



# Technical Assistance Document (TAD) for Precursor Gas Measurements in the NCore Multi-pollutant Monitoring Network

Version 4

**Technical Assistance Document (TAD)  
For Precursor Gas Measurements in the NCore Multi-Pollutant  
Monitoring Network**

**VERSION 4**

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Contract No. 68-D-02-061  
Work Assignment 3-02

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## **ACKNOWLEDGMENTS**

Significant contributions to the TAD content were made by Kevin Cavender, Dennis Mikel, Michael Papp, Joann Rice, Solomon Ricks, Nealson Watkins, and Lewis Weinstock of the U.S. EPA, Office of Air Quality Planning and Standards, and Anna Kelly, of the Hamilton County Department of Environmental Services (Ohio).

The U.S. Environmental Protection Agency wishes to acknowledge the assistance and input provided by the following advisors in the preparation of this guidance document: George Allen, of the Northeast States of Coordinated Air Use Management (NESCAUM); James Schwab, of the State University of New York at Albany; William McClenny of the U.S. EPA Office of Research and Development; and Eric Edgerton of Atmospheric Research and Analysis, Inc.

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## ACRONYMS

CFR	Code of Federal Regulations
CO	carbon monoxide
EPA	U.S. Environmental Protection Agency
FPD	flame photometric detection
FRM	Federal Reference Method
GFC	gas filter correlation
HCN	hydrogen cyanide
IR	infrared
LDL	lower detectable limit
MDL	method detection limit
Mo	molybdenum
N <sub>2</sub>	nitrogen
NAAMS	National Ambient Air Monitoring Strategy
NAAQS	National Ambient Air Quality Standards
NAMS	National Air Monitoring Station
NCore	national core monitoring network
NDIR	non-dispersive infrared
NH <sub>3</sub>	ammonia
NH <sub>4</sub> <sup>+</sup>	ammonium
NIST	National Institute of Standards and Technology
NO	nitrogen oxide
NO <sub>2</sub>	nitrogen dioxide
NO <sub>x</sub>	nitrogen oxides
NO <sub>y</sub>	reactive nitrogen oxides
NPN	n-propyl nitrate
O <sub>3</sub>	ozone
Pd	palladium
Pt	platinum

PM	particulate matter
PMT	photomultiplier tube
ppb	part per billion
ppm	part per million
ppt	part per trillion
QA	quality assurance
QC	quality control
SLAMS	State and Local Air Monitoring Station
SO <sub>2</sub>	sulfur dioxide
SOP	standard operating procedure
TAD	technical assistance document
VOC	volatile organic compound
UV	ultraviolet

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## **TECHNICAL ASSISTANCE DOCUMENT FOR PRECURSOR GAS MEASUREMENTS IN THE NCORE MULTI-POLLUTANT MONITORING NETWORK**

### **1.0 INTRODUCTION**

The U.S. EPA is currently implementing the National Ambient Air Monitoring Strategy (NAAMS).<sup>[1]</sup> The NAAMS goals include improvement of the scientific and technical competency of the nation's air monitoring networks and increased value in protecting public health and the environment. Monitoring of ambient air pollution is a critical part of the nation's air program infrastructure. Monitoring data are used to characterize air quality and associated health and ecosystem impacts, develop emission strategies to reduce impacts, and account for progress over time. Substantial improvements in ambient air quality have been observed over the last two decades, despite increases in the U.S. population, vehicle usage, and industrial productivity. Ambient concentrations of several of the criteria air pollutants [specifically, lead (Pb), carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), and nitrogen dioxide (NO<sub>2</sub>)] are now well below the applicable National Ambient Air Quality Standards (NAAQS).

While the obvious problems of widespread elevated concentrations have been largely solved for some criteria pollutants, problems related to particulate matter (PM), ozone (O<sub>3</sub>), 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, new approaches in air monitoring are needed to measure these low levels and to incorporate these measurements with other data into comprehensive assessments of human and environmental health.

One of the major areas of investment in the NAAMS is the use of highly sensitive commercial air pollutant monitors for the characterization of the precursor gases CO, SO<sub>2</sub>, and total reactive oxides of nitrogen (NO<sub>y</sub>) in a new national core monitoring network (NCORE). The high sensitivity CO and SO<sub>2</sub> analyzers are fundamentally the same as those designated as Federal Reference and Equivalent methods (<http://www.epa.gov/ttn/amtic/criteria.html>), but with

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. This capability for accurate measurements at low concentrations will support long-term epidemiological studies, reduce uncertainties in data for modeling of air pollution episodes, and support source apportionment and observational analyses.

The implementation of high sensitivity monitoring for CO, SO<sub>2</sub>, and NO<sub>y</sub> 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 this Technical Assistance Document (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.

## **1.1 Development of the NCore Network**

NCore is both a repackaging and an enhancement of existing networks. The emphasis on the term “Core” reflects a multi-faceted, multi-pollutant national network that can be complemented by more specific efforts, such as intensive field campaigns to understand atmospheric processes, or personal and indoor measurements to assess human exposure and health effects. The NCore network will replace the current National Air Monitoring Station (NAMS) and State and Local Air Monitoring Station (SLAMS) programs, and leverages all of the major existing networks to produce an integrated multi-pollutant approach to air monitoring. Emphasis is placed on a backbone of multi-pollutant sites, continuous monitoring methods, and measurement of important pollutants other than the criteria pollutants (e.g., ammonia and NO<sub>y</sub>). When complete, NCore will meet a number of important data needs: improved flow and timely reporting of data to the public, including supporting air quality forecasting and information systems such as AIRNow; continued determination of NAAQS compliance; improved development of emissions control strategies; enhanced accountability for the effectiveness of

emission control programs; and more complete information for scientific, public health, and ecosystem assessments. Structurally, NCore will establish three levels of monitoring sites:

- Level 1— a small number of research-oriented sites accommodating the greatest diversity of instrumentation with specific targeted objectives, reasonably analogous to the current PM Supersite program;
- Level 2 – the backbone network of approximately 75 long-term, nationwide multi-pollutant sites, encompassing both urban (about 55 sites) and rural (about 20 sites) locations;
- Level 3 – sites focused primarily on specific pollutants of greatest concern (PM and O<sub>3</sub>), with as few as one measured parameter. It is estimated that over 1,000 Level 3 sites will be part of NCore.

While each of these three levels has specific objectives, there will likely be a continuum of site capabilities. Level 2 sites, for example, may meet a minimum level of multi-pollutant measurements, or may be augmented as necessary with other measurements so that the most heavily equipped Level 2 sites approach Level 1 in scope. Similarly, Level 3 sites may be single pollutant sites, but as necessary, may be augmented by other monitors to approach Level 2 site capabilities. These variations will be dictated by the needs of the particular area or agency responsible for air monitoring programs. The Level 2 sites are the primary platform for new implementation of high sensitivity precursor gas monitors.

## **1.2 The Need for High Sensitivity Precursor Gas Data in NCore**

The precursor gases CO, SO<sub>2</sub>, and NO<sub>y</sub> play important roles in the formation of atmospheric ozone, air toxics, and PM, on both local and regional scales. This interconnection among distinct air quality issues requires an integrated multiple pollutant air quality monitoring and management approach. For example, multi-pollutant monitoring data can allow health

studies to separate confounding effects, particularly in the face of varying ambient concentrations and PM composition. Air quality models and source attribution methods can benefit because multi-pollutant data allow more robust diagnostic evaluations (i.e., ensuring the model produces correct results for the correct reasons). Many emission sources release multiple pollutants, and consequently source apportionment models may yield more conclusive results with the use of multi-pollutant monitoring data. The NCore Level 2 sites are focused on providing multi-pollutant monitoring data to address these issues.

Equally important is that monitoring in NCore accurately quantify the low precursor gas concentrations that often typify conditions across the U.S. National health assessments and air quality model evaluations require data that are representative of broad urban (e.g., 5 to 40 km) and regional/rural (> 50 km) spatial scales, and long-term epidemiological studies must represent a variety of airshed characteristics across different population regimes. These requirements drive the mixed urban/rural placement of the NCore Level 2 sites. The NCore sites thus should be perceived as developing a representative report card on air quality across the nation, capable of delineating differences among geographic and climatological regions. While relatively high precursor gas concentrations may once have characterized all urban areas, emission reductions have changed that situation. For example, even in Atlanta, GA, median precursor gas concentrations are only a few times the detection limits of the conventional monitors currently in use.<sup>[2]</sup> Characterization of rural/regional environments is also important to understanding background conditions, transport corridors, regional-urban dynamics, and influences of global transport, as air quality modeling domains continue to expand. Localized source-oriented dispersion modeling evolved throughout the 1970's and 80's into broader urban scale modeling (e.g., EKMA and Urban airshed modeling for ozone), then into Regional approaches in the 1980's and 1990's (e.g., the Regional Oxidant (ROM) and Acid Deposition (RADM) Models), and currently into national scale approaches (e.g., the Community Multiscale Air Quality (CMAQ) models). This movement toward broader spatial scale modeling coincides with increased recognition of the importance of the regional/rural transport environment on urban conditions. As peak urban air pollution levels decline, rural and regional levels also decline. For example, in rural Centreville, AL, median precursor gas concentrations are at or below the

detection limits of the conventional monitors currently in use.<sup>[2]</sup> Measurements of low precursor gas concentrations thus are needed throughout the NCore network so that models can incorporate these low concentrations accurately.

The overarching objective of the high sensitivity precursor gas monitoring in NCore is to determine concentrations in well-mixed representative rural and urban atmospheres. NCore provides an opportunity to address new directions in monitoring and to begin to fill measurement and technological gaps that have accumulated in the existing networks. The NAAMS recognizes that there are both nationally and locally oriented objectives in monitoring that require different design approaches. The multipollutant high sensitivity monitoring approach in NCore addresses national level needs and makes the most of available resources.

### **1.3 Precursor Gas Monitoring in the NCore Network**

The use of high sensitivity precursor gas monitors for the characterization of CO, SO<sub>2</sub>, and NO<sub>y</sub> at NCore Level 2 monitoring stations is one of the major areas of investment for the NAAMS. In most cases, the adoption of improved precursor gas monitoring methods and associated calibration procedures will be necessary given the low levels of these pollutants at many of the likely NCore Level 2 sites. The use of high sensitivity monitors will also be valuable at Level 2 sites in urban areas, since at many such locations the concentrations of these gases are not consistently at elevated levels. In addition, as emissions reductions are realized and concentrations shift downward, high sensitivity monitors in urban areas will support the detection of trends. The applicability of high sensitivity monitors to urban Level 2 sites will be addressed on a site-by-site basis.

Precursor gas monitoring of CO, SO<sub>2</sub>, and NO<sub>y</sub> at NCore Level 2 sites will be accomplished by use of commercially available, continuous high sensitivity monitors. This document provides the technical guidance needed for implementation of these monitors in the NCore network. The following is a brief summary of the measurement principles and limitations of these monitors:

- CO: Commercially available, non-dispersive infrared (NDIR) monitors will be used that include modifications to enhance performance and sensitivity. The principal constraints on lower detection limits of these devices are water vapor interference and background drift. These limitations are reduced by drying the sample air and by automated determination of the monitor's baseline reading (i.e., auto-zeroing) using an appropriate CO oxidation system.
- SO<sub>2</sub>: Commercially available, ultraviolet (UV) fluorescence monitors will be used that include modifications to enhance performance and sensitivity. A more intense UV light source and improved optical filtering to minimize interference from nitric oxide (NO), are modifications typically made to increase sensitivity of these monitors. As with CO measurements, precursor SO<sub>2</sub> measurements also may be affected by water vapor and background drift.
- NO<sub>y</sub>: Commercially available monitors based on the chemiluminescent reaction of NO with O<sub>3</sub> will be used. Since the chemiluminescence method detects only NO, other trace nitrogen species including NO<sub>2</sub> must first be converted to NO in order to be measured using this method. Consequently, appropriate means of sampling and converting the chemical species that constitute NO<sub>y</sub> are critical to accurate measurements. Typical improvements made to these monitors for high sensitivity measurements include increased sample flow rate, placement of the converter at the sample inlet, improved cooling of the detector, and reduction of interferences through a prereactor for baseline determination.

#### **1.4 Data Quality Objectives**

Data Quality Objectives (DQOs) are qualitative and quantitative statements that clarify the monitoring objectives, define the appropriate type of data, and specify the tolerable levels of measurement errors for the monitoring program. By applying the DQO process to the

development of a quality system for NCore precursor gas monitoring, EPA guards against committing resources to data collection efforts that might not support the decisions for which the data are collected. The DQO process is iterative and allows for the incorporation of new information and modifying outputs from previous steps as inputs for a subsequent step. The final outcome of the DQO process is a design for collecting data (e.g., the type of measurements or number of samples to collect, and when, where, and how to collect samples), together with limits on the probabilities of making decision errors. During calendar year 2005 a Workgroup made up of personnel representing decision makers, technical experts, quality assurance manager, and statisticians will work their way through the seven step DQO process to address requirements for precursor gas monitoring in NCore. The results of that process will be reflected in additional guidance provided for the NCore network.

## **1.5 Format and Purpose**

Section 2 of this TAD provides detailed procedures for the use and calibration of high sensitivity CO monitoring equipment at Level 2 NCore sites. Sections 3 and 4 provide the same information for high sensitivity SO<sub>2</sub> and NO<sub>y</sub> measurements, respectively. Section 5 of this TAD describes the QA/QC procedures needed to support precursor gas monitoring at the NCore Level 2 sites, and Section 6 provides guidance about the acquisition and management of data from the precursor gas monitors. Each major section concludes with a list of the references cited in that section. Appendix A of this TAD is a description prepared by EPA of sampling manifold designs for precursor gas monitoring.

Although this TAD is not intended to be a Standard Operating Procedure (SOP), several topics addressed here are discussed in the 2001 EPA guidance on preparing Standard Operating Procedures (SOPs).<sup>[3]</sup> S/L/T agencies will find this document useful in preparing SOPs for the specific precursor gas analyzers employed at their sites. Furthermore, SOP's prepared by EPA for selected precursor gas monitoring and calibration equipment are included as Appendix B.

Electronic versions of these SOP's are also located at

<http://www.epa.gov/ttn/amtic/precursop.html>.

This TAD was written to help field operators, data managers, and data users understand why (not just how) key procedures are performed, what issues exist with the analyzers that they should be aware of, and how to address these issues. Special attention is paid to interferences, equipment selection, and calibration procedures. Users of this TAD should also consult Part 1, General Principles, of EPA's Quality Assurance Handbook, Volume II,<sup>[4]</sup> which contains detailed information pertinent to all measurement methods.

## 1.6 References

1. "National Ambient Air Monitoring Strategy," U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, April 2004, Final Draft.
2. Data from sites in the Southeastern Aerosol Research and Characterization (SEARCH) Study, summarized in personal communication by Eric Edgerton, Atmospheric Research and Analysis, Inc., June 10, 2005. SEARCH data are available at <http://www.atmospheric-research.com/studies/SEARCH/index.html>.
3. "Guidance for Preparing Standard Operating Procedures (SOPs)," EPA QA/G-6, EPA/240/B-01/004, U.S. Environmental Protection Agency, Office of Environmental Information, Washington, DC, 20460, March 2001.
4. "Quality Assurance Handbook for Air Pollution Measurements," Volume II, EPA-454/R-98-004, U. S. Environmental Protection Agency, Research Triangle Park, NC 27711, August 1998.

## **2.0 HIGH SENSITIVITY CARBON MONOXIDE MEASUREMENTS**

### **2.1 Introduction**

The NAAMS<sup>[1]</sup> builds upon research from the late 1990s, which indicated that carbon monoxide (CO) could be used as a background tracer for industrial processes and as a world-wide tracer for long-range pollution transport.<sup>[2-4]</sup> The Strategy also calls for monitoring to ascertain whether CO can be used as an indicator for volatile organic compounds (VOCs).

In response to the need for ambient CO monitoring, researchers and academia have worked with commercial instrument manufacturers to create high sensitivity CO instruments, with manufacturer-stated detection limits as low as 0.04 parts per million (ppm) (40 parts per billion (ppb)) in air.

#### **2.1.1 Properties of Carbon Monoxide**

CO is a colorless, odorless, tasteless, and highly poisonous gas. It affects the oxygen carrying capacity of the blood by diffusing through the alveolar walls of the lungs and competing with oxygen for the four iron sites in the hemoglobin molecule. Since the affinity of the iron site for CO is approximately 240 times greater than for oxygen<sup>[5]</sup> even low levels of CO can cause a number of symptoms including headache, mental dullness, dizziness, weakness, nausea, vomiting, and loss of muscular control. In extreme cases, collapse, unconsciousness, and death can occur. CO is only slightly soluble in water (2.3 ml/100 ml H<sub>2</sub>O at 20 °C and 760 mm Hg)<sup>[5]</sup> and consequently CO is not readily deposited or washed out of the atmosphere.

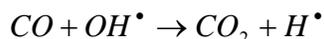
#### **2.1.2 Sources and Sinks of Carbon Monoxide**

CO has both natural and anthropogenic sources. The two primary CO production mechanisms are the oxidation of hydrocarbons in the atmosphere and the combustion of carbonaceous fuels. Global background concentrations of CO typically fall between 50 and 120 ppb and fluctuate seasonally, as well as geographically. In general, higher concentrations

occur during winter and are found in the northern hemisphere, due to the preponderance of anthropogenic sources in that part of the world.<sup>[5]</sup> CO is also produced naturally from the photochemical oxidation of methane (CH<sub>4</sub>) and other hydrocarbons in the atmosphere.

In urban environments, human activity results in CO levels that can greatly exceed background levels. Along with carbon dioxide (CO<sub>2</sub>), CO is a primary gaseous product of the combustion of carbonaceous fuels and is emitted from both mobile and stationary sources. In most urban areas, automobiles are a substantial source of CO. Consequently, CO levels tend to build up during morning and evening commute times, and maximum mixing ratios exceeding 50 ppm have been observed in congested intersections. Typically, however, one-hour average concentrations greater than 10 ppm are rare.

CO is relatively stable in the atmosphere and has an average global atmospheric lifetime of between 1 and 4 months.<sup>[5]</sup> The primary mechanism for removal of CO from the atmosphere is the oxidative reaction with hydroxyl radical to form CO<sub>2</sub>:



The hydroxyl radical coincidentally is part of a chain reaction that also produces CO from hydrocarbons in the atmosphere.

### **2.1.3 Historical Overview of CO Measurement Method**

The standard reference method for the determination of ambient CO is non-dispersive infrared spectrophotometry (NDIR). The NDIR CO measurement principle is the absorption of infrared (IR) radiation, with a wavelength of 4.7 micrometers (μm), by CO. The first instrumental method introduced, the Luft-type instrument, was granted Federal Reference Method (FRM) designation in 1976. In 1981, instrument manufacturers developed several modifications of the NDIR FRM and submitted those modified instruments for FRM designation. The gas filter correlation (GFC) method became the most popular modification in

the monitoring community because of its improved linearity and detection capabilities. EPA sponsored the development of the GFC technique at Ford AeroNutronics in Newport Beach, CA. Instrument manufacturers used the original analyzer developed in that work as a guide for designing commercial versions. 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.

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). Modifications in commercial GFC CO instruments have lowered estimated LDL values to 0.04 ppm (40 ppb). This chapter focuses on the GFC method and on those modifications to the GFC method that allow for high sensitivity CO measurements.

## **2.2 Summary of Method**

### **2.2.1 CO Measurement by NDIR Spectrophotometry**

GFC analyzers operate on the principle that the CO molecule has a sufficiently characteristic IR absorption spectrum that absorption can be used as a measure of CO concentration in the presence of other gases. CO absorbs IR radiation maximally at a wavelength of 4.7  $\mu\text{m}$ , which is in a spectral region where few other atmospherically significant species absorb to interfere with the accurate quantification of CO. The few potential interferences are discussed in Section 2.5.1.

Since NDIR is a spectrophotometric method, the concentration of CO can be determined based upon the Beer-Lambert Law. The Beer-Lambert law relates the concentration of an absorbing species to the degree of light attenuation according to the equation shown below:

$$I / I_0 = e^{(-axC)}$$

where:

$I$  = light intensity after absorption by absorbing species

$I_0$  = light intensity before absorption by the absorbing species

$a$  = absorption coefficient for absorbing species

$x$  = path length between light source and detector

$C$  = concentration of the absorbing species.

By measuring the degree of light attenuation through a sample cell of known length in both the presence and absence of CO, the concentration can be accurately determined if the absorption coefficient of CO is known.

In Luft-type instruments, IR radiation is passed alternately between a reference cell, containing a non-absorbing gas, and the sample cell. Prior to the introduction of sample gas containing CO to the sample cell, the intensity of the light passing through the sample cell is adjusted to match the intensity passing through the reference cell. As sample gas containing CO is introduced to the sample cell, an imbalance in the light transmitted through the two cells develops. This imbalance results in a detectable signal that is related to the CO concentration in the sample cell. However, although CO has a strong characteristic absorption at 4.7  $\mu\text{m}$ , other gaseous atmospheric species can contribute to the light attenuation by the sample and, thus, interfere with the accurate quantification of CO. Consequently, gas filter correlation (GFC) techniques were developed to address this problem.

## 2.2.2 Gas Filter Correlation (GFC)

A schematic of a GFC CO monitor is shown in Figure 2-1. In GFC monitors, there is only one sample cell, which acts both as the sample and reference cell. In this technique, a broad band of IR radiation is emitted from an IR source and enters the sample cell. Mirrors are used to reflect the light across the length of the cell multiple times which increases the effective pathlength and sensitivity of the monitor. Depending on instrument design, the light passes

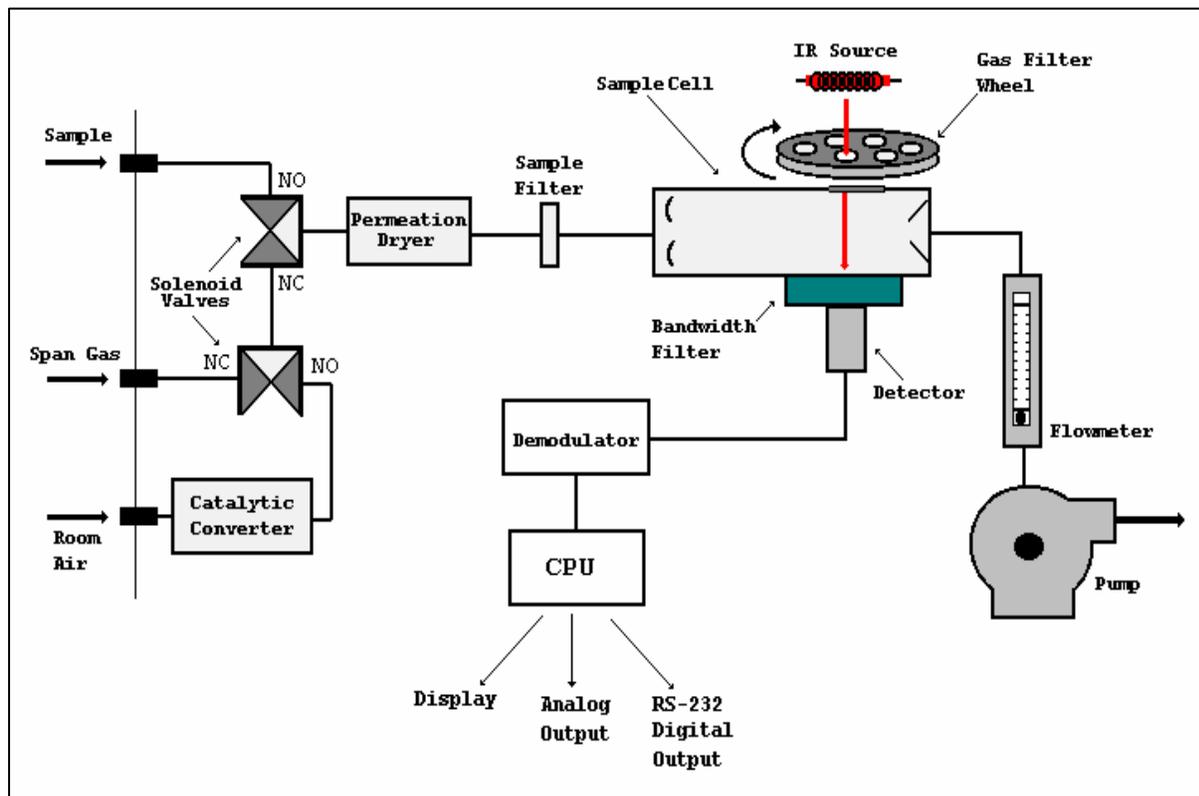


Figure 2-1. General schematic of a typical GFC CO analyzer.

through a bandpass filter either before or after the sample cell. This bandpass filter blocks most wavelengths from passing and allows only a narrow bandwidth of radiation centered on 4.7  $\mu\text{m}$  to reach the detector. In GFC monitors, a mechanical chopper assembly with cells containing either pure nitrogen ( $\text{N}_2$ ) or pure CO is positioned between the IR source and the sample cell, and acts as a gas filter. As the gas filter assembly rotates, the IR energy alternately passes through the cells containing the CO or  $\text{N}_2$  gases. When the light passes through a cell containing CO, all the light at 4.7  $\mu\text{m}$  is absorbed by the CO in the gas filter cell. This technique effectively “scrubs out” any light at wavelengths where CO absorbs prior to the sample cell, but allows other wavelengths of light to pass through the sample cell and reach the detector. As the chopper wheel spins, the gas filter cell containing  $\text{N}_2$  in the chopper assembly then crosses the IR energy beam. Since  $\text{N}_2$  is transparent to IR radiation, this gas filter cell allows all IR light to pass through unattenuated by the  $\text{N}_2$ . A neutral attenuator is used in the gas filter to reduce the overall light intensity exiting the  $\text{N}_2$  cell to match the intensity exiting the CO cell.

In the absence of CO in the sample cell, no change in light intensity is detected as the gas filter rotates. However, when CO is introduced to the sample cell, some of the light that passes through the  $\text{N}_2$  cell of the wheel is absorbed by CO in the sample cell, resulting in a difference in light intensity at the detector that is proportional to the concentration of CO in the sample cell. As the gas filter rotates, the light intensity is modulated and creates a signal from the detector that is electronically demodulated using phase-sensitive amplifiers and subsequently processed to generate a CO concentration reading.

### **2.3 Recommendations for NCore**

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, and provides examples of commercial high sensitivity CO 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.

### **2.3.1 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.<sup>[6]</sup> 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 the following method performance criteria.

#### **2.3.1.1 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 (see Sections 2.7.4 and 5.3.3). Calculations to assess precision are given below 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  $\pm 15$  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. The resulting percent differences are then used as described below. For each single point precision check, calculate the percent difference,  $d_i$ , as follows:

Equation 1

$$d_i = \frac{\text{reported} - \text{challenge}}{\text{challenge}} \cdot 100$$

where *reported* is the concentration indicated by the high sensitivity CO analyzer and *challenge* is the concentration of the standard used in the precision check. The precision estimator is then calculated as the coefficient of variation (CV) upper bound, using Equation 2 as follows:

Equation 2

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^n d_i^2 - \left(\sum_{i=1}^n d_i\right)^2}{n(n-1)}} \cdot \sqrt{\frac{n-1}{X^2_{0.1, n-1}}}$$

where  $n$  is the number of data points (i.e., precision check comparisons), the  $d_i$  values are the resulting percent differences, and  $X_{0.1, n-1}$  is the 10th percentile of a chi-squared distribution with  $n-1$  degrees of freedom.

### **2.3.1.2 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 (see Section 2.3.1.1 above). The bias estimator is an upper bound on the mean absolute value of the percent differences as described in Equation 3 as follows:

Equation 3

$$|bias| = AB + t_{0.95, n-1} \cdot \frac{AS}{\sqrt{n}}$$

where  $n$  is the number of challenge comparisons being aggregated;  $t_{0.95, n-1}$  is the 95th quantile of a t-distribution with  $n-1$  degrees of freedom; the quantity  $AB$  is the mean of the absolute values of the individual  $d_i$ 's and is calculated using Equation 4 as follows:

Equation 4

$$AB = \frac{1}{n} \cdot \sum_{i=1}^n |d_i|$$

and the quantity  $AS$  is the standard deviation of the absolute value of the  $d_i$ 's and is calculated using Equation 5 as follows:

Equation 5

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^n |d_i|^2 - \left( \sum_{i=1}^n |d_i| \right)^2}{n(n-1)}}$$

Since the bias statistic as calculated in Equation 3 uses absolute values, it does not have a direction or sign (negative or positive) associated with it. The sign of the calculated bias is to be determined by rank ordering the percent differences of the QC check samples from a given analyzer for a particular assessment interval. Calculate the 25<sup>th</sup> and 75<sup>th</sup> percentiles of the percent differences for each analyzer. The absolute bias upper bound should be flagged as positive if both the 25<sup>th</sup> and 75<sup>th</sup> percentiles are positive, and as negative if both these percentiles are negative. The absolute bias upper bound would not be flagged if the 25<sup>th</sup> and 75<sup>th</sup> percentiles

are of different signs. It is recommended that high sensitivity CO analyzers have an upper bound for the average bias of  $\pm 15$  percent or less.

#### **2.3.1.3 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).

#### **2.3.1.4 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.

#### **2.3.1.5 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, this TAD describes the recommended characteristics of high sensitivity CO analyzers and the procedures for their installation and use. For example, all

monitoring agencies should purchase instruments that have the additional features described in Section 2.3.2, and should adhere to the sampling requirements described in Section 2.3.3.

#### **2.3.1.6 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. 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.

The MDL should be established on-site by supplying the analyzer at least seven times with a test atmosphere containing CO at a concentration that is approximately one to five times greater than the estimated MDL, and recording the response. To perform the MDL test, run zero air through the analyzer and establish an acceptable zero; dilute pollutant gas to the targeted concentration (one to five times the estimated MDL) and collect 20 to 25 one minute observations. Repeat this seven times over the course of 5 to 14 days. Average the concentration from the 20-25 readings; calculate the standard deviation (S) of the average readings and compute the MDL. The MDL is then calculated as the standard deviation of the response values

times the Student's t-value for the number of test measurements (40 CFR Part 136, Appendix B). The MDL for high sensitivity CO analyzers should 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.

#### **2.3.1.7 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 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.

#### **2.3.1.8 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. A range of 5 ppm may not be sufficient in all areas and situations. 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.

#### **2.3.1.9 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  $\pm 1$  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.

### **2.3.2 Recommended 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 GFC CO instrument is described in Section 2.2, and examples of specific instruments are provided in Section 2.3.3. In general, each of the analyzers contains the following systems:

- *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.
- *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.
- *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:

- The sample stream is dried using a permeation tube or Nafion® Dryer prior to introduction to the sample cell;
- 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, on-board, converter that is based on palladium (Pd), platinum (Pt), or other composition;
- The temperature of the optical bench is tightly controlled (i.e., within  $\pm 1$  °C) to maintain detector stability;
- The instrument uses an ultra-sensitive detector, in order to detect very small changes in light intensity.

It is recommended that the high sensitivity CO analyzers deployed in NCore employ these features. Examples of commercial analyzers with these features are presented below.

### **2.3.3 Commercial High Sensitivity GFC CO Monitors**

Several vendors of commercial GFC CO analyzers supply instruments for both ambient and high sensitivity monitoring. Only high sensitivity GFC CO analyzers with nominal LDLs of 40 ppb or below are discussed in detail in this document. Three such analyzers [from Ecotech, Thermo Electron Corporation, and Teledyne Advanced Pollution Instrumentation (API)] are

described here as examples of available high sensitivity CO monitors (no endorsement should be inferred). The descriptions provided for these instruments and the performance claimed for them are based solely on information provided by the respective vendors, and confirmation by EPA should not be inferred.

### 2.3.3.1 *Ecotech Model EC9830T*

The Model EC9830T (Figure 2-2) is the high-sensitivity version of the Model EC9830, which has a U.S. EPA Reference Method designation of RFCA-0992-088.<sup>[7]</sup>



**Figure 2-2. Ecotech EC9830T high sensitivity CO analyzer (courtesy of Ecotech).**

This analyzer has a vendor-specified LDL of 20 ppb, which is achieved in part by the implementation of the features described in Section 2.3.2 and through the use of a cell with a 6 m path length. This LDL is achieved by use of a Kalman digital filter to provide a compromise between response time and noise reduction. The 95% response time of the EC9830T is 300 seconds with the Kalman filter. The recommended operating temperatures for the Model EC9830T are 20 °C to 30 °C, but it may be operated between 15 °C and 35 °C. Since temperature stability of the analyzer is crucial to maintaining its high sensitivity, an automatic background correction will be initiated if the internal temperature of the instrument changes by more than 4 °C. The automatic zeroing feature allows the analyzer to periodically check and

correct for background light intensity, and significantly reduces zero drift. The Model EC9830T incorporates a second order polynomial correction curve that is custom calibrated for each analyzer in the range of 0 to 3,000 ppb (3 ppm), with linearity within 5 percent. Outputs are provided in both analog and digital formats. Table 2-1 shows the specifications of the Model EC9820T.<sup>[7]</sup>

**Table 2-1. Ecotech Model EC9830T high sensitivity CO analyzer specifications**

Parameter	EC9830T Specifications
Precision	± 5 % of reading for range 0-1 ppm ± 1% of reading for range 1-20 ppm
Bias	Not Available
Method Detection Limit	Not Available
Lower Detectable Limit	0.020 ppm (20 ppb) with Kalman 300 sec filter active
Linearity	± 5% 0-1 ppm scale ± 1% of full scale from 1-20 ppm
Zero Drift	Temperature dependence, 0.1% per degree C change. 24 hours; less than 0.020 ppm (20 ppb) 30 days; less than 0.020 ppm (20 ppb)
Span Drift	Temperature dependence, 0.05 % per degree C change. 24 hours less than 0.5% of reading 30 days less than 1.0% of reading

**2.3.3.2 Thermo Electron Corporation Model 48C-TLE**

The Thermo Electron Corporation Model 48C-TLE Enhanced Trace Level CO analyzer<sup>[8-10]</sup> (Figure 2-3) is an improved version of the standard Model 48C Ambient CO analyzer (U.S. EPA Designation Method RFCA-0981-054). In addition to the features described in Section 2.3.2, the primary modifications to the Model 48C-TLE analyzer that improve its sensitivity over the Model 48C include the use of higher reflectance gold-coated mirrors, incorporation of a baseline auto-zeroing function, and the implementation of ± 1 ° C control of optical bench temperature. The recommended operating temperature for the instrument ranges

from 20 °C to 30 °C, but the Model 48C-TLE CO analyzer can be operated over the range of 5 °C to 45°C. The Model 48C-TLE CO analyzer has an LDL of 0.02 ppm (20 ppb) with a 30 second averaging time. The analyzer has ten operating ranges from 0 to 1 ppm through 0 to 1,000 ppm, including a 0 to 5 ppm range. Data can be provided in analog or digital formats. Table 2-2 shows the specifications of the Model 48C-TLE CO.



**Figure 2-3. Thermo Electron Model 48C-TLE CO analyzer (courtesy of Thermo Electron).**

**Table 2-2. Thermo Electron Model 48C-TLE CO analyzer specifications**

Performance Parameters	Model 48C-TLE CO Analyzer Specifications
Precision	±2% of reading or 0.02 ppm (20 ppb) (whichever is larger)
Bias	Not Available
Method Detection Limit	Not Available
Lower Detectable Limit	0.04 ppm (40 ppb) ; 60 sec averaging time
Linearity	± 1% full-scale
Zero Drift	< 0.100 ppm (100 ppb) (24 hour)
Span Drift	± 1% full-scale (24 hour)

### 2.3.3.3 Teledyne Advanced Pollution Instrumentation (API) Model 300E

The Teledyne/API Model 300E high sensitivity CO analyzer<sup>[11-12]</sup> (Figure 2-4) has a U.S. EPA Reference Method designation of RFCA-1093-093. The Model 300E is a high-sensitivity version of the Model 300, which has the same Reference Method designation, and incorporates the recommended features described in Section 2.3.2 to achieve enhanced sensitivity. The Model 300E CO instrument has selectable measurement ranges that can be set anywhere from 0 to 1 ppm up to 0 to 1,000 ppm. The operational temperature range for the instrument is between 5 °C and 40 °C. Table 2-3 shows the specifications of the Model 300E.



Figure 2-4. Teledyne API Model 300E CO analyzer (courtesy of Teledyne API).

Table 2-3. Teledyne API Model 300E high sensitivity CO analyzer specifications

Performance Parameters	Model 300E CO Analyzer Specifications
Precision	0.5% of reading
Bias	Not Available
Method Detection Limit	Not Available
Lower Detectable Limit	0.04 ppm (40 ppb); 30 second averaging time
Linearity	1% full-scale
Zero Drift	<0.1 ppm (100 ppb) per 24 hours; 0.2 ppm (200 ppb) per 7 days
Span Drift	<0.5% reading per 24 hours, 1% reading per 7 days

## **2.3.4 Sampling Requirements**

Proper siting of the sampling equipment and sampling probes is necessary to ensure that the precursor gas analyzers are obtaining representative samples of the ambient air. Likewise, proper environmental control and proper sampling is critical to ensuring that the analyzers are operating correctly and that the CO measurements are comparable to CO measurements recorded at other sites.

### **2.3.4.1 Analyzer Siting**

Analyzer siting should follow the criteria in 40 CFR 58, Appendix E. The installation of the CO analyzer should allow for the sample manifold inlet to be located between 3 and 15 meters above ground level, with at least one meter of vertical and horizontal separation from supporting structures. The probe should be positioned with at least 270 degrees of unrestricted airflow including the predominant wind direction. The probe should be separated from the drip line of nearby trees or structures by at least 20 meters, and should be positioned at least twice as far from nearby obstacles as the height of the obstacles.

### **2.3.4.2 Instrument Shelter**

To help ensure proper performance, the precursor gas analyzers and supporting equipment should be installed and operated in a temperature controlled environment. An insulated instrument shelter should be used to protect the analyzers from precipitation and adverse weather conditions, maintain operating temperature within the analyzers' temperature range requirements, and provide security and electrical power. The environmental control of the shelter should be sufficient to minimize fluctuations in shelter temperature. The recommended shelter temperature range is 20 °C to 30 °C, and daily changes in temperature should not exceed 5 °C over a 24-hour period. Condensation of moisture must be prevented, and it may be

necessary to impose seasonal temperature ranges to assure remaining above the ambient dewpoint.

#### **2.3.4.3 Sample Inlet or Manifold**

Sample air for a high sensitivity CO analyzer should be drawn directly to the analyzer through FEP (Fluoroethylpropylene) or PTFE (Polytetrafluoroethylene) tubing (e.g., ¼ inch outer diameter (OD)), equipped with a 1-micron Teflon® filter at the inlet to remove particles from the sample air. The filter should be changed weekly, or more often in excessively dirty conditions. In this configuration the CO analyzer does not share its inlet system with any other analyzer.

Some existing air monitoring stations may provide air to multiple analyzers through a common manifold. In such a case, it is recommended that manifolds for high sensitivity CO measurements be made of glass. Since neither zero air nor sample air is totally particulate-free, over time sample manifolds will collect particulate matter on the internal walls. A glass manifold is transparent, and can be inspected easily and cleaned readily by rinsing with distilled water and air drying. However, caution must be used with glass manifolds because of their fragility. The CO analyzer should be located as close to the inlet manifold as possible, to minimize the length of sampling lines, and sampling lines should be constructed of FEP or PTFE. The sample manifold must be of sufficient diameter that outside air is drawn into the manifold at as close to atmospheric pressure as possible. The manifold must also allow for excess gas flow to be exhausted without over-pressurization (e.g., during delivery of gases from high-pressure cylinders.) If the pressure in the manifold differs from atmospheric pressure, the CO readings obtained will not be representative. A manifold of 1 inch inner diameter should be sufficient to avoid pressure differences. A detailed description of sample manifold designs is presented in Appendix A.

## **2.4 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. Operators are encouraged to report any observations or anecdotal data that might add to the understanding or awareness of interferences or other anomalies in CO measurements.

### **2.4.1 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. Section 2.4.1.1 describes the most common positive interferences (water vapor and CO<sub>2</sub>), and Section 2.4.1.2 describes the most common negative interferences and sources of bias (incomplete removal of CO during instrumental auto-zeroing and loss of CO by reaction or adsorption in dirty inlet lines or filters). In each section recommended procedures to minimize these interferences or sources of bias are described.

#### **2.4.1.1 Positive Interferences**

GFC CO analyzers determine CO concentration by measuring the amount of light that is absorbed at a select wavelength (4.7  $\mu\text{m}$ ) 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 results 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<sub>2</sub>, which are both generally present in the atmosphere at concentrations greatly exceeding those of CO. Studies have shown conclusively that water vapor interferes with the ability of NDIR analyzers to accurately quantify CO. Water absorbs very strongly in the 3.1, 5.0

to 5.5, and 7.1 to 10.0  $\mu\text{m}$  regions of the IR spectrum. Since water vapor absorbs light in regions in close proximity to the CO absorptions, removal of water vapor from the sample air is necessary 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 that selectively removes water vapor from the sample gas without removing CO.

CO<sub>2</sub> absorbs in the IR spectrum at 2.7, 5.2, and 8.0 to 12.0  $\mu\text{m}$ . 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<sub>2</sub> 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  $\mu\text{m}$ . Manufacturers of high sensitivity CO analyzers select the bandpass filter to effectively remove CO<sub>2</sub> interference. An added benefit of such filters is that they also limit interference from water vapor.

#### **2.4.1.2 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<sub>2</sub>. 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<sub>2</sub> 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, then a CO calibration mixture, all with the internal heated CO scrubber engaged. Zero air and sample air readings should be within  $\pm 0.010$  ppm (10 ppb), and scrubber efficiency should be >99%.

### **2.4.2 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.

## **2.5 Supporting Equipment**

In addition to the precursor gas analyzers, several pieces of supporting equipment should be maintained at each NCore site. At a minimum, this equipment includes a data acquisition device and calibration equipment.

### **2.5.1 Data Acquisition Device**

Many types of equipment can be used to record the concentration measurements obtained from the analyzer. Recommended options for data acquisition are described in Section 6 of this TAD.

### **2.5.2 Calibration Equipment**

The following equipment is recommended for calibration of a high sensitivity CO analyzer.

#### ***2.5.2.1 Calibration Standard and Standard Delivery System***

The calibration standards used for the calibration of high sensitivity CO analyzers should be generated by dilution of a commercially-prepared and certified compressed gas CO standard

using a mass flow controlled (MFC) calibration unit. The method of generating calibration standards by dilution involves the accurate measurement of the analyte gas flow rate and the diluent gas flow rate prior to blending these gas streams. The calibration unit includes mass flow controllers that are based upon small thermistors that are sensitive to heat loss. A potential voltage is applied to the thermistor and, as the gas flow increases across the thermistor, the resistance of the thermistor changes proportionally with the flow rate. This change in resistance can be measured very accurately by electronic circuitry and a feedback loop within the MFC circuitry monitors the gas flow and controls the flow rate to maintain the desired rate. Using two channels in parallel, the MFC calibrator unit controls the analyte gas flow rate and the diluent gas flow rate such that upon mixing these gases generates a working standard with the desired concentration. Typical flow ranges of the MFC units are up to 10 L/min for the diluent gas flow and up to 100 cm<sup>3</sup>/min for the analyte gas flow. These systems allow for accurate dilution of CO standard gases from high concentration (usually 200 to 250 ppm) to low ambient working standard concentrations (e.g., from 0.04 to 0.8 ppm). When the analyte concentration in the commercially-prepared standard cylinder is certified by reference to NIST standards, and the MFCs are calibrated to NIST-traceable standards, the resulting working standard concentration is considered to be NIST-traceable.

It is highly important when purchasing a MFC calibrator that it meet the 40 CFR 50 requirements of  $\pm 2$  percent flow accuracy, and that the calibrations of both MFC channels be checked periodically using a NIST traceable flow standard. Routine MFC checks must be standard procedure. To accomplish such check, a NIST traceable flow standard must be on hand as part of every calibration system.

#### **2.5.2.2      *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.

## **2.6 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.

### **2.6.1 Calibration Standards**

The primary CO standards used must be certified, commercially-prepared compressed gas standards with a certified accuracy of no worse than  $\pm 2$  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., N<sub>2</sub>), or may be a mixed component standard that also contains known concentrations of other precursor gases (e.g., SO<sub>2</sub>, NO). (Note that mixtures containing both SO<sub>2</sub> and NO may not be suitable for SO<sub>2</sub> calibration, depending on the NO rejection ratio of the SO<sub>2</sub> analyzer – see Section 3 SO<sub>2</sub> Measurements.)

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.

### **2.6.2 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 noted in Section 2.5.2.2. Commercial zero air further scrubbed of CO may be used to crosscheck the purity of air provided by a commercial continuous air purification system.

## **2.7 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.

### **2.7.1 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 (see Section 6).

### **2.7.2 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 samples (Section 5.4.1) differ from the certified standard values by  $\pm 15$  percent.

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

### **2.7.3 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  $\pm 15$  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 in Section 2.7.2.

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.

- 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.

#### **2.7.4 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, according to the equations provided in Section 2.3.1.1. 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.

### **2.8 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. Despite active preventive maintenance, occasional problems may arise with the high sensitivity CO analyzers. 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 this TAD.

### **2.8.1 Preventive Maintenance**

Routine preventive maintenance procedures should be in place to prevent down-time and data loss. 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 2-4 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.

**Table 2-4. Example of a preventive maintenance schedule for high sensitivity CO analyzers.**

<b>Item</b>	<b>Schedule</b>
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

### **2.8.2 Troubleshooting**

High sensitivity CO analyzers are subject to many factors that can cause inaccurate measurements or down-time. Table 2-5 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 2-5. Instrument troubleshooting for high sensitivity CO analyzers.**

<b>Problem</b>	<b>Possible Cause</b>	<b>Possible Solution</b>
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	N <sub>2</sub> leak from correlation wheel	Replace wheel

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.

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### **3.0 HIGH SENSITIVITY SULFUR DIOXIDE MEASUREMENTS**

#### **3.1 Introduction**

Sulfur dioxide (SO<sub>2</sub>) has been identified as a key precursor of fine particulate matter (PM<sub>2.5</sub>) and, thus, plays an important role in PM-related health effects. A variety of sulfur compounds are released to the atmosphere from both natural and anthropogenic sources. Ninety-five percent of sulfur emitted to the air from anthropogenic sources is released as sulfur dioxide, mainly from stationary sources that burn fossil fuels (e.g., coal and oil) that contain sulfur. The major human sources of SO<sub>2</sub> are coal-burning electrical utilities, refineries, and ore smelters. The amount of SO<sub>2</sub> released depends on the sulfur content of the fuel; high-sulfur coal may contain as much as six percent sulfur by weight.

##### **3.1.1 Properties of SO<sub>2</sub>**

SO<sub>2</sub> is a colorless gas that can be detected by taste and odor in ambient air at concentrations as low as 0.3 ppm. Above 3 ppm, SO<sub>2</sub> has a pungent, irritating odor similar to a struck match. In addition to having a bad odor, high concentrations of sulfur dioxide can affect breathing, cause respiratory illnesses, and aggravate existing respiratory and cardiovascular diseases.

SO<sub>2</sub> is found at appreciable levels (i.e., low ppb) in the lower atmosphere (troposphere), where it is oxidized to sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), by both gas-phase photochemical reactions and aqueous-phase reactions with hydrogen peroxide and other oxidants in cloud water. The gas-phase and aqueous-phase oxidation pathways are roughly equally important in converting SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>. Sulfuric acid is non-volatile and condenses into particulate form, typically with partial to complete neutralization by atmospheric ammonia (NH<sub>3</sub>). Sulfates account for a substantial fraction of suspended particulate matter in urban air. They can be transported long distances and return to the earth as a major component of acid rain.

### **3.1.2 Historical Overview of Measurement Method**

The UV fluorescence monitoring method for atmospheric SO<sub>2</sub> was developed to improve upon the flame photometric detection (FPD) method for SO<sub>2</sub>, which in turn had displaced the pararosaniline wet chemical method for SO<sub>2</sub> measurement. The pararosaniline method is still the U.S. EPA's Reference Method for atmospheric SO<sub>2</sub>, but is rarely used because of its complexity and slow response, even in its automated forms. Both the UV fluorescence and FPD methods are designated as Equivalent Methods by EPA, but UV fluorescence has largely supplanted the FPD approach because of the UV method's inherent linearity, sensitivity, and the absence of consumables, such as the hydrogen gas needed for the FPD method. Numerous vendors supply UV fluorescence SO<sub>2</sub> analyzers, including a few who supply high sensitivity analyzers (examples are provided below).

### **3.2 Summary of SO<sub>2</sub> Measurement by UV Fluorescence**

The current method for the measurement of SO<sub>2</sub> is based on the principle that SO<sub>2</sub> molecules absorb ultraviolet (UV) light at one wavelength and emit UV light at a different wavelength. This process is known as fluorescence, and involves the excitation of the SO<sub>2</sub> molecule to a higher energy electronic state by light absorption. Once excited, the molecule decays non-radiatively to a lower energy electronic state from which it then decays to the original, or ground, electronic state by emitting a photon of light at a longer wavelength (i.e., lower energy) than the original excitation light. The process can be summarized in the following equations:



where  $SO_2^*$  represents the excited state of  $SO_2$ ,  $h\nu_1$  and  $h\nu_2$  represent the energy of the excitation and fluorescence photons, respectively, and  $h\nu_2 < h\nu_1$ . The intensity of the emitted light is proportional to the number of  $SO_2$  molecules in the sample gas.

Figure 3-1 shows a schematic illustration of the optical chamber of a commercial  $SO_2$  analyzer. Light from a high intensity UV lamp passes through a bandwidth filter, allowing only photons with wavelengths around the  $SO_2$  absorption peak (near 214 nm) to enter the optical chamber. The light passing through the source bandwidth filter is collimated using a UV lens and passes through the optical chamber, where it is detected on the opposite side of the chamber by the reference detector. A photomultiplier tube (PMT) is offset from and placed perpendicular to the light path to detect the  $SO_2$  fluorescence. Since the  $SO_2$  fluorescence (330 nm) is at a wavelength that is different from the excitation wavelength, an optical bandwidth filter is placed in front of the PMT to filter out any stray light from the UV lamp. A lens is located between the filter and the PMT to focus the fluorescence onto the active area of the detector and optimize the fluorescence signal.

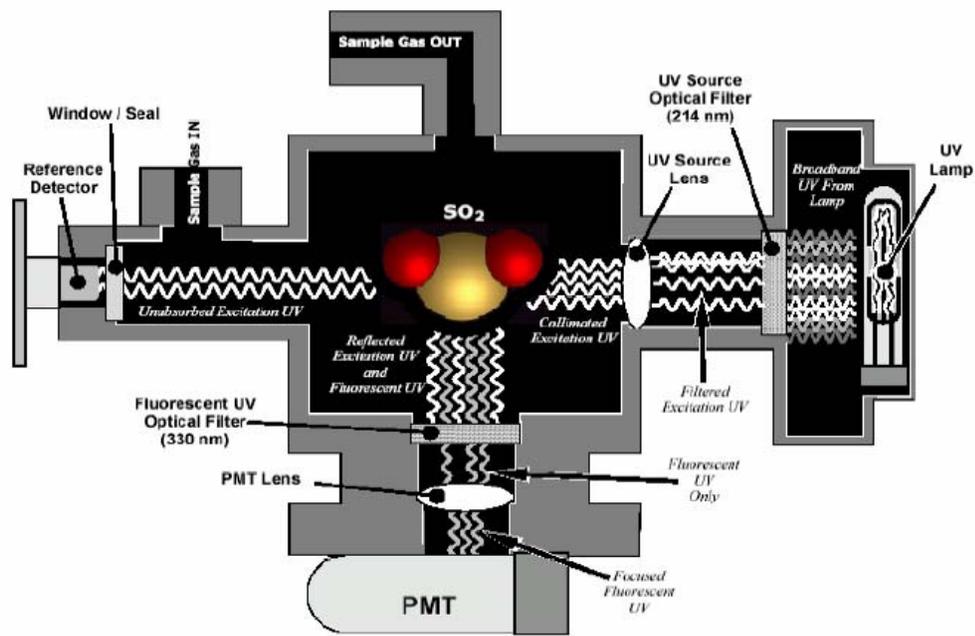


Figure 3-1. Schematic illustration of the optical chamber of a precursor  $SO_2$  analyzer.

### **3.3 Recommendations for NCore**

Since the high sensitivity SO<sub>2</sub> analyzers deployed at NCore sites are intended to monitor low ambient SO<sub>2</sub> concentrations, it is important that they meet a variety of performance criteria. Many of these performance criteria are more stringent than those for routine SO<sub>2</sub> analyzers; consequently, a number of features are required in the high sensitivity SO<sub>2</sub> analyzers 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 SO<sub>2</sub> 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.

#### **3.3.1 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.<sup>[1]</sup> 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 SO<sub>2</sub> analyzers that are deployed at NCore sites meet the following method performance criteria.

### 3.3.1.1 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 (see Sections 3.7.4 and 5.3.3). Calculations to assess precision are given below and should be used to assess precision on a quarterly basis. It is recommended that high sensitivity SO<sub>2</sub> 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. The resulting percent differences are then used as described below. For each single point precision check, calculate the percent difference,  $d_i$ , as follows:

#### Equation 1

$$d_i = \frac{\text{reported} - \text{challenge}}{\text{challenge}} \cdot 100$$

where *reported* is the concentration indicated by the high sensitivity SO<sub>2</sub> analyzer and *challenge* is the concentration of the standard used in the precision check. The precision estimator is then calculated as the coefficient of variation (CV) upper bound, using Equation 2 as follows:

#### Equation 2

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^n d_i^2 - \left(\sum_{i=1}^n d_i\right)^2}{n(n-1)}} \cdot \sqrt{\frac{n-1}{X^2_{0.1, n-1}}}$$

where  $n$  is the number of data points (i.e., precision check comparisons), the  $d_i$  values are the resulting percent differences, and  $X_{0.1, n-1}$  is the 10th percentile of a chi-squared distribution with  $n-1$  degrees of freedom.

### 3.3.1.2 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 (see Section 3.3.1.1 above). The bias estimator is an upper bound on the mean absolute value of the percent differences as described in Equation 3 as follows:

Equation 3

$$|bias| = AB + t_{0.95, n-1} \cdot \frac{AS}{\sqrt{n}}$$

where  $n$  is the number of challenge comparisons being aggregated;  $t_{0.95, n-1}$  is the 95th quantile of a t-distribution with  $n-1$  degrees of freedom; the quantity  $AB$  is the mean of the absolute values of the individual  $d_i$ 's and is calculated using Equation 4 as follows:

Equation 4

$$AB = \frac{1}{n} \cdot \sum_{i=1}^n |d_i|$$

and the quantity  $AS$  is the standard deviation of the absolute value of the  $d_i$ 's and is calculated using Equation 5 as follows:

Equation 5

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^n |d_i|^2 - \left( \sum_{i=1}^n |d_i| \right)^2}{n(n-1)}}$$

Since the bias statistic as calculated in Equation 3 uses absolute values, it does not have a direction or sign (negative or positive) associated with it. The sign of the calculated bias is to be determined by rank ordering the percent differences of the QC check samples from a given analyzer for a particular assessment interval. Calculate the 25<sup>th</sup> and 75<sup>th</sup> percentiles of the percent differences for each analyzer. The absolute bias upper bound should be flagged as positive if both the 25<sup>th</sup> and 75<sup>th</sup> percentiles are positive, and as negative if both these percentiles are negative. The absolute bias upper bound would not be flagged if the 25<sup>th</sup> and 75<sup>th</sup> percentiles are of different signs. It is recommended that high sensitivity SO<sub>2</sub> analyzers have an upper bound for the average bias of  $\pm 15$  percent or less.

### **3.3.1.3 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 SO<sub>2</sub> 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).

### **3.3.1.4 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 SO<sub>2</sub> concentrations in NCore, EPA requires a minimum data completeness of 75 percent. In practice typical completeness values can often approach 90 to 95 percent.

### **3.3.1.5 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, this TAD describes the recommended characteristics of high sensitivity SO<sub>2</sub> analyzers and the procedures for their installation and use. For example, all monitoring agencies should purchase instruments that have the additional features described in Section 3.3.2, and should adhere to the sampling requirements described in Section 3.3.3.

### **3.3.1.6 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. 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.

The MDL should be established on-site by supplying the analyzer at least seven times with a test atmosphere containing SO<sub>2</sub> at a concentration that is approximately one to five times greater than the estimated MDL, and recording the response. To perform the MDL test, run zero air through the analyzer and establish an acceptable zero; dilute pollutant gas to the targeted concentration (one to five times the estimated MDL) and collect 20 to 25 one minute observations. Repeat this seven times over the course of 5 to 14 days. Average the concentration from the 20-25 readings; calculate the standard deviation (S) of the average readings and compute the MDL. The MDL is then calculated as the standard deviation of the response values times the Student's t-value for the number of test measurements (40 CFR Part 136, Appendix B). The MDL for high sensitivity SO<sub>2</sub> analyzers should be 0.30 ppb or lower over an averaging time of no more than 5 minutes.

#### **3.3.1.7 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 SO<sub>2</sub> readings is determined according to 40 CFR 53.23(b). The vendor-specified LDL for the most sensitive range of high sensitivity SO<sub>2</sub> analyzers should be 0.20 ppb or lower, over an averaging time of no more than 5 minutes.

#### **3.3.1.8 Linear Range**

The linear range of each high sensitivity SO<sub>2</sub> analyzer should extend from approximately 0.20 ppb to at least 100 ppb. Users should determine if their range should exceed 100 ppb and adjust accordingly. A range of 100 ppb may not be sufficient in all areas and situations. Note that some high sensitivity SO<sub>2</sub> 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 SO<sub>2</sub> concentrations.

### **3.3.1.9 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 SO<sub>2</sub> analyzer into service. Such SO<sub>2</sub> analyzers should have 12- and 24-hour zero drift less than 0.20 ppb, and should have a span drift of less than  $\pm 1$  percent of the full scale measurement range of the analyzer per 24 hours.

### **3.3.1.10 NO Rejection Ratio**

The NO rejection ratio refers to the effectiveness with which fluorescent emission from nitric oxide (NO) is blocked in a UV fluorescence SO<sub>2</sub> analyzer. This interfering emission can be greatly reduced by optical filtering of the light reaching the PMT. For high sensitivity SO<sub>2</sub> monitoring in NCore, it is recommended that the NO rejection ratio of the SO<sub>2</sub> analyzer be at least 100 to 1, i.e., 100 ppb of NO must produce a response equivalent to that from no more than 1 ppb of SO<sub>2</sub>.

## **3.3.2 Recommended Features for High Sensitivity SO<sub>2</sub> Measurements**

Continuous UV fluorescence SO<sub>2</sub> 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 UV fluorescence instrument is shown above in Section 3.2, and examples of specific instruments are provided in Section 3.3.3. In general, each of the analyzers contains the following systems:

- Pneumatic System: This portion of the analyzer consists of sample probe, sample inlet line, particulate filter, hydrocarbon scrubber/kicker, dryer (if

needed), sample cell, flow meter, and pump, all used to bring ambient air from the inlet to the deflector.

- *Analytical System*: This portion of the analyzer consists of the UV source with the associated source filters, lenses, and optics, as well as the light baffles, the detector (photomultiplier tube), and bandpass filters.
- *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 addition to these general systems, the high sensitivity versions of the commercial UV fluorescence SO<sub>2</sub> analyzers typically have the following features that allow them to measure SO<sub>2</sub> at sub-ppb levels:

- A high intensity pulsed UV light source that provides a greater degree of sensitivity;
- Multiple reflective optical filters that allow only light at the wavelength causing excitation of the SO<sub>2</sub> molecules to enter the optical chamber, while excluding all light at wavelengths that may cause interference; and
- Optical filtering to maximize the rejection of fluorescence from NO molecules.

It is recommended that the high sensitivity SO<sub>2</sub> analyzers deployed in NCore employ these features. Examples of commercial analyzers with these features are presented below.

### **3.3.3 Commercial High Sensitivity UV Fluorescence SO<sub>2</sub> Monitors**

High sensitivity SO<sub>2</sub> analyzers are commercially available from a number of vendors. Examples of such analyzers discussed in this section are closely similar to instrumentation designated as Federal Equivalent Methods; however, modifications to improve measurement sensitivity have been made. The following three instruments are shown as examples of commercially available high sensitivity SO<sub>2</sub> analyzers (no endorsement should be inferred). The descriptions provided for these instruments and the performance claimed for them are based solely on information provided by the respective vendors, and confirmation by EPA should not be inferred.

#### **3.3.3.1 *Ecotech Model EC9850T***

The Ecotech Model EC9850T SO<sub>2</sub> analyzer<sup>[2]</sup> shown in Figure 3-2 is a UV fluorescence SO<sub>2</sub> analyzer specifically designed to measure background concentrations of SO<sub>2</sub> with a lower detection limit of 200 ppt (0.2 ppb). The EC9850T is a high sensitivity version of the Ecotech ML9850/EC9850 that has a U.S. EPA Equivalent Method Designation of EQSA-0193-092. The higher sensitivity is achieved in part by using a specially selected high output UV lamp operating at 214 nm, a Kalman digital filter that continuously provides a compromise between response time and noise reduction, and a special high performance SO<sub>2</sub> scrubber impregnated with Na<sub>2</sub>CO<sub>3</sub> solution. Scrubbed sample air is used for zeroing of the analyzer's response. The EC9850T SO<sub>2</sub> analyzer uses a 360 nm filter to reduce interference from NO and potential interference from other species. The analyzer has multiple range settings up to 0 to 200 ppb full scale, and has a recommended operating temperature range of 20 °C to 30 °C, but may be operated between 15 °C and 35 °C. The EC9850T SO<sub>2</sub> analyzer has both analog and digital outputs. Table 3-1 shows the specifications of the Model EC9850T.



Figure 3-2. Ecotech EC9850T SO<sub>2</sub> analyzer (courtesy of Ecotech).

Table 3-1. Ecotech EC9850T SO<sub>2</sub> analyzer specifications.

Performance Parameters	EC9850T SO <sub>2</sub> Analyzer Specifications
Precision	± 2% of reading
Bias	Not available
Method Detection Limit	Not available
Lower Detectable Limit	200 ppt (0.2 ppb) (with Kalman or 300 sec filter active)
Linearity	Not available
Zero Drift	Temperature dependence, 0.1% per degree C changes. 24 hours; less than 200 ppt (0.2 ppb)
Span Drift	Temperature dependence, 0.05 % per degree C changes. 24 hours less than 0.5% of reading 30 days less than 1.0% of reading
NO Rejection Ratio	Not available <sup>a</sup>

<sup>a</sup>: Vendor states rejection ratio is high, but difficult to quantify; dependent on water vapor content of air.

### 3.3.3.2 Thermo Electron Corporation Model 43C-TLE

The Model 43C-TLE enhanced high sensitivity pulsed fluorescence SO<sub>2</sub> analyzer<sup>[3]</sup> is shown in Figure 3-3. The Model 43C-TLE SO<sub>2</sub> analyzer is a successor to the Model 43C analyzer, which has a U.S. EPA Equivalent Method Designation of EQSA-0486-060. As

recommended in Section 3.3.2, the Model 43C-TLE achieves higher sensitivity than the Model 43C through the use of additional reflective bandpass filters to further reduce stray light, and by operation of the UV flash lamp at a higher voltage, which increases the total output light intensity. Additionally, the Model 43C-TLE also includes a longer optical bench that increases the effective sample path length and improves sensitivity. Furthermore, optimization of the optical properties of the detector filter allows for greater rejection of NO interference. This feature allows an instrument originally designed for rural background monitoring applications to also be used in urban monitoring programs such as NCore Level 2.

The Model 43C-TLE SO<sub>2</sub> analyzer has multiple range settings up to 1 ppm full scale and may be safely operated in the temperature range of 0 °C to 45 °C. The Model 43C-TLE analyzer displays the SO<sub>2</sub> concentration on a screen on the front panel of the analyzer, and has both analog and digital outputs. An optional capability of the 43C-TLE is for generation of internal zero and span mixtures using an SO<sub>2</sub> permeation tube, although this means of calibration is not recommended for use in NCore. Table 3-2 shows the specifications of the Model 43C-TLE.



**Figure 3-3. Thermo Electron Model 43C-TLE SO<sub>2</sub> analyzer (courtesy Thermo Electron).**

**Table 3-2. Thermo Electron Model 43C-TLE SO<sub>2</sub> analyzer specifications.**

Performance Parameters	Model 43C-TLE SO <sub>2</sub> Analyzer Specifications
Precision	1% of reading or 0.2 ppb
Bias	Not available
Method Detection Limit	Not available
Lower Detectable Limit	0.2 ppb (10 sec avg. time) 0.10 ppb (60 sec avg. time) 0.05 ppb (300 sec avg. time)
Linearity	± 1% of full scale
Zero Drift	less than 0.2 ppb per day
Span Drift	± 1% per week
NO Rejection Ratio	<2.5 ppb equivalent with 500 ppb NO interference

### 3.3.3.3 Teledyne Advanced Pollution Instrumentation (API) Model 100AS

The Teledyne API Model 100AS SO<sub>2</sub> analyzer<sup>[4, 5]</sup> shown in Figure 3-4 is based on the Model 100A fluorescence SO<sub>2</sub> Analyzer. Both the Model 100A and the Model 100AS analyzers are designated as U.S. EPA Equivalent Method Number EQSA-0495-100. The sensitivity and stability of the Model 100AS analyzer is achieved in part through the use of an optical shutter to compensate for PMT drift and a reference detector to correct for changes in UV lamp intensity. A hydrocarbon “kicker” and advanced optical design combine to minimize inaccuracies due to interferences, including NO. The Model 100AS has sensitivity ranges of 0 to 10 ppb full scale up to 0 to 1 ppm full scale and can measure SO<sub>2</sub> with a lower detectable limit of 0.10 ppb. The analyzer may be safely operated in the temperature range of 5 °C to 40 °C. The Model 100AS has both analog and digital outputs. An optional capability of the Model 100AS is for generation of internal zero and span mixtures, using an SO<sub>2</sub> permeation tube. Table 3-3 shows the specifications of the Model 100AS.

*Note: The Model 100AS is not API’s “true high sensitivity” analyzer, and the Model 100EU high sensitivity analyzer is expected to be commercially available this year.*



Figure 3-4. Teledyne API Model 100AS SO<sub>2</sub> analyzer (courtesy Teledyne API).

Table 3-3. Teledyne API Model 100AS SO<sub>2</sub> analyzer specifications.

Performance Parameters	Teledyne API Model 100AS SO <sub>2</sub> Analyzer Specifications
Precision	0.5% of reading
Bias	Not available
Method Detection Limit	Not available
Lower Detectable Limit	100 ppt (0.1 ppb) (4 minute averaging time)
Linearity	1% full scale
Zero Drift	< 0.2 ppb/24 hours
Span Drift	< 0.5% reading/24 hours
NO Rejection Ratio	100:1 standard; 250:1 with optional filter

### **3.3.4 Sampling Requirements**

Proper siting of the sampling equipment and sampling probes is necessary to ensure that the gas analyzers are obtaining representative samples of the ambient air. Likewise, proper environmental control of the analyzer and proper sampling are critical to ensuring that the analyzers are operating correctly and that the SO<sub>2</sub> measurements are comparable to SO<sub>2</sub> measurements recorded at other sites.

#### **3.3.4.1 Analyzer Siting**

Analyzer siting should follow the criteria in 40 CFR58, Appendix E. The installation of the precursor SO<sub>2</sub> analyzer should allow for the sample manifold inlet to be located between 3 and 15 meters above ground level, with at least one meter of vertical and horizontal separation from supporting structures. The probe should be positioned with at least 270 degrees of unrestricted airflow including the predominant wind direction. The probe should be separated from the drip line of nearby trees or structures by at least 20 meters, and should be positioned at least twice as far from of nearby obstacles as the height of the obstacles.

#### **3.3.4.2 Instrument Shelter**

To help ensure proper performance, the precursor analyzers and supporting equipment should be installed and operated in a temperature controlled environment. An insulated instrument shelter should be used to protect the analyzer from precipitation and adverse weather conditions, maintain operating temperature within the analyzer's temperature range requirements, and provide security and electrical power. The environmental control of the shelter should be sufficient to minimize fluctuations in shelter temperature. The recommended shelter temperature range is 20°C to 30°C, and daily changes in temperature should not exceed 5°C over a 24-hour period. Condensation of moisture must be prevented, and it may be necessary to impose seasonal temperature ranges to assure remaining above the ambient dewpoint.

#### **3.3.4.3 Sample Inlet or Manifold**

Sample air for a high sensitivity SO<sub>2</sub> analyzer should be drawn directly to the analyzer through FEP or PTFE tubing (e.g., ¼ inch outer diameter (OD)), equipped with a 1-micron Teflon® filter at the inlet to remove particles from the sample air. The filter should be changed weekly, or more often in excessively dirty conditions. In this configuration the SO<sub>2</sub> analyzer does not share its inlet system with any other analyzer.

Some existing air monitoring stations may provide air to multiple analyzers through a common manifold. In such a case it is recommended that manifolds for precursor SO<sub>2</sub> measurements be made of glass. Since neither zero air nor sample air is totally particulate-free, over time sample manifolds will collect particulate matter on the internal walls. A transparent glass manifold can be inspected easily and cleaned readily by rinsing with distilled water and air drying. However, caution must be used with glass manifolds because of their fragility.

The SO<sub>2</sub> analyzer should be located as close to the inlet manifold as possible, to minimize the length of sampling lines, and sampling lines should be constructed of FEP or PTFE. The sample manifold must be of sufficient diameter that outside air is drawn into the manifold at as close to atmospheric pressure as possible. The manifold must also allow for excess gas to be exhausted in the event of over pressurization (i.e., during delivery of gases from high-pressure cylinders.) If the pressure in the manifold differs from atmospheric pressure, the SO<sub>2</sub> readings obtained will not be representative. A manifold of 1 inch inner diameter should be sufficient to avoid pressure differences. A detailed description of sample manifold designs is presented in Appendix A.

### **3.4 Potential Problems and Solutions**

This section describes several of the potential problems associated with precursor SO<sub>2</sub> measurements, and discusses the practical solutions to these problems, many of which the SO<sub>2</sub> analyzer vendors have already implemented in their analyzers.

The following sections describe several potential positive and negative sources of interference or bias. Section 3.4.1 describes the most common positive interferences (volatile aromatic and poly-nuclear aromatic hydrocarbons, and NO), and the most common source of positive bias (stray light). Section 3.4.2 describes the most common sources of negative bias (collisional quenching of SO<sub>2</sub> and loss of SO<sub>2</sub> in sampling lines). In each section recommended procedures to minimize these interferences or sources of bias are described.

In addition to these potential problems, other problems may arise in the routine operation of precursor SO<sub>2</sub> analyzers. Operators are encouraged to report any observations or anecdotal data that might add to the understanding or awareness of interferences or other anomalies in SO<sub>2</sub> measurements with UV fluorescence analyzers in general.

### **3.4.1 Sources of Positive Interference or Bias**

Positive interference in precursor SO<sub>2</sub> monitoring can result from other gases in the sample that happen to fluoresce at the same wavelength as SO<sub>2</sub>. Perhaps the most prevalent sources of this type of interference are volatile aromatic (e.g., xylenes) and poly-nuclear aromatic (PNA) (e.g., naphthalene) hydrocarbons. Such compounds absorb UV photons and fluoresce in the region of the SO<sub>2</sub> fluorescence. Consequently, any such aromatic hydrocarbons that are in the optical chamber can act as a positive interference. To remove this source of interference, the high sensitivity SO<sub>2</sub> analyzers have hydrocarbon scrubbers or “kickers” to remove these compounds from the sample stream before the sample air enters the optical chamber. Another potential source of positive interference is nitric oxide (NO). NO fluoresces in a spectral region that is close to the SO<sub>2</sub> fluorescence. However, in high sensitivity SO<sub>2</sub> analyzers, the bandpass filter in front of the PMT is designed to prevent NO fluorescence from reaching the PMT and being detected. Care must be exercised when using multicomponent calibration gases containing both NO and SO<sub>2</sub> that the NO rejection ratio of the SO<sub>2</sub> analyzer is sufficient to prevent NO interference.

The most common source of positive bias (as opposed to positive spectral interference) in high sensitivity SO<sub>2</sub> monitoring is stray light reaching the optical chamber. Since SO<sub>2</sub> can be excited by a broad range of UV wavelengths, any stray light with an appropriate wavelength that enters the optical chamber can excite SO<sub>2</sub> in the sample and increase the fluorescence signal. Furthermore, stray light at the wavelength of the SO<sub>2</sub> fluorescence that enters the optical chamber may impinge on the PMT and increase the fluorescence signal. The analyzer manufacturers incorporate several design features to minimize the stray light that enters the

chamber. These features include the use of light filters, dark surfaces, and opaque tubing to prevent light from entering the chamber.

### **3.4.2 Sources of Negative Interference or Bias**

Non-radiative deactivation (quenching) of excited SO<sub>2</sub> molecules can occur from collisions with common molecules in air, including nitrogen, oxygen, and water. During collisional quenching, the excited SO<sub>2</sub> molecule transfers energy kinetically allowing the SO<sub>2</sub> molecule to return to the original lower energy state without emitting a photon. Collisional quenching results in a decrease in the SO<sub>2</sub> fluorescence and results in the underestimation of SO<sub>2</sub> concentration in the air sample. The concentrations of nitrogen and oxygen are constant in the ambient air, so quenching from those species at a surface site is also constant, but the water vapor content of air can vary. Despite this variability, in routine ambient monitoring the effect of water vapor on SO<sub>2</sub> fluorescence measurements is negligible. Only if high or highly variable water vapor concentrations were a concern (as in source sampling), should it be necessary to dry the sample air using optional equipment available from the analyzer vendors. Condensation of water vapor in sampling lines must be avoided, as it can absorb SO<sub>2</sub> from the sample air. The simplest approach to avoid condensation is to heat sampling lines to a temperature above the expected dew point, and within a few degrees of the controlled optical bench temperature. An alternative approach would be to maintain all sampling lines at reduced pressure by locating the analyzer's critical orifice at the sample inlet point.

### **3.5 Supporting Equipment**

In addition to the precursor gas analyzers, several pieces of supporting equipment should be maintained at each NCore site. At a minimum, this equipment includes a data acquisition device and calibration equipment.

### **3.5.1 Data Acquisition Device**

Many types of equipment can be used to record the concentration measurements obtained from the analyzer. Recommended options for data acquisition are described in Section 6 of this TAD.

### **3.5.2 Calibration Equipment**

The equipment required for calibration of a high sensitivity SO<sub>2</sub> analyzer include a MFC calibrator unit, and a source of zero air. The following equipment is recommended for calibration of a high sensitivity SO<sub>2</sub> analyzer.

#### ***3.5.2.1 Calibration Standard and Standard Delivery System***

The calibration standards used for the calibration of high sensitivity SO<sub>2</sub> analyzers should be generated by dilution of a commercially-prepared and certified compressed gas SO<sub>2</sub> standard using a MFC calibration unit. That commercially-prepared standard may contain only SO<sub>2</sub> in an inert gas (e.g., N<sub>2</sub>), or may be a mixed component standard that also contains known concentrations of other precursor ambient gases (e.g., CO, NO). However, note the caution stated in Section 3.4.1 regarding potential NO interference in mixed standards containing SO<sub>2</sub> and NO.

It is important when purchasing a MFC calibrator that it meets the 40 CFR 50 requirements of  $\pm 2$  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 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.

### **3.5.2.2 Zero Air Source/Generator**

Zero air is required for the calibration of precursor SO<sub>2</sub> instruments. This air must contain no detectable SO<sub>2</sub> (i.e., SO<sub>2</sub> content must be less than the LDL of the SO<sub>2</sub> analyzer) and be free of particulate matter. Suitable zero air may be supplied from compressed gas cylinders of purified air. However, it may be expensive to maintain a sufficient supply of zero air cylinders to operate a precursor SO<sub>2</sub> analyzer continuously. As an alternative, many commercially available zero air generation systems can supply suitably SO<sub>2</sub>-free air.

To ensure that the zero air used is free from contaminants, the SO<sub>2</sub> analyzer should be independently supplied with zero air from different sources. If the analyzer responds differently to the different sources, generally the source with the lowest response is the highest quality source. Confirmation of zero air quality can be achieved using various additional scrubbing traps. For example, ambient air can be scrubbed of SO<sub>2</sub> using 24 x 7 purged activated carbon. The carbon type used for scrubbing is important; Barnebey & Sutcliffe Corp. (formerly Barnebey-Cheney) type GI ([www.bscarbon.com](http://www.bscarbon.com), Columbus, Ohio) has been shown to work well. As an alternative to using an activated carbon scrubber, a sodium carbonate coated denuder, such as the Sunset Laboratory Model #DN-315 stainless steel concentric denuder, can be used. Alternatively, a cartridge of soda lime attached to the outlet of the zero air system will last for extended periods (potentially over one year) and maintain SO<sub>2</sub> at less than 0.05 ppb.

*Note: For zero-air sources based on removing SO<sub>2</sub> by means of soda lime, charcoal, or a denuder as described above, the inlet air must be outside ambient air rather than instrument shelter air. Contaminant levels inside the shelter may greatly exceed those in outside air. Also to the extent possible, the components of the zero-air system should be free of materials that might outgas hydrocarbons.*

## **3.6 Reagents and Standards**

Routine operation of high sensitivity SO<sub>2</sub> 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.

### **3.6.1 Calibration Standards**

The primary SO<sub>2</sub> standards used must be certified, commercially-prepared compressed gas standards, with a certified accuracy of no worse than  $\pm 2$  percent. SO<sub>2</sub> gas standards of 10 to 20 ppm are conveniently diluted with a MFC calibrator down to working concentrations of 20 ppb or less. The commercially-prepared standard may contain only SO<sub>2</sub> in an inert gas (e.g., N<sub>2</sub>), or may be a mixed component standard that also contains known concentrations of other precursor ambient gases (e.g., CO, NO). The potential for NO interference must be kept in mind if a standard containing both SO<sub>2</sub> and NO is used for SO<sub>2</sub> calibration, as noted in Sections 3.4.1 and 3.5.2.1. It is critical when placing an SO<sub>2</sub> gas standard into service that the cylinder regulator be fully purged to avoid the effect of trace moisture on the delivered SO<sub>2</sub> concentration. Evacuating the regulator by means of a vacuum line attached to the regulator outlet, before purging for a few minutes with the cylinder gas, is an effective procedure to dry and condition the regulator.

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.

### **3.6.2 Zero Air**

Zero air used as dilution gas for calibration purposes should have an SO<sub>2</sub> concentration below the LDL of the SO<sub>2</sub> analyzer. Multiple zero air sources should be checked, and soda lime, charcoal, or sodium carbonate scrubbers may be necessary to achieve adequate zero air quality, as noted in Section 3.5.2.2. A canister of soda lime followed by a particle filter on the outlet of the zero air source will remove SO<sub>2</sub> for extended periods. Breakthrough can be tested by temporarily adding a carbonate denuder and observing zero gas readings.

## **3.7 Quality Control**

### **3.7.1 Site Visit Checklists and Remote Diagnostic Checks**

To determine whether the SO<sub>2</sub> 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 (see Section 6).

### **3.7.2 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 SO<sub>2</sub> analyzers provide inherently linear response over their entire operating range; therefore, four points should be sufficient. Multipoint calibrations must be done prior to the precursor SO<sub>2</sub> analyzer being put into service and at least every six months 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 samples (Section 5.4.1) differ from the certified standard values by  $\pm 15$  percent.

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

### **3.7.3 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 SO<sub>2</sub> 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. They are conducted by challenging the analyzer with zero air and a test atmosphere containing SO<sub>2</sub> 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. The span check should not exceed  $\pm 15$  percent and the zero drift should not exceed  $\pm 0.5$  percent of full scale. 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 in Section 3.7.2.

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.
- New generation DASs can record calibration data and allow remote users to track daily Level I check and zero drift. This is important for data validation, verification and troubleshooting.

### **3.7.4 Precision Checks**

At least once every two weeks a precision check should be conducted by challenging the SO<sub>2</sub> analyzer with a known low SO<sub>2</sub> concentration to assess the performance of the analyzer. The precision checks should be conducted by challenging the SO<sub>2</sub> analyzer with a standard gas of known concentration between 10 and 50 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, according to the equations provided in section 3.3.1.1. 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.

### **3.8 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. Despite active preventive maintenance, occasional problems may arise with the precursor SO<sub>2</sub> analyzers. This section briefly describes several key items that might be included in the preventive maintenance program established for precursor SO<sub>2</sub> 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 this TAD.

### **3.8.1 Preventive Maintenance**

Routine preventive maintenance procedures should be in place to prevent down-time and data loss. 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. SO<sub>2</sub> 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. Sampling lines should be replaced 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.

Table 3-4 illustrates items that monitoring agencies should include in their preventive maintenance program for high sensitivity SO<sub>2</sub> monitoring.

**Table 3-4. Example of a preventive maintenance schedule for high sensitivity SO<sub>2</sub> analyzers.**

<b>Item</b>	<b>Schedule</b>
Replace particle filter	Weekly
Replace internal span permeation tube (if applicable)	Annually
Perform pneumatic system leak check	At least quarterly
Inspect internal, external tubing; replace if necessary	At least quarterly
Rebuild or replace pump	Annually
Replace UV lamp	As needed
Clean optic bench	As needed
Replace PMT	As needed

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. The pump should be rebuilt or replaced when it is unable to maintain a vacuum of at least 25 inches of Hg.
- 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.

### **3.8.2 Troubleshooting**

High sensitivity SO<sub>2</sub> analyzers are subject to many factors that can cause inaccurate measurements or down-time. Table 3-5 summarizes common problems seen with high sensitivity SO<sub>2</sub> analyzers, their possible causes, and possible solutions. More specific information can be found in the manufacturer's operations manual.

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 SO<sub>2</sub> 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 3-5. Instrument troubleshooting for precursor SO<sub>2</sub> analyzers.**

Problem	Possible Cause	Possible Solution
Noisy output	Defective DC power supply	Replace power supply
	Dirty optics	Clean optics bench
	PMT failure	Replace PMT
High positive zero drift	Defective bandpass filter	Replace filter
	PMT failure	Replace PMT
No response to span gas	UV source is defective	Replace UV lamp
	UV power supply defective	Replace UV power supply
	PMT failure	Replace PMT
Zero output at ambient levels	Pump failure	Check pump
	UV lamp failure	Replace UV lamp
	UV power supply defective	Replace power supply
	PMT failure	Replace PMT
No flow through analyzer	Pump failure	Replace/ rebuild pump head

### 3.9 References

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## 4.0 HIGH SENSITIVITY TOTAL REACTIVE NITROGEN OXIDES MEASUREMENTS

### 4.1 Introduction

Measurement of ambient nitrogen oxides differs from measurement of CO or SO<sub>2</sub> 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<sub>2</sub>), which collectively are termed NO<sub>x</sub> (i.e., NO<sub>x</sub> = NO + NO<sub>2</sub>). These primary emitted species are converted by atmospheric processes to numerous other inorganic and organic nitrogen oxides, which collectively are called NO<sub>z</sub>, and the total of all reactive gaseous nitrogen species present in ambient air is called NO<sub>y</sub> (i.e., NO<sub>y</sub> = NO<sub>x</sub> + NO<sub>z</sub>).

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<sub>y</sub>). Measuring NO<sub>y</sub> is a valuable adjunct to NO and NO<sub>x</sub> monitoring because the individual species comprising NO<sub>z</sub> 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<sub>y</sub> concentrations is useful in establishing nitrogen oxide emission patterns and temporal trends, and in assessing the photochemical age and reactivity of air masses.<sup>(e.g., 1-4)</sup> NO<sub>y</sub> 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.<sup>[e.g., 1, 5, 6]</sup>

#### **4.1.1 Properties of NO<sub>y</sub>**

NO<sub>y</sub> includes all of the nitrogen oxide compounds that react or are formed in the lower atmosphere and that contribute to the photochemical formation of O<sub>3</sub> and the transport and ultimate fate of nitrogen oxides.<sup>[1-4]</sup> NO<sub>y</sub> compounds include NO<sub>x</sub> (NO + NO<sub>2</sub>) and NO<sub>z</sub>, which include nitrogen acids [nitric acid (HNO<sub>3</sub>) and nitrous acid (HONO)], organic nitrates

[e.g., peroxy acetyl nitrate (PAN), methyl peroxy acetyl nitrate (MPAN), and peroxy propionyl nitrate (PPN)], other organic nitrogen oxides, particulate nitrates, nitrate radical (NO<sub>3</sub>), nitrogen trioxide (N<sub>2</sub>O<sub>3</sub>), nitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) and halogen-nitrogen species (e.g., ClONO<sub>2</sub> and BrONO<sub>2</sub>). In typical urban environments, the principal NO<sub>y</sub> compounds include NO, NO<sub>2</sub>, HNO<sub>3</sub>, 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<sub>y</sub> differ widely in their physical properties and chemical reactivity. For example, some species, such as NO<sub>2</sub> and HONO, are readily photolyzed, whereas others, such as PAN, decompose rapidly at moderate temperatures. NO and NO<sub>2</sub> are chemically reactive but have relatively low solubility in water, whereas the key product species HNO<sub>3</sub> is highly soluble and relatively unreactive. Consequently, physical removal of HNO<sub>3</sub> from the atmosphere is a key removal process for NO<sub>y</sub>. Organic nitrogen oxides can vary widely in volatility and stability, and HNO<sub>3</sub> is known to be highly “sticky”; that is, adsorptive on surfaces. In addition, particulate ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) is volatile under certain ambient conditions, and can decompose to release HNO<sub>3</sub> and ammonia (NH<sub>3</sub>) into the gas phase. These factors make accurate sampling and measurement of atmospheric NO<sub>y</sub> much more challenging than determination of CO or SO<sub>2</sub>. A discussion of sampling and measurement issues that must be addressed in order to make more useful measurements of NO<sub>y</sub> is provided in Section 4.3.2.

#### **4.1.2 Sources of NO<sub>y</sub>**

Nitrogen oxides are emitted to the atmosphere principally as NO and NO<sub>2</sub>, 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<sub>2</sub> are oxidized by photochemical processes to a wide variety of products. Oxidation of NO to NO<sub>2</sub> 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<sub>3</sub>) and free radical species. When NO<sub>x</sub> 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<sub>z</sub> (and, in turn, NO<sub>y</sub>). The extent of conversion of NO<sub>x</sub> species to NO<sub>y</sub> 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.<sup>(2-4)</sup>

#### **4.1.3 Historical Overview of NO<sub>y</sub> Measurement Method**

Ambient NO<sub>y</sub> must be measured in a practical, standardized manner, as it is not possible to measure individually all the compounds that comprise NO<sub>y</sub>. Instruments used to measure NO<sub>y</sub> 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<sub>x</sub> 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<sub>2</sub> is listed in 40 CFR Part 53.<sup>[7]</sup> Instruments designated as Reference methods for NO<sub>2</sub> are also approved for measuring NO. It must be noted that the designated instruments may not truly measure NO<sub>x</sub> (i.e., NO plus NO<sub>2</sub>) in urban areas where photochemical processes have occurred, but NO<sub>x</sub> plus some poorly defined fraction of NO<sub>z</sub>.

For NO<sub>y</sub>, a standard reference method has not yet been designated; however, EPA has suggested a modification of the NO<sub>x</sub> 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<sub>3</sub>. The original ambient NO is measured by bypassing the converter. This procedure is similar to the current methodology used to monitor NO<sub>x</sub> except that, in the NO<sub>y</sub> methodology, the converter has been moved to the sample inlet to

avoid line losses of adsorbent NO<sub>y</sub> species like HNO<sub>3</sub>, and additional calibration procedures recommended for adequate measurement of the various NO<sub>z</sub> species.

#### 4.2 Summary of NO<sub>y</sub> Measurement by Chemiluminescence Method

NO<sub>y</sub> concentrations are determined by photometrically measuring the light intensity at wavelengths greater than 600 nm from the chemiluminescent reaction of NO with O<sub>3</sub>.<sup>(8)</sup> This principle is identical to that on which the measurement of NO and NO<sub>x</sub> is based, which is designated by EPA as the Reference method for determining NO<sub>2</sub> in ambient air.<sup>[9]</sup>

The chemiluminescence approach is based on the gas-phase reaction of NO and O<sub>3</sub>, 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. Specifically,



where:

NO<sub>2</sub>\* = an electronically excited NO<sub>2</sub> molecule

hν = E, the emitted photon energy (where h is Planck's constant, and ν is the frequency of the emitted photon)

M = inert molecules, predominantly N<sub>2</sub> and O<sub>2</sub> in air.

The reaction of NO with O<sub>3</sub> produces predominantly ground state NO<sub>2</sub> molecules, as in reaction (4-1a), but in a small fraction of the reactions, the NO<sub>2</sub> produced is in an excited state,

as in reaction (4-1b). The resulting excited NO<sub>2</sub> molecules lose their excess energy either through collisions with other inert molecules (M), as in reaction (4-2a), or by releasing a photon of light, as in reaction (4-2b). Monitoring instruments based on chemiluminescence are designed to enhance the emission and detection of the light produced in reaction (4-2b). For example, to minimize the unproductive pathway in reaction (4-2a), the concentration of other molecules (M) is kept low by carrying out the NO/O<sub>3</sub> reaction at low pressure.

To determine the concentration of NO by chemiluminescence, the sample gas flow is mixed with O<sub>3</sub> in a reaction chamber causing reactions (4-1) and (4-2) to occur. The chemiluminescence that results from the reaction is monitored by an optically filtered high-sensitivity photomultiplier, that responds to NO<sub>2</sub> chemiluminescence emission at wavelengths longer than 600 nm. The electronic signal produced in the photomultiplier is proportional to the NO concentration in the sample air.

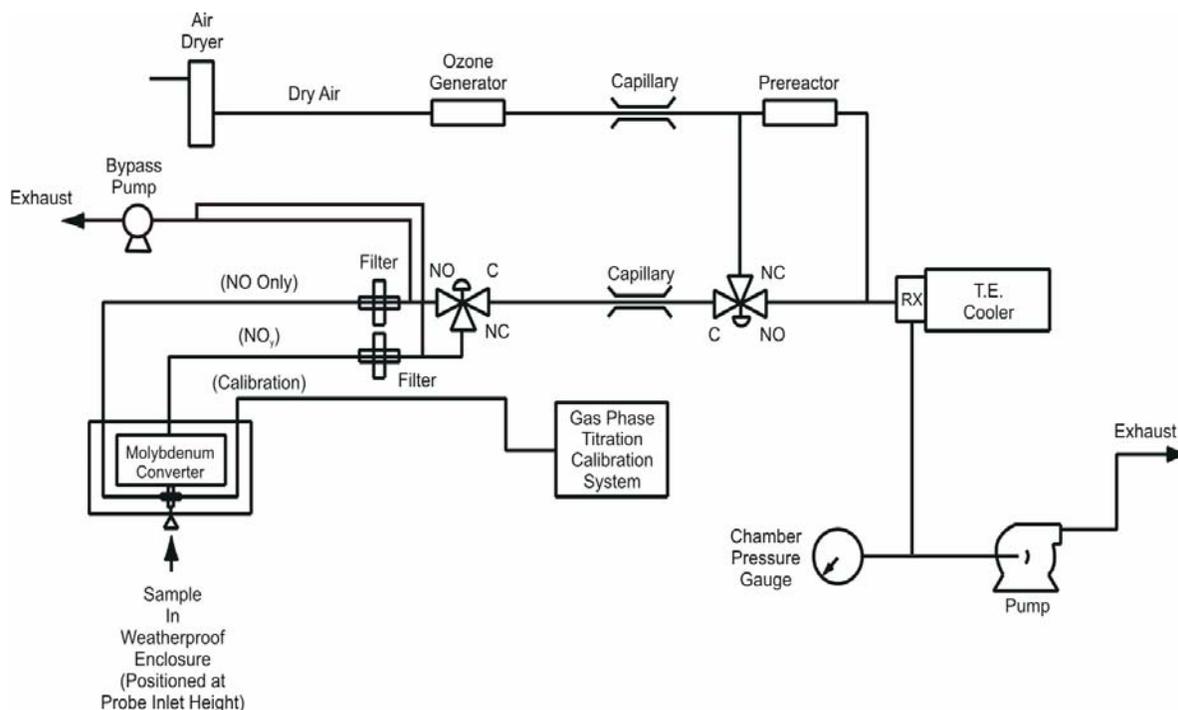
To measure NO<sub>y</sub>, sample air is passed through a chemical reductant (molybdenum) converter placed at the extreme sample air inlet point, and the nitrogen oxide compounds present are reduced to NO.<sup>[10]</sup> The NO resulting from the reduction of these nitrogen oxide compounds, plus any native NO, is reacted with O<sub>3</sub>, and the resulting chemiluminescent light is measured as an indication of the total NO<sub>y</sub> 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<sub>3</sub>, and the resulting chemiluminescent light intensity is proportional to the NO concentration.

The primary differences between this method, as implemented for NO<sub>y</sub> monitoring and as implemented for conventional NO<sub>x</sub> 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<sub>y</sub> species to NO immediately upon entry of sample air into the sampling system. This approach minimizes loss of NO<sub>y</sub> constituents such as HNO<sub>3</sub> in sampling, and help to assure complete capture of the total NO<sub>y</sub>. Calibration procedures

for NO<sub>y</sub> monitoring go beyond those used for NO<sub>x</sub> monitoring, in that more stringent tests of converter efficiency are required (see Section 4.4.2 for a discussion of converter efficiency).

Figure 4-1 shows a schematic illustration of a typical NO<sub>y</sub> 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<sub>3</sub> and the resultant chemiluminescence is measured, or the sample is directed to a prereactor vessel where it is mixed with O<sub>3</sub> before passage into the reaction chamber. The use of the prereactor allows the NO/O<sub>3</sub> 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<sub>3</sub> reaction (e.g., reactions of hydrocarbons and O<sub>3</sub>). The PMT is housed in a thermoelectric (TE) cooler to minimize thermal noise.

As shown in Figure 4-1, separate sample transfer lines downstream of the sample inlet point are used for the NO<sub>y</sub> 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<sub>y</sub> measurement mode of the NO<sub>y</sub> instrument, since all NO<sub>y</sub> 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<sub>3</sub>. These two species can react [by reactions 4-1a and b] to decrease the NO reaching the chemiluminescence detector, resulting in an under-estimation of the ambient NO level. This



**Figure 4-1. General schematic of a typical chemiluminescence NO<sub>y</sub> instrument.**

effect can be substantial: assuming 100 ppbv of O<sub>3</sub>, 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<sub>y</sub> 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<sub>y</sub> 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<sub>y</sub> flow paths by reducing the gas pressure.

### **4.3 Recommendations for NCore**

Since the high sensitivity analyzers deployed at NCore sites are intended to monitor low ambient NO<sub>y</sub> concentrations, it is important that they meet a variety of performance criteria as described below. Many of these performance criteria for high sensitivity NO<sub>y</sub> analyzers are more stringent than those for routine NO<sub>x</sub> analyzers; consequently, there are a number of recommended features that the NO<sub>y</sub> 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<sub>y</sub> 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.

#### **4.3.1 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.<sup>[11]</sup> 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<sub>y</sub> 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<sub>y</sub> than for NO.

#### 4.3.1.1 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 (see Sections 4.7.4 and 5.3.3). Calculations to assess precision are given below and should be used to assess precision on a quarterly basis. It is recommended that high sensitivity NO<sub>y</sub> 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. The resulting percent differences are then used as described below. For each single point precision check, calculate the percent difference,  $d_i$ , as follows:

##### Equation 1

$$d_i = \frac{\text{reported} - \text{challenge}}{\text{challenge}} \cdot 100$$

where *reported* is the concentration indicated by the high sensitivity NO<sub>y</sub> analyzer and *challenge* is the concentration of the standard used in the precision check. The precision estimator is then calculated as the coefficient of variation (CV) upper bound, using Equation 2 as follows:

##### Equation 2

$$CV = \sqrt{\frac{n \cdot \sum_{i=1}^n d_i^2 - \left(\sum_{i=1}^n d_i\right)^2}{n(n-1)}} \cdot \sqrt{\frac{n-1}{X^2_{0.1, n-1}}}$$

where  $n$  is the number of data points (i.e., precision check comparisons), the  $d_i$  values are the resulting percent differences, and  $X_{0.1, n-1}$  is the 10th percentile of a chi-squared distribution with  $n-1$  degrees of freedom.

#### 4.3.1.2 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 (see Section 4.3.1.1 above). The bias estimator is an upper bound on the mean absolute value of the percent differences as described in Equation 3 as follows:

Equation 3

$$|bias| = AB + t_{0.95, n-1} \cdot \frac{AS}{\sqrt{n}}$$

where  $n$  is the number of challenge comparisons being aggregated;  $t_{0.95, n-1}$  is the 95th quantile of a t-distribution with  $n-1$  degrees of freedom; the quantity  $AB$  is the mean of the absolute values of the individual  $d_i$ 's and is calculated using Equation 4 as follows:

Equation 4

$$AB = \frac{1}{n} \cdot \sum_{i=1}^n |d_i|$$

and the quantity  $AS$  is the standard deviation of the absolute value of the  $d_i$ 's and is calculated using Equation 5 as follows:

Equation 5

$$AS = \sqrt{\frac{n \cdot \sum_{i=1}^n |d_i|^2 - \left( \sum_{i=1}^n |d_i| \right)^2}{n(n-1)}}$$

Since the bias statistic as calculated in Equation 3 uses absolute values, it does not have a direction or sign (negative or positive) associated with it. The sign of the calculated bias is to be determined by rank ordering the percent differences of the QC check samples from a given analyzer for a particular assessment interval. Calculate the 25<sup>th</sup> and 75<sup>th</sup> percentiles of the percent differences for each analyzer. The absolute bias upper bound should be flagged as positive if both the 25<sup>th</sup> and 75<sup>th</sup> percentiles are positive, and as negative if both these percentiles are negative. The absolute bias upper bound would not be flagged if the 25<sup>th</sup> and 75<sup>th</sup> percentiles are of different signs. It is recommended that high sensitivity NO<sub>y</sub> analyzers have an upper bound for the average bias of  $\pm 15$  percent or less.

#### **4.3.1.3 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<sub>y</sub> 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).

#### **4.3.1.4 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<sub>y</sub> concentrations in NCore, EPA requires a minimum data completeness of 75 percent. In practice typical completeness values can often approach 90 to 95 percent.

#### **4.3.1.5 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, this TAD describes the recommended characteristics of high sensitivity NO<sub>y</sub> analyzers and the procedures for their installation and use. For example, all monitoring agencies should purchase instruments that minimally have the features described in Section 4.3.2, and should adhere to the sampling requirements described in Section 4.3.3.

#### **4.3.1.6 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. 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.

To perform the MDL test, run zero air through the analyzer and establish an acceptable zero; dilute pollutant gas to the targeted concentration (one to five times the estimated MDL) and collect 20 to 25 one minute observations. Repeat this seven times over the course of 5 to 14 days. Average the concentration from the 20-25 readings; calculate the standard deviation (S) of the average readings and compute the MDL. The MDL is then calculated as the standard deviation of the response values times the Student's t-value for the number of test measurements (40 CFR Part 136, Appendix B). The MDL for high sensitivity NO<sub>y</sub> analyzers should 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.

#### **4.3.1.7 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<sub>y</sub> analyzers should be 0.10 ppb or lower, over an averaging time of no more than 5 minutes.

#### **4.3.1.8 Linear Range**

The linear range of each high sensitivity NO<sub>y</sub> 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<sub>y</sub> 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<sub>y</sub> concentrations.

#### **4.3.1.9 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<sub>y</sub> analyzer into service. Such NO<sub>y</sub> analyzers should have 12- and 24-hour zero drift less than 0.10 ppb, and should have a span drift of less than  $\pm 1$  percent of the full scale measurement range of the analyzer per 24 hours. Zero tests should be performed with the internal zero prereactor engaged.

#### **4.3.2 Recommended Features for High Sensitivity Ambient NO<sub>y</sub> Measurements**

Continuous chemiluminescence NO<sub>y</sub> 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 chemiluminescence analyzer is described in Section 4.2, and examples of specific instruments are provided below in Section 4.3.3. In general, each of the analyzers contains the following systems:

- *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.
- *Analytical System*: This portion of the analyzer consists of the reaction chamber, photomultiplier, and bandpass filters.
- *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<sub>y</sub> analyzers to allow them to measure NO<sub>y</sub> at levels well below 1 ppb.

- Locate the sample inlet at 10 meters to avoid the physical removal of HNO<sub>3</sub>. 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<sub>y</sub> measurements, and provides a practical solution to ward off larger insects.
- Locate the site in an area that is not obstructed by nearby trees and obstacles (see Section 4.3.4.1)
- Ensure that the sample residence time in the NO sample transfer line is less than 2 seconds to address the O<sub>3</sub>/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.
- 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 (H<sub>2</sub>), and provides no clear advantage in determining total NO<sub>y</sub> in urban and suburban air.<sup>[10]</sup>
- 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<sub>y</sub> 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<sub>y</sub> species are not converted. It is equally important that the converter not be operated below 350 °C to ensure optimal conversion of NO<sub>y</sub> species.

- Automatic over-range capabilities are used to track the rapid changes that may occur in ambient NO<sub>y</sub> 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<sub>y</sub> analyzers deployed in NCore include these additional siting and operational features in order to ensure useful measurements.

### **4.3.3 Commercial Chemiluminescent NO<sub>y</sub> Monitors**

Vendors of commercial NO<sub>y</sub> analyzers typically supply instruments for both routine ambient and high sensitivity monitoring. In this case, only analyzers with an LDL of 0.1 ppb or less for NO are considered to have high sensitivity. (Note that the LDL for NO may be lower than that for NO<sub>y</sub>.) Analyzers from Thermo Electron Corporation, Teledyne Advanced Pollution Instrumentation (API), Ecotech, and ECO PHYSICS are described here as examples (no endorsement should be inferred), though not all have both the requisite detection limit and NO<sub>y</sub> measurement capabilities. A summary of each monitor follows. The descriptions provided for these instruments, and the performance claimed for them, are based solely on information provided by the respective vendors, and confirmation by EPA should not be inferred.

#### ***4.3.3.1 Thermo Electron Corporation Model 42C-Y***

The Model 42C-Y NO<sub>y</sub> analyzer<sup>[12, 13]</sup> shown in Figure 4-2 is based on the Model 42C NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer, and employs an external molybdenum converter that is typically operated at 325 °C. The Model 42C-Y NO<sub>y</sub> analyzer has a lower detection limit of 0.05 ppb, and

has adjustable range settings from 0 to 5 ppb up to 0 to 200 ppb. The recommended operating temperature range is between 15 °C and 35 °C. The Model 42C-Y NO<sub>y</sub> analyzer uses increased pumping speed to minimize residence time and enhance chemiluminescent detection, and has increased ozone production capabilities.



**Figure 4-2. Thermo Electron Model 42C-Y NO<sub>y</sub> analyzer (courtesy Thermo Electron).**

Table 4-1 shows the vendor specifications of the Model 42C-Y NO<sub>y</sub> analyzer.

**Table 4-1. Thermo Electron Model 42C-Y NO<sub>y</sub> Analyzer Specifications.**

Performance Parameters	Model 42C-Y NO <sub>y</sub> Analyzer Specifications
Precision	Not available
Bias	Not available
Method Detection Limit	Not available
Lower Detectable Limit	50 ppt (0.05 ppb) (120 second average time)
Linearity	± 1% of full scale
Zero Drift	Negligible (24-hour)
Span Drift	± 1% of full scale (24-hour)

#### 4.3.3.2 API Model 200AU with Model 501Y Converter

The API Model 200AU high sensitivity analyzer<sup>[14-16]</sup> shown in Figure 4-3 is based on the Model 200A NO/NO<sub>2</sub>/NO<sub>x</sub> analyzer, and uses the optional Model 501Y molybdenum NO<sub>y</sub> converter that places the converter at the sample inlet point.



**Figure 4-3. API Model 200AU/501Y NO<sub>y</sub> analyzer (courtesy Teledyne API).**

The Model 200AU has operating ranges from 0 to 5 ppb up to 0 to 2,000 ppb (2 ppm), with a lower detectable limit of 0.05 ppb, and may be safely operated in the temperature range of 5 °C to 35 °C. Table 4-2 shows the vendor specifications for the Model 200AU/501 NO<sub>y</sub> Analyzer.

**Table 4-2. API Model 200AU/501 NO<sub>y</sub> Analyzer Specifications.**

Performance Parameters	API Model 200AU/501NO <sub>y</sub> Analyzer Specifications
Precision	0.5% of reading
Bias	Not available
Method Detection Limit	Not available
Lower Detectable Limit	50 ppt (0.05 ppb); 120 second averaging time
Linearity	1% full scale
Zero Drift	<0.1 ppb/24 hours, <0.2 ppb/7 days
Span Drift	<0.5% full scale/7 days or 50 ppt/7 days, whichever is greater

#### **4.3.3.3 Ecotech Model EC9841**

High sensitivity NO<sub>y</sub> capabilities are only partly established in the Ecotech line of analyzers. Although an Ecotech high sensitivity nitrogen oxides analyzer exists, it is not yet available in an NO<sub>y</sub> configuration.

The high sensitivity Ecotech analyzer is the Model EC9841T Trace Nitrogen Oxides Analyzer, which has a LDL of 0.05 ppb, and a maximum full scale reading of 200 ppb. However, at this time the Model EC9841T is not available in a configuration consistent with the NO<sub>y</sub> requirements illustrated in Figure 4-1. On the other hand, Ecotech's Model EC9841-NO<sub>y</sub> does incorporate the needed NO<sub>y</sub> configuration, but has an LDL of 0.5 ppb. On the assumption that Ecotech may later adapt the high sensitivity EC9841T analyzer for NO<sub>y</sub> detection, the capabilities of both the EC9841-T and the EC9841-NO<sub>y</sub> are summarized below.

The EC9841-NO<sub>y</sub> analyzer<sup>[17, 18]</sup> shown in Figure 4-4 has a lower detection limit of 500 ppt (0.5 ppb). It uses a programmable temperature-controlled molybdenum (Mo) converter that is typically operated at 350 °C and is mounted directly onto the system's sample manifold (external to the analyzer). The sample manifold and inlet lines are heated to ensure there is no condensation as the sample gas is transported from the converter to the analyzer. The EC9841-NO<sub>y</sub> analyzer also uses a high-vacuum pump to minimize residence time, and to decrease reaction cell pressure and thus increase the sensitivity of the chemiluminescent detection. Interferences are minimized in the EC9841-NO<sub>y</sub> through the use in the converter of Mo chips that have a greater gas contact area than solid Mo granules to provide greater converter efficiency with low flow restriction at atmospheric pressure. Under typical operating conditions, the converter has less than a 5 percent conversion efficiency for ammonia, cyanides, and amines, thereby limiting interference from these non-NO<sub>y</sub> species. The analyzer has automatically selected range settings up to 20 ppm full scale, and has a recommended operating temperature range of 20 °C to 30 °C, but may be operated between 15 °C and 35 °C. The Model EC9841T differs from the EC9841-NO<sub>y</sub> primarily in its higher sensitivity and lower zero and span drift. Table 4-3 shows the vendor specifications of both analyzers.



Figure 4-4. Ecotech EC9841-NO<sub>y</sub> analyzer (courtesy of Ecotech).

Table 4-3. Ecotech EC9841-NO<sub>y</sub> Analyzer Specifications.

Performance Parameters	EC9841-NO <sub>y</sub>	EC9841T
Precision	± 2% of reading	± 2% of reading
Bias	Not available	Not available
Method Detection Limit	Not available	Not available
Lower Detectable Limit	500 ppt (0.5 ppb) (with Kalman or 300 sec filter active)	50 ppt (0.05 ppb) (with Kalman or 300 sec filter active)
Linearity	Not available	Not available
Zero Drift	Temperature dependence, 0.1% per degree C changes. 24 hours; less than 1 ppb	Temperature dependence, 0.1% per degree C changes. 24 hours; less than 50 ppt (0.05 ppb)
Span Drift	Temperature dependence, 0.1 % per degree C changes. 24 hours less than 1.0% of reading 30 days less than 1.0% of reading	Temperature dependence, 0.05 % per degree C changes. 24 hours less than 0.5% of reading 30 days less than 1.0% of reading

**4.3.3.4 ECO PHYSICS Models CLD 88 p or CLD 780 TR with CON 765 NO<sub>y</sub> Converter**

ECO PHYSICS produces two different chemiluminescent analyzers with the requisite high sensitivity for trace level measurements.<sup>[19]</sup> The ECO PHYSICS Model CLD 88 p analyzer has a lower detection limit of 50 ppt (0.05 ppb), and the CLD 780 TR is a research grade NO instrument capable of a lower detection limit of 10 ppt (0.01 ppb) with a 60 second integration

time. The CLD 88 p has four selectable operating ranges from 5 to 5,000 ppb (5 ppm) and may be safely operated in the temperature range of 5 °C to 40 °C. The CLD 780 TR has five selectable operating ranges from 5 to 500 ppb, and may be safely operated in the temperature range of 5 °C to 50 °C. However, at this time these analyzers are not available in a configuration consistent with the NO<sub>y</sub> requirements illustrated in Figure 4-1. On the assumption that the manufacturer may adapt one or both analyzers to the required configuration, the capabilities of both the CLD 88 p and the CLD 780 TR are summarized below.

The limitation of the ECO PHYSICS analyzers lies in the ECO PHYSICS CON 765 NO<sub>y</sub> converter, which is designed to be used with either of the CLD 88 p or CLD 780 TR NO analyzers.<sup>[19]</sup> The CON 765 reduces NO<sub>y</sub> species to NO by chemical reaction with CO on a gold surface maintained at 315 °C. This converter has a reported NO<sub>y</sub> conversion efficiency that exceeds 95%, and due to the nature of the reduction process the presence of water vapor in the sample air is said to keep interference from NH<sub>3</sub> and HCN to a negligible level. Despite these attractive features, the CON 765 is not the type of NO<sub>y</sub> converter recommended for use in precursor gas monitoring in NCore. The need for a constant supply of highly toxic high purity CO is a serious disadvantage of this converter, especially since the gold converter offers essentially the same NO<sub>y</sub> conversion efficiency as the molybdenum converter recommended for use in NCore.

Figure 4-5 shows the Model CLD 88 p with the CON 765 converter. Table 4-4 shows the information available on the specifications of both the CLD 88 p and CLD 780 TR NO analyzers.



**Figure 4-5. ECO PHYSICS Model CLD 88 p and CON 765 NO<sub>y</sub> Converter**

**Table 4-4. ECO PHYSICS CLD 88 p and CLD 780 TR Analyzer Specifications.**

Performance Parameters	CLD 88 p	CLD 780 TR
Precision	Not available	Not available
Bias	Not available	Not available
Method Detection Limit	Not available	Not available
Lower Detectable Limit	50 ppt (0.05 ppb)	10 ppt (0.01 ppb) w. 60 sec response
Linearity	1% of full scale	1% of full scale
Zero Drift	0.05% of full scale (24 hours)	None (i.e., zero)
Span Drift	1% of full scale (24 hours)	Not available

#### **4.3.4 Sampling Requirements**

Proper siting of the sampling equipment and sampling probes is necessary to ensure that the gas analyzers are obtaining representative samples of the ambient air. Likewise, proper environmental control of the analyzer and proper sampling are critical to ensuring that the analyzers are operating correctly and that the NO<sub>y</sub> measurements are comparable to NO<sub>y</sub> measurements recorded at other sites.

#### **4.3.4.1 Analyzer Siting**

Analyzer siting should follow the criteria in 40 CFR 58, Appendix E. The installation of the precursor NO<sub>y</sub> analyzer should allow for the sample probe inlet to be approximately 10 meters above ground level with the inlet facing the prevailing wind direction. The probe should be positioned with at least 270 degrees of unrestricted airflow including the predominant wind direction. The probe should be separated from the drip line of nearby trees or structures by at least 20 meters, and should be positioned at least twice as far from of nearby obstacles as the height of the obstacles.

#### **4.3.4.2 Instrument Shelter**

To help ensure proper performance, the precursor analyzers and supporting equipment should be installed and operated in a temperature controlled environment. An insulated instrument shelter should be used to protect the analyzer from precipitation and adverse weather conditions, maintain operating temperature within the analyzer's temperature range requirements, and provide security and electrical power. The environmental control of the shelter should be sufficient to minimize fluctuations in shelter temperature. The recommended shelter temperature range is 20 °C to 30 °C, and daily changes in temperature should not exceed 5 °C over a 24-hour period. Condensation of moisture must be avoided and it may be necessary to impose seasonal temperature ranges to assure remaining above the ambient dewpoint.

#### **4.3.4.3 Sampling Issues**

Studies of NO<sub>y</sub> sampling inlet issues have focused primarily on airborne NO<sub>y</sub> measurements, where it is not feasible to locate the converter directly at the sample inlet point.<sup>[20-22]</sup> The purpose of these studies was to identify the material that causes the least adsorptive loss of NO<sub>y</sub> components during sampling. Nitric acid, as both a key component of NO<sub>y</sub> and a strongly adsorbed species, has generally been the target compound in these studies. Adsorption of NO and NO<sub>2</sub> is of much less concern. Numerous tubing materials, including TFE,

PFA, and FEP Teflon®, have been investigated for use in sampling inlets.<sup>[20]</sup> In testing these materials for HNO<sub>3</sub> adsorption, less than 5 percent of the HNO<sub>3</sub> 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<sub>3</sub> transmission through aluminum, steel, and nylon tubes did not increase in over 1 hour of HNO<sub>3</sub> exposure. HNO<sub>3</sub> loss on aluminum and steel tubes heated to 50 °C was irreversible. However, HNO<sub>3</sub> adsorption on glass decreased over time, so that over a period of several hours of continuous HNO<sub>3</sub> exposure, glass will be passivated to HNO<sub>3</sub> 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<sub>3</sub>. PFA Teflon® causes the least adsorption of HNO<sub>3</sub>, and so is recommended for sampling inlets.

Although PFA Teflon® is far superior to other materials in minimizing HNO<sub>3</sub> adsorption, it has the disadvantage that any previously adsorbed HNO<sub>3</sub> can be released back into the air stream by changes in temperature and/or relative humidity.<sup>[20]</sup> Thus, the best approach to NO<sub>y</sub> 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 4-1, 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.

#### **4.4 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<sub>y</sub> in ambient air.

#### **4.4.1 Interferences**

Interferences in NO<sub>y</sub> measurements are of two types. One potential interference is the presence of nitrogen-containing species in ambient air that are not components of NO<sub>y</sub>, but that can potentially be converted to NO by the heated converters used to achieve NO<sub>y</sub> measurement. The primary examples of such an interferent are ammonia (NH<sub>3</sub>), and particulate ammonium (NH<sub>4</sub><sup>+</sup>), 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 Section 4.4.2.

The other type of potential interferent consists of non-NO<sub>y</sub> species that can react with O<sub>3</sub> 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<sub>y</sub> monitoring is minimized by the use of a prereactor vessel in the NO<sub>y</sub> 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<sub>3</sub> reaction occurs rapidly and the resulting NO<sub>2</sub> chemiluminescent emission occurs entirely within the prereactor, where it cannot be detected by the photomultiplier. However, the O<sub>3</sub> reactions with unsaturated hydrocarbons occur more slowly, so light emission from these reactions is not completed within the prereactor volume. As the sample/O<sub>3</sub> 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<sub>3</sub> reaction. Commercial high sensitivity NO<sub>y</sub> 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.

## **4.4.2 Converter Efficiency**

### **4.4.2.1 Overview**

The heated molybdenum converters used in commercial high sensitivity NO<sub>y</sub> 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<sub>y</sub> total.<sup>[e.g., 10, 23]</sup> These studies indicate that the molybdenum converters can provide accurate measurements of NO<sub>y</sub>. The goal with such converters is to achieve 100 percent conversion efficiency of NO<sub>y</sub> species to NO, while approaching zero percent conversion of other non-NO<sub>y</sub> nitrogen-containing species. Note that, as used in commercial high sensitivity NO<sub>y</sub> monitors, the molybdenum converters are designed to convert particulate nitrate compounds, as well as the numerous gaseous components of NO<sub>y</sub>, to NO for detection.<sup>[10]</sup>

As noted in Section 4.4.1, non-NO<sub>y</sub> 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 conversion or less) by maintaining the converter temperature at 350 °C. At sub-ppb NO<sub>y</sub> 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<sub>y</sub> readings, even though the conversion efficiency for ammonia is much less than that for NO<sub>2</sub> or the various NO<sub>z</sub> compounds. In general, the efficiency of a converter system at sub-ppb levels may vary depending on the mix of NO<sub>y</sub> 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.

#### **4.4.2.2 Challenge Species for Converter Efficiency Checks**

Studies of converter efficiencies have established that among NO<sub>y</sub> species, NO<sub>2</sub> is relatively easily reduced to NO. As a result calibration with NO and NO<sub>2</sub>, as described in Section 4.7.2, is a necessary but not entirely sufficient approach to characterizing an NO<sub>y</sub> monitoring system. A more stringent approach is to also calibrate with an NO<sub>y</sub> 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<sub>y</sub> 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<sub>y</sub> levels. Diluted NPN mixtures (Scott-Marrin, Inc., Riverside, CA; [www.scottmarrin.com](http://www.scottmarrin.com)) are supplied to the monitor through the calibration line to the monitor's inlet (Figure 4-1), and provide a more challenging test of the conversion efficiency than testing with NO<sub>2</sub> alone.

Conversion efficiency testing with NPN is in addition to, not in place of, routine calibration with NO and NO<sub>2</sub>. Changes in pollutant levels and meteorological conditions over time can significantly alter the instrument's conversion efficiency. Thus, NO<sub>y</sub> 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<sub>y</sub> monitoring. An NPN conversion efficiency of 95 percent or greater is considered acceptable for NO<sub>y</sub> 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.

The most rigorous way to perform NO or NO<sub>2</sub> calibrations and NPN conversion efficiency checks would be by standard addition (i.e., by adding known concentrations of these species to the ambient air sampled by the monitor). This approach would provide the most accurate and realistic calibration because it includes the effects of water vapor and other

constituents in the sample air. However, this procedure may not fit well into the routine data acquisition used at many monitoring sites. Often, data acquisition is keyed to recording one-hour average data. Over that period, the ambient air background NO and NO<sub>y</sub> levels are not likely to remain constant enough for an accurate standard addition calibration or efficiency check. As a result, it is recommended to perform calibrations and conversion efficiency checks by diluting appropriate standards with high purity air using a MFC dilution system. Personnel at NO<sub>y</sub> monitoring sites are advised to consider the calibration approaches that fit best within their programs.

Although HNO<sub>3</sub> is a key component of NO<sub>z</sub> and in turn of NO<sub>y</sub>, and is known to be especially difficult to sample, it is not advisable to attempt routine calibration checks with HNO<sub>3</sub> in the field. The complexities of maintaining an HNO<sub>3</sub> source and delivering accurate HNO<sub>3</sub> levels to the sample inlet outweigh the potential benefits. The best way to assure adequate sampling of HNO<sub>3</sub> and other NO<sub>y</sub> species is to use a properly configured NO<sub>y</sub> monitor, as described in Section 4.3.2 and 4.3.4. 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<sub>2</sub>, a converter efficiency check with NPN, and perhaps a test of the conversion efficiency for NH<sub>3</sub> (the most likely gas-phase interferent) using a certified permeation source of NH<sub>3</sub>. 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.

## **4.5 Equipment and Supplies**

### **4.5.1 Data Acquisition Device**

Many types of equipment can be used to record the concentration measurements obtained from the analyzer. Recommended options for data acquisition are described in Section 6 of this TAD.

## **4.5.2 Calibration Equipment**

The equipment required for calibration of a precursor NO<sub>y</sub> analyzer include a MFC calibrator unit as described in Section 2.5.2, with gas phase titration capability, and a source of zero air. The following equipment is recommended for calibration of a high sensitivity NO<sub>y</sub> analyzer.

### **4.5.2.1 Calibration Standard and Standard Delivery System**

The calibration standards used for the calibration of precursor NO<sub>y</sub> 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 meet the 40 CFR 50 requirements of  $\pm 2$  percent accuracy, and that the flow rates of both MFC channels be 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.

### **4.5.2.2 Zero Air Source/Generator**

Zero air is required for the calibration of high sensitivity NO<sub>y</sub> instruments. This air must contain no detectable NO<sub>y</sub> species (i.e., NO<sub>y</sub> 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<sub>y</sub> analyzer continuously. As an alternative, many commercially-available zero-air generation systems can supply suitably NO<sub>y</sub>-free air, provided additional external scrubbing is provided as noted above.

## 4.6 Reagents and Standards

Routine operation of precursor NO<sub>y</sub> 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.

### 4.6.1 Calibration Standards

The primary NO standards must be certified commercially-prepared compressed gas standards of NO in N<sub>2</sub>, with a certified accuracy of no worse than  $\pm 2$  percent. NO gas standards of 5 to 20 ppm (with less than 1 ppm NO<sub>2</sub>) 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, SO<sub>2</sub>). This standard must be traceable to a NIST NO in N<sub>2</sub> Standard Reference Material (SRM 1683 or SRM 1684), NIST NO<sub>2</sub> 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<sup>[24]</sup> gives a recommended protocol for certifying NO gas cylinders against either a NO SRM or CRM. Procedures for certifying a NO gas cylinder against a NIST NO<sub>2</sub> SRM and for determining the amount of NO<sub>2</sub> impurity in a NO cylinder are presented by Ellis.<sup>[25]</sup> Commercial gas standards for NO<sub>2</sub> and NPN should be obtained with a certified accuracy no worse than  $\pm 2$  percent, and  $\pm 5$  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.

## **4.6.2 Zero Air**

Zero air used as dilution gas for calibration purposes should have an NO<sub>y</sub> concentration below the LDL of the NO<sub>y</sub> monitor. Commercial grades of zero air may be suitable as a starting point, provided additional cleanup is employed as noted in Section 4.5.2.2. Commercial zero air further scrubbed of NO<sub>y</sub> 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<sub>y</sub> analyzer.

## **4.7 Quality Control**

### **4.7.1 Site Visit Checklists and Remote Diagnostic Checks**

To determine whether the high sensitivity NO<sub>y</sub> 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 (see Section 6).

### **4.7.2 Multipoint Calibrations**

Calibration procedures for high sensitivity NO<sub>y</sub> analyzers are more complicated than for other high sensitivity precursor gas analyzers (i.e., for CO and SO<sub>2</sub>), in that they include calibration with NO and NO<sub>2</sub>,<sup>[9]</sup> as well as checks of the converter efficiency for NO<sub>z</sub> 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

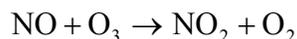
analyzers typically provide linear response over their entire operating range; therefore, four points should be sufficient. Multipoint calibrations must be done prior to the high sensitivity NO<sub>y</sub> analyzer being put into service and at least quarterly thereafter. An analyzer should be calibrated (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 samples (Section 5.4.1) differ from the certified standard values by  $\pm 15$  percent.

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<sub>2</sub>, as a check of the conversion efficiency of the molybdenum converter for NO<sub>2</sub>. This calibration is conducted by gas phase titration of NO with O<sub>3</sub>. MFC calibration systems in common use at ambient monitoring sites have GPT capability. The multipoint NO<sub>2</sub> 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<sub>2</sub> calibration are: a stable O<sub>3</sub> 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<sub>3</sub> to produce equal stoichiometric quantities of NO<sub>2</sub> in accordance with the following equation:



This is the same overall reaction detailed in reactions (4-1a and b) and (4-2a and b) above. 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<sub>y</sub> 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<sub>3</sub> the decrease in NO reading observed is equivalent to the concentration of NO<sub>2</sub> produced. The amount of NO<sub>2</sub> generated may be varied by adding variable amounts of O<sub>3</sub> from a stable O<sub>3</sub> generator, which is a component of the GPT system of the calibrator. Comparison of the NO and NO<sub>y</sub> responses of the analyzer then allows determination of the ratio of NO<sub>2</sub> response to NO<sub>2</sub> generated, which indicates the converter efficiency for NO<sub>2</sub>. Maintenance or replacement of the converter should be undertaken whenever the NO<sub>2</sub> conversion efficiency falls below 96 percent.

#### **4.7.3 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<sub>y</sub> 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<sub>y</sub> 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 in Section 4.7.2.

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.
- 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.

#### **4.7.4 Precision Checks**

At least once every two weeks a precision check should be conducted by challenging the NO<sub>y</sub> 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<sub>y</sub> 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, according to the equations provided in Section 4.3.1.1. 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.

### **4.8 Preventive Maintenance and Troubleshooting**

Long-term operation of continuous gas analyzers requires a preventive maintenance program to avoid instrument down-time and data loss. Despite active preventive maintenance, occasional problems may arise with the high sensitivity NO<sub>y</sub> analyzers. This section briefly describes several key items that might be included in the preventive maintenance program established for high sensitivity NO<sub>y</sub> 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 this TAD.

#### **4.8.1 Preventive Maintenance**

Routine preventive maintenance procedures should be in place to prevent down-time and data loss. 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<sub>y</sub> 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<sub>y</sub> inlet should be inspected every time the NO<sub>y</sub> filter is changed.

Table 4-5 illustrates items that monitoring agencies should include in their preventive maintenance program for high sensitivity NO<sub>y</sub> monitoring.

**Table 4-5. Example of a preventive maintenance schedule for NO<sub>y</sub> 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 <sub>2</sub> conversion efficiency	At least every 6 months
Monitor NPN conversion efficiency	At least every month

#### **4.8.2 Troubleshooting**

Table 4-6 summarizes common problems seen with precursor NO<sub>y</sub> 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<sub>y</sub> 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.
- Leaks

**Table 4-6. Instrument troubleshooting for high sensitivity NO<sub>y</sub> 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 <sub>3</sub> supply	Clean or replace O <sub>3</sub> generator
Low or declining response to span gas	O <sub>3</sub> source failing	Clean or replace O <sub>3</sub> generator
	Dirty reaction cell window	Clean window
Zero output at ambient levels	Pump failure	Check pump
	PMT failure	Replace PMT
Low NO <sub>2</sub> or NPN efficiency	Aging or dirty converter	Replace converter
No flow through analyzer	Pump failure	Replace/ rebuild pump head

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## **5.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) PROCEDURES**

### **5.1 Introduction**

One of the primary objectives of the NAAMS is to accurately measure CO, SO<sub>2</sub>, and NO<sub>y</sub> at low concentrations.<sup>[1]</sup> Therefore, a rigorous quality assurance (QA) program, with appropriate quality control (QC) activities, must be maintained to ensure that the precursor monitoring data collected in the NCore network are of suitable quality to meet the objectives of the program. Quality assurance is defined by EPA as “an integrated system of management activities involving planning, implementation, assessment reporting and quality improvement to ensure that a process, item or service is of the type and quality needed and the client expects.”<sup>[2]</sup> QA is an overall process, described in a management plan, to guarantee the integrity of the data, and QA activities ensure that the process is appropriately defined and implemented. Quality control (QC) is defined as “the overall system of technical activities that measures the attributes and performance of a process, item or service against defined standards to verify that they meet the stated requirements established by the customer.”<sup>[2]</sup> QC activities are a series of analytical measurements taken throughout the air monitoring process that are used to assess the quality of the monitoring data. This section of the NCore TAD describes the QA/QC activities that should be implemented for precursor gas monitoring in NCore.

### **5.2 QA/QC Management**

The overall QA/QC program should be defined in a Quality Assurance Project Plan (QAPP). Each State or Local monitoring agency should develop a QAPP in accordance with the guidance document prepared by EPA.<sup>[3]</sup> The primary purpose of the QAPP is to “provide an overview of the project, describe the need for the measurements, and define QA/QC activities to be applied to the project, all within a single document. The QAPP should be detailed enough to provide a clear description of every aspect of the project and include information for every member of the project staff, including samplers, lab staff, and data reviewers.”<sup>[4]</sup>

### **5.3 Network Calibration and Instrument Check Procedures**

The following sections describe the instrument calibration and routine instrument check procedures for precursor analyzers that should be implemented within NCore. In general, these procedures may be followed for all the precursor pollutant monitors (i.e., CO, SO<sub>2</sub>, NO<sub>y</sub>) unless noted.

#### **5.3.1 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 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 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 samples (Section 5.4.1) differ from the certified standard values by  $\pm 15$  percent.

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

#### **5.3.1.1 Precautions**

A primary precaution is to check the calibration of the mass flow controllers in the calibration system before calibration of the precursor gas analyzers, rather than relying solely on the vendor-supplied calibration. This check should be conducted by comparison of readings over the full range of each flow controller, using an independent and NIST-traceable flow measurement device, such as an electronically timed bubble or piston-type flow meter. Commonly used MFC calibrators allow the input of regression data from such comparisons, so that corrections to the flow readings are made automatically by the calibration system.

Once the calibration system has been inspected, tested, and NIST traceability established, the precursor analyzers can be calibrated in a field situation. The following additional precautions should be observed.

- FEP or PTFE is the recommended material for all components and lines throughout the calibration system, and all tubing and connection from the gas standard cylinders. It is also preferred for any surfaces contacting the gas flows in solenoid valves in the calibration system.
- When connecting cylinders to a MFC, make sure that the cylinder regulator is purged. Fill and vent the regulator at least three successive times before connecting the regulator to the delivery tubing. If a cylinder is changed, regulator purging is needed, and the resulting calibration should be monitored very closely. If the response of the analyzer is lower than before the cylinder change, then it can most likely be traced to improper regulator purging. Purging and drying of a regulator can be aided by the application of vacuum, as described in Section 3.6.1.

- It is recommended that stainless steel regulators with internal diaphragms that are coated with Teflon® or other inert material be used with all calibration and audit cylinders.

### **5.3.1.2 Calibration Procedures**

Analyzer-specific SOPs should be developed based on the manufacturer's recommended calibration procedures. Example SOP's prepared by EPA are included in Appendix B of this TAD. However, the following steps outline the multipoint calibration procedure for the precursor gas analyzers. If appropriate, a NIST-traceable multicomponent gas mixture (i.e., CO, SO<sub>2</sub>, NO in N<sub>2</sub>) may be used to calibrate multiple precursor gas analyzers.

1. Allow both the calibration system and the analyzer to warm up properly. Consult the manufacturer's instruction manual for specific details.
2. Record the normal QC check information. Especially note the zero and span dial/readout values before starting the calibration.
3. Start introduction of zero air to the sampling manifold or the NO<sub>y</sub> inlet, and flag this event in the data. With the zero air supplied at a constant flow rate, allow the analyzer readings to stabilize on zero air. When stability is satisfactory, record the response of the analyzer.
4. Set the MFC calibration unit to allow diluted calibration gas to flood the manifold or NO<sub>y</sub> inlet at a concentration that is 80 to 90 percent of full scale of the analyzer measurement range.
5. Allow the analyzer readings to stabilize at the working concentration. Record the response from the analyzer.

6. Lower the concentration of the diluted calibration standard to 40 to 50 percent of the analyzer's full scale. Repeat the previous step.
7. Lower the concentration of the diluted calibration standard to 15 to 20 percent of the analyzer's full scale. Repeat Step 5.
8. Once three concentration levels are tested and all values recorded, allow the analyzer to sample zero air again (Step 3), and again record the reading. Once the calibration is completed, return the instrument to its normal ambient operational status.

The responses of the precursor analyzer should be analyzed by linear regression to assess the results of the calibration. Acceptance criteria for the linear regressions are left to the discretion of the monitoring agency, but the following are suggested: slope,  $1 \pm 0.10$ ; intercept,  $zero \pm 1 \times \text{analyzer LDL}$  or  $\pm 1\%$  of the tested range (whichever is greater); and correlation coefficient ( $r$ ),  $> 0.995$ , where the  $\pm$  values represent 95% confidence intervals. Regardless of what criteria are selected, the instrument still must also pass audit tests, which require an absolute difference between the analyzer reading and the standard gas concentration of no more than 15 percent.

### **5.3.2 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  $\pm 15$  percent. If zero drift is internally adjusted by the analyzer, the zero check is used to verify that the internal zero is working properly. Zero checks are conducted by challenging the analyzer with zero air and a test

atmosphere containing concentrations 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 in Section 5.3.1.

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.

- New generation DASs can record calibration data and allow remote users to track daily Level I check and zero drift. This is important for data validation, verification and troubleshooting.

### **5.3.3 Precision Checks**

At least once every two weeks a precision check should be conducted by challenging each precursor analyzer with a known concentration of a standard gas mixture to assess the ability of the analyzers to measure a gas under reproducible conditions. The precision checks should be conducted by challenging the precursor analyzer with a standard gas of known concentration in the ranges shown in Table 5-1. The gas must be supplied through all filters, scrubbers, and other conditioners and should be supplied through as much of the sample inlet system as possible. After completion of the precision check, the actual concentration of the working standard and the measured concentration indicated by the analyzer should be reported along with the percent difference between these values. Precision should be calculated at the end of each calendar quarter as described in Section 2.3.1.1, 3.3.1.1, or 4.3.1.1.

**Table 5-1. Concentration levels for biweekly precision checks.**

<b>Target</b>	<b>Concentration Range</b>
CO	250 to 500 ppb
SO <sub>2</sub>	10 to 50 ppb
NO <sub>y</sub>	Approx. 20 ppb

## **5.4 Independent Audits and Assessments**

The effectiveness of the QA/QC procedures in place at each site should be evaluated routinely through a series of independent audits and assessments. These assessments should include:

- Proficiency test samples;
- Technical systems audits; and

- Audits of data quality.

#### **5.4.1 Proficiency Test Samples**

Proficiency test (PT) samples are used to ensure the performance of the precursor gas analyzers used to collect the monitoring data. PT samples are challenges of the gas analyzers with standards of known concentration that are independent of those standards used to calibrate the analyzers. 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. Clearly, the appropriate concentration values to be used for PT samples will be different for the different precursor gases (CO, SO<sub>2</sub>, and NO<sub>y</sub>). In addition, for any one of these gases, the appropriate PT concentrations may vary with the analyzer operating range, which is selected based on the characteristics of the monitoring site. Consequently, the recommended concentration ranges for PT samples are given in Table 5-2 relative to the full scale range of the analyzer, rather than in concentration units. At least one PT sample of known concentration is to be delivered to the analyzer from each of the applicable ranges shown in Table 5-2. The indicated ranges are consistent with the requirements of 40 CFR 58 Appendix A, Section 3.2.1.

**Table 5-2. Concentration ranges for PT samples.**

<b>Audit Point</b>	<b>Percent of Full Scale Range<sup>a</sup></b>
1	3 to 8
2	15 to 20
3	35 to 45
4	80 to 90

a: Applies to operating range of CO, SO<sub>2</sub>, or NO<sub>y</sub> analyzer.

PT sample challenges should be conducted at least annually on each analyzer, and can be conducted (a) by a person outside of the agency, or an independent QA group within the agency, or (b) by having an independent audit device, such as used in the National Performance Audit Program (NPAP), sent to the monitoring station. In the former case, an independent audit system

or standard is brought to the monitoring station and used to produce working standards of the target gases that are supplied to the analyzers by the auditor. In the latter case, the audit device provided to the monitoring agency produces working standards of the calibration gases that are supplied to the analyzers. The operators and auditor do not know the concentrations of the standards that are produced by the audit equipment. Responses of the precursor analyzers are recorded and provided to the agency that supplied the audit device. That agency compares the responses of the analyzers to the calculated concentrations from the audit device and provides an audit report to the monitoring agency. In both cases, the PT sample audit should be conducted by supplying the analyzer with the PT sample gas in its normal sampling mode such that the audit gas passes through all sample inlet components used during normal ambient sampling.

Both the actual concentration of the PT sample gases and the concentration measured by the analyzer being audited should be reported, along with the percent differences between these concentrations for each audit point. The calculated percent differences are used to confirm the analyzer precision and bias estimates obtained from routine checks.

The PT audit should also include an independent check of the gas flow controllers in the calibration system, using a NIST-traceable flow standard.

#### **5.4.2 Technical Systems Audit**

A technical systems audit (TSA) is an on-site review and inspection of the operation of an air monitoring station to assess its compliance with established QA/QC procedures and any applicable regulations. TSAs assess whether all procedures for the monitoring program are being followed and documented. A TSA should be conducted immediately before or shortly after the start of monitoring and should be repeated at least every three years. TSAs should be performed by a regional auditor who is knowledgeable of the monitoring program but independent of routine operations.

### **5.4.3 Audits of Data Quality**

An audit of data quality (ADQ) process is an examination of data after they have been collected and verified. ADQs are conducted to determine how well the measurement system performed with respect to goals specified in the Quality Assurance Project Plan (QAPP) and whether the data were accumulated, transferred, calculated, summarized, and reported correctly. The ADQ documents and evaluates the methods by which decisions were made during the data treatment process.

### **5.5 References**

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## **6.0 DATA ACQUISITION AND MANAGEMENT**

### **6.1 Introduction**

The ambient pollutant data generated by the high sensitivity precursor gas analyzers in the NCore network must be captured, organized, and verified in order to be useful. The process of capturing the precursor gas data is known as data acquisition, whereas the organization of the data is known as data management. Within both of these areas, quality assurance efforts and data reviews must be carried out to verify the quality of the ambient data. This chapter of the NCore TAD provides guidance in these areas, including identification of advanced equipment and procedures that are recommended for implementation in NCore. The recommended procedures rely on digital communication by the data acquisition system to collect a wider variety of information from the precursor gas analyzers, to control instrument calibrations, and to allow for more routine, automated, and thorough data quality efforts.

### **6.2 Data Acquisition and Analysis**

Many S/L/T agencies currently perform precursor gas data acquisition by recording an analog output from each precursor gas analyzer, using an electronic data logger. The analog readings are converted and stored in digital memory in the data logger, for subsequent automatic retrieval by a remote data management system. This approach can reliably capture the monitoring data, but does not allow complete control of monitoring operations, and the recorded analog signals are subject to noise that limits the detection of low concentrations. Furthermore, with this data acquisition approach, the data review process is typically labor-intensive and not highly automated. For these reasons, EPA discourages this approach, and instead strongly recommends adoption of digital data acquisition methods. In that regard, the common analog data acquisition approach often does not fully utilize the capabilities of the electronic data logger. For example, a data logger used by many agencies for analog data acquisition is the ESC Model 8816 Data Logger/Controller (Environmental Systems Corporation, Knoxville, Tennessee). This and similar data loggers have the capability to acquire data in

digital form, and to control some aspects of calibrations and analyzer operation, but these capabilities are not exercised in typical analog data acquisition approaches.

The recommended data acquisition approach for precursor gas monitoring in NCore is a system that records analyzer readings and diagnostic information in digital form, and allows direct digital communication between the data system and the precursor analyzers and calibration systems, at one or more monitoring sites. Digital data acquisition reduces noise in the recording of precursor gas monitoring data, thereby improving sensitivity, and also allows recording and control of the instrument settings, internal diagnostics, and programmed activities of monitoring and calibration equipment. Such data acquisition systems (DAS) also typically provide automated data quality assessment as part of the data acquisition process.

It may be cost-effective for S/L/T agencies to adopt digital data acquisition and calibration control simply by more fully exploiting the capabilities of their existing electronic data loggers, such as the ESC 8816 noted above. For example, many high sensitivity gas analyzers are capable of being calibrated under remote control. The opportunity to reduce travel and personnel costs through automated calibrations is a strong motivator for S/L/T agencies to make greater use of the capabilities of their existing data acquisition systems. Alternatively, Section 6.2.1 presents one example of a new commercial data logger that is capable of performing the recommended digital data acquisition. Also, Section 6.2.2 presents an example of a highly sophisticated environmental data system capable of performing such digital data acquisition and equipment control at multiple monitoring sites. Section 6.2.3 summarizes the process by which precursor gas data is transferred from the high sensitivity analyzers to ultimate use in public data systems such as EPA's Air Quality System (AQS).<sup>[1]</sup>

### **6.2.1 Example Data Logger: ESC 8832 Data System Controller**

The ESC Model 8832 Data System Controller<sup>[2,3]</sup> (Environmental Systems Corporation, Knoxville, Tennessee), shown in Figure 6-1, is an example of a digital data logger suitable for



**Figure 6-1. ESC 8832 data system controller.**

use in NCore precursor gas monitoring. The ESC 8832 is the most recent version in a line of ESC digital data loggers that have been used in ambient monitoring, such as the ESC 8816, which has been widely used by S/L/T agencies for recording analog monitoring data. Relative to the Model 8816, the Model 8832 uses a 32-bit rather than 16-bit processor, provides more memory capacity and somewhat faster data transfer, and allows comma-delimited parsing of serial data. The ESC 8832 uses a 32-bit 50 MHz processor, and is designed for acquisition or calculation of up to 99 data channels, with the capability of updating each channel once per second. “Calculated” data channels include vector wind speed and direction and sigma theta. In the standard configuration, the ESC 8832 can store over 100,000 data records and, with an optional memory expansion card, can store over 300,000 data records. The ESC 8832 incorporates high-speed serial ports for data polling, and for downloads of configuration and software upgrades without changing the data logger’s EPROM. The ESC 8832 can record internal diagnostic parameters of precursor gas analyzers, and program the performance of zeroing and calibration procedures. Digital output relays can control valve switching or other devices, with up to 32 events programmable. Up to 64 programmable alarms can be used to flag recorded data values, and up to 32 calibrations can be applied to recorded data. The ESC 8832 can record analog inputs with 14-bit resolution over voltage ranges from  $\pm 100$  mV to  $\pm 10$  V full

scale. An Ethernet port and VGA analyzer output port are also available. The ESC 8832 is capable of network communication with analyzers that have network ports installed (e.g., Thermo Environmental and API analyzers can provide this feature). Once configured as a network client, the data logger can gather data from the instrument as if via a serial port.

Obtaining the maximum benefit from using a digital data logger, as exemplified by the ESC 8832, requires using suitable software to manage the collected data. This requirement especially applies when operating multiple ambient monitoring sites. To continue this example, the E-DAS/ATX Ambient software developed by ESC is capable of polling one or more data loggers at widely dispersed sites to process, edit, archive, and report the ambient data. The Windows-based software can be used to perform data retrieval with error checking, automatic time synchronization for multiple sites, graphical display of data, data storage and archiving, data editing, and reporting of data in specified formats such as for EPA's AQS.<sup>[1]</sup>

### **6.2.2 Example Environmental Data System: ENVIDAS System**

An example of the type of data system recommended for precursor gas monitoring at NCore sites is the ENVIDAS environmental data acquisition system<sup>[4]</sup> (Envitech Ltd., Ramat Gan, Israel). The ENVIDAS system uses non-proprietary desktop or industrial personal computer (PC) hardware to run flexible, Windows-based data acquisition software. A wide variety of data acquisition cards may be installed for use with the ENVIDAS system. Typically, the ENVIDAS system can accept up to 64 inputs, either analog or digital, with analog ranges from  $\pm 1.25$  V to  $\pm 10$  V, and supports up to eight RS232C serial communication channels. Data sampling rates (1, 2, 5, or 10 seconds) and averaging periods (e.g., 1, 5, 6, 15, or 60 minutes) are user-selectable. Data storage includes calculated parameters such as vector wind speed and direction and sigma theta. The multi-tasking software assures that data are not lost during data polling or user interaction with the software. Data can be averaged, archived, displayed, and reported in various formats including wind roses, pollution roses, histograms, and time series plots.

The advantage of systems such as ENVIDAS, relative to data logging systems, is that ENVIDAS is designed to communicate with and control a variety of precursor analyzers and dilution calibrators at multiple monitoring sites. Thus, ENVIDAS facilitates remote control of analyzer and calibrator operations at a monitoring site, as well as data acquisition. This communication is achieved by means of RS232C protocols specific to each manufacturer's analyzer or calibrator. For example, ENVIDAS supports RS232C protocols for analyzers made by Thermo Environmental, API, Environnement S.A., and Monitor Labs, and for calibrators made by Thermo Environmental, API, Horiba, Sabio, and Envirionics. Digital communication and data acquisition means that the ENVIDAS system can access the internal software of an analyzer or calibrator, and control the device's internal settings and parameters. Control of such a device can be accomplished as fully through the ENVIDAS system as by an operator through the front panel push buttons of the analyzer or calibrator itself. Basic analyzer settings, such as the time and date, measurement range, units of concentration, time constant or averaging time, and zero and calibration factors, can be controlled by the ENVIDAS system.

As in the data loggers exemplified in Section 6.2.1, a key feature for precursor monitoring is recording of internal diagnostic information from the analyzers, to document the status of the analyzer or diagnose data quality problems. For example, Table 6-1 lists several internal status parameters for a typical CO, SO<sub>2</sub>, and NO<sub>y</sub> analyzer that could be recorded and controlled through the ENVIDAS (or a digital data logging) system.

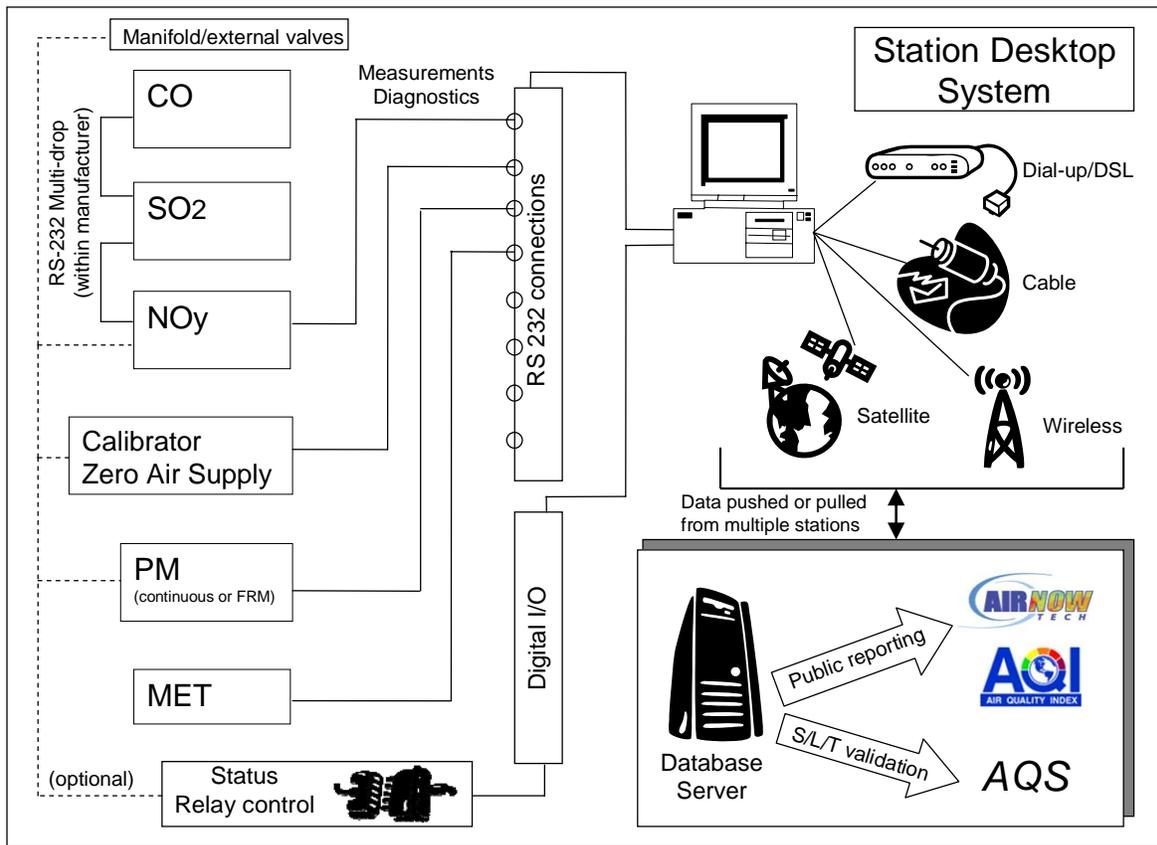
EPA recommends that a high-performance data acquisition system such as ENVIDAS, or a system such as the ESC 8832 data logger with digital data transfer and suitable software, be used for precursor gas monitoring at NCore sites. Implementation of such a system offers a monitoring agency the most up-to-date capabilities in instrument control, data acquisition, and data analysis, especially when multiple monitoring sites are in operation.

**Table 6-1. Example Internal Diagnostic Parameters of High Sensitivity Precursor Gas Analyzers Accessible to a Digital Data Acquisition System.**

CO Analyzer	SO <sub>2</sub> Analyzer	NO <sub>y</sub> Analyzer
Optical chamber temperature	Optical chamber temperature	Reaction chamber temperature
Optical chamber pressure	Optical chamber pressure	Reaction chamber pressure
Temperature correction	Temperature correction	P/T correction
Pressure correction	Pressure correction	Converter temperature
Sample flow rate	Sample flow rate	PMT cooler temperature
Power supply voltage	Power supply voltage	Sample flow rate
Sample/reference intensity ratio	Flash lamp voltage	Power supply voltage
Auto gain control frequency	PMT high voltage	Alarms and max/min settings
Chopper motor speed	Alarms and max/min settings	Prereactor zero reading
Alarms and max/min settings		Internal temperature

### **6.2.3 Summary Data Acquisition Process**

Figure 6-2 illustrates the recommended digital data acquisition approach, in the form of a schematic of the data flow from NCore precursor gas monitors through a local digital data acquisition system, to final reporting of the data in various public databases. This schematic shows several of the key capabilities of the recommended approach. A basic capability is the acquisition of digital data from multiple analyzers and other devices, thereby reducing noise and minimizing the effort needed in data processing. Another capability is two-way communication, so that the data acquisition system can interrogate and/or control the local analyzers, calibration systems, and even sample inlet systems, as well as receive data from the analyzers. Data transfer to a central location is also illustrated, with several possible means of that transfer shown. S/L/T agencies are urged to take advantage of the state of the art in this part of the process, as even sophisticated technologies such as satellite data communication are now well established, commercially available, and inexpensive to implement for monitoring operations. Finally, it is important that data are reported in formats of immediate use in public data bases such as AQS, and air quality index sites such as the multi-agency AIRNow site.<sup>[5]</sup> An advantage of software such as the ESC E-DAX/ATS or ENVIDAS systems introduced above is their ability to facilitate the assembly, formatting, and reporting of monitoring data to these data databases.



**Figure 6-2. Flow of data from precursor gas analyzers to final reporting.**

### 6.3 Data Acquisition System Quality Assurance

The use of a data acquisition system such as those described above is strongly encouraged for the NCore precursor gas monitoring community. However, several practices should be followed to ensure the quality of the data that are collected.

#### 6.3.1 Personnel

Each organization conducting precursor gas monitoring should identify one or more persons within the organization to implement and oversee the data acquisition and management system. These personnel must have adequate education, training, and experience to perform

these functions, and must recognize the performance of these functions as a key (if not primary) component of their responsibilities. These personnel contribute to quality assurance of the data acquisition system through reviews and audits of the DAS and the collected data.

### **6.3.2 Security**

The data acquisition system must be safeguarded against accidental or deliberate actions that could result in the following potential problems:

*Modification, destruction, or unwanted disclosure of data.* The integrity of the data should be maintained by (e.g.) implementing password protection and user authorization for setup of the DAS, control of monitoring and calibration equipment, data acquisition and editing, and data reporting.

*Unavailability of the DAS or collected data.* Protection against data loss may be avoided by redundant data storage, and assurance of DAS operation may require hardware maintenance or upgrades, surge protection, or backup systems.

### **6.3.3 Data Entry and Formatting**

Electronic data acquisition systems such as those described above can record, average, and compile the monitoring data in a variety of reporting formats. The personnel responsible for the DAS should assure that the reported data are in the formats required for reporting to databases such as AQS. Information on AQS requirements is available in the AQS Users Guide<sup>[1]</sup> (Volume II, Air Quality Data Coding, and Volume III, Air Quality Data Storage).

Precursor gas monitoring data from NCore sites are to be reported to AQS as hourly average values. However, it is suggested that S/L/T agencies also consider recording and archiving data with shorter time resolution, e.g., as five minute averages. Such data can easily be used to compute averages over longer time periods, and are valuable for diverse data analyses beyond the purposes of AQS. For example, short time period data can be used to assess the

variability and uncertainty in hourly or longer time period data, and to evaluate temporal trends, source impacts, and special research topics. The availability of high time resolution data will be valuable to the data user community, and is likely to foster analyses of air quality that could not be attempted with hourly or longer data periods.

#### **6.3.4 Data Review**

The review of collected data is the most important means to assure data quality in ambient monitoring. The review process has multiple stages, beginning with observations in the field, continuing through the analysis of electronic data, and ending with the reporting of final data. Data review should be the subject of an SOP that defines the criteria an agency will apply in processing and reporting the monitoring data.

Data review in the field should involve the observations and records of site operators on topics such as the operational status of precursor analyzers, the need for maintenance or repair, the occurrence of unexpected or unexplained readings, the existence of difficult or unusual meteorological conditions, and the observation of ambient data outside the normal range for the site. At a minimum, such observations must be recorded in a site notebook or other document. Preferably, such observations should be recorded by electronic word processor, and ideally such records are associated with the ambient data through the data acquisition system. Data review in the field is the first step in flagging suspect data for subsequent review.

Data review is a key component of the data analysis process. Electronic data acquisition systems allow automatic flagging of data based on the status (i.e., alarms, internal diagnostics, calibration results) of the precursor analyzer, or based on other criteria such as expected data ranges. However, review of the data by experienced personnel is still necessary. This review should be carried out promptly after data collection and should take into account any field observations such as those noted above. The aim of this review is to identify and remove suspect data, and to identify and retain valid data based on the variety of information recorded. Software associated with an electronic data acquisition system can be used to automatically compare

various types of data to flag or confirm the validity of the ambient measurements. This capability should be exploited in data review for NCore.

The final step of data review is conducted in appropriately averaging and formatting data to be reported. The usefulness of the AQS database, or other such publicly accessible data repositories, is dependent on the consistency and accuracy of the processed data submitted to it. Careful review of the data should take place to assure submission of complete and correctly formatted data sets.

### **6.3.5 Calibrations and Audits**

Quality assurance of the DAS is based on the system being operated within some range of performance; i.e., that the data collected on the DAS and reported to the central database is the same as that generated by the monitoring equipment. Among the practices used to document DAS performance are routine calibration checks of the data acquisition system itself, data trail audits, and performance audits.

#### **6.3.5.1 *DAS Calibration***

In the case where analog signals from monitoring equipment are recorded by the DAS, the calibration of a DAS is similar to the approach used for calibration of a strip chart recorder. To calibrate the DAS, known voltages are supplied to each of the input channels and the corresponding measured response of the DAS is recorded. Specific calibration procedures in the DAS owner's manual should be followed when performing such DAS calibrations. The DAS should be calibrated at least once per year.

In addition, precursor gas analyzers typically have an option to set output voltages to full scale, or to ramp the analog output voltages supplied by the analyzer over the full output range. Such a function can be used to check the analog recording process from the analyzer through the DAS.

### **6.3.5.2 Data Trail Audit**

A data trail audit consists of following one or more data values from the analyzer through collection by the DAS, and through data processing to reporting to the central data repository. This audit should be conducted by those personnel assigned to manage the data acquisition hardware and software, and should be conducted at least annually. The procedure to be followed is that one or more data points or data averages reported from the analyzer (e.g., hourly values) should be collected by the DAS and checked on the DAS storage medium, and, in the final format, reported to the data repository. The same values must be traceable through all steps of the data acquisition and reporting process.

## **6.4 Data and Records Management**

All raw data, averaged or processed data, operator documentation, correspondence on data recording or processing issues, and other records should be retained for an appropriate period of time after data have been collected, processed, and reported in the required format. The following sections summarize specific data management recommendations for key types of records.

### **6.4.1 Calibration Data**

Calibration data should be recorded in the same manner as all other precursor gas analyzer data, but appropriately flagged to distinguish it from routine ambient data. Any hard copy records associated with calibration data must be linked or cross-referenced to the electronic data, and the personnel who prepared the hard copy data must be fully identified. Calibration data should be sequestered from ambient data in the data review process, and the appropriate calibration results accurately applied to the relevant time periods of ambient monitoring.

Digital data acquisition systems such as those exemplified in Sections 6.2.1 and 6.2.2 offer a great advantage over analog systems in the tracking of calibration data, because of their

ability to control and record the internal readings of gas analyzers and calibration systems. That is, a digital data acquisition system not only can record the analyzer's output readings, but can schedule and direct the performance of analyzer calibrations, and record calibrator settings and status. Thus flagging of calibration data to distinguish them from ambient monitoring data is conducted automatically during data acquisition, with no additional effort or post-analysis. These capabilities greatly reduce the time and effort needed to organize and quantify calibration results.

#### **6.4.2 Electronic Data Files**

Electronic data files from different stages of the data collection and reporting process should be retained for an appropriate period of time. The files to be retained should at first include raw data files, intermediate files (e.g., edited to remove calibration or suspect data), and the final data files submitted to the data repository. Any supporting information (including hard copy records) should also be retained. Subsequent to final reporting of the data, a judgment may be made to reduce the extent of the files retained. However, any data files that directly support decisions made in the data review and editing process should be retained. In storing the electronic data files, use should be made of file compression methods that reduce the size of files for storage.

#### **6.4.3 Hard Copies**

As is evident from the discussion above, hard copy records are discouraged for precursor gas monitoring in NCore, in favor of electronic data acquisition systems. However, some hard copy records may be unavoidable; e.g., a site operator's personal laboratory notebook. There are two key requirements for hard copy records. First, these records must be carefully reviewed by the staff who recorded them and the personnel who oversee the electronic data acquisition to assure that relevant information from the hard copy records is recognized and used in the data analysis process. Second, in storing hard copy records, care must be taken to properly and completely identify the records, and link them with the corresponding electronic data records.

## 6.5 References

1. "AQS User Guide: Air Quality System", U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, November 15, 2004; available at <http://www.epa.gov/ttnairs1/airsaqs/manuals/AQSUserGuide.pdf>.
2. Information on ESC Model 8832 data system controller, Environmental Systems Corporation, Knoxville, Tennessee, available at [http://www.escdas.com/cem/cem\\_8832.html](http://www.escdas.com/cem/cem_8832.html).
3. Information on ESC EDAS data software, Environmental Systems Corporation, Knoxville, Tennessee, available at <http://www.escdas.com/ambient/atx.html>.
4. Information on ENVIDAS data acquisition system, Envitech Ltd., Givataim, Israel, available at <http://www.envitech.co.il/EnvidasFW.aspx>.
5. AIRNow Web site, developed by the U.S. Environmental Protection Agency, State/Local/Tribal Agencies, National Park Service, and National Oceanic and Atmospheric Administration, with international and media partners. (<http://www.epa.gov/airnow>)

**APPENDIX A**

**SAMPLE MANIFOLD DESIGN FOR PRECURSOR  
GAS MONITORING**

# Sample Manifold Design for Precursor Gas Monitoring

Many important variables affect sampling manifold design for ambient precursor gas monitoring: residence time of sample gases, materials of construction, diameter, length, flow rate, and pressure drop. Considerations for these parameters are discussed below.

Residence Time Determination: The residence time of air pollutants within the sampling system (defined as extending from the entrance of the sample inlet above the instrument shelter to the bulkhead of the precursor gas analyzer) is critical. Residence time is defined as the amount of time that it takes for a sample of air to travel through the sampling system. This issue is discussed in detail for NO<sub>y</sub> monitoring in Section 4.2, and recommendations in Section 4 for the arrangement of the molybdenum converter and inlet system should be followed. However, residence time is also an issue for other precursor gases, and should be considered in designing sample manifolds for those species. For example, Code of Federal Regulations (CFR), Title 40 Part 58, Appendix E.9 states, “Ozone in the presence of NO will show significant losses even in the most inert probe material when the residence time exceeds 20 seconds. Other studies indicate that 10-second or less residence time is easily achievable.”<sup>1</sup> Although 20-second residence time is the maximum allowed as specified in 40 CFR 58, Appendix E, it is recommended that the residence time within the sampling system be less than 10 seconds. If the volume of the sampling system does not allow this to occur, then a blower motor or other device (such as a vacuum pump) can be used to increase flow rate and decrease the residence time. The residence time for a sample manifold system is determined in the following way. First the total volume of the cane (inlet), manifold, and sample lines must be determined using the following equation:

$$\text{Total Volume} = C_v + M_v + L_v \quad \text{Equation 1}$$

Where:

$C_v$  = Volume of the sample cane or inlet and extensions

$M_v$  = Volume of the sample manifold and moisture trap

$L_v$  = Volume of the instrument lines from the manifold to the instrument bulkhead

The volume of each component of the sampling system must be measured individually. To measure the volume of the components (assuming they are cylindrical in shape), use the following equation:

$$V = \pi * (d/2)^2 * L \qquad \text{Equation 2}$$

Where:

V = volume of the component, cm<sup>3</sup>

$\pi$  = 3.14

L = Length of the component, cm

d = inside diameter of the component, cm

Once the total volume is determined, divide the total volume by the total sample flow rate of all instruments to calculate the residence time in the inlet. If the residence time is greater than 20 seconds, attach a blower or vacuum pump to increase the flow rate and decrease the residence time.

**Laminar Flow Manifolds:** In the past, vertical laminar flow manifolds were a popular design. By the proper selection of a large diameter vertical inlet probe and by maintaining a laminar flow throughout, it was assumed that the sample air would not react with the walls of the probe. Numerous materials such as glass, plastic, galvanized steel, and stainless steel were used for constructing the probe. Removable sample lines constructed of FEP or PTFE were placed to protrude into the manifold to provide each instrument with sample air. A laminar flow manifold could have a flow rate as high as 150 L/min, in order to minimize any losses, and large diameter tubing was used to minimize pressure drops. However, vertical laminar flow manifolds have many disadvantages which are listed below:

- Since the flow rates are so high, it is difficult to supply enough audit gas to provide an adequate independent assessment for the entire sampling system;
- Long laminar flow manifolds may be difficult to clean due to size and length;
- Temperature differentials may exist that could change the characteristics of the gases, e.g., if a laminar manifold's inlet is on top of a building, the temperature at the bottom of the building may be much lower, thereby dropping the dew point and condensing water.

For these technical reasons, EPA strongly discourages the use of laminar flow manifolds in the national air monitoring network. It is recommended that agencies that utilize laminar manifolds migrate to conventional manifold designs that are described below.

**Sampling Lines as Inlet and Manifold:** Often air monitoring agencies will place individual sample lines outside of their shelter for each instrument. If the sample lines are manufactured out of Polytetrafluoroethylene (PTFE) or Fluoroethylpropylene (FEP) Teflon®, this is acceptable to the EPA. The advantages to using single sample lines are: no breakage and ease of external auditing. However, please note the following caveats:

1. PTFE and FEP lines can deteriorate when exposed to atmospheric conditions, particularly ultraviolet radiation from the sun. Therefore, it is recommended that sample lines be inspected and replaced regularly.
2. Small insects and particles can accumulate inside of the tubing. It has been reported that small spiders build their webs inside of tubing. This can cause blockage and affect the response of the instruments. In addition, particles can collect inside the tubing, especially at the entrance, thus affecting precursor gas concentrations. Check the sampling lines and replace or clean the tubing on a regular basis.
3. Since there is no central manifold, these configurations sometimes have a “three-way” tee, i.e., one flow path for supplying calibration mixtures and the other for the sampling of ambient air. If the three-way tee is not placed near the outermost limit of the sample inlet tubing, then the entire sampling system is not challenged by the provision of calibration gas. It is strongly recommended that at least on a periodic basis calibration gas be supplied so that it floods the entire sample line. This is best done by placing the three-way tee just below the sample inlet, so that calibration gas supplied there is drawn through the entire sampling line.
4. The calibration gas must be delivered to the analyzers at near ambient pressure. Some instruments are very sensitive to pressure changes. If the calibration gas flow is excessive, the analyzer may sample the gas under pressure. If a pressure effect on calibration gas response is suspected, it is recommended that the gas be introduced at more than one place in the sampling line (by placement of the tee, as described in item #3 above). If the response

to the calibration gas is the same regardless of delivery point, then there is likely no pressure effect.

**Conventional Manifold Design** - A number of “conventional” manifold systems exist today. However, one manifold feature must be consistent: the probe and manifold must be constructed of borosilicate glass or Teflon® (PFA or PTFE). These are the only materials proven to be inert to gases. EPA will accept manifolds or inlets that are made from other materials, such as steel or aluminum, that are lined or coated with borosilicate glass or the Teflon® materials named above. However, all of the linings, joints and connectors that could possibly come into contact with the sample gases must be of glass or Teflon®. It is recommended that probes and manifolds be constructed in modular sections to enable frequent cleaning. It has been demonstrated that there are no significant losses of reactive gas concentrations in conventional 13 mm inside diameter (ID) sampling lines of glass or Teflon® if the sample residence time is 10 seconds or less. This is true even in sample lines up to 38 m in length. However, when the sample residence time exceeds 20 seconds, loss is detectable, and at 60 seconds the loss can be nearly complete. Therefore, EPA requires that residence times must be 20 seconds or less (except for NO<sub>y</sub>). Please note that for particulate matter (PM) monitoring instruments, such as nephelometers, Tapered Element Oscillating Microbalance (TEOM) instruments, or Beta Gauges, the ambient precursor gas manifold is not recommended. Particle monitoring instruments should have separate intake probes that are as short and as straight as possible to avoid particulate losses due to impaction on the walls of the probe.

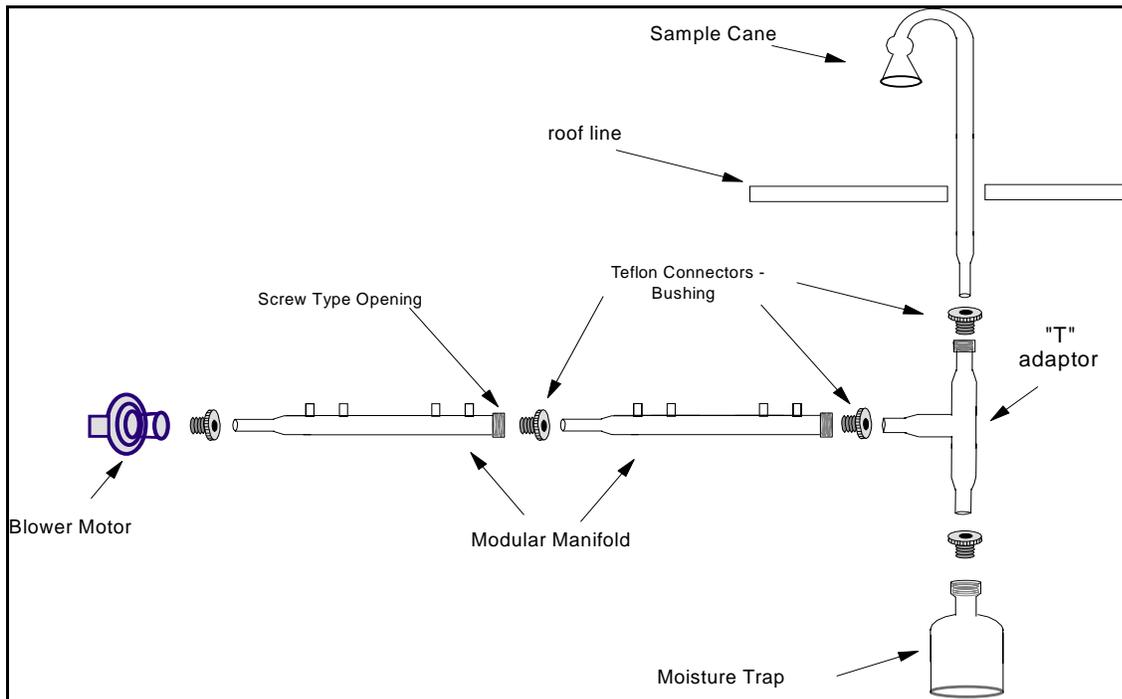
**T-Type Design:** The most popular gas sampling system in use today consists of a vertical "candy cane" protruding through the roof of the shelter with a horizontal sampling manifold connected by a tee fitting to the vertical section (Figure 1). This type of manifold is commercially available. At the bottom of the tee is a bottle for collecting particles and moisture that cannot make the bend; this is known as the “drop out” or moisture trap bottle. Please note that a small blower at the exhaust end of the system (optional) is used to provide flow through the sampling system. There are several issues that must be mitigated with this design:

- The probe and manifold may have a volume such that the total draw of the precursor gas analyzers cannot keep the residence time less than 20 seconds (except NO<sub>y</sub>), thereby requiring a blower motor. However, a blower motor may prevent calibration and audit

gases from being supplied in sufficient quantity, because of the high flow rate in the manifold. To remedy this, the blower motor must be turned off for calibration.

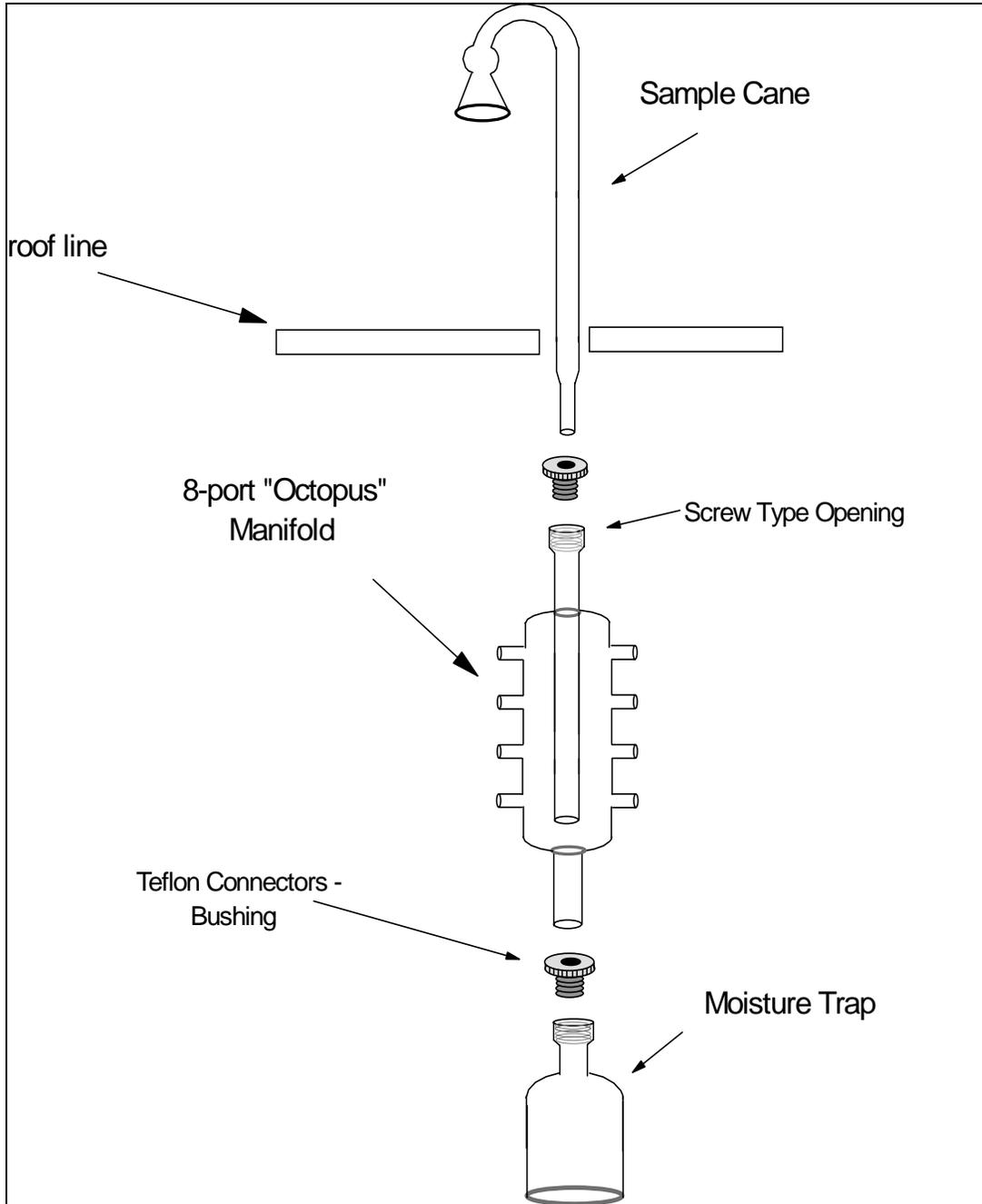
However, this may affect the response of the instruments since they are usually operated with the blower on.

- Horizontal manifolds have been known to collect water, especially in humid climates. Standing water in the manifold can be pulled into the instrument lines. Since most monitoring shelters are maintained at 20-30 °C, condensation can occur when warm humid outside air enters the manifold and is cooled. Station operators must be aware of this issue and mitigate this situation if it occurs. Tilting the horizontal manifold slightly and possibly heating the manifold have been used to mitigate the condensation problem. Water traps should be emptied whenever there is standing water.



**Figure 1. Conventional T-Type Glass Manifold System**

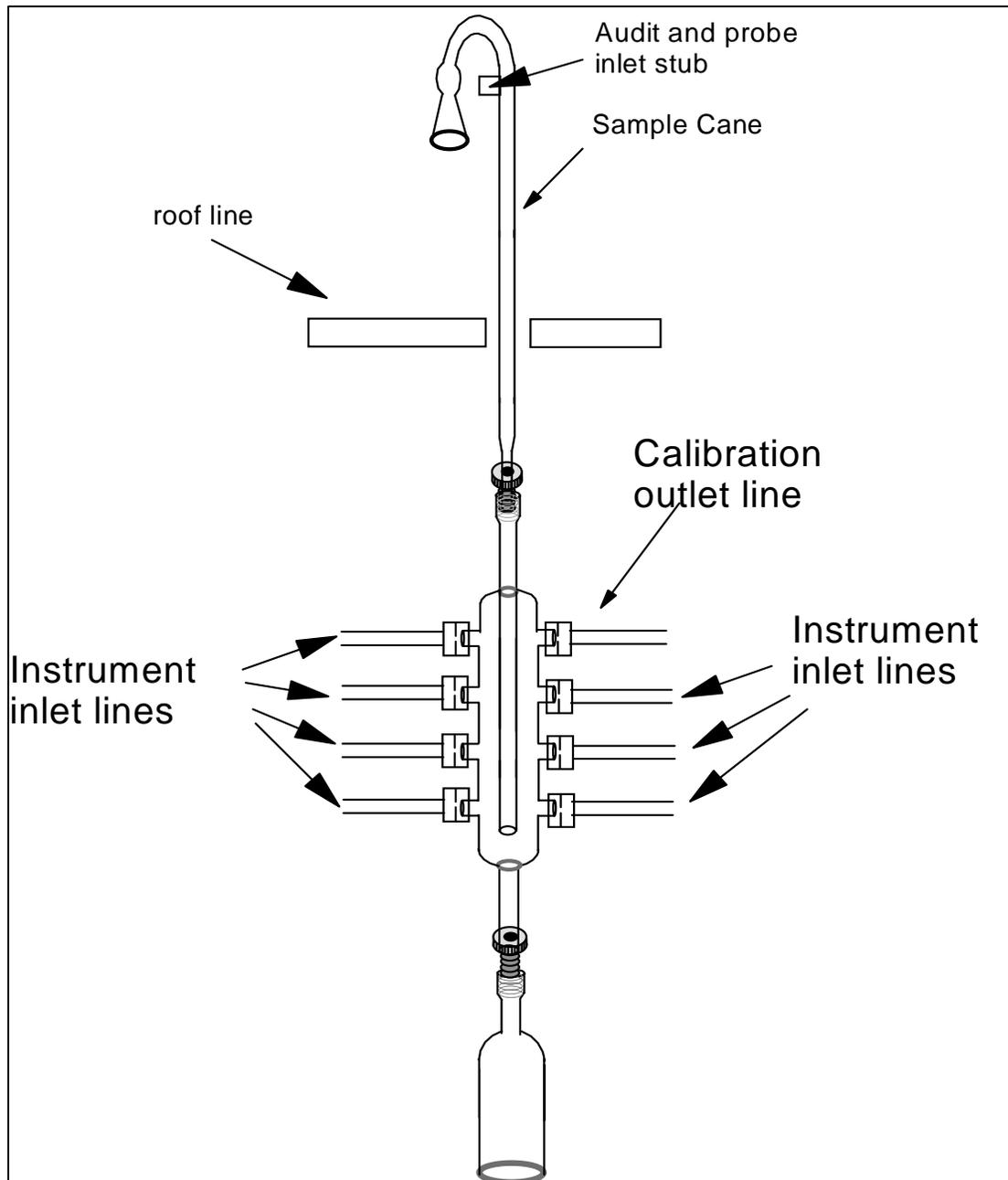
**California Air Resources Board “Octopus” Style:** Another type of manifold that is being widely used is known as the California Air Resources Board (CARB) style or “Octopus” manifold, illustrated in Figure 2. This manifold has a reduced profile, i.e., there is less volume in the cane and manifold; therefore, there is less need for a blower motor. If the combined flow rates of the gas analyzers are high enough, then an additional blower is not required.



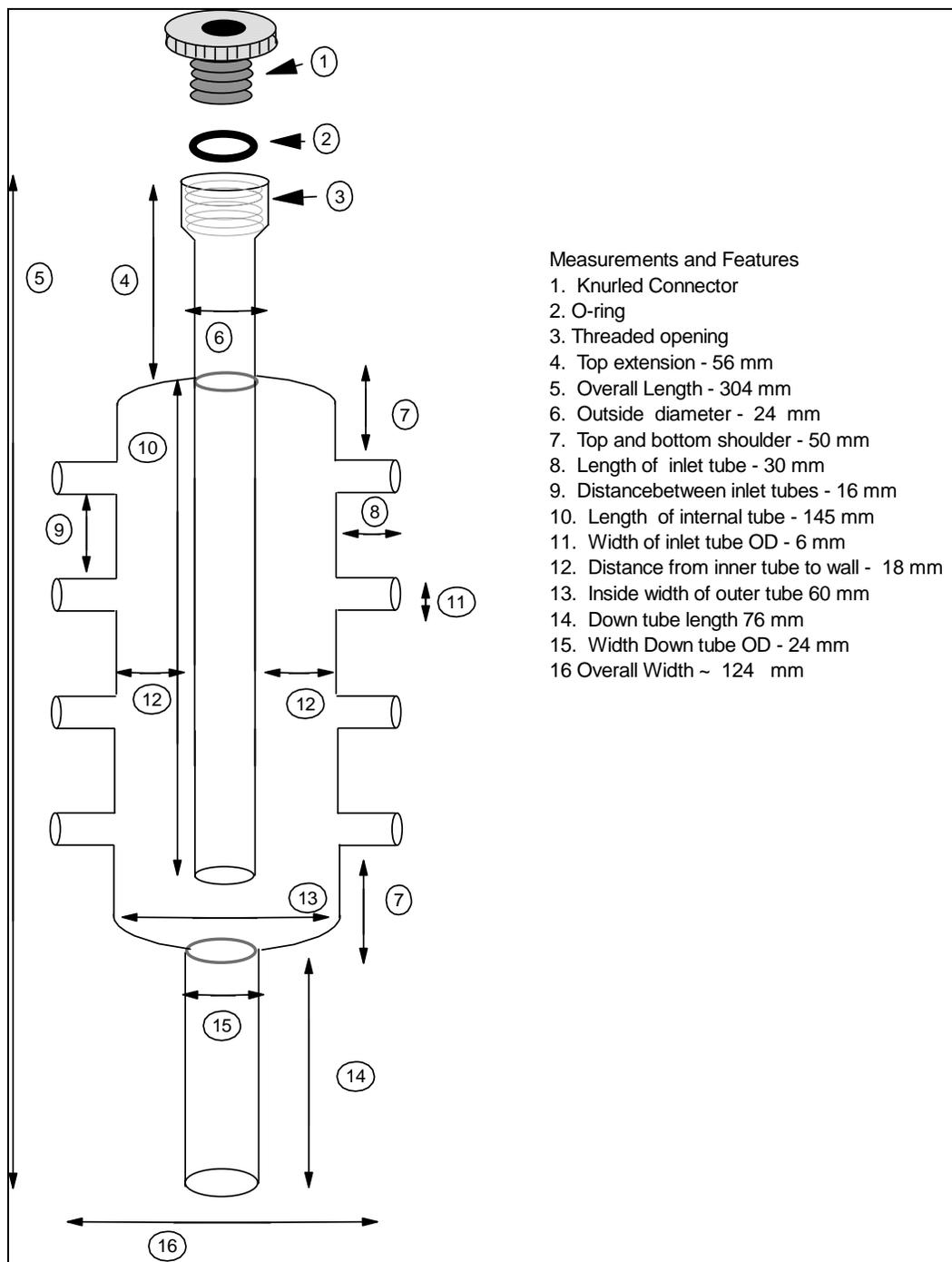
**Figure 2. CARB or “Octopus” Style Manifold**

**Placement of Tubing on the Manifold:** If the manifold employed at the station has multiple ports (as in Figure 2) then the position of the instrument lines relative to the calibration input line can be crucial. If a CARB “Octopus” or similar manifold is used, it is suggested that sample connections for analyzers requiring lower flows be placed towards the bottom of the manifold.

Also, the general rule of thumb states that the calibration gas delivery line (if used) should be in a location so that the calibration gas flows past the analyzer inlet points before the gas is evacuated out of the manifold. Figure 3 illustrates two potential locations for introduction of the calibration gas. One is located at the ports on the “Octopus” manifold, and the other is upstream near the air inlet point, using an audit or probe inlet stub. This stub is a tee fitting placed so that “Through-the-Probe” audit line or sampling system tests and calibrations can be conducted.



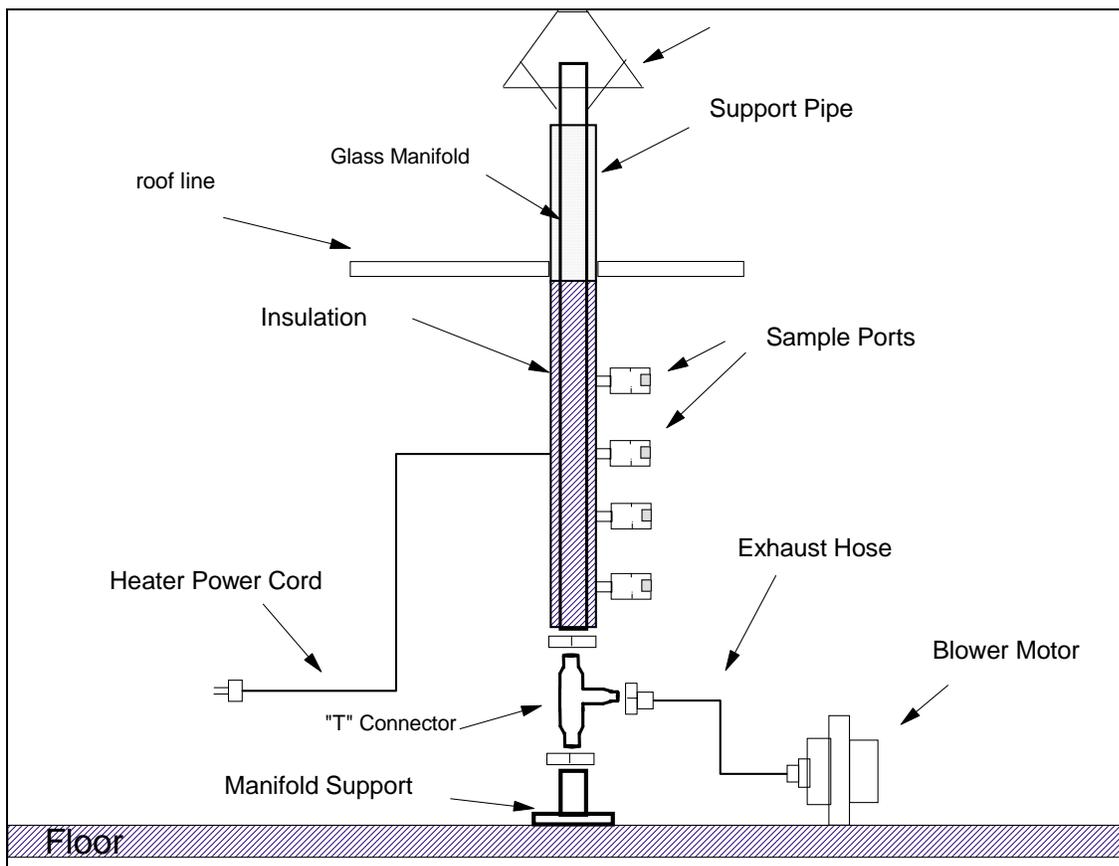
**Figure 3. Placement of Lines on the Manifold**



**Figure 4. Specifications for an ‘Octopus’ Style Manifold**

Figure 4 illustrates the specifications of an Octopus style manifold. Please note that EPA-OAQPS has used this style of manifold in its precursor gas analyzer testing program. This type of manifold is commercially available.

**Vertical Manifold Design:** Figure 5 shows a schematic of the vertical manifold design. Commercially available vertical manifolds have been on the market for some time. The issues with this type of manifold are the same with other conventional manifolds, i.e., when sample air moves from a warm humid atmosphere into an air-conditioned shelter, condensation of moisture can occur on the walls of the manifold. Commercially available vertical manifolds have the option for heated insulation to mitigate this problem. Whether the manifold tubing is made of glass or Teflon®, the heated insulation prevents viewing of the tubing, so the interior must be inspected often. The same issues apply to this manifold style as with horizontal or “Octopus” style manifolds: additional blower motors should not be used if the residence time is less than 20 seconds, and the calibration gas inlet should be placed upstream so that the calibration gas flows past the analyzer inlets before it exits the manifold.

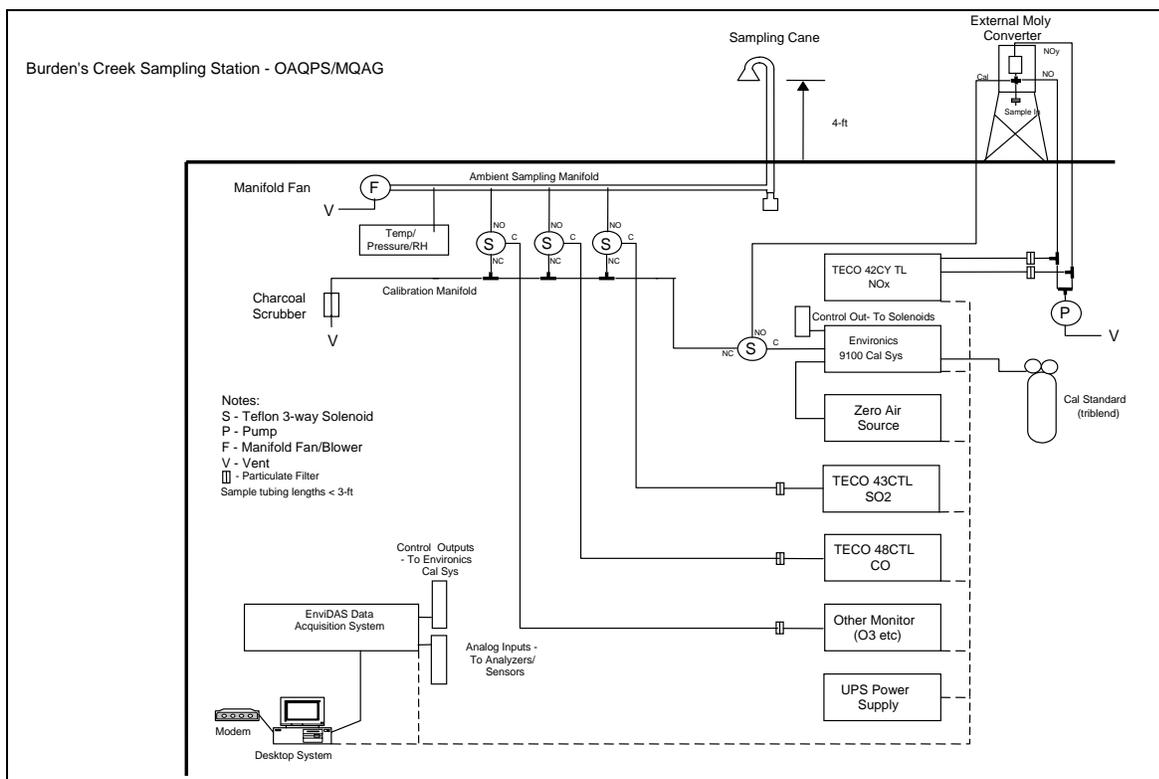


**Figure 5. Example of Vertical Design Manifold**

**Manifold/Instrument Line Interface:** A sampling system is an integral part of a monitoring station, however, it is only one part of the whole monitoring process. With the continuing integration of advanced electronics into monitoring stations, manifold design must be taken into consideration. Data Acquisition Systems (DASs) are able not only to collect serial and analog data from the analyzers, but also to control Mass Flow Calibration (MFC) equipment and solid state solenoid switches, communicate via modem or Ethernet, and monitor conditions such as shelter temperature and manifold pressure. As described in Chapter 6, commercially available DASs may implement these features in an electronic data logger, or via software installed on a personal computer. Utilization of these features allows the DAS and support equipment to perform automated calibrations (Autocal). In addition to performing these tasks, the DAS can flag data during calibration periods and allow the data to be stored in separate files that can be reviewed remotely.

Figure 6 shows a schematic of the integrated monitoring system at EPA's Burden Creek NCore monitoring station. Note that a series of solenoid switches are positioned between the ambient air inlet manifold and an additional "calibration" manifold. This configuration allows the DAS to control the route from which the analyzers draw their sample. At the beginning of an Autocal, the DAS signals the MFC unit to come out of standby mode and start producing zero or calibration gas. Once the MFC has stabilized, the DAS switches the analyzers' inlet flow (via solenoids) from the ambient air manifold to the calibration manifold. The calibration gas is routed to the instruments, and the DAS monitors and averages the response, flagging the data appropriately as calibration data. When the Autocal has terminated, the DAS switches the analyzers' inlet flow from the calibration manifold back to the ambient manifold, and the data system resets the data flag to the normal ambient mode.

The integration of DAS, solenoid switches, and MFC into an automated configuration can bring an additional level of complexity to the monitoring station. Operators must be aware that this additional complexity can create situations where leaks can occur. For instance, if a solenoid switch fails to open, then the inlet flow of an analyzer may not be switched back to the ambient manifold, but instead will be sampling interior room air. When the calibrations occur, the instrument will span correctly, but will not return to ambient air sampling. In this case, the data collected must be invalidated. These problems are usually not discovered until there is an



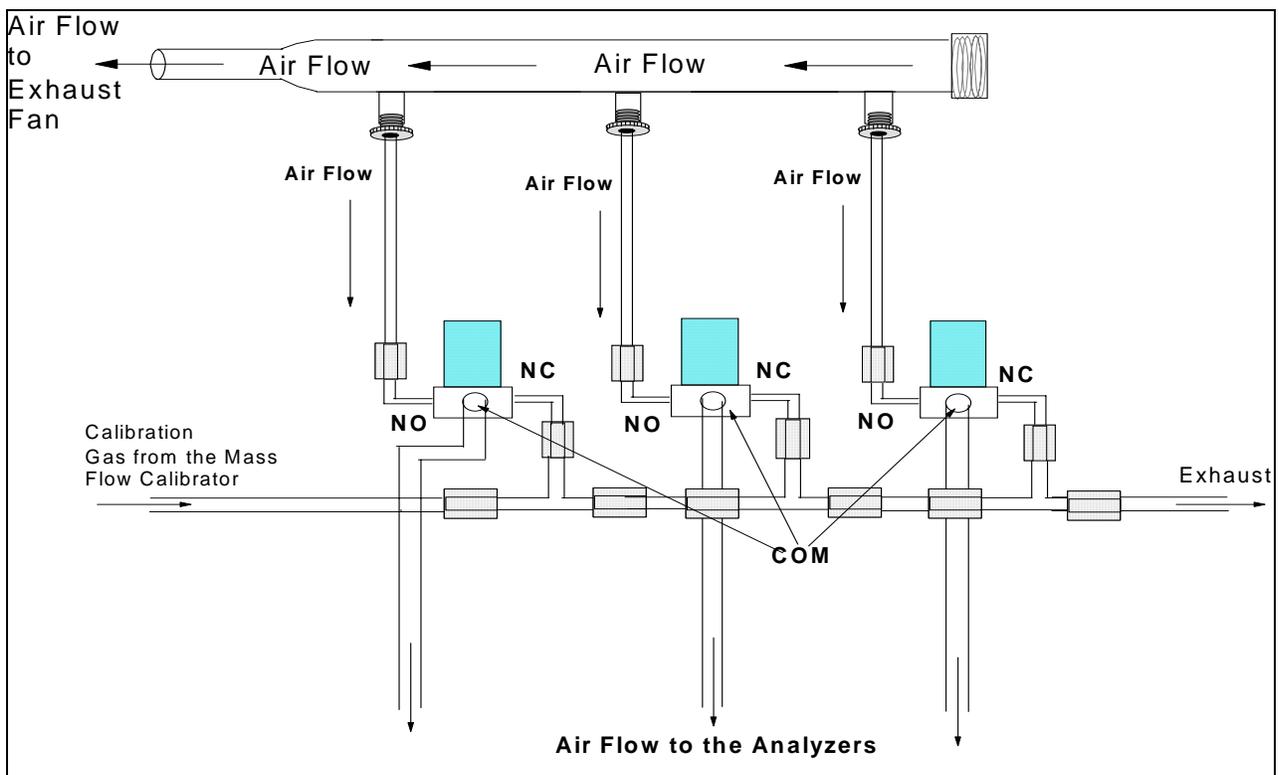
**Figure 6. Example of a Manifold/Instrument Interface**

external “Through-the Probe” audit, but by then extensive data could be lost. It is recommended that the operator remove the calibration line from the calibration manifold on a routine basis and challenge the sampling system from the inlet probe. This test will discover any leak or switching problems within the entire sampling system.

Figure 7 shows a close up of an ambient/calibration manifold, illustrating the calibration manifold – ambient manifold interface. This is the same interface used at EPA’s Burden’s Creek monitoring station. The interface consists of three distinct portions: the ambient manifold, the solenoid switching system and the calibration manifold. In this instance, the ambient manifold is a T-type design that is being utilized with a blower fan at the terminal. Teflon® tubing connects the manifold to the solenoid switching system. Two-way solenoids have two configurations. Either the solenoid is in its passive state, at which time the ports that are connected are the normally open (NO) and the common (COM). In the other state, when it is energized, the ports that are connected are the normally closed (NC) and the COM ports. Depending on whether the

solenoid is 'active' or not, the solenoid routes the air from the calibration or ambient manifold to the instrument inlets. There are two configurations that can be instituted with this system.

1. Ambient Mode: In this mode the solenoids are in "passive" state. The flow of air (under vacuum) is routed from the NO port through the solenoid to the COM port.
2. Calibration Mode: In this mode, the solenoids are in the "active" state. An external switching device, usually the DAS, must supply direct current to the solenoid. This causes the solenoid to be energized so that the NO port is shut and the NC port is now connected to the COM port. As in all cases, the COM port is always selected. The switching of the solenoid is done in conjunction with the MFC unit becoming active; generally, the MFC is controlled by the DAS. When the calibration sequences have finished, the DAS stops the direct current from being sent to the solenoid and switches automatically back to the NO to COM (inactive) port configuration. This allows the air to flow through the NO to COM port and the instrument is now back on ambient mode.



**Figure 7. Ambient – Calibration Manifold Interface**

## Reference

1. Code of Federal Regulations, Title 40, Part 58, Appendix E.9

## **APPENDIX B**

### **STANDARD OPERATING PROCEDURES FOR SELECTED TRACE LEVEL PRECURSOR GAS MONITORING AND CALIBRATION EQUIPMENT**

SOP's also available at: <http://www.epa.gov/ttn/amtic/precursop.html>

**STANDARD OPERATING PROCEDURES**  
**THERMO ELECTRON CORPORATION MODEL 48C-TLE**  
**TRACE LEVEL CO INSTRUMENT**

**Version 2**



## **Section 1.1 Acknowledgments**

This Standard Operating Procedure (SOP) for Carbon Monoxide – Trace Level is the product of EPA’s Office of Air Quality, Planning and Standards. The following individuals are acknowledged for their contributions.

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## STANDARD OPERATING PROCEDURES THERMO 48C-TLE TRACE-LEVEL CO INSTRUMENT

### 3.0 PROCEDURES

#### 3.1 Scope and Applicability

Carbon Monoxide (CO), a colorless, odorless, tasteless, highly poisonous gas has detrimental effects on human health. CO originates from the partial oxidation of hydrocarbon fuels, coal and coke<sup>1</sup>. CO affects the oxygen carrying capacity of the blood. CO can diffuse through the alveolar walls of the lungs and compete with oxygen for one of the four iron sites in the hemoglobin molecule. The affinity of the iron site for CO is approximately 210 times greater than oxygen<sup>2</sup>. Low levels of CO can cause a number of symptoms including headache, mental dullness, dizziness, weakness, nausea, vomiting and loss of muscular control. In extreme cases, collapse, unconsciousness and death can occur.

The Thermo Electron Corporation (TECO) model 48C-TLE is a state of the science instrument for the determination of trace levels of CO by Non-Dispersive Infrared Spectrophotometry (NDIR) using Gas Filter Correlation (GFC). This SOP will detail the operation, preventive maintenance, cautions and health warnings.

The Detection Limit (DL) for non-trace levels of CO is 1.0 parts per million (ppm) (*Code of Federal Regulations*, Volume 40, Part 53.23c, or, in the shortened format used hereafter, 40 CFR 53.23c)<sup>3</sup>. However, the 48C-TLE has a DL to 20 parts per billion (ppb), which is accomplished by modifications to the Federal Reference Method (FRM) instruments. This document will discuss the Trace Level (TL) operating procedures in detail.

#### 3.2 Summary of Method

The analytical principle is based on absorption of IR light by the CO molecule. NDIR-GFC analyzers operate on the principle that CO has a sufficiently characteristic IR absorption spectrum such that the absorption of IR by the CO molecule can be used as a measure of CO concentration in the presence of other gases. CO absorbs IR maximally at 2.3 and 4.6  $\mu\text{m}$ . Since NDIR is a spectrophotometric method, it is based upon the Beer-Lambert Law. The degree of reduction depends on the length of the sample cell, the absorption coefficient, and CO concentration introduced into the sample cell, as expressed by the Beer-Lambert law shown below:

$$T = I/I_0 = e^{(-axC)} \quad (\text{equation 1})$$

where:

- T = Transmittance of light through the gas to the detector
- I = light intensity after absorption by CO
- I<sub>0</sub> = light intensity at zero CO concentration
- a = specific CO molar absorption coefficient
- x = path length, and
- C = CO concentration

For Gas Filter Correlation, there is only one sample cell. This cell acts as the sample and reference cell. The broad band of IR radiation is emitted from an IR source. The IR light passes through a very narrow band pass filter which screens out most wavelengths and allows only the light that CO absorbs to enter the sample cell. The GFC analyzer has a chopper wheel with two pure gases: Nitrogen and CO. As the chopper wheel rotates and allows the IR energy to enter “CO side” of the wheel, all IR energy that could be absorbed by CO in the sample stream is absorbed by the CO in the wheel. This technique effectively “scrubs out” any light that could possibly be attenuated. The single detector records the light level ( $I_0$ ). As the wheel spins, the “N<sub>2</sub> side” of the wheel reaches the IR energy beam. This side of the wheel allows all IR light to pass through the wheel and be absorbed by any CO that might be in the sample gas. This light level is CO sensitive ( $I$ ). The detector records the attenuation of this light, compares the two light levels ( $I/I_0$ ) and sends a signal to the electrometer board that calculates the concentration. The voltage is related to the CO concentration according to the Beer-Lambert law in equation 1 shown above. Thus, TECO 48C-TLE can be measured continuously. The 48C-TLE version has four distinct features that allow it to measure CO at ppb levels:

- Required sample stream dried using permeation dryer;
- Analyzer baseline determined and corrected using heated Carolite catalytic converter;
- Frequent auto-zero, at a minimum once per hour, through the catalytic converter;
- The instrument has an ultra-sensitive or “hot” detector.

The 48C-TLE instrument operates in the following fashion:

1. In sample mode, ambient air is allowed to enter through the rear bulkhead sample port. Solenoid #1 is in its Normally Open (NO) mode. The ambient air flows through the solenoid to the permeation dryer, which removes the moisture and water from the air stream.
2. The sample stream then passes through a sample filter, which removes particles that can build up on the mirror and sample chamber and attenuate the IR beam.
3. The sample then enters the sample cell. A major difference between a non-TL and TL instrument is the detector. The TL instrument has a detector that is more sensitive to the light emitted and absorbed in the sample cell. This detector must be more sensitive because the amount of attenuation by the CO gas in the sample stream is much lower. Therefore, the detector must be sensitive at lower ambient levels. Temperature of the sample cell is also critical. The sample cell and detector must be maintained at a constant temperature in order for the detector to keep a stable background. Fluctuations of more than 1° Centigrade can cause the baseline to drift, giving false readings at low levels.
4. The detector sends the signal to the demodulator which interprets the signal. The demodulator sends a digital value to the Central Processor Unit (CPU).
5. At the end of the hour, the CPU sends a voltage signal to the Solenoid #1 and switches it to the “Normally Closed” (NC) position. This allows room air to be drawn into the instrument and to pass through the catalytic converter. The catalytic converter uses a Carolite bed heated to 50° Centigrade to convert all CO to Carbon Dioxide ( $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ ). This effectively “scrubs” all CO from the sample stream. The CO “free” air flows through the sample cell and the CPU interprets the signal from the demodulator as the “background” or “baseline” value. The baseline is then adjusted at that time. The baseline adjustment takes 10 minutes.
6. The CPU then switches Solenoid #1 to its NO position and ambient air then drawn into the analyzer.

### 3.3 Definitions

Here are some key terms for this method.

**Table 3-1 Definitions of Key Terms**

Term	Definition
DAS	Data acquisition system. Used for automatic collection and recording of CO concentrations.
Interferences	Physical or chemical entities that cause CO measurements to be higher (positive) or lower (negative) than they would be without the entity. (See Section 3.6).

### 3.4 Health and Safety Warnings

To prevent personal injury, please heed these warnings concerning the 48C-TLE.

1. CO is a poisonous gas. Vent any CO or calibration span gas to the atmosphere rather than into the shelter or other sampling area. If this is impossible, limit exposure to CO by getting fresh air every 5 to 10 minutes. If the operator experiences light headedness, headache or dizziness, leave the area immediately.
2. The IR source is a filament resistor that has an electrical current running through it. The IR source can become very hot. When troubleshooting, allow the instrument to cool off especially if you suspect the IR source as the cause of trouble.
3. Always use a third ground wire on all instruments.
4. Always unplug the analyzer when servicing or replacing parts.
5. If it is mandatory to work inside an analyzer while it is in operation, use extreme caution to avoid contact with high voltages. The analyzer has a 110 volt Volts Alternating Current (VAC) power supply. Refer to the manufacturer's instruction manual and know the precise locations of the VAC components before working on the instrument.
6. Avoid electrical contact with jewelry. Remove rings, watches, bracelets, and necklaces to prevent electrical bums.

### 3.5 Cautions

To prevent damage to the 48C-TLE, all cautions should immediately precede the applicable step in this SOP. The following precautions should be taken:

1. Normally, if Teflon™ filters are used in the sample train, cleaning the optical bench will not be required. However, in the event that the bench is cleaned, be careful to avoid damaging the interior of the sample chamber. In addition, some GFC instruments have a series of mirrors that deflect the light in order to increase the path length. The mirrors are aligned at the factory. If the mirrors become misaligned, the IR light beam will not be directed to the detector. Use extreme caution when cleaning or servicing the sample chamber(s). In addition the mirrors are very fragile. Avoid dropping the instrument. This may damage, misalign or crack the mirrors and cause expensive repairs.
2. Keep the interior of the analyzer clean.
3. Inspect the system regularly for structural integrity.

4. To prevent major problems with leaks, make sure that all sampling lines are reconnected after required checks and before leaving the site.
5. Inspect tubing for cracks and leaks. The permeation dryer may rest upon parts that vibrate, such as the air pump. Check the areas of the permeation dryer where they come into contact with other parts.
6. It is recommended that the analyzer be leak checked after replacement of any pneumatic parts.
7. If cylinders are used in tandem with Mass Flow Control (MFC) calibrators, use and transport of cylinders are a major concern. Gas cylinders can sometimes contain pressures as high as 2000 pounds per square inch. Handling of cylinders must be done in a safe manner. If a cylinder is accidentally dropped and valve breaks off, the cylinder can become explosive or a projectile.
8. Transportation of cylinders is regulated by the Department of Transportation (DOT). It is strongly recommended that all agencies contact the DOT or Highway Patrol to learn the most recent regulations concerning transport of cylinders.
9. CO is a highly poisonous gas. Long term exposure can cause problems with motor coordination and mental acuity. It is strongly recommended that all agencies have Material Safety Data Sheets (MSDS) at all locations where CO cylinders are stored or used. MSDS can be obtained from the DOT or from your vendor.
10. It is possible (and practical) to blend other compounds with CO. If this is the case, it is recommended that MSDS for all compounds be made available to all staff that use and handle the cylinders or permeation tubes.
11. Shipping of cylinders is governed by the DOT. Contact the DOT or your local courier about the proper procedures and materials needed to ship high-pressure cylinders.

### 3.6 Interferences

**Water Vapor:** Studies have shown conclusively that NDIR analyzers have interference from water vapor. Water absorbs very strongly across several bands of IR spectra. Water vapor interference occurs because water vapor absorption of light in the region of 3.1, 5.0 -5.5 and 7.1 -10.0  $\mu\text{m}$  in the IR region. Since water vapor absorbs light in this region, this has a quenching effect on the reaction of CO. The TECO 48C-TLE is equipped with a permeation drier, which effectively scrubs all water and water vapor. No maintenance is required on the dryer.

**Carbon Dioxide:** CO<sub>2</sub> absorbs in the IR spectrum at 2.7, 5.2, and 8.0 to 12.0  $\mu\text{m}$ . This is very close to the regions that CO absorbs within as well. However, since atmospheric carbon dioxide is much higher in concentration than CO, this UV spectral range must be avoided. To prevent light in this spectral region, the TECO 48C-TLE analyzer has a band pass filter that blocks these wavelengths.

### 3.7 Personal Qualifications

The person(s) chosen to operate the TECO 48C-TLE should have a minimum of qualifications. The understanding of basic chemistry and electronics are a must. The understanding of digital circuitry is helpful, but not required. Also, courses in data processing and validation are also welcome.

### 3.8 Equipment and Supplies

**Monitoring Apparatus:** The design of the 48C-TLE is identical to the 48C, with several major variations. A diagram of the TECO 48C-TLE instrument is described in Figure 3-1. The three main components are:

- Pneumatic System: Consists of sample inlet line, particulate filter, filter holder, permeation dryer, reaction chamber, flowmeter, and pump, all used to bring ambient air samples to the analyzer inlet.

- **Analytical System:** This portion of the instrument consists of the IR source, the correlation wheel, motor, mirrors, detector and band pass filter.
- **Electronic Hardware:** The part of the analyzer that generally requires little or no maintenance. The brain of the 48C series is the CPU. It monitors and regulates motor speed, temperatures, flows and pressure. It also monitors and stores diagnostic information. If the 48C-TLE is operated above the manufacturer's recommended temperature limit, however, individual integrated chips can fail and cause problems with data storage or retrieval.

Other apparatus and equipment includes the following.

**Instrument Shelter:** A shelter is required to protect the analyzer from precipitation and adverse weather conditions, maintain operating temperature within the analyzer's temperature range requirements, and provide security and electrical power. The recommended shelter temperature range is 20-30°C.

**Spare Parts and Incidental Supplies:** See the TECO 48C-TLE operating manual, Section 5-1 for specific maintenance and replacement requirements.

**Calibration System:** A system that creates concentrations of CO of known quality is necessary for establishing traceability. This is described in detail in the "EnviroNics 9100 SOP." Please reference this document.

**DAS:** A data acquisition system is necessary for storage of ambient and ancillary data collected by the 48C-TLE.

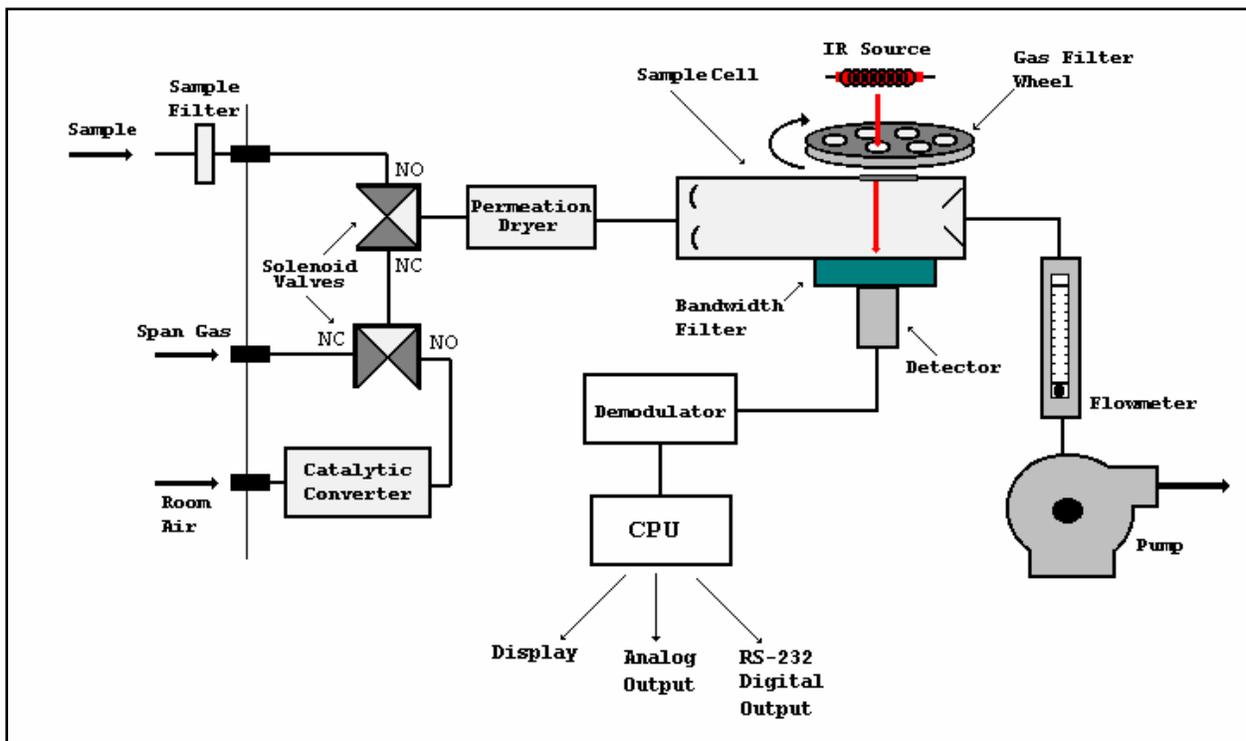


Figure 3-1 Schema of the TECO 48C-TLE

**Wiring, Tubing and Fittings:** Teflon™ and borosilicate glass are inert materials that should be used exclusively throughout the intake system. It is recommended that Polytetrafluoroethylene (PTFE) or Fluoroethylpropylene (FEP) Teflon™ tubing be used. PTFE and FEP are the best choice for the connection between the intake manifold and the 48C-TLE bulkhead fitting. Examine and discard if particulate matter collects in the inlet tubing. All fittings and ferrules should be made of Teflon™ or stainless steel. Connection wiring to the DAS should be shielded two strand wire or RS-232 cables for digital connections.

**Reagents and Standard:** The TECO 48C-TLE does not require any reagents since the instrument uses photometry to analyze for CO. All standards for the CO method can be obtained in compressed cylinders and must be NIST traceable. Please see the “Calibration of Trace Gas Analyzers” SOP.

### 3.9 Procedure

**3.9.1 Sample Collection:** Sampling for Trace Level CO is performed by drawing ambient air through a sample manifold directly into the analyzer continuously via a vacuum pump. All inlet materials must be constructed from Teflon™ or borosilicate glass as detailed in 40 CFR 58. The siting criteria for CO Trace Level instruments is detailed in 40 CFR 58, appendix A<sup>4</sup>.

**3.9.2 Sample Handling and Preservation:** CO samples receive no special preparation prior to analysis. Therefore this SOP does not need a section on Sample Handling and Preservation.

#### 3.9.3 Instrument Operation, Startup and Maintenance

This section discusses startup, operation and maintenance of the 48C-TLE. The TECO 48C-TLE series instrument has a digital front panel screen with selection switches below. This allows the user to check functions, switch operating parameters, adjust zero and span and read warnings messages. **It is extremely important that the users familiarize themselves with the menus available. Inadvertently changing parameters within the analyzer can damage the instrument and possibly invalidate data as well. Please reference the TECO 48C-TLE owner’s manual and read it carefully before adjusting any parameters that are set by the factory.**

##### 3.9.3.1 Start up

The following text is taken from the TECO 48C-TL manual. It is identical for the 48C-TLE model.

The Model 48C Trace Level is shipped complete in one container. If, upon receipt of the analyzer, there is obvious damage to the shipping container, notify the carrier immediately and hold for inspection. The carrier, and not Thermo Environmental Instruments Inc., is responsible for any damage incurred during shipment. Follow the procedure below to unpack and inspect the instrument.

1. Remove the instrument from the shipping container and set on a table or bench that allows easy access to both the front and rear of the instrument.
2. Remove the instrument cover to expose the internal components and remove any packing material.
3. Check for possible damage during shipment and check that all connectors and printed circuit boards are firmly attached.
4. Re-install the instrument cover.
5. Connect the sample line to the sample bulkhead on the rear panel. Ensure that the sample line is not contaminated by dirty, wet or incompatible materials. All tubing should be constructed of Teflon™ or borosilicate glass with an OD of 1/4” and a minimum ID of 1/8”.

6. The length of the tubing should be less than 10 feet.
7. All gas must be delivered to the instrument at atmospheric pressure. It may be necessary to employ an atmospheric bypass plumbing arrangement or attach the instrument inlet line to a manifold that is vented to the atmosphere.
8. Connect the exhaust bulkhead to a suitable vent. The exhaust line should be ¼" OD (outside diameter) with a minimum ID of 1/8" OD. The length of the exhaust line should be less than 10 feet. Verify that there is no restriction in this line.
9. Connect a suitable recording device to the rear panel terminals. The EPA recommends, but does not require, recording of the data digitally. The TECO 48C-TLE has this option. Please refer to the "Data Acquisition and Management" SOP. If the DAS system that you have does not have the RS-232 capabilities, then proceed to the next section, Diagnostic Checks/Manual Checks. If you have connected the 48C-TLE to a computer or DAS, review the Diagnostic Check from your computer screen. TECO offers TECO communication software, a computer program that allows the operator to log the diagnostic data that is collected by the 48C-TLE CPU. Several DAS manufacturers offer this type of software as well.
10. Plug the instrument into an outlet of the appropriate voltage and frequency. The Model 48C Trace Level is supplied with a three-wire grounding cord. Under no circumstances should this grounding system be defeated.
11. Turn the power on.

### 3.9.3.2 Operation and Range Setting

1. The exhaust fan will start and the display will come on. The Central Processing Unit (CPU) will boot the system and load the firmware.
2. The display has a 4 line by 20 character alphanumeric display that shows the sample concentration, instrument parameters, instrument controls and help/warning messages. The menus for access (as described in sections 3.9.3.4 and 3.9.3.5 of this SOP) are performed using the display and the 6 push-buttons just below the display.
3. Once the instrument loads the firmware, the display will display "CO PPM XX.XX, below this value is the time and "REMOTE." This is the "RUN" menu and should always be left in the "RUN" menu when it is collecting ambient data.
4. To access the Main Menu, press the "Menu." This will put you into the Main Menu.
5. From the Main Menu, Use the ↑ and ↓ pushbuttons move the cursor down so that the arrow is next to "Range" selection. Press "Enter."
6. The Range menu contains the gas units, CO ranges, and the custom ranges. In the upper right corner of the display, the words "SINGLE, DUAL, or AUTO" is displayed to indicate the active mode. The "Range" menu in the dual and auto-range modes appear the same except for the word DUAL or AUTO, displayed in the upper right corner. For more information about the SINGLE, DUAL, or AUTO-range modes, see page 3-6 of the owner's manual. The default is set to single range.
7. To set the upper scale range, use the ↑ and ↓ pushbuttons to move the cursor down so that the arrow is next to "CO Range" selection. Press "Enter."
8. Use the "↑↓→←" buttons on the front panel to enter in the desired concentration, this should be "5." Press "Enter."
9. Press "Menu" and then press "Run." The full scale range has now been set to 5.00 ppm. The default for the units is "ppm." It is recommended that this not be changed.
10. In single range mode, there is one range, one averaging time, and one span coefficient. The two CO analog outputs are arranged on the rear panel terminal strip as shown in Figure 3-3 of the owner's manual. To use the single range mode, set option switches 4 and 5 off. For more information about

setting the internal option switches, see .Internal Option Switches, on page 3-7.

### 3.9.3.3 Diagnostic Checks/Manual Checks

To determine whether the 48C-TLE is working properly, the field operators should perform the Diagnostic Checks every time they visit the monitoring station. It is good practice for the operator to check these Diagnostic Checks either by the computer or manually. Figure 3-2 of this SOP has the menu “tree” that was taken from the TECO 48 C-TL manual. By pressing the “menu” button and following the tree, an operator can easily get to the location needed.

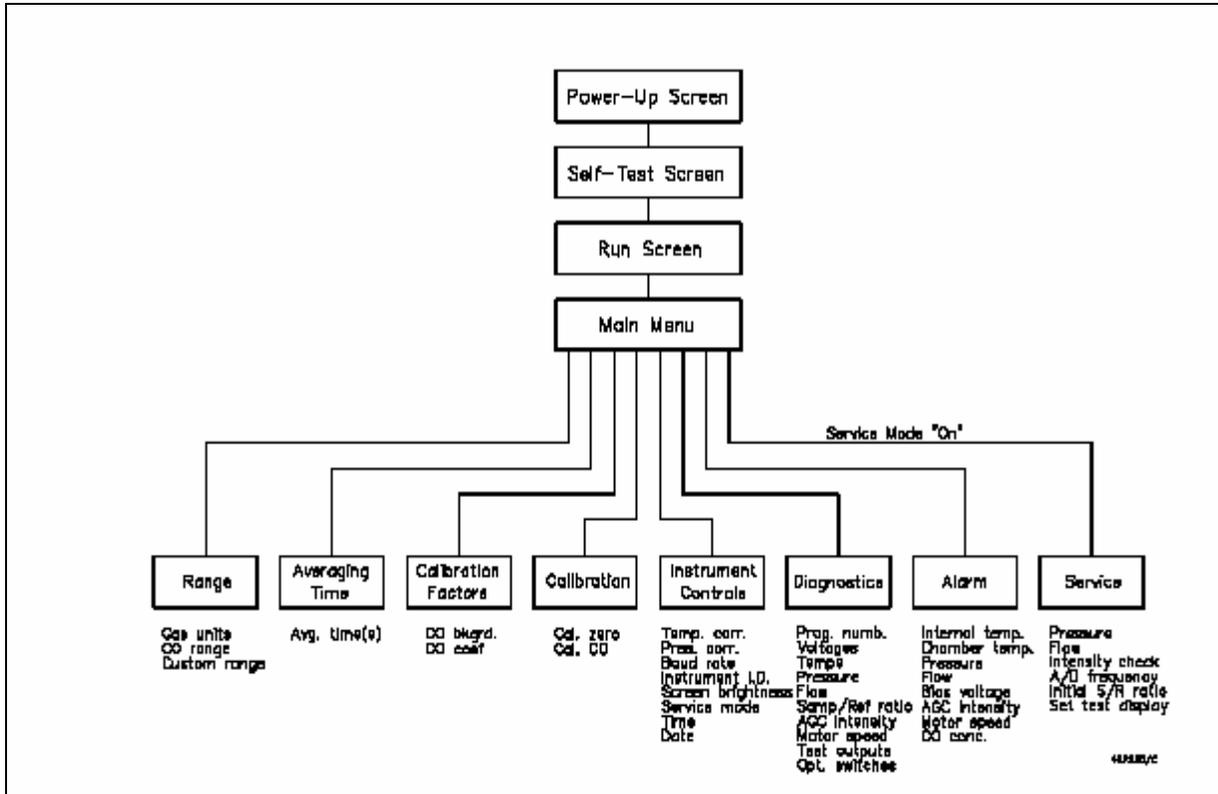


Figure 3-2 Menu Tree Schema

Below are instructions on how to perform the diagnostic checks manually. Please note that the TECO 48C-TLE has set upper and lower ranges for some of these Diagnostic checks. Please reference the owner’s manual for these ranges. Please use the following instructions to access the Diagnostic data.

1. While in the “Run” menu, press the “Menu” button. This will put you into the Main Menu.
2. From the Main Menu, Use the ↑ and ↓ pushbuttons move the cursor down so that the arrow is next to “Diagnosics” selection. Press “Enter.”
3. In the Diagnostics Menu, the operator can toggle the arrow using the ↑ and ↓ pushbuttons to align the arrow to the selection. Once the operator has toggled the arrow to the diagnostic check desired, press “Enter.” This will allow you to see the desired information. Record this information on your field work sheet. Please see Table 3-2 for a list of Diagnostic Checks and a brief explanation. Please check the Owners Manual for the manufacturer’s recommended ranges.

4. Once the operator has reviewed all of the diagnostic information, return to the Main Menu by pressing “Menu” followed by “Run.”

**Table 3-2 Diagnostic Checks**

Check	Explanation
Program Number	The current software version used by the instrument
Voltages	There are four voltages that should be recorded.
Temperatures	There are two temperatures that should be recorded: internal and chamber. Reference Page 3-47 for details.
Pressure	This is the pressure inside of the optics bench.
Flow	This is the actual flow rate through the optics bench. Reference page 3-53 for specifications.
S/R Ratio	Sample/Reference Ratio. This is the ratio of the intensities of the light source through the sample side and the reference side of the correlation wheel. Please See page 3-38 for the optimal values.
AGC Intensity	Automatic Gain Control. The AGC displays the intensity (in Hertz) of the reference channel. The AGC circuit optimizes the noise and resolution level of the analyzer. Please see page 3-39 for details.
Motor Speed	This displays, in percentage, the status of the chopper motor. This value should be 100%.

Once the Diagnostic checks have been established and recorded for the 48C-TLE, it is time to calibrate the instrument. Please refer to section 3.9.4 of this SOP.

### 3.9.3.4 Preventive Maintenance

Preventive maintenance should **prevent** down-time and data loss. Table 3.3 lists the preventive maintenance items that are should be performed. Please see section 5-1 of the owner’s manual. Section 5-1 also has a list of the spare parts that the operator should keep in stock.

**Table 3-3 Preventive Maintenance Schedule the TECO 48C-TLE**

Item	Schedule
Replace particle filter	Weekly
Diagnostics Checks	Weekly
Perform Level I calibration	Daily
Replace IR source	As needed
Leak Check and Pump Check Out	Annually
Inspect Pneumatic Lines	Semi-annually
Clean inside of Chassis	As needed

Rebuild or replace pump	As needed
Clean optic bench	As needed
Replace wheel motor	As needed
Replace gases in correlation wheel	As needed

### 3.9.3.5 Instrument Troubleshooting

The TECO 48C-TLE manual has an excellent troubleshooting guide in Section 6-1 of the manual. For details on using the Test Functions for predicting failures, please reference this section.

### 3.9.4 Calibration and Standardization

The calibration of the TECO 48C-TLE is performed by comparing the digital or analog output of the instrument against standardized gases of known quality. Generation of these gases is detailed in the "Calibration of Trace Gas Analyzers" SOP. The recommended ranges for the calibration are detailed in Table 4-2. This section will detail how to adjust the 48C-TLE to the standardized gases. Once the calibration has been performed, compare the response of your DAS to the calculated "source" value. If this is outside of +/-10%, then adjust the instrument response as detailed in the next sections of this SOP.

#### 3.9.4.1 Adjustment to Zero Air

In order to adjust the output of the 48C-TLE to zero air, perform the following:

1. Allow the instrument to sample zero air from a manifold that is at near atmospheric pressure for a minimum of 15 minutes.
2. On the front panel press the "Menu" button. This will bring up the main menu. Using the ↓ arrow until the cursor is on the "Calibration" selection. Press "Enter."
3. This next screen is the "Calibration" screen. In this screen press the ↑↓ buttons until you align the cursor at the "Calibrate Zero" selection. Press "Enter."
4. The next screen will show a "CO PPM X.X above the words "SET TO ZERO?" If the analyzer has stabilized to zero air, press "Enter." Then Press "Menu" and then press "Run." This will adjust the baseline to the zero air. If you decide to adjust the higher range response, continue on to Section 3.9.4.2.

#### 3.9.4.2 Adjustment to Calibration Gas

In order to adjust the output of the 48C-TLE to NIST traceable calibration gas, perform the following:

1. Switch the calibration unit to generate a known concentration of CO. Allow the instrument to sample calibration gas from a manifold that is at near atmospheric pressure for a minimum of 15 minutes.
2. On the front panel press the "Menu" button. This will bring up the main menu. Using the ↓ arrow until the cursor is on the "Calibration" selection. Press "Enter."
3. This next screen is the "Calibration" screen. In this screen press the ↑↓ buttons until you align the cursor at the "Calibrate CO" selection. Press "Enter."
4. The first line of the display shows the current CO concentration reading. The second line shows the instrument range and the third line states, "SET TO..... XX.XX." The next line shows "↑↓ INC/DEC." The cursor should be under one of the digits in the third line. Use the "↑↓→←" buttons on the front panel to enter in the desired concentration, that is being generated by the calibration system. Press "Enter."

5. Then Press “Menu” and then press “Run.” This will adjust the response of the instrument to the calibration gas concentration. The instrument is now calibrated.

### 3.10 Data Analysis and Calculations

Data analysis for this analyzer is detailed in “Data Acquisition and Management” SOP. For the TECO 48C-TLE, there is one design detail of which the operator must be aware; the auto-zero function. As detailed in Section 3.1 of this SOP, the TECO 48C-TLE has an auto-zero sequence that occurs at the end of the hour (default). During this period, the 48C-TLE analog output will be at or close to zero, since the detector is sampling air with the CO “scrubbed out.” While this occurs the display will illustrate “ZERO.” If the operator records the data during this sequence via the analog output, then the operator must be aware and flag this data in the DAS. The digital output via the RS-232 is flagged; therefore, no other flagging is required. The auto-zero function can be modified from once per hour to any increment up to once per day. It is recommended that the factory default not be changed from once per hour at this time.

## 4.0 QUALITY CONTROL AND QUALITY ASSURANCE

The following section has brief definitions of the QA/QC indicators. Table 4-1 has the Measurement Quality Objectives (MQOs) of the TECO 48C-TLE. Please note that this section details primarily with the QA indicators. Quality Control for continuous electronic instruments, such as the TECO 48C-TLE consists of performing the diagnostic checks, maintenance and calibrations. These procedures are detailed in sections 3.9.3 and 3.9.4: Instrument Operation, Startup and Maintenance and Calibration and Standardization. Appendix A has an example of a Quality Control and Maintenance Record developed by the EPA for this instrument. In addition, please review Table 4-2, which has the recommended operation parameters for the TECO 48C-TLE. The operation parameters include recommended operating full scale range, calibration ranges and recommended cylinder concentrations.

### 4.1 Precision

Precision is defined as the measure of agreement among individual measurements of the same property taken under the same conditions. For CO, this refers to testing the CO analyzer in the field at concentrations between 0.250 and 0.500 ppm. The test must be performed, at a minimum, once every two weeks. Calculations for Precision can be found in Reference 4.

### 4.2 Bias

Bias is defined as the degree of agreement between a measured value and the true, expected, or accepted value. Quantitative comparisons are made between the measured value and the true, standard value during audits. Generally, three upscale points and a zero point are compared. Two audit types commonly used for CO, direct comparison and blind, are discussed below. The SOP should discuss plans for each type of audit.

- **Direct Comparison Audits:** An independent audit system is brought to the monitoring location and produces gas concentrations that are assayed by the monitoring station's CO analyzer. In most cases, a person outside of the agency or part of an independent QA group within the agency performs the audit. The responses of the on-site analyzer are then compared against the calculated concentration from the independent audit system and a linear regression is generated
- **Blind Audits:** In blind audits (also called performance evaluation audits) State or Local agency staff are sent an audit device, such as the National Performance Evaluation Program (NPEP). The agency

staff does not know the CO concentrations produced by the audit equipment. Responses of the on-site analyzer are then compared against those of the generator and a linear regression is calculated.

### 4.3 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. Since the NCORE Level I and II siting criteria are urban and regional, the CO Trace Level criteria are the same. Please reference the National Monitoring Strategy<sup>5</sup> for a discussion of NCORE Level II CO monitoring scale.

### 4.4 Completeness

Completeness is defined as the amount of data collected compared to a pre-specified target amount. For CO, EPA requires a minimum completeness of 75% (40 CFR 50, App.H.3). Typical completeness with the TECO 48C-TLE values can approach 90-93%.

### 4.5 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 TECO 48C-TLE meets the MQOs for a Trace Level CO instrument. Please see Table 4-1.

### 4.6 Method Detection Limit

The method detection limit (MDL) or detectability refers to the lowest concentration of a substance that can be determined by a given procedure. The TECO 48C-TLE must be able to detect a minimum value of 0.040 ppm of CO.

**Table 4-1 Measurement Quality Assurance Objectives**

Requirement	Frequency	Acceptance Criteria	Reference	Information or Action
Bias	NCORE, once per year	To be Determined from Data Quality Objectives	40 CFR Pt.58	Use of NIST generated gas concentrations with Mass Flow Calibration unit that is NIST traceable
Precision	1 every 2 weeks	Concentration: 0.250 -0.500 ppm, Coefficient of Variance: To be determined	40 CFR Pt.58 Appendix A	To be determined
Completeness	Quarterly, Annually	NCORE, 75%	National Monitoring Strategy.	If under 75%, institute Quality Control Measures
Representativeness	N/A	Neighborhood, Urban or Regional Scale	40 CFR 58	N/A
Comparability	N/A	Must be a Trace Level instrument. See Sections 3.1 and 3.2 of this document.	National Monitoring Strategy.	N/A
Method Detection Limit	NA	0.040 ppm	National Monitoring Strategy	Testing is performed at the factory.

**Table 4-2 Operating Parameters for the TECO 48C-TLE Trace Gas Instrument**

Item	Range	Comments
Full Scale Range	0 to 5.000 ppm	Suggested Range. Reduce to 1.000 ppm if rural site
Units	Part per million (ppm)	Recommended
Compressed Gas Cylinder	200 – 250 ppm	NIST Traceable Protocol #1 cylinder with CO concentration between 200 – 250 ppm.
Calibration Ranges		
a. zero	0 – 0.010 ppm	There are a number of commercially available vendors.
b. Level I Span	4.000 – 5.000 ppm	NIST Traceable Protocol #1 cylinder with CO concentration between 200 – 250 ppm. Recommended gas flow range 75 – 90 cc/min. Zero air flow 4.80 – 5.00 liters/min.
c. Mid Point Span	2.000 – 2.500 ppm	NIST Traceable Protocol #1 cylinder with CO concentration between 200 – 250 ppm. Recommended gas flow range 75 – 90 cc/min. Zero air flow 8.00 10.00 liters/min.
d. Precision Level	0.250 – 0.500 ppm	NIST Traceable Protocol #1 cylinder with CO concentration between 200 – 250 ppm. Recommended gas flow range 20 - 35 cc/min. Zero air flow 18.00 – 20.00 liters/min.

**5.0 REFERENCES**

1. Merck Index, twelfth edition 1996, page 296
2. Seinfeld,, John H., Atmospheric Chemistry and Physics of Air Pollution, 1986, page 54
3. Code of Federal Regulations, Title 40, Part 53.23c
4. Code of Federal Regulation, Title 40, Part 58, Appendix A
5. The National Air Monitoring Strategy, Final Draft, 4/29/04, <http://www.epa.gov/ttn/amtic/monstratdoc.html>

**Appendix A**

Environmental Protection Agency  
Monthly Quality Control and Maintenance Records  
TECO 48C-TLE CO Analyzer

Site Name/Location \_\_\_\_\_

Technician \_\_\_\_\_  
Month/Year \_\_\_\_\_  
Serial Number \_\_\_\_\_ Range \_\_\_\_\_

Parameter	Date	Date	Date	Acceptance Criteria
Program Number				48 TR007 00 Communications 48LTR007 00
Bias Voltage				-105-115V
+5 volt supply				NA
+15 volt supply				NA
-15 volt supply				NA
Battery				NA
Internal Temp				8.0 – 47 deg. C
Chamber Temp				48.0 – 52.0 deg. C
Pressure				250 – 1000 mm Hg
Flow				0.35 - 2.5 LPM
S/R Ratio				1.14 – 1.18
AGC Intensity				200,000 – 300,000 Hz
Motor Speed				100%
Test Analog Outputs*				See note below
Option Switches**				See note below

\* When the operator needs to set the analog output against the DAS, this function should be utilized. Please refer to page 3-41 to 3-44 of the owner’s manual to initiate this feature.  
\* \*The option switches are set at the factory. Please reference owner’s manual, Page 3-62 “Service Mode Menu” on changing these options switches.

Date	Comments and Notes

**Figure A-1 TECO 48C-TLE Quality Control and Maintenance Record**

**STANDARD OPERATING PROCEDURES**  
**TELEDYNE - ADVANCED POLLUTION INSTRUMENTS**  
**MODEL 300EU TRACE LEVEL**  
**CARBON MONOXIDE INSTRUMENT**  
**Version 2**



## **Section 1.1 Acknowledgments**

This Standard Operating Procedure (SOP) for Carbon Monoxide – Trace Level is the product of EPA's Office of Air Quality, Planning and Standards. The following individuals are acknowledged for their contributions.

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**STANDARD OPERATING PROCEDURES**  
**TELEDYNE - ADVANCED POLLUTION INSTRUMENTS**  
**MODEL 300EU TRACE LEVEL CARBON MONOXIDE INSTRUMENT**

### 3.0 PROCEDURES

#### 3.1 Scope and Applicability

Carbon Monoxide (CO), a colorless, odorless, tasteless, highly poisonous gas has detrimental effects on human health. Carbon Monoxide originates from the partial oxidation of hydrocarbon fuels, coal and coke<sup>1</sup>. Carbon Monoxide affects the oxygen carrying capacity of the blood. Carbon Monoxide can diffuse through the alveolar walls of the lungs and compete with oxygen for one of the four iron sites in the hemoglobin molecule. The affinity of the iron site for CO is approximately 210 times greater than oxygen<sup>2</sup>. Low levels of CO can cause a number of symptoms including headache, mental dullness, dizziness, weakness, nausea, vomiting and loss of muscular control. In extreme cases, collapse, unconsciousness and death can occur.

The Teledyne – Advanced Pollution Instruments (TAPI) model 300EU is a state of the science instrument for the determination of trace levels of Carbon Monoxide by Non-Dispersive Infrared Spectrophotometry (NDIR) using Gas Filter Correlation (GFC). This SOP will detail the operation, preventive maintenance, cautions and health warnings.

The Detection Limit (DL) for non-trace levels of CO is 1.0 parts per million (ppm) (*Code of Federal Regulations*, Volume 40, Part 53.23c, or, in the shortened format used hereafter, 40 CFR 53.23c)<sup>3</sup>. However, the 300EU has a DL to 20 parts per billion (ppb), which is accomplished by modifications to the Federal Reference Method (FRM) instruments. This document will discuss the Trace Level (TL) operating procedures in detail.

#### 3.2 Summary of Method

The analytical principle is based on absorption of IR light by the CO molecule. NDIR-GFC analyzers operate on the principle that CO has a sufficiently characteristic IR absorption spectrum such that the absorption of IR by the CO molecule can be used as a measure of CO concentration in the presence of other gases. Carbon Monoxide absorbs IR maximally at 2.3 and 4.6  $\mu\text{m}$ . Since NDIR is a spectrophotometric method, it is based upon the Beer-Lambert Law. The degree of reduction depends on the length of the sample cell, the absorption coefficient, and CO concentration introduced into the sample cell, as expressed by the Beer-Lambert law shown below:

$$T = I/I_0 = e^{(-axC)} \quad (\text{equation 1})$$

where:

- T = Transmittance of light through the gas to the detector
- I = light intensity after absorption by Carbon Monoxide
- I<sub>0</sub> = light intensity at zero Carbon Monoxide concentration
- a = specific Carbon Monoxide molar absorption coefficient
- x = path length, and
- C = Carbon Monoxide concentration

For Gas Filter Correlation, there is only one sample cell. This cell acts as the sample and reference cell. The broad band of IR radiation is emitted from an IR source. The IR light passes through a very narrow band pass filter which screens out most wavelengths and allows only the wavelength of light that CO absorbs to enter the sample cell. The GFC analyzer has a chopper wheel with two pure gases: Nitrogen and Carbon Monoxide. As the chopper wheel rotates and allows the IR energy to enter “CO side” of the wheel, all IR energy that could be absorbed by CO in the sample stream is absorbed by the CO in the wheel. This technique effectively “scrubs out” any light that could possibly be attenuated. The single detector records the light level ( $I_0$ ). As the wheel spins, the “N<sub>2</sub> side” of the wheel reaches the IR energy beam. This side of the wheel allows all IR light to pass through the wheel and be absorbed by any CO that might be in the sample gas. This light level is CO sensitive ( $I$ ). The detector records the attenuation of this light, compares the two light levels ( $I/I_0$ ) and sends a signal to the electrometer board that calculates the concentration. The voltage is related to the CO concentration according to the Beer-Lambert law in equation 1 shown above. Thus, TAPI 300EU can measure CO continuously. The 300EU version has four distinct features that allow it to measure CO at ppb levels:

- The sample stream is dried using permeation or Nafion™ Dryer;
- The analyzer baseline is determined and corrected using heated palladium catalytic converter;
- The baseline is frequently auto-zeroed, at a minimum once per hour, through the palladium converter;
- The instrument has an ultra-sensitive or “hot” detector.

The 300 EU instrument operates in the following fashion:

1. In sample mode, ambient air is allowed to enter through the rear bulkhead sample port. Solenoid #1 is in its Normally Open (NO) mode. The ambient air flows through the solenoid to the permeation dryer, which removes the moisture and water from the sample air stream.
2. The sample stream then passes through a sample filter, which removes particles that can build up on the mirror and sample chamber and attenuate the IR beam.
3. The sample then enters the sample cell. A major difference between a non-TL and TL instrument is the detector. The TL instrument has a detector that is more sensitive to the light emitted and absorbed in the sample cell. This detector must be more sensitive because the amount of attenuation by the CO gas in the sample stream is much lower. Therefore, the detector must be sensitive at lower ambient levels. Temperature of the sample cell is also critical. The sample cell and detector must be maintained at a constant temperature in order for the detector to keep a stable background. Fluctuations of more than 1° Centigrade can cause the baseline to drift, giving false readings at low levels.
4. The detector sends the signal to the demodulator which interprets the signal. The demodulator sends a digital value to the Central Processor Unit (CPU).
5. At the end of the hour, the CPU sends a voltage signal to the Solenoid #1 and switches it to the “Normally Closed” (NC) position. This allows room air to be drawn into the instrument and to pass through the catalytic converter. The catalytic converter uses a palladium bed heated to 50° Centigrade to convert all Carbon Monoxide to Carbon Dioxide ( $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ ). This effectively “scrubs” all CO from the sample stream. The CO “free” air flows through the sample cell and the CPU interprets the signal from the demodulator as the “background” or “baseline” value. The baseline is then adjusted at that time. The baseline adjustment usually takes between 7-10 minutes.
6. The CPU then switches Solenoid #1 to its NO position and ambient air then drawn into the analyzer.

### 3.3 Definitions

Here are some key terms for this method.

**Table 3-1, Definitions of Key Terms**

<u>Term</u>	<u>Definition</u>
DAS	Data acquisition system. Used for automatic collection and recording of CO concentrations.
Interferences	Physical or chemical entities that cause CO measurements to be higher (positive) or lower (negative) than they would be without the entity. (See Section 3.6).

### 3.4 Health and Safety Warnings

**To prevent personal injury, please heed these warnings concerning the 300EU.**

1. Carbon Monoxide is a poisonous gas. Vent any CO or calibration span gas to the atmosphere rather than into the shelter or other sampling area. If this is impossible, limit exposure to CO by getting fresh air every 5 to 10 minutes. If the operator experiences light headedness, headache or dizziness, leave the area immediately.
2. The IR source is a filament resistor that has an electrical current running through it. The IR source can become very hot. When troubleshooting, allow the instrument to cool off especially if you suspect the IR source as the cause of trouble.
3. Always use a third ground wire on all instruments.
4. Always unplug the analyzer when servicing or replacing parts.
5. If it is mandatory to work inside an analyzer while it is in operation, use extreme caution to avoid contact with high voltages. The analyzer has a 110 volt Volts Alternating Current (VAC) power supply. Refer to the manufacturer's instruction manual and know the precise locations of the VAC components before working on the instrument.
6. Avoid electrical contact with jewelry. Remove rings, watches, bracelets, and necklaces to prevent electrical burns.

### 3.5 Cautions

**To prevent damage to the 300EU, all cautions should immediately precede the applicable step in this SOP. The following precautions should be taken:**

1. Normally, if Teflon™ filters are used in the sample train, cleaning the optical bench will not be required. However, in the event that the bench is cleaned, be careful to avoid damaging the interior of the sample chamber. In addition, some GFC instruments have a series of mirrors that deflect the light in order to increase the path length. The mirrors are aligned at the factory. If the mirrors become misaligned, the IR light beam will not be directed to the detector. Use extreme caution when cleaning or servicing the sample chamber(s). In addition the mirrors are very fragile. Avoid dropping the instrument. This may damage, misalign or crack the mirrors and cause expensive repairs.
2. Keep the interior of the analyzer clean.
3. Inspect the system regularly for structural integrity.
4. To prevent major problems with leaks, make sure that all sampling lines are reconnected after required checks and before leaving the site.

5. Inspect tubing for cracks and leaks.
6. It is recommended that the analyzer be leak checked after replacement of any pneumatic parts.
7. If cylinders are used in tandem with Mass Flow Control (MFC) calibrators, use and transport is a major concern. Gas cylinders can sometimes contain pressures as high as 2000 pounds per square inch (psi). Handling of cylinders must be done in a safe manner. If a cylinder is accidentally dropped and valve breaks off, the cylinder can become explosive or a projectile.
8. Transportation of cylinders is regulated by the Department of Transportation (DOT). It is strongly recommended that all agencies contact the DOT or Highway Patrol to learn the most recent regulations concerning transport of cylinders.
9. Carbon Monoxide is a highly poisonous gas. Long term exposure can cause problems with motor coordination and mental acuity. It is strongly recommended that all agencies have Material Safety Data Sheets (MSDS) at all locations where CO cylinders are stored or used. MSDS can be obtained from the DOT or from your vendor.
10. It is possible (and practical) to blend other compounds with CO. If this is the case, it is recommended that MSDS for all compounds be made available to all staff that use and handle the cylinders or permeation tubes.
11. Shipping of cylinders is governed by the DOT. Contact the DOT or your local courier about the proper procedures and materials needed to ship high-pressure cylinders.

### 3.6 Interferences

**Water Vapor:** Studies have shown conclusively that NDIR analyzers have interference from water vapor. Water absorbs very strongly across several bands of IR spectra. Water vapor interference occurs because water vapor absorption of light in the region of 3.1, 5.0 5.5 and 7.1 -10.0  $\mu\text{m}$  in the IR region. Since water vapor absorbs light in this region, this has a quenching effect on the reaction of CO. The TAPI 3000EU is equipped with a Nafion™ drier, which effectively scrubs all water and water vapor. No maintenance is required on the dryer.

**Carbon Dioxide:** Carbon dioxide absorbs in the IR spectrum at 2.7, 5.2, and 8.0 to 12.0  $\mu\text{m}$ . This is very close to the regions that CO absorbs within as well. However, since atmospheric CO<sub>2</sub> is much higher in concentration than CO, this UV spectral range must be avoided. To prevent light in this spectral region, the TAPI 300EU analyzer has a band pass filter that blocks these wavelengths.

### 3.7 Personal Qualifications

The person(s) chosen to operate the TAPI 300EU should have a minimum of qualifications. The understanding of basic chemistry and electronics are a must. The understanding of digital circuitry is helpful, but not required. Also, courses in data processing and validation are also welcome.

### 3.8 Equipment and Supplies

**Monitoring Apparatus:** The design of the 300EU is identical to the 300E with several major variations. A diagram of the TAPI 300EU instrument is described in Figure 3-1. The three main components are:

- *Pneumatic System:* Consists of sample inlet line, particulate filter, permeation dryer, reaction chamber, flowmeter, and pump, all used to bring ambient air samples to the analyzer inlet.
- *Analytical System:* This portion of the instrument consists of the IR source, the correlation wheel, motor, mirrors, detector and band pass filter.

- **Electronic Hardware:** The part of the analyzer that generally requires little or no maintenance. If the 300EU is operated above the manufacturer's recommended temperature limit, however, individual integrated chips can fail and cause problems with data storage or retrieval.

Other apparatus and equipment includes the following.

**Instrument Shelter:** A shelter is required to protect the analyzer from precipitation and adverse weather conditions, maintain operating temperature within the analyzer's temperature range requirements, and provide security and electrical power. The recommended shelter temperature range is 20-30°C.

**Spare Parts and Incidental Supplies:** See the TAPI 300EU operating manual, Appendix B for specific maintenance and replacement requirements.

**Calibration System:** A system that creates concentrations of CO of known quality is necessary for establishing traceability. This is described in detail in the "EnviroNics 9100 SOP." Please reference this document.

**DAS:** A data acquisition system is necessary for storage of ambient and ancillary data collected by the 300EU.

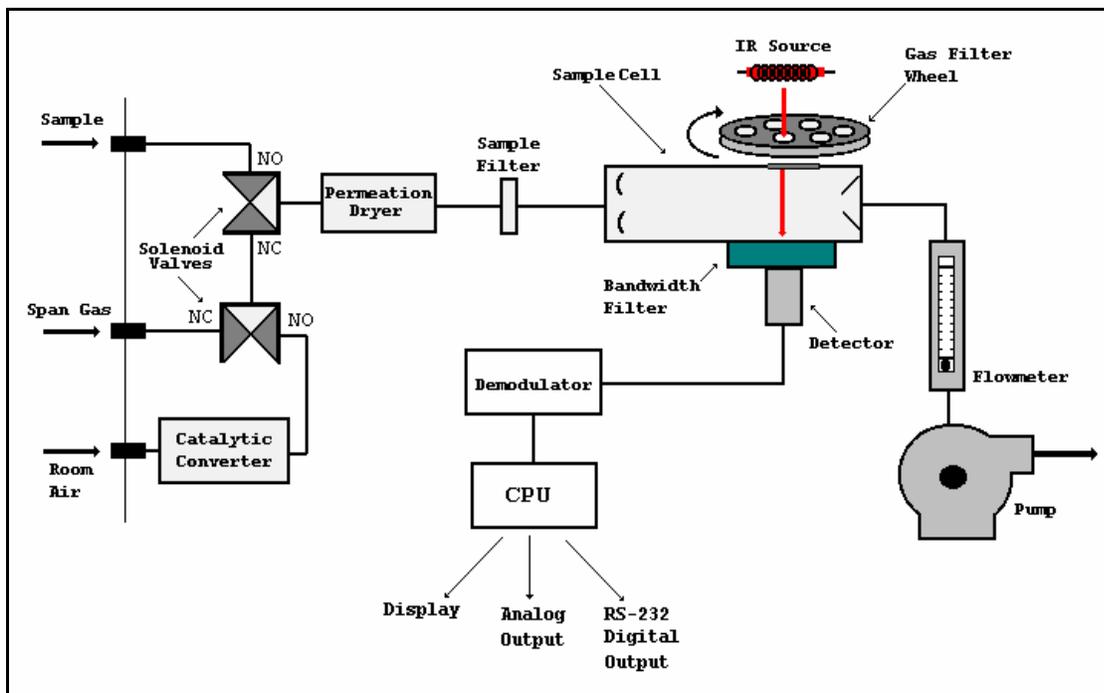


Figure 3-1 Schema of the Teledyne API 300EU

**Wiring, Tubing and Fittings:** Teflon™ and borosilicate glass are inert materials that should be used exclusively throughout the intake system. It is recommended that Polytetrafluoroethylene (PTFE) or Fluoroethylpropylene (FEP) Teflon™ tubing be used. PTFE and FEP are the best choice for the connection between the intake manifold and the 300EU bulkhead inlet. Examine and discard if particulate matter collects in the tubing. All fittings and ferrules should be made of Teflon™ or stainless

steel. Connection wiring to the DAS should be shielded two strand wire or RS-232 cables for digital connections.

**Reagents and Standard:** The TAPI 300EU does not require any reagents since the instrument uses photometry to analyze for CO. All standards for the CO method can be obtained in compressed cylinders and must be NIST traceable. Please see the “Calibration of Trace Gas Analyzers” SOP.

### 3.9 Procedure

**3.9.1 Sample Collection:** Sampling for Trace Level CO is performed by continuously drawing ambient air through a sample manifold directly into the analyzer via a vacuum pump. All inlet materials must be constructed from Teflon™ or borosilicate glass as detailed in 40 CFR 58. The siting criteria for CO Trace Level instruments is detailed in 40 CFR 58, Appendix A<sup>4</sup>.

**3.9.2 Sample Handling and Preservation:** Carbon Monoxide samples receive no special preparation prior to analysis. Therefore this SOP does not have a section on Sample Handling and Preservation.

### 3.9.3 Instrument Operation, Startup and Maintenance

This section discusses startup, operation and maintenance of the 300EU. The TAPI 300EU series instrument has a digital front panel screen with toggle switches below. This allows the user to check functions, switch operating parameters, adjust zero and span and read warnings messages. **It is extremely important that the user familiarize themselves with the menus available. Inadvertently changing parameters within the analyzer can damage the instrument and possibly invalidate data as well. Please reference the TAPI 300EU owner’s manual and read it carefully before adjusting any parameters that are set by the factory.**

#### 3.9.3.1 Start up

Before the instrument is operated, inspect the instrument for any damage. If damage is observed to the shipping box or the instrument, contact your shipping personnel.

Carefully remove the cover and check for internal damage. Please see Section 3.1 of the TAPI 300EU manual.

Remove the 6 red shipping screws that hold down the internal bench and parts. See Section 3.1 of the TAPI 300EU manual.

Once you have removed the shipping screws and performed your inspection, replace the cover.

Plug the instrument into a grounded power strip that has surge protection. It is also advisable to purchase an Uninterrupted Power Supply (UPS). An UPS will protect the 300EU from power surges and keep the unit operating until an operator can shut it down.

Check to see that the 300EU has enough clearance so that it gets proper ventilation. Check the TAPI 300EU manual Section 3.1.

Connect the output of the analog to a DAS via shielded two wire cable. Please see EPA SOP on “Data Management” for details.

Connect the digital RS-232 port to an appropriate cable and connect it to the DAS. Please see EPA SOP on “Data Management” for further details.

Connect the sample inlet port to the station intake manifold.

Press the power rocker switch to “ON.”

### 3.9.3.2 Operation and Range Setting

1. The exhaust fan will start and the display will come on. The Central Processing Unit (CPU) will boot the system and load the firmware. You will see in the upper right hand corner that the fault warning light will be flashing red. This is letting you know that the analyzer has been off.
2. To clear the fault warning, press the "CLR" button below the display. This will clear the warning and the sample green light will flash. If the red fault light continues to flash, and clearing it does not change this condition, then reference section 6.2.1 of the TAPI 300EU manual for instruction.
3. Once the red fault light is cleared, the operator will see the main menu. At this time, the time of day and date must be verified and reset if necessary.
4. From main menu press the toggle button under the "SETUP" label.
5. In this menu, you will see "8 1 8" on the bottom of the display. This is the default password. In addition, you will see on the top of the display the words "ENTER SETUP PASS:818."
6. At this time, press the toggle under "ENTR."
7. This will bring up the "PRIMARY SETUP MENU" screen.
8. In this menu, press the toggle button under "CLK."
9. In the next menu, press the "TIME" toggle switch.
10. In the next menu, you will see the time above 3 or 4 toggle switches. Adjust these toggles so that the time is correct. Press the "ENTR" toggle switch.
11. This returns you to the "TIME OF DAY CLOCK" menu. Press the toggle switch under "DATE."
12. This will put you in the date menu. You should see the day (digits), month and year (digits) above 5 toggle switches. Adjust these toggles until the correct date is obtained. Press the "ENTR" toggle switch. Press the "EXIT" toggle switch twice. This returns you to the main menu.
13. The range should be illustrated in the top middle of the main menu. This value should be set to 5000 ppb. If it is not set to this range, then it must be reset.
14. To change the range of the instrument, press the toggle under "SETUP." If the password is correct, then press "ENTR."
15. In this menu, you will see "8 1 8" on the bottom of the display. This is the default password. In addition, you will see on the top of the display the words "ENTER SETUP PASS:818."
16. At this time, press the toggle under "ENTR."
17. This will bring up the "PRIMARY SETUP MENU" screen.
18. Press the toggle switch under the "RNGE."
19. This is the "RANGE CONTROL MENU." Press the toggle switch under the "UNIT."
20. This display will show the range options. Press the toggle under the "PPB." Press the toggle under the "ENTR."
21. This will put you into the "RANGE CONTROL MENU." Press the toggle switch under the "SET."
22. This display will show the full scale range value. Press the toggles under the digits to adjust the instrument to the full scale value desired. Press the toggle under the "ENTR."
23. Press the "EXIT" toggle switch twice.
24. The instrument is now set with the appropriate time, date and full scale range.
25. It is recommended that you allow the 300EU 24 hours before you attempt function checks or calibration.
26. If the DAS system that you have does not have the RS-232 capabilities, then proceed to the next section, Diagnostic Checks/Manual Checks. If you have connected the 300EU to a computer or DAS, review the Diagnostic Check from your computer screen. TAPI offers API.COM, a computer program that allows the operator to log the diagnostic data that is collected by the 300EU CPU. Several DAS manufacturers offer this type of software as well.

### 3.9.3.3 Diagnostic Checks/Manual Checks

To determine whether the 300EU is working properly, the field operators should perform the Diagnostic Checks every time they visit the monitoring station. It is good practice for the operator to check these Diagnostic Checks either by the computer or manually. Below are instructions on how to perform this manually. Please note that the TAPI 300EU has set upper and lower ranges for some of these Diagnostic checks. Please reference the owner’s manual for these ranges.

1. If you observe the display, it should show “Sample” in the left hand corner, “Range” in the middle of the display and “CO= XX.XX.” Below this line there should be one line that read “<TST”, “TST>”, “CAL” and “SETUP.”
2. There is a series of toggle switches/ buttons below the display. These correspond to the bottom row of the display.
3. If you press the button below the left hand “<TST,” you will toggle the display into function check tree in one direction. The button under the “TST>,” will allow you to access the function check tree in the opposite direction.
4. Toggle through the function check tree. The following table illustrates the functions that should be recorded. Please see section 6.2.2 of the TAPI 300EU manual for more details. A manual check list on maintenance check sheet is attached in Appendix A of this SOP.

**Table 3-2 Diagnostic Checks**

Check	Explanation
Range	The full scale range of the instrument
Stabil	The standard deviation of CO concentrations for the last 25 readings
CO Meas	The demodulated peak of the IR detector output on the measure side of the wheel
CO Ref	The demodulated peak of the IR detector on the reference side of the wheel
MR ratio	The result of the CO meas/CO Ref
Azero ratio	The result of the CO meas/CO Ref during the Azero cycle
Sample Pres	The absolute pressure of the sample gas in the sample chamber
Sample FL	Mass flow rate of sample air
Sample Temp	The temperature of the gas inside the sample chamber
Bench Temp	Optical bench temperature
Wheel Temp	Filter wheel temperature
Box Temp	The temperature inside the instrument chassis.
PHT Drive	The voltage needed to the thermoelectric coolers of the IR detector board
Slope	The sensitivity of the instrument as calculated during the last calibration.
Offset	The overall offset of the instrument calculated during the last calibration
Time	Displays current time.

Once the Diagnostic checks have been established and recorded for the 300EU, it is time to calibrate the instrument. Please refer to section 3.9.4 of this SOP.

### 3.9.3.4 Preventive Maintenance

Preventive maintenance should **prevent** down-time and data loss. Table 3.3 lists the preventive maintenance items that are listed in the Model 300EU manual, section 9.1.

**Table 3-3 Preventive Maintenance Schedule the TAPI 300EU**

<b>Item</b>	<b>Schedule</b>
Replace particle filter	Weekly
Verify Test Function	Weekly
Perform Level I calibration	Daily
Pump Diaphragm	Bi-annually
Perform Leak Check	Annually
Inspect Pneumatic Lines	Annually
Clean inside of Chassis	As needed
Rebuild or replace pump	As needed
Replace IR source	As needed
Clean optic bench	As needed
Replace wheel motor	As needed
Replace gases in correlation wheel	As needed

### **3.9.3.5 Instrument Troubleshooting**

The TAPI 300EU manual has an excellent troubleshooting guide in Section 9.2. Please reference page 143 of the manual for details on using the Test Functions for predicting failures.

### **3.9.4 Calibration and Standardization**

The calibration of the TAPI 300EU is performed by comparing the output of the instrument against standardized gases of known quality. Generation of these gases is detailed in the “Calibration of Trace Gas Analyzers” SOP. This section will detail how to adjust the 300EU to the standardized gases. Once the calibration has been performed, compare the response of your DAS to the calculated “source” value. If this is outside of +/-10%, then adjust the instrument response as detailed in the next sections.

#### **3.9.4.1 Adjustment to Zero Air**

In order to adjust the output of the 300EU to zero air, perform the following:

1. Allow the instrument to sample zero air from a manifold that is at near atmospheric pressure for a minimum of 15 minutes.
2. On the bottom of the front panel screen there is a toggle switch/ button that is beneath the “CAL” label. Press this button.
3. This next screen is the “M-P CAL” screen. In this screen press the button below the “ZERO” label.
4. The next screen will show an “ENTR, SPAN and CONC” above the toggle switches on the bottom of the panel. Press the button below the “ENTR” label. This operation changes the calculation equation and zeros the instrument.
5. Press the button below the “EXIT” label. This returns the operator to the main “SETUP” menu.

#### **3.9.4.2 Adjustment to Calibration Gas**

In order to adjust the output of the 300EU to NIST traceable calibration gas, perform the following:

1. Switch the calibration unit to generate a known concentration of CO. Allow the instrument to sample calibration gas from a manifold that is at near atmospheric pressure for a minimum of 15 minutes.
2. On the bottom of the front panel screen of the main menu there is a button that is beneath the "CAL" label. Press this button.
3. This next screen is the "M-P CAL" screen. The next screen will show an "ENTR, SPAN and CONC" above the toggle switches on the bottom of the panel. Press the button below the "CONC" label. On the bottom line, there will be digits below each toggle button. In order to change the concentration, toggle each digit before and after the decimal place to get the concentration that is being generated in the manifold by the calibrator. At this time, press the "ENTR."
4. At this time, press the toggle below the "SPAN" switch.
5. This operation changes the calculation equation and adjusts the slope of the instrument.
6. Press the button below the "EXIT" label. This returns the operator to the main "SETUP" menu.

### **3.10 Data Analysis and Calculations**

Data analysis for this analyzer is detailed in the "Data Acquisition and Management" SOP. For the TAPI 300EU, there is one design detail of which the operator must be aware; the auto-zero (Azero) function. As detailed in Section 3.1, the TAPI 300EU has an Azero sequence that occurs at the end of the hour. During this period, the 300EU "freezes" the output to the CPU at the last value calculated by the CPU and the display will illustrate "AZERO." During the auto-zero sequence, the display and analog output are "frozen" on one value. If the operator records the data via the analog output, then the operator must be aware of this sequence and flag this data in the DAS. The digital output via the RS-232 is flagged; therefore, no other flagging is required. The Azero function can be modified from once per hour to any increment up to once per day. It is recommended that the factory default not be changed from once per hour at this time.

## **4.0 QUALITY CONTROL AND QUALITY ASSURANCE**

The following section has brief definitions of the QA/QC indicators. Table 4-1 has the Measurement Quality Objectives (MQOs) of the TAPI 300EU. Please note that this section deals primarily with the data quality indicators. Quality Control for continuous electronic instruments, such as the TAPI 300EU consists of performing the diagnostic checks, maintenance and calibrations. These procedures are detailed in sections 3.9.3 and 3.9.4: Instrument Operation, Startup and Maintenance and Calibration and Standardization. Appendix A has an example of a Quality Control and Maintenance Record developed by the EPA for this instrument.

### **4.1 Precision**

Precision is defined as the measure of agreement among individual measurements of the same property taken under the same conditions. For CO, this refers to testing the CO analyzer in the field at concentrations between 0.250 and 0.500 ppm (250 – 500 ppb). The test must be performed, at a minimum, once every two weeks. Calculations for Precision can be found in Reference 4.

## 4.2 Bias

Bias is defined as the degree of agreement between a measured value and the true, expected, or accepted value. Quantitative comparisons are made between the measured value and the true, standard value during audits. Generally, three upscale points and a zero point are compared. Two audit types commonly used for CO, direct comparison and blind, are discussed below. The SOP should discuss plans for each type of audit.

- **Direct Comparison Audits:** An independent audit system is brought to the monitoring location and produces gas concentrations that are assayed by the monitoring station's CO analyzer. In most cases, a person outside of the agency or part of an independent QA group within the agency performs the audit. The responses of the on-site analyzer are then compared against the calculated concentration from the independent audit system and a linear regression is generated
- **Blind Audits:** In blind audits (also called performance evaluation audits), State or Local Agency staff are sent an audit device, such as done in the National Performance Audit Program (NPAP). The agency staff does not know the CO concentrations produced by the audit equipment. Responses of the on-site analyzer are then compared against those of the audit device and a linear regression is calculated.

## 4.3 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. Since the NCORE Level I and II siting criteria are urban and regional, the TL-CO criteria are the same. Please reference the National Monitoring Strategy<sup>5</sup> for a discussion of NCORE Level II CO monitoring scale.

## 4.4 Completeness

Completeness is defined as the amount of data collected compared to a pre-specified target amount. For CO, EPA requires a minimum completeness of 75% (40 CFR 50, App.H.3). Typical completeness with the TAPI 300EU values can approach 90-93%.

## 4.5 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 TAPI 300EU meets the MQOs for a TL-CO instrument. Please see Table 4-1.

## 4.6 Method Detection Limit

The method detection limit (MDL) or detectability refers to the lowest concentration of a substance that can be determined by a given procedure. The TAPI 300EU must be able to detect a minimum value of 0.020 ppm of CO.

**Table 4-1 Measurement Quality Assurance Objectives**

<b>Requirement</b>	<b>Frequency</b>	<b>Acceptance Criteria</b>	<b>Reference</b>	<b>Information or Action</b>
Bias	NCORE, once per year	To be Determined from Data Quality Objectives	40 CFR Pt.58	Use of NIST generated gas concentrations with Mass Flow Calibration unit that is NIST traceable
Precision	1 every 2 weeks	Concentration: 0.250 - 0.500 ppm, Coefficient of Variance: To be determined	40 CFR Pt.58 Appendix A	To be determined
Completeness	Quarterly, Annually	NCORE, 75%	National Monitoring Strategy.	If under 75%, institute Quality Control Measures
Representativeness	N/A	Neighborhood, Urban or Regional Scale	40 CFR 58	N/A
Comparability	N/A	Must be a Trace Level instrument. See Sections 3.1 and 3.2 of this document.	National Monitoring Strategy.	N/A
Method Detection Limit	NA	0.020 ppm	National Monitoring Strategy	Testing is performed at the factory.

**Table 4-2 Operating Parameters for the TAPI 300EU Trace Gas Instrument**

Item	Range	Comments
Full Scale Range	0 to 5000 ppb	Suggested Range. Reduce to 1000 ppb if rural site
Units	Part per billion (ppb)	Recommended
Compressed Gas Cylinder	200 – 250 ppm	NIST Traceable Protocol #1 cylinder with CO concentration between 200 – 250 ppm.
Calibration Ranges		
a. zero	0 – 10 ppb	There are a number of commercially available vendors.
b. Level I Span	4000 – 5000 ppb	NIST Traceable Protocol #1 cylinder with CO concentration between 200 – 250 ppm. Recommended gas flow range 75 – 90 cc/min. Zero air flow 4.80 – 5.00 liters/min.
c. Mid Point Span	2000 – 2500 ppb	NIST Traceable Protocol #1 cylinder with CO concentration between 200 – 250 ppm. Recommended gas flow range 75 – 90 cc/min. Zero air flow 8.00 10.00 liters/min.
d. Precision Level	250 – 500 ppb	NIST Traceable Protocol #1 cylinder with CO concentration between 200 – 250 ppm. Recommended gas flow range 20 – 35 cc/min. Zero air flow 18.00 – 20.00 liters/min.

## 5.0 REFERENCES

1. Merck Index, twelfth edition 1996, page 296
2. Seinfeld,, John H., Atmospheric Chemistry and Physics of Air Pollution, 1986, page 54
3. Code of Federal Regulations, Title 40, Part 53.23c
4. Code of Federal Regulation, Title 40, Part 58, Appendix A
5. The National Air Monitoring Strategy, Final Draft, 4/29/04,  
<http://www.epa.gov/ttn/amtic/monstratdoc.html>

**Appendix A**

Environmental Protection Agency  
 Monthly Quality Control and Maintenance Records  
 Teledyne API 300EU CO Analyzer

Site Name/Location \_\_\_\_\_

Technician \_\_\_\_\_

Month/Year \_\_\_\_\_

Serial Number \_\_\_\_\_ Range \_\_\_\_\_

Parameter	Date	Date	Date	Acceptance Criteria
Offset				
Slope				
PHT Drive				
Box Temp				
Wheel Temp				
Bench Temp				
Sample Temp				
Sample Flow				
Sample Pressure				
A-zero Ratio				
MR Ratio				
CO Reference				
CO Measured				
Stability				
Range				
Other Tests				
Dark Current				

Date	Comments and Notes

**Figure A-1 Teledyne API 300 EU Quality Control and Maintenance Record**

**STANDARD OPERATING PROCEDURES**  
**TELEDYNE – ADVANCED POLLUTION INSTRUMENTATION**  
**MODEL 100AS TRACE LEVEL**  
**SULFUR DIOXIDE INSTRUMENT**  
**Version 2**



## **Section 1.1 Acknowledgments**

This Standard Operating Procedure (SOP) for Sulfur Dioxide – Trace Level is the product of EPA's Office of Air Quality, Planning and Standards. The following individuals are acknowledged for their contributions.

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**STANDARD OPERATING PROCEDURES**  
**TELEDYNE – ADVANCED POLLUTION INSTRUMENTATION**  
**MODEL 100AS TRACE LEVEL SULFUR DIOXIDE INSTRUMENT**

### 3.0 PROCEDURES

#### 3.1 Scope and Applicability

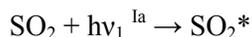
Sulfur Dioxide (SO<sub>2</sub>) is a colorless, nonflammable gas that has a strong suffocating odor. SO<sub>2</sub> originates from fuel containing sulfur (mainly coal and oil) burned at power plants and during metal smelting and other industrial processes. High levels of SO<sub>2</sub> can result in temporary breathing impairment for asthmatic children and adults who are active outdoors. Long-term exposure to high levels of SO<sub>2</sub>, in the presence of high levels of particulate matter, may aggravate existing cardiovascular disease and respiratory illness.

The Teledyne-Advanced Pollution Instrumentation (T-API) model 100AS combines proven detection technology for the determination of trace levels of SO<sub>2</sub>. This SOP will detail the operation, preventive maintenance, cautions and health warnings.

The Detection Limit (DL) for a non-trace level SO<sub>2</sub> analyzer is 10 parts per billion (ppb) (*Code of Federal Regulations*, Volume 40, Part 53.23c, or, in the shortened format used hereafter, 40 CFR 53.23c)<sup>3</sup>. However, the T-API model 100AS has an estimated DL of 100 parts per trillion (ppt), which is accomplished by an increased detector sensitivity, as well as increasing the length of the standard instrument's optics bench. This document will discuss the Trace Level (TL) operating procedures in detail.

#### 3.2 Summary of Method

The Model 100AS Trace Level operating principle is based on measuring the emitted fluorescence of SO<sub>2</sub> produced by the absorption of ultraviolet (UV) light. The UV lamp emits ultraviolet radiation which passes through a 214 nm band pass filter, excites the SO<sub>2</sub> molecules, producing fluorescence which is measured by a photomultiplier tube (PMT) with a second UV band pass filter. SO<sub>2</sub> absorbs in the 190 nm – 230 nm region free of quenching by air and relatively free of other interferences. The equations describing the above reactions are as follows:



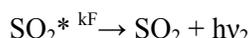
The excitation ultraviolet light at any point in the system is given by:

$$I_a = I_0[1 - \exp(-ax(\text{SO}_2))]$$

where:

$I_0$  = UV light intensity,  
 $a$  = the absorption coefficient of SO<sub>2</sub>  
 $x$  = the path length  
SO<sub>2</sub> = concentration of SO<sub>2</sub>

The excited SO<sub>2</sub> decays back to the ground state emitting a characteristic fluorescence:



When the SO<sub>2</sub> concentration is relatively low, the path length of exciting light is short and the background is air, the above expression reduces to:

$$F = k(\text{SO}_2)$$

where:

F = amount of fluorescent light given off

k = rate at which SO<sub>2</sub>\* decays into SO<sub>2</sub>

The 100AS instrument operates in the following fashion:

1. In sample mode, the sample is drawn into the analyzer through the SAMPLE bulkhead. The sample flows through a hydrocarbon “kicker,” which operates on a selective permeation principle, allowing only hydrocarbon molecules to pass through the tube wall. The driving force for the hydrocarbon removal is the differential partial pressure across the wall. This differential pressure is produced within the instrument by passing the sample gas through a capillary tube to reduce its pressure and feeding it into the shell side of the hydrocarbon kicker. The SO<sub>2</sub> molecules pass through the hydrocarbon “kicker” unaffected.
2. The sample flows into the fluorescence chamber, where UV light is focused through a narrow 214 nm band pass filter into the reaction chamber, exciting the SO<sub>2</sub> molecules; the molecules then give off their characteristic decay radiation. A second filter allows only the decay radiation to fall on the PMT. The PMT transfers the light energy into the electrical signal which is directly proportional to the light energy in the sample stream being analyzed. The preamp board converts this signal into a voltage which is further conditioned by the signal processing electronics.
3. The UV light source is measured by a UV detector. Software calculates the ratio of the PMT output and the UV detector in order to compensate for variations in the UV light energy. Stray light is the background light produced with zero ppb SO<sub>2</sub>. Once this background light is subtracted, the CPU will convert this electrical signal into the SO<sub>2</sub> concentration which is directly proportional to the number of SO<sub>2</sub> molecules.

### 3.3 Definitions

Here are some key terms for this method.

**Table 3-1 Definitions of Key Terms**

Term	Definition
DAS	Data acquisition system. Used for automatic collection and recording of Sulfur Dioxide concentrations.
Interferences	Physical or chemical entities that cause Sulfur Dioxide measurements to be higher (positive) or lower (negative) than they would be without the entity. (See Section 3.6).

### 3.4 Health and Safety Warnings

To prevent personal injury, please heed these warnings concerning the T-API 100AS.

1. Always use a third ground wire on all instruments.
2. Always unplug the analyzer when servicing or replacing parts.
3. If it is mandatory to work inside an analyzer while it is in operation, use extreme caution to avoid contact with high voltages. The analyzer has a 110 volt Volts Alternating Current (VAC) power supply. Refer to the manufacturer's instruction manual and know the precise locations of the VAC components before working on the instrument.
4. Avoid electrical contact with jewelry. Remove rings, watches, bracelets, and necklaces to prevent electrical burns.

### 3.5 Safety Precautions

To avoid damaging internal components of the T-API 100AS, the following precautions should be taken:

1. Wear an anti-static wrist strap that is properly connected to earth ground (note that when the analyzer is unplugged, the chassis is not at earth ground);
2. If an anti-static wrist strap is not available, be sure to touch a grounded metal object before touching any internal components;
3. Handle all printed circuit boards by the edge;
4. Carefully observe the instructions in each procedure specified in Section 8 of the manual;
5. Normally, if Teflon™ filters are used in the sample train, cleaning the optical bench will not be required. However, in the event that the bench is cleaned, be careful to avoid damaging the interior of the sample chamber. Use extreme caution when cleaning or servicing the sample chamber(s). In addition the mirrors are very fragile; avoid dropping the instrument. This may damage, misalign or crack the mirrors and cause expensive repairs;
6. Keep the interior of the analyzer clean;
7. Inspect the system regularly for structural integrity;
8. To prevent major problems with leaks, make sure that all sampling lines are reconnected after required checks and before leaving the site;
9. Inspect tubing for cracks and leaks;
10. It is recommended that the analyzer be leak checked after replacement of any pneumatic parts;
11. If cylinders are used in tandem with Mass Flow Control (MFC) calibrators, use and transport is a major concern. Gas cylinders can sometimes contain pressures as high as 2000 pounds per square inch (psi). Handling of cylinders must be done in a safe manner. If a cylinder is accidentally dropped and valve breaks off, the cylinder can become explosive or a projectile;
12. Transportation of cylinders is regulated by the Department of Transportation (DOT). It is strongly recommended that all agencies contact the DOT or Highway Patrol to learn the most recent regulations concerning transport of cylinders;
13. It is possible (and practical) to blend other compounds with SO<sub>2</sub>. If this is the case, it is recommended that MSDS for all compounds be made available to all staff that use and handle the cylinders or permeation tubes; and
14. Shipping of cylinders is governed by the DOT. Contact the DOT or your local courier about the proper procedures and materials needed to ship high-pressure cylinders.

### 3.6 Interferences

The most common source of interference is from other gases that fluoresce in a similar fashion to SO<sub>2</sub> when exposed to UV light. The most significant of these is a class of hydrocarbons called polynuclear aromatic hydrocarbons (PAH); of which naphthalene is a prominent example. Xylene is another hydrocarbon that can cause interference. These hydrocarbons are removed via the hydrocarbon “kicker” (see section 3.2 for explanation on the hydrocarbon “kicker”).

Nitrogen oxide (NO) fluoresces in a spectral range close to SO<sub>2</sub>. Interference from NO is addressed by the presence of the band pass filter, which allows only the wavelengths emitted by the excited SO molecules to reach the PMT.

### 3.7 Personnel Qualifications

The person(s) chosen to operate the T-API 100AS should have a minimum of qualifications. The understanding of basic chemistry and electronics are a must. The understanding of digital circuitry is helpful, but not required. Also, courses in data processing and validation are also welcome.

### 3.8 Equipment and Supplies

**Monitoring Apparatus:** The T-API 100AS combines proven detection technology with advanced diagnostics for greater flexibility and reliability. A diagram of the T-API 100AS instrument is described in Figure 3-1. The three main components are:

- *Pneumatic System:* Consists of sample inlet line, particulate filter, reaction chamber, flowmeter, and pump, all used to bring ambient air samples to the analyzer inlet.
- *Analytical System:* This portion of the instrument consists of the UV lamp, mirrors, photo-detector and band pass filter.
- *Electronic Hardware:* The part of the analyzer that generally requires little or no maintenance. If the T-API 100AS is operated above the manufacturer's recommended temperature limit, however, individual integrated chips can fail and cause problems with data storage or retrieval.

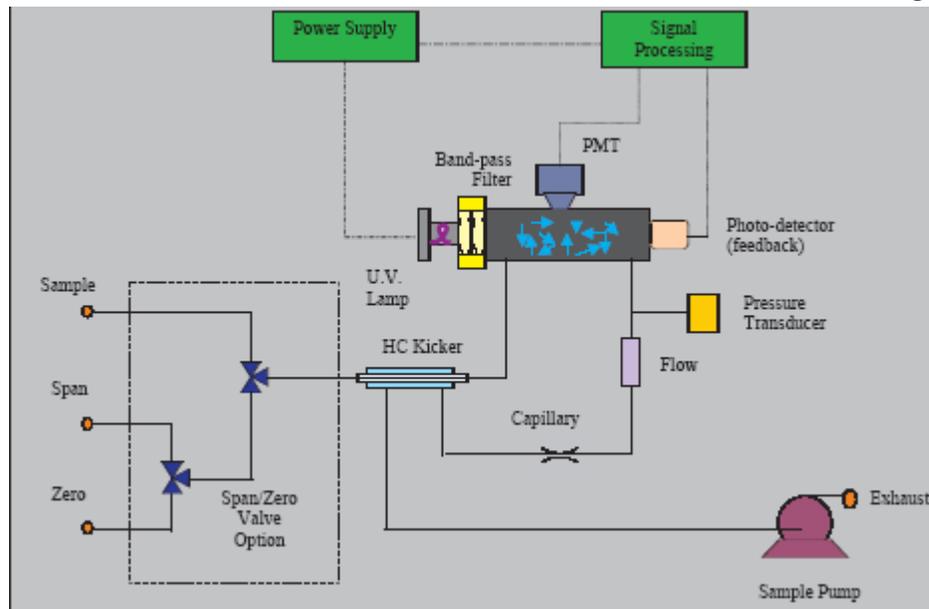
Other apparatus and equipment includes the following.

**Instrument Shelter:** A shelter is required to protect the analyzer from precipitation and adverse weather conditions, maintain operating temperature within the analyzer's temperature range requirements, and provide security and electrical power. The recommended shelter temperature range is 20-30°C.

**Spare Parts and Incidental Supplies:** See the T-API 100AS manual, Section 10, for a list of recommended spare parts.

**Calibration System:** A system that creates concentrations of SO<sub>2</sub> of known quality is necessary for establishing traceability. This is described in detail in the Environics Series 9100 Computerized Ambient Monitoring Calibration System SOP. Please reference this document.

**DAS:** A data acquisition system is necessary for storage of ambient and ancillary data collected by the T-API 100AS.



**Figure 3-1 T-API Model 100AS Flow Diagram**

**Wiring, Tubing and Fittings:** Teflon™, stainless steel, and borosilicate glass are inert materials that should be used exclusively throughout the intake system. Stainless steel tubing should be avoided because it is expensive, hard to clean, and can develop micro-cracks that are difficult to detect. Teflon™ tubing is the best choice for the connection between the intake manifold and the T-API 100AS inlet. Examine and discard if particulate matter collects in the tubing. All fittings and ferrules should be made of Teflon™ or stainless steel. Connection wiring to the DAS should be shielded two strand wire or RS-232 cables for digital connections.

**Reagents and Standard:** The T-API 100AS does not require any reagents since the instrument uses photometry to analyze for sulfur dioxide. All standards for the SO<sub>2</sub> method can be obtained in compressed cylinders and must be NIST traceable. Please see the EnviroNics Series 9100 Computerized Ambient Monitoring Calibration System SOP.

### 3.9 Procedure

**3.9.1 Sample Collection:** Sampling for trace level SO<sub>2</sub> is performed by drawing ambient air through a sample manifold directly into the analyzer continuously via a vacuum pump. All inlet materials must be constructed from Teflon™, or borosilicate glass. The siting criteria for SO<sub>2</sub> Trace Level instruments is detailed in 40 CFR 58, appendix A<sup>4</sup>.

**3.9.2 Sample Handling and Preservation:** SO<sub>2</sub> samples receive no special preparation prior to analysis. Therefore this SOP does not need a section on Sample Handling and Preservation.

### 3.9.3 Instrument Operation, Startup and Maintenance

This section discusses startup, operation and maintenance of the T-API 100AS. The T-API 100AS has a digital front panel screen with pushbuttons below. This allows the user to check functions, switch operating parameters, and adjust zero and span. Recommend at start-up of instrument and after a warm-up period for the instrument, run through the menu items and record the current settings. **It is extremely important that the user familiarize themselves with the menus available. Inadvertently changing parameters within the analyzer can damage the instrument and possibly invalidate data as well.**

**Please reference the T-API 100AS owner's manual and read it carefully before adjusting any parameters that are set by the factory.**

### **3.9.3.1 Start up**

Before the instrument is operated, inspect the instrument for any damage. If damage is observed to the shipping box or the instrument, contact your shipping personnel.

Carefully remove the cover and check for internal damage. Please see Section 2 of the T-API 100AS manual.

Remove the red shipping screws that hold down the internal bench and parts. See Section 2 of the T-API 100AS manual.

Once you have removed the shipping screws and performed your inspection, replace the cover.

Plug the instrument into a grounded power strip that has surge protection. It is also advisable to purchase an Uninterrupted Power Supply (UPS). An UPS will protect the T-API 100AS from power surges and keep the unit operating until an operator can shut it down.

Check to see that the 100AS has enough clearance so that it gets proper ventilation. Check the T-API 100AS manual, Section 2.

Connect the output of the analog to a DAS via shielded two wire cable. Please see EPA SOP on "Data Management" for details.

Connect the digital RS-232 port to an appropriate cable and connect it to the DAS. Please see EPA SOP on "Data Management" for further details.

Connect the sample inlet port to the station intake manifold.

Press the power rocker switch to "ON."

### **3.9.3.2 Operation and Range Setting**

1. The exhaust fan will start and the display will come on. The Central Processing Unit (CPU) will boot the system and load the firmware. You will see in the upper right hand corner that the fault warning light will be flashing red. This is letting you know that the analyzer has been off.
2. To clear the fault warning, press the "CLR" button below the display. This will clear the warning and the sample green light will flash.
3. Once the red fault light is cleared, the operator will see the main menu. At this time, the time of day and date must be verified and reset if necessary.
4. From main menu press the toggle button under the "SETUP" label.
5. In this menu, you will see "8 1 8" on the bottom of the display. This is the default password. In addition, you will see on the top of the display the words "ENTER SETUP PASS: 818."
6. At this time, press the toggle under "ENTR."
7. This will bring up the "PRIMARY SETUP MENU" screen.
8. In this menu, press the toggle button under "CLK."
9. In the next menu, press the "TIME" toggle switch.
10. In the next menu, you will see the time above 3 or 4 toggle switches. Adjust these toggles so that the time is correct. Press the "ENTR" toggle switch.
11. This returns you to the "TIME OF DAY CLOCK" menu. Press the toggle switch under "DATE."
12. This will put you in the date menu. You should see the day (digits), month and year (digits) above 5 toggle switches. Adjust these toggles until the correct date is obtained. Press the "ENTR" toggle switch. Press the "EXIT" toggle switch twice. This returns you to the main menu.
13. The range should be illustrated in the top middle of the main menu. This value should be set to 100 ppb. If it is not set to this range, then it must be reset.
14. To change the range of the instrument, press the toggle under "SETUP." If the password is correct, then press "ENTR."

15. In this menu, you will see “8 1 8” on the bottom of the display. This is the default password. In addition, you will see on the top of the display the words “ENTER SETUP PASS: 818.”
16. At this time, press the toggle under “ENTR.”
17. This will bring up the “PRIMARY SETUP MENU” screen.
18. Press the toggle switch under the “RNGE.”
19. This is the “RANGE CONTROL MENU.” Press the toggle switch under the “UNIT.”
20. This display will show the range options. Press the toggle under the “PPB.” Press the toggle under the “ENTR.”
21. This will put you into the “RANGE CONTROL MENU.” Press the toggle switch under the “SET.”
22. This display will show the full scale range value. Press the toggles under the digits to adjust the instrument to the full scale value desired. Press the toggle under the “ENTR.”
23. Press the “EXIT” toggle switch twice.
24. The instrument is now set with the appropriate time, date and full scale range.
25. It is recommended that you allow the T-API 100AS 24 hours before you attempt function checks or calibration.

If your DAS does not have RS-232 capabilities, then proceed to the next section, Diagnostic Checks/Manual Checks. If you have connected the T-API 100AS to a computer or DAS, review the Diagnostic Check from your computer screen. T-API offers API.COM, a computer program that allows the operator to log the diagnostic data that is collected by the T-API 100AS CPU. Several DAS manufacturers offer this type of software as well.

### 3.9.3.3 Diagnostic Checks/Manual Checks

To determine whether the T-API 100AS is working properly, the field operators should perform the Diagnostic Checks every time they visit the monitoring station. It is good practice for the operator to check these Diagnostic Checks either by the computer or manually. Below are instructions on how to perform this manually. Please note that the T-API 100AS has set upper and lower ranges for some of these Diagnostic checks. Please reference the owner's manual for these ranges.

1. If you observe the display, it should show “Sample” in the left hand corner, “Range” in the middle of the display and “SO<sub>2</sub>= XX.X.” Below this line there should be one line that read “<TST”, “TST>”, “CAL” and “SETUP.”
2. There is a series of toggle switches/ buttons below the display. These correspond to the bottom row of the display.
3. If you press the button below the left hand “<TST,” you will toggle the display into function check tree in one direction. The button under the “TST>,” will allow you to access the function check tree in the opposite direction.
4. Toggle through the function check tree. The following table illustrates the functions that should be recorded. Please see the T-API 100AS manual for more details. A maintenance checklist is attached in Appendix A of this SOP.

**Table 3-2 Diagnostic Checks**

Check	Explanation
Range	The full scale limit at which the reporting range of the instrument's analog outputs are currently set.
Stability	The standard deviation of SO <sub>2</sub> concentrations for the last 25 readings.
Pressure	The current pressure of the sample gas as it enters the sample chamber.
Sample flow	The flow rate of the sample gas through the sample chamber.
PMT	The raw output voltage of the PMT.
Norm PMT	The output voltage of the PMT after normalization.
UV lamp	The output voltage of the UV reference detector.
Lamp ratio	The current output of the UV reference detector divided by the reading stored in the CPU's memory from the last time a UV lamp calibration was performed.
Stray light	The offset due to stray light recorded by the CPU during the last zero-point calibration.
Dark PMT	The PMT output reading recorded the last time the UV source lamp shutter was closed.
Dark lamp	The UV reference detector output reading recorded the last time the UV source lamp shutter was closed.
Slope	The sensitivity of the instrument as calculated during the last calibration.
Offset	The overall offset of the instrument as calculated during the last calibration.
HVPS	The PMT high voltage power supply.
DCPS	The composite of the +5 and ± 15 VDC supplies.
RCell temp	The current temperature of the sample chamber.
Box temp	The ambient temperature of the inside of the analyzer case.
PMT temp	The current temperature of the PMT.

Once the Diagnostic checks have been established and recorded for the T-API100AS, it is time to calibrate the instrument. Please refer to section 3.9.4 of this SOP.

### 3.9.3.4 Preventive Maintenance

Preventive maintenance should **prevent** down-time and data loss. Table 3.3 lists the preventive maintenance items that are listed in the T-API 100AS manual, Section 8.

**Table 3-3 Preventive Maintenance Schedule for the 100AS**

Item	Schedule
Visual inspection and cleaning	Bi-annually
Sample particulate filter inspection	Weekly
TEST Functions	Weekly
Perform Level I calibration	Daily
Pneumatic sub-system	Annually, or after repairs
PMT sensor hardware calibration	On PMT or preamp changes
Sample chamber windows and filters	As necessary
Leak check	Annually
Pump diaphragm	Change annually
Factory calibration	Annually, or after repairs

### **3.9.3.5 Instrument Troubleshooting**

The T-API 100AS manual has an excellent troubleshooting guide in Section 9.

### **3.9.4 Calibration and Standardization**

The calibration of the T-API 100AS is performed by comparing the output of the instrument against standardized gases of known quality. Generation of these gases is detailed in the Enviroics Series 9100 Computerized Ambient Monitoring Calibration System SOP. This section will detail how to adjust the T-API 100AS to the standardized gases. Once the calibration has been performed, compare the response of your DAS to the calculated “source” value. If this is outside of +/-10%, then adjust the instrument response as detailed in the next sections.

#### **3.9.4.1 Adjustment to Zero Air**

Before running the zero air through the T-API 100AS, ensure that the zero air is free from contaminants. One way to determine if the zero air is free from contaminants is through the use of multiple zero air sources, and determining which source produces the lowest response.<sup>5</sup>

To adjust the output of the T-API 100AS to zero air, perform the following:

1. Allow the instrument to sample zero air from a manifold that is at or near atmospheric pressure for a minimum of 15 minutes.
2. On the bottom of the front panel screen there is a toggle switch/ button that is beneath the “CAL” label. Press this button.
3. This next screen is the “M-P CAL” screen. In this screen press the button below the “ZERO” label.
4. The next screen will show an “ENTR, SPAN and CONC” above the toggle switches on the bottom of the panel. Press the button below the “ENTR” label. This operation changes the calculation equation and zeros the instrument.

Press the button below the “EXIT” label. This returns the operator to the main “SETUP” menu.

#### **3.9.4.2 Adjustment to Calibration Gas**

It is desirable, but not essential, to calibrate the T-API 100AS at low SO<sub>2</sub> levels (typically, less than 20 ppb). However, fluorescence SO<sub>2</sub> analyzers have been shown to be inherently linear over a wide dynamic range. If low concentration SO<sub>2</sub> calibration cylinders (less than 50 ppm) are used, there is the potential for contamination by back diffusion from a poorly purged regulator. Contamination with even a small amount of moisture from back diffusion can cause the SO<sub>2</sub> concentration to become unstable; the lower the cylinder concentration, the more susceptible it is to any contamination from “abuse” in the field<sup>5</sup>. The best way to ensure low concentration cylinders are not contaminated by back diffusion is to make sure whenever the cylinder valve is open, there is gas flow out of the cylinder.

To adjust the output of the T-API 100AS to NIST traceable calibration gas, perform the following:

1. Switch the calibration unit to generate a known concentration of SO<sub>2</sub>. Allow the instrument to sample calibration gas from a manifold that is at near atmospheric pressure for a minimum of 15 minutes.

2. On the bottom of the front panel screen of the main menu there is a button that is beneath the "CAL" label. Press this button.
3. This next screen is the "M-P CAL" screen. The next screen will show an "ENTR, SPAN and CONC" above the toggle switches on the bottom of the panel. Press the button below the "CONC" label. On the bottom line, there will be digits below each toggle button. In order to change the concentration, toggle each digit before and after the decimal place to get the concentration that is being generated in the manifold by the calibrator. At this time, press the "ENTR."
4. At this time, press the toggle below the "SPAN" switch.
5. This operation changes the calculation equation and adjusts the slope of the instrument.

Press the button below the "EXIT" label. This returns the operator to the main "SETUP" menu.

### 3.10 Data Analysis and Calculations

Data analysis for this analyzer is detailed in the "Data Acquisition and Management SOP."

## 4.0 QUALITY CONTROL AND QUALITY ASSURANCE

The following section has brief definitions of the QA/QC indicators. Table 4-1 has the Measurement Quality Objectives (MQOs) of the T-API 100AS. Please note that this section details primarily with the QA indicators. Quality Control for continuous electronic instruments, such as the T-API 100AS consists of performing the diagnostic checks, maintenance and calibrations. These procedures are detailed in sections 3.9.3 and 3.9.4: Instrument Operation, Startup and Maintenance and Calibration and Standardization. Appendix A has an example of a Quality Control and Maintenance Record developed by the EPA for this instrument.

### 4.1 Precision

Precision is defined as the measure of agreement among individual measurements of the same property taken under the same conditions. For SO<sub>2</sub>, this refers to testing the SO<sub>2</sub> analyzer in the field at concentrations between 0.0003 and 0.005 ppm. The test must be performed, at a minimum, once every two weeks. Calculations for Precision can be found in Reference item 3.

### 4.2 Bias

Bias is defined as the degree of agreement between a measured value and the true, expected, or accepted value. Quantitative comparisons are made between the measured value and the true, standard value during audits. Generally, three upscale points and a zero point are compared. Two audit types commonly used for SO<sub>2</sub>, direct comparison and blind, are discussed below. The SOP should discuss plans for each type of audit.

- **Direct Comparison Audits:** An independent audit system is brought to the monitoring location and produces gas concentrations that are assayed by the monitoring station's SO<sub>2</sub> analyzer. In most cases, a person outside of the agency or part of an independent QA group within the agency performs the audit. The responses of the on-site analyzer are then compared against the calculated concentration from the independent audit system and a linear regression is generated
- **Blind Audits:** In blind audits (also called performance evaluation audits); agency staff are sent an audit device, such as the National Performance Evaluation Program (NPEP). The agency staff does

not know the SO<sub>2</sub> concentrations produced by the audit equipment. Responses of the on-site analyzer are then compared against those of the generator and a linear regression is calculated.

### **4.3 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. Since the NCORE Level I and II siting criteria are urban and regional, the trace level SO<sub>2</sub> criteria are the same. Please reference the National Monitoring Strategy<sup>5</sup> for a discussion of NCORE Level II SO<sub>2</sub> monitoring scale.

### **4.4 Completeness**

Completeness is defined as the amount of data collected compared to a pre-specified target amount. For SO<sub>2</sub>, EPA requires a minimum completeness of 75% (40 CFR 50, App.H.3). Typical completeness with the T-API 100AS values can approach 90-93%.

### **4.5 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 MQOs for a trace level SO<sub>2</sub> instrument are still to be determined. Please see Table 4-1.

### **4.6 Method Detection Limit**

The method detection limit (MDL) or detectability refers to the lowest concentration of a substance that can be determined by a given procedure. The T-API 100AS must be able to detect a minimum value of 300 ppt of SO<sub>2</sub>.

**Table 4-1 Measurement Quality Assurance Objectives**

<b>Requirement</b>	<b>Frequency</b>	<b>Acceptance Criteria</b>	<b>Reference</b>	<b>Information or Action</b>
Bias	NCORE, once per year	To be determined.	40 CFR Pt.58	To be determined.
Precision	1 every 2 weeks	Concentration: 0.0003 -0.005 ppm, Coefficient of Variance: To be determined.	40 CFR Pt.58 Appendix A	To be determined.
Completeness	Quarterly, Annually	NCORE, 75%	National Monitoring Strategy.	If under 75%, institute Quality Control Measures
Representativeness	N/A	Neighborhood, Urban or Regional Scale	40 CFR 58	N/A
Comparability	N/A	Must be a Trace Level instrument. See Sections 3.1 and 3.2 of this document.	National Monitoring Strategy.	N/A
Method Detection Limit	N/A	300 ppt	National Monitoring Strategy	Testing is performed at the factory.

**5.0 REFERENCES**

1. Code of Federal Regulations, Title 40, Part 53.23c
2. Code of Federal Regulation, Title 40, Part 58, Appendix A
3. The National Air Monitoring Strategy, Final Draft, 4/29/04, <http://www.epa.gov/ttn/amtic/monstratdoc.html>
4. Instruction Manual, T-API Model 100AS Trace Level SO<sub>2</sub> Analyzer.
5. Trace SO<sub>2</sub> Monitoring Guidance for the MANE-VU Regional Aerosol Intensive Network (RAIN) program, Draft (dated March 7, 2005).

**Appendix A**

Environmental Protection Agency  
 Monthly Quality Control and Maintenance Records  
 Teledyne – API 100AS Ultra-Sensitivity SO<sub>2</sub> Analyzer

Site Name/Location \_\_\_\_\_

Technician \_\_\_\_\_

Month/Year \_\_\_\_\_

Serial Number \_\_\_\_\_ Range \_\_\_\_\_

Date Time				Parameters Acceptance Criteria
Range				
Stability				
Pressure				
Sample flow				
PMT				
Norm PMT				
UV lamp				
Lamp ratio				
Stray light				
Dark PMT				
Dark lamp				
Slope				
Offset				
HVPS				
DCPS				
RCell temp				
Box temp				
PMT temp				
Other Tests				
ETest				
OTest				

Date	Comments and Notes

**Figure A-1. T-API 100AS Quality Control and Maintenance Record**

**STANDARD OPERATING PROCEDURES**

**THERMO ELECTRON CORPORATION**

**MODEL 43C-TLE TRACE LEVEL**

**SULFUR DIOXIDE INSTRUMENT**

**Version 3**



## **Section 1.1 Acknowledgments**

This Standard Operating Procedure (SOP) for Sulfur Dioxide – Trace Level is the product of EPA's Office of Air Quality, Planning and Standards. The following individuals are acknowledged for their contributions.

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**STANDARD OPERATING PROCEDURES  
THERMO ELECTRON CORPORATION  
MODEL 43C-TLE TRACE LEVEL SULFUR DIOXIDE INSTRUMENT**

**3.0 PROCEDURES**

**3.1 Scope and Applicability**

Sulfur Dioxide (SO<sub>2</sub>) is a colorless, nonflammable gas that has a strong suffocating odor. SO<sub>2</sub> originates from fuel containing sulfur (mainly coal and oil) burned at power plants and during metal smelting and other industrial processes. High levels of SO<sub>2</sub> can result in temporary breathing impairment for asthmatic children and adults who are active outdoors. Long-term exposure to high levels of SO<sub>2</sub>, in the presence of high levels of particulate matter, may aggravate existing cardiovascular disease and respiratory illness.

The Thermo Electron Corporation model 43C-TLE combines proven detection technology and advanced diagnostics for the determination of trace levels of SO<sub>2</sub>. This SOP will detail the operation, preventive maintenance, cautions and health warnings.

The Detection Limit (DL) for a non-trace level SO<sub>2</sub> analyzer is 10 parts per billion (ppb) (*Code of Federal Regulations*, Volume 40, Part 53.23c, or, in the shortened format used hereafter, 40 CFR 53.23c)<sup>3</sup>. However, the 43C-TLE has an estimated DL of 100 parts per trillion (ppt), which is accomplished by an increased detector sensitivity, as well as increasing the length of the standard instrument's optics bench. This document will discuss the Trace Level (TL) operating procedures in detail.

**3.2 Summary of Method**

The Model 43C-TLE Trace Level operating principle is based on measuring the emitted fluorescence of SO<sub>2</sub> produced by the absorption of ultraviolet (UV) light. Pulsating UV light is focused through a narrow band-pass filter mirror allowing only light wavelengths of 190 to 230 nm to pass into the fluorescent chamber. SO<sub>2</sub> absorbs light in this region without any quenching by air or most other molecules found in polluted air. The SO<sub>2</sub> molecules are excited by UV light and emit a characteristic decay radiation. A second filter allows only this decay radiation to contact a photomultiplier tube (PMT). Electronic signal processing transfers the light energy impinging on the PMT into a voltage which is directly analyzed. Specifically,



where:

$hv_1$  = incidence light,  
 $hv_2$  = fluoresced light, and  
 $\text{SO}_2^*$  = SO<sub>2</sub> in its excited state

The 43C-TLE instrument operates in the following fashion:

1. In sample mode, the sample is drawn into the analyzer through the SAMPLE bulkhead. The sample flows through a hydrocarbon “kicker,” which operates on a selective permeation principle, allowing only hydrocarbon molecules to pass through the tube wall. The driving force for the hydrocarbon removal is the differential partial pressure across the wall. This differential pressure is produced within the instrument by passing the sample gas through a capillary tube to reduce its pressure and feeding it into the shell side of the hydrocarbon kicker. The SO<sub>2</sub> molecules pass through the hydrocarbon “kicker” unaffected.
2. The sample flows into the fluorescence chamber, where pulsating UV light excites the SO<sub>2</sub> molecules. The condensing lens focuses the pulsating UV light into the mirror assembly. The mirror assembly contains eight selective mirrors that reflect only the wavelengths which excite SO<sub>2</sub> molecules.
3. As the excited SO<sub>2</sub> molecules decay to lower energy states they emit UV light that is proportional to the SO<sub>2</sub> concentration. The band pass filter allows only the wavelengths emitted by the excited SO<sub>2</sub> molecules to reach the PMT. The PMT detects the UV light emission from the decaying SO<sub>2</sub> molecules. The photo detector, located at the back of the fluorescence chamber, continuously monitors the pulsating UV light source and is connected to a circuit that compensates for fluctuations in the UV light.
4. The sample then flows through a flow sensor, a capillary, and the shell side of the hydrocarbon “kicker.” The model 43C-TLE trace level outputs the SO<sub>2</sub> concentration to the front panel display and the analog or digital outputs.

### 3.3 Definitions

Here are some key terms for this method.

**Table 3-1 Definitions of Key Terms**

<u>Term</u>	<u>Definition</u>
DAS	Data acquisition system. Used for automatic collection and recording of Sulfur Dioxide concentrations.
Interferences	Physical or chemical entities that cause Sulfur Dioxide measurements to be higher (positive) or lower (negative) than they would be without the entity. (See Section 3.6).

### 3.4 Health and Safety Warnings

To prevent personal injury, please heed these warnings concerning the 43C-TLE.

1. Always use a third ground wire on all instruments.
2. Always unplug the analyzer when servicing or replacing parts.
3. If it is mandatory to work inside an analyzer while it is in operation, use extreme caution to avoid contact with high voltages. The analyzer has a 110 volt Volts Alternating Current (VAC) power supply. Refer to the manufacturer's instruction manual and know the precise locations of the VAC components before working on the instrument.
4. Avoid electrical contact with jewelry. Remove rings, watches, bracelets, and necklaces to prevent electrical bums.

### 3.5 Safety Precautions

To avoid damaging internal components of the 43C-TLE, the following precautions should be taken:

1. Wear an anti-static wrist strap that is properly connected to earth ground (note that when the analyzer is unplugged, the chassis is not at earth ground);
2. If an anti-static wrist strap is not available, be sure to touch a grounded metal object before touching any internal components;
3. Handle all printed circuit boards by the edge;
4. Carefully observe the instructions in each procedure specified in Chapter 7 of the manual;
5. Normally, if Teflon™ filters are used in the sample train, cleaning the optical bench will not be required. However, in the event that the bench is cleaned, be careful to avoid damaging the interior of the sample chamber. Use extreme caution when cleaning or servicing the sample chamber(s). In addition the mirrors are very fragile; avoid dropping the instrument. This may damage, misalign or crack the mirrors and cause expensive repairs;
6. Keep the interior of the analyzer clean;
7. Inspect the system regularly for structural integrity;
8. To prevent major problems with leaks, make sure that all sampling lines are reconnected after required checks and before leaving the site;
9. Inspect tubing for cracks and leaks;
10. It is recommended that the analyzer be leak checked after replacement of any pneumatic parts;
11. If cylinders are used in tandem with Mass Flow Control (MFC) calibrators, use and transport is a major concern. Gas cylinders can sometimes contain pressures as high as 2000 pounds per square inch (psi). Handling of cylinders must be done in a safe manner. If a cylinder is accidentally dropped and valve breaks off, the cylinder can become explosive or a projectile;
12. Transportation of cylinders is regulated by the Department of Transportation (DOT). It is strongly recommended that all agencies contact the DOT or Highway Patrol to learn the most recent regulations concerning transport of cylinders;
13. It is possible (and practical) to blend other compounds with SO<sub>2</sub>. If this is the case, it is recommended that MSDS for all compounds be made available to all staff that use and handle the cylinders or permeation tubes; and
14. Shipping of cylinders is governed by the DOT. Contact the DOT or your local courier about the proper procedures and materials needed to ship high-pressure cylinders.

### **3.6 Interferences**

The most common source of interference is from other gases that fluoresce in a similar fashion to SO<sub>2</sub> when exposed to UV light. The most significant of these is a class of hydrocarbons called polynuclear aromatic hydrocarbons (PAH); of which naphthalene is a prominent example. Xylene is another hydrocarbon that can cause interference. These hydrocarbons are removed via the hydrocarbon “kicker” (see section 3.2 for explanation on the hydrocarbon “kicker”).

Nitrogen oxide (NO) fluoresces in a spectral range close to SO<sub>2</sub>. Interference from NO is addressed by the presence of the band pass filter, which allows only the wavelengths emitted by the excited SO molecules to reach the PMT.

### 3.7 Personnel Qualifications

The person(s) chosen to operate the Thermo 43C-TLE should have a minimum of qualifications. The understanding of basic chemistry and electronics are a must. The understanding of digital circuitry is helpful, but not required. Also, courses in data processing and validation are also welcome.

### 3.8 Equipment and Supplies

**Monitoring Apparatus:** The design of the 43C-TLE combines proven detection technology with advanced diagnostics for greater flexibility and reliability. A diagram of the 43C-TLE instrument is described in Figure 3-1. The three main components are:

- Pneumatic System: Consists of sample inlet line, particulate filter, reaction chamber, flowmeter, and pump, all used to bring ambient air samples to the analyzer inlet.
- Analytical System: This portion of the instrument consists of the UV lamp, mirrors, photo-detector and band pass filter.
- Electronic Hardware: The part of the analyzer that generally requires little or no maintenance. If the 43C-TLE is operated above the manufacturer's recommended temperature limit, however, individual integrated chips can fail and cause problems with data storage or retrieval.

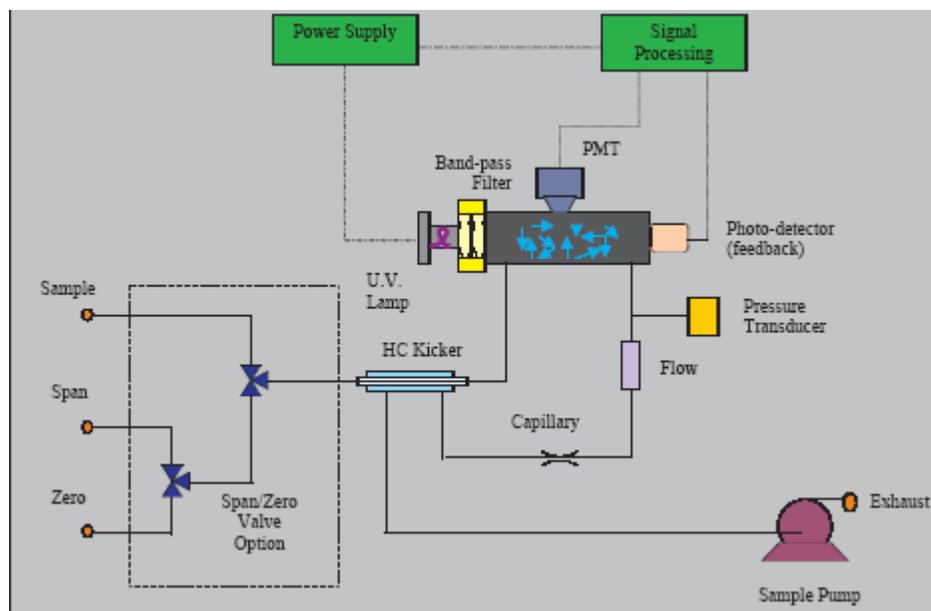
Other apparatus and equipment includes the following.

**Instrument Shelter:** A shelter is required to protect the analyzer from precipitation and adverse weather conditions, maintain operating temperature within the analyzer's temperature range requirements, and provide security and electrical power. The recommended shelter temperature range is 20-30°C.

**Spare Parts and Incidental Supplies:** See the 43C-TLE manual, Chapter 5, for a list of recommended spare parts.

**Calibration System:** A system that creates concentrations of SO<sub>2</sub> of known quality is necessary for establishing traceability. This is described in detail in the Environics Series 9100 Computerized Ambient Monitoring Calibration System SOP. Please reference this document.

**DAS:** A data acquisition system is necessary for storage of ambient and ancillary data collected by the 43C-TLE.



**Figure 3-1 Model 43C-TLE Flow Diagram**

**Wiring, Tubing and Fittings:** Teflon™, stainless steel, and borosilicate glass are inert materials that should be used exclusively throughout the intake system. Stainless steel tubing should be avoided because it is expensive, hard to clean, and can develop micro-cracks that are difficult to detect. Teflon™ tubing is the best choice for the connection between the intake manifold and the 43C-TLE inlet. Examine and discard if particulate matter collects in the tubing. All fittings and ferrules should be made of Teflon™ or stainless steel. Connection wiring to the DAS should be shielded two strand wire or RS-232 cables for digital connections.

**Reagents and Standard:** The 43C-TLE does not require any reagents since the instrument uses photometry to analyze for sulfur dioxide. All standards for the SO<sub>2</sub> method can be obtained in compressed cylinders and must be NIST traceable. Please see the EnviroNics Series 9100 Computerized Ambient Monitoring Calibration System SOP.

### 3.9 Procedure

**3.9.1 Sample Collection:** Sampling for trace level SO<sub>2</sub> is performed by drawing ambient air through a sample manifold directly into the analyzer continuously via a vacuum pump. All inlet materials must be constructed from Teflon™, or borosilicate glass. The siting criteria for SO<sub>2</sub> Trace Level instruments is detailed in 40 CFR 58, appendix A<sup>4</sup>.

**3.9.2 Sample Handling and Preservation:** SO<sub>2</sub> samples receive no special preparation prior to analysis. Therefore this SOP does not need a section on Sample Handling and Preservation.

### 3.9.3 Instrument Operation , Startup and Maintenance

This section discusses startup, operation and maintenance of the 43C-TLE. The 43C-TLE has a digital front panel screen with pushbuttons below. This allows the user to check functions, switch operating parameters, and adjust zero and span. Recommend at start-up of instrument and after a warm-up period for the instrument, run through the menu items and record the current settings. **It is extremely important that the user familiarize themselves with the menus available. Inadvertently changing parameters within the analyzer can damage the instrument and possibly invalidate data as well. Please reference the Thermo 43C-TLE owner's manual and read it carefully before adjusting any parameters that are set by the factory.**

### 3.9.3.1 Start up

Before the instrument is operated, inspect the instrument for any damage. If damage is observed to the shipping box or the instrument, contact your shipping personnel.

Carefully remove the cover and check for internal damage. Please see Chapter 2 of the 43C-TLE manual.

Check that all connectors and printed circuit boards are firmly attached.

Once you have removed any packing material and performed your inspection, replace the cover.

Connect the sample line to the **SAMPLE** bulkhead on the rear panel of the instrument. See Chapter 2 of the 43C-TLE manual.

Connect the **EXHAUST** bulkhead to a suitable vent.

Connect a suitable recording device to the rear panel terminals. Please see EPA SOP on “Data Management” for details.

Plug the instrument into a grounded power strip that has surge protection. It is also advisable to purchase an Uninterrupted Power Supply (UPS). An UPS will protect the 43C-TLE from power surges and keep the unit operating until an operator can shut it down.

Press the power rocker switch to “ON.”

### 3.9.3.2 Operation and Range Setting

1. The exhaust fan will start and the Power-Up and Self-Test screens will be displayed. These screens are displayed each time the instrument is turned on, and will continue to be displayed till the instrument has completed its warm up and self-checks. You should allow 30 minutes for the instrument to stabilize.
2. After the warm-up period the Run screen, the normal operating screen, is displayed. This screen is where the SO<sub>2</sub> concentration is displayed.
3. From the Run screen, the Main Menu, which contains a list of submenus, can be displayed by pressing the **MENU** pushbutton. If the instrument is in **REMOTE** mode, press **ENTER** and select **LOCAL** mode in order to be able to change parameters.
4. Instrument parameters and features are divided into the submenus according to their function. Use the **UP/DOWN ARROW** pushbuttons to move the cursor to each submenu. **Note:** When the Main Menu is entered directly from the Run screen, the **LEFT ARROW** pushbutton may be used to jump to the most recently displayed submenu screen.
5. To set the range for the instrument, press the **DOWN ARROW** pushbutton till the cursor is on “Range.” Press the **ENTER** pushbutton to display the Range Menu.
6. In the upper right corner of the display, the word SINGLE, DUAL, or AUTO is displayed to indicate the active mode. For a detailed explanation about the SINGLE, DUAL, or AUTORANGE mode, see Chapter 3 (page 3-7) of the manual. This SOP addresses setting the range for a single range.
7. Press the **ENTER** pushbutton for the Gas Units screen. Use the **DOWN ARROW** pushbutton to select “PPB” and press **ENTER**. Press **MENU** to return to the Range Menu.
8. Use the **DOWN ARROW** pushbutton to display the Range screen and press **ENTER**.
9. Use the **UP/DOWN ARROW** pushbuttons to scroll through the preset ranges. Select “100.0” and press **ENTER**. Press **MENU** to return to the Range Menu.
10. Press **RUN** to return to the Run screen.
11. To set the correct time and date on the instrument, press **MENU** to return to the Main Menu. Press the **DOWN ARROW** pushbutton till the cursor is on Instrument Controls. Press **ENTER** to display the Instrument Controls screen.
12. Use the **UP/DOWN ARROW** pushbuttons to scroll through the choices. Select “Time” and press **ENTER**.
13. Use the **UP/DOWN ARROW** pushbuttons to increase/decrease the hours and minutes; use the **LEFT/RIGHT ARROW** pushbuttons to move the cursor left and right. Set the appropriate time and press **ENTER**. Press **MENU** to return to the Instrument Controls screen.

14. Select "Date" and press **ENTER**.
15. Use the **UP/DOWN ARROW** pushbuttons to increase/decrease the month, day, and year; use the **LEFT/RIGHT ARROW** pushbuttons to move the cursor left and right. Set the appropriate date and press **ENTER**. Press **RUN** to return to the Run screen.
16. The instrument is now set with the appropriate time, date, full scale range and units.
17. It is recommended that you allow the 43C-TLE 24 hours before you attempt function checks or calibration.
18. If your DAS does not have RS-232 capabilities, then proceed to the next section, Diagnostic Checks/Manual Checks. If you have connected the 43C-TLE to a computer or DAS, review the Diagnostic Check from your computer screen.

### **3.9.3.3 Diagnostic Checks/Manual Checks**

To determine whether the 43C-TLE is working properly, the field operators should perform the Diagnostic Checks every time they visit the monitoring station. It is good practice for the operator to check these Diagnostic Checks either by the computer or manually. Below are instructions on how to perform this manually. Please note that the 43C-TLE has set upper and lower ranges for some of these Diagnostic checks. Please reference the owner's manual for these ranges.

1. To display the Diagnostics menu, from the Run screen press the **MENU** pushbutton to display the Main Menu. Use the **UP/DOWN ARROW** pushbuttons to move the cursor to "Diagnostics." Press **ENTER** for the Diagnostics screen.
2. Use the **UP/DOWN ARROW** pushbuttons to toggle through the function check tree. The following table illustrates the functions that should be recorded. Please see Chapter 3 (page 3-34) 43C-TLE manual for more details. A maintenance check sheet is attached in Appendix A of this SOP.
3. On the Program Number screen, the version numbers of the program installed are displayed. Prior to contacting the factory with any questions regarding the instrument, note the program numbers.

**Table 3-2 Diagnostic Checks**

Check	Explanation
Voltages	The current DC power supply and PMT power supply voltages
Temperatures	The current internal instrument and chamber temperatures
Pressure	The current chamber pressure
Flow	The current sample flow rate
Lamp intensity	The current UV lamp intensity
Optical Span Test	A quick way of checking the optics and electronics for span drift
Test Analog Outputs	Enable analog outputs to be set to zero and full scale to adjust analog outputs to agree with the front panel display

Once the Diagnostic checks have been established and recorded for the 43C-TLE, it is time to calibrate the instrument. Please refer to section 3.9.4 of this SOP.

### 3.9.3.4 Preventive Maintenance

Preventive maintenance should **prevent** down-time and data loss. Table 3.3 lists the preventive maintenance items that are listed in the model 43C-TLE manual, Chapter 5. The maintenance procedures described in Chapter 5 of the manual should be performed every six months.

**Table 3-3 Preventive Maintenance Schedule for the 43C-TLE**

Item	Schedule
Visual inspection and cleaning	Bi-annually
Sample particulate filter inspection	Weekly
Verify Test Function	Weekly
Perform Level I calibration	Daily
Capillary inspection and replacement	Bi-annually
Perform flow check	Bi-annually
Fan filter inspection and cleaning	Bi-annually
Lamp voltage check	Bi-annually

### 3.9.3.5 Instrument Troubleshooting

The 43C-TLE manual has an excellent troubleshooting guide in Chapter 6.

## 3.9.4 Calibration and Standardization

The calibration of the 43C-TLE is performed by comparing the output of the instrument against standardized gases of known quality. Generation of these gases is detailed in the EnviroNics Series 9100 Computerized Ambient Monitoring Calibration System SOP. This section will detail how to adjust the 43C-TLE to the standardized gases. Once the calibration has been performed, compare the response of your DAS to the calculated “source” value. If this is outside of +/-10%, then adjust the instrument response as detailed in the next sections.

### 3.9.4.1 Adjustment to Zero Air

Before running the zero air through the 43C-TLE, ensure that the zero air is free from contaminants. One way to determine if the zero air is free from contaminants is through the use of multiple zero air sources, and determining which source produces the lowest response<sup>5</sup>. Appendix D of the 43C-TLE manual provides suggestions for generating trace-quality zero air.

In order to adjust the output of the 43C-TLE to zero air, perform the following:

1. Allow the instrument to sample zero air from a manifold that is at near atmospheric pressure for a minimum of 15 minutes.
2. From the Main Menu select the Calibration menu; select the “Calibrate Zero” screen.
3. Press **ENTER** to set the SO<sub>2</sub> reading to zero.
4. Press **MENU** to return to the Calibration menu.
5. Press **RUN** to return to the Run screen.

### 3.9.4.2 Adjustment to Calibration Gas

It is desirable, but not essential, to calibrate the 43C-TLE at low SO<sub>2</sub> levels (typically, less than 20 ppb). However, fluorescence SO<sub>2</sub> analyzers have been shown to be inherently linear over a wide dynamic range. If low concentration SO<sub>2</sub> calibration cylinders (less than 50 ppm) are used, there is the potential for contamination by back diffusion from a poorly purged regulator. Contamination with even a small amount of moisture from back diffusion can cause the SO<sub>2</sub> concentration to become unstable; the lower the cylinder concentration, the more susceptible it is to any contamination from “abuse” in the field<sup>5</sup>. The best way to ensure low concentration cylinders are not contaminated by back diffusion is to make sure whenever the cylinder valve is open, there is gas flow out of the cylinder.

Appendix D of the 43C-TLE manual offers additional discussion on trace level calibration issues.

In order to adjust the output of the 43C-TLE to NIST traceable calibration gas, perform the following:

1. Switch the calibration unit to generate a known concentration of SO<sub>2</sub>. Allow the instrument to sample calibration gas from a manifold that is at near atmospheric pressure for a minimum of 15 minutes.
2. From the Main Menu select the Calibration menu; select the “Calibrate SO<sub>2</sub>” screen.
3. On the bottom line, there will be individual digits with which the span value can be set. In order to change the concentration, use the **UP/DOWN ARROW** pushbuttons to increase/decrease each digit; use the **LEFT/RIGHT ARROW** pushbuttons to move the cursor left and right.
4. Press **ENTER** to calibrate the SO<sub>2</sub> reading to the SO<sub>2</sub> calibration gas.
5. This operation changes the calculation equation and adjusts the SO<sub>2</sub> span coefficient of the instrument.
6. Press **MENU** to return to the Calibration menu.
7. Press **RUN** to return to the Run screen.

### 3.10 Data Analysis and Calculations

Data analysis for this analyzer is detailed in the “Data Acquisition and Management SOP.”

## 4.0 QUALITY CONTROL AND QUALITY ASSURANCE

The following section has brief definitions of the QA/QC indicators. Table 4-1 has the Measurement Quality Objectives (MQOs) of the Thermo 43C-TLE. Please note that this section details primarily with the QA indicators. Quality Control for continuous electronic instruments, such as the 43C-TLE consists of performing the diagnostic checks, maintenance and calibrations. These procedures are detailed in sections 3.9.3 and 3.9.4: Instrument Operation, Startup and Maintenance and Calibration and Standardization. Appendix A has an example of a Quality Control and Maintenance Record developed by the EPA for this instrument.

## 4.1 Precision

Precision is defined as the measure of agreement among individual measurements of the same property taken under the same conditions. For SO<sub>2</sub>, this refers to testing the SO<sub>2</sub> analyzer in the field at concentrations between 0.0003 and 0.005 ppm. The test must be performed, at a minimum, once every two weeks. Calculations for Precision can be found in Reference item 3.

## 4.2 Bias

Bias is defined as the degree of agreement between a measured value and the true, expected, or accepted value. Quantitative comparisons are made between the measured value and the true, standard value during audits. Generally, three upscale points and a zero point are compared. Two audit types commonly used for SO<sub>2</sub>, direct comparison and blind, are discussed below. The SOP should discuss plans for each type of audit.

- **Direct Comparison Audits:** An independent audit system is brought to the monitoring location and produces gas concentrations that are assayed by the monitoring station's SO<sub>2</sub> analyzer. In most cases, a person outside of the agency or part of an independent QA group within the agency performs the audit. The responses of the on-site analyzer are then compared against the calculated concentration from the independent audit system and a linear regression is generated
- **Blind Audits:** In blind audits (also called performance evaluation audits); agency staff are sent an audit device, such as the National Performance Evaluation Program (NPEP). The agency staff does not know the SO<sub>2</sub> concentrations produced by the audit equipment. Responses of the on-site analyzer are then compared against those of the generator and a linear regression is calculated.

## 4.3 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. Since the NCORE Level I and II siting criteria are urban and regional, the trace level SO<sub>2</sub> criteria are the same. Please reference the National Monitoring Strategy<sup>5</sup> for a discussion of NCORE Level II SO<sub>2</sub> monitoring scale.

## 4.4 Completeness

Completeness is defined as the amount of data collected compared to a pre-specified target amount. For SO<sub>2</sub>, EPA requires a minimum completeness of 75% (40 CFR 50, App.H.3). Typical completeness with the 43C-TLE values can approach 90-93%.

## 4.5 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 43C-TLE meets the MQOs for a trace level SO<sub>2</sub> instrument. Please see Table 4-1.

## 4.6 Method Detection Limit

The method detection limit (MDL) or detectability refers to the lowest concentration of a substance that can be determined by a given procedure. The 43C-TLE must be able to detect a minimum value of 300 ppt of SO<sub>2</sub>.

**Table 4-1 Measurement Quality Assurance Objectives**

<b>Requirement</b>	<b>Frequency</b>	<b>Acceptance Criteria</b>	<b>Reference</b>	<b>Information or Action</b>
Bias	NCORE, once per year	To be determined.	40 CFR Pt.58	To be determined.
Precision	1 every 2 weeks	Concentration: 0.0003 -0.005 ppm, Coefficient of Variance: To be determined.	40 CFR Pt.58 Appendix A	To be determined.
Completeness	Quarterly, Annually	NCORE, 75%	National Monitoring Strategy.	If under 75%, institute Quality Control Measures
Representativeness	N/A	Neighborhood, Urban or Regional Scale	40 CFR 58	N/A
Comparability	N/A	Must be a Trace Level instrument. See Sections 3.1 and 3.2 of this document.	National Monitoring Strategy.	N/A
Method Detection Limit	N/A	300 ppt	National Monitoring Strategy	Testing is performed at the factory.

## **5.0 REFERENCES**

1. Code of Federal Regulations, Title 40, Part 53.23c
2. Code of Federal Regulation, Title 40, Part 58, Appendix A
3. The National Air Monitoring Strategy, Final Draft, 4/29/04, <http://www.epa.gov/ttn/amtic/monstratdoc.html>
4. Instruction Manual, Model 43C Trace Level SO<sub>2</sub> Analyzer
5. Trace SO<sub>2</sub> Monitoring Guidance for the MANE-VU Regional Aerosol Intensive Network (RAIN) program, Draft (dated March 7, 2005).

**Appendix A**

Environmental Protection Agency  
 Monthly Quality Control and Maintenance Records  
 Thermo 43C-TLE SO<sub>2</sub> Analyzer

Site Name/Location \_\_\_\_\_

Technician \_\_\_\_\_

Month/Year \_\_\_\_\_

Serial Number \_\_\_\_\_ Range \_\_\_\_\_

<b>Parameter</b>	<b>Date</b>	<b>Date</b>	<b>Date</b>	<b>Acceptance Criteria</b>
DC Voltage				
PMT Voltage				
Internal Temp				
Chamber Temp				
Chamber Pressure				
Sample Flow				
UV Lamp Intensity				
Other Tests				
Optical Span Test				

<b>Date</b>	<b>Comments and Notes</b>

**Figure A-1 Thermo 43C-TLE Quality Control and Maintenance Record**

**STANDARD OPERATING PROCEDURES**  
**THERMO ENVIRONMENTAL INSTRUMENTS**  
**42CY NO<sub>y</sub> TRACE LEVEL**  
**REACTIVE NITROGEN COMPOUNDS INSTRUMENT**

**Version 3**



## **Section 1.1 Acknowledgments**

This Standard Operating Procedure (SOP) for Trace Level Reactive Nitrogen Compounds is the product of EPA's Office of Air Quality, Planning and Standards. The following individuals are acknowledged for their contributions.

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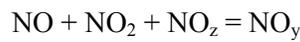
**STANDARD OPERATING PROCEDURES**  
**THERMO ENVIRONMENTAL INSTRUMENTS**  
**42CY NO<sub>y</sub> TRACE LEVEL**  
**REACTIVE NITROGEN COMPOUNDS INSTRUMENT**

**3.0 PROCEDURES**

**3.1 Scope and Applicability**

Reactive nitrogen compounds (NO<sub>y</sub>) have been identified as precursors for both ozone and fine particulate matter (PM<sub>2.5</sub>). Measurements of NO<sub>y</sub> constitute a valuable adjunct to current NO and NO<sub>2</sub> monitoring because the individual species comprising NO<sub>y</sub> include not only NO and NO<sub>2</sub> but also other organic nitroxyl compounds that have recently been shown to play a significant role in the photochemical O<sub>3</sub> formation process.

NO<sub>y</sub> consists of all oxides of nitrogen in which the oxidation state of the N atom is +2 or greater, ie, the sum of all reactive nitrogen oxides including NO<sub>x</sub> (NO + NO<sub>2</sub>) and other nitrogen oxides referred to as NO<sub>z</sub>. The major components of NO<sub>z</sub> include nitrous acids [nitric acid (HNO<sub>3</sub>), and nitrous acid (HONO)], organic nitrates [peroxyl acetyl nitrate (PAN), methyl peroxyl acetyl nitrate (MPAN), and peroxyl propionyl nitrate, (PPN)], and particulate nitrates.



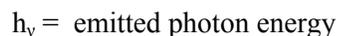
The Thermo Environmental Instruments (TECO) model 42CY is an instrument for the determination of trace levels of NO<sub>y</sub> by its chemiluminescent reaction with O<sub>3</sub>. This SOP will detail the operation, calibration, preventive maintenance, cautions and health warnings.

**3.2 Summary of Method**

The analytical principle is based on the chemiluminescent reaction of NO with an excess of O<sub>3</sub>. This reaction produces a characteristic near infrared luminescence with an intensity that is linearly proportional to the concentration of NO present. Specifically,



where:

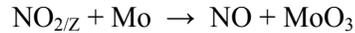


The reaction results in electronically excited NO<sub>2</sub> molecules which revert to their ground state, resulting in an emission of light or chemiluminescence.

To determine the concentration of NO, the sample gas is blended with O<sub>3</sub> in a reaction chamber causing the reaction to occur. The chemiluminescence that results from the reaction is monitored by an optically filtered high-sensitivity photomultiplier. The optical filter and photomultiplier respond to light in a narrow-wavelength band unique to the NO and O<sub>3</sub> reaction. The electronic signal produced in the photomultiplier is proportional to the NO concentration.

To measure NO<sub>y</sub>, sample air is passed through a probe-mounted chemical reduction converter and the nitroxyl compounds present are reduced to NO. The sample is then blended with O<sub>3</sub> and the

chemiluminescent response is proportional to the concentration of NO<sub>y</sub> entering the converter. The chemical reduction converter uses heated molybdenum to convert non-NO NO<sub>y</sub> species to NO. Specifically,



where:

Mo = heated molybdenum reductant

The concentration of NO<sub>2</sub> + NO<sub>z</sub> is calculated as the difference between a measured NO<sub>y</sub> value and a measured NO value representing approximately the same point in time. This procedure is similar to the current methodology used to measure NO<sub>x</sub>, however, the converter temperature is higher in order to enhance conversion of NO<sub>z</sub> species. In addition, the converter has been moved to the sample inlet to avoid line losses of “sticky” NO<sub>y</sub> species such as HNO<sub>3</sub>.

A diagram of the 42CY instrument is presented in Figure 3-1. For the 42CY, ambient sample is first drawn through a short Teflon sample line and split into two parallel flow channels using a ½ inch PFT Teflon tee. Channel 1 passes through a Teflon filter and then directly to the monitor. Channel 2 first passes through a catalytic converter before going through a Teflon filter to the monitor. Flow from each channel is alternately fed to the reaction chamber to detect the NO. The converter is operated outside of the analyzer, close to the ambient sampling point. This allows for a short flow path upstream of the converter and minimizes the loss of species such as HNO<sub>3</sub>. In addition to alternating flows from Channel 1 and Channel 2 to the reactor, the analyzer also alternates a flow of internal zero air, produced by pre-reacting the sample flow with a high concentration of ozone before reaching the chemiluminescent detector. The signal from this zero air stream is used to correct for analyzer drift, and allows the analyzer to achieve very low detection limits (0.05 ppb) compared with standard NO<sub>x</sub> analyzers.

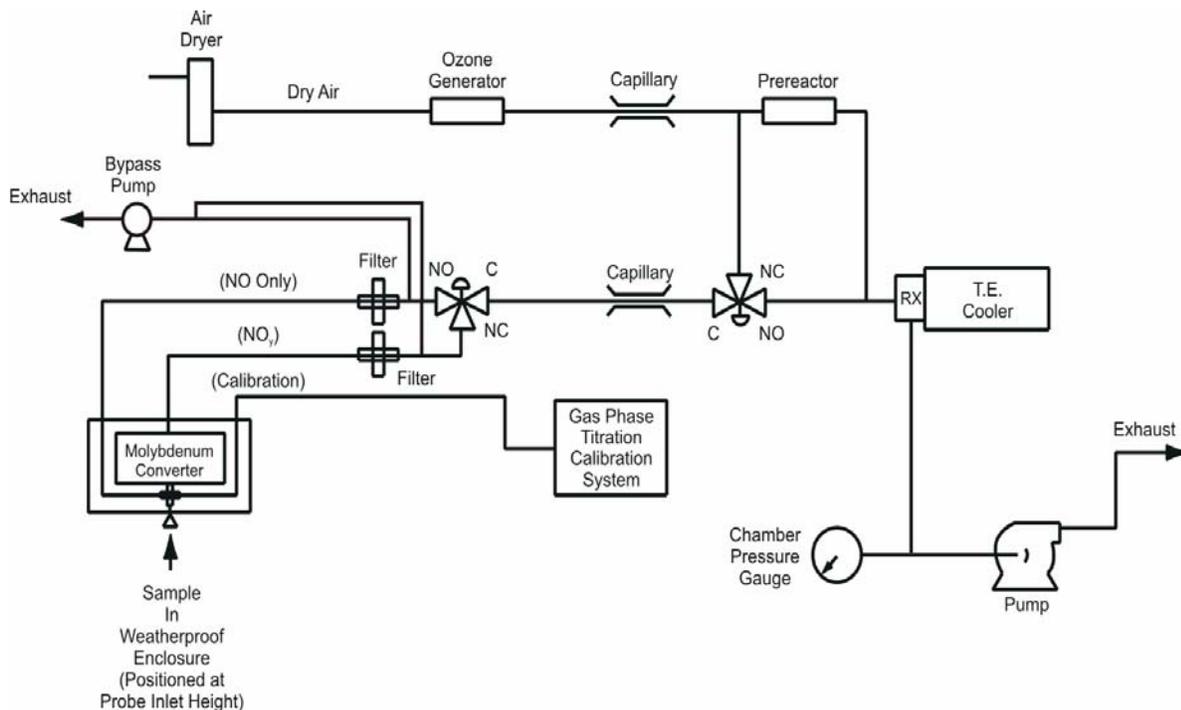


Figure 3-1. Simplified Flow Diagram of 42CY NO<sub>y</sub> Monitor

### 3.3 Definitions

Here are some key terms for this method.

**Table 3-1 Definitions of Key Terms**

<u>Term</u>	<u>Definition</u>
NO <sub>y</sub>	Total reactive nitrogen including NO, NO <sub>2</sub> , HNO <sub>3</sub> , and other reactive organic nitrogen compounds.
NO <sub>z</sub>	Reactive nitrogen compounds other than NO and NO <sub>2</sub> .
DAS	Data acquisition system. Used for automatic collection and recording of Carbon Monoxide concentrations.
Interferences	Physical or chemical entities that cause NO <sub>y</sub> measurements to be higher (positive) or lower (negative) than they would be without the entity. (See Section 3.6).

### 3.4 Health and Safety Warnings

**To prevent personal injury, please heed these warnings concerning the 42CY.**

1. Nitrogen oxides are a poisonous gas. Vent any nitrogen oxide or calibration span gas to the atmosphere rather than into the shelter or other sampling area. If this is impossible, limit exposure to nitrogen oxide by getting fresh air every 5 to 10 minutes. If the operator experiences light headedness, headache or dizziness, leave the area immediately.
2. Always use a third ground wire on all instruments.
3. Always unplug the analyzer when servicing or replacing parts.
4. If it is mandatory to work inside an analyzer while it is in operation, use extreme caution to avoid contact with high voltages. The analyzer has a 110 volt Volts Alternating Current (VAC) power supply. Refer to the manufacturer's instruction manual and know the precise locations of the VAC components before working on the instrument.
5. Avoid electrical contact with jewelry. Remove rings, watches, bracelets, and necklaces to prevent electrical burns.

### 3.5 Cautions

**To prevent damage to the 42CY, all cautions should immediately precede the applicable step in this SOP. The following precautions should be taken:**

1. Keep the interior of the analyzer clean.
2. Inspect the system regularly for structural integrity.
3. To prevent major problems with leaks, make sure that all sampling lines are reconnected after required checks and before leaving the site.
4. Inspect tubing for cracks and leaks.
5. It is recommended that the analyzer be leak checked after replacement of any pneumatic parts.
6. If cylinders are used in tandem with Mass Flow Control (MFC) calibrators, use and transport is a major concern. Gas cylinders can sometimes contain pressures as high as 2000 pounds per square inch (psi). Handling of cylinders must be done in a safe manner. If a cylinder is accidentally dropped and valve breaks off, the cylinder can become explosive or a projectile.

7. Transportation of cylinders is regulated by the Department of Transportation (DOT). It is strongly recommended that all agencies contact the DOT or Highway Patrol to learn the most recent regulations concerning transport of cylinders.
8. Low levels of nitrogen oxides in the air can irritate your eyes, nose, throat, and lungs, possibly causing you to cough and experience shortness of breath, tiredness, and nausea. Exposure to low levels can also result in fluid build-up in the lungs 1 or 2 days after exposure. Breathing high levels of nitrogen oxides can cause rapid burning, spasms, and swelling of tissues in the throat and upper respiratory tract, reduced oxygenation of body tissues, a build-up of fluid in your lungs, and death.
9. It is possible (and practical) to blend other compounds with NO. If this is the case, it is recommended that MSDS for all compounds be made available to all staff that use and handle the cylinders or permeation tubes.
10. Shipping of cylinders is governed by the DOT. Contact the DOT or your local courier about the proper procedures and materials needed to ship high-pressure cylinders.

### 3.6 Interferences

**Ammonia:** Depending on the converter temperature, the converter may convert a small amount of ammonia ( $\text{NH}_3$ ) to NO, resulting in increased NO readings. However, under normal circumstances  $\text{NH}_3$  concentrations are low compared to NO and this positive interference is negligible. Nonetheless, care should be taken when siting the monitor to be sure that it is not located near significant  $\text{NH}_3$  sources which could cause elevated  $\text{NH}_3$  concentrations (e.g., concentrated animal feeding operations).

### 3.7 Personal Qualifications

The person(s) chosen to operate the 42CY should have a minimum of qualifications. The understanding of basic chemistry and electronics are a must. The understanding of digital circuitry is helpful, but not required. Also, courses in data processing and validation are also welcome.

### 3.8 Equipment and Supplies

**Monitoring Apparatus:** The design of the 42CY is similar to the 42C with several major variations. A diagram of the 42CY instrument is presented in Figure 3-1. The four main components are:

- Remote Inlet and Converter: This component consists of a weather resistant enclosure that houses the molybdenum converter and supports the sample inlet.
- Pneumatic System: Consists of sample inlet lines, sample bypass pump, particulate filters, reaction chamber, flowmeters, and vacuum pump, all used to bring ambient air samples to the analyzer.
- Analytical System: This portion of the instrument consists of the ozone generator, pre-reaction chamber, reaction chamber, and photomultiplier tube.
- Electronic Hardware: The part of the analyzer that generally requires little or no maintenance. If the 42CY is operated above the manufacturer's recommended temperature limit, however, individual integrated chips can fail and cause problems with data storage or retrieval.

Other apparatus and equipment includes the following.

**Instrument Shelter:** A shelter is required to protect the analyzer from precipitation and adverse weather conditions, maintain operating temperature within the analyzer's temperature range requirements, and provide security and electrical power. The recommended shelter temperature range is 20-30°C.

**Spare Parts and Incidental Supplies:** See the 42CY operating manual, Chapter 5, for specific maintenance and replacement requirements.

**Calibration System:** A system that creates concentrations of nitrogen oxide of known quality is necessary for establishing traceability. The calibration system must also include a high precision ozone generator in order to generate concentrations of nitrogen dioxide by gas phase titration with nitrogen oxide. This is described in detail in the “EnviroNics 9100 SOP.” Please reference this document.

**DAS:** A data acquisition system is necessary for storage of ambient and ancillary data collected by the 42CY. The 42CY requires a minimum of two analog outputs, one each for NO and NO<sub>y</sub> outputs. A third output is also needed if the monitor is to be run in auto-ranging mode to capture the range information. Note, a digital DAS is preferred because diagnostic information can also be collected which will greatly help troubleshooting and validation of data.

**Wiring, Tubing and Fittings:** PFT Teflon™ should be used exclusively throughout the intake system. Examine the tubing and discard if particulate matter is collected in the tubing. All fittings and ferrules should be made of Teflon™ or stainless steel. Connection wiring to the DAS should be shielded two strand wire or RS-232 cables for digital connections.

**Reagents and Standard:** The 42CY does not require any reagents since the instrument uses photometry to analyze for NO<sub>y</sub>. All standards for the NO<sub>y</sub> method can be obtained in compressed cylinders and must be NIST traceable. Please see the “Calibration of Trace Gas Analyzers” SOP.

### 3.9 Procedure

**3.9.1 Sample Collection:** Ambient air is drawn through a sample inlet located on the remote inlet/converter. The sampling point should be located 3 to 5 meters above ground level, at least 1 meter from all obstructions, and at least 10 meters from obstructions over a range of at least 180 degrees. These requirements necessitate mounting the catalytic converter outside the shelter. The sample bypass lines from the converter to the instrument should not exceed 10 meters in length.

**3.9.2 Sample Handling and Preservation:** NO<sub>y</sub> samples receive no special preparation prior to analysis. Therefore this SOP does not need a section on Sample Handling and Preservation.

### 3.9.3 Instrument Operation, Startup and Maintenance

This section discusses startup, operation and maintenance of the 42C-NO<sub>y</sub>. The 42CY series instrument has a digital front panel screen with control buttons below. This allows the user to check functions, switch operating parameters, adjust zero and span and read warnings messages. **It is extremely important that the user familiarize themselves with the menus available. Inadvertently changing parameters within the analyzer can damage the instrument and possibly invalidate data as well. Please reference the 42CY owner’s manual and read it carefully before adjusting any parameters that are set by the factory.**

#### 3.9.3.1 Installation and Start up

1. Before the instrument is operated, inspect the instrument for any damage. If damage is observed to the shipping box or the instrument, contact your shipping personnel.
2. Remove the instrument from its shipping container and set on a table or bench that allows easy access to both the front and rear of the instrument.

3. Carefully remove the instrument cover and remove any packing material.
4. Check for possible internal damage.
5. Check that all connectors and printed circuit boards are firmly attached.
6. Once you have performed your inspection, replace the cover.
7. Remove the remote inlet enclosure and place on a bench that allows easy access.
8. Open the enclosure and check for internal damage.
9. Using ¼ inch PFT Teflon™ tubing, plumb the inlet as shown in Figure 3-2.
10. Mount the enclosure at the desired sampling location being sure to meet the requirements detailed in 3.9.1, above.
11. Determine the distance from the point where the sample tubing exits the converter enclosure to the point where the tubing will enter the monitoring station, including ample length to account for any curves or obstructions. Cut the two plastic conduits to this length.
12. Run the two sample lines, calibration line, and thermocouple wire through one conduit, and the converter power cable through the second.
13. Connect the two sample lines, calibration line, thermocouple wire, and power cable inside the converter enclosure as shown in Figure 3-2, and secure the conduits to the converter enclosure.
14. Run the tubing, thermocouple wire, and power cable in to the monitoring station.
15. Mount the 42CY in its rack being sure that the 42CY has enough clearance so that it gets proper ventilation.
16. Connect the sample lines to the bypass pump, filters, and analyzer as shown in Figure 3-1.
17. Connect the Dryrite™ air dryer to the dry air bulkhead.
18. Connect the intake of the vacuum pump to the exhaust bulkhead.
19. Connect the charcoal container to the outlet of the vacuum pump.
20. Connect the converter power cable and thermocouple wire to the back of the 42CY.
21. Connect the power cable and plug the instrument, vacuum pump, and bypass pump into a grounded power strip that has surge protection. It is also advisable to purchase an Uninterrupted Power Supply (UPS). An UPS will protect the 42CY from power surges and keep the unit operating until an operator can shut it down.
22. Connect the output of the analog to a DAS via shielded two wire cable. Please see EPA SOP on “Data Management” for details.
23. Connect the digital RS-232 port to an appropriate cable and connect it to the DAS. Please see EPA SOP on “Data Management” for further details.
24. Press the power rocker switch to “ON.”
25. After an adequate warm-up period, run through the menu and record factory/start-up settings. Compare to recommended limits located in the manual and listed on the daily worksheet.
26. Perform a leak check. Press the **MENU** pushbutton to display the Main Menu. Use the **UP/DOWN ARROW** pushbuttons to move the cursor to “Diagnostics.” Press **ENTER** for the Diagnostics screen. Use the **UP/DOWN ARROW** pushbuttons to select **Flow**. The sample flow rate should be approximately 1 lpm. Cap or otherwise plug the sample inlet on the remote converter. The sample flow rate should drop to less than 0.1 lpm within 15 seconds. Slowly remove the cap. Do not leave the inlet capped for more than a minute as it can cause damage to the monitor. If the sample flow does not drop to below 0.1 lpm, tighten all connections and repeat leak test.

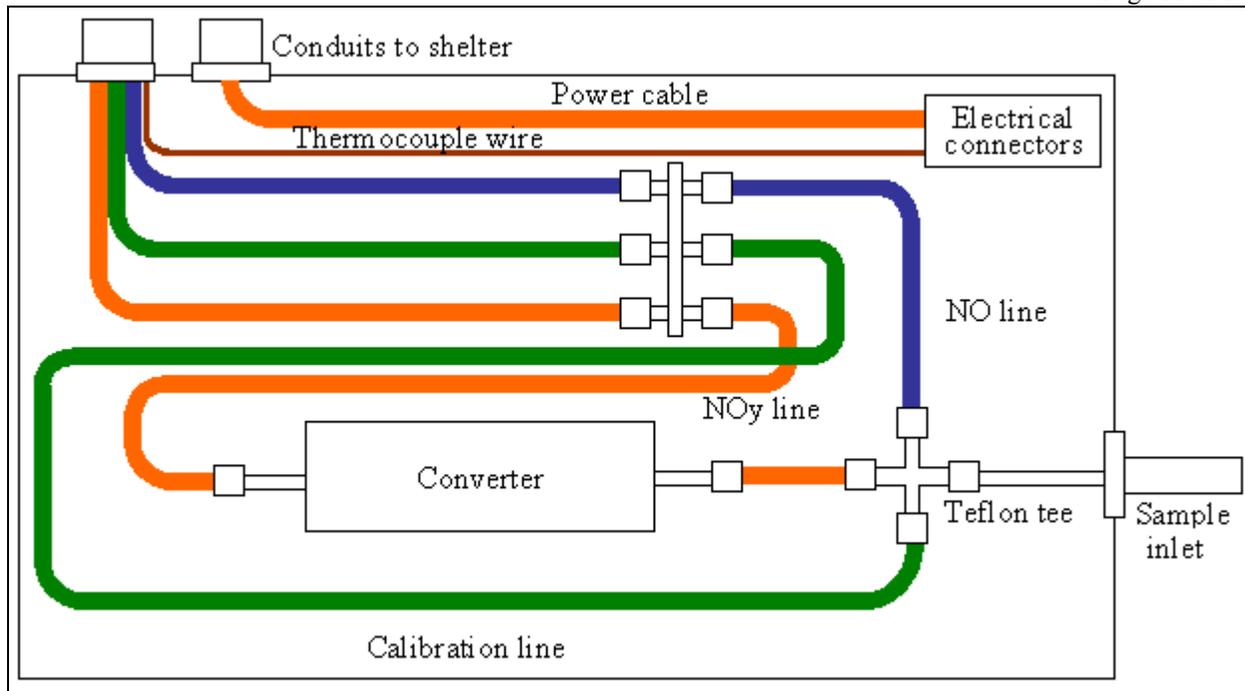


Figure 3-2. Schematic of plumbing and wiring for 42CY External Converter

### 3.9.3.2 Operation and Range Setting

1. The exhaust fan will start and the Power-Up and Self-Test screens will be displayed. These screens are displayed each time the instrument is turned on, and will continue to be displayed till the instrument has completed its warm up and self-checks. You should allow 30 minutes for the instrument to stabilize.
2. After the warm-up period the Run screen, the normal operating screen, is displayed. This screen is where the NO and NO<sub>y</sub> concentration is displayed. The display for the model that EPA is using currently mis-reports the data. The data reported as NO<sub>x</sub> is actually NO<sub>y</sub>. The data reported as NO<sub>2</sub> is actually NO<sub>2</sub> + NO<sub>z</sub>. Future versions should correct this, and are expected to report NO, NO<sub>y</sub> and "DIFF" which would represent NO<sub>2</sub> + NO<sub>z</sub>.
3. In the bottom right hand corner the word "**LOCAL**" or "**REMOTE**" will be displayed. The analyzer must be in local mode to adjust the configuration using the keys on the front panel. Press the **ENTER** button until the analyzer is in local mode.
4. From the Run screen, the Main Menu, which contains a list of submenus, can be displayed by pressing the **MENU** pushbutton.
5. Instrument parameters and features are divided into the submenus according to their function. Use the **UP/DOWN ARROW** pushbuttons to move the cursor to each submenu. **Note:** When the Main Menu is entered directly from the Run screen, the **LEFT ARROW** pushbutton may be used to jump to the most recently displayed submenu screen.
6. To set the range for the instrument, press the **DOWN ARROW** pushbutton till the cursor is on "Range." Press the **ENTER** pushbutton to display the Range Menu.
7. In the upper right corner of the display, the word single, dual, or auto is displayed to indicate the active mode. For a detailed explanation about the single, dual, or autorange mode, see Chapter 3 (page 3-7) of the manual. This SOP addresses setting the range for a single range.

8. Press the **ENTER** pushbutton for the Gas Units screen. Use the **DOWN ARROW** pushbutton to select “PPB” and press **ENTER**. Press **MENU** to return to the Range Menu.
9. Use the **DOWN ARROW** pushbutton to display the Range screen and press **ENTER**.
10. Use the **UP/DOWN ARROW** pushbuttons to scroll through the preset ranges. Select “100.0” and press **ENTER**. Press **MENU** to return to the Range Menu. Note, a higher range may be required in areas with higher NO<sub>y</sub> concentrations.
11. Press **RUN** to return to the Run screen.
12. To set the averaging time, press the **MENU** button to return to the Main Menu. Press the **DOWN ARROW** pushbutton till the cursor is on Averaging Time.
13. Press **ENTER** for the averaging time screen. Use the **DOWN ARROW** pushbutton to select the desired averaging time and press **ENTER**. Press **RUN** to return to the Range Menu.
14. To set the correct time and date on the instrument, press **MENU** to return to the Main Menu. Press the **DOWN ARROW** pushbutton till the cursor is on Instrument Controls. Press **ENTER** to display the Instrument Controls screen.
15. Use the **UP/DOWN ARROW** pushbuttons to scroll through the choices. Select “Time” and press **ENTER**.
16. Use the **UP/DOWN ARROW** pushbuttons to increase/decrease the hours and minutes; use the **LEFT/RIGHT ARROW** pushbuttons to move the cursor left and right. Set the appropriate time and press **ENTER**. Press **MENU** to return to the Instrument Controls screen.
17. Select “Date” and press **ENTER**.
18. Use the **UP/DOWN ARROW** pushbuttons to increase/decrease the month, day, and year; use the **LEFT/RIGHT ARROW** pushbuttons to move the cursor left and right. Set the appropriate date and press **ENTER**. Press **RUN** to return to the Run screen.
19. The instrument is now set with the appropriate time, date and full scale range.
20. It is recommended that you allow the 42CY 24 hours before you attempt function checks or calibration.
21. If the DAS system that you have does not have the RS-232 capabilities, then proceed to the next section, Diagnostic Checks/Manual Checks. If you have connected the 42CY to a computer or DAS, review the Diagnostic Check from your computer screen.

### 3.9.3.3 Diagnostic Checks/Manual Checks

To determine whether the 42CY is working properly, the field operators should perform the Diagnostic Checks every time they visit the monitoring station. It is good practice for the operator to check these Diagnostic Checks either by the computer or manually. Below are instructions on how to perform this manually. Please note that the 42CY has set upper and lower ranges for some of these Diagnostic checks. Please reference the owner’s manual for these ranges.

1. To display the Diagnostics menu, from the Run screen press the **MENU** pushbutton to display the Main Menu. Use the **UP/DOWN ARROW** pushbuttons to move the cursor to “Diagnostics.” Press **ENTER** for the Diagnostics screen.
2. Use the **UP/DOWN ARROW** pushbuttons to toggle through the function check tree. The following table illustrates the functions that should be recorded. Please see Chapter 3 (page 3-36) 42CY manual for more details. A manual checklist on maintenance is attached in Appendix A of this SOP.
3. On the Program Number screen, the version numbers of the program installed are displayed. Prior to contacting the factory with any questions regarding the instrument, note the program numbers.

**Table 3-2 Diagnostic Checks**

Check	Explanation
Voltages	The current DC power supply and PMT power supply voltages
Temperatures	The current internal instrument and chamber temperatures
Pressure	The current chamber pressure
Flow	The current ozonator and sample flow rate
Test Analog Outputs	Enable analog outputs to be set to zero and full scale to adjust analog outputs to agree with the front panel display

Reference the owners manual or the worksheet in Appendix A of this SOP for acceptable limits. Once the Diagnostic checks have been established and recorded for the 42CY, it is time to calibrate the instrument. Please refer to section 3.9.4 of this SOP.

### 3.9.3.4 Preventive Maintenance

Preventive maintenance should prevent down-time and data loss. Table 3.3 lists the preventive maintenance items that are listed in the 42CY manual, section 5.

**Table 3-3 Preventive Maintenance Schedule the TECO 42CY**

Item	Schedule
Replace ozonator air feed drying column	As needed
Inspect and replace sample filters	Weekly
Inspect and replace capillaries	Quarterly
Digital to analog converter test	As needed
Inspect and clean cooler fins	Semi-annually
Inspect and clean fan filters	Semi-annually

### 3.9.3.5 Instrument Troubleshooting

The 42CY manual has an excellent troubleshooting guide in Chapter 6. Please reference the manual for details on troubleshooting the 42CY analyzer.

## 3.9.4 Calibration and Standardization

The calibration of the 42CY is performed by comparing the output of the instrument against standardized gases of known quality. Generation of these gases is detailed in the “Calibration of Trace Gas Analyzers” SOP. This section will detail how to adjust the 42CY to the standardized gases. Once the calibration has been performed, compare the response of your DAS to the calculated “source” value. If this is outside of +/-10%, then adjust the instrument response as detailed in the next sections.

### 3.9.4.1 Adjustment to Zero Air

In order to adjust the output of the 42CY to zero air, perform the following:

1. Connect the calibration line to a source of zero air. Supply a sufficient amount of zero air to supply the analyzer and to ensure that a small amount of excess zero air exits from the sample inlet.

2. Allow the analyzer to sample zero air for at least 15 minutes or until stable NO, NO<sub>y</sub>, and NO<sub>2</sub>+NO<sub>z</sub> readings are obtained.
3. From the Main Menu, choose Calibration. From the calibration menu, choose Calibrate Zero.
4. The Calibrate Zero screen displays the NO, NO<sub>y</sub>, and Prereactor readings.
5. Press **ENTER** to set the NO, NO<sub>y</sub>, and Prereactor readings to zero.
6. The message "Savings Parameters(s)" is briefly displayed to indicate that the background readings have been set to zero.
7. Press **MENU** to return to the Calibration menu.
8. Press **RUN** to return to the Run screen.

### 3.9.4.2 Adjustment to Calibration Gas

In order to adjust the output of the 42CY to NIST traceable calibration gas, perform the following:

1. Switch the calibration unit to generate a known concentration of NO corresponding to approximately 80% of full scale.
2. Supply a sufficient amount of calibration air to supply the analyzer and to ensure that a small amount of excess calibration air exits from the sample inlet.
3. Allow the instrument to sample calibration gas for a minimum of 15 minutes, or until stable NO, NO<sub>y</sub>, and NO<sub>2</sub>+NO<sub>z</sub> readings are obtained.
4. From the Main Menu select the Calibration menu; select the "Calibrate NO" screen.
5. On the bottom line, there will be individual digits with which the span value can be set. In order to change the span value, use the **UP/DOWN ARROW** pushbuttons to increase/decrease each digit; use the **LEFT/RIGHT ARROW** pushbuttons to move the cursor left and right.
6. Change the span value to reflect the known concentration of NO in the calibration gas being sampled.
7. Press **ENTER** to calibrate the NO reading to the NO calibration gas.
8. This operation changes the calculation equation and adjusts the NO span coefficient of the instrument.
9. Press **MENU** to return to the Calibration menu.
10. Select "Calibrate NO<sub>y</sub>".
11. Change the span value to reflect the known concentration of NO plus any known NO<sub>2</sub> impurity in the calibration gas being sampled.
12. Press **ENTER** to calibrate the NO<sub>y</sub> reading to the NO calibration gas.
13. This operation changes the calculation equation and adjusts the NO<sub>y</sub> span coefficient of the instrument.
14. Press **MENU** to return to the Calibration menu.
15. Adjust the calibrator to add a known concentration of ozone to the calibration gas corresponding to approximately 60% of full scale. The ozone will react with the NO in the calibration gas to form NO<sub>2</sub>.
16. Supply a sufficient amount of calibration air to supply the analyzer and to ensure that a small amount of excess calibration air exits from the sample inlet.
17. Allow the instrument to sample calibration gas for a minimum of 15 minutes, or until stable NO, NO<sub>y</sub>, and NO<sub>2</sub>+NO<sub>z</sub> readings are obtained.
18. Select "Calibrate NO<sub>2</sub>" from the Calibration menu.
19. Change the span value to reflect the known concentration of ozone added to the calibration gas plus any known NO<sub>2</sub> impurity in the calibration gas being sampled.
20. Press **ENTER** to calibrate the NO<sub>2</sub> reading to the NO calibration gas.
21. This operation changes the calculation equation and adjusts the NO<sub>2</sub> span coefficient of the instrument.

22. Press **RUN** to return to the Run screen.

### 3.10 Data Analysis and Calculations

Data analysis for this analyzer is detailed in “Data Acquisition and Management” SOP.

## 4.0 QUALITY CONTROL AND QUALITY ASSURANCE

The following section has brief definitions of the QA/QC indicators. Table 4-1 has the Measurement Quality Objectives (MQOs) of the 42CY. Please note that this section details primarily with the data quality indicators. Quality Control for continuous electronic instruments, such as the 42CY consists of performing the diagnostic checks, maintenance and calibrations. These procedures are detailed in sections 3.9.3 and 3.9.4: Instrument Operation, Startup and Maintenance and Calibration and Standardization. Appendix A has an example of a Quality Control and Maintenance Record developed by the EPA for this instrument.

### 4.1 Precision

Precision is defined as the measure of agreement among individual measurements of the same property taken under the same conditions. For NO<sub>y</sub>, this refers to testing the NO<sub>y</sub> analyzer in the field at concentrations between 0.2 and 100 ppb (note, higher test levels may be required in areas with higher NO<sub>y</sub> concentrations). The test must be performed, at a minimum, once every two weeks. Calculations for Precision can be found in Reference 4.

### 4.2 Bias

Bias is defined as the degree of agreement between a measured value and the true, expected, or accepted value. Quantitative comparisons are made between the measured value and the true, standard value during audits. Generally, three upscale points and a zero point are compared. Two audit types commonly used for NO<sub>y</sub>, direct comparison and blind, are discussed below. The SOP should discuss plans for each type of audit.

- **Direct Comparison Audits:** An independent audit system is brought to the monitoring location and produces gas concentrations that are assayed by the monitoring station's NO<sub>y</sub> analyzer. In most cases, a person outside of the agency or part of an independent QA group within the agency performs the audit. The responses of the on-site analyzer are then compared against the calculated concentration from the independent audit system and a linear regression is generated
- **Blind Audits:** In blind audits (also called performance evaluation audits); agency staff are sent an audit device, such as the National Performance Evaluation Program (NPEP). The agency staff does not know the NO<sub>y</sub> concentrations produced by the audit equipment. Responses of the on-site analyzer are then compared against those of the generator and a linear regression is calculated.

### 4.3 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. Since the NCORE Level I and II siting criteria are urban and regional, the TL-NO<sub>y</sub> criteria are the same. Please reference the National Monitoring Strategy<sup>5</sup> for a discussion of NCORE Level II NO<sub>y</sub> monitoring scale.

#### 4.4 Completeness

Completeness is defined as the amount of data collected compared to a pre-specified target amount. The EPA does not have a minimum completeness requirement for NO<sub>y</sub> sampling. However, for NO<sub>x</sub>, EPA requires a minimum completeness of 75% (40 CFR 50, App.H.3). Typical completeness with the 42CY values can approach 90-93%.

#### 4.5 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 42CY meets the MQOs for a Trace Level NO<sub>y</sub> instrument. Please see Table 4-1.

#### 4.6 Method Detection Limit

The method detection limit (MDL) or detectability refers to the lowest concentration of a substance that can be determined by a given procedure. The 42CY must be able to detect a minimum value of 50 ppt of NO<sub>y</sub>.

**Table 4-1 Measurement Quality Assurance Objectives**

<b>Requirement</b>	<b>Frequency</b>	<b>Acceptance Criteria</b>	<b>Reference</b>	<b>Information or Action</b>
Bias	NCORE, once per year	Slope: 1.00 +/- 0.15 Intercept: +/- 3% of full scale Regression: <0.9950	40 CFR Pt.58	Use of NIST generated gas concentrations with Mass Flow Calibration unit that is NIST traceable
Precision	1 every 2 weeks	Concentration: 0.2 - 600 ppb, Coefficient of Variance less than 15%.	40 CFR Pt.58 Appendix A	If CV is greater than 15%, institute Quality Control measures
Completeness	Quarterly, Annually	NCORE, 75%	National Monitoring Strategy.	If under 75%, institute Quality Control Measures
Representativeness	N/A	Neighborhood, Urban or Regional Scale	40 CFR 58	N/A
Comparability	N/A	Must be a Trace Level instrument. See Sections 3.1 and 3.2 of this document.	National Monitoring Strategy.	N/A
Method Detection Limit	NA	50 ppt	National Monitoring Strategy	Testing is performed at the factory.

## 5.0 REFERENCES

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4. Code of Federal Regulations, Title 40, Part 53.23c
4. Code of Federal Regulation, Title 40, Part 58, Appendix A
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<http://www.epa.gov/ttn/amtic/monstratdoc.html>
6. Model 42CY Instruction Manual, Thermo Environmental Instruments



**STANDARD OPERATING PROCEDURES**

**ENVIRONICS SERIES 9100**

**COMPUTERIZED AMBIENT MONITORING CALIBRATION  
SYSTEM**

**Version 1**



## **Section 1.1 Acknowledgments**

This Standard Operating Procedure (SOP) for the Environics Series 9100 Computerized Ambient Monitoring Calibration System is the product of EPA's Office of Air Quality, Planning and Standards. The following individuals are acknowledged for their contributions.

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## 3.0 Scope and Procedures

### 3.1 Scope and Applicability

This Standard Operating Procedure (SOP) is applicable for the Environics Series 9100 Computerized Ambient Monitoring Calibration System integrated with several ambient air monitoring analyzers. The SOP outlines the steps to run calibrations and verifications either automatically through programming sequences or through manual commands.

### 3.2 Summary of Method

#### 3.2.1 Summary of Specific Procedures

This SOP will use the following methods to unpack, check and set-up, and execute a multi-point calibration, and daily zero, span and one point QC checks.

##### 3.9.1.1 Unpack the Instrument

##### 3.9.1.2 Warm up the Environics

##### 3.9.1.3 Leak check the Environics

##### 3.9.1.4 Flow Verification

#### 3.9.2 Assign the Calibrator Ports to the Gaseous Standards

#### 3.9.3 Multi-point Calibrations

#### 3.9.4 Verifications: Zero, Span and One Point Quality Checks

##### 3.9.4.1 Setting up a Sequence

##### 3.9.4.2 Setting up a Timer Control

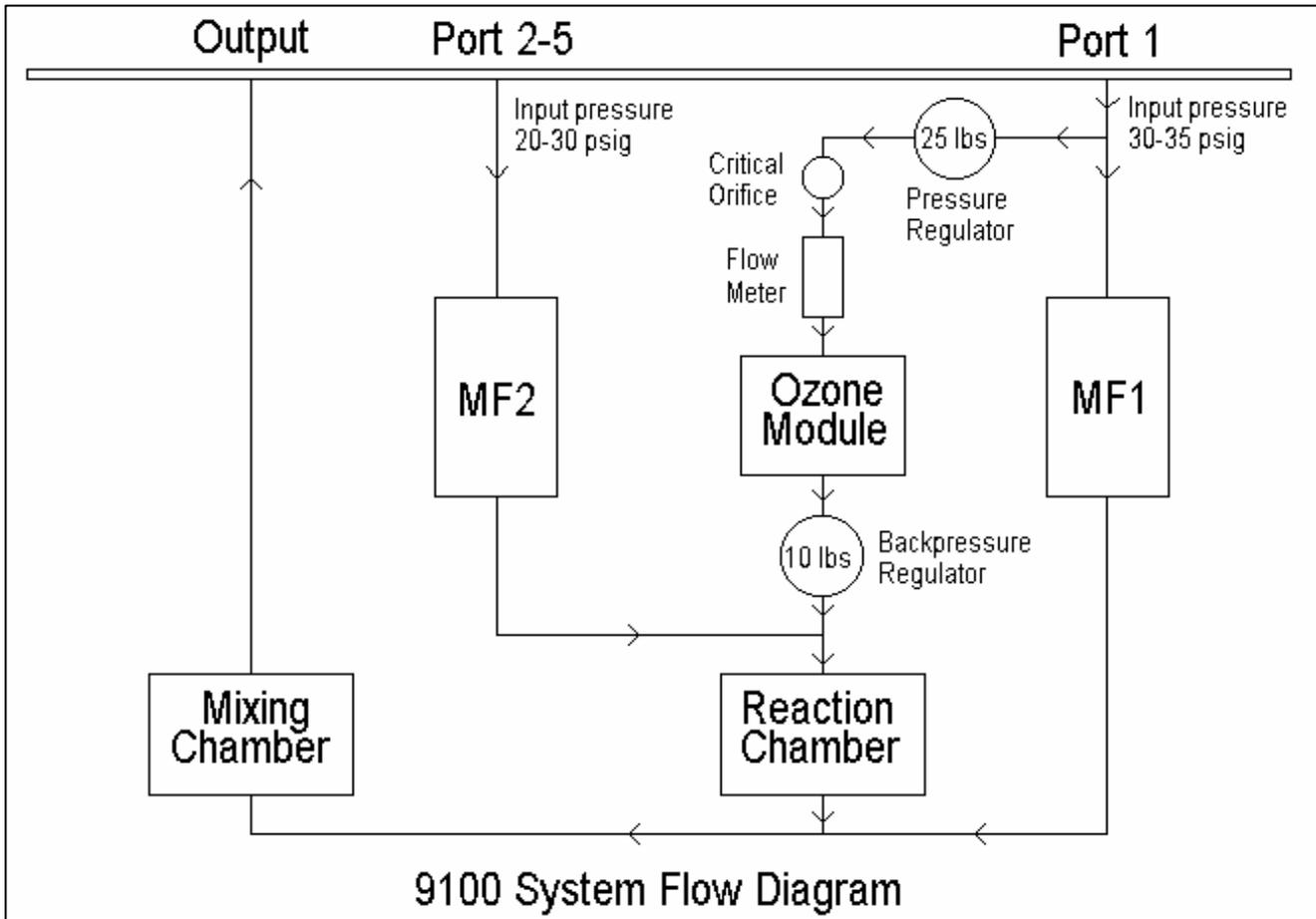
##### 3.9.4.3 Running the Timer Control

##### 3.9.4.4 Zero, Span, and One-Point Quality Checks

##### 3.9.4.5 Calibrator Automation

#### 3.2.2 Summary of Analyzer Operation *Refer to the Flow Diagram, Figure 1.*

In the Environics 9100 Calibrator, Port 1 is connected to mass flow controller (MFC) 1. Port 1 is used for Zero Air. MFC 2 can choose any of the remaining available ports. When nitrogen dioxide (NO<sub>2</sub>) is required pollutant, ozone flows into the reaction chamber along with gases from the other ports except 1. It is here that ozone reacts with the gas. The resultant gas is then sent to the Mixing Chamber and is diluted with zero air from Port 1 before exiting the calibrator and sent to the appropriate analyzer. If diluting gases for CO and SO<sub>2</sub>, this process is by-passed.



**Figure 1.0 Flow Diagram: Enviroics 9100**

3.3 Definitions

MFC

Mass Flow Controller

Scm

Standard Cubic Centimeter per minute

DAS

Digital Acquisition System

Span Check

a one point verification of the monitoring system challenging an analyzer with a known concentration of gas and measuring the analyzer response. Span checks are the highest concentration test point approximately 80 to 90% of full scale range.

One Point Quality Check

a one point verification of the analyzer made by challenging the analyzer with a known concentration of gas and measuring the analyzer response. This concentration ideally should be in the range of daily observed acceptable quality. A response outside the limits initiates a series of actions to determine data quality.

### 3.4 Health and Safety Warnings

1. Some gases can be explosive or otherwise reactive when blended. Users must check gas compatibility before blending. Please consult a gas handbook, a specialty gas manufacturer or other competent source for information about gas compatibility. Failure to observe these precautions may result in damage to the instrument, serious injury or death.
2. Pressurized cylinders are extremely dangerous if improperly handled. Proper regulators, use of safety caps and proper restraints are mandatory. Avoid cross contamination when attaching regulators or making manifold connections. Always consult your gas supplier for proper safety procedures. Failure to observe these precautions may result in serious injury or death.
3. Rules and regulations regarding the transportation of gas cylinders are governed by the Department of Transportation. Each agency should familiarize themselves with these regulations and follow them when involved in transporting gas cylinders. Failure to follow these precautions may result in serious injury or death.
4. Secure Material Safety Data Sheets (MSDS) for all gases and keep in specially designated binder in any easily accessible location.
5. Power to the unit should be disconnected before working on it to prevent injury or electrical shock.
6. If it is necessary to work on the inside of the unit with power connected, extreme caution should be taken. Failure to do so can result in injury or electrical shock.
7. Because the electronic circuit boards contain static sensitive components, always use static discharge equipment when working on the unit and handling circuit boards.
8. A line should be run to the outside or a fume hood, whichever is more readily available, to vent the outflow of gases from the entire system: Envionics 9100, the Zero Air Generator, and the analyzers. This should be done to prevent the possibility of a build-up of gases in a closed room/monitoring station and the potential for gaseous poisoning to the unaware station operator.

### 3.5 Cautions

1. The Envionics 9100 operates at a line voltage between 100-120 VAC (optional 220-240 VAC). Operating at an incorrect line voltage will damage the instrument and void the manufacturer's warranty.
2. Because the RS-232 ports and the parallel printer port are especially susceptible to damage if the unit is powered ON while any computer or printer equipment is being connected or disconnected, the unit must be powered OFF before connecting or disconnecting any cables, wiring harnesses or other sources of potential electrical impulses.

3. If routine maintenance is performed, prior to putting the unit back into service check the following items:

- Inspect the power cord and internal wiring
- Check all fittings for tightness and leak check if possible
- Clean circuit boards using a vacuum or air gun to remove dust
- Check all tubing for splits, kinks, or cuts

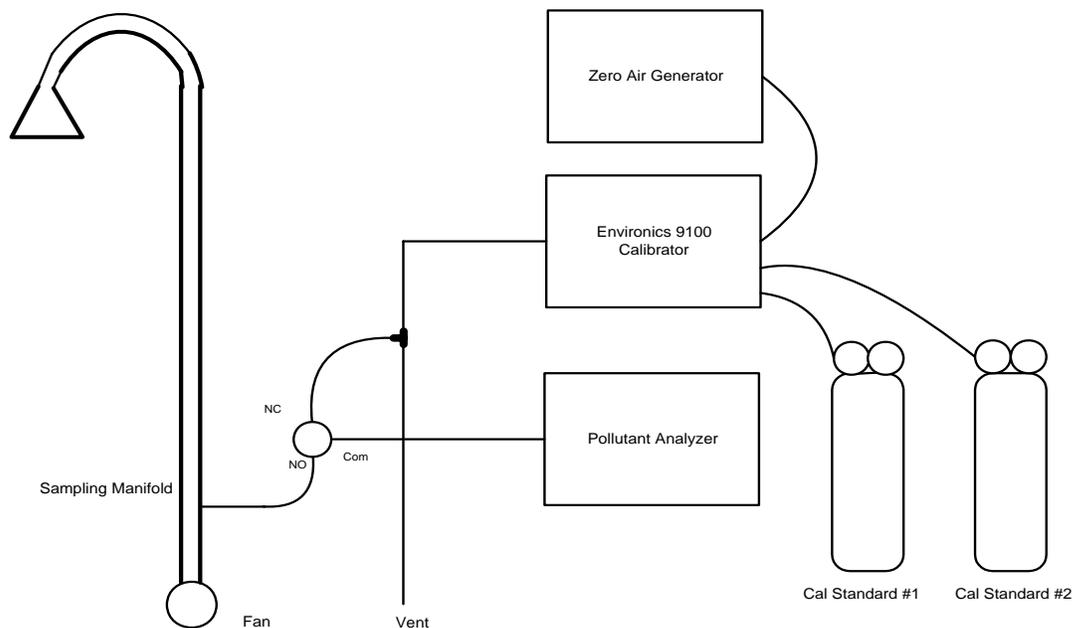
### 3.6 Interferences

The calibrator as well as the zero air supply and any gaseous cylinders should be stored and operated in a temperature and humidity controlled shelter as extremes of either can effect the final concentration. Condensation of humidity in the sampling and associated lines can also dilute the concentration of gases delivered to the analyzers.

### 3.7 Personnel Qualifications

Persons setting up and operating this system should have an understanding of gaseous systems and/or a good background in chemistry, physics, and the scientific process. For someone unfamiliar with gaseous systems and/or setting up analyzers and related equipment at a monitoring site, an instructional course would be beneficial. Other sources of instruction include any US EPA guidance documents and training with other experienced personnel.

### 3.8 Equipment and Supplies



**Figure 2.0: Sampling System Set-up**

Environics Series 9100: used to blend gases to desired concentration to run check calibration of ambient air analyzers through not only a calibration of each but also through the daily zero, span, and one point quality checks.

Zero Air Source: For this study, an API Model 701 Zero Air Generator is used. Carbon monoxide and hydrocarbon scrubbers are available as an option when purchasing. For precursor gas applications, the CO scrubber is required. Please see the manual for a recommended maintenance schedule on the unit. The purpose of the zero air source is to dilute the gases to achieve the desired final concentration of gaseous pollutants in question. Zero Air should be filtered before entering the calibrator to ensure it is free of any particulate contaminants. A cylinder of zero air may also be used. However, the latter may not be cost effective or practical for monitoring organizations given the frequency of use of the zero air supply. It is also imperative for the monitoring organization to verify/recertify their zero air supply annually using an independent zero air source. The independent source should be of a higher quality than what is routinely used. Most high purity cylinder air sources are not of the quality needed as an independent source. High quality cylinders can be used, but they require external scrubbers for the precursor gases of interest.

It is not recommended that the API 701 be used to generate air at a flow rate greater than 10 LPM. The internal CO scrubber is not as efficient at the higher flow rates (e.g., 20 LPM); therefore, caution should be taken when exceeding 10 LPM. Decreased scrubber efficiency presents itself as an increased CO analyzer baseline. An external Hopcalite or Carulite scrubber can be added to the API 701 to remove any CO not eliminated by the scrubber at higher flow rates. CO scrubbers can fail. The manual recommends replacement on an annual schedule depending on CO levels in the source air.

It is also recommended that ambient air, not air from the inside of the monitoring station, is used as a source for the API zero air generator.

Reagents and Standards: Gas Cylinders are used as the source of the target pollutant concentration. Cylinders used should be of the highest purity available, specifically for multi-point calibrations and performance evaluations. All gases used should be either NIST traceable or EPA Protocol Gases having acceptance criteria of 2%. Three different gas cylinders were used in the initial testing project. The concentrations used to obtain the desired blend for the routine span and precision checks follow:

Concentration of gases, cylinder one:

- |                   |  |                     |
|-------------------|--|---------------------|
| • NO              | 50 ppm nominal in N <sub>2</sub> balance @ 2000 psig   | Tolerance: ± 1% EPA |
| • CO              | 5000 ppm nominal in N <sub>2</sub> balance @ 2000 psig | Tolerance: ± 1% EPA |
| • NO <sub>x</sub> | 50 ppm nominal in N <sub>2</sub> balance @ 2000 psig   |                     |
| • NO <sub>2</sub> | <0.2 ppm in N <sub>2</sub> balance @ 2000 psig         |                     |
| • SO <sub>2</sub> | 50 ppm nominal in N <sub>2</sub> balance @ 2000 psig   | Tolerance: ±1% EPA  |

Concentration of gases used in cylinder two:

- CO 350 ppm nominal in N<sub>2</sub> balance @ 2000 psig Tolerance ± 1% EPA
- NO 10 ppm nominal in N<sub>2</sub> balance @ 2000 psig Tolerance ± 1% EPA
- NO<sub>2</sub> <0.05 ppm in N<sub>2</sub> balance @ 2000 psig
- NO<sub>x</sub> 10 ppm nominal in N<sub>2</sub> balance @ 2000 psig
- SO<sub>2</sub> 10 ppm nominal in N<sub>2</sub> balance @ 2000 psig Tolerance ± 1% EPA

Cylinder three (span and precision checks)

- CO 60 ppm nominal

Targeted concentrations of the span and precision checks:

Pollutant	Range	Span	Precision Check
CO	5000 ppb	4000 ppb	250-500 ppb
SO <sub>2</sub>	100 ppb	80 ppb	20 ppb
NO <sub>y</sub>	100 ppb	80 ppb	20 ppb

**Data Acquisition, Storage and Communication Package:** A data acquisition package is necessary to retrieve the data from a remote site and store it for further analysis. Two data acquisition systems were used in this project: Environmental Data Acquisition System (EDAS) for Windows both models 8816 and 8832, Environmental Services Corporation and Envidas, by Envotech. For further information, please refer to the Data Management SOP.

### 3.9 Procedures

#### 3.9.1 Start-up

##### 3.9.1.1 Unpack the instrument

1. Remove the unit from the shipping container and inspect for damages.
2. Note any damage to the shipping case and report to freight carrier immediately.
3. Removing the screws on each side of the top removes the top cover.
4. Inspect the interior of the calibrator for any loose parts or visible damage.
5. Check for any loose circuit boards. If loose, press down to reseat them before connecting the power.
6. Report any instrument damage to Environics or the local distributor.
7. If no damage is found, replace the cover and screws.

The above procedure should be done upon immediate receipt of the instrument or can be moved to the location the calibrator will be sited and then inspected for damage. However, do not wait too long to do the inspection to ensure validation of the warranty period. Please refer to inside the front cover of the manual for specifics on the warranty period and specific coverage.

### 3.9.1.2 Warm-up

When bringing zero air supply and calibrator together for initial checks, suggested warm up time is 24 hours. If moving to sampling location after initial checks, suggested warm up time would be 3-4 hours.

1. Set-up Calibrator in place and connect zero air supply to Port 1.  
**Note:** Pressure of zero air supply should be between 30-35 PSI
2. Secure the appropriate electrical power supply to the Environics and switch to the "ON" position
3. Allow calibrator and zero air supply to warm-up and stabilize before proceeding.

**3.9.1.3 Leak Check** Refer to Section 5.14 in the Environics Manual for further information on the Leak Check

A leak check of the calibrator should be performed before beginning other work. A leak in the calibrator will result an incorrect dilution of gases delivered to analyzers yielding incorrect calibration and verifications of concentrations by the analyzer(s). It is strongly recommended to perform the leak check even if the calibrator is brand new. This ensures integrity of the system and prevents aggravation to the operator.

1. Set the pressure of the zero air supply to 10 PSI
2. At the READY screen, press the MORE key (F8) in the lower right hand corner of the screen. This will take you to the second screen.
3. Once on the second screen, press the LEAK CHECK key (F7)
4. Adjust the PSI reading on the external pressure gage on the front of the zero air supply source as necessary.  
**Note:** The PSI should NOT be above 13. A PSI over 13 will activate the pressure safety.
5. Press the START key (F1) on the front panel.
6. Allow the Environics to run through the leak test cycle. The factory acceptance criterion for a leak check is less than 3 sccm.  
Automatic sequence of events during the LEAK CHECK cycle:
  1. Acquire atmospheric pressure (approximately 59 seconds)
  2. Pressurize system - calibrator and zero air supply (approximately 89 seconds)
  3. Shut down solenoids in calibrator – actual leak check of the calibrator and zero air supply  
**Note:** The test may be cancelled at any time by pressing any key.
7. Once the LEAK CHECK is complete, the Environics will display the results. If less than 3 sccm, the results are acceptable.
8. Record results in appropriate lab notebook
9. Press the EXIT (F8) key located in the lower right hand corner of the screen.
10. Adjust the zero air supply to read 30 PSI on the external pressure gage

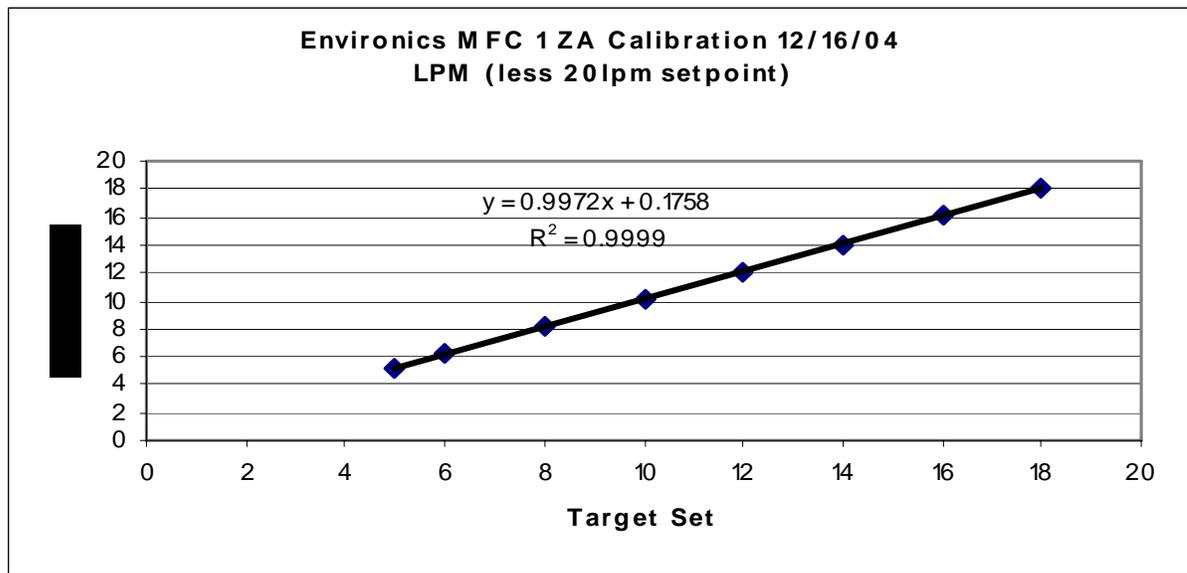
### 3.9.1.4 Flow Verification

Although the mass flow controllers have been factory set, it is strongly recommended to verify the flows through the calibrator using a NIST traceable source. This ensures accuracy as the flow measurement standard must be more accurate than the specified flow accuracy of the MFC. For this study, a BIOS Dry-Cal device was used. Flow devices must be certified annually. Flow checks should be verified at the start-up of the sampling system. Additional verifications should be performed annually or when the gaseous pollutant flow is questioned.

To complete flow verification of Port 1, zero air, and Port 2, cylinder gases, a BIOS Dry-Cal device was used. If another type of flow device is used, these procedures may differ. Consult the manual that accompanies that device for specific instructions.

1. Attach the appropriate BIOS cell to the base of the dry-cal.
2. Attach tubing to the exhaust end of the dry-cal.
3. Attach the calibration output tubing to the dry-cal. **Note:** the tubing from the calibrator output may not be the correct size to connect to the input of the dry-cal. Therefore, it may be necessary to have a small adapter/connector between two different sizes of tubing.
4. Turn on dry-cal
5. From the READY screen on the front panel of the Environics calibrator, press the CONC MODE (F1) soft key
6. When the Concentration Mode Screen appears, move cursor using the arrow keys on the soft key pad to Port 1.
7. Enter Port 1 and the cursor will move to the Target Gas area
8. Once in the Target Gas area, the concentration should be 0 for all gases. If not, change to 0 in those pollutant concentration fields as needed using the numeric key pad and the arrow keys.
9. After work in Target Gas area is complete, cursor should be in Total Flow area. If not move cursor to that area and enter total flow desired: 5.0 SLPM.
10. Move the cursor to another field using the arrow keys. This will update and confirm on the screen the current requested information.
11. Press START (F1) on the soft key pad at the bottom of the screen. This initiates the calibrator to open the appropriate solenoids and start the air flow through the calibrator.
12. Observing the display on the dry cal and the front of the calibrator, begin to record the actual readings from the dry cal when the flows are constant on both. It is recommended to record eight to ten readings.
13. After the readings are completed for a specific flow, select STOP (F ) on the bottom of the front panel of the calibrator, repeat steps 9-12. Five or more Target Flows up to 20 LPM should be used to create a line.
14. When completed with Port 1, EXIT (F8) to the READY screen and switch to the cell for flows on the dry cal device. The flow of Port 2 will now be verified.
15. At the READY screen, select the FLOW MODE (F2) at the bottom of the screen.
16. Cursor should appear at Port 1. Move to Target Flow area and enter 0 SLPM.
17. Move cursor to Port 2 and enter desired SCCM: 90.
18. Move the cursor to another field using the arrow keys. This will update and confirm on the screen the current requested information.
19. Turn on dry-cal

20. Select the START key (F1) on the soft key pad at the bottom of the screen. This initiates the calibrator to open the appropriate solenoids and start the air flow through the calibrator.
21. Observing the display on the dry cal and the front of the calibrator, begin to record the actual readings from the dry cal when the flows are constant on both. It is recommended to record eight to ten readings.
22. After the readings are completed for a specific flow, select EXIT (F8) on the bottom of the front panel of the calibrator, repeat steps 17, 18, and 20. Five or more Target Flows down to 10 SCCM should be used to create a line.
23. When completed with Port 2, EXIT (F8) to the READY screen.
24. Turn off dry-cal, disconnect tubing, and replace all tubing to original set-up as necessary.
25. Average each of the flow points.
26. Perform a linear regression analysis and plot the actual vs. target concentration flows.



**Figure 3: Calibration Graph of Envionics 9100 Mass Flow**

### **Controller**

#### **3.9.2 IDENTIFYING THE CALIBRATOR PORTS TO THE GASEOUS STANDARDS**

*Refer to Section 5.8 in the Envionics Series 9100 Manual*

The purpose of this section is to assign gaseous cylinders to a specific port located on the rear of the Envionics 9100 Calibrator.

1. From the **READY SCREEN**, select **MAINTAIN PORTS (F6)**
2. Using the soft number key pad on the right front screen, choose the desired gas port to be configured. Once a port number is selected, the cursor will appear in front of the word **BALANCE**
3. Using the Right Arrow key, move to the Gas ID column. Lines 1 will be used to name the **BALANCE** of the gas in the cylinder. Lines 2-6 will be used to name the individual gases in that cylinder.
4. Enter the first gas to be configured on line 2

**Note:** If it is intended to use nitric oxide to perform a Gas Phase Titration, “NO” must be used as the GAS ID. The system will compute the NO<sub>2</sub> while running. System recognizes NO only for this process.

5. Use the “Exit” key to return to the CGC area or use the “Up and/or Down” keys to move to a different CGC field.
6. Enter the CGC for each GAS ID

**Note:** The cylinder concentration can either be entered as parts per million (ppm) or percent (%). Percent of a concentration is more typically used for higher blending higher concentration of gases.

**Note:** Concentrations of up to five (5) gases may be added for one multi blend gas cylinder. Beneath the CGC, the first cell is labeled **BALANCE**. If using a multi blend gas and contains nitric oxide (NO), this must be the first gas entered.

7. Repeat steps 2-4 for all gases to be entered for that cylinder
8. Press CYL ID (F6), to move to cylinder ID field and enter a name for that cylinder.  
Suggestion: use the cylinder number listed on the cylinder tag
9. After completing set-up for a desired port, press EXIT (F8) to select a different port. Press EXIT(F8) again to go to the Main Menu.

### **3.9.3 CALIBRATIONS – Multi-point**

Running a multipoint calibration, a zero point and three separate concentrations are to be run to determine linearity of the instrument. The proposed audit ranges concentrations found in 40 CFR Part 58 Appendix A Section 3.2.2 combined with actual ambient concentrations observed would serve as a guideline of concentrations to choose for a multi-point calibration. The recommended sequence when performing the multi-point calibration is to perform a zero first, making any necessary adjustments to the zero, then move to the highest concentration working backwards ending with the low concentration and a final zero. Performing the points in this order more completely coats the exposed surfaces allowing for a more stable concentration. An added benefit to performing the concentration points in this sequence is the time savings element.

#### **3.9.3.1 Determination of Concentrations for the Multi-point Calibration**

Before performing the actual multi-point calibration, calculate the desired concentration of each point based upon the gas cylinder concentrations and gas flow. A recommendation: calculate these values before purchasing your pollutant gas standards to ensure having the desired concentrations when ready to perform the multi-point calibration.

Based on the flow verification of the mass flow controllers in the calibrator performed earlier, use the actual flow of the zero air and gases in the multi-blend cylinder to calculate what concentrations are needed for each pollutant for the multi-point calibration. Refer to Example #1 as you follow the step by step process.

1. Determine the range of the each pollutant, example CO is 0-5000 ppb

- Next, determine 10 and 90 percent of the range, 500 and 4500 ppb respectively. By solving for the minimum and maximum concentrations, you will be able to determine what concentration of pollutant gas cylinder(s) is needed.

**Note:** It will be necessary to determine your total air flow needed through your system. This will be based on the set-up of the entire sampling system including manifold.

- Using the following equation and referring to **Example #1**, Steps 2 & 3, determine what flow is needed to generate these concentrations.

$$\frac{\text{Concentration of pollutant in cylinder} \times \text{pollutant flow}}{\text{Total flow through system: pollutant flow} + \text{zero air flow}} = \text{desired concentration}$$

- In this example, make the pollutant flow, the unknown value and solve the equation for it.
- Once the 10 and 90 percent of range have been determined, solve for several more concentration values between those two.

#### **Example #1 – Calculations for actual one point quality checks**

Actual flow of gases through the system:

Zero air: 6.843 = 6.999.6 ccm; gaseous concentrations: 100 ccm = 98.05 ccm, 16.73 ccm = 13.63 ccm

Step 1: Zero air is run through the system to flush out any sample air before beginning the precision check

Step 2: Zero air is mixed with a gas containing

X concentration of CO at a flow of 100 ccm:

10.07 ppm of CO resulting concentration of CO: 139.1 ppb  
[10.07 ppm x 98.05/ (98.05 + 6999.6)] x 1000 = 139.1 ppb

X concentration of SO<sub>2</sub> at a flow of 100 ccm:

13.13 ppm of SO<sub>2</sub> resulting concentration of SO<sub>2</sub>: 181.4 ppb  
[13.13 ppm x 98.05/ (98.05 + 6999.6)] x 1000 = 181.4 ppb - Over Range

X concentration of NO at a flow of 100 ccm:

10.26 ppm of NO resulting concentration of NO: 141.7 ppb  
[10.26 x 98.05/ (98.05 + 6999.6)] x 1000 = 141.7 ppb - Over Range

Step 3: Zero air is mixed with a gas containing 13.13 ppm SO<sub>2</sub> , 10.26 ppm NO, and 10.07 ppm CO resulting in 25.5 ppb of SO<sub>2</sub> , 19.9 ppb NO, and 19.6 ppb.

X concentration of CO at a flow of 16.73 ccm:

10.07 ppm of CO resulting concentration of CO: 19.6 ppb  
[10.07 ppm x 13.63./ (13.63 + 6999.6)] x 1000 = 19.6 ppb - Under Range

X concentration of SO<sub>2</sub> at a flow of 16.73 ccm

13.13 ppm of SO<sub>2</sub> resulting concentration of SO<sub>2</sub>: 25.5  
 $[13.13 \text{ ppm} \times 13.63 / (13.63) + 6999.6] \times 1000 = 25.5 \text{ ppb}$   
X concentration of NO at a flow of 16.73 ccm  
10.26 ppm of NO resulting concentration of NO: 19.9 ppb  
 $[10.26 \text{ ppm} \times 13.63 / (13.63) + 6999.6] \times 1000 = 19.9 \text{ ppb}$

Step 4: Zero air only is run through the system

Audit Level	Concentration Range, PPM			
	O <sub>3</sub>	SO <sub>2</sub> ,	NO <sub>2</sub>	CO
1.....	0.02-0.05	0.0003-0.005	0.0002-0.002	0.08-0.10
2.....	0.06-0.10	0.006-0.01	0.003-0.005	0.50-1.00
3.....	0.11-0.20	0.02-0.10	0.006-0.10	1.50-4.00
4.....	0.21-0.30	0.11-0.40	0.11-0.30	5-15
5.....	0.31-0.90	0.41-0.90	0.31-0.60	20-50

**Table 1.0 Proposed Audit Levels, 40 CFR, Part 58 Appendix A, Section 3.2.2**

Example concentrations used for Multipoint Calibration

CO	SO <sub>2</sub>	NO/NO <sub>y</sub>
421 ppb	8.69 ppb	12.54 ppb
855 ppb	18.57 ppb	28.6 ppb
1078 ppb	40.56 ppb	50.04 ppb
2660 ppb	59.98 ppb	71.3 ppb
2990 ppb	82.5 ppb	92.28 ppb
3534 ppb	93.0 ppb	
4081 ppb		

### 3.9.3.2 Performing the Multi-point Calibration

- 1 From the READY screen, select **Concentration Mode** screen. This goes into the MANUAL Mode of Calibrations. Calibrations will occur for each analyzer and each point at a time. The cursor will appear at the first TARGET GAS concentration.
- 2 Enter the desired gas concentration in the TARGET GAS area by moving the cursor using the arrows.
- 3 Using the arrow keys, move to the TOTAL FLOW area and enter the flow, 10 LPM
- 4 Using the arrow keys, cursor to the OZONE area and enter desired concentration if applicable for the pollutant needed for NO<sub>2</sub>
- 5 Press START. This will initiate the blending of the gases to the analyzer.
- 6 Allow the analyzer to stabilize.
- 7 Once stable, wait ten minutes, record the reading for that concentration.
- 8 Continue to the next concentration level repeating steps 1 through 5.

- The above steps can be automated by programming each step into a Sequence and assigning a designated time to *Run*.

### 3.9.4 VERIFICATIONS – Zero, Span and One Point Quality Checks

These steps will assess and confirm the upper range of the multi-point calibration, the zero base line and the ambient working range of the instrument. The one point quality checks will determine both precision and bias of the analyzers.

This step may be either automated to occur as directed or manually. If performing a manual operation, follow the same procedure in *Section 3.9.3.2 Performing the Multi-Point Calibrations*. To operate in AUTOMATIC Mode, it is first necessary to program the **Sequences** and name the **Programs**.

#### 3.9.4.1 SET-UP A SEQUENCE Refer to Section 5.6.1 in the EnviroNics Series 9100 Manual

In this step, the steps necessary to automate the zero and span check will be set up. Below is an automated **Sequence** used in the project. Refer to **Example # 1** for a detailed explanation of each step.

ID	Run Time Conc.	Mode	Port	Zero			O <sub>3</sub>	Gas
				Air Flow (ccm)	Gas (ccm)	Total		
1	10 (min)	Conc.	2	6.843	0.0	6.843 0.0	NO	0.0
2.	20	Conc.	2	6.843	100	6.943 0.0	NO	0.142
3.	20	Conc.	2	6.843	16.73	6.8597 0.0	NO	0.025
4.	10	Conc.	2	6.843	0.0	6.843 0.0	NO	0.0

- From the **READY**, select **Program Mode (F4)**
- Once in **Program Mode**, select **Sequence (F2)**
- At the blank screen, the cursor is in the **RUNTIME** column
- Enter the desired run time for the first step Refer to Row 1 - 10 minutes  
Note: If “0” is entered, the step will be skipped and not displayed.  
Valid run times are 1 to 60 minutes.  
Twenty lines (20) are available for programming one **SEQUENCE**
- Move the cursor to the **MODE** column. Using the function keys, choose the appropriate **MODE**  
**Note:** For zero, span, and precision checks use **Concentration (CONC) Mode**
- Move the cursor to the **PORT** column; enter the desired span gas port which has been established in section 3.9.2 (In this case, it is not necessary to use Port 1. Using Port 2 and telling it not to send any gas from port 2 serves the same purpose as using Port 1 only)
- Move to the **Total Flow** column and enter the desired flow.
- Move to the **Gas ID** column; when at this column, the GAS ID should default to those provided in section 3.9.2  
**Note:** **Gas ID** number refers to the order of gases entered in the **MAINTAIN PORTS** screen.

9. Move to **CONC** column; enter desired concentration for that gas. Enter concentration in ppm.

**Note:** Moving cursor from column to column initiates a check to determine if the value entered is legal. If the value is not possible, an Error message is displayed at the bottom of the screen.

**Note:** When using the **CONC MODE**, the calibrator will automatically calculate the amount of gas needed to produce the required concentration. It is considered Good Laboratory Practice to check to determine calculations are correct. This can be a random check on one or more of the calculations.

10. Follow steps 3-9 for additional rows in the **Sequence**. Example 1 has four rows: zero, one quality check - CO; one point quality check – NO and SO<sub>2</sub>, and a zero.
11. After entering all steps in a specific sequence, **SAVE (F2)** the **Sequence** in the Register. Use the function keys to type the name of the **Sequence**. We'll call **Example # 1** PC-1 and saved as sequence line number 01
12. When the **SAVE** is complete, press EXIT (F8) to return to the **Program Mode**
13. Pressing EXIT again, returns to the **READY** screen.

#### **3.9.4.2 SET-UP TIMER CONTROL (TIMER CTL)** *Section 5.6.2 in the Envionics Series 9100 Manual*

This is used to automate a number of sequences which allow for automating zero, span and one-point quality checks.

1. If this is the first set-up and no previous **Timer CTL** are stored in the register, the cursor will be in the Sequence line and it will be necessary to enter the desired sequence for the specific day(s) and time (s) the **Timer CTL**
  1. From the **Main Menu**, select **Program Mode**
  2. From **Program Mode**, select **TIMER CTL**
  3. Go to the day you want a specific **Sequence** to Run.
  4. Select the **Sequence**, 01, to be run.
  5. Enter the time to start the **Sequence**. Once the time is entered, the system will display the duration of the **Sequence** and calculate the end time.

**Note:** Time is based on a 24 hour clock with 12:00 being noon and 24:00 being midnight. Entering 0:00 will cause the **Sequence** to be skipped and will not be displayed; therefore must enter time as low as 00:01

Note: Three sequences per day may be entered for each day of the week.

6. Once the desired sequences are in the desired order, press the **SAVE (F2)** key.
7. Enter the desired register number. A name may also be entered.
8. Press EXIT (F8)

### 3.9.4.3 RUN TIMER CTL

1. If a program has been previously saved press the RECALL (F3) key to bring the program to the screen
2. Press the START (F1) key.

**Note:** The day and time of the next sequence will be displayed in the lower right hand corner of the screen.

### 3.9.4.4 Zero, Span, and One-Point Quality Checks

1. At the Concentration Mode, Manual Operation screen, enter the TARGET GAS concentration for the desired gas. The system will determine the actual flows for each port to achieve the requested gas concentration(s). Remember: Port 1 is Zero Gas.
2. Once the TARGET GAS concentrations have been set for the desired gas, press the START (F1) key, to begin the operation.

**Note:** A similar process is to go to the FLOW MODE and enter the desired flow. The EnviroNics will calculate the actual concentration based on the flow.

If the desire is to automate the zero, span and one point quality checks, set-up a **Sequence** and SAVE the sequence. Then to Run the **Sequence**, go to Timer Control and set the desired time to run your **Sequence**. Below is an example of a **Sequence** set-up for *Precision Checks* used in the testing program. Refer to previous sections 3.9.4.2 and 3.9.4.3. Note: A tri-blend standard was used in the testing process. An example of the gases used and the concentrations are found on pages 8 and 9.

### 3.9.4.5 Calibrator Automation

A Data Acquisition System can control the running of a programmed sequence. To use this function, the EnviroNics calibrator must have the optional status board. The INPUTS option provides the ability to trigger various actions within the system. The OUTPUTS option will signal external devices when certain operating conditions occur. In order for the data acquisition system to run the calibrator, the INPUTS option is needed.

1. Using the key pad, press the STATUS SETUP – INPUT soft key at the **Main Menu** screen.
2. At the INPUT screen add the desired function(s), **Sequence, Timer Control**, etc to be run in the Status Line. The desired function(s) can be chosen from the soft keys at the bottom of the screen.
3. When the desired function(s) have been entered, select the EXIT soft key returning to the **Main Menu** and the READY mode.

**Note:** the calibrator must be in the READY mode for the automation to occur

For further detailed information on communications between the data acquisition system, calibrator and analyzers, refer to the Data Acquisition SOP.

#### 4.0 Quality Control and Quality Assurance

After confirming the flows through the calibrator, a multi-point calibration for each analyzer should be performed. A different certified gas cylinder should be used other than the cylinder used for span and precision check gas.

Operating the MFC below 10% of its rated full-scale flow may result in flow inaccuracies.

The system may produce gas blends that fall outside the accuracy specifications of the system if the gas pressures do not stay within the ranges specified for each gas port.

The operator of the system should not be the same person who performs the multi-point calibrations, but

MQO Table for Enviroics 9100 Calibrator			
Criteria	Acceptable Range	Minimum Frequency	Reference
Mass Flow Controllers			
Zero Air Source			

in the case of the Trace Gas Analyzers, it could be.

#### 5.0 References

1. 40 CFR Part 58, Appendix A
2. Enviroics Series 9100 Computerized Ambient Monitoring Calibration System, Operating Manual, Revision 6, October 1999

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United States  
Environmental Protection  
Agency

Office of Air Quality Planning and Standards  
Emissions, Monitoring and Analysis Division  
Research Triangle Park, NC

Publication No. EPA-454/R-05-003  
September 2005

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