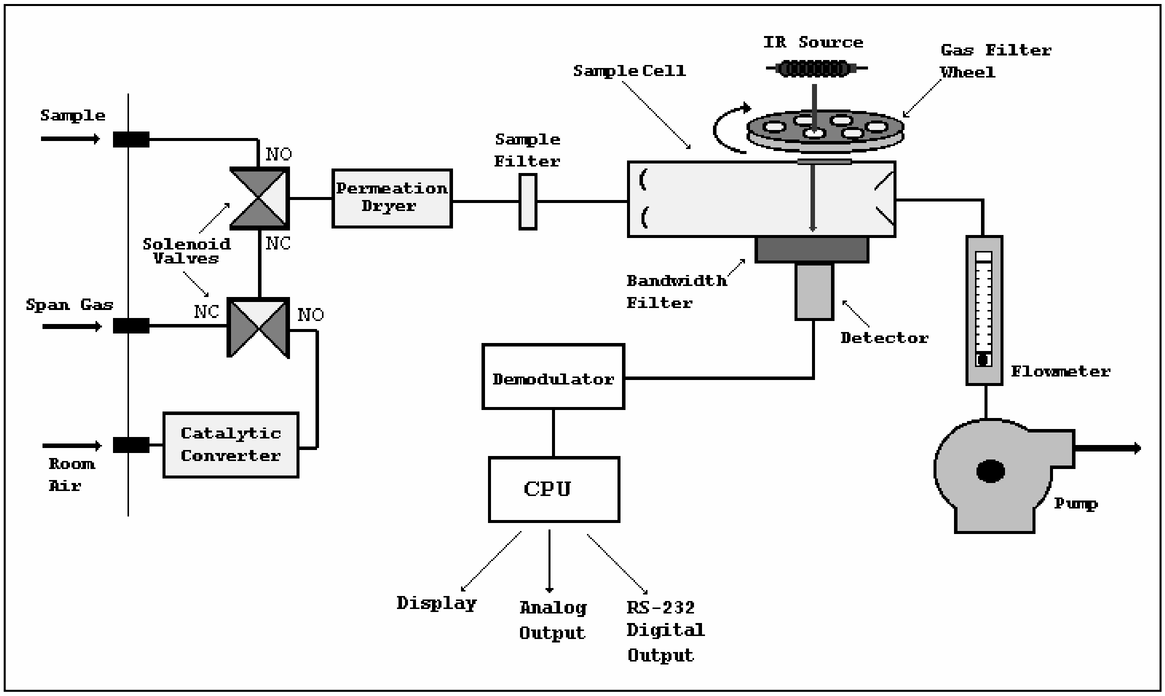
1. Pneumatic System: This portion of the analyzer consists of a sample probe, sample inlet line, particulate filter, dryer, catalytic converter, flow meter, and pump, all used to condition the ambient sample air and bring it to the analyzer;
2. Analytical System: This portion of the analyzer consists of the IR source, the gas correlation filter, motor, optical multipass cell, detector, and bandpass filter. Being a mechanical device, the motor can and will wear out. The gas correlation filter can be subject to leakage and the IR source will eventually burn out. Extra IR sources should be stocked as replacement parts and the gas correlation filters should be replaced as necessary; and,
3. Electronic Hardware: This portion of the analyzer consists of the electronic components that control the analyzer and process the signals. This part of the analyzer generally requires little or no maintenance. However, if the instrument is operated near the manufacturer's recommended upper temperature limit, individual integrated chips can fail and cause problems with data storage or retrieval.

In addition to these general systems, the high sensitivity versions of the commercial GFC CO instruments typically have four distinct features that allow them to measure CO at ppb levels:

1. The sample stream is dried using a permeation tube or Nafion® Dryer prior to introduction to the sample cell;
2. The analyzer baseline is determined and corrected automatically and frequently by introducing into the sample cell CO-free air, that is generated using a heated, onboard, converter that is based on palladium (Pd), platinum (Pt), or other composition;
3. The temperature of the optical bench is tightly controlled (i.e., within ± 1 °C) to maintain detector stability; and,
4. The instrument uses an ultra-sensitive detector, in order to detect very small changes in light intensity. For example, the detector used on TECO Model 48C (Trace Level Analyzer) is a Photo Conductive, Lead-Selenide (PbSe) device, with an internal thermoelectric cooler. The PbSe detector operates through use of the internal photoelectric effect.

It is recommended that the high sensitivity CO analyzers deployed in NCore employ these features.

Figure 8-9. Diagram of a typical GFC CO analyzer.



Potential Problems and Solutions

This section describes several of the potential problems associated with high sensitivity

CO measurements, and discusses the practical solutions to these problems, some of which the vendors have already implemented in their analyzers. In addition to these potential problems, other problems may arise in the routine operation of high sensitivity CO analyzers.

Interferences and Sources of Bias

Preventing interferences or biases is crucial to the accurate measurement of low ambient levels of CO. The following sections describe several potential positive and negative sources of interference or bias and recommended procedures to minimize these interferences or sources of bias.

Positive Interferences

GFC CO analyzers determine CO concentration by measuring the amount of light that is absorbed at a select wavelength (4.7 µm) as it passes through a sample cell containing CO. Any other gas in the air sample that also absorbs at those wavelengths could present an interference that would result in an inaccurate determination of CO concentration. Removal of potential interferences must be done selectively such that these interferences are completely removed without affecting the CO concentration. For CO measurements at low ambient levels, this is particularly critical in order to achieve the desired sensitivity. Of particular concern are water vapor and CO_2, which are both generally present in the atmosphere at concentrations which greatly exceeding those of CO.

Water absorbs very strongly in the 3.1, 5.0 to 5.5, and 7.1 to 10.0 µm regions of the IR spectrum and therefore must be removed from the sample air to avoid positive interferences in the determination of CO concentration. To achieve this goal, high sensitivity CO analyzers are equipped with a permeation tube or Nafion™ drier (discussed earlier in this Chapter) that selectively removes water vapor from the sample gas without removing CO.

CO_2 absorbs in the IR spectrum at 2.7, 5.2, and 8.0 to 12.0 µm. These regions are also very close to the regions of CO absorption. Since atmospheric carbon dioxide is typically much higher in concentration than CO and has properties that are similar to CO, it is impractical to selectively remove CO_2 from the sample air without removing a fraction of the CO. Therefore, it is important that the bandpass filter used to limit the interrogating radiation is sufficiently selective to restrict the wavelengths to a small region centered on the CO absorption band of 4.7 µm. Manufacturers of high sensitivity CO analyzers select the bandpass filter to effectively remove CO_2 interference. An added benefit of such filters is that they also limit interference from water vapor.

Negative Interferences and Biases

High sensitivity CO analyzers are equipped with a solenoid switching system to draw sample air into a heated internal scrubber that converts all CO to CO_2. The analyzer then measures the light absorption of this CO-free air and uses that light intensity to establish the zero reading. However, any CO that is not converted to CO_2 would remain in the sample gas and decrease the light intensity (i.e., absorb the light) used to establish the zero reading, resulting in an artificially high zero reading and a negative bias when measuring the CO in ambient air.

To avoid this situation, it is important that the heated scrubber be maintained at the manufacturer's recommended temperature. Scrubber efficiency must be checked periodically, e.g., every 30 days. A convenient means to check CO scrubber efficiency is to sample ambient air, then zero air, and then a CO calibration mixture, all with the internal heated CO scrubber engaged. Zero air and sample air readings should be within ±0.010 ppm (10 ppb), and scrubber efficiency should be >99%.

Detector Stability

The temperature of the detector in a high sensitivity CO analyzer must remain stable in order to allow for ppb sensitivity. Commercial high sensitivity CO analyzers provide a display of the detector temperature. This temperature should be checked periodically for compliance with the vendor's required temperature setting. Bench temperature should be checked both with and without the zero scrubber engaged, to ensure that scrubber effluent does not cause heating of the optical bench.

Zero Air Source/Generator

Zero air is required for the calibration of high sensitivity CO analyzers. This air must contain no detectable CO (i.e., CO content must be less than the LDL of the CO analyzer) and must be free of particulate matter. Suitable zero air may be supplied from compressed gas cylinders of purified air, with additional external CO scrubbers (e.g. hopcalite or carulite) to remove residual CO in the commercial product. However, it is likely too expensive and impractical to maintain a sufficient supply of zero air cylinders to operate a high sensitivity CO analyzer continuously. As an alternative, many commercially available zero-air generation systems can greatly reduce CO levels in air. However, depending on the required zero air flow rates, it may be difficult to reduce CO levels to 0.040 ppm or less, unless a Pd or Pt scrubber is used. A recommended approach to test zero air quality is to compare the readings of the high sensitivity CO analyzer in zero air in sample mode vs. the analyzer output in the "auto zero" mode. This comparison should be done at least quarterly and can only be done with those analyzers that provide a digital recording of the output in the "auto zero" mode.

Reagents and Standards

Routine operation of precursor CO analyzers requires the use of calibration standards and zero air to conduct periodic calibrations and instrument checks. This section describes the requirements for these gases.

Calibration Standards

The primary CO standards used must be certified, commercially-prepared compressed gas standards with a certified accuracy of no worse than ±2 percent. Standards in the concentration range of 200 to 250 ppm are suitable choices for dilution to prepare low concentration calibration mixtures. The commercially-prepared CO standard may contain only CO in an inert gas (e.g., N2), or may be a mixed component standard that also contains known concentrations of other precursor gases (e.g., SO_2, NO). (Note that mixtures containing both SO_2 and NO may not be suitable for SO2 calibration, depending on the NO rejection ratio of the SO_2 analyzer.)

Every gas standard used in precursor gas monitoring must be accompanied by a certificate of calibration from the vendor stating the concentration of the standard, the uncertainty of that certification, and the expiration date of the certification. Standards traceable to NIST are preferred. Certification documents for all standards must be retained in a common location and reviewed periodically so that standards for which the vendor's certification has expired may be removed from service and replaced.

Zero Air

Zero air used as dilution gas for calibration purposes should have a CO concentration below the LDL of the high sensitivity CO monitor. Commercial cylinder gas grades such as Ultra Zero and CEM grade may be suitable as a starting point, provided additional cleanup is employed as discussed in the previous section. Commercial zero air further scrubbed of CO may be used to crosscheck the purity of air provided by a commercial continuous air purification system.

Quality Control

A thorough quality control program is critical to the collection of high sensitivity CO monitoring data, and must be implemented at each NCore site. Components of such a program are described below.

Site Visit Checks and Remote Diagnostic Checks

To determine whether the CO analyzer is working properly, field operators should conduct routine checks of instrument diagnostics and performance every time they visit the monitoring station. Each agency needs to develop diagnostic or maintenance checklists or electronic spreadsheets to document that all required checks have been made. Such lists and sheets should be useful both for collecting diagnostic information and for assessing the quality of the monitoring data. To the extent possible, diagnostic checks can be done remotely, provided the data acquisition system allows remote access to instrument diagnostic information.

Multipoint Calibrations

A multipoint calibration includes a minimum of four points (three spaced over the expected range and a zero point), generated by the calibration system. Although more points may be preferable, current high sensitivity CO analyzers typically provide linear response over the entire operating range; therefore, four points should be sufficient. Multipoint calibrations must be done prior to the high sensitivity CO analyzer being put into service and should be repeated at least quarterly thereafter. An analyzer should be calibrated (or recalibrated) if any of the following conditions occur:

- Upon initial installation;

- The Level 1 span check or precision check difference exceeds 15 percent;
- After repairs or service is conducted that may affect the calibration;
- Following physical relocation or an interruption in operation of more than a few days;
- Upon any indication that the analyzer has malfunctioned or a there has been a change in calibration; or
- The measured concentration values during challenges with performance test (audit) samples differ from the certified standard values by ±15 percent. (Generally this challenge is conducted as a blind audit, such that the site operator is not aware of the gas standard concentrations delivered to the analyzers.)

The analyzers should be calibrated *in-situ* without disturbing the normal sampling inlet system to the degree possible.

Level 1 Zero/Span Checks

Level 1 zero and span calibrations are simplified, two-point calibrations used when adjustments may be made to the analyzer. When no adjustments are made to the analyzer, the Level 1 calibration may also be called a zero/span "check" and must not be confused with a level 2 zero and span check. Level 1 zero and span checks should be conducted nightly. They are used to assess if the analyzers are operating properly and to assess if any drift in instrument response has occurred. The level 1 check should not exceed ±15 percent. Zero drift is internally adjusted by the analyzer. The zero check is used to verify that the internal zero is working properly. They are conducted by challenging the analyzer with zero air and a test atmosphere containing CO at a concentration of between 70 percent and 90 percent of the full measurement range in which the analyzer is operating. The challenge gas should be sampled through as much of the sampling inlet system as practical to mimic the actual sampling of ambient air. The results of the Level 1 zero/span check should be plotted on control charts to graphically illustrate the trends in the response of the analyzer to the challenge gases. If the measured concentrations fall outside of the control limits, the accuracy of the MFC calibration system should be checked with a NIST-traceable flow standard. If the MFC flow accuracy is confirmed, the data recorded since the last successful Level 1 check should be flagged and the analyzer should be recalibrated using the multipoint calibration procedures described earlier.

State-of-the-art calibration equipment now exists that is fully automated. These "new generation" calibration units are fully integrated with computers, mass flow calibrators, and the associated hardware and software where they can create test atmospheres manually or automatically. For the precursor gas program, it is recommended that the NCore sites have fully automated calibration capability. Below are a number of reasons why this is advantageous:

- By performing the calibrations or checks automatically, agencies no longer expend the extra manpower needed to perform them manually.
- Automated calibrations or checks can be triggered internally or by a DAS. Since newer

DASs allow remote access; this allows a remote user to challenge the analyzers without actually being present.

- High sensitivity precursor gas analyzers are expected to have more zero and span drift than less sensitive analyzers; therefore, it is important that a zero and Level I check be performed daily.
- New generation DASs can record calibration and check data and allow remote users to track daily Level I check and zero drift. This is important for data validation, verification and troubleshooting.

Precision Checks

At least once every two weeks, a precision check should be conducted by challenging the CO analyzer with a known (low) CO concentration to assess the performance of the analyzer. The precision checks should be conducted by challenging the precursor CO analyzer with a standard gas of known concentration between 0.25 and 0.50 ppm (250 and 500 ppb). After completion of the precision check, the operator should calculate the percent difference between the measured value and the known standard value. Precision should be calculated quarterly, using the calculated percent differences from the precision checks (For more detail on calculating precision, refer to Technical Assistance Document (TAD) for Precursor Gas Measurements in the NCore Multi-pollutant Monitoring Network Version 4 (EPA-454/R-05-003). For acceptable precision to be maintained it is recommended that the calibration system's gas flows be verified frequently against a NIST flow standard, and adjusted if necessary before making any adjustments to the analyzer.

Preventive Maintenance and Troubleshooting

Long-term operation of continuous high sensitivity precursor gas analyzers requires a preventive maintenance program to avoid instrument down-time and data loss. This section briefly describes several key items that might be included in the preventive maintenance program established for high sensitivity CO analyzers deployed at NCore sites, as well as some of the troubleshooting activities that may be useful in resolving unexpected problems with these analyzers. This discussion is not meant to be exhaustive or comprehensive in detail. More thorough discussions can be found in the analyzer operation manuals, and should be included in SOPs developed for these analyzers. Example SOP's prepared by EPA are included as Appendix B of the Technical Assistance Document (TAD) for Precursor Gas Measurements in the NCore Multi-pollutant Monitoring Network Version 4 (EPA-454/R-05-003).

Preventive Maintenance

Management and field operators should jointly develop their preventive maintenance program. A program designed by persons unfamiliar with analyzer operations may include unnecessary items or omit mandatory ones.

Several factors linked to shelter and sampling manifold design can contribute to data loss. CO values can be low if the sample probe, manifold, and lines are dirty, cracked, or leaky.

The sample probe and manifold should be cleaned at least every six months. FEP and PTFE sampling lines should be replaced every two years. Teflon® filters used in the sampling train to remove fine particles should be replaced at least once per month, but may need to be replaced as often as every week, depending on the condition of the filter and the particulate loading around the monitoring site.

Table 8-6 illustrates items that monitoring agencies should include in their preventive maintenance program for precursor CO monitoring. In addition to a schedule, the preventive maintenance plan should also include more detailed task descriptions, such as illustrated below:

- Because the analyzer pneumatic system requires so much preventive maintenance, the tubing, solenoids, and pump should be inspected regularly. Cracked tubing or loose fittings can cause the instrument to analyze room air rather than ambient air and lead to invalid data. A faulty pump can also cause problems with pneumatic systems. When oscillations in the flow rate force the operator to adjust the flow continually, the pump is failing and should be either repaired or replaced.
- Check the instrument for vibration. When pumps get old, they sometimes will vibrate more than is normal. If this occurs, it can cause cracks if the tubing is touching another surface.
- Consult the analyzer operations manual for complete details on operation and maintenance.

Table8-6. Example of a preventive maintenance schedule for high sensitivity CO analyzers.

Item	Schedule
Replace particle filter	Weekly
Clean fan/fan filter	Semi-annually
Inspect internal, external tubing; replace if necessary	Annually
Rebuild or replace pump	Every two years, or as needed
Replace IR source	As needed based on manufacturer's diagnostics
Clean optic bench	As needed
Replace wheel motor	As needed
Replace gases in correlation wheel	As needed

Troubleshooting

When troubleshooting, an operator must constantly be aware of environmental factors that may affect the instruments. Environmental factors can also cause sporadic problems that can be difficult to diagnose. Examples of factors that may affect the performance of the high sensitivity CO analyzers are:

- Variable shelter temperature (fluctuations greater than several degrees);
- Excessive vibration from other equipment;
- Voltage instability; fluctuations in the 110 VAC line voltage;

- Air conditioning system blowing on the instrument;
- Frequent opening of the door of the shelter.

Table 8-7 summarizes common problems seen with high sensitivity CO analyzers, their possible causes, and possible solutions. More specific information can be found in the manufacturer’s operations manual.

Table 8-7. Instrument troubleshooting for high sensitivity CO analyzers.

Problem	Possible Cause	Possible Solution
Noisy output	Defective DC power supply	Replace power supply
	Dirty optics	Clean optics bench
High positive zero drift	Defective bandpass filter	Replace filter
No Response to Span Gas	IR source is defective	Replace IR source
	IR power supply defective	Replace IR power supply
Differential Signal at Zero	IR source is defective	Replace IR source
	IR power supply is defective	Replace IR power supply
	CO leak from correlation wheel	Replace wheel
Zero output at ambient levels	Pump failure	Check pump
	IR source failure	Replace IR source
	IR power supply defective	Replace power supply
No flow through analyzer	Pump failure	Replace/ rebuild pump head
Reference signal at zero	N2 leak from correlation wheel	Replace wheel

References

Technical Assistance Document (TAD) For Precursor Gas Measurements in the NCore Multi-Pollutant Monitoring Network Version 4, EPA-454/R-05-003, September 2005.

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Chapter 9

Oxides of Nitrogen Measurement Principle and Calibration Procedures

The prescribed procedure for measurement of nitrogen dioxide (NO_2) consists of a reference measurement principle and calibration procedure. Any analyzer that uses the specified measurement principle, meets the prescribed specification, and is calibrated in accordance with the specified calibration procedure may be designated a Reference Method by EPA. The reference measurement principle for nitrogen dioxide (NO_2) employs gas phase chemiluminescence similar to the process used in the reference measurement principle for ozone. The chemiluminescent reaction used is based on the light-emitting reaction of nitric oxide (NO) and ozone (O_3). NO_2 is measured indirectly, due to the necessity of reducing NO_2 to NO before it can be measured by the NO-O_3 chemiluminescent reaction. The NO_2 to NO reduction is achieved by the use of a converter, while NO_2 concentration is calculated by the use of electronic processing circuitry. The calibration procedure consists of checking the analyzer's carbon monoxide response by "challenging" the analyzer with known concentrations of carbon monoxide.

While the obvious problems of widespread elevated concentrations have been largely solved for some criteria pollutants, problems related to particulate matter (PM), ozone (O_3), and toxic air pollutants remain. It is now clear that even very low air pollution levels can be associated with adverse environmental and human health effects. As a result, the use of highly sensitive commercial air pollutant monitors for the characterization of the precursor gases CO, SO_2, and total reactive oxides of nitrogen (NO_y) in a new national core monitoring network (NCore). The high sensitivity CO and SO_2 analyzers are fundamentally the same as those designated as Federal Reference and Equivalent methods (http://www.epa.gov/ttn/amtic/criteria.html), but with Precursor Gas Technical Assistance Document (TAD) modifications to improve sensitivity and accuracy or reduce interferences. The use of such precursor gas analyzers in the NCore network will still allow determination of compliance with the NAAQS, but will provide measurements at much lower detection limits than are achievable by current monitors. The implementation of high sensitivity monitoring for CO, SO_2, and NO_y in the NCore network will require installation of new analyzers at selected sites, and implementation of new monitoring, calibration, and data acquisition procedures. The purpose of Precursor Gas TAD is to provide state, local, and tribal (S/L/T) agencies with guidance on the equipment, procedures, data acquisition, and quality assurance/quality control (QA/QC) efforts needed to properly implement high sensitivity precursor gas monitoring.

The beginning of this chapter will discuss the nitrogen dioxide (NO_2) measurement principle and calibration procedures for use with traditional ambient monitors. The latter sections of this chapter will focus on high sensitivity (NO_y) precursor gas monitoring instrumentation, their calibration and related sampling issues. The (NO_y) precursor gas analyzers are very similar to the traditional analyzers used to monitor for NO_2. They share the measurement principle of the chemiluminescent reaction of nitric oxide and ozone ($NO\text{-}O_3$) and utilize essentially the same calibration procedure.

Overtime, high sensitivity analyzers will increasingly be brought online; however, traditional analyzers will remain part of the NAAQS monitoring network for many years to come.

Nitrogen Dioxide (NO_2) Measurement Principle

The basis of the measurement principle for NO_2 is the same as that for ozone. The only difference between the two principles is the chemiluminescent reaction involved, and the indirect determination (as opposed to direct for ozone) of the NO_2 concentration.

When nitric oxide reacts with ozone, some electronically activated nitrogen dioxide is formed. In order to lose its energy of activation, the activated nitrogen dioxide emits a quantum of light. This released light energy has a characteristic band of 600 to 2400 nm with a strong peak at 1200 nm. This light emission spectrum is unique to the $NO\text{-}O_3$ reaction. The light intensity released from the chemiluminescent reaction is proportional to the reactant concentration of NO, and, therefore, can be used to measure NO concentrations. As in the ozone measurement method, a photomultiplier tube is used to convert the light-energy emitted from the reaction to an electrical impulse (Clough and Thrush 1967) (Fontijn, Sabadell, and Ronco 1970).

In order to utilize the $NO\text{-}O_3$ chemiluminescent reaction for the measurement of NO_2, it is necessary to reduce NO_2 to NO so that it can react with ozone. NO_2 analyzers employ a converter which reduces all NO_2 present in the air sample to NO. Two basic types of converters are used: a thermal reduction converter, or a chemical reduction converter. Both types of converters reduce only NO_2, while allowing NO to pass through the converter unchanged. Chemical reduction is the preferred method in modern ambient air monitoring instruments since the reduction of NO_2 to NO can occur at a lower temperature.

In the NO_2 measurement process, the sampled air is first passed directly into the chemiluminescent reaction chamber, and the concentration of NO is measured. The NO concentration is then stored electronically for later use. The analyzer then passes a sample of air through the converter, thereby transforming NO_2 to NO but leaving the original NO content unchanged. This sample is then measured and the resultant concentration is stored as total oxides of nitrogen ($[NO_2] + [NO]$) or, as it is sometimes termed, $[NO_x]$. The analyzer electronically subtracts the original NO concentration (which was stored) from the NO_x concentration to yield the concentration of NO_2. This $[NO] – [NO_x]$ determination sequence is sometimes reversed, depending on the instrument's design.

Chemistry

The reaction between nitric oxide and ozone is straightforward with few interferences:

(Eq. 9-1) $$NO + O_3 \rightarrow NO_2 * + O_2$$

NO_2* denotes the activated nitrogen dioxide molecule. The chemiluminescent process evolves from this activated molecule returning to its natural ground energy state. This requires the loss of energy in the form of light (Clough and Thrush 1967):

(Eq. 9-2) $$NO_2 * \rightarrow NO_2 + hv$$

The term, hv, represents a photon of light emitted at a characteristic-wavelength as the excited NO_2* molecule returns to a lower energy state.

Equipment

An NO_2 continuous ambient air analyzer is composed of the following basic components: an ozone generator, a solenoid or sample separation tree, an NO_2-NO converter, ozone and sample air flow controllers, a chemiluminescent reaction chamber, a photomultiplier tube (PMT), and signal storage/processing electronics. Figure 9-1 is a schematic off a typical NO_2 analyzer.

The source of ozone for the NO-O_3 reaction is a self-contained ozone generator. The ozone generator used in most commercial analyzers is a gas discharge type. Ozone is formed when a high voltage, applied to an internal electrode, discharges through the surrounding sample air to an outer electrode. The outer electrode is formed by a conductive coating applied to the exterior of the glass tube, wherein sample air flows through the generator. This generator doesn’t have provisions for adjusting the ozone output. The ozone produced is of one concentration that is adequate for a complete reaction with any expected concentration of NO. The source of oxygen for irradiation should first be passed through a drying agent. This precaution will assure that the ozone concentration produced will not be affected by variations in the moisture content of the source air and will prevent formation of nitric acid, which could damage the ozone generator and reaction chamber. A solid desiccant, such as drierite ™, which must be replace periodically (prior to it becoming saturate), or a continuously operating permeation type air drier may be used as the drying agent.

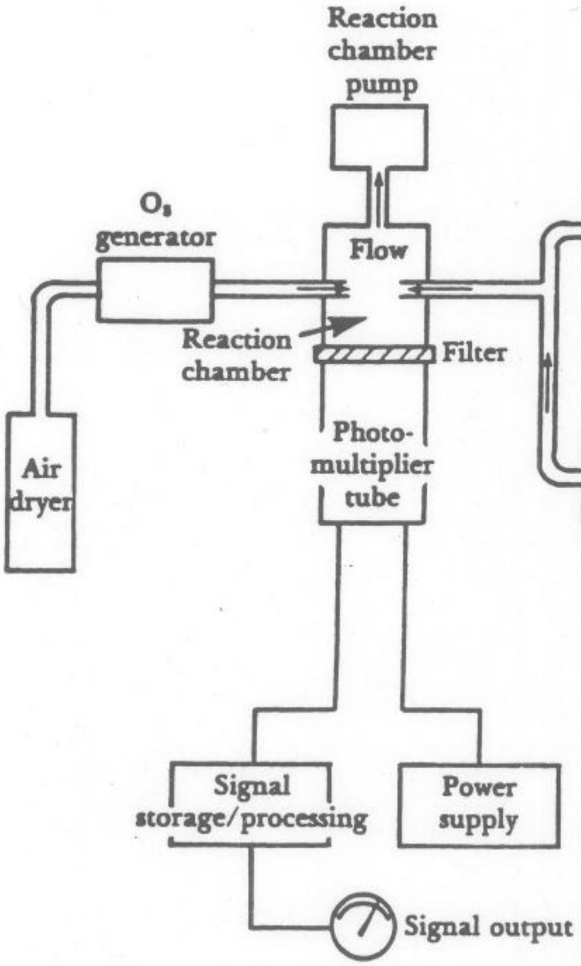


Figure 9-1. Chemiluminescent NO_2 analyzer.

The use of a solenoid or a sample separation tee depends on the method employed by the manufacturer to separate the air sample for the NO and NO_2 determinations. NO_2 analyzers can employ one of two basic configurations, dual or cyclic, for the NO and NO_x measurements. In dual-type analyzers, the air sample is divided at the analyzer inlet and half passes continuously through a converter to one reaction chamber (NO_x) while the other half passes continuously (though an equivalent converter volume) to a second reaction chamber (NO). The NO and NO_x concentrations are measured continuously with either a single detector time shared between the two reaction cells or a pair of matched detectors (one for each reaction cell).

In contrast, the more common cyclic analyzers have a single reaction chamber and detector and utilize a solenoid to direct the sample through the converter (for NO_x determinations) or around the converter (for NO determinations). The sample partitioning solenoid of the cyclic-type instruments is connected electronically to the signal processing circuitry. When the solenoid is in the bypass (NO) mode of operation, it signals the NO measurement/memory circuitry to activate. Meanwhile, the NO_x measurement/memory circuitry is in the hold position, and the memory retains the photomultiplier tube signal

(NO_x concentration) from the last time it was in the "on" position (solenoid directing sample through the converter). This sample-hold process alternates to the corresponding NO-NO_x cycles of the solenoid valve (Ellis 1975).

As discussed earlier, chemical reduction converters are the preferred over thermal converters and are made from a variety of materials: pure metals such as gold, tungsten, platinum or molybdenum; various alloys; or carbon-based compounds such as nonabsorptive charcoals or carbon impregnated with various metals. Although their compositions differ, chemical converters reduce NO_2 to NO by forming an oxide of the converter material. In the case of carbon-based converters, reduction occurs as follows:

(Eq. 9-4) $$C + NO_2 \xrightarrow{\Delta T} CO + NO$$

Due to the nature of this conversion process, chemical converters will eventually lose their effectiveness. This is no great advantage, however, since the carbon-type converters are inexpensive to replace and the metal-based converters are easily reactivated by exposing the converter surface to a reducing gas such as hydrogen. Although ammonia is not oxidized to NO by chemical converters at normal operating temperatures (200 to 375 ºC), other unstable nitrogen compounds such as peroxyacetyl nitrate (PAN), some amines, and certain organic nitrates and nitrites will decompose quantitatively to NO. The ambient concentrations of these compounds are usually so low in most areas of the country that this interference can be disregarded (Breitenbach and Shelef 1973) (Winter et al. 1974) (Ellis 1975).

Ozone and sample flow control is an important consideration in the proper use of an NO_2 analyzer due to the stoichiometric properties of the chemiluminescent reaction. For the instrument's response to remain stable, it is essential that constant flow rates be maintained. This is achieved by the use of capillaries and pressure regulators. The use of these flow controllers results in a constant flow to the reaction chamber over a wide range of sample source pressures and flow rates.

A schematic representation of an NO_2 analyzer's reaction chamber is shown in Figure 9-2. The reaction chamber is a light-tight container of a size which is sufficient to allow the total chemiluminescent reaction to take place. The two reactant gases (0_3 + NO) are metered into the chamber, mixed, and the resultant light energy is passed to the photomultiplier tube via a "window" at one end of the chamber. To facilitate proper mixing and flow through the chamber, a vacuum pump maintains a partial vacuum within the chamber of about 200-300 mm Hg. A red, sharp-cut optical filter, which absorbs any light emissions below 600 nm, is placed between the reaction chamber and the photomultiplier tube. This filter is required to eliminate interfering emissions of shorter wavelengths which are emitted from the chemiluminescent reaction of ozone with certain unsaturated hydrocarbons.

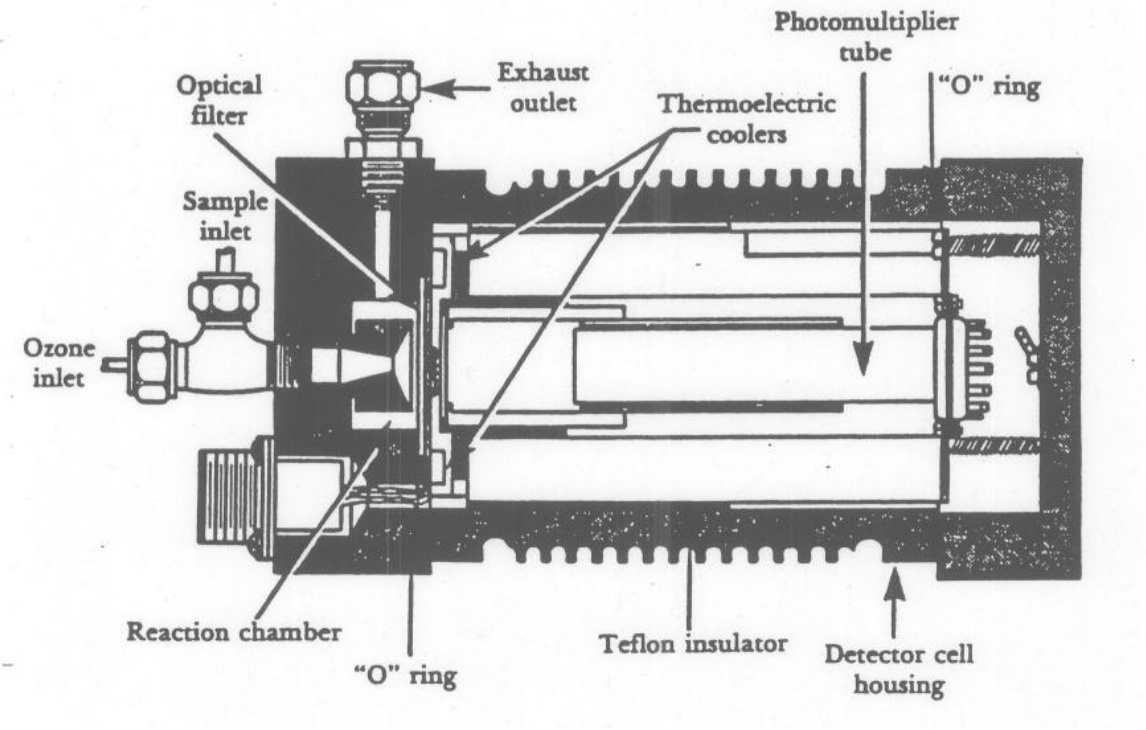


Figure 9-2. Reaction chamber/photomultiplier assembly.

The photomultiplier tube is contained in a thermoelectrically cooled housing, which maintains the photomultiplier tube at a temperature of approximately 8°C or less. By cooling the PMT, its sensitivity and response time are enhanced, thus resulting in lower limits of detectability.

As explained previously, the signal processing components of an NO_2 analyzer operate in conjunction with the sample cycling valves. This is accomplished by independent timer controls which alternate the NO-NO_2 measurement cycles every 5 to 30 seconds. Each mode's PMT signal is fed to a corresponding analog circuit where that signal is stored. At the end of the double cycle (NO-NO_2 measurement), the two modes' output signals are subtracted by an electronic subtraction circuit and the NO_2 concentration is registered by readout circuitry.

Calculations

Most NO_2 ambient analyzers have direct readout capability, indicating NO_2 concentration in ppm. If it is necessary to record NO_2 data in concentrations of µg/std m^3 the following conversion factor is used:

(Eq. 9-3)
$$\frac{\mu g\ NO_2}{\mathrm{std}\ m^3} = \mathrm{ppm}\, NO_2 \times 1880$$

Calibration Procedures

EPA allows either of two different methods for the calibration of NO_2 analyzers: gas phase titration (GPT) or, alternatively, calibration with an NO_2 permeation tube/dilution system (for further details see 40 CFR 50 Appendix F). Both of these calibration methods essentially satisfy the two requirements for NO_2 analyzer calibration which are:

1. calibration of NO and NO_x responses of the analyzer using an NO standard, and
2. calibration of NO_2 response of the analyzer with NO_2, generated directly, or indirectly, from an NO_2 standard.

Gas Phase Titration (GPT) Method

This calibration technique is based on the rapid gas phase reaction of NO and O_3 to produce stoichiometric quantities of NO_2. The reaction proceeds according to the following reaction (Hodgeson et al. 1972):

(Eq. 9-4)

$$NO + O_3 \rightarrow NO_2 + O_2$$

The quantitative nature of the reaction is used in a manner such that, once the concentration of reacted NO is known, the concentration of NO_2 is determined. Ozone is added to excess NO in a dynamic calibration system, and the previously calibrated NO channel of the analyzer is used to measure changes in NO concentration. Upon the addition of O_3, the decrease in NO concentration observed by the calibrated NO channel is equivalent to the concentration of NO_2 produced. The amount of NO_2 generated is varied by changing the concentration of O_3 added.

Figure 9-3 shows the recommended configuration of a typical GPT calibration system. Dynamic calibration systems utilizing this basic configuration are available commercially or can be assembled using Figure 9-3 as a guide. However, before either a commercial or self-assembled GPT/NO_2 calibrator is used, the following conditions must be met:

1. provide an adequate flow and concentration range for the analyzer to be calibrated
2. have a stable ozone source with an adjustment output
3. have a reaction chamber residence time of less than 2 minutes (refer to EPA 600/4-75-003)
4. have a dynamic parameter specification of 2.75 ppm-minutes or greater at the operating conditions at which calibration will be performed (refer to EPA 600/4-75-003)

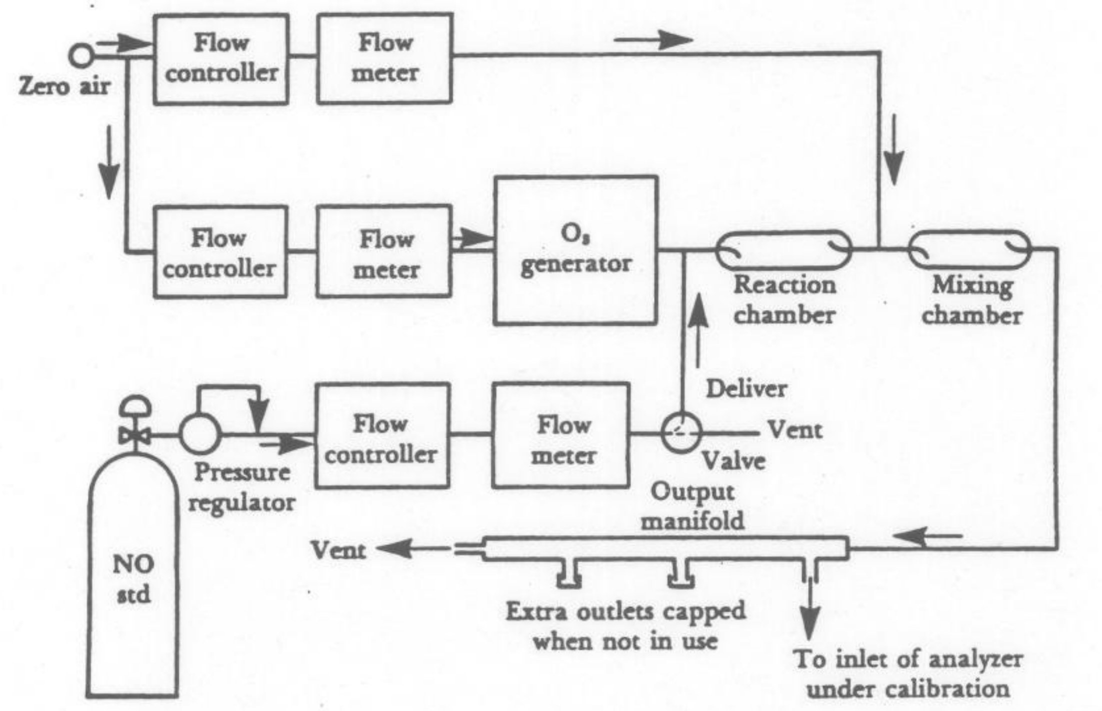


Figure 9-3. Schematic diagram of a typical GPT calibration system.

In addition to the requirements listed above, there are some other items which are important in performing a valid NO_2 calibration. Pressurized cylinders of NO in nitrogen (N_2) at levels between 50 to 100 ppm are recommended for use in the GPT system. Care should be taken to use only cylinders containing NO in oxygen-free N_2, and assayed to contain no more than 1.0 ppm NO_2 as impurity. It is preferable to have no NO_2 impurity. Some agencies will reject a cylinder of NO with any NO_2 impurity. To assure that the cylinder's concentration is as stated, it should be certified against a National Institute of Standards and Technology's (NIST) Standard Reference Material (SRM) for NO. It is important to select a cylinder pressure regulator of a non-reactive material, such as stainless steel to avoid oxidation of the NO. Additionally, the pressure regulator and as much of the connecting non-reactive connecting tubing (e.g., glass, teflon™) should be properly purged to remove contaminants which may react with the NO. A slow and steady decline in instrument response during challenge with a span concentration may be a result of an improperly purged regulator and sample line.

Only a clean, dry source of oxygen should be used for ozonation by the ozone generator. In addition, it is very important that the flow of oxygen to the ozone generator be regulated so as to allow no variation in the resulting O_3 concentration.

As mentioned before, gas phase titration requires the use of the NO channel of the analyzer to determine the amount of NO_2 generated by titration. Therefore, it is necessary to calibrate and determine the linearity of the NO channel before proceeding with the NO_2

calibration. In some analyzers it is also necessary to calibrate the NO_x channel. This can be done simultaneously with the NO calibration.

To calibrate the NO-NO_x channels, several concentrations (normally six covering the selected range) of NO are generated by the GPT system and measured by the chemiluminescence analyzer. Adjustments are made to the zero and span controls of the analyzer to reflect the responses to these various NO concentrations. The number and nature of adjustments is dependent on the design of the instrument. Following the actual calibration of the instrument's NO-NO_x response, calibration curves are prepared by plotting instrument response against the different concentrations of NO and NO_x.

After calibrating the NO-NO_x channels, the ozone generator is activated on the dynamic multi-gas calibrator/GPT system and NO_2 is generated for calibrating the instrument's NO_2 response. Again, to determine the NO_2 concentration the analyzer's NO channel is used to measure the initial NO concentration and then the resultant NO concentrations as the ozone output is changed. Generally, six separate NO_2 concentrations are generated by adjusting the concentration of ozone (see Chapter 6, "Ozone Generator"). These concentrations should cover the entire NO_2 response range chosen. A calibration curve reflecting instrument response vs. NO_2 concentration (calculated from NO response) is plotted for future use.

The accuracy of the NO_2 calibration is dependent on the analyzer's converter efficiency. Therefore, a determination of converter efficiency is a required part of the calibration procedures. To determine the converter efficiency, the total NO_2 concentration generated during the GPT calibration is calculated:

(Eq. 9-5)

$$[NO_2]_{out} = [NO]_{orig} - [NO]_{rem} + NO_2 \text{ impurity}$$

Where:

$[NO_2]_{out}$ = the total NO_2 concentration generated

$[NO]_{orig}$ = the original NO concentration at 90% of NO range (taken from NO calibration curve)

$[NO]_{rem}$ = the NO concentration at 80% of NO_2 range-ozone generator on (taken from NO calibration curve)

NO_2 impurity = NO_2 concentration resulting from NO_2 present in the NO cylinder, if any.

The total NO_2 concentration converted to NO in the analyzer's converter is calculated:

(Eq. 9-6)

$$[NO_2]_{conv} = [NO_2]_{out} - \left([NO_x]_{orig} - [NO_x]_{rem}\right)$$

Where:

$[NO_2]_{conv}$ = total NO_2 concentration converted to NO

The slope of a plot of $[NO_2]_{conv}$ vs. $[NO_2]_{out}$ is the average converter efficiency of the analyzer. A converter efficiency of less than 96% is considered unacceptable.

A detailed description of the GPT calibration procedure and the associated calculations is contained in the manufacturer's instruction manual and in the following publications:

USEPA, Quality Assurance Guidance Document 2.3, Reference Method for the Determination of Nitrogen Dioxide in the Atmosphere (Chemiluminescence) (1998 Draft)

Ellis, E.C., Technical Assistance Document for the Chemiluminescence Measurement of Nitrogen Dioxide. EPA 600/4-75-003, December 1975.

In addition, Appendix A of this manual is a reprint of the reference measurement principle and calibration procedures for NO_2 contained in Title 40 of the *Code of Federal Regulations*, Part 50.

NO_2 Permeation Tube Method

Instead of generating NO_2 indirectly using NO and O_3, it is possible to calibrate the NO_2 channel directly using an NO_2 permeation tube. The NO_2 permeation tube is an inert, polymeric material (usually Teflon®) which contains a quantity of liquefied NO_2. The walls of the tube are semi-permeable, due to the structure of the polymeric material. The liquid NO_2, due to its high vapor pressure, changes into NO_2 gas which can permeate the walls of the polymeric tube. This permeation rate is a temperature dependent, time constant rate, and is usually determined in μg/min.

In this calibration procedure, the NO and NO_2 responses of the chemiluminescent NO_2 analyzer are first calibrated with an NO standard, essentially using the same procedure as discussed for the GPT method. The NO_2 channel is calibrated with various concentrations of NO_2 produced by accurately diluting the effusion from the NO_2 permeation tube with metered flows of zero air.

Figure 9-4 is a diagram of a typical dynamic multi-gas calibrator with an integrated permeation tube calibration system. Such systems are commercially available or can be assembled with the indicated components. The system consists of four functional sections:

1. A temperature-controlled section that houses the NO_2 permeation tube. A continuous flow of purified, dry zero air or nitrogen is passed through this section to effect transport of the permeation NO_2;
2. A regulated source of clean, dry zero air for dilution of the NO_2 gas from the permeation tube;
3. An NO standard (cylinder gas) and delivery system; and,
4. A dilution-mixing, sampling, and exhaust section.

The first two of the above are unique for the NO_2 permeation tube calibrator, while the last two are essentially the same as, and their operations follow, the GPT procedure.

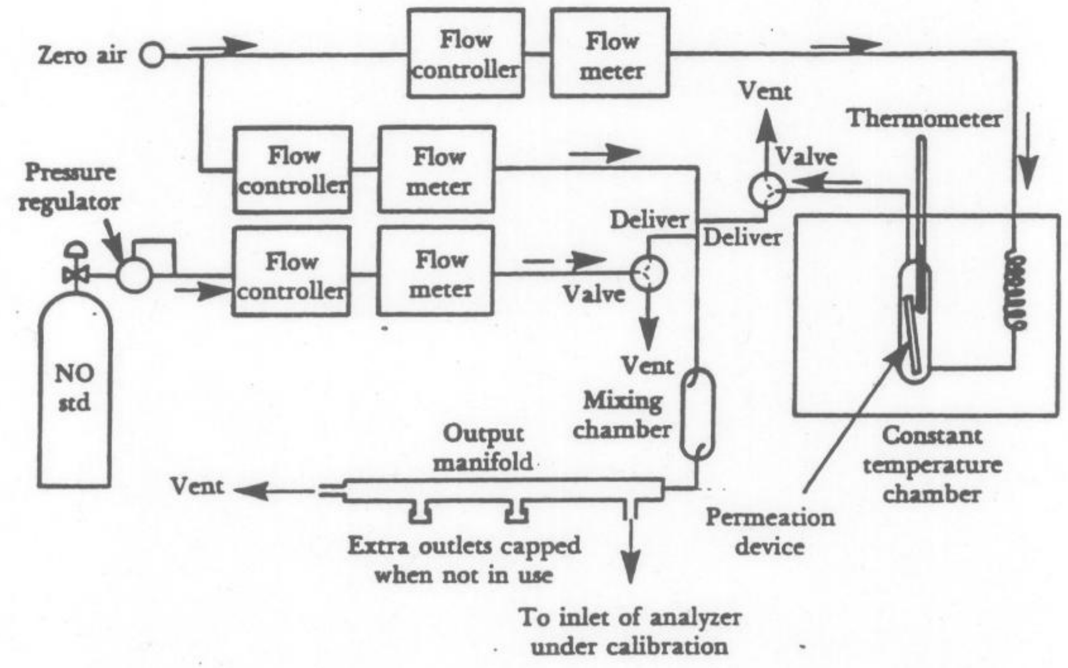


Figure 9-4. Schematic diagram of a typical calibration apparatus using an NO_2 permeation tube.

An essential element of the NO_2 permeation calibrator is the maintenance of the permeation tube at a constant temperature. In order for the calibration to be accurate and valid, a constant temperature with ±0.1°C must be maintained and monitored while the calibrator is in use. This requires that the permeation tube be contained in a temperature controllable, constant temperature chamber.

In addition to maintaining the permeation tube at a constant temperature, it is also necessary to maintain the purge gas at the same temperature. The purge gas is a small, fixed zero air or nitrogen flow that carries the NO_2 out of the permeation area into a mixing chamber where the NO_2 is diluted with clean, dry zero air. To maintain the purge gas's temperature, it is necessary to pass the air (or nitrogen) through a heat exchanger (e.g., a coil of copper tubing), contained in the constant temperature chamber. The gas is then passed over the permeation tube.

Once the permeation tube calibration system has been assembled, is operative, and the NO cylinder and NO_2 permeation tube have been intercompared with respect to certified standards, the actual calibration of an NO_2 chemiluminescence analyzer is straight forward. The object of the calibration is to determine NO, NO_2, and NO_x response of the analyzer as a function of known NO and NO_2 concentrations. Also, it is an important part of the calibration to determine the converter efficiency of the instrument.

The NO and NO_x channels of the analyzer are calibrated from NO concentrations generated by dilutions of the NO cylinder's contents. The procedure used in the GPT method for these two channels is applicable. The instrument's span and zero controls are adjusted to reflect these concentrations. Also, calibration curves are prepared.

The NO_2 channels is calibrated by generating several (usually six) concentrations of NO_2. This is done by diluting the effluent from the permeation tube. The instrument's controls are set based on the span concentration (approximately 80% of the upper range limit), and a calibration curve is prepared for the NO_2 response.

Converter efficiency is determined using the same basic procedure as in the GPT method. The total NO_2 concentration generated, $[NO_2]_{out}$, is calculated from the permeation rate and the total flow (dilution gas + purge gas) of the system. The amount of NO_2 converted to NO ($[NO_2]_{conv}$) by the analyzer is determined by the instrument's NO_x response to the generated NO_2 concentrations. $[NO_2]_{conv}$ (y-axis), is plotted verses $[NO_2]_{out}$ (x-axis), to give the converter efficiency curve. The slope of this curve multiplied by one hundred gives the converter's efficiency in percent. In modern instruments the converter efficiency is determined by the instrument's software and displayed digitally. If efficiency is less than 96%, the converter should be replaced or recharged.

The publications cited in the gas phase titration section also contain pertinent information concerning the NO_2 permeation tube method. These publications should be consulted before performing the calibration of the NO_2 chemiluminescence by means of the permeation tube method.

Reference Measurement Principle - Characteristics and Capabilities

Advantages

Chemiluminescence NO_2 analyzers have a relatively fast response time, due to the mechanism of the gas phase reaction of ozone and nitric oxide. They also tend to be reliable and easy to operate, requiring little in the way of ancillary equipment.

Interferences

Interference from air pollutants commonly found in the environment- ozone, sulfur dioxide, carbon monoxide, methane, and ammonia- are negligible for chemiluminescence NO_2 analyzers. The selectivity of the NO-O_3 reaction, the use of low temperature catalytic converters, and selective optical filters, preclude almost all possible interferences. The only possible interferences of any significance are organic nitrates, organic nitrites, and PAN. The ambient concentrations of these compounds are usually so low in most areas of the country that this interference can be disregarded. However, for highly quantitative ambient air studies, under circumstances where relatively low concentrations off NO_2 occur simultaneously with high concentrations of PAN and other nitrogen-containing compounds (1:10 ratio), the results of these particular interferences could be significant. If this situation exists, then it may be necessary to determine independently the concentrations of the interfering species by gas chromatography, infrared spectroscopy, or other methods. Upon determining their concentrations, corrections to the chemiluminescent NO_2 determinations can be made. Further discussion is included in the latter section of this chapter specifically regarding interferents on high sensitivity precursor gas monitoring.

Range and Sensitivity

Most chemiluminescence NO_2 analyzers are equipped to measure several different concentration ranges. Typically, the lowest range is up to 0.05 ppm NO_2, with the largest range being up to 100 ppm NO_2. It is possible to select several ranges between these two cited, but a range of 0 to 0.5 ppm is the usual range used in most ambient air monitoring applications. It is typical for modern analyzers to be equipped with an auto-ranging feature.

Normal minimum sensitivity (Lower Detectable Limit – LDL) for the determination of NO, NO_x, NO_2 is reported as 0.4 ppb (0.0004 ppm).

Problems, Precautions, Troubleshooting

Problems and precautions regarding the use of chemiluminescent NO_2 instruments for ambient monitoring have been discussed at various points within this chapter. These precautions mainly involve the NO_2-NO converter's design/operation, ozone generator design/operation, and calibration procedures. The operating manual of any NO_2 analyzer contains specific instructions in these areas. A thorough maintenance and calibration program will assure that problems will be kept at a minimum.

Troubleshooting will only be necessary when instrument conditions or sample results deviate from normal or the instrument's diagnostics indicate some malfunctions. Table 9-1 is intended to serve as a brief guide to diagnosing and remedying some sampling problems.

Table 9-1. Typical NO_x monitor problems

Observation	Problem Cause	Remedy
NO Mode		
NO sample result too low or zero	1. Sample line clogged or closed 2. Ozonizer inoperative 3. Photomultiplier tube failure 4. Signal amplifier open 5. Vacuum pump inoperative	1. Check inlet line and flow meter 2. Check O_3 supply and ozonizer lamp 3. Check photomultiplier tube 4. Check all circuits 5. Check pump
NO sample results too high	1. Photomultiplier tube too sensitive 2. Sample too large	1. Check photomultiplier tube and amplifier circuits 2. Check inlet flow meter
NO_2 Mode		
NO_2 sample results too low	1. Sample line clogged or closed 2. Ozonizer inoperative 3. Photomultiplier tube failure 4. Signal amplifier open 5. Vacuum pump inoperative 6. NO_2 converter ineffective	1. Check inlet line and flow meter 2. Check O_2 supply and ozonizer lamp 3. Check photomultiplier tube 4. Check all circuits 5. Check pump 6. Check converter heater, or replace catalyst
	1. Photomultiplier tube too sensitive	1. Check photomultiplier tube and amplifier
Interference		
All sampling results too low or high	1. NH_3 or PAN 2. Photomultiplier tube may be failing	1. Monitor for NH_3/PAN 2. Check photomultiplier tube and amplifier circuits against manufacturer's specifications

Additional guidance in troubleshooting instrument problems can be found in the individual instrument's operating manual.

Quality Assurance

To assure that the data obtained from a chemiluminescence NO_2 monitor is valid, a conscientious quality assurance program should be carried out on various aspects of the ambient monitoring/data production process. Five general areas of concern for an NO_2 monitoring quality assurance program are:

1. calibration;
2. operation;
3. data reduction;
4. performance audits; and
5. system audits.

Calibration

The details of performing an NO_2 analyzer calibration are contained in preceding sections. However, after the calibration procedures have been performed there is still a tendency for the instrument to drift from the set calibration responses. A one point span check performed at least once per week using a GPT or perm tube system, will determine if the instrument's precision is being maintained. The accuracy of the instrument is determined by a check of three different NO_2 concentrations. This should be performed at least once each quarter. If either of these audit processes shows a deviation from the original calibration, a full recalibration should be performed.

Operation

An essential part of the quality assurance program is scheduled series of checks for the purpose of verifying the operational status of the monitoring system. The operator should visit the site at least once per week, noting such items as: temperature inside the monitoring shelter, condition of the sample introduction system (i.e., water in lines, conditions of prefilters, leaks/breaks in lines, etc.), status of the recorder or data acquisition system (i.e., proper ink level and trace, adequate paper supply, chart drive working), and the condition of the NO_2 analyzer (i.e., flow controls at proper settings, temperature indicators at proper levels, span and zero stable).

Data Reduction

Before data is considered valid, it should be subjected to several quality assurance activities. Begin by visually inspecting the strip chart or data printout to determine if there are signs of instrument malfunction. The data can then be reduced to a suitable reporting format.

Performance Audits

An audit is an independent assessment of data accuracy. Independence is achieved by having the audit performed by an operator other than the one conducting the routine field measurements and by using audit standards and equipment different from those routinely used in monitoring.

For an NO_2 monitoring system, two performance audits are recommended: a multipoint calibration audit and a data audit. The multipoint calibration audit consists of challenging the analyzer with three different, known concentrations of NO_2 covering the analyzer's range. The difference between these known concentrations and the analyzer's response is used to calculate the accuracy of the analyzer. This multipoint calibration audit should be carried out at least once per quarter.

Data reduction audit involves reading a strip chart record, calculating an average, and transcribing or recording the results on the AIRS data form. This independent check of the entire data reduction should be performed by an individual other than the one who originally reduced the data. Initially the data processing check should be performed 1 day out of every 2 weeks of data. For two l-hour periods within each day audited, make independent readings of the strip chart record and continue tracing the data reduction steps through the actual transcription of the data on the AIRS data form. The 2 hours that are selected during each day that is audited should be those for which either the analyzer response is most dynamic in terms of spikes or the average concentration is high.

The data processing check is made by calculating the accuracy:

$$A = [NO_2]_R - [NO_2]_{CHECK}$$

where
A = the difference in measured and check values
$[NO_2]_R$ = the recorded analyzer response, ppm
$[NO_2]_{CHECK}$ = the data processing NO_2 concentration, ppm.

If A exceeds ±0.02 ppm, check all of the remaining data in the 2-week period.

System Audit

A systems audit is an on-site inspection and review of the quality assurance activities used for the total measurement system (sample collection, sample analysis, data processing, etc.); it is a qualitative appraisal of system quality. See Section 15 ("Assessment and Corrective Action") in Volume II, Part 1, of EPA's *Quality Assurance Handbook for Air Pollution Measurement Systems* (EPA 1998). A checklist for a systems audit can be found in Figure 6.4 (QA Handbook). Questions in this checklist should be reviewed for applicability to the particular local, state, or federal agency.

The systems audit is to be conducted at the startup of a new monitoring system and periodically (as appropriate) as significant changes in system operations occur.

Measurement Quality Objectives

Table 9-2: An example (prepared by USEPA) of measurement quality objectives (MQO) for the ambient measurement of NO_2 by chemiluminescence.

Measurement Quality Objectives - Parameter NO_2 (Chemiluminescence)				
Requirement	**Freq.**	**Acceptance Criteria**	**Reference**	**Information/Action**
Standard Reporting Units	All data	ppm	40 CFR, Pt 50.11	
Shelter Temp.				
Temp. range	Daily	20 to 30 °C	40 CFR, Pt. 53.20	Instruments designated as reference or equivalent has been tested over this temp. range. Maintain shelter temp. above sample dewpoint. Shelter should have a 24- hour temp. recorder. Flag all data for which temp. range or fluctuations are outside acceptance criteria.
Temp. control	Daily	±2 °C	Vol II, S 7.1 1/ Vol II, MS 2.3.2	
Equipment				
NO_2 analyzer	Purchase Specs	Reference or equivalent method	40 CFR, Pt 53.9	
Air flow controllers	"	Flow rate regulated to ±2%	40 CFR, Pt 50, App F, S2.2	
Flowmeters		Accuracy ±2%	EPA-600/4-75-003	
Detection				
Noise	Purchase specs	0.005 ppm	40 CFR, Pt 53.20 & 23	Instruments designated as reference or equivalent have been determined to meet these acceptance criteria
Lower Detection level		0.01 ppm	"	
Completeness				
Hourly Data	Quarterly	75 %	40 CFR, Pt 50.11	
Compressed Gases				
Dilution gas (zero air)	Purchase specs	Free of contaminants	EPA-600/4-75-003	Return cylinder to supplier.
Gaseous standards	"	NIST Traceable (e.g., EPA Protocol Gas)	40 CFR, Pt 50, App F, S1.3 EPA-600/R-97/121	Nitric oxide in nitrogen EPA Protocol Gases have a 24-month certification period and must be recertified to extend the certification.

Measurement Quality Objectives - Parameter NO_2 (Chemiluminescence)

Requirement	**Freq.**	**Acceptance Criteria**	**Reference**	**Information/Action**
Calibration				
Multipoint calibration (at least 5 points)	> 1/6 months., after failure of QC check or after maintenance	Res. time < 2 min Dynam. parameter > 2.75 ppm-min All points w/in ±2% of full scale of best-fit straight line	40 CFR, Pt 50, App F, S 1 Vol II, S 12.6Vol II, MS 2.3.2	Zero gas and at least four upscale calibration points. Points outside acceptance criterion are repeated. If still outside consult manufacturer's manual and invalidate data to last acceptable multipoint calibration or zero/span check.
Convertor efficiency	During multipoint calibration	96%	40 CFR, Pt. 50, App F Vol II, MS.2.3.2	Replace or service converter.
Zero/span check–level 1	1/ 2 weeks	Zero drift ±20 - 30 ppb Span drift ±20 to 25% Zero drift ± 10 to 15 ppb Span drift ± 15%	Vol II, MS 2.3.2 Vol II, S 12.6 Vol II, S 12.6 Vol II, MS 2.3.2	**If calibration factors are updated after each zero/span,** invalidate data to last acceptable zero/span check, adjust analyzer, and perform multipoint calibration. **If fixed calibration factors are used to calculate data,** invalidate data to last acceptable zero/span check, adjust analyzer, and perform multipoint calibration.
Flowmeters	1/3 months	Accuracy ± 2%	Vol II, App 12	Flowmeter calibration should be traceable to NIST standards.
Performance Evaluation				
(NPAP)	1/year at selected sites	Mean absolute difference 15%	NPAP QAPP	Use information to inform reporting agency for corrective action and technical systems audits.
State audits	1/year	State requirements	Vol II, App 15, S 3	
Precision				
Single analyzer	1/ 2 weeks	None	40 CFR, Pt 58, App A	Concentration. = 0.08 - 0.10 ppm.
Reporting organization	1/3 months	95% Confidence Interval ± 15%	EPA-600/4-83-023 Vol II, App 15, S 6	
Accuracy				
Single analyzer	25% of sites quarterly	None	40 CFR, Pt 58, App A	Four concentration ranges. If failure, recalibrate analyzer and reanalyze samples. Repeated failure requires corrective action.
Reporting organization	(all sites yearly)	95% Confidence Interval # ± 20%	EPA-600/4-83-023 Vol II, App 15, S 3	

1/ - reference refers to the QA Handbook for Air Pollution Measurement Systems, Volume II. The use of "S" refers to sections within Part 1 of Volume II. The use of "MS" refers to method-specific sections in Volume II.

In theory, if these MQOs are met, measurement uncertainty should be controlled to the levels necessary to provide reliable data.

High Sensitivity Total Reactive Nitrogen Oxides (NO_y) Measurements

Introduction

Measurement of ambient nitrogen oxides differs from measurement of CO or SO_2 in that the target air pollutant is not a single chemical but a group of chemicals of differing properties, and is not a criteria air pollutant. Nitrogen oxides released from emission sources are primarily nitric oxide (NO) with lesser amounts of nitrogen dioxide (NO_2), which collectively are termed NO_x (i.e., $NO_x = NO + NO_2$). These primary emitted species are converted by atmospheric processes to numerous other inorganic and organic nitrogen oxides, which collectively are called NO_z, and the total of all reactive gaseous nitrogen species present in ambient air is called NO_y (i.e., $NO_y = NO_x + NO_z$).
Precursor gas monitoring in the NCore network builds upon capabilities of EPA's Photochemical Assessment Measurement Stations (PAMS) network and Southern Oxidants Study to measure ozone precursors, including total reactive oxides of nitrogen (NO_y). Measuring NO_y is a valuable adjunct to NO and NO_x monitoring because the individual species comprising NO_z include numerous organic and inorganic nitrogen oxide compounds, that are difficult to measure individually, but collectively contribute to a more complete and conservative measure of nitrogen oxides. Determining NO_y concentrations is useful in establishing nitrogen oxide emission patterns and temporal trends, and in assessing the photochemical age and reactivity of air masses. NO_y measurements are a critical tool in accounting for progress in large-scale nitrogen emission reduction programs, providing input for a variety of source apportionment and observation based models, and assisting in the evaluation of air quality models.

Properties of NO_y

NO_y includes all of the nitrogen oxide compounds that reacts or is formed in the lower atmosphere and that contribute to the photochemical formation of O_3 and the transport and ultimate fate of nitrogen oxides. NO_y compounds include NO_x (NO + NO_2) and NO_z, which include nitrogen acids [nitric acid (HNO_3) and nitrous acid (HONO)], organic nitrates [e.g., peroxyl acetyl nitrate (PAN), methyl peroxyl acetyl nitrate (MPAN), and peroxyl propionyl nitrate (PPN)], other organic nitrogen oxides, particulate nitrates, nitrate radical (NO_3), nitrogen trioxide (N_2O_3), nitrogen pentoxide (N_2O_5) and halogen-nitrogen species (e.g., $ClONO_2$ and $BrONO_2$). In typical urban environments, the principal NO_y compounds include NO, NO_2, HNO_3, and PAN, and in some cases particulate nitrate.

In terms of precursor monitoring in NCore, a key factor is that the numerous species making up the total NO_y differ widely in their physical properties and chemical reactivity. For example, some species, such as NO_2 and HONO, are readily photolyzed, whereas others, such as PAN, decompose rapidly at moderate temperatures. NO and NO_2 are chemically reactive, but have relatively low solubility in water, whereas the key product species HNO_3 is highly soluble and relatively unreactive. Consequently, physical removal of HNO_3 from the atmosphere is a key removal process for NO_y. Organic nitrogen oxides can vary widely in volatility and stability, and HNO_3 is known to be highly "sticky"; that is, adsorptive on surfaces. In addition, particulate ammonium nitrate (NH_4NO_3) is volatile under certain ambient conditions, and can decompose to release HNO_3 and ammonia (NH_3) into the gas phase. These factors make accurate sampling and measurement of atmospheric NO_y much more challenging than determination of CO or SO_2. A discussion of sampling and measurement issues that must be addressed in order to make more useful measurements of NO_y is provided in the following sections.

Sources of NO_y

Nitrogen oxides are emitted to the atmosphere principally as NO and NO_2, by both natural and man-made sources. Important natural sources include lightning and natural fires. The major man-made emissions result from transportation and combustion of fossil fuels for energy production. Once released into the atmosphere, NO and NO_2 are oxidized by photochemical processes to a wide variety of products. Oxidation of NO to NO_2 can occur by reaction with atmospheric oxygen (only at high NO concentrations that may exist very near the emissions source), or by reaction with atmospheric ozone (O_3) and free radical species. When NO_x is mixed with hydrocarbon air pollutants and exposed to sunlight, a complex set of reactions occurs that constitutes the phenomenon known as photochemical smog. This photochemical process involves free radicals generated by photolysis and maintained through chain reactions, and results in the production of large amounts of ozone. Depending on the nature of co-pollutants, this process can also produce fine particulate matter containing nitrate, sulfate, and organic material, and the more complex nitrogen oxide species that make up NO_z (and, in turn, NO_y). The extent of conversion of NO_x species to NO_y species is a measure of the "photochemical age" of an air mass; i.e., a measure of the time of transport and the reactivity of the mix of pollutants in that air mass.

Historical Overview of NO_y Measurement Method

Ambient NO_y must be measured in a practical, standardized manner, as it is not possible to measure individually all the compounds that comprise NO_y. Instruments used to measure NO_y must be sensitive enough to measure the low concentrations typically encountered in rural locations as well as the higher concentrations encountered in urban smog. The standard reference method for the determination of NO and NO_x at ambient levels is chemiluminescence (40 CFR Part 53), with several manufacturers offering EPA-approved instruments.

Instrumentation designated as Reference or Equivalent methods for measuring ambient concentrations of NO_2 is listed in 40 CFR Part 53. Instruments designated as Reference Methods for NO_2 are also approved for measuring NO. It must be noted that the designated instruments may not truly measure NO_x (i.e., NO plus NO_2) in urban areas where photochemical processes have occurred, but NO_x plus some poorly defined fraction of NO_z. For NO_y, a standard reference method has not yet been designated; however, EPA has suggested a modification of the NO_x chemiluminescence monitoring approach that uses a heated converter to reduce all reactive nitrogen species to NO, followed by detection of that NO by its chemiluminescence reaction with an excess of O_3. The original ambient NO is measured by bypassing the converter. This procedure is similar to the current methodology used to monitor NO_x except that, in the NO_y methodology, the converter has been moved to the sample inlet to avoid line losses of adsorbent NO_y species like HNO_3, and additional calibration procedures recommended for adequate measurement of the various NO_z species.

Summary of NO_y Measurement by Chemiluminescence Method

NO_y concentrations are determined by photometrically measuring the light intensity at wavelengths greater than 600 nm from the chemiluminescent reaction of NO with O3. This principle is identical to that on which the measurement of NO and NO_x is based, which is designated by EPA as the Reference Method for determining NO_2 in ambient air. The chemiluminescence approach is based on the gas-phase reaction of NO and O_3, which produces a characteristic near-infrared luminescence (broad-band radiation from 500 to 3,000 nm, with a maximum intensity at approximately 1,100 nm) with an intensity that is proportional to the concentration of NO. However, it differs in that, the NO resulting from the reduction of nitrogen oxide compounds, plus any native NO, is reacted with O_3, and the resulting chemiluminescent light is measured as an indication of the total NO_y concentration, not NO_x concentration.

To measure NO separately and specifically, sample air is by-passed around the chemical reductant converter so that no reduction of the other nitrogen oxide compounds to NO occurs. The NO (i.e., native NO only) is reacted with O_3, and the resulting chemiluminescent light intensity is proportional to the NO concentration. The primary differences between this method, as implemented for NO_y monitoring and as implemented for conventional NO_x monitoring, are in the location of the molybdenum (Mo) converter and in the calibration procedures required. The converter location at the extreme inlet of the sampling system is designed to convert all NO_y species to NO immediately upon entry of sample air into the sampling system. This approach minimizes loss of NO_y constituents, such as HNO_3 in sampling, and help to assure complete capture of the total NO_y. Calibration procedures for NO_y monitoring go beyond those used for NO_x monitoring, in that more stringent tests of converter efficiency are required (dicussed later in this chapter).

Figure 9-5 shows a schematic illustration of a typical NO_y instrument. Sample air is drawn either from the ambient air or from calibration sources (i.e., zero/span gas), using a three-way solenoid valve (not shown). At the sample inlet, the sample flow is either directed through a heated molybdenum converter to reduce the reactive oxides of nitrogen to NO, or directed around the converter to allow detection of only NO. The sample air flow then passes through a filter to remove particulate matter and then through a flow control capillary to another three-way valve. This three-way valve directs the sample flow either directly to the reaction chamber (RX) where it is mixed with O_3 and the resultant chemiluminescence is measured, or the sample is directed to a prereactor vessel where it is mixed with O_3 before passage into the reaction chamber. The use of the prereactor allows the NO/O_3 chemiluminescence to occur out of view of the PMT, providing for an accurate measurement of background chemiluminescence resulting from reactions other than the NO/O_3 reaction (e.g., reactions of hydrocarbons and O_3). The PMT is housed in a thermoelectric (TE) cooler to minimize thermal noise.

As shown in Figure 9-5, separate sample transfer lines downstream of the sample inlet point are used for the NO_y and NO measurement channels, and a third transfer line is used to deliver calibration and converter efficiency assessment standards from the gas phase titration (GPT) calibration system to the sample inlet. Because of the remote location of the converter relative to the analyzer itself, these transfer lines may be of considerable length (i.e., up to 20 m). The length of the sample transfer line presents no problem in the NO_y measurement mode of the NO_y instrument, since all NO_y species are converted to NO in the heated converter, and since that same converter destroys any ozone present in the sample air. However, in the instrument's NO mode, the ambient air drawn down the sample transfer line contains both ambient NO and ambient O_3. These two species can react to decrease the NO reaching the chemiluminescence detector, resulting in an under-estimation of the ambient NO level.

This effect can be substantial: assuming 100 ppbv of O_3, loss of 10 percent of the NO can occur within a few seconds. One way to counteract this effect, is for sample air to be drawn rapidly through the sample transfer line. For example, at a sample flow rate of 6 L/min, a sampling line with an inner diameter of 4 mm and a length of 15 m (50 feet) would result in a residence time of less than 2 seconds. Rapid transport of the sample can best be accomplished using an auxiliary sampling pump (not shown in Figure 4-1) to draw sample down the transfer line to a "T" fitting at the back panel of the NO_y analyzer. The sample flow to the chemiluminescence detector is then drawn from that "T" by the analyzer's internal sample pump. If implemented, it is recommended that this approach be implemented on both the NO and NO_y sample lines, to achieve consistent residence times in the two lines. However, implementing rapid sample transport through the Mo converter in this way may reduce converter efficiency and/or lifetime.
Consequently, a preferable approach may be to reduce sample transport time in both the NO and NO_y flow paths by reducing the gas pressure.

Recommendations for NCore

Since the high sensitivity analyzers deployed at NCore sites are intended to monitor low ambient NO_y concentrations, it is important that they meet a variety of performance criteria as described below. Many of these performance criteria for high sensitivity NO_y analyzers are more stringent than those for routine NO_x analyzers; consequently, there are a number of recommended features that the NO_y analyzers should have in order to achieve the performance criteria. This section describes the recommended performance criteria and the analyzer features that are recommended in order to achieve the performance criteria, and provides examples of commercial high sensitivity NO_y analyzers that are available for deployment at the NCore sites.

Additionally, this section discusses some important sampling requirements that should be considered during the installation of the analyzers.

Recommended Method Performance Criteria

The U.S. EPA has recently assessed the measurement quality objectives needed for high sensitivity precursor gas monitoring in NCore, relative to the long-established statistics stated in 40 CFR 58. In particular, EPA recommends that measurement quality objectives for bias and precision be based on upper confidence limits at the monitoring site level, to provide a higher probability of reaching appropriate conclusions (e.g., in comparisons to NAAQS). The intent of this recommendation is to move S/L/T agencies to a performance-based quality system i.e., allowing organizations that show tight control of precision and bias to reduce the frequency of certain QC checks, and to focus their quality system efforts where most needed.

The U.S. EPA recommends that the high sensitivity NO_y analyzers that are deployed at NCore sites meet the following method performance criteria. It is to be expected that these criteria may be more difficult to meet for NO_y than for NO.

Precision

Precision is defined as the measure of agreement among individual measurements of the same property taken under the same conditions. Precision is assessed from checks that are performed at least once every two weeks and should be used to assess precision on a quarterly basis. It is recommended that high sensitivity NO_y analyzers have a 95 percent probability limit for precision of ±15 percent or less. Calculation of precision starts with the comparison of the known challenge concentration used in the precision checks to the corresponding measured concentrations reported by the analyzer.

Bias

Bias is defined as a systematic or persistent distortion of a measurement process that causes errors in one direction. Bias is assessed from the degree of agreement between a measured value and the true, expected, or accepted value. Analyzer bias is calculated using comparisons of known challenge concentrations to the corresponding measured concentrations reported by the analyzer. The challenge comparisons used to assess bias should be the same as those used to assess precision. It is recommended that high sensitivity NO_y analyzers have an upper bound for the average bias of ± 15 percent or less.

Representativeness

Representativeness refers to whether the data collected accurately reflect the conditions being measured. It is the data quality indicator most difficult to quantify. Unless the samples are truly representative, the other indicators are meaningless. Representativeness for monitoring of low ambient levels of NO_y in NCore is different than for routine monitoring, since the objectives of the monitoring are much different. Representativeness can only be assured in terms of the appropriate selection of the sampling site, proper implementation of ambient air sampling, and reasonable coverage of the sampling schedule (i.e., continuous).

Completeness

Completeness is defined as the amount of data collected relative to the total expected amount. Ideally, 100 percent of the expected amount of data would always be collected; in practice, completeness will be less for many reasons, ranging from calibration time and site relocation to power outages and equipment failure. For monitoring of ambient NO_y concentrations in NCore, EPA requires a minimum data completeness of 75 percent. In practice typical completeness values can often approach 90 to 95 percent.

Comparability

Comparability is defined as the process of collecting data under conditions that are consistent with those used for other data sets of the same pollutant. The goal is to ensure that instruments purchased and operated by different states and local agencies produce comparable data. To promote comparability, the USEPA Technical Assistance Document (TAD) for Precursor Gas Measurements in the NCore Multi-Pollutant Monitoring Newtwork, Version 4, (EPA-454/R-05-003), describes the recommended characteristics of high sensitivity NO_y analyzers and the procedures for their installation and use.

Method Detection Limit

The MDL refers to the lowest concentration of a substance that can be reliably determined by a given procedure. The MDL is typically not provided by the vendor. Based on the objectives of the Precursor Gas Program, it is expected that most sites will be measuring pollutant concentrations at lower ranges than the typical SLAMS/NAMS network. Therefore, the ability to quantify concentrations at these lower levels will be very important. The use of a vendors advertised LDL is sufficient to make intelligent purchasing decisions; however, vendors quantify LDLs under ideal conditions and therefore one might consider this value as the best possible detection that can be achieved. As these monitors are deployed into monitoring networks, where both environmental conditions, equipment (calibration, dilution devices, sampling lines, gaseous standards) and operator activities can vary, it is important to estimate what pollutant concentrations can truly be detected, above background noise (the potential conditions mentioned above). The site specific MDL establishes an estimate based on the routine operation (and conditions) of that instrument in the network and provides a more meaningful evaluation of data as it is aggregated across the precursor gas network. By establishing site specific MDLs, values less than the MDL can be flagged which would allow data users a more informed decision on the use of that data.

It is recommended the MDL for high sensitivity NO_y analyzers be established prior to putting the analyzers into service, and should be 0.20 ppb or lower over an averaging time of no more than 5 minutes.

Lower Detectable Limit

The LDL is the minimum pollutant concentration that produces a signal of twice the noise level. To estimate the LDL, zero air is sampled and the noise level of the readings is determined according to 40 CFR 53.23(b). The vendor-specified LDL for the most sensitive range of high sensitivity NO_y analyzers should be 0.10 ppb or lower, over an averaging time of no more than 5 minutes.

Linear Range

The linear range of each high sensitivity NO_y analyzer should extend from approximately 0.10 ppb to at least 200 ppb. Users should determine if their range should exceed 200 ppb and adjust accordingly. A range of 200 ppb may not be sufficient in all areas and situations. Note that some high sensitivity NO_y analyzers can operate simultaneously on a number of ranges, with each range recorded on a separate data logger channel with its own calibration curve. Although requiring slightly more effort to calibrate and maintain, recording of multiple ranges would allow capture of a wide range of NO_y concentrations.

Zero/Span Drift

Zero drift is defined as the change in response to zero pollutant concentration, over 12- and 24-hour periods of continuous unadjusted operation. Span drift is defined as the percent change in response to an upscale pollutant concentration over a 24-hour period of continuous unadjusted operation. Zero and span drift should be obtained from the vendor prior to putting a high sensitivity NO_y analyzer into service. Such NO_y analyzers should have 12- and 24-hour zero drift less than 0.10 ppb, and should have a span drift of less than ±1 percent of the full scale measurement range of the analyzer per 24 hours. Zero tests should be performed with the internal zero prereactor engaged.

Recommended Analyzer Features for High Sensitivity Ambient NO_y Measurements

Continuous chemiluminescence NO_y analyzers are commercially available from a number of vendors. The design of these analyzers is similar among vendors with some slight variations. A diagram of the typical high sensitivity NO_y chemiluminescence analyzer is described in Figure 9-5. In general, each of the analyzers contains the following systems:

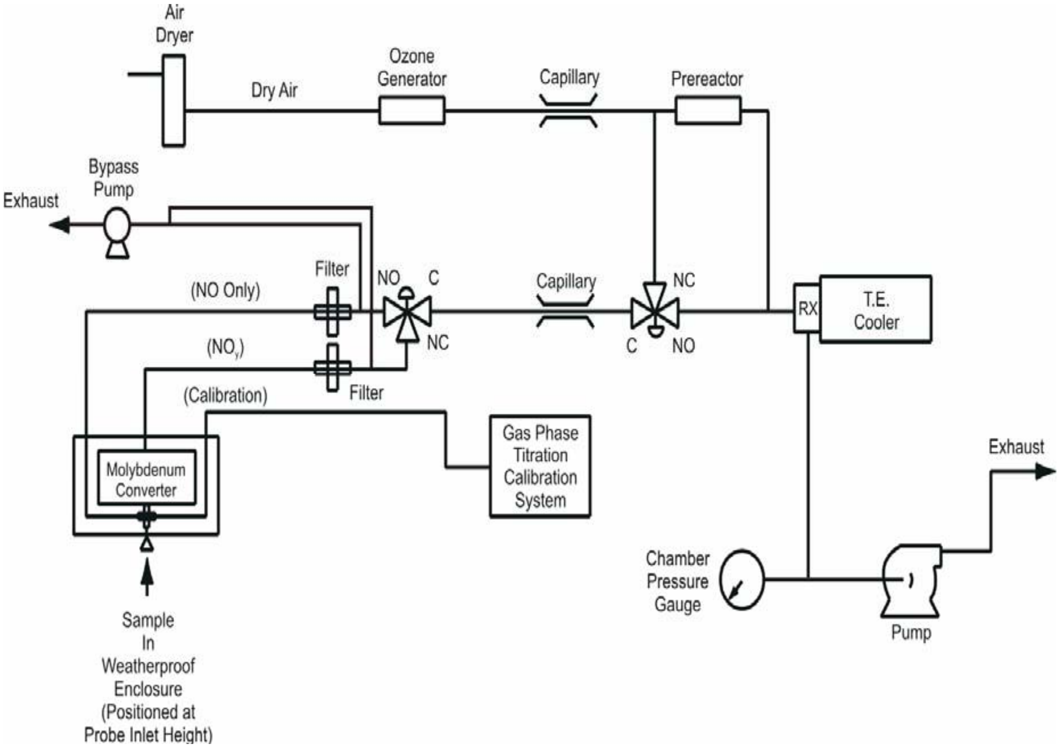
1. Pneumatic System: This portion of the analyzer consists of a sample inlet incorporating a heated converter, sample inlet line, particulate filter, gas phase titration calibration unit, ozone generator, prereactor, flow meter, and pump, all used to bring ambient air samples to the analyzer inlet.
2. Analytical System: This portion of the analyzer consists of the reaction chamber, photomultiplier, and bandpass filters.
3. Electronic Hardware: This portion of the analyzer consists of the electronic components that control the analyzer and process the signals. This part of the analyzer generally requires little or no maintenance. If the instrument is operated outside the manufacturer's recommended temperature range, however, individual integrated chips can fail and cause problems with operation, data storage, or retrieval.

In operation of these systems, the following recommendations should be followed with precursor NO_y analyzers to allow them to measure NO_y at levels well below 1 ppb.

1. Locate the sample inlet at 10 meters to avoid the physical removal of HNO_3. The inlet should face the prevailing wind direction, be as short as possible, and be constructed of PFA Teflon®. Half of a Teflon® filter holder with the filter support used as a "bug screen" should have a negligible effect on NO_y measurements, and provides a practical solution to ward off larger insects.
2. Locate the site in an area that is not obstructed by nearby trees and obstacles.
3. Ensure that the sample residence time in the NO sample transfer line is less than 2 seconds to address the O_3/NO reaction and subsequent loss of NO in the line, and protect the sample transfer lines from light through the use of opaque conduit normally provided by the vendor.
4. A heated molybdenum converter rather than a heated gold/reactant converter is recommended, since the latter requires a supply of either a toxic reductant gas (CO) or a flammable reductant gas (H2), and provides no clear advantage in determining total NO_y in urban and suburban air.
5. The temperature of the molybdenum converter should be maintained at 350 °C. Higher temperatures than recommended may result in converting significant amounts of non-NO_y species such as ammonia, organic amines, or particulate ammonium. If a manufacturer recommends a converter temperature above 350 °C, he should show evidence that such non-NO_y species are not converted. It is equally important that the converter not be operated below 350 °C to ensure optimal conversion of NO_y species.
6. Automatic over-range capabilities are used to track the rapid changes that may occur in ambient NO_y levels. High sensitivity analyzers often have an analog output range limited to 200 ppb full scale; digital ranges of up to 400 ppb may be needed to track peak concentrations in urban areas.

It is recommended that the NO_y analyzers deployed in NCore include these additional siting and operational features in order to ensure useful measurements.

Figure 9-5. General schematic of a typical chemiluminescence NO_y instrument.



Sampling Issues

Studies of NO_y sampling inlet issues have focused primarily on airborne NO_y measurements, where it is not feasible to locate the converter directly at the sample inlet point. The purpose of these studies was to identify the material that causes the least adsorptive loss of NO_y components during sampling. Nitric acid, as both a key component of NO_y and a strongly adsorbed species, has generally been the target compound in these studies. Adsorption of NO and NO_2 is of much less concern. Numerous tubing materials, including TFE, PFA, and FEP Teflon®, have been investigated for use in sampling inlets. In testing these materials for HNO_3 adsorption, less than 5 percent of the HNO_3 was lost with Teflon® tubing, while greater than 70 percent was lost with tubing made of stainless steel, glass, fused silica, aluminum, nylon, silica-steel, and silane-coated steel. HNO_3 transmission through aluminum, steel, and nylon tubes did not increase in over 1 hour of HNO_3 exposure. HNO_3 loss on aluminum and steel tubes heated to 50 °C was irreversible. However, HNO_3 adsorption on glass decreased over time, so that over a period of several hours of continuous HNO_3 exposure, glass will be passivated to HNO_3 adsorption. Furthermore, heated glass tubing passivates faster than room temperature tubing, and larger diameter glass tubing takes longer than smaller diameter glass tubing to passivate with HNO_3. PFA Teflon® causes the least adsorption of HNO_3, and so is recommended for sampling inlets.

Although PFA Teflon® is far superior to other materials in minimizing HNO_3 adsorption, it has the disadvantage that any previously adsorbed HNO_3 can be released back into the air stream by changes in temperature and/or relative humidity. Thus, the best approach to NO_y monitoring is to expose the incoming sample air to as little surface area as possible upstream of the heated converter. Therefore, the best approach is to minimize the length of PFA tubing at the inlet.

The inlet system must also be configured to allow calibration through the same inlet plumbing used in monitoring. As shown in Figure 9-5, this is easily accomplished by means of a PFA cross fitting on the inlet of the converter, with one arm of the cross connected to the GPT calibration system.

Potential Problems and Solutions

In addition to the potential problems with sampling described above, there are other potential problems with the high sensitivity measurement of NO_y in ambient air.

Interferences

Interferences in NO_y measurements are of two types. One potential interference is the presence of nitrogen-containing species in ambient air that are not components of NO_y, but that can potentially be converted to NO by the heated converters used to achieve NO_y measurement. The primary examples of such an interferent are ammonia (NH_3), and particulate ammonium (NH_4^+), but other amines and even cyanide compounds (e.g., hydrogen cyanide, HCN) could be present. This type of interference is addressed in the discussion of converter efficiency in the following section.

The other type of potential interferent consists of non-NO_y species that can react with O_3 to produce chemiluminescence in the relevant wavelength region, thereby artificially increasing the apparent signal from NO in the sample air. The most important such interferents in ambient air are unsaturated hydrocarbons (e.g., ethylene, propylene, and naturally emitted species such as terpenes). Interference from such compounds in ambient NO_y monitoring is minimized by the use of a prereactor vessel in the NO_y monitor (see Figure 4-1). The prereactor is a part of the normal flow path of ozone to the reaction chamber in the monitor. When the sample air flow is diverted into the prereactor, the NO/O_3 reaction occurs rapidly and the resulting NO_2 chemiluminescent emission occurs entirely within the prereactor, where it cannot be detected by the photomultiplier. However, the O_3 reactions with unsaturated hydrocarbons occur more slowly, so light emission from these reactions is not completed within the prereactor volume. As the sample/ O_3 mixture flows from the prereactor into the reaction chamber, the photomultiplier detects the background chemiluminescence from the hydrocarbon interferents, without emission from the NO/O_3 reaction. Commercial high sensitivity NO_y analyzers typically determine their background readings automatically using this prereactor mode and, thus, this type of interference is automatically accounted for by the analyzer software through subtraction of the background readings.

Converter Efficiency

Overview

The heated molybdenum converters used in commercial high sensitivity NO_y analyzers have undergone extensive testing and intercomparison in both laboratory and field studies to confirm the wide variety of species that can be converted to NO and measured as part of the NO_y total. These studies indicate that the molybdenum converters can provide accurate measurements of NO_y. The goal with such converters is to achieve 100 percent conversion efficiency of NO_y species to NO, while approaching zero percent conversion of other non-NO_y nitrogen-containing species. Note that, as used in commercial high sensitivity NO_y monitors, the molybdenum converters are designed to convert particulate nitrate compounds, as well as the numerous gaseous components of NO_y, to NO for detection.

As noted in the discussion of interferences, non-NO_y species such as ammonia, particulate ammonium, or hydrogen cyanide can also be oxidized to NO, although this conversion can be minimized (to a few percent or less) by maintaining the converter temperature at 350 °C. At sub-ppb NO_y concentrations, interference from such compounds can be substantial, and even at higher levels the potential for interferences must be kept in mind. Sampling near a large source of ammonia, for example, could produce erroneously high NO_y readings, even though the conversion efficiency for ammonia is much less than that for NO_2 or the various NO_z compounds. In general, the efficiency of a converter system at sub-ppb levels may vary depending on the mix of NO_y species present, the age and condition of the converter, the converter temperature, ambient humidity, or ozone levels and cannot be entirely predicted even from the behavior of a similar system. For these reasons, converter efficiency must be evaluated.

Challenge Species for Converter Efficiency Checks

Studies of converter efficiencies have established that among NO_y species, NO_2 is relatively easily reduced to NO. As a result, calibration with NO and NO_2 is a necessary but not entirely sufficient approach to characterizing a NO_y monitoring system. A more stringent approach is to also calibrate with a NO_y species that is both more difficult to convert to NO and relatively easy to prepare in known concentrations. The most common choice for such an additional compound to determine NO_y converter efficiency is n-propyl nitrate (NPN). This organic nitrate is used in the form of compressed gas standards that are readily diluted to near-ambient NO_y levels. Diluted NPN mixtures (Scott-Marrin, Inc., Riverside, CA; www.scottmarrin.com) are supplied to the monitor through the calibration line to the monitor's inlet (Figure 9-5), and provide a more challenging test of the conversion efficiency than testing with NO_2 alone.

Conversion efficiency testing with NPN is in addition to, not in place of, routine calibration with NO and NO_2. Changes in pollutant levels and meteorological conditions over time can significantly alter the instrument's conversion efficiency. Thus, NO_y monitoring requires routine NPN converter efficiency checks and consistent procedures to maintain or repair the converter when its efficiency falls below acceptable levels. A single-point conversion efficiency check with NPN is recommended every month in continuous NO_y monitoring. An NPN conversion efficiency of 95 percent or greater is considered acceptable for NO_y

monitoring, converters falling below 95 percent efficiency should be replaced. Note that a new converter should be allowed to "burn in" over one to three days of use before performance of an NPN test. Also, the NPN standard may not be certified to better than ±5%, so it is recommended to track conversion over time and use 95% of the original efficiency as the performance cutoff.

Although HNO_3 is a key component of NO_z and in turn of NO_y, and is known to be especially difficult to sample, it is not advisable to attempt routine calibration checks with HNO_3 in the field. The complexities of maintaining an HNO_3 source and delivering accurate HNO_3 levels to the sample inlet outweigh the potential benefits. The best way to assure adequate sampling of HNO_3 and other NO_y species is to use a properly configured NO_y monitor. However, an annual or more frequent challenge of the monitor with multiple compounds may be a valuable test of instrument performance. If performed, such a challenge should involve several different tests, i.e., calibrations with NO and NO_2, a converter efficiency check with NPN, and perhaps a test of the conversion efficiency for NH_3 (the most likely gas-phase interferent) using a certified permeation source of NH_3. An NPN conversion efficiency of at least 95 percent, and a simultaneous ammonia conversion efficiency of, at most, 5 percent, should be the target performance criteria for such a challenge.

Equipment and Supplies

Calibration Equipment

The equipment required for calibration of a precursor NO_y analyzer include a MFC calibrator unit, with gas phase titration capability, and a source of zero air. The following equipment is recommended for calibration of a high sensitivity NO_y analyzer.

Calibration Standard and Standard Delivery System

The calibration standards used for the calibration of precursor NO_y analyzers should be generated by dilution of a commercially-prepared and certified compressed gas NO standard using a MFC calibration unit. It is important when purchasing a MFC calibrator that it meets the 40 CFR 50 requirements of ±2 percent accuracy, and that the flow rates of both MFC channels are calibrated using a NIST-traceable flow standard.

When the analyte concentration in the commercially-prepared standard cylinder is vendor certified by reference to NIST standards, and the MFCs are calibrated to NIST-traceable standards, the resulting working gas concentration is considered to be NIST-traceable.

Zero Air Source/Generator

Zero air is required for the calibration of high sensitivity NO_y instruments. This air must contain no detectable NO_y species (i.e., NO_y content must be less than the LDL of the analyzer) and must be free of particulate matter. Suitable zero air may be supplied from compressed gas cylinders, with additional scrubbing by passage through a soda lime trap, sodium carbonate trap, or carbonate coated denuder. However, it is likely too expensive and impractical to maintain a sufficient supply of zero air cylinders to operate a high sensitivity NO_y analyzer continuously. As an alternative, many commercially-available zero-air generation systems can supply suitably NO_y-free air, provided additional external scrubbing is provided as noted above.

Reagents and Standards

Routine operation of precursor NO_y analyzers requires the use of calibration standards and zero air to conduct periodic calibrations and instrument checks. This section describes the requirements for these gases.

Calibration Standards

The primary NO standards must be certified commercially-prepared compressed gas standards of NO in N_2, with a certified accuracy of no worse than ±2 percent. NO gas standards of 5 to 20 ppm (with less than 1 ppm NO_2) are conveniently diluted with a MFC calibrator down to working concentrations of 10 ppb or less. The commercially-prepared standard may contain only NO, or may be a mixed component standard that also contains known concentrations of other non-reactive precursor gases (e.g., CO, SO2). This standard must be traceable to a NIST NO in N_2 Standard Reference Material (SRM 1683 or SRM 1684), NIST NO_2 Standard Reference Material (SRM 1629), or a NIST/EPA-approved commercially available Certified Reference Material (CRM). Section 2.0.7 of EPA's Quality Assurance Handbook gives a recommended protocol for certifying NO gas cylinders against either a NO SRM or CRM. Commercial gas standards for NO_2 and NPN should be obtained with a certified accuracy no worse than ±2 percent, and ±5 percent, respectively.

Every gas standard used in precursor gas monitoring must be accompanied by a certificate of calibration from the vendor stating the type of traceability, concentration of the standard, the uncertainty of that certification, and the expiration date of the certification. Standards traceable to NIST are preferred. Certification documents for all standards must be retained in a common location and reviewed periodically so that standards for which the vendor's certification has expired may be removed from service and replaced.

Zero Air

Zero air used as dilution gas for calibration purposes should have a NO_y concentration below the LDL of the NO_y monitor. Commercial grades of zero air may be suitable as a starting point, provided additional cleanup is employed as discussed earlier. If the zero air used for dilution and for establishing baseline conditions has impurity levels greater than several tenths of a ppb, the accuracy of the analyzer being calibrated may be severely jeopardized. A 0.5 ppb impurity level is equivalent to a 10% relative error for a 5 ppb concentration. Commercial zero air further scrubbed of NO_y may be used to crosscheck the purity of air provided by a commercial continuous air purification system, or a rapid check of the purity of a zero air source can be made by intercomparison of zero air readings when sampled directly vs. through the prereactor mode of the NO_y analyzer.

Quality Control

Site Visit Checklists and Remote Diagnostic Checks

To determine whether the high sensitivity NO_y analyzer is working properly, field operators conduct many routine checks of instrument diagnostics and performance every time they visit the monitoring station. Each agency needs to develop maintenance checklists or electronic spreadsheets to document that all required checks have been made. The lists and sheets should be useful both for collecting data and for assessing the quality of that data. Management must review them regularly and change them if necessary. To the extent possible, diagnostic checks can be done remotely, provided the data acquisition system allows remote access to instrument diagnostic information.

Multipoint Calibrations

Calibration procedures for high sensitivity NO_y analyzers are more complicated than for other high sensitivity precursor gas analyzers (i.e., for CO and SO_2), in that they include calibration with NO and NO_2, as well as checks of the converter efficiency for NO_z species and potential interferents. A basic requirement is for a multipoint NO calibration that includes a minimum of four points (three spaced over the expected range and a zero point), generated by the calibration system. Although more points may be preferable, current high sensitivity analyzers typically provide linear response over their entire operating range; therefore, four points should be sufficient. Multipoint calibrations must be done prior to the high sensitivity NO_y analyzer being put into service and at least quarterly thereafter. An analyzer should be calibrated (or recalibrated) if any of the following conditions occur:

- Upon initial installation;
- The Level 1 span check or precision check difference exceeds 15 percent;
- After repairs or service is conducted that may affect the calibration;
- Following physical relocation or an interruption in operation of more than a few days;
- Upon any indication that the analyzer has malfunctioned or a there has been a change in calibration; or
- The measured concentration values during challenges with performance test (audit) samples differ from the certified standard values by ±15 percent. (Generally this challenge is conducted as a blind audit, such that the site operator is not aware of the gas standard concentrations delivered to the analyzers.)

The analyzers should be calibrated in-situ without disturbing the normal sampling inlet system to the degree possible. A second requirement is for multipoint calibration with NO_2, as a check of the conversion efficiency of the molybdenum converter for NO_2. This calibration is conducted by gas phase titration of NO with O_3. MFC calibration systems in common use at ambient monitoring sites have GPT capability. The multipoint NO_2 calibration should be done at approximately the same three concentration levels as the NO calibration noted above. The major equipment/components required for the GPT NO_2

calibration are: a stable O_3 generator, a data acquisition and display device, and the NO concentration standard used for the multipoint NO calibration. The principle of this calibration technique is the rapid gas phase reaction of NO with O_3 to produce equal stoichiometric quantities of NO_2 in accordance with the following equation:

$$NO + O_3 \rightarrow NO_2 + O_2$$

This is the same overall reaction detailed earlier in this chapter for the GPT calibration procedure for the traditional NO_x ambient analyzers. For calibration purposes, ozone is added to a stable and excess concentration of NO in a dynamic calibration system, and the NO reading of the chemiluminescence NO_y instrument is used as an indicator of changes in NO concentration. The NO standard is diluted sufficiently to produce an upscale NO reading on the measurement range of interest, and upon addition of O_3 the decrease in NO reading observed 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 O_3 generator, which is a component of the GPT system of the calibrator. Comparison of the NO and NO_y responses of the analyzer then allows determination of the ratio of NO_2 response to NO_2 generated, which indicates the converter efficiency for NO_2. Maintenance or replacement of the converter should be undertaken whenever the NO_2 conversion efficiency falls below 96 percent.

Level 1 Zero/Span Checks

Level 1 zero and span calibrations are simplified, two-point calibrations used when adjustments may be made to the analyzer. When no adjustments are made to the analyzer, the Level 1 calibration may also be called a zero/span "check" and must not be confused with a level 2 zero and span check. Level 1 zero and span checks should be conducted nightly if the calibration system and NO_y analyzers used can be programmed to automatically perform these. They are used to assess if the analyzers are operating properly and to assess if any drift in instrument response has occurred. The level 1 span check should not exceed ±15 percent. They are conducted by challenging the analyzer with zero air and a test atmosphere containing NO_y at a concentration of between 70 percent and 90 percent of the full measurement range in which the analyzer is operating. The challenge gas should be sampled through as much of the sampling inlet system as practical to mimic the actual sampling of ambient air. The results of the Level 1 zero/span check should be plotted on control charts to graphically illustrate the trends in the response of the analyzer to the challenge gases. If the measured concentrations fall outside of the control limits, the accuracy of the MFC calibration system should be checked with a NIST traceable flow standard. If the MFC flow accuracy is confirmed, the data recorded since the last successful Level 1 check should be flagged and the analyzer should be recalibrated using the multipoint calibration procedures described above.

State-of-the-art calibration equipment now exists that is fully automated. These "new generation" calibration units are fully integrated with computers, mass flow calibrators, and the associated hardware and software where they can create test atmospheres manually or automatically. For the precursor gas program, it is recommended that the NCore sites have fully automated calibration capability. Below are a number of reasons why this is advantageous:

- By performing the calibrations or checks automatically, agencies no longer spend the manpower needed to perform them;
- Automated calibrations or checks can be triggered internally or by a DAS. Since newer DASs allow remote access, this allows a remote user to challenge the analyzers without actually being present;
- High sensitivity precursor gas analyzers are expected to have more zero and span drift than less sensitive analyzers; therefore, it is important that a zero and Level I check be performed daily; and,
- New generation DASs can record calibration or check data and allow remote users to track daily Level I check and zero drift. This is important for data validation, verification and troubleshooting.

Precision Checks

At least once every two weeks a precision check should be conducted by challenging the NO_y analyzer with a known (low) NO concentration to assess the performance of the analyzer. The precision checks should be conducted by challenging the precursor NO_y analyzer with a calibration mixture of a known NO concentration near 20 ppb. After completion of the precision check, the operator should calculate the percent difference between the measured value and the standard value. Precision should be calculated quarterly, using the calculated percent differences from the precision checks (For more detail on calculating precision, refer to Technical Assistance Document (TAD) for Precursor Gas Measurements in the NCore Multi-pollutant Monitoring Network Version 4 (EPA-454/R-05-003). For acceptable precision to be maintained it is recommended that the calibration system's gas flows be verified frequently against a NIST flow standard, and adjusted if necessary before making any adjustments to the analyzer.

Preventive Maintenance and Troubleshooting

Long-term operation of continuous gas analyzers requires a preventive maintenance program to avoid instrument down-time and data loss. This section briefly describes several key items that might be included in the preventive maintenance program established for high sensitivity NO_y analyzers deployed at NCore sites, as well as some of the troubleshooting activities that may be useful in resolving unexpected problems with these analyzers. This discussion is not meant to be exhaustive or comprehensive in detail. More thorough discussions should be included in the analyzer operation manuals and SOPs developed for these analyzers. Example SOP's prepared by EPA are included as Appendix B of the Technical Assistance Document (TAD) for Precursor Gas Measurements in the NCore Multi-pollutant Monitoring Network Version 4 (EPA-454/R-05-003).

Preventive Maintenance

Management and field operators should jointly develop their preventive maintenance program. A program designed by persons unfamiliar with analyzer operations may include unnecessary items or omit mandatory ones.

NO_y values can be erroneous if the sample inlet and lines become dirty, cracked, or leaky. PFA lines should be inspected at least quarterly and replaced as needed, but at least every two years. Teflon® filters used in the sampling train to remove fine particles may need to be replaced as often as every week, depending on the condition of the filter and the particulate loading around the monitoring site. The NO_y inlet should be inspected every time the NO_y filter is changed.

Table 9-2 illustrates items that monitoring agencies should include in their preventive maintenance program for high sensitivity NO_y monitoring.

Table 9-2. Example of a preventive maintenance schedule for NO_y monitoring.

Item	Schedule
Maintain air dryer	As needed
Replace particle filter	Weekly
Perform pneumatic system leak check	At least quarterly
Inspect internal, external tubing; replace if necessary	Inlet, weekly; other, quarterly
Clean optical bench	As needed
Replace PMT	As needed
Monitor NO_2 conversion efficiency	At least every 6 months
Monitor NPN conversion efficiency	At least every month

Troubleshooting

Table 9-3 summarizes common problems seen with precursor NO_y analyzers, possible causes, and possible solutions. More specific information can be found in the manufacturer's operations manuals. When troubleshooting, an operator must constantly be aware of environmental factors that may affect the instruments. Environmental factors can also cause sporadic problems that can be difficult to diagnose. Examples of factors that may affect the performance of the precursor NO_y analyzers are:

- Variable shelter temperature (fluctuations greater than several degrees);
- Excessive vibration from other equipment;
- Voltage instability; fluctuations in the 110 VAC line voltage;
- Air conditioning system blowing on the instrument;
- Frequent opening of the door of the shelter; and,
- Leaks.

Table 9-3. Instrument troubleshooting for high sensitivity NO_y analyzers.

Problem	Possible Cause	Possible Solution
Noisy output	Defective DC power supply	Replace power supply
	Dirty reaction cell	Clean cell
	PMT failure	Replace PMT
High positive zero drift	Defective bandpass filter	Replace filter
	PMT failure	Replace PMT
High Prereactor zero reading	Moisture in PMT housing	Allow PMT housing to warm up; purge with dry gas, reassemble
No response to span gas	PMT failure	Replace PMT
	Voltage failure	Replace high voltage source
	No O_3 supply	Clean or replace O_3 generator
Low or declining response to span gas	O_3 source failing	Clean or replace O_3 generator
	Dirty reaction cell window	Clean window
Zero output at ambient levels	Pump failure	Check pump
	PMT failure	Replace PMT
Low NO_2 or NPN efficiency	Aging or dirty converter	Replace converter
No flow through analyzer	Pump failure	Replace/ rebuild pump head

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Chapter 10

National Ambient Air Monitoring Programs

Introduction

Ambient air monitoring systems are a critical part of the nation's air quality management program infrastructure. Environmental management officials and other environmental professionals use the ambient air monitoring data for a wide variety of purposes in managing air quality. As depicted in Figure 10-1, air quality management involves a cycle of setting standards and objectives, designing and implementing control strategies, assessing the results of those control strategies, and measuring progress. Ambient monitoring data have many uses throughout this process, such as determining compliance with the National Ambient Air Quality Standards (NAAQS); characterizing air quality and trends; estimating health risks and ecosystem impacts; developing and evaluating emission control strategies; evaluating source-receptor relationships; providing data for input to run and evaluate models; and measuring overall progress of air pollution control programs. Ambient air monitoring data provide accountability for emission strategy progress through tracking long-term trends of criteria and non-criteria pollutants and their precursors. The data also form the basis for air quality forecasting and other public air quality reports. They also can provide valuable information for broader ecosystem impacts.

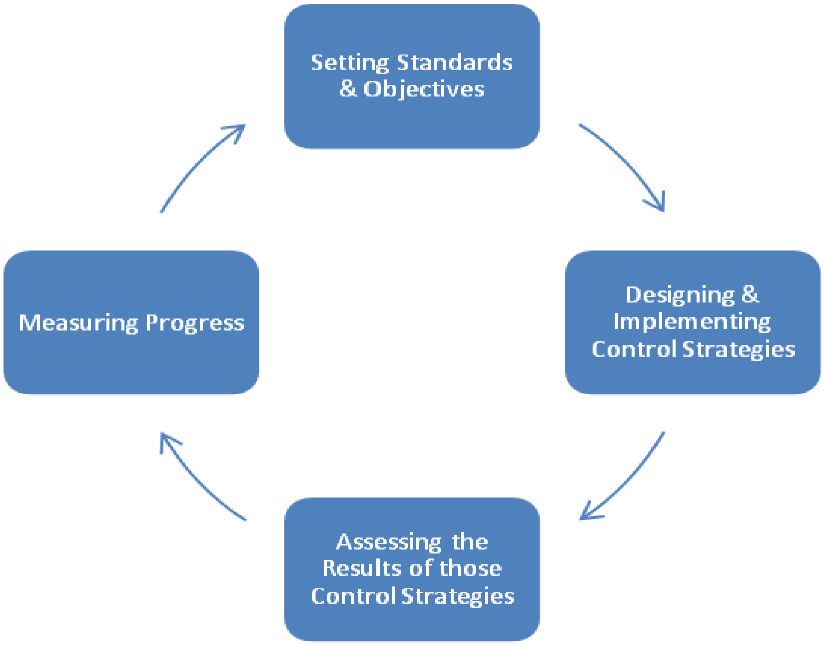

Figure 10-1. Process of associated with assessing an air quality management program.

State and local agencies and Tribes (SLTs) have primary responsibility for urban air monitoring in order to demonstrate that areas attain national ambient air quality standards

(NAAQS). Many SLTs maintain additional monitoring to assess local air issues and air toxics. In addition, the federal government operates or supports several networks, such as atmospheric deposition and visibility monitoring networks that provide data on specific issues, particularly focused on rural ambient conditions.

Monitoring programs are subject to continual changes in SLT, federal, and research priorities. New and revised NAAQS, changing air quality (e.g., significantly reduced concentrations of some criteria pollutants), and an influx of scientific findings and technological advancements challenge the response capability of the nation's networks.

Thus, a coordinated national strategy needs to update SLT networks (which largely grew out of efforts dating back to the 1970s), recognize the importance of other monitoring, such as atmospheric deposition monitoring, integrate that other monitoring with the SLT networks where appropriate, and maintain continuity so that an appropriate set of monitors continue to provide valid comparisons of long-term trends.

Given this backdrop, the overarching goals of the recently adopted (2006) National Ambient Air Monitoring Strategy (NAAMS) are:

(1) To ensure that the existing SLT monitoring networks are reconfigured to be consistent with the basic environmental and programmatic needs for current environmental management;

(2) To seek ways to integrate various monitoring networks where opportunities for integration exist;

(3) To improve the scientific and technical competency of the nation's air monitoring networks to ensure high quality data; and

(4) To enhance data storage, dissemination, and analyses so that government agencies, researchers, and the general public have improved access to ambient monitoring data, both in terms of completeness and timeliness.

In developing a strategy that can meet these objectives, EPA and its partners must consider resource constraints and look for opportunities to streamline and integrate existing monitoring resources in a way that maximizes the benefit of the monitoring data collected.

Overview of Ambient Air Monitoring

NAAQS Monitoring

State and local ambient monitoring stations (SLAMS) and national ambient monitoring stations (NAMS) represent the majority of all criteria pollutant (SO_2, NO_2, CO, O_3, Pb, $PM_{2.5}$, PM_{10}) monitoring across the nation, with over 5,000 monitors at approximately 3,000 sites. These stations use federal reference or equivalent methods (FRM/FEM) for direct comparison to the NAAQS that lead to determining whether areas are listed as in attainment or nonattainment. NAMS are a subset of SLAMS that are designated as national trends sites and, in some cases, also serve as the design value sites for an area. The EPA has established a suite of regulations that specifies the design and measurement requirements for these networks: 40 CFR Part 58 (design and quality assurance); Part 53 (equivalent methods); and Part 50 (reference methods).

The SLAMS and NAMS were developed in the 1970s. In the early 1980s, the networks began to add PM_{10} monitors, and then expanded to include $PM_{2.5}$ monitors, starting in 1999, to assess attainment with the $PM_{2.5}$ NAAQS promulgated in 1997. The $PM_{2.5}$ network consists of ambient air monitoring sites that make mass or chemical speciation measurements. As of 2005, there were about 900 FRM/FEM filter-based sites and 540 continuous measurement sites for mass measurements.[1] Chemical speciation measurements were made at over 50 trends sites, about 210 SLT sites were used in support of SLT monitoring objectives (including state implementation plan (SIP) development), and there were about 110 IMPROVE (Interagency Monitoring of Protected Visual Environments) sites in Class I visibility protection areas. These sites collect aerosol samples and analyze the filters for trace elements, major ions, and carbon fractions. Most of the IMPROVE sites are operated by other federal agencies within the Department of the Interior. IMPROVE sites support implementation of the NAAQS by providing data to assess $PM_{2.5}$ concentrations from rural areas that may impact urban areas.

The number of monitoring sites for total suspended particulates has declined sharply, as has the number of sites for other pollutants such as lead, NO_2, and SO_2. The number of ozone and carbon monoxide sites has stayed relatively stable (Figure 10-2). Given the long history of using these sites, and the changing nature of NAAQS attainment and control strategy issues, rethinking the design of SLAMS/NAMS is one of the central topics of this Strategy.

In addition to the SLAMS/NAMS networks, the Photochemical Assessment Monitoring Stations (PAMS) was developed in the 1990s to measure ozone precursors, volatile organic compounds (VOC), and NO_x. The PAMS consists of 75 sites in 25 metropolitan areas that were classified as serious ozone nonattainment areas. The addition of PAMS in the early- to mid-1990s was a major addition to the state/local networks, introducing near research grade measurement technologies to produce continuous data for over 50 VOC compounds during summer ozone seasons.

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[1] The $PM_{2.5}$ continuous monitoring network is the only criteria pollutant reported and forecasted nationally on a year-round basis as part of the Air Quality Index (AQI) -- see http://airnow.gov.

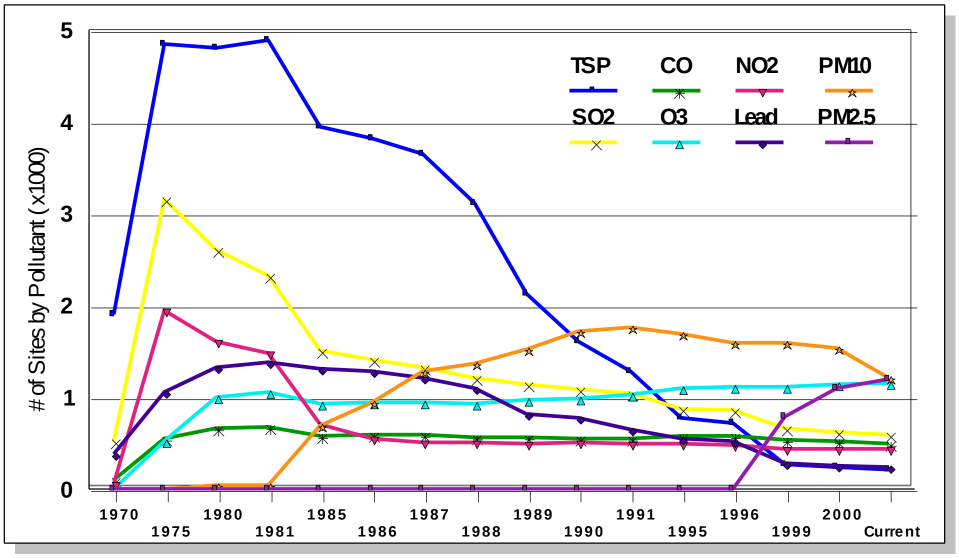


Figure 10-2: Growth and decline of criteria pollutant networks.

Acid Rain/Deposition Monitoring in Rural Areas

The Clean Air Status and Trends Network (CASTNET) originally was designed mostly to account for progress of strategies targeting major electrical generating utilities throughout the eastern U.S., which release acid rain precursor emissions, sulfur, and nitrogen oxides. Network operations are contracted out to private firms funded through Science and Technology (S&T) funds and managed by EPA's Office of Air and Radiation. CASTNET consists of over 80 sites located predominantly throughout the East, with greatest site densities in states along the Ohio River Valley and central Appalachian Mountains (Figure 10-3). Unlike SLAMS/NAMS, most CASTNET sites are located away from local sources of pollution in order to assess broad, regional air quality trends.

The National Atmospheric Deposition Program (NADP) comprises three subnetworks: the National Trends Network (NTN), the Mercury Deposition Network (MDN), and the Atmospheric Integrated Research Monitoring Network (AIRMoN). NTN collects weekly samples for hydrogen, sulfate, nitrate, ammonium, chloride, and base cations (such as calcium and magnesium).

NTN provides a long-term, high-quality database that is useful for assessing the magnitude of the acid rain problem and for determining spatial and temporal trends in the chemical composition of the atmosphere and the removal of atmospheric compounds as deposition. The NTN has grown from 22 sites in 1978 to over 200 sites currently.

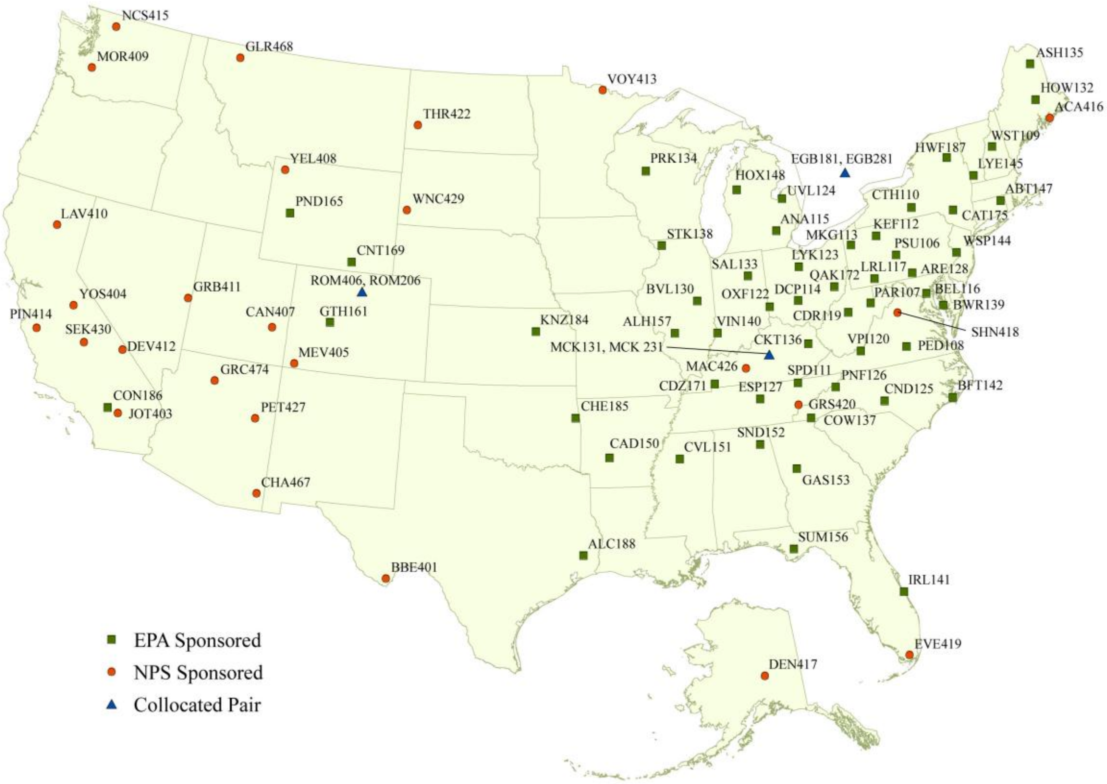
MDN collects mercury samples, and supports a regional database of the weekly concentrations of total mercury in precipitation and the seasonal and annual flux of total mercury in wet deposition.

Lastly, AIRMoN was formed for the purpose of studying precipitation chemistry with greater temporal resolution (precipitation samples are collected daily). The samples are analyzed for the same constituents as NTN sites. AIRMoN currently operates eight sites, with the full network expected to grow to about 20-30 wet and dry deposition sites. The

AIRMoN sites provide a research-based foundation for operations of the other deposition monitoring networks (NADP for wet deposition and CASTNET for dry deposition).

Visibility Monitoring

The Interagency Monitoring of Protected Visual Environments (IMPROVE) program is a cooperative measurement effort by a steering committee composed of representatives from Federal and regional-state organizations. The IMPROVE program was established in 1985 to aid the creation of Federal and state implementation plans for the protection of visibility in Class 1 areas (156 national parks and wilderness areas) as stipulated in the 1977 amendments to the Clean Air Act (CAA). The IMPROVE network presently comprises 110 monitoring sites. These sites also provide $PM_{2.5}$ speciation data, as noted above.



CASTNET Site Locations

Figure 10-3: Clean Air Status and Trends Network (CASTNET)

Air Toxics Monitoring

Unlike NAAQS pollutants, the Clean Air Act does not require monitoring for air toxics. Because the primary focus of the air toxics program to date has been on reducing air toxics emissions by application of available control technology for industrial sources and more stringent mobile source emission standards, the success of the program so far has been measured more often by the level of emissions reductions achieved as opposed to measured changes in air quality. EPA has used air dispersion modeling to estimate the impact of air toxics emissions on ambient air concentrations of air toxics and, ultimately, on human health.

EPA now has an active national air toxics monitoring program that includes three distinct monitoring efforts:

- National Air Toxics Trends Stations (NATTS);
- EPA funded local-scale projects to assess conditions at the local level; and
- Existing state and local program monitoring.

The NATTS network is intended to provide long-term monitoring data for certain priority air toxics across representative areas of the country in order to establish overall trends for these pollutants. EPA has established 23 NATTS, 17 of which are in urban areas and six of which are in rural areas. In the near term, the NAAMS documents EPA's commitment to maintain NATTS.

Initial ambient air toxics monitoring pilot studies have shown that across a city significant variations in pollutant concentrations occur that cannot be characterized by a single monitoring site. Thus, EPA has incorporated into the national air toxics monitoring strategy support for local-scale projects consisting of several monitors operated for one to two years.

Many state and local agencies for some years have operated ambient air toxics monitoring networks in support of their state or local air toxics programs. These can include monitors to address "hot spots," environmental justice concerns, or citizen complaints. About 250 separate air toxics sites exist at the state and local levels.

In addition to these air toxic-specific monitoring activities, other monitoring programs primarily intended to address other air pollution concerns incorporate aspects of air toxics monitoring. EPA's Photochemical Assessment Monitoring Stations (PAMS) collect data on certain volatile organic compound and carbonyl air toxics, while the IMPROVE and CASTNET networks collect data on certain air toxics metals. To identify certain air toxics compounds, the results of some particulate matter monitoring is speciated.

In addition to these existing efforts, EPA has an ongoing effort to develop a strategy for persistent bioaccumulative toxics (PBT) monitoring, and expanded mercury monitoring.

Tribal Monitoring

Currently, there are well over 100 Tribal air quality programs in various stages of development across the United States. This is a dramatic increase from only nine programs in 1995. Many of these Tribes currently report data to EPA's Air Quality Subsystem (AQS) from about 120 monitors in Indian country for several types of pollutants, including $PM_{2.5}$ and PM_{10}, ozone, nitrogen and sulfur oxides. Tribes also operate monitors in other national networks such as CASTNET, IMPROVE and NADP.

EPA's Tribal air policy emphasizes that, as sovereign governments, Tribes set their own air program goals and determine how monitoring is to be used in achieving these goals. Thus, EPA's role for Tribal air programs is to help the Tribes understand their air quality problems and to establish and meet their air quality goals, rather than to set goals or timetables for the Tribes.

Current Air Quality Management Challenges and Opportunities

Dramatic and mostly positive changes in air quality have been observed over the last two decades, despite increasing population, vehicle usage, and productivity. Most criteria pollutant measurements read well below national standards (see Figure 10-4).

As Figure 10-4 shows, control measures adopted under the CAA and state and local laws have generally solved the widespread, elevated levels of lead and gaseous criteria pollutants. However, current and future problems in particulate matter, ozone, and air toxics damage continue to challenge air programs.

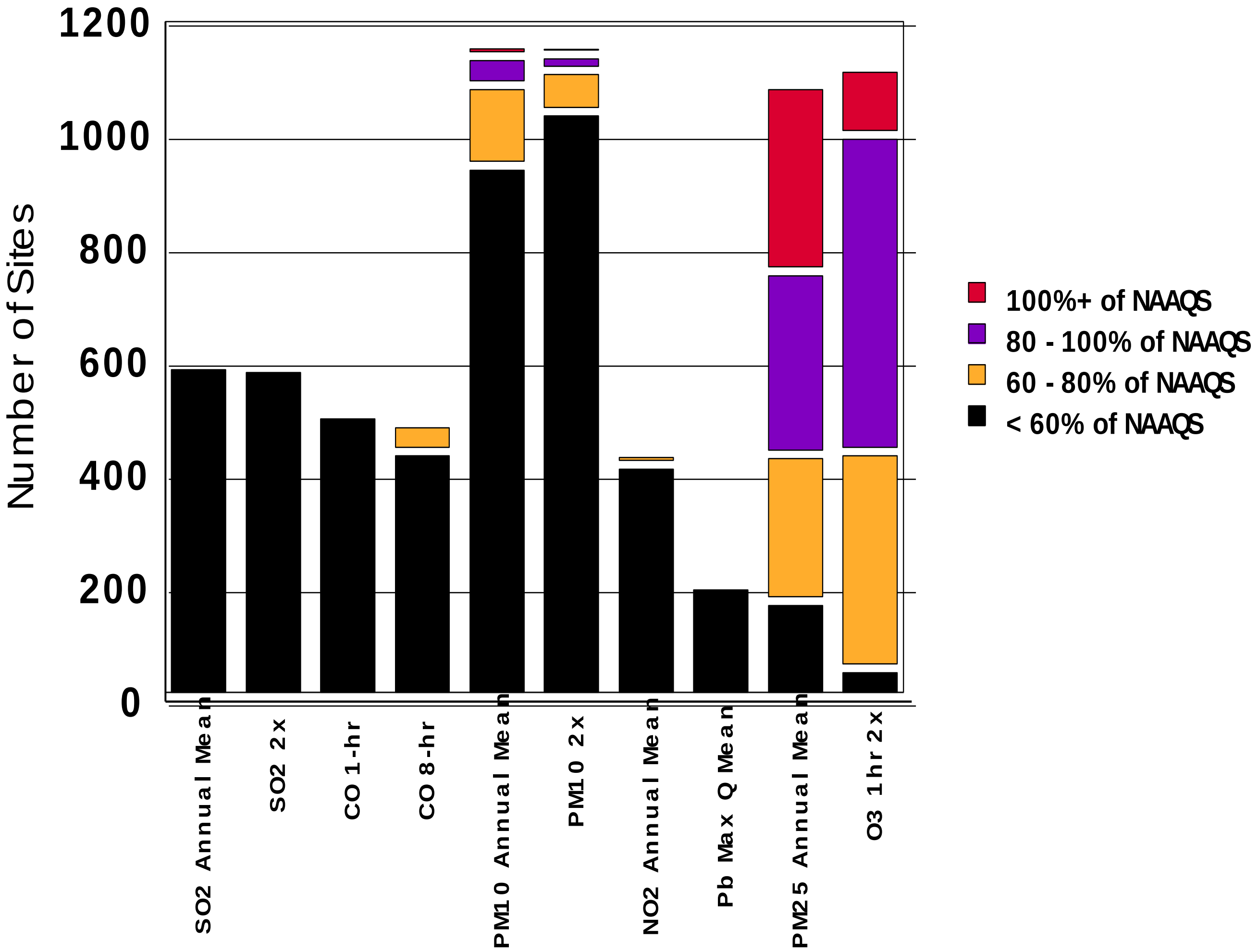


Figure 10-4. Number of monitors measuring values relative to the National Ambient Air Quality Standards based on AIRS data through 1999. Great progress has been made in reducing ambient concentrations of most criteria measurements. Ozone and $PM_{2.5}$ dominate the nonattainment picture on a national scale.

Many of the key air quality management challenges were outlined recently in a major National Academy of Sciences (NAS) report: Air Quality Management in United States (2004). These include:

- Meeting new standards for ozone, particulate matter, and regional haze;
- Understanding and addressing the human health risks from exposure to air toxics;
- Responding to evidence that there may be no identifiable threshold exposure below which harmful effects cease to occur for some pollutants;
- Mitigating pollution effects that may disproportionately occur in minority and low-income communities;
- Understanding and protecting ecosystems affected by air pollution;
- Understanding and addressing multistate and international transport of pollutants; and
- Adapting the air quality management system to a changing climate.

Among the NAS recommendations to address those challenges were enhancing assessments of air quality and health, ecosystem monitoring, and exposure assessment. Reconfiguring existing monitoring networks can reflect our progress in reducing many forms of air pollution and incorporate new scientific findings and technologies to address the remaining challenges. The NAAMS is one prong of working to implement those recommendations by coordinating ambient monitoring efforts and looking for ways to strengthen, update, and link together existing monitoring systems.

Identifying the Need for a National Strategy

As EPA looks at the air quality management challenges ahead, it is clear that a national strategy to maintain effective ambient monitoring systems is a vital component of meeting those challenges. The Strategy needs to address the following types of gaps, inefficiencies, and overlaps:

- The existing NAAQS compliance networks, SLAMS/NAMS, need to be reconfigured to emphasize persistent attainment problems, such as 0_3 and $PM_{2.5}$, and $PM_{10\text{-}2.5}$ (see subsequent section on PM Coarse). In part, this will require shifting resources currently being expended on NAAQS attainment problems that largely have been addressed (such as CO, lead, NO_2, and SO_2). While reducing the overall number of NAAQS-oriented sites for these pollutants, the national networks need to maintain adequate sites for these pollutants to address other objectives such as long-term trends analysis, photochemical reaction evaluations, inputs for regional modeling efforts, and a variety of other purposes.

- The existing networks need to move toward enhanced data collection by incorporating continuous and multipollutant measurements where possible.

- The importance of rural background monitoring for evaluating long range transport, cross-border flux concerns, NAAQS control strategies (such as the 2005 Clean Air Interstate Rule and Clean Air Mercury Rule), and long-term NAAQS trends needs to be recognized. EPA must seek opportunities for better integrating non-NAAQS networks, such as IMPROVE and CASTNET, with NAAQS monitoring networks.

- The linkages between ambient air monitoring and ecosystem impacts need to be recognized. These ecosystem impacts can include acid, nitrogen, and mercury deposition, and ecosystem impacts of elevated ozone levels. These linkages are important not only for developing general ecosystem protection strategies, but also for evaluating secondary NAAQS established under the Clean Air Act to protect the public welfare.

- The quality system and other technical requirements for monitors need to be performance-based, which ensures high quality data but allows for technological advances in monitor design and components.

- Storage and dissemination of the full range of ambient data that SLTs and EPA collect needs to be improved. This will enhance the usefulness of the data for modeling, other research, and general public access.

Strategy Development

A National Monitoring Steering Committee (NMSC) was developed to provide oversight and guidance to develop the NAAMS.[2] The NMSC included representatives from SLTs and EPA's Office of Air Quality Planning and Standards (OAQPS), Office of Research and Development (ORD), and Regional Offices. This NMSC structure reflected both the partnership across EPA and its major grantees as well as an intent to limit participation initially to focus on a manageable subset of clients and increase probability for progress. With input from the NMSC, EPA released a series of draft Strategy materials. The December 2005 draft updated an earlier April 2004 draft, which in turn was a combination of work on a series of earlier draft documents. This update reflects input from other EPA offices, such as Office of Atmospheric Programs and Office of Transportation and Air Quality, so that this draft Strategy reflects an Office of Air and Radiation-wide position, and addresses the full array of critical national ambient air monitoring components.

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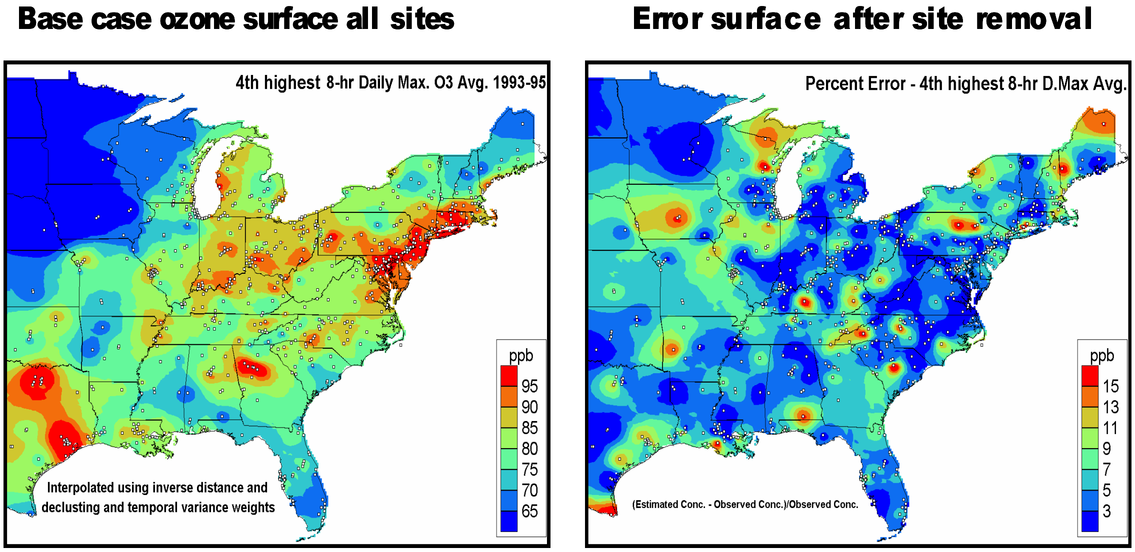
[2] The NMSC has evolved into the present National Ambient Air Monitoring Steering Committee.

In addition, EPA has been conducting national assessments of the criteria pollutant monitoring networks. An assessment was conducted in 2000 to catalyze subsequent regional level assessments. A copy of the FY 2000 national assessment can be found on the Web at: www.epa.gov/ttn/amtic/netamap. This assessment established weighting parameters to determine relative "value" of individual sites. The weighting factors included concentration level, site representation of area and population, and error uncertainty created by site removal. In addition, the assessment evaluated site redundancy. The national assessment calculated error uncertainty by modeling (i.e., interpolating between measurement sites) surface concentrations with and without a specific monitor. The difference reflects the error uncertainty (Figure 10-5). Areas of low uncertainty (e.g., less than five ppb error difference for ozone) suggest that removal of a monitor would not compromise the ability to estimate air quality in the region of that monitor as nearby stations would provide adequate acceptable predictions.



Base case ozone surface all sites

Error surface after site removal

Figure 10-5: Surface depiction of estimated absolute errors (right) in ozone concentrations produced by removing existing monitors on a site by site basis, relative to base case (left). Areas showing low errors (<5 ppb) suggest neighboring monitors could accurately predict ozone in area of a removed site. Areas of high error suggest necessity to retain existing monitors and perhaps increase monitoring.

National Strategy

Overview

The National Ambient Air Monitoring Strategy (NAAMS) which was promulgated in 2006 has a number of different elements, not all of which apply to all forms of ambient air monitoring. The major impetus behind this Strategy is EPA's recognition that the monitoring historically undertaken to determine NAAQS compliance needs to be significantly reconfigured and updated to meet the challenges facing air quality management in the U.S. At the same time, EPA recognizes that other ambient monitoring networks and programs, including some that are just now coming into development, play a vital role in responding to those challenges as well, and that continued maintenance, and in places enhancement, of those networks is an important element of a national monitoring strategy. Finally, EPA also realizes that while these various monitoring programs may have developed initially to provide data for different objectives, there are synergies and needs between those objectives that provide opportunities to integrate some of these systems.

Thus, this Strategy has three main elements:

- in place of the current SLAMS/NAMS networks, implement the NCore multipollutant sites and streamline the number of single pollutant sites (still called SLAMS) that are designed principally to assess NAAQS compliance and long-term NAAQS trends;
- maintain and enhance where necessary other existing monitoring programs so they meet their environmental objectives effectively and efficiently; and
- identify and pursue opportunities for integrating monitoring networks and programs where synergies exist.

In addition to these primary elements, the Strategy includes several secondary elements as well:

- Encourage quality system enhancements.
- Update outdated technology and streamline requirements to encourage technology innovations over time.
- Promote data management, access, and analysis tools to maximize agency, research, and public use of the data collected.
- Ensure adequate resources to implement all necessary elements of the Strategy and take on other elements of the Strategy in a way that is consistent with available resources.

These primary and secondary elements of the Strategy are applied to specific monitoring programs in the following sections entitled, Strategy for Urban Areas and Strategy for Rural Areas.

Strategy for Urban Areas

NCore Multipollutant Sites

Urban monitoring systems need to build on the current air monitoring networks, but also incorporate changes to address new directions in air monitoring and to begin filling measurement and technological gaps that have accumulated over the years. This Strategy emphasizes multipollutant sites, continuous monitoring methods, and important pollutants previously not included in SLAMS/NAMS, such as ammonia and reactive nitrogen compounds (NO_y). When completed, this modified network will meet a number of important needs: improved data flow and timely reporting to the public; NAAQS compliance determinations; support for development of emissions strategies; improved accountability for control programs; and support for scientific and health-based studies.

Structurally, the central component of this Strategy will be a network of National Core (NCore) multipollutant monitoring sites. Monitors at NCore multipollutant sites will measure particles ($PM_{2.5}$, speciated $PM_{2.5}$, $PM_{10-2.5}$), O_3, SO_2, CO, nitrogen oxides ($NO/NO_2/NO_y$), and basic meteorology. Monitors for all the gases except for O_3 would be more sensitive than standard FRM/FEM monitors, so they could accurately report concentrations that are well below the respective NAAQS but that can be important in the formation of O_3 and PM.

EPA expects that each state would have from one to three NCore sites, and EPA will collaborate on site selection with states individually and through multistate organizations. The objective is to locate sites in broadly representative urban (about 55 sites) and rural (about 20 sites) locations throughout the country to help characterize regional and urban patterns of air pollution. In many cases, states likely will collocate these new stations with PAMS sites already measuring O_3 precursors and/or NATTS sites measuring air toxics. By combining these monitoring programs at a single location, EPA and its partners can maximize the multipollutant information available. This greatly enhances the foundation for future health studies and NAAQS revisions.

The NCore multipollutant stations are part of an overall strategy to integrate multiple monitoring networks and measurements, including research grade and SLAMS sites. Research grade sites would provide complex, research-grade monitoring data for special studies. The SLAMS monitors would provide NAAQS comparisons and other data needs of monitoring agencies. The number and placement of SLAMS monitors would vary according to the pollutant, population, and level of air quality problem.

Rationalization of NAAQS Pollutants Networks

In shifting to the new framework outlined above, EPA and its partners will seek to continue to assess existing monitoring, reduce monitoring where no longer needed to assure NAAQS attainment or meet other policy needs (such as trends analysis), and move to continuous monitoring where possible. The key efforts in this area include:

- a significant reduction in the number of sites, especially for pollutants such as lead that no longer pose widespread air quality problems in the U.S.; and

- the regulatory framework necessary to restructure the existing SLAMS/NAMS networks, harmonize quality assurance requirements, and provide additional changes necessary to implement elements of this Strategy.

The efforts will ensure that the NAAQS monitoring networks focus resources on the most pressing needs and continue to modernize technology in ways that will enhance use of the data and timely access to the data. In addition, these changes need to take into account the possibility of more stringent NAAQS being established in the future, especially for $PM_{2.5}$.

Coarse PM

Prior to the adoption of the fine-particle fraction NAAQS in 1997, EPA determined that the fine and coarse fractions of PM_{10} should be considered separately. At this time, EPA added new standards, using $PM_{2.5}$ as the indicator for fine particles (with $PM_{2.5}$ referring to particles with a nominal aerodynamic diameter less than or equal to 2.5 μm), and using PM_{10} as the indicator for purposes of regulating the coarse fraction of PM_{10} (referred to as thoracic coarse particles or coarse-fraction particles; generally including particles with a nominal aerodynamic less than or equal to 10 μm).

In the more recent review and adoption (October 17, 2006) of revised PM NAAQS, some consideration had been given to a more narrowly defined indicator that did not include fine particles (*e.g.*, $PM_{10–2.5}$); however, EPA decided that it was more appropriate to continue to use PM_{10} as the indicator for standards to control thoracic coarse particles.

Although NAAQS for $PM_{10–2.5}$ have not been established, EPA is promulgating a new reference method (FRM) for measurement of mass concentrations of $PM_{10–2.5}$ in the atmosphere. This new FRM will be defined as the standard of reference for measurements of $PM_{10–2.5}$ concentrations in ambient air. This should provide a basis for approving Federal Equivalent Methods (FEMs) and promote the gathering of scientific data to support future reviews of the PM NAAQS. One of the reasons for not finalizing a $PM_{10–2.5}$ standard was the limited body of evidence on health effects associated with thoracic coarse particles from studies that use $PM_{10–2.5}$ measurements of ambient thoracic coarse particle concentrations. If an FRM is available, researchers will likely include $PM_{10–2.5}$ measurements of thoracic coarse particles in health studies either by directly using the FRM or by utilizing approved equivalent methods based on the FRM.

The NAAMS, promulgated on the same day (October 17, 2006) as the revised PM NAAQS, has a requirement for a new multi-pollutant monitoring network that takes an integrated approach to air quality measurements. One of the required measurements at these multi-pollutant monitoring stations is $PM_{10–2.5}$. The availability of an FRM, and subsequently approved equivalent methods for $PM_{10–2.5}$, will support State and local agencies' efforts to deploy robust methods at these monitoring stations for the measurement of thoracic coarse particles that do not include fine particles. These multi-pollutant monitoring stations will provide a readily available dataset at approximately 75 urban and rural locations for atmospheric and health researchers to compare particle and gaseous air pollutants.

Finally, the $PM_{10–2.5}$ FRM, by definition, provides a reference measurement. Because it is a filter based system, this method can itself be used to provide speciated data and EPA will be issuing guidance to ensure the use of a consistent national approach for speciated coarse particle monitors as soon as possible. The reference measurement from this instrument is also important in the development of alternative $PM_{10–2.5}$ speciation samplers.

PAMS

Consistent with the NCore multipollutant objectives, the PAMS sites already provide reasonably comprehensive data pertinent to ozone air pollution in non-attainment areas classified as serious, severe, or extreme. There are four types of PAMS sites, but the primary focus of the new urban monitoring strategy will promote the continued use of Type 2 PAMS sites: those areas where maximum ozone precursor emissions are expected. As shown in Table 10-1, the primary changes to PAMS would include:

- The number of required PAMS sites would be reduced. Only one Type 2 site would be required per area regardless of population and Type 4 sites would not be required. Only one Type 1 or one Type 3 site would be required per area.

- The requirements for speciated VOC measurements would be reduced. Speciated VOC measurements would only be required at Type 2 sites and one other site (either Type 1 or Type 3) per PAMS area.

- Carbonyl sampling would only be required in areas classified as serious or above for the 8-hour O_3 standard.

- NO_2/NO_x monitors would only be required at Type 2 sites.

- NO_y will be required at one site per PAMS area (either Type 1 or Type 3).

- Precursor gas (trace level) CO would be required at Type 2 sites.

Table 10-1. Proposed New Minimum Requirements for PAMS Sites.

Measurement	Where Required	Sample Frequency (except upper air meteorology)
Speciated VOC	Two sites per area; one must be at a Type 2 site	During PAMS monitoring periods: • hourly auto GC • (8) 3-hr canisters • 1 morning, 1 afternoon canister plus continuous NMHC measurement
NO_x	All type 2 sites	Hourly during ozone season
NO_y	One site per area, either at Type 1 or Type 3 site	Hourly during ozone season
CO (ppb level)	All sites	Hourly during ozone season
Ozone	All sites	Hourly during ozone season
Surface met	All sites	Hourly during ozone season
Upper air met	One site in PAMS area	Sample frequency must be approved as part of the PAMS Network Description

See Chapter 7, Ozone Precursors, in this Manual, for further discussions of PAMS monitoring.

PM Speciation

As of 2005, $PM_{2.5}$ chemical speciation measurements are collected at approximately 50 Speciation Trend Network (STN), about 210 SLAMS, and 110 IMPROVE Class I area sites (Figure 10-6).[3] The majority of these sites collect aerosol samples over 24 hours every third day on filters that are analyzed for trace elements, major ions (sulfates, nitrates, and ammonium), and organic and elemental carbon fractions.

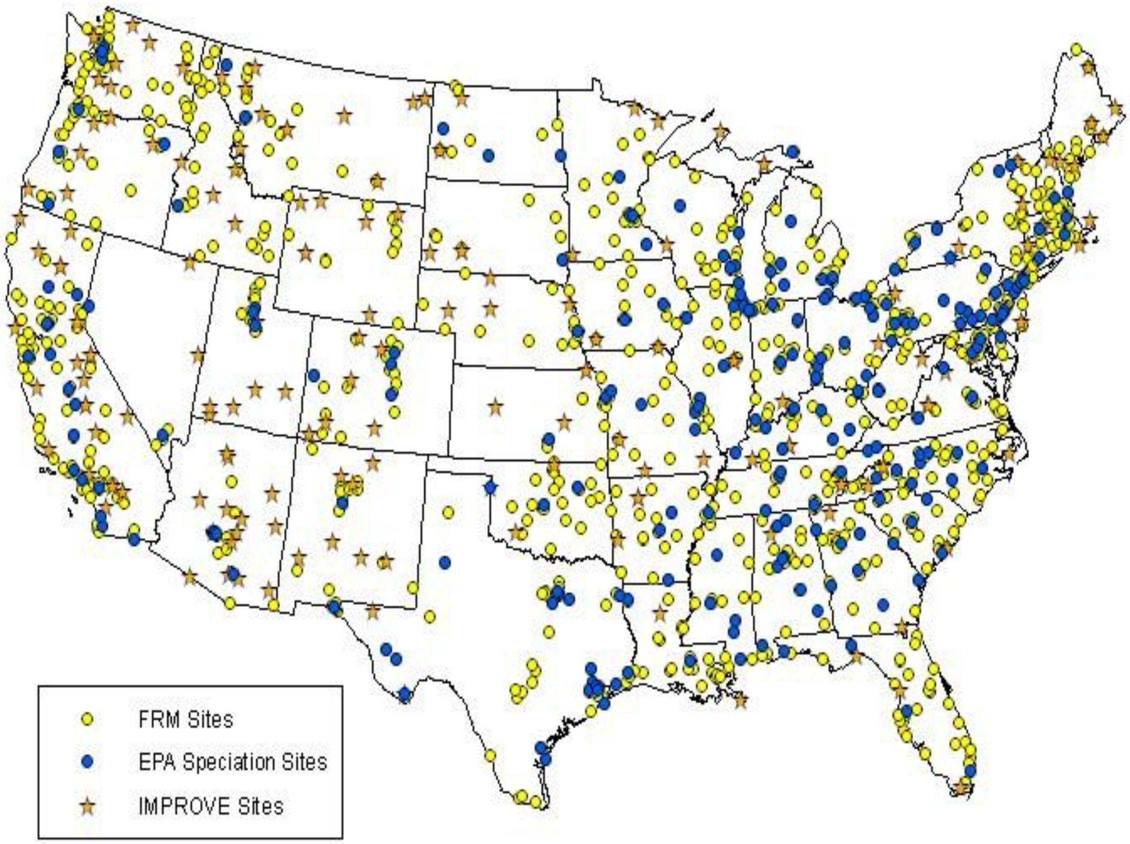


Figure 10-6. $PM_{2.5}$ Monitoring Sites, Including Chemical Speciation Sites.

In addition, under the new urban monitoring strategy, continuous or semi-continuous speciation monitors will provide the ability for monitoring networks to deliver data with a high temporal resolution so that the atmosphere can be characterized on a time scale relevant to how it changes and how people are exposed under dynamic processes. Initially,

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[3] The 250 SLAMS sites currently use either of two sampling and speciation analysis protocols, one the same as the STN sites and the other the same as the IMPROVE Class I area sites.

the strategy will not require states to operate continuous speciation samplers, with the exception of 22 National Air Toxics Trend Stations (NATTS). These NATTS locations use the Aethalometer™ instrument to measure black carbon (for more discussion on Aethalometers see EPA Course 435, Atmospheric Sampling). Nevertheless, EPA's strategy is that there should be a gradual evolution of continuous sampler operations at NCore multipollutant sites. EPA is committed to supporting a 10-site continuous speciation network, including carbon, sulfate, and nitrate.

This network evolved from early discussions with the health effects community related to a series of recommendations forwarded by the National Academy of Sciences in the late 1990s and continued by CASAC. EPA will continue to take a cautious approach toward continuous speciation monitoring, based largely on findings from the Supersites and other programs indicating mixed performance across a variety of monitors.

Air Toxics

In 1999, EPA began designing a national ambient air toxics monitoring network. As set out in the July 2004 National Monitoring Strategy Air Toxics Component, EPA is developing a national air toxics program that increases the role of ambient monitoring in support of efforts to reduce human exposure and health risks from air toxics. The primary objectives of ambient air toxics monitoring include (1) to discern trends and account for program progress by measuring key air toxics in representative locations to provide a basic measure of air quality differences across cities and regions, and over time in specific areas; (2) to support exposure assessments by providing ambient concentration levels for comparison with personal measurements; and (3) to provide basic grounding for models used for exposure assessments, development of emission control strategies, and related assessments of program effectiveness.

The NAAMS includes four elements of a national air toxics monitoring program:

- National Air Toxics Trends Stations (NATTS);
- EPA funded local-scale projects to assess conditions at the local level;
- Existing state and local program monitoring; and
- Long-range strategy development to address persistent bioaccumulative toxics (PBT) monitoring within existing resource constraints.

The NATTS network is intended to provide long-term monitoring data for certain priority air toxics across representative areas of the country in order to establish overall trends for these pollutants. As of January 2004, EPA had established 23 NATTS in 22 cities. In the near-term, this Strategy documents EPA's commitment to maintain NATTS. EPA intends to review with stakeholders the list of pollutants monitored at NATTS sites.

In FY 2004, EPA selected 16 local-scale project proposals for grant awards totaling $6.2 million. For FY 2005, EPA solicited bids for $6.3 million in grant funds. EPA works with SLTs to define the goals and priorities for this monitoring. In FY 2005, EPA reduced the emphasis on community-scale assessments and increased the emphasis on source characterization and monitoring methods development. Under this Strategy, EPA anticipates continued funding for these types of local-scale projects, and a continued dialogue with SLTs on the appropriate priorities for these efforts.

Many state and local agencies for some years have operated ambient air toxics monitoring networks in support of their state or local air toxics programs. EPA has assisted these monitoring efforts since 1997 by providing laboratory analysis of air toxics samples collected by state and local agency monitors. In FYs 2003 and 2004, EPA re-directed $6.5 million in Section 105 grant funding from criteria pollutant monitoring to air toxics monitoring, and anticipates maintaining this approach under the NAAMS in the future.

In the area of PBT monitoring, EPA currently has been developing a draft strategy that has not been implemented to date because of resource constraints. Within those constraints, EPA remains committed to developing further monitoring of PBTs. At this time, EPA's primary focus will be to work towards a mercury network that can provide ambient concentration and meteorological data for estimating dry deposition (see “Strategy for Rural Area,” below, for further discussion).

Near Roadway Exposure

Monitoring near roadways has, to date, been limited to research-level monitoring. As the national air monitoring network matures, it is vital that monitoring near roadways continue and that EPA and others evaluate strategies for incorporating this monitoring into the other components of the NAAMS as a means of determining health risks and impacts on urban attainment. EPA fully intends to consult with SLT and other stakeholders in developing the near roadway component of the Strategy, and issuing more detailed elements of this component of the Strategy (scheduled for release in January 2007).

Strategy for Rural Areas

EPA has a multi-prong strategy for rural monitoring networks, including CASTNET, NADP, IMPROVE, and smaller scale rural programs (such as specific Prevention of Significant Deterioration (PSD) monitoring sites):

(1) Recognize that these existing systems represent a core element in our national monitoring framework that is vital to assessing progress in the program areas for which they were created (such as atmospheric deposition and visibility). Based on that recognition, maintain their ability to continue that function and upgrade equipment and data dissemination as necessary.

(2) Use these systems to track rural background ambient conditions in support of regional control strategies aimed at reducing long range $PM_{2.5}$ and ozone transport, including the 2005 Clean Air Interstate Rule (CAIR). This objective has emerged in recent years as an important rationale for continued support to these systems, in addition to their other primary purposes (including tracking atmospheric deposition, trends, and visibility). Data from these systems are important to understand both in terms of identifying solutions to urban NAAQS attainment problems and tracking progress of regional control strategies in reducing background ambient concentrations of $PM_{2.5}$ and ozone.

(3) Identify opportunities to use these systems for integrated ecosystem assessments.

(4) Consistent with items (2) and (3), seek ways to formally integrate these systems with the urban monitoring networks where such integration would enhance our ability to manage current and future air quality management challenges. From a technology standpoint, integration includes measuring the same constituents on the same time scale, and using similar, if not the same, methods. In addition, integration includes coordinating the management infrastructure so that decisions about network modifications and other issues are coordinated, both internally at EPA and externally with EPA's partners.

(5) Strengthen existing mercury monitoring to assess the long term effectiveness of strategies to reduce mercury exposure, including CAIR and the 2005 Clean Air Mercury Rule (CAMR).

For mercury monitoring, EPA has proposed collaboration with the NADP to design and implement an ambient, speciated mercury monitoring network for temporally and spatially characterizing total mercury concentrations in the atmosphere. The Mercury Deposition Network (MDN) provides the beginning of a network which currently measures wet deposition. However, an enhanced mercury network will be necessary to assess progress under CAIR and CAMR. The network EPA is proposing in collaboration with the NADP would begin to fill the national data gap in dry ambient mercury compounds by initiating a core federal component of a broader, spatially representative mercury monitoring network in the United States. The goals in filling this gap are to better understand atmospheric mercury and to track its fate. EPA believes that it is important to build on the successes of the existing long-term monitoring infrastructure. The Agency hopes that using an existing and successful long-term multi-stakeholder model, like NADP, as a foundation for long-term mercury monitoring will encourage other agencies and states to join the effort.

Common Elements Applicable to All Monitoring

Quality System

Quality assurance is a major component of the air monitoring programs. The goal of the NAAMS is that all of the ambient monitoring networks produce high quality data that maximize the usefulness and confidence in the monitoring results. The specific steps for implementing a quality system for the NAAMS include:

- move toward a performance-based measurement process with specified data quality objectives;
- minimize start-up problems with a phased implementation approach;
- provide a reasonable estimate of the costs associated with QA programs;
- develop certification and/or accreditation programs;

- develop generic quality assurance program plans (QAPPs);

- accelerate data review and certification programs for quicker data access into the national air quality data system (AQS);

- eliminate redundancies in performance evaluation programs;

- develop appropriate data quality assessment tools (e.g., software); and

- streamline regulations, and more specifically identify those actions that should be mandated through regulation and that should be recommended through guidance.

Both regulatory changes and necessary guidance will be developed as separate actions to accommodate the implementation of the Strategy. Additional actions that will have to be part of the implementation plan include:

- development of standard operating procedures (SOPs) to accompany the employment of new instrumentation; and

- set appropriate requirements for the infrastructure necessary to accommodate monitoring sites (e.g., so that sufficient space, power, access, etc, are included in site designs).

Monitoring Technology - Development and Transfer

The explosion of computer and communications technologies over the past 15 years presents significant opportunities for air quality monitoring networks. The potential for improving monitoring methods; monitoring support capabilities such as computer controlled instrument calibrations and quality assurance functions; and information transfer (i.e., getting data quickly to the public) is greater in recent years than at any time in the past. However, some components of our monitoring networks are still functioning under more manual and time consuming regimes.

EPA, working with its state and local partners, has established a Technology Working Group to examine the prospects for incorporating new technologies and making recommendations as to the best ways to embrace these. The focus is in three key areas:

- moving toward continuous PM monitors in place of the more cumbersome, labor-intensive filter-based methods;

- encouraging the utilization of new technologies to measure a more robust suite of pollutants, such as reactive nitrogen compounds (NO_y); and

- fostering the utilization of advanced information transfer technologies (e.g., replacing antiquated phone communication telemetry systems with internet-based, radio, and satellite communications media).

There are several recognized impediments in moving forward in these areas:

- regulations that support the "old" way of doing things need to be revised to reflect the current technological environment;
- special funding needs to be identified to invest in the equipment capital costs of replacing older monitors and data transfer systems;
- investments in staff training are needed to ensure that EPA and SLT staff will be able to operate and maintain the new equipment; and
- in some cases, currently available instrumentation has not been demonstrated to operate successfully without extensive operator oversight and maintenance.

In addressing these impediments, regulation changes are in progress as part of the NAAMS, and funding/training issues will be addressed as part of the implementation plan.

Planning and Assessment Processes

State and local agencies typically conduct an annual network review, and recommend changes to their networks. As a result, the networks are ever-changing to meet more current needs. However, for many years there was no concerted effort to take a critical look at our monitoring sites and determine if there were redundancies and inefficiencies in network designs. Furthermore, our networks have traditionally been laid out in overlapping fashion, such as an ozone network, a carbon monoxide network, a PM_{10} and $PM_{2.5}$ network, an atmospheric deposition network, a visibility network, and so forth.

In 2000, EPA commissioned a national assessment of the SLAMS/NAMS networks, with considerations for population, pollutant concentrations, pollutant deviations from the NAAQS, pollutant estimation uncertainty, and the geographic area represented by each site. Based on this national assessment, it was determined that substantial reductions in monitors could be made for pollutants that are no longer violating national air standards on a widespread basis, namely lead, sulfur dioxide, nitrogen dioxide, and PM_{10}, with the caveat that the measurement of some pollutants, such as sulfur dioxide, may be useful as source tracers even though ambient levels may be low. Even for those pollutants of greatest national concern, ozone and $PM_{2.5}$, sufficient redundancy was found to suggest reductions of 5 to 20% of our monitors without seriously compromising the information from our monitors.

With this as a backdrop, each of the 10 EPA Regional Offices was charged with conducting regional assessments of the SLAMS/NAMS networks. This process began in early 2001, and the NAAMS reflects many of the findings of these assessments and the 2000 national assessment. As part of EPA's commitment to maintaining the NAAMS as a living document, EPA intends to continue the assessment process, with regional assessments targeted to occur on a five year cycle basis. EPA also is developing standardized guidelines for these assessments. The procedures for previous regional assessments were not standardized. Even though differences in air quality, population, monitoring density, and other factors necessitate some varying approaches in evaluating networks, generalized guidelines are needed to avoid unwarranted regional inconsistencies. A Subcommittee of CASAC (Clean Air Science Advisory Committee) met in July 2003 and recommended that regional assessment guidelines be developed, and in response, definitive guidelines will be in place for subsequent regional assessments.

The network assessment process, too, is a collaborative effort between EPA and the SLTs. While some factors for network changes may be developed from statistical evaluations, there are also local policy considerations that have a bearing on decisions to change monitors. Ultimately, the combined efforts among national, regional, and local perspectives and needs will result in an optimized realignment of air monitoring networks that remains responsive to the many objectives for conducting the monitoring.

In summary, network assessment is not a new process. State and local agencies historically have conducted annual network evaluations, and changes to monitoring networks have been undertaken and reported as part of this process. However, periodically, it is necessary to take a more holistic review on a multi-level basis: national, regional, and local. As part of the NAAMS, EPA intends to conduct a multi-level network assessment every five years.

The primary objectives of the network assessments are to ensure that the right parameters are being measured in the right locations, and that network costs are kept at a minimum. Some of the related secondary objectives include the following:

- Identify new data needs and associated technologies;
- Increase multipollutant sites versus single pollutant sites;
- Increase network coverage;
- Reduce network redundancy;
- Preserve important trends sites; and
- Reduce manual methods in favor of continuous methods.

Data Access

A primary objective of the NAAMS is to enhance access to ambient monitoring data. Within resource constraints, EPA's ongoing approach will be to make available more timely and effective data than is currently available. EPA already is addressing these issues with a variety of approaches emerging from a long range "Data Warehouse" OAQPS planning effort as well inter office collaboration with the Agency's Office of Environmental Information (OEI). Several pilot projects to gauge the usefulness of new data products and access methods are being launched as part of these efforts. For instance, EPA's air quality data system (AQS) was taken off-line for several days so that a "static" copy of the data could be made available, at the request of a community of EPA research grant recipients.

Another effort is underway to make all measured (versus reduced) data in AQS available on demand, allowing a customer to extract a data file based on his or her selection of geographic area, time frame, and pollutants of interest. A subsequent addition of the more timely AIRNow data (including quality assurance caveats) would provide an exponential enhancement in data delivery.

Another goal is to make detailed air quality data summaries available to anyone at any time by offering a variety of self-service tools to access the data. Currently web pages exist allowing querying of annual summary information, and air quality professionals can access any data in the system. The relevant databases and tools are being upgraded to enable public availability of daily summary information through internet access. The timeliness of this information also will improve as EPA reduces the time necessary to process data before making it available to the public and its external partners.

Finally, the collaboration with OEI offers the longer range potential to merge multimedia data sets that could be used, for instance, to support ecosystem assessments. EPA will continue to examine those responsibilities and to broaden its outreach efforts beyond traditional SLT partners to key consumer communities, such as academia, public health organizations, and the private sector, to ensure delivery of effective products and services.