APTI 464

Analytical Methods for Air Quality Standards

Laboratory Exercise Manual

March 2010

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Appendixes

Nomenclature

A_1	assay of original ozone concentration
A_2	assay of diluted ozone concentration
B_L	CO analyzer response to 1 ppm CO
B_Z	CO analyzer response to zero air
C	concentration of SO_2 in test atmosphere
C_c	certified concentration of calibration gas
C_f	final dilution concentration of CO standard gas
C_{fs}	full scale reading of CO analyzer
C_s	concentration of CO span gas
C_{std}	concentration of CO standard gas
%E	linearity error in percent
F_D	flowrate of dilution air
F_{NO}	flowrate of NO standard air
F_o	flowrate of air through air generator
F_p	flowrate of gas through the UV absorption cell
F_Z	flowrate of zero air thorough UV photometric calibration system
FPD	flame photometric detection
GPT	gas phase titration
LDL	lower detectable limit
M	molecular weight of SO_2
NIST-SRM	National Institute of Standards and Technology - Standard Reference Material
NDIR	nondispersive infrared
$[NO]_{ORIG}$	NO concentration before addition of ozone
$[NO_{OUT}$	NO concentration as the output manifold
$[NO]_{REM}$	NO concentration after addition of ozone
$[NO]_{std}$	concentration of undiluted NO standard gas
$[NO_x]_{OUT}$	NO_x concentration at the output manifold
$[NO_2]_{OUT}$	NO_2 concentration at the output manifold
N_{span}	span number of UV photometer
P_b	barometer pressure
P_R	dynamic parameter specification
ppb	parts per billion
ppm	parts per million
PR	permeation rate
psi	pounds per square inch
P_{80}	precision at SO_2 analyzer's 80±5% upper range limit
Q_t	total flowrate of gases through SO_2 permeation tube calibration system
Q_{SO2}	flowrate from cylinder of SO_2 standard gas
Q_{std}	flowrate of CO standard gas
Q_D	flowrate of diluent (zero air)
R	dilution ratio of ozone concentration flowrates

S/N	serial number
S_o	standard deviation of CO analyzer's mean response to zero air
STP	EPA's standard temperature and pressure for ambient air monitoring (25ºC, 760 mm Hg pressure)
T	Temperature
t_R	reaction chamber gas residence time
URL	upper range limit
UV	ultraviolet
V	molar volume of SO_2 at STP
V_{RC}	volume of calibrator's reaction chamber
Z	recorder response to zero air
$\mu g/m^3$	micrograms per cubic meter

Course 464
Analytical Methods for Air Quality Standards

Course Goal and Objectives

Course Goal

The goal of this course is to develop familiarity with selected reference and equivalent instrumental methods used to measure the gaseous criteria pollutants in ambient air. This includes calibration, operation, and determination of performance specifications in instrumental methods.

Course Objectives

At the conclusion of this course, you should be able to:

(a) Properly operate and calibrate various gaseous ambient air analyzers;
(b) prepare dynamic calibration curves for instrumental methods using such primary standards as permeation tubes or cylinder gases and appropriate dynamic dilution systems, and
(c) determine performance specifications of various ambient air monitors.

Chapter 1

Laboratory A

Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere (UV Photometry)

Laboratory Objectives

Upon completion of this laboratory, you should be able to:

1. Properly use the Equivalent Method Measurement Principle and Reference Method Calibration Procedure to calibrate an ozone (O_3) analyzer using UV photometry.
2. Understand the difference between a UV photometer used for measurement and a UV photometer used for calibration.
3. Determine the following instrument performance parameters:
    - Rise time
    - Fall time
    - Lag time.

INTRODUCTION

Historical Review

The ozone reference measurement principle and calibration procedure, promulgated in 1971 and amended in 1979, is based on detection of chemiluminescence resulting from the reaction of ozone with ethylene gas. Later, Rhodamine B, an organic dye embedded in a disc, was approved for use in place of ethylene to detect chemiluminescence. But neither method was problem-free. The flammability of ethylene was a constant concern, especially when monitoring was conducted in or near a public facility. The Rhodamine B analytical system did not regain a stable baseline rapidly enough after exposure to ozone. Thus, when UV analyzers were first approved as equivalent methods in 1977, they gained rapid, almost universal acceptance. Today, users have their choice of many approved UV instruments from several manufacturers. For more information on reference and equivalent methods, see the Student Manual for EPA Course 464.

Ultraviolet Absorption by Ozone

The analytical principle is based on absorption of UV light by the ozone molecule and subsequent use of photometry to measure reduction of the quanta of light reaching the detector at 254 nm. The degree of reduction depends on the path length of the UV sample cell, the ozone concentration introduced into the sample cell, and the wavelength of the UV light, as expressed by the Beer-Lambert law shown below:

$I = I_o \exp(-aLC)$

where:

I = light intensity after absorption by ozone
I_o = light intensity at zero ozone concentration
a = specific ozone molar absorption coefficient
L = path length, and
C = ozone concentration

The air sample is drawn into an optical absorption cell where it is irradiated by a low pressure, cold cathode mercury vapor lamp fitted with a Vycor sheath to filter out radiation with a wavelength of less than 254 nm. A photodetector, located at the opposite end of the sample cell, measures the reduction in UV intensity at 254 nm caused by the presence of ozone in the sample cell. To compensate for possible irregularities in output, another photodetector is used in some instruments to monitor the intensity of the mercury vapor lamp.

Although some ozone analyzers measure reference and sample air simultaneously using two absorption cells, most analyzers alternate these measurements, using only one cell. In the first part of the cycle, sample air is passed through a scrubber with manganese dioxide to remove ozone. The scrubbed sample air then enters the sample absorption cell to establish a reference light intensity at zero ozone concentration (I_o). In the second part of the cycle, sample air is re-directed to bypass the scrubber and enter the sample cell directly for measurement of the attenuated light intensity (I). The difference is related to the ozone concentration according to the Beer-Lambert law shown above. Thus, ozone in a sample stream can be measured continuously by alternately measuring the light level at the sample detector, first with ozone removed and then with ozone present.

Any ozone analyzer used for routine ambient air monitoring must be calibrated against a suitable ozone primary standard or a secondary standard directly traceable to a primary standard. An ozone primary standard is a photometer similar to a UV analyzer that meets the specifications in 40 CFR 50, Appendix D.

Potential interferences to the UV detection of ozone, including water, aromatic hydrocarbons, and mercury, are discussed in the Student Manual for EPA Course 464.

Definitions

Learning new acronyms, abbreviations, and specialized terms is an important task of a new staff member because these items are a part of the organizational culture. Standard operating procedures (SOPs) should contain similar lists of terms specific to them, while also defining each term upon first usage in the document. Table 1-1 lists some key terms for this method.

Table 1-1. Definitions of Key Terms

Term	Definition

DAS	**Data acquisition system. Used for automatic collection and recording of ozone concentrations.**
Interferences	**Physical or chemical entities that cause ozone measurements to be higher (positive) or lower (negative) than they would be without the entity.**
Local primary standard	**Master standard for all calibrations by a monitoring agency. NIST-traceable when verified by comparison to a standard reference photometer, usually through a transfer standard. Must meet requirements found in 40 CFR 50 Appendix D.**
NIST	**National Institute of Standards and Technology (formerly the National Bureau of Standards.) Holder of the standard reference photometer for establishing NIST traceability.**
Ozone analyzer	**Designation reserved for an air monitoring instrument.**
Ozone photometer	**Designation reserved for a UV instrument used as a primary or transfer standard. (See also Section 9.1.1 through 9.1.5).**
SRP	**Standard reference photometer. (See also Section 9.1.2).**
Transfer standard	**A transportable device or apparatus which, together with associated operational procedures, is capable of accurately reproducing ozone concentrations or of producing accurate assays of ozone concentrations which are quantitatively related to an authoritative master standard. (See2 also Sections 9.1.5 through 9.1.7).**
Zero air	**Must be free of ozone, to 0.001 ppm, and of substances that react with ozone, including nitric oxide (NO), nitrogen dioxide (NO), particulates,2 and hydrocarbons. (See also Section 8.2).**

Monitoring Apparatus and Materials

Because of the complexity of ozone monitoring equipment and procedures, this Section includes much more information than the customary list of equipment and supplies, to give field operators an in-depth understanding of their task and tools.

UV Ozone Analyzer: The design of a *UV ozone analyzer* is similar to that of the *photometer,* but with one important difference. An ozone analyzer uses a special internal scrubber that removes ozone but not other gases to provide a zero-concentration ozone reference for the analyzer's zero reference. Maintaining the distinction between an analyzer and a photometer is very important. The term "analyzer" is reserved for the air monitoring instrument, the term "photometer" for the calibration standard instrument. For use in State and Local Air Monitoring Stations (SLAMS) networks, an analyzer must be one designated by EPA as an equivalent method under 40 CFR 53.

Calibration Apparatus

The following equipment is required for calibration of an ozone analyzer.

Ozone Transfer Standard: A transfer standard, such as an ozone analyzer or ozone generator, that has been certified as a transfer standard against the local primary standard in accordance with stipulated procedures. A primary ozone standard may also be used directly for calibration, in which case it should be intercompared periodically with another primary ozone standard to check its veracity.

Ozone Generator: A generator providing stable ozone concentrations that can be varied manually or by automatic electronic feedback circuitry. If the transfer standard is an ozone generator, no other ozone generator is needed.

Zero Air Generator: Zero air is required for the calibration of ozone instruments. This air must be ozone-free to 0.001 ppm, and also free of nitric oxide (NO), nitrogen dioxide (NO_2), particulates, and hydrocarbons. Although there are many commercially available zero-air systems, zero air can also be generated by using a series of canisters that contain thermally cracked carbon, Purafil, and desiccant. Because NO may be difficult to remove, frequent changing of the carbon or use of an NO-to-NO_2 converter may be necessary. When such a converter is used, test the output with an NO/NO_x analyzer to ensure that the residence time in the system is long enough for complete conversion of NO to NO_2.
The desiccant used with the zero-air system should be changed regularly. Changing humidity can affect the response of UV photometers. Very dry zero air may also be a problem. The scrubber needs time to adjust if the zero air is much drier than the ambient air.

***Output Manifold*:** Although the output manifold can be constructed of borosilicate glass, Teflon, or stainless steel, glass is recommended. The manifold must have an opening that vents excess air to the atmosphere such that the pressure in the manifold is as close to atmospheric pressure as possible. If ozonated air is delivered under too high a pressure, the ozone readings obtained will not be representative.

***Barometer*:** The internal barometric pressure of a transfer standard needs to be determined accurately if measurements are made above 1000 feet in elevation (approximately 730 mm Hg). Many commercially available analyzers or photometers with built-in barometric pressure sensors automatically correct the measured ozone values to 760 mm Hg. If automatically adjusting instruments are not available, pressure corrections need to be made manually.

***Temperature Sensor*:** The internal temperature of a photometer must be measured accurately. Many newer photometers have built-in temperature sensors to automatically correct the measured ozone values to 298K. If automatic adjusting instruments are not available, temperature corrections need to be made manually.

***Tubing and Fittings*:** Teflon and Kynar are two inert materials that should be used exclusively throughout the 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 because it can be examined and discarded if particulate matter is collecting in it. It is also very pliable. All fittings and ferrules must also be made of Teflon or Kynar.

ANALYZER CALIBRATION

Calibration Standards

No Standard Reference Materials (SRMs) exist for ozone because ozone is unstable in cylinders. Therefore, ozone standard concentrations must be generated dynamically *in situ*, either with (1) an ozone generator certified as an ozone transfer standard; or (2) an uncertified ozone generator whose output concentration levels are assayed with a primary standard photometer or an ozone assay instrument certified as an ozone transfer standard. Ozone can be generated by irradiating zero air with UV light from a cold cathode mercury vapor lamp.

Primary Standards

EPA has established UV photometry as the primary standard for ozone concentrations (40 CFR 50, Appendix D). Ozone primary standard concentrations are determined by a primary standard photometer. A primary standard ozone photometer is an instrument that measures ozone using the Beer-Lambert law at 254 nm, uses the absorption coefficient for ozone (308.8 $atm^{-1}cm^{-1}$ at 273K and 760 mm Hg), and meets all other requirements. Most commercially available photometers make these corrections automatically. An auxiliary ozone generator is also required to provide stable ozone concentrations to be assayed by the photometer.

An ozone standard photometer is very similar to the ozone analyzer, but **has no built in scrubber for removing ozone.** Therefore, the photometer must be supplied with zero air from the same source that supplies zero air to the ozone generator.

Standard Reference Photometers

EPA and the National Institute of Standards and Technology (NIST) jointly developed a special, highly accurate standard photometer known as a Standard Reference Photometer (SRP) to serve in lieu of an SRM for ozone concentrations. NIST maintains one or more "master" SRPs. EPA maintains 10 other SRPs: one in Research Triangle Park, NC; seven in EPA Regional Office laboratories; one at the California Air Resources Board; and a traveling one used for intercomparisons. Each SRP is a standard in its own right and is not "calibrated" against the NIST unit. Instead, all SRPs are intercompared periodically to **verify** that they all agree with one another and to establish NIST-traceability. If one does **not** agree with the others, it is **not** recalibrated--it is repaired. The EPA SRPs provide NIST-traceable ozone standards that are accessible to states and local agencies for verifying their own local primary standards. In some cases, the SRPs may also be available for certification of transfer standards.

Local Primary Standard

Each monitoring agency needs its own local primary standard photometer that serves as the single master standard for all ozone calibrations carried out by the agency. Other ozone photometers or transfer standards are used as working standards to calibrate the ozone monitoring analyzers. These transfer standards are all referenced to the local primary standard. Calibration photometers are commercially available from a number of vendors, or a UV analyzer can be modified to become a calibration photometer.

Because even primary standard photometers can malfunction, each local primary standard should be compared at least annually to an SRP to reverify its accuracy and recertify its NIST traceability. Although a local primary standard may be moved to an SRP laboratory for the comparison, a transfer standard that has recently been recertified against the local standard is usually moved instead, to protect the local standard from damage during transit.

The local primary standard photometer is not calibrated against a verified SRP, because it is a standard in its own right. Instead, it is compared with the SRP to verify its continued accuracy. If there is a substantial difference (more than ± 5%, preferably ± 3%) between the local standard and the SRP, the local standard is considered to be malfunctioning and must be repaired and reverified before further use.

Agencies needing SRP verification should contact their EPA Regional Office.

Ozone Generators

Ozone generators, one type of commonly used transfer standard, frequently are mass flow-controlled calibration units with a very accurate ozone generator system. They operate by establishing the authority of a thumbwheel setting or digital display to the primary standard.

Transfer Standards

A transfer standard is a secondary standard that is used to transfer the accuracy (or authority) of the local primary ozone standard to the ozone analyzers at the monitoring sites. A transfer standard is first calibrated against the local primary standard and then used in the field to calibrate ozone analyzers. A transfer standard may be an ozone generator or an ozone photometer. For the latter, a stable auxiliary ozone generator is also required to produce certifiable ozone concentrations. Commercially available transfer standards usually have a built-in ozone generator.

Clean Teflon tubing should be used between the primary and the transfer standards. The zero air should have less than 0.001 ppm of ozone. If the transfer standard has a zero air scrubber, the transfer standard should be plumbed to take in zero air through that scrubber during the zero air cycle. Normal manufacturer's recommended maintenance procedures should be performed for the primary standards and for cleaning the optical system. To eliminate the need for frequent cleaning of the optical system, a Teflon filter (pore size of 10 microns) should be used on the inlet of the primary standard.

Temperature- and pressure-sensing hardware must be calibrated annually. The temperature-sensing unit should be submersible and compared against a NIST-traceable thermometer in water at three different temperatures. The barometer should be compared against a Fortin barometer or equivalent.

Calibration/Certification of Transfer Standards

Several conditions must be met before an instrument can be certified as a transfer standard.

- The transfer standard must be capable of generating or assaying ozone concentrations very precisely and repeatably. The same instrument must never be used both as a transfer standard and as an analyzer to collect data.

- A transfer standard has no intrinsic authority of its own and must be referenced and certified to a primary standard before use for calibrating analyzers.

- Once authority has been established, a transfer standard should be recalibrated or recertified at least every three months against a primary standard.

- Transfer standards are always used with clean, filtered zero air.

- A transfer standard can be operated with or without an ozone-zero air scrubber. If a scrubber is used, it should be changed regularly, depending on how much the photometer is used between recertifications and on the manufacturer's recommendation. Scrubbers should be replaced at least annually. If an internal scrubber is not used, then some type of external scrubber, such as activated charcoal in an air-tight canister, is needed during the zero-air cycle. Once certified against a local primary standard, a transfer standard must keep the same scrubber configuration during use.

- Use the same zero air for the primary and transfer standards if the zero air scrubber is removed from the transfer standard.

- A transfer standard must be a rugged device readily transportable in airplane cargo holds and motor vehicles, yet light enough to be carried across difficult terrain.

- The primary and transfer standards must analyze the same air under the same atmospheric conditions. The manifold to which they are connected must have an opening large enough so that excess air can leave the manifold without any back pressure.

- If an independent ozone generator is used, then the lines to the primary and transfer standards should be approximately the same length. Use only Teflon lines.

- Vent the ozone to the outside, if possible. Ozone exposure in an enclosed area can contribute to health problems.

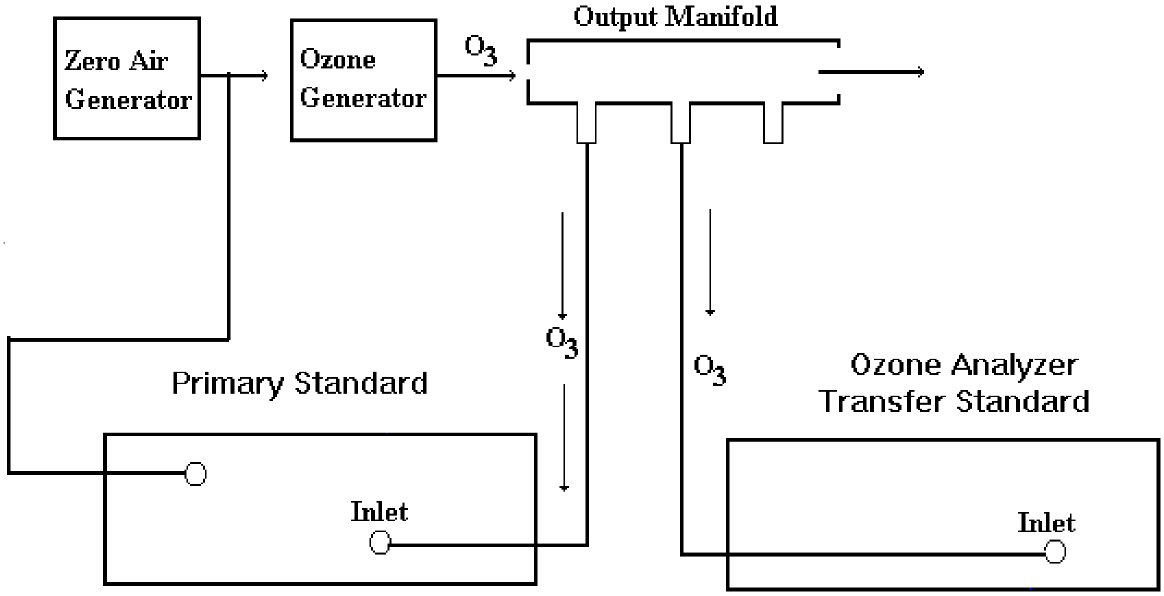


Figure 1.1 Calibration of an ozone analyzer-type transfer standard

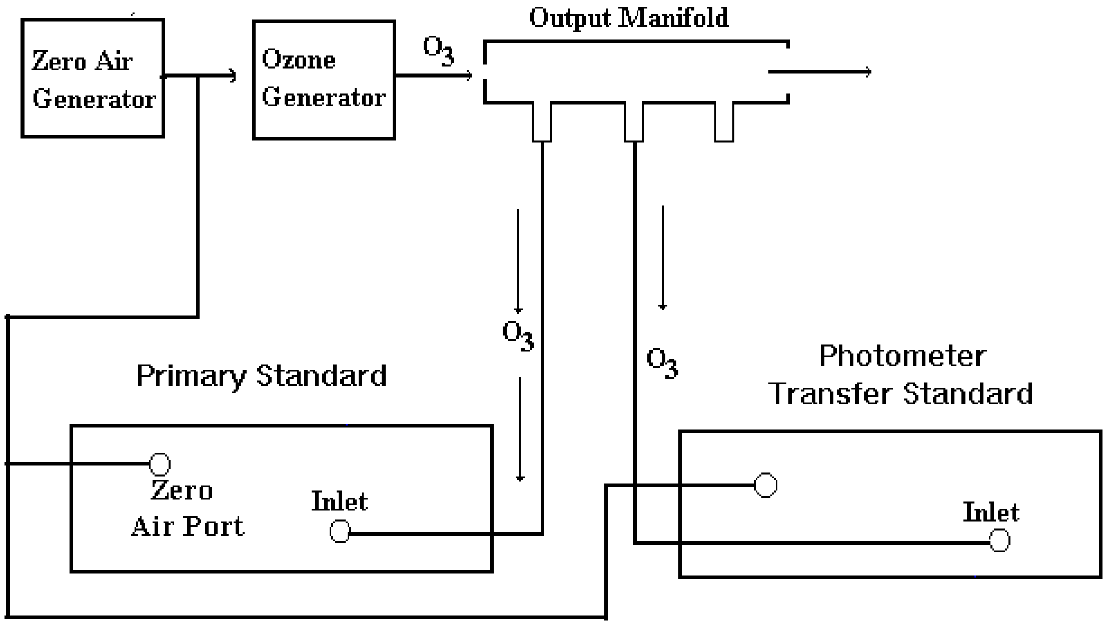


Figure 1.2 Calibration of a photometer-type transfer standard

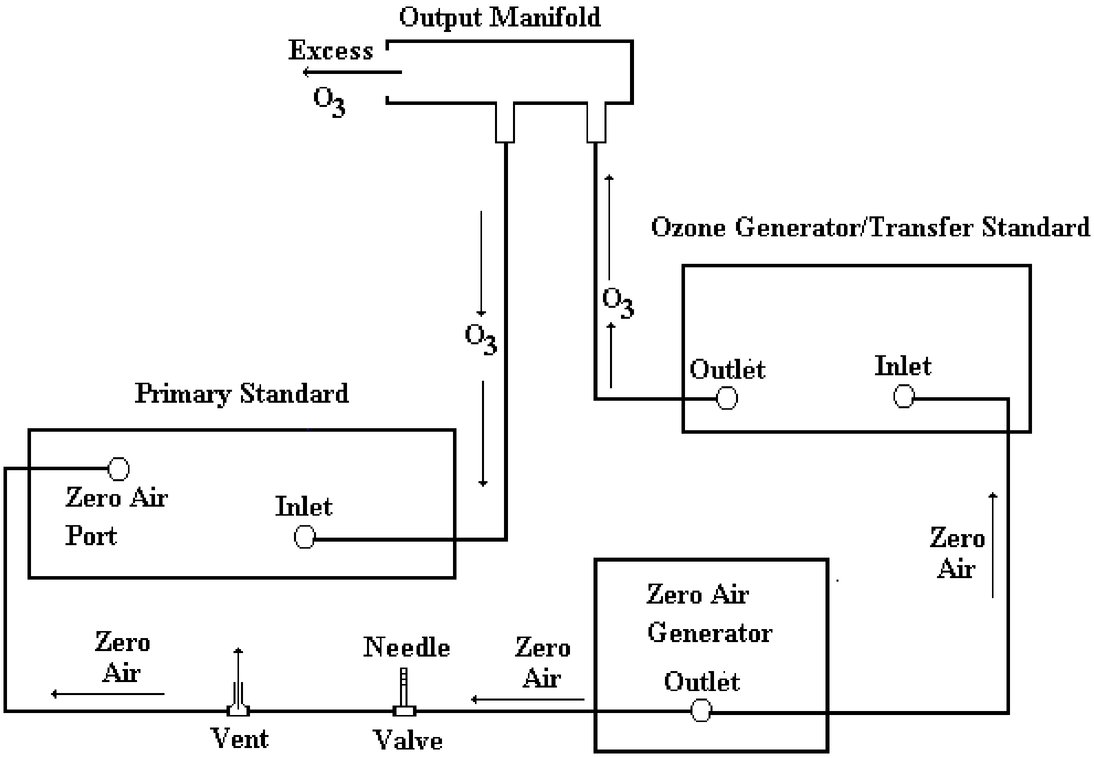


Figure 1.3 Calibration of an ozone generator-type transfer standard

Calibration Procedure for the Transfer Standard

1. Select the proper equipment configuration from Figure 1.1, 1.2, or 1.3 depending on the type of equipment being utilized.

2. Allow the transfer and primary standards to warm up properly. Generally, one hour is sufficient. Consult the manufacturer's operating manual for details.

3. Record the span and the count frequency settings, temperature, and barometric pressure (if applicable) on both the primary and transfer standards.

4. Attach the inlet of the primary and transfer standard to the ozone manifold. Make sure that there is proper venting of ozonated air.

5. With the ozone lamp off, allow both the primary and the transfer standards to stabilize to zero air. Record 10 readings from the primary and the transfer standard simultaneously (record a reading each time the analyzer refreshes – typically indicated by the blink of the decimal point). If an ozone generator is used as a transfer standard, a control setting rather than a reading may need to be recorded.

6. After 10 readings have been recorded, switch on the ozone lamp and set the lamp for 80-90% of the full scale of the ozone transfer standard.

7. Allow the primary and the transfer standard to stabilize at this ozone concentration and record 10 readings from the both instruments simultaneously.

8. Repeat the two previous steps at each of at least four lower ozone concentrations.

9. After six concentrations of ozone have been tested against the primary and transfer standard and all values have been recorded, turn off the ozone lamp and allow both instruments to sample zero air.

10. Record the temperature and barometric pressure of the primary standard once the tests are finished. Then examine the data for evidence of temperature or pressure instability.

11. Average all data points at each level. Perform a linear regression on this data set.

12. Repeat this entire procedure on five more days within a two-week period to complete the 6x6.

Ozone Analyzer Calibration

Once a primary standard and all transfer standards have been selected and authority established, the ozone analyzer can be calibrated by referencing its ozone response at the monitoring station against the transfer standard. See Figure 1.4 for equipment configuration.

The same precautions should be observed when calibrating an ozone analyzer against a transfer standard.

Multipoint Analyzer Calibrations

A multipoint calibration includes a minimum of four points (three spaced over the expected range and a zero point), each collected simultaneously from the transfer standard and the ozone analyzer. Although five to seven points are preferable, current analyzers are very linear over their entire operational range. The following steps outline the multipoint calibration procedure. Field operators should consult the manufacturer's operations manual for detailed, step-by-step instructions on how to use their particular analyzer.

1. Allow both the transfer standard and the ozone analyzer to warm up properly. Usually, one hour is sufficient, but consult the manufacturer's instruction manual for specific details.

2. Record the span and frequency setting and the temperature and barometric pressure (if available) for the ozone analyzer and transfer standard, to use as QC checks. Use calibration data sheets at the end of the chapter to organize your data collection.

3. Start the flow of zero air from the dynamic calibration unit [mark the strip chart, and flag the DAS data]. With the ozone lamp off, allow both ozone analyzer and transfer standard to stabilize to zero air. When stability is satisfactory, record 10 readings from the DAS ozone channel and transfer standard simultaneously.

4. Switch on the ozone lamp and set it to 80-90% of full scale of the transfer standard. Allow the analyzer and transfer standard to stabilize at this reading.

5. Then record 10 readings from the analyzer (or DAS ozone channel) and the transfer standard simultaneously.

6. Lower the ozone lamp setting to 40-50% of full scale. Repeat the previous two steps.

7. Lower the ozone lamp setting to 15-20% of full scale. Repeat as above.

8. Once three ozone levels are tested and all values recorded, turn off the ozone lamp and allow both instruments to sample zero air to see if the baseline of the transfer standard has drifted. Once the tests are completed, record the temperature and barometric pressure (if available).

9. Average all data points at each level and record on data sheet.

10. Generate a calibration curve by plotting the Ozone analyzer responses (y-axis) versus the corresponding transfer standard (or primary standard) concentrations (x-axis) to obtain the calibration relationships and verify linearity. Determine the straight line of best fit determined by the method of least squares regression. This regression can be done with a programmed calculator with this capability.

Acceptance criteria for the linear regressions are left to the discretion of the monitoring agency, but the following are suggested: slope, 1 ± 0.10; intercept, ± 0.010; correlation coefficient, > 0.995.

Whatever criteria are selected, the instrument still must pass audit tests, which require a difference of no more than ± 15%. These regular multipoint calibrations must be done at least every six months. In between times, however, other calibrations and checks are used whenever analyzer zero or span drift has been detected.

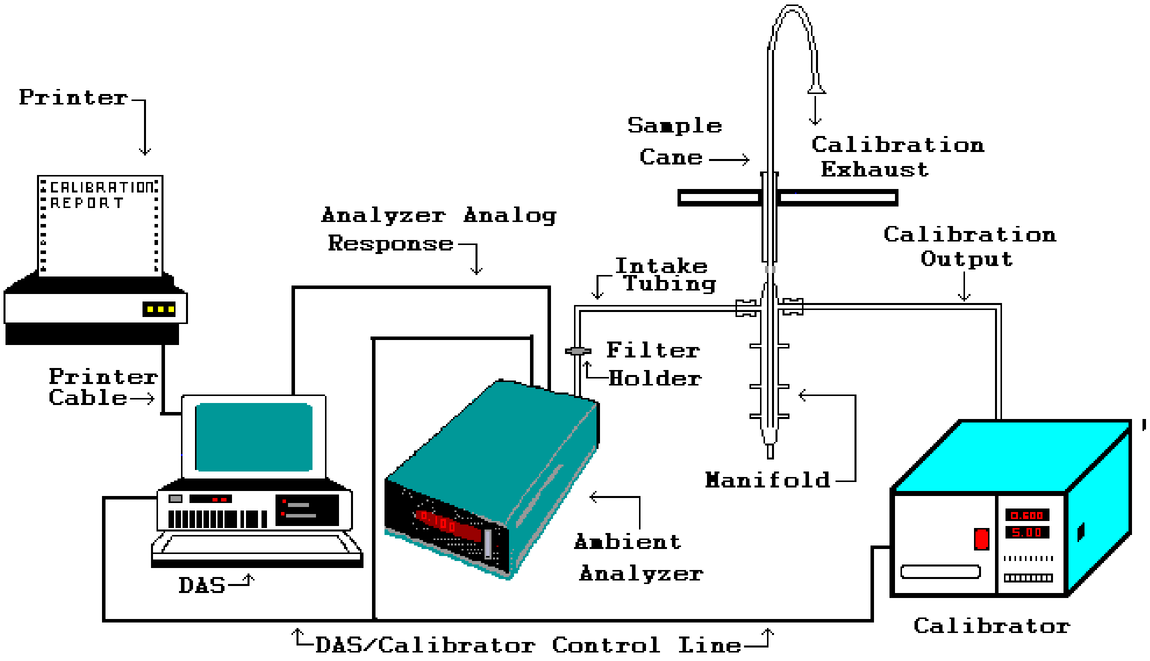


Figure 1.4 DAS calibration system

Instrument Performance Specifications Check

After completing the calibration of the ozone analyzer verify the instrument performance specifications for:

- Rise time
- Fall time
- Lag time.

The procedures for conducting these tests can be found in Appendix A of this manual and in 40 CFR Part 53.

Data collected during these tests should be recorded on the Instrument Performance Data Sheets found at the end of the chapter.

Laboratory A – Ozone

Calibration Data Form

Multipoint Analyzer Calibration

NAME______________________________

GROUP NO._________________________________

DATE ______________________________

Analyzer
Mfg.______________________________________
S/N______________________ **Zero Setting**_____________
Model No.________________ **Span Setting**_____________

Calibrator
Mfg.______________________________________
S/N______________________ **Zero Setting**_____________
Model No.________________ **Span Setting**_____________

Conc.	**Data Point**	**Calibrator Instrument**[1]	**Ozone Analyzer**	**Conc.**	**Data Point**	**Calibrator Instrument**[1]	**Ozone Analyzer**
Zero	1			80-90% URL			
	2						
	3						
	4						
	5						
	6						
	7						
	8						
	9						
	10						
	Avg						
40-50% URL	1			15-20% URL			
	2						
	3						
	4						
	5						
	6						
	7						
	8						
	9						
	10						
	Avg						

Note 1: The calibrator instrument maybe an ozone generator-, an analyzer-, or photometer-type transfer standard. If the calibrator is an ozone generator-type transfer standard the instrument is set at a level within the desired range while a series of 10 reading are measured for the analyzer under calibration. Therefore, only a single value corresponding to the ozone generator setting will be entered in this column. For all other transfer

standards simultaneous reading will be taken for each instrument and recorded on the data form under the appropriate column.

Laboratory A – Ozone

Calibration Data Form

Multipoint Analyzer Calibration

NAME______________________________
_

GROUP NO.________________________________

DATE ______________________________

Analyzer
Mfg.______________________________________
S/N______________________ **Zero Setting**_____________
Model No._______________ **Span Setting**_____________

Calibrator
Mfg._____________________________________
S/N______________________ **Zero Setting**_____________
Model No._______________ **Span Setting**_____________

Conc.	**Data Point**	**Calibrator Instrument[1]**	**Ozone Analyzer**	**Conc.**	**Data Point**	**Calibrator Instrument[1]**	**Ozone Analyzer**
Zero	1			80-90% URL			
	2						
	3						
	4						
	5						
	6						
	7						
	8						
	9						
	10						
	Avg						
40-50% URL	1			15-20% URL			
	2						
	3						
	4						
	5						
	6						
	7						
	8						
	9						
	10						
	Avg						

Note 1: The calibrator instrument maybe an ozone generator-, an analyzer-, or photometer-type transfer standard. If the calibrator is an ozone generator-type transfer standard the instrument is set at a level within the desired range while a series of 10 reading are measured for the analyzer under calibration. Therefore, only a single value corresponding to the ozone generator setting will be entered in this column. For all other transfer

standards simultaneous reading will be taken for each instrument and recorded on the data form under the appropriate column.

Laboratory A – Ozone

Instrument Performance Data Form

Name_________________________________

Group No._____________________________

Analyzer S/N______________________________

Model No._________________________________

Analyzer Mfg______________________________

Instrument Performance		
Parameter	**EPA Specification**	**Actual Performance**
Lag time	**20 minutes**	
Rise time	**15 minutes**	
Fall time	**15 minutes**	

Laboratory A – Ozone

Instrument Performance Data Form

Name__________________________________

Group No.______________________________

Analyzer S/N________________________________

Model No.__________________________________

Analyzer Mfg________________________________

Instrument Performance		
Parameter	**EPA Specification**	**Actual Performance**
Lag time	**20 minutes**	
Rise time	**15 minutes**	
Fall time	**15 minutes**	

Chapter 2

Laboratory B

Measurement Principle and Calibration Procedure for the Measurement of Nitrogen Dioxide in the Atmosphere (Gas Phase Titration)

Laboratory Objectives

Upon completion of this laboratory, you should be able to:

4. Calibrate the NO, NO_2, NO_x response channels of a NO-NO_2-NO_x analyzer by the Gas Phase Titration (GPT) method.
5. Construct dynamic calibration curves for each channel of a NO-NO_2-NO_x chemiluminescence analyzer using the GPT technique and a known concentration of nitric oxide (NO).
6. Determine the converter efficiency of a NO-NO_2-NO_x analyzer.

Introduction

Concentrations of nitrogen dioxide (NO_2) in ambient air are determined indirectly by photometrically measuring the light intensity, at wavelengths greater than 600 nm, resulting from the chemiluminescent reaction of nitric oxide (NO) with ozone (O_3). NO_2 is first quantitatively reduced to NO by a converter. The NO, which commonly exists in association with NO_2, passes through the converter unchanged, resulting in a total nitrogen oxides (NO_X) concentration of NO plus NO_2. A portion of the ambient air is also reacted with O_3 without having passed through the converter, and the NO concentration is measured. This value is subtracted from the NO_X concentration yielding the concentration of NO_2.

When purchasing or designing a calibration system, be sure that the calibration system meets the guidelines outlined in the reference method (40 CFR 50 Appendix F).

Two methods for dynamic multipoint calibration of NO_2 analyzers are specified in the reference method:

1. GPT of an NO compressed gas calibration standard with O_3 to generate known concentrations of NO_2, and
2. NO_2 permeation tube and a dynamic dilution system to produce known concentrations of NO_2, and an NO compressed gas calibration standard.

Only the first method is discussed in this chapter (laboratory exercise). Those wishing to use the second method should read Section 2 of the Technical Assistance Document (TAD) for the

Chemiluminescence Measurement of Nitrogen Dioxide (EPA-600/4-75-003). The first method requires four major components. They are:

1. NO compressed gas calibration standard;
2. Stable O_3 generator;
3. Source of zero air; and
4. GPT system (the GPT is typically part of a commercially available dynamic dilution system).

The NO standard must be traceable to an NIST-SRM. The specific NO SRMs available from NIST are listed in the NIST-SRM catalog (https://srmors.nist.gov/tables/view_table.cfm?table=107-1.htm). An acceptable protocol to demonstrate the traceability of a commercially produced NO standard to an NIST-SRM is described in the EPA traceability protocol for gaseous calibration standards (EPA. 1997. EPA traceability protocol for assay and certification of gaseous calibration standards. Publication No. EPA-600/R-97/121).

Zero air (free of contaminants that can cause a detectable response with the NO_X analyzer or that can react with either NO, O_3, or NO_2) is commercially available, or it can be generated by the user. Detailed procedures for generating zero air are given in the TAD.

As a precaution, all new GPT apparatus should be checked out against a calibrator of known reliability.

Calibration of Equipment

Dynamic calibration involves introducing gas samples of known concentrations into an instrument in order to adjust the instrument to a predetermined calibration relationship. This relationship is derived from the instrument's response to successive samples of different known concentrations. These samples may be introduced in an order of decreasing concentration to minimize response times. At a minimum, three reference points and a zero point are recommended to define this relationship. The certified values of the NO standards must be traceable to NIST-SRMs.

Most monitoring instrument systems are subject to drift and variation in internal parameters and cannot be expected to maintain stable calibration over long periods of time. Therefore, it is necessary to dynamically check the calibration relationship on a predetermined schedule. Precision is determined by a one-point check at least once every 2 weeks. Accuracy is determined by a three-point audit once each quarter. Zero and span checks must be used to document within-control conditions, these checks are also used in data reduction and validation.

Dynamic Multipoint Calibration Principles Using Gas-Phase Titration (GPT)

The principle of GPT is based on the rapid gas-phase reaction between NO and O_3 that produces stoichiometric quantities of NO_2 as shown by the following reaction:

$NO + O_3 \tau NO_2 + O_2$

If the initial and final NO concentrations for this reaction are known, the resulting concentration of NO_2 can be determined. Ozone is added to excess NO in a dynamic calibration system, and the NO channel of the chemiluminescent analyzer detects the changes in NO concentration. After the addition of O_3, the observed decrease in NO concentration is equivalent to the concentration of NO_2 produced. The concentration of NO_2 generated may be varied by increasing or decreasing the concentration of O_3 produced by a stable O_3 generator.

Dynamic calibration systems based on this GPT principle are commercially available, or may be assembled by the user. A recommended calibration system is described in the reference method and detailed in the TAD. Figure 2.1 shows a diagram of the GPT apparatus.
Both the assembled and the purchased calibration systems must meet the following conditions before being used for NO_2 calibrations.

- Use an NO standard traceable to an NIST-SRM.
- Have a stable O_3 source with an adjustable output.

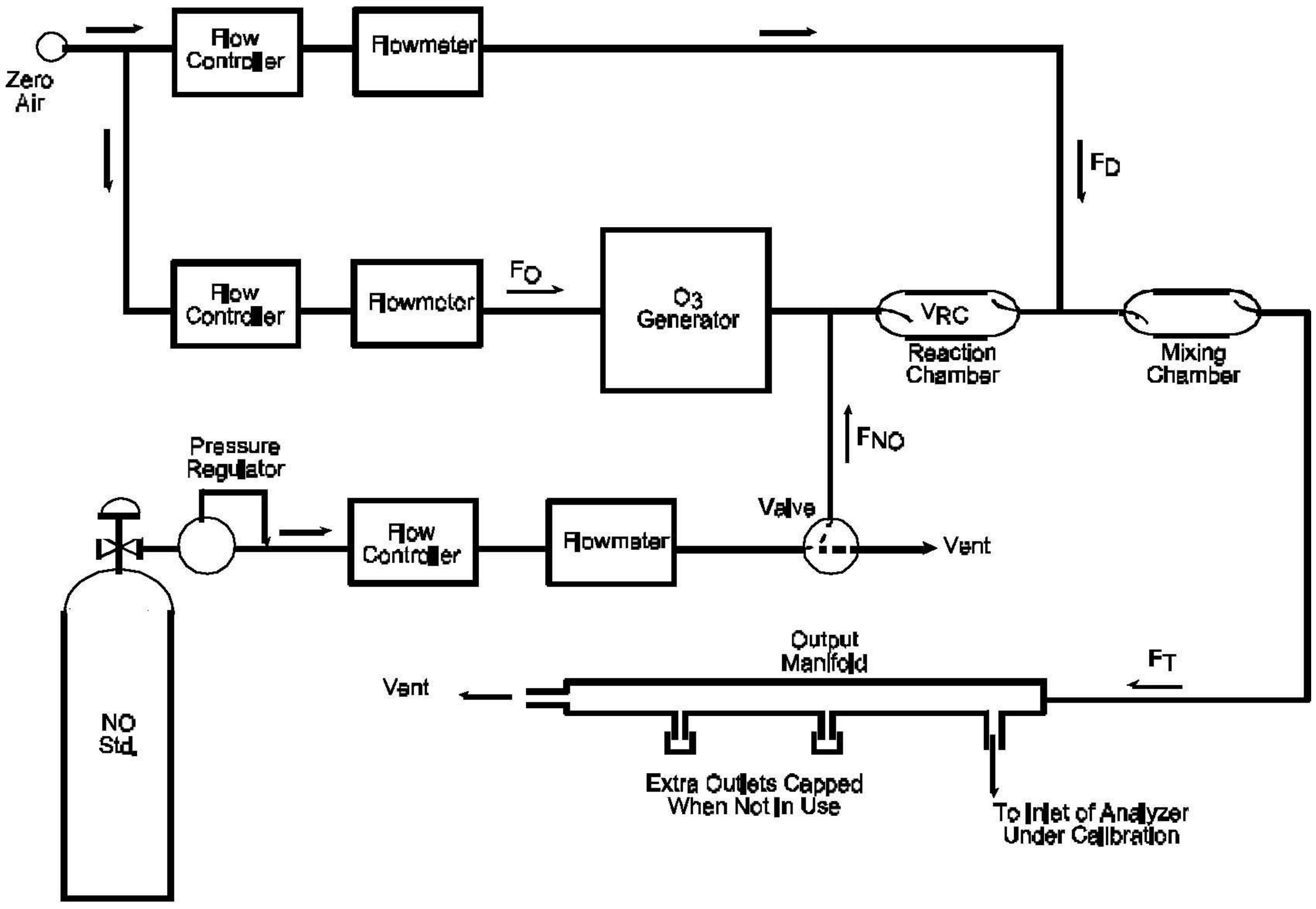


Figure 2.1. Schematic diagram of a typical GPT calibration system.

- Have a minimum total flow rate output that exceeds the analyzer flow rate demand by at least 10% to avoid reverse leakage into the calibration system.
- Be capable of generating an NO concentration that is approximately 90% of the upper range limit (URL) of the NO_2 range to be calibrated.
- Have a reaction chamber residence time of $\leq$2 minutes.
- Have a dynamic parameter specification of $\geq$2.75 ppm-min at the operating conditions at which the calibration will be performed.

It has been determined empirically that the NO-O_3 reaction goes to completion (<1% residual O_3) if the NO concentration in the reaction chamber (parts per million) multiplied by the residence time (minutes) of the reactants in the chamber is $\geq$2.75 ppm-min. The theory behind the development of this equation is discussed in the reference method and TAD.

General Calibration Recommendations

Calibration must be performed with a calibrator that meets all conditions specified in the TAD. Flow settings (with the exception of the NO flow rate, F_{NO}) and the concentration of the NO standard, $[NO]_{STD,}$ used in the GPT calibration for NO_2 must be the same as those used in the calculations of specified conditions.

The user should be sure that all flowmeters are calibrated under the conditions of use against a reliable standard such as a piston or soap bubble flowmeter or wet test meter. All volumetric flow rates should be corrected to standard temperature and pressure (STP) of 25 °C (77 °F) and 760 mm (29.92 in.)Hg. Calibrations of flowmeters are discussed in Appendix 12 (“Calibration of Primary and Secondary Standards for Flow Measurements”) in Volume II, Part 1, of the EPA Quality Assurance Handbook.

Precautions must be taken to purge O_2 and other contaminants from the NO standard’s pressure regulator and the delivery system prior to the start of calibration to avoid any premature conversion of the NO to NO_2. Failure to do so can cause significant errors in calibration. This problem may be minimized by:
- Carefully evacuating the pressure regulator, when possible, after it has been connected to the NO standard and before opening the cylinder hand valve;
- Thoroughly flushing the regulator and the delivery system with NO after opening the cylinder valve; and
- Not removing the regulator from the cylinder between calibrations unless absolutely necessary.

Sampling lines and manifolds should be constructed of Teflon® or glass to minimize possible reaction and degradation of NO_X. The residence time within the sampling line should be minimized to reduce the possibility of interreaction. For example, the reaction of ambient concentrations of NO and O_3 in the sample lines and manifold would lead to erroneous measurements.

Calibration Procedure for NO and NO_X

The GPT requires the use of the NO channel of the analyzer to determine the amount of NO_2 generated by titration. Therefore, it is necessary to calibrate and determine the linearity of the NO channel before proceeding with the NO_2 calibration. In some analyzers, it is also necessary to calibrate the NO_X channel. This can be done simultaneously with the NO calibration. The following procedure uses the calibration data form to aid in the collection and documentation of calibration data. An example form is shown in Figure 2.2. Blank forms can be found at the end of the chapter.

During the calibration, the analyzer should be operating in its normal sampling mode, and the test atmosphere should pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling and as much of the ambient air inlet system as is practicable. All operational adjustments to the analyzer should be completed prior to the calibration.

1. Record the station name and address on the calibration data form. Identify individual stations by their official names and addresses. Where appropriate, the station name and address should be the same as those appearing on the AIRS site identification form for that station. This will help to eliminate any confusion by persons not familiar with the station.

2. Identify the person performing the calibration and record the date of calibration.

3. Identify the analyzer being calibrated. Record the manufacturer's name, model, and serial number.

4. Identify the calibration apparatus used. If the calibrator was purchased, record the manufacturer's name, model, and serial number. Calibrators assembled by the user should be assigned an identification number so that calibrations can be referenced to that particular apparatus.

5. Identify, by supplier and stamped cylinder number, the NO standard to be used. Record the certified concentration of the NO standard ($[NO]_{STD}$) and the amount of NO_2 impurities ($[NO_2]_{IMP}$). Do not use NO standards with pressures <200 psig for calibration. It has been shown that some NO concentrations become unstable at low pressures. Provide a record of traceability to NIST for any NO standard used in a calibration, and include the date and the name of the person or organization that conducted the analysis.

6. Record the zero and the span settings after the calibration is complete so that these settings can be used at a later date to determine changes in the instrument performance characteristics.

1. Station Redbank

417 Redbank Road

Millsville, Ohio

2. Calibrated by Joe Smith

Date 3-2-00

3. Analyzer mfgr. ACME

Model $NO/NO_2/NO_X$ (No. 9876)

S/N 14782

4. Calibrator mfgr. State Agency

Model GPT

S/N 2A

5. NO reference standard

Supplier Gas Supplier

Concentration $[NO]_{STD}$ 50.5

NO_2 impurity, $[NO_2]_{IMP}$ 0

Traceable to NIST-SRM No. 1683d

Cylinder number 6783

Cylinder pressure 1500 psig

Cylinder No. AL-9323517

	NO	NO_X	NO_2
6. Zero knob setting	1.48	1.46	1.42
Span knob setting	6.43	6.29	6.71

7. Temperature 25°C

Barometric pressure 760 mm Hg

NO/NO_X Calibration and Linearity Check

	1	2	3	4	5	6
Calibration points NO/NO_X	$F_D + F_O$ (cm^3/min)	F_{NO} (cm^3/min)	$[NO]_{OUT}$ (ppm)	NO channel response (volts)	$[NO_X]_{OUT}$ (ppm)	NO_X channel response (volts)
Zero	2,720	0.0	0.000	0.050	0.000	0.050
80% URL	2,720	21.8	0.405	0.860	0.405	0.860
1	2,720	10.8	0.200	0.450	0.200	0.450
2	2,720	5.4	0.100	0.250	0.100	0.250

NO_2 Calibration by GPT

	7	8	9	10	11	12
Calibration points NO_2	$[NO_X]$ (ppm)	$[NO]_{ORIG}$ (ppm)	$[NO]_{REM}$ (ppm)	$[NO_2]_{IMP}$ (ppm)	$[NO_2]_{OUT}$ (ppm)	NO_2 channel response (volts)
Zero	—	—	—	0	0.000	0.050
ORIG	0.450	0.450	—	0	0.000	—
80% URL	0.440	0.450	0.050	0	0.400	0.850
1	0.445	0.450	0.250	0	0.200	0.450
2	0.450	0.450	0.350	0	0.100	0.250

Figure 2.2. Example Calibration Data Form.

Note: Some analyzers may have separate zero controls knobs for NO, NO_X, and NO_2; others may have separate zero controls only for NO and NO_X; still others may have only one zero control common to all three channels.

Note: Some analyzers may not have physical zero and span knobs to adjust because their signal processing is being performed digitally by a microprocessor in the analyzer. For such analyzers, there may not be a zero or span setting that can be recorded and there may not be a means to obtain an offset analyzer response to zero air. Consult the operating manual for such an analyzer to determine whether it has this feature.

7. Record the shelter temperature and barometric pressure at the time of calibration.

8. Use the NO/NO_X part of the data form (Figure 2.2) for the systematic recording of data determined during calibration of the NO and NO_X channels of the analyzer. Because zero and span adjustments differ between analyzers, the manufacturer's manual should be consulted before calibration is performed.

    a. Auto-ranging analyzers should be calibrated on all ranges that are likely to be used. Select the operating range of the analyzer to be calibrated. Precision and accuracy for NO_2 calibration are best obtained when all three channels of the analyzer are set to the same range.

    b. Connect the signal output cable(s) of the analyzer to the input terminals of the strip chart recorder(s) or DAS. Make all adjustments to the analyzer based on the appropriate analyzer responses. Analyzer responses in the procedures given herein refer to strip chart recorder or DAS responses.

    c. Adjust the flow rate of the diluent air to ensure that the total air flow rate exceeds the total demand of the analyzer(s) connected to the output manifold so that no ambient air will be pulled into the manifold vent. Record the sum of the flow rates of diluent air (F_D) and O_3 generator air (F_O) in Column 1 of Figure 2.2 Typically, F_o is not a separate air flow; it is a fraction of the F_D flow rate. Check the operations manual for the specific analyzer being used to make this determination. If this is the case, simply record the flow rate for F_D in column 1 of the calibration data form.

    d. Allow the analyzer to sample zero air until stable NO, NO_X, and NO_2 responses are obtained. After the responses have stabilized, adjust the analyzer zero control(s). (Offsetting the analyzer zero adjustments to 0.050 volts is recommended to facilitate observing any negative zero drift.) Record the stable zero air responses (Z_{NO} and Z_{NOx}) under Column 4 of Figure 2.2 for NO and under Column 6 for NO_X. Record the NO_2 zero air response (Z_{NO2}) in Column 12.

e. Adjust the flow rate from the NO standard to generate an NO concentration of approximately 80% of the URL of the NO channel. Measure the NO flow rate (F_{NO}) and record it under Column 2 on the 80% URL line.

f. Calculate the output NO concentration $[NO]_{OUT}$ using Equation 2-1.

(Eq. 2-1)
$$[NO]out = \frac{F_{no} \times [NO]_{std}}{F_{no} + F_o + F_D}$$

Calculate the output NOX concentration $[NO_X]_{OUT}$ using Equation 2-2.

(Eq. 2-2)
$$[NO_2]_{out} = \frac{F_{no} \times ([NO]_{std} + [NO]_{imp})}{F_{no} + F_o + F_D}$$

Record the $[NO]_{OUT}$ under Column 3 and the $[NO_X]_{OUT}$ under Column 5 on the 80% URL line.

1. Sample the generated concentration until the NO and the NO_X responses have stabilized. Adjust the NO span control to obtain an analyzer response as determined by Equation 2-3.

(Eq. 2-3)
$$Recorder\ response\ (\%\ scale) = \left(\frac{[NO]_{out}}{URL} \times 100\right) + Z_{NO}$$

where URL = nominal upper range limit of the NO channel being calibrated in parts per million.
Z_{NO} = recorder response, NO channel to zero air.

Note: Some analyzers may have separate span controls for NO, NO_X, and NO_2; others may have separate span controls only for NO and NO_X; while still others may have only one span control common to all three channels. If only one span control is available, make the span adjustment on the NO channel. When adjusting the analyzer's NO_X span control, substitute the $[NO_X]_{OUT}$ and the Z_{NO} in Equation 2-3 to determine the analyzer response. If substantial adjustments of the span controls are necessary, recheck the zero span adjustments by repeating Steps 8f and 8g. Record the NO analyzer response under Column 4 and the NO_X analyzer response under Column 6 on the 80% URL line.

2. After the zero and the 80% URL points have been set, determine two approximately evenly spaced points between zero and the 80% URL without further adjustment to the analyzer. These additional points can be generated by either increasing the dilution flow rate (F_D) or by decreasing the F_{NO}. For each concentration generated, calculate the NO and NO_X concentrations using Equations 2-1 and 2-2. Record the required information for each point under the appropriate column in the NO/NO_X table in Figure 2.2.

9. Plot the NO analyzer responses (y-axis) versus the corresponding calculated concentrations $[NO]_{OUT}$ (x-axis) to obtain the calibration relationships shown in Figure 2.3. Determine the straight line of best fit determined by the method of least squares regression. This regression can be done with a programmed calculator with this capability.

10. After determining the slope (b) and the y-intercept (a) where the regression line crosses the y-axis, draw the fitted line for each set of points. On the y-axis of the graph, locate and plot the value of a. Using the equation y = a + bx, calculate the predicted y value using the 80% URL concentration for the x-value. Plot this second point on the graph. Draw a straight line through these two points to give a best-fit line. Figure 2.3 shows a calibration line plotted using this procedure. Steps 9 and 10 should be repeated for the NO_X values.

11. After the best-fit line has been drawn for the NO and the NO_X calibrations, determine whether the analyzer response is linear. To be considered linear, no calibration point should differ from the best-fit line by more than 2% of the URL. A simple test for linearity can be made by plotting a point 2% of the URL above and 2% of the URL below the point where the fitted line crosses the 0.4-ppm line. Repeat this procedure where the fitted line crosses the 0.1-ppm line. Draw a straight line through the +2% URL points and the -2% URL points (Figure 2.3). These two lines define the limits between which the calibration points can fall and the calibration curve be considered linear. Repeat any points falling outside these limits; if repeated points still fall outside the limits, consult the manufacturer's manual on how to correct the nonlinearity.

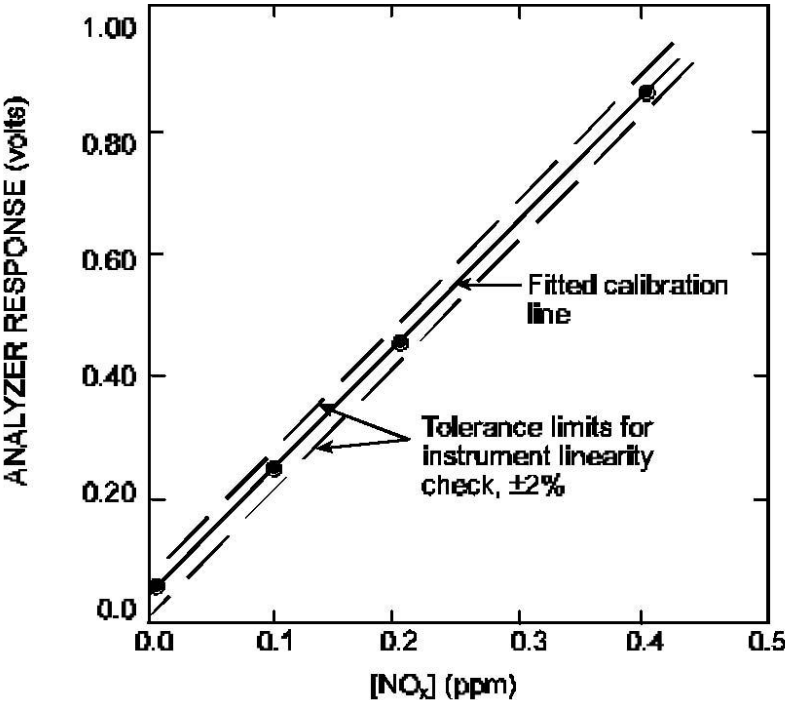


Figure 2.3. Example of an NO_X calibration relationship.

Gas-Phase Titration Procedure for NO_2

Having completed the calibration of the NO and NO_X channels, the NO_2 channel may now be calibrated by GPT. Figure 2.2 allows for the systematic recording of the data determined during the calibration of the NO_2 channel of the analyzer. Do not readjust the zero and span settings for the NO and the NO_X channels.

1. The NO_2 zero adjustment was made in Step 8d of the NO/NO_X calibration and need not be repeated. Record the analyzer response under Column 12 of the NO_2 calibration table.

2. The NO_2 impurity concentration, $[NO_2]_{IMP}$, found in the NO standard must be recorded under Column 10; if there is no impurity, disregard this column.

3. Adjust the NO flow rate (F_{NO}) to generate an NO concentration near 90% of the URL. Sample this NO concentration until the NO and NO_X responses stabilize. Using the NO calibration relationship determined in Step 10 in the previous section, measure and record the NO concentration under Column 8, $[NO]_{ORIG}$. Using the NO_X calibration relationship obtained in Step 10, measure and record the NO_X concentration under Column 7, $[NO_X]$. Record both values on the line marked “ORIG.”

4. Adjust the O_3 generator to produce sufficient O_3 to decrease the NO concentration from 90% to 10% of the URL. This decrease will be equivalent to 80% of the URL of the uncalibrated NO_2 channel. The decrease must not exceed 90% of the NO concentration determined in Step 3. After the analyzer responses stabilize, determine the new NO and NO_X concentrations from their respective calibration relationships. Record the NO_X concentration under Column 7, and the remaining NO concentration under Column 9, $[NO]_{REM}$. The $[NO]_{ORIG}$ will be the same value determined in Step 3.

5. Calculate the resulting NO_2 concentration, $[NO_2]_{OUT}$, using Equation 2-4, and record it under Column 11, $[NO_2]_{OUT}$.

(Eq. 2-4)

$$[NO_2]_{out} = [NO]_{orig} - [NO]_{rem} + \frac{F_{NO} \times [NO_2]IMP}{F_{NO} + F_O + F_D}$$

If there was no NO_2 impurity in the NO reference standard, Equation 2-4A may be used to calculate $[NO_2]_{OUT}$.

(Eq. 2-4A)

$$[NO_2]_{out} = [NO]_{orig} - [NO]_{rem}$$

6. Adjust the NO_2 span control to obtain the analyzer response calculated in Equation 2-10A. This equation is derived from Equation 2-3 by substituting $[NO_2]_{OUT}$ and Z_{NO2} for $[NO]_{OUT}$ and Z_{NO}, respectively.

(Eq. 2-3A)

$$Recorder\ response\ (\%\, scale) = \left(\frac{[NO_2]_{out}}{URL} \times 100\right) + Z_{NO_2}$$

Note: If the analyzer has only one or two span controls, the span adjustments are made on the NO channel or on the NO and NO_X channels, and no further adjustment is made here for NO_2. If substantial adjustment of the NO_2 span control is necessary, it may be necessary to recheck the zero and span adjustments. Record the NO_2 analyzer response under Column 12.

7. While maintaining all other conditions, adjust the ozone generator to obtain two other concentrations of NO_2 evenly spaced between the 80% URL point and the zero point. Record the information for each point on the respective lines of the NO_2 calibration table.

8. Repeat Steps 9, 10, and 11 of Calibration Procedure for the NO_2 analyzer response, Column 12, and the corresponding calculated concentration $[NO_2]_{OUT,}$ Column 11.

Example NO and NO_2 Calibration

1. Complete Steps 1 through 5 and Step 7 of the NO/NO_X calibration before starting the calibration to document all information concerning the station, analyzer, NO standard, and person performing the calibration. Because analyzers have different operating characteristics, consult the manufacturer's operation manual before starting the calibration procedure.

2. Select the operating range (parts per million) of the analyzer to be calibrated. For this example, assume that all three channels (NO, NO_X, and NO_2) will be calibrated on the range of 0 to 0.5 ppm (or 500 ppb).

3. Be sure that the strip chart recorders or the DAS are operating properly and are connected to the correct output terminals of the analyzer.

4. Connect the analyzer's sample line to the manifold of the calibrator.

5. Adjust the diluent air flow rate (F_D) and the O_3 generator air flow rate (F_O) to obtain the flow rates close to those determined in the previous section. Re-measure these flows for each calibration:

   F_D = 2460 cm^3/min at STP
   F_O = 260 cm^3/min at STP
   Record the sum of F_D and F_O under Column 1.
   $F_D + F_O$ = 2720 cm^3/min at STP

6. Allow the analyzer to sample the zero air until the NO, NO_X, and NO_2 analyzer responses stabilize. Then adjust the analyzer zero control(s) to offset the analyzer responses to 0.05 volts to facilitate observing any negative zero drift. Record the stable zero air responses (Z_{NO} and Z_{NO}) under Column 4 for NO and Column 6 for NO_X. Record the NO_2 zero air response (Z_{NO}) in Column 12.

7. Adjust the NO flow rate from the NO standard to generate an NO concentration of approximately 80% of the URL of the NO channel. Measure the NO flow rate (F_{NO}), and record this under Column 2 on the 80% URL line.

$$\mathbf{F_{NO} = 21.8\ cm^3/min}$$

8. Calculate the NO concentration $[NO]_{OUT}$ using Equation 2-1.

$$[NO]out = \frac{F_{no} \times [NO]_{std}}{F_{no} + F_o + F_D}$$

$$[NO]out = \frac{21.8 \times 50.5}{2720 + 21.8} = 0.405\ ppm$$

Record this value on the 80% URL line of Column 3. Calculate the exact NO_X concentration $[NO_X]_{OUT}$ using Equation 2-2.

$$[NO_2]_{out} = \frac{F_{no} \times ([NO]_{std} + [NO]_{imp})}{F_{no} + F_o + F_D}$$

$$[NO_2]_{out} = \frac{21.8 \times (50.5 + 0)}{2720 + 21.8} = 0.405\ ppm$$

Record this value on the 80% URL line of Column 5.

9. Sample the generated concentration until the NO and NO_X analyzer responses have stabilized. Calculate the expected analyzer response for this concentration using Equation 2-3.

$$Recorder\ response\ (volts) = \left(\frac{[NO]_{out}}{URL} \times 100\right) + Z_{NO}$$

$$Recorder\ response\ (volts) = \left(\frac{0.405}{0.5} \times 100\right) + 5 = 0.860\ \text{volts}$$

Adjust the NO span control to obtain an analyzer response of 0.860 volts, and record this response on the 80% URL line of Column 4.

Substitute the NO_X values in Equation 2-3; an analyzer response of 0.860 volts is determined. Adjust the NO_X span control and record this response under Column 6.

10. Generate two approximately evenly spaced points between zero and the 80% URL by changing either F_{NO} or F_D. In this example, F_{NO} was changed. Allow the analyzer response to

stabilize before moving to the next calibration point. When the response has stabilized, record it in the appropriate column of the NO/NO_X calibration table.

11. Plot the analyzer response from Column 4 (y-axis) versus the corresponding calculated concentration $[NO]_{OUT}$ from Column 3 (x-axis). A straight line of best fit is now calculated by the method of least squares. For this example, the slope (b) is 1.00 with a y-intercept (a) of 0.050 volts. Plot the calibration relationship as in Figure 2.3. To check linearity, draw the +2% and -2% URL lines parallel to this calibration line. In this example, the analyzer response is linear.

12. Adjust the NO flow rate (F_{NO}) to generate an NO concentration near 90% of the NO range. For this example, a concentration of 0.450 ppm is used. This value need only be approximated.

After the response has stabilized, use the NO calibration relationship determined in Step 11 to obtain the actual concentrations. Record this value on the line marked "ORIG" under Column 8 $[NO]_{ORIG}$. If the NO_X channel is monitored, determine NO_X concentrations from the NO_X calibration relationship, and record the values under Column 7.

13. Adjust the O_3 generator to produce sufficient O_3 to reduce the NO concentration from 90% of the URL (0.450 ppm) to 10% of the URL (0.050 ppm). Determine the actual NO concentration remaining from the calibration relationship, and record the value on the 80% URL line under Column 9 $[NO]_{REM}$. $[NO]_{ORIG}$ is the same value determined in Step 12.

14. The resulting NO_2 concentration is now calculated. Because there were no NO_2 impurities present in the NO standard, Equation 2-4A may be used.

$$[NO_2]_{out} = [NO]_{orig} - [NO]_{rem}$$

$$[NO_2]_{out} = 0.45 - 0.05 = 0.40\ ppm\ NO_2$$

15. Calculate the required recorder response using Equation 2-3.

$$Recorder\ response\ (volts) = \left(\frac{[NO]_{out}}{URL} \times b\right) + a$$

$$Recorder\ response\ (volts) = \left(\frac{0.400}{0.500} \times 1.00\right) + 0.050 = 0.85\ volts$$

Adjust the NO_2 span control to obtain an analyzer response of 0.850 volts. Record this value under Column 12.

16. Adjust the ozone generator for two additional concentrations of NO_2, approximately evenly spaced between the 80% URL point and the zero point. Record the required data under the appropriate columns of the NO_2 calibration table (Figure 2.2).

17. Plot the analyzer response from Column 12 (y-axis) versus the corresponding calculated concentration $[NO_2]_{OUT}$ from Column 11 (x-axis). Proceed as in Step 11 to determine a straight line of best fit and linearity.

Determination of NO_2 to NO Converter Efficiency

Note: Some analyzers whose signal processing is handled by a microprocessor may have manual or automatic software for correcting for the converter efficiency. For such analyzers, it may not be possible to determine the analyzer's converter efficiency and this section should be ignored. Consult the operating manual for the analyzer to determine if it has this feature.

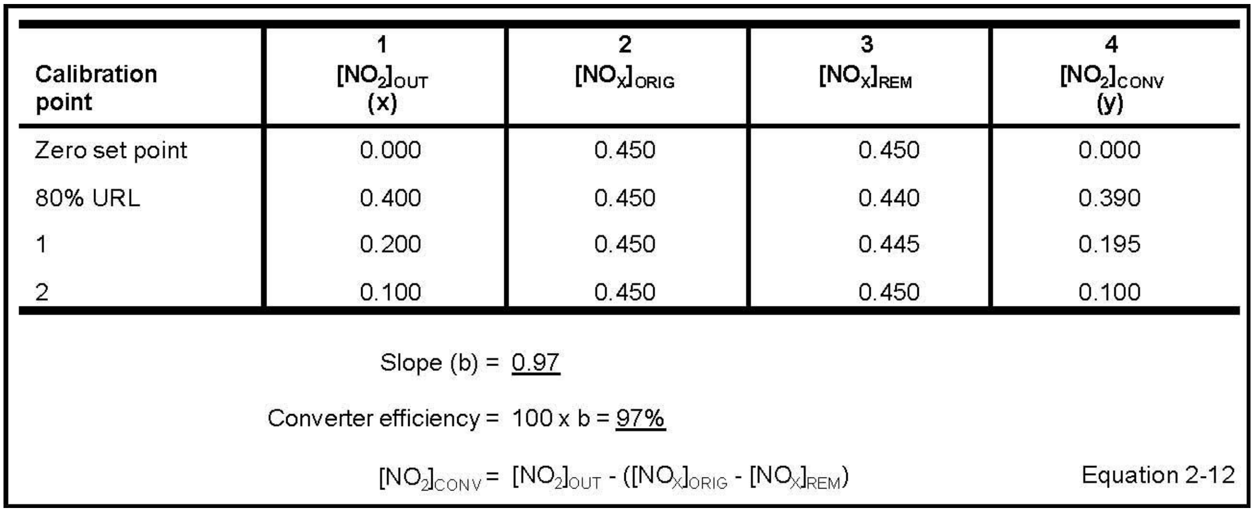
A converter efficiency data form has been developed to aid in the collection and documentation of calibration data. An example form is shown in Figure 2.4. Blank forms can be found at the end of the chapter. The following procedure is for use with this data form.

1. Values for Columns 1, 2, and 3 of the converter efficiency data form are taken directly from the NO_2 table of the calibration data form.

2. Calculate the quantity of NO_2 converted to NO, labeled $[NO_2]_{CONV}$, for each point using Equation 2-12.

(Eq. 2-5) $$[NO]_{CONV} = [NO_2]_{OUT} - ([NO_X]_{ORIG} - [NO_X]_{REM})$$

Note: Converters may fail gradually or catastrophically. A gradual failure may manifest itself first at the highest value of $[NO_2]_{CONV}$ by the inability to attain a stable analyzer response. The converter efficiency may remain within the 96% acceptance limit at lower values of $[NO_2]_{CONV}$ while falling outside the limit at higher values of $[NO_2]_{CONV}$. The failing converter may appear to recover after sampling ambient air with low $[NO_2]$. Consult the operating manual for the analyzer for other information regarding troubleshooting converter problems.



Calibration point	1 $[NO_2]_{OUT}$ (x)	2 $[NO_X]_{ORIG}$	3 $[NO_X]_{REM}$	4 $[NO_2]_{CONV}$ (y)
Zero set point	0.000	0.450	0.450	0.000
80% URL	0.400	0.450	0.440	0.390
1	0.200	0.450	0.445	0.195
2	0.100	0.450	0.450	0.100

Slope (b) = 0.97

Converter efficiency = 100 x b = 97%

$[NO_2]_{CONV} = [NO_2]_{OUT} - ([NO_X]_{ORIG} - [NO_X]_{REM})$ Equation 2-12

Figure 2.4. Converter efficiency data form.

Column l, $[NO_2]_{OUT}$, is from Column 11, $[NO_2]_{OUT}$, of the table from Figure 2.2.
Column 2, $[NO_X]_{ORIG}$, is from the line marked "ORIG" of Column 7, $[NO_X]$, of the table; this value will be the same for all lines of Column 2.
Column 3, $[NO_X]_{REM}$, is from the appropriate calibration points of Column 7 of the table.

3. Plot $[NO_2]_{CONV}$ (y-axis) versus $[NO_2]_{OUT}$ (x-axis), and the converter efficiency curve (Figure 2.5), and then calculate the slope (b) of the curve using an appropriate calculator capable of the method of least squares regression.

4. Multiply the slope (b) of the curve by 100 to determine average converter efficiency; if the efficiency is <96%, either replace or service the converter.

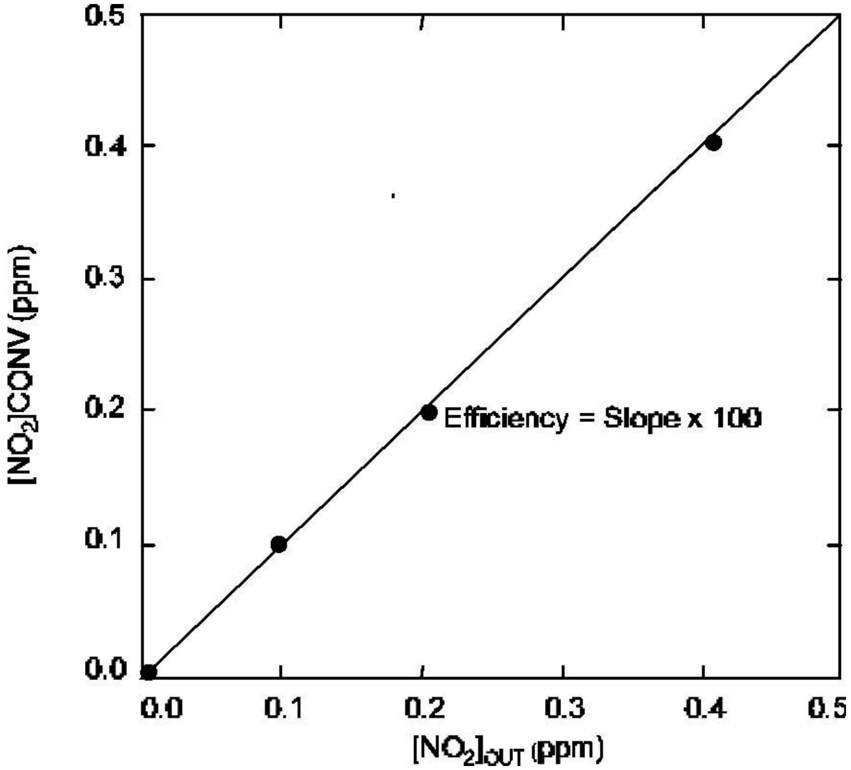


Figure 2.5. Converter efficiency relationship.

Calibration Frequency

1. To ensure accurate measurements of the NO and NO_2 concentrations, calibrate the analyzer at the time of installation and recalibrate it:

2. No later than 3 months after the most recent calibration or performance audit that indicated analyzer response to be acceptable; or

3. Following any one of the activities listed below:

   i. An interruption of more than a few days in analyzer operation;

   ii. Any repairs that might affect its calibration;

   iii. Physical relocation of the analyzer; or

   iv. Any other indication (including excessive zero or span drift) of possible significant inaccuracy of the analyzer.

Following any of the activities listed in Item 2 above, the zero and span should be checked to determine if a calibration is necessary. If the analyzer zero and span drifts do not exceed the acceptance limits, a calibration need not be performed. If either the zero or span drift exceed their respective acceptance limit, investigate the cause of the drift, take corrective action, and calibrate the analyzer. See Section 12 (“Instrument Calibration and Frequency”) in Volume II, Part 1, of the handbook.

Laboratory B – Nitrogen Dioxide
Calibration Data Form

NAME____________________________ **Analyzer Serial No.**________________
GROUP NO.______________________ **Model No.**________________________
DATE ____________________________

Station ______________________________
____
____

Calibrated by__________________________ **Date**______________________________
Analyzer Mfgr.________________________ **Calibrator Mfgr.**______________________
Model______________________________ **Model**______________________________
S/N______________________________ **S/N**______________________________
NO reference standard
Supplier______________________________ **Cylinder No**__________________________
Concentration $[NO]_{STD}$___________________ **Cylinder Pressure**_____________________
NO_2 impurity $[NO2]_{IMP}$___________________
Traceable to NIST-SRM No.______________

NO **NO_X** **NO_2** **Temperature**_________________________
Zero Setting ______ _______ ______ **Barometric Pressure**____________________
Span Setting ______ _______ ______

NO/NO_X Calibration and Linearity Check

Calibration Points NO/NO_X	1	2	3	4	5	6
	$F_D + F_O$ (cm^3/min)	F_{NO} (cm^3/min)	$[NO]_{out}$ (ppm)	NO channel Response (volts)	$[NO_X]_{out}$ (ppm)	NO_X channel Response (volts)
Zero						
80% URL						
1						
2						

NO2 Calibration by GPT

Calibration Points NO_2	7	8	9	10	11	12
	$[NO_X]$ (ppm)	$[NO]_{ORIG}$ (ppm)	$[NO]_{REM}$ (ppm)	$[NO_2]_{IMP}$ (ppm)	$[NO_2]_{OUT}$ (ppm)	NO_2 channel Response (volts)
Zero						
80% URL						
1						
2						

Laboratory B – Nitrogen Dioxide

Calibration Data Form

NAME____________________________ **Analyzer Serial No.**________________

GROUP NO._______________________ **Model No.**________________________

DATE ___________________________

Station ______________________________

____

____

Calibrated by__________________________ **Date**________________________________

Analyzer Mfgr._________________________ **Calibrator Mfgr.**________________________

Model______________________________ **Model**______________________________

S/N_______________________________ **S/N**_______________________________

NO reference standard

Supplier______________________________ **Cylinder No**__________________________

Concentration [NO]$_{STD}$___________________ **Cylinder Pressure**______________________

NO$_2$ impurity [NO2]$_{IMP}$__________________

Traceable to NIST-SRM No._____________

NO **NO$_X$** **Temperature**_________________________

NO$_2$

Zero Setting ______ _______ ______ **Barometric Pressure**____________________

Span Setting ______ _______ ______

NO/NO$_X$ Calibration and Linearity Check						
Calibration Points NO/NO$_X$	1	2	3	4	5	6
	$F_D + F_O$ (cm^3/min)	F_{NO} (cm^3/min)	$[NO]_{out}$ (ppm)	NO channel Response (volts)	$[NO_X]_{out}$ (ppm)	NO$_X$ channel Response (volts)
Zero						
80% URL						
1						
2						

NO2 Calibration by GPT						
Calibration Points NO$_2$	7	8	9	10	11	12
	$[NO_X]$ (ppm)	$[NO]_{ORIG}$ (ppm)	$[NO]_{REM}$ (ppm)	$[NO_2]_{IMP}$ (ppm)	$[NO_2]_{OUT}$ (ppm)	NO$_2$ channel Response (volts)
Zero						
80% URL						
1						
2						

Laboratory B – Nitrogen Dioxide

Converter Efficiency Data Form

NAME_____________________________ **Analyzer Serial No.**_________________
GROUP NO.________________________ **Model No.**_________________________
DATE _____________________________

Calibration Point	1 $[NO_2]_{OUT}$ (x)	2 $[NO_X]_{ORIG}$	3 $[NO_X]_{REM}$	4 $[NO_2]_{CONV}$ (y)
Zero set point				
80% URL				
1				
2				

Slope (b) = ___________________

Converter efficiency = 100 x b = ____________________

$[NO_2]_{CONV} = [NO_2]_{OUT} - ([NO_X]_{ORIG} - [NO_X]_{REM})$

Laboratory B – Nitrogen Dioxide

Converter Efficiency Data Form

NAME_____________________________ **Analyzer Serial No.**_________________
GROUP NO.________________________ **Model No.**_________________________
DATE _____________________________

Calibration Point	1 $[NO_2]_{OUT}$ (x)	2 $[NO_X]_{ORIG}$	3 $[NO_X]_{REM}$	4 $[NO_2]_{CONV}$ (y)
Zero set point				
80% URL				
1				
2				

Slope (b) = ___________________

Converter efficiency = 100 x b = ____________________

$[NO_2]_{CONV} = [NO_2]_{OUT} - ([NO_X]_{ORIG} - [NO_X]_{REM})$

Chapter 3

Laboratory C

Instrumental Method for the Determination of Sulfur Dioxide in the Atmosphere

Laboratory Objectives

Upon completion of this laboratory, you should be able to:

(a) recall the principles of operation of the ultraviolet (UV) fluorescence sulfur dioxide analyzer;
(b) calculate SO_2 concentration from permeation rate and dilution flow rate; and
(c) perform a least squares linear regression analysis on calibration data.

Introduction

The UV fluorescence monitoring method for atmospheric SO_2 was developed to improve upon the flame photometric detection (FPD) method for SO_2, which in turn had displaced the pararosaniline wet chemical method for SO_2 measurement. The pararosaniline method is still the U.S. EPA's Reference Method for atmospheric SO_2, 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.

The current method for the measurement of SO_2 is based on the principle that SO_2 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_2 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:

$$SO_2 + h\nu_1 \rightarrow SO_2^*$$

$$SO_2^* \rightarrow SO_2 + h\nu_2$$

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 ($h\nu_2$) is proportional to the number of SO_2 molecules in the sample gas.

Instructions

Ultraviolet (UV) Fluorescent SO_2 Analyzer

Prepare calibration curve using known concentrations of SO_2 from calibration source and generalized calibration procedure detailed in the section entitled Generalized Calibration, Operation for both a FPD Analyzer as well as an UV Fluorescent Analyzer of this chapter. Record data on appropriate calibration data form. Perform least squares linear regression on the calibration data as directed in instructions.

Generalized Calibration and Operations Procedures

This section describes the procedure for performing zero and span checks and also details the procedure used in calibrating a SO_2 analyzer. A discussion of the calibration gas types (i.e., cylinder gas and permeation tube) and a dynamic dilution calibrator which has the capability of accommodating a permeation tube (i.e, permeation oven) as the SO_2 calibration gas source is also provided.

Gas Generation Systems Required

1. Zero Gas Source/Generator

A SO_2 free air supply is required for the proper calibration and checkout of the monitor. There are several methods that are acceptable to generate the required “zero air”.

Zero air is required for the calibration of precursor SO_2 instruments. This air must contain no detectable SO_2 (i.e., SO_2 content must be less than the LDL of the SO_2 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_2 analyzer continuously. As an alternative, many commercially available zero air generation systems can supply suitably SO_2-free air.

To ensure that the zero air used is free from contaminants, the SO_2 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_2 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, 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_2 at less than 0.05 ppb.

Note: For zero-air sources based on removing SO_2 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.

2. SO_2 Calibration Gas Source

The source of SO_2 gas maybe either certified, commercially-prepared compressed gas standards or certified, commercially-prepared permeation tube standards.

The primary SO_2 standards used must be certified, commercially-prepared compressed gas standards, with a certified accuracy of no worse than ±2 percent. SO_2 gas standards of 50 to 100 ppm are conveniently diluted with a dynamic calibrator down to working concentrations of 0.5 ppm or less. The commercially-prepared standard may contain only SO_2 in an inert gas (e.g., N_2), or may be a mixed component standard that also contains known concentrations of other ambient gases (e.g., CO, NO).

3. Calibration Gas Generator

The dynamic dilution calibration gas generator should be capable of providing seven accurate levels of SO_2 calibration gas between 0.000 and 0.500 parts per million. One point must be at approximately 0.40 ppm while another point must be 0.000 ppm. The remaining five points should be spaced approximately equally between these limits. In addition, it must provide a flow of this span gas at a rate required by the analyzer (see manufacturer's operating manual). Commercial systems are available which reliably and accurately dilute a high concentration gas mixture to provide a reliable span gas.

If a SO_2 permeation tube is to be used as the calibration standard then the dynamic calibrator must be equipped with a permeation oven to accommodate this use. Permeation tube capable calibration systems must precisely maintain a set temperature to within ±0.05% and hold a zero air flow rate to within ±0.2% to be used for generation of span gas and other working standards (intermediate concentrations). Refer to the instrument manufacturer's instructions for proper use of such systems.

The accuracy of the calibration gas generated must be known. This is accomplished by reference to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) permeation device, or by a tank of cylinder gas (SO_2) traceable to a NIST-SRM. All flows (e.g., calibration of mass flow controller) should be referenced to NIST calibration standards. This is most easily done by using a certified soap bubble meter, piston meter, or mass flow meter.

All plumbing lines, fittings should be constructed of FEP Teflon or borosilicate glass to minimize calibration gas interaction.

Calibration

The calibration procedure discussed here is for calibration of the SO_2 analyzer using either a permeation tube or cylinder gas as the standard reference material (SRM) of SO_2 and a dynamic dilution calibration generator and zero gas generator as previously described (or similar). It is suggested that a calibration curve have at least (7) points between 0.000 and 0.500 parts per million SO_2 concentration. Though the seven (7) point curve is optional, two (2) out of whatever number of points is chosen, should be located t the 0.000 and 0.400 ppm levels (approximately 80% URL) and the remaining points, equally spaced between these values.

Multipoint Calibration of a SO_2 Analyzer

A multipoint calibration must be performed when the analyzer is first set up and periodically thereafter. The frequency of calibration will depend upon the type of sample the analyzer receives, the environmental conditions under which the analyzer operates, and the requirements for data accuracy. Calibrations are very useful for maintaining and assessing the reliability and accuracy of air quality data. Dramatic changes in calibration results alert the user to problems with the analyzer or calibrator. Periodic calibrations are an important part of the quality control and quality assurance aspects of an air monitoring program.

The following procedure is intended for use with instruments that are designed to sample the ambient atmosphere for SO_2. Under these conditions, the SO_2 level often will be low (often 0.1 ppm or less) and measurements of the highest accuracy are sought. To help insure the accuracy of the data, the analyzer should be operated under controlled environmental conditions of temperature, voltage, and humidity, and the calibration procedure should be performed frequently.

Step-by-step instructions for dynamic calibration of a typical SO_2 analyzer are given below. Each step is numbered. Special explanations or precautions are given immediately following the instructions.

1. *Verify that preliminary steps, such as zero and span checks, and maintenance and replacement steps are complete.* Record all actions and results in a notebook or the calibration logbook. Record the requested information on the appropriate Calibration Data Form in this Chapter. This form will become the results table for your laboratory report.

2. *Interface the analyzer and the calibration system.* Disconnect the analyzer's Teflon ambient air sampling line from the station ambient air sampling manifold and connect it to the calibration system manifold. The ambient air sampling line should be used for calibration purposes. In this way the calibration gas passes through the same pathway (including the Teflon particulate filter) as the ambient air and the same pressures and flow rates are maintained. Do not change the length of the Teflon sampling line. Use of other zero or span gas entry ports to the instrument is not recommended for either multipoint calibration or for zero and span checks.

3. *Sample zero air.* Leave the analyzer in the sample mode and allow it to sample zero air from the calibration manifold until a stable reading on the strip chart trace, DAS, or voltmeter is obtained. Record the voltage reading or strip chart or DAS reading in the Calibration Data Form.
    a. Compare the zero gas reading to the value set at the previous calibration. The values should be nearly the same if no significant zero drift has occurred. Do not adjust zero setting at this time. As long as 30 minutes or more may be required to obtain a stable zero baseline. This is usually the case when a high SO_2 concentration has been sampled just prior to sampling zero air.
    b. The analyzer should have been on for at least 24 hours prior to calibration.
    c. Be certain that your zero air meets all requirements for zero air. It *should not* contain sulfur compounds or large amounts of water vapor.

d. The zero airflow (and in later steps the working standard airflow) must be in excess of the analyzer sample flow demand, preferably 50 percent greater. Thus, if an analyzer's sample flow is 200 cm^3/min, the zero airflow must be at least 300 cm^3/min. Do no pressurize the calibration manifold since this will alter the analyzer's response. Provide unobstructed exhaust of excess air. Do not allow back diffusion of room air. The pressure (as measured at the calibration manifold) must not exceed 1 inch of water, either positive or negative, from the ambient pressure. Use a water manometer for measuring pressure.

4. *Set the zero of the analyzer.* Set the zero adjust setting so that the analyzer output, the pen of the strip chart recorder, traces a line at the point on the chart paper corresponding to 0.000 V (or the voltage value assigned to zero ppm SO_2). Strip chart divisions, percent of full scale chart readings, or ppm SO_2 values taken from the recorder or a DAS may be used instead of voltmeter readings. Be certain the recorder itself is properly zeroed, spanned, and its response is linear.

Note: Some analyzers may not have physical zero and span knobs to adjust because their signal processing is being performed digitally by a microprocessor in the analyzer. For such analyzers, there may not be a zero or span setting that can be recorded and there may not be a means to obtain an offset analyzer response to zero air. Consult the operating manual for such an analyzer to determine whether it has this feature.

5. *Sample SO_2 span gas.* Adjust the flow rate of the calibration assembly to produce a SO_2 span gas of concentration equal to approximately 80 percent of the value of the analyzer's range. The usual ranges used are 0 to 0.5 or 0 to 1.0 ppm. If, for example, the analyzer is set to a 0-0.5 ppm range, 80 percent of the upper range limit (URL) would be (0.80)(0.5) = 0.4 ppm. Generate this concentration (0.400 ppm) or an accurately known value close to it based on the equation below. Use this as the span gas concentration. Sample the span gas until a stable signal is obtained (as indicated by the strip chart trace). Record this value.

Select the appropriate equation based on the SO_2 calibration gas being used.

Permeation Tube SO_2 Gas Standard:

$$C = \frac{(PR)(\bar{V})\left(\frac{760}{Pb}\right)\left(\frac{T}{298}\right)}{(M)(Q_t)}$$

Where:

C = Concentration of SO_2

PR = Permeation Rate (ug/min)

$\bar{V}$ = Molar Volume, 24.26 uL/u mole at STP

M = Molecular Weight of SO_2, 64 ug/u mole

Q_t = Total Flow Rate ($Q_t = Q_{SO2} + Q_D$)

Q_{SO2} = Flow rate of the gas stream through the permeation oven.

Q_D = Flow rate of the diluent gas (i.e., zero air gas)

Pb = Barometric pressure (mm Hg)

T = Temperature, Absolute (K = degrees Celsius + 273)

Cylinder SO_2 Gas Standard:

$$C = \frac{Q_{co} \times [SO_2]_{std}}{Q_t}$$

Where:

C = Concentration of SO_2

Q_t = Total Flow Rate ($Q_t = Q_{SO2} + Q_D$)

Q_{SO2} = Flow rate of the gas stream from the SO_2 cylinder

Q_D = Flow rate of the diluent gas (i.e., zero air gas)

$[SO_2]_{std}$ = Cylinder gas concentration, SO_2

6. *Compare "unadjusted span" value to previous calibration results.* If the values are within ±10 percent, proceed to Step 7. If the present span concentration is greater than ±10 percent of the value predicted by the previous calibration data, a problem may exist in the present calibration setup, a problem was present at the last calibration, or the analyzer has drifted significantly and needs maintenance.

7. *Set the analyzer span setting.*

Note*: Some analyzers may not have physical zero and span knobs to adjust because their signal processing is being performed digitally by a microprocessor in the analyzer. For such analyzers, there may not be a zero or span setting that can be recorded and there may not be a means to obtain an offset analyzer* *response to zero air. Consult the operating manual for such an analyzer to determine whether it has this feature.*

8. Adjust the calibrator flow rates in succession the following standard SO_2 calibration levels (expressed as percent of instrument range) using the appropriate equation in Step 5:

Approximate percent of range	**ppm, if 0.5 range**
75	0.375
60	0.300
45	0.225
30	0.150
15	0.075

Other levels may be introduced if desired. Values less than 0.100 ppm are suggested since ambient SO_2 concentrations are usually in this range. Values less than 0.040 ppm (40 ppb) are very slow to give a stable response.

   a. Important! Make no adjustments to the zero or span pots while these points are being entered.

   b. Record the strip chart response (in ppm) for each level. Allow sufficient time for each SO_2 level to stabilize ("level off" as indicated by the strip chart) before proceeding to the next value. The instrument response time and stabilization time will be slower at the lower concentration values.

9. Return the analyzer sampling line to the station sampling manifold and ambient air. Make note of this action and the time in the notebook.

10. Construct a plot of the calibration data on graph paper.
   a. Use a high quality graph paper with fine graduation marks so that data points may be clearly entered. A good choice is 18 x 25 cm graph paper with 10 x 10 divisions to the centimeter.
   b. Assign the SO_2 concentration values to the x-axis (horizontal axis). These are the calculated values from the calibration system. Subdivide the x-axis in ppm extending from zero to the analyzer's full scale range. Units of micrograms of SO_2 per cubic meter ($\mu g/m^3$) may also be plotted: 1 ppm SO_2 = 2,165 $\mu g/m^3$ SO_2 at 1 atmosphere (760 mm Hg) and 25°C. Assign the analyzer response (in ppm) to the y-axis (vertical axis) and subdivide this axis into portions of the full scale output for the particular analyzer.

c. Enter the zero and span values on the graph, also enter all intermediate calibration values.

d. Check the quality of the calibration curve in the following way:

    1) With the aid of a straightedge (ruler, etc.) connect the zero and span points with a light pencil line.

    2) Look at the positions of the intermediate calibration points with respect to the straight line. The intermediate points should fall on or very near the line. They are all off, either above or below the line, this may suggest:

        i. The span point is incorrectly set. Recheck the air flow and calculations used for spans.

        ii. The zero point is incorrectly set.

    3) All possible error sources should be investigated before adjustments are made to the circuitry (i.e., PMT, lamp intensity, etc). Consult the analyzer's operating manual for advice.

11. *Determine the calibration equation.* Determine the equation for the least squares line of best fit for all the calibration points, including zero and span. Many hand-held calculators now have the capacity to compute the least squares linear regression equation. The equation will be of the form:

$$y = a + bx$$

Where:

y = analyzer response, ppm
b = slope of calibration line, ppm
x = concentration of SO_2, ppm, and
a = intercept of calibration line with the y-axis, ppm.

Using this equation, calculate the location of any two points on the line (one point near zero, one point near full scale). Connect these points with a light line and extend the line through the y-axis as well as beyond the span point. This line should pass through or very near to the intermediate calibration points, the span point, and the zero point.

Laboratory C- Sulfur Dioxide

Permeation Calibration Data Sheet

Name_______________________________ Date_________________________

Group no.____________________________

Barometric Pressure P_b_________ mm Hg

Analyzer manufacturer/serial no.______________________ /____________________

Calibrator manufacturer/serial no.______________________ / ____________________

Temperature of permeation oven (T) ____°C____K Permeation rate (PR)_____µg/min

Q **Total Flow (L/min)**	**C** **Concentration of SO_2 (ppm)**	**NET Instrument Response** **(Volts, % scale)**	**Instrument Response** **(PPM)**
	ZERO		

$$C = \frac{(PR)(\bar{V})\left(\frac{760}{Pb}\right)\left(\frac{T}{298}\right)}{(M)(Q_t)}$$

T = Absolute Temperature (K), °C + 273 = K
M = molecular weight of SO_2, 64 µg/µ mole
$\bar{V}$ = molar volume at 25°C (298 K) and 760 mm Hg pressure, 24.46 µL/µ mole
Q_t = Total Flow Rate ($Q_t = Q_{SO2} + Q_D$)
Q_{SO2} = Flow rate of the gas stream through the permeation oven.
Q_D = Flow rate of the diluent gas (i.e., zero air gas)

Laboratory C- Sulfur Dioxide

Permeation Calibration Data Sheet

Name________________________________ Date__________________________

Group no._____________________________

Barometric Pressure P_b_________ mm Hg

Analyzer manufacturer/serial no.________________________ /_____________________

Calibrator manufacturer/serial no.________________________ / _____________________

Temperature of permeation oven (T) ____°C____K Permeation rate (PR)_____µg/min

Q **Total Flow (L/min)**	**C** **Concentration of SO_2 (ppm)**	**NET Instrument Response** **(Volts, % scale)**	**Instrument Response** **(PPM)**
	ZERO		

$$C = \frac{(PR)(\bar{V})\left(\frac{760}{Pb}\right)\left(\frac{T}{298}\right)}{(M)(Q_t)}$$

T = Absolute Temperature (K), °C + 273 = K

M = molecular weight of SO_2, 64 µg/µ mole

$\bar{V}$ = molar volume at 25°C (298 K) and 760 mm Hg pressure, 24.46 µL/µ mole

Q_t = Total Flow Rate ($Q_t = Q_{SO2} + Q_D$)

Q_{SO2} = Flow rate of the gas stream through the permeation oven.

Q_D = Flow rate of the diluent gas (i.e., zero air gas)

Laboratory C- Sulfur Dioxide

Cylinder/Dilution Calibration Data Sheet

Name________________________________ Date__________________________

Group no.____________________________

Concentration of SO_2 in standard cylinder, $[SO_2]$_________ ppm

Analyzer manufacturer/serial no.________________________ /____________________

Calibrator manufacturer/serial no._______________________ / ____________________

SO_2 cylinder flow Q_t (mL/min)	Zero air flow Q_D (mL/min)	Concentration of SO_2, C (ppm)	Net Instrument Response	
			% Scale or volts	ppm

$$C = \frac{Q_{co} \times [SO_2]_{std}}{Q_t}$$

Where:

C = Concentration of SO_2

Q_t = Total Flow Rate ($Q_t = Q_{SO2} + Q_D$)

Q_{SO2} = Flow rate of the gas stream from the SO_2 cylinder

Q_D = Flow rate of the diluent gas (i.e., zero air gas)

$[SO_2]_{std}$ = Cylinder gas concentration, SO_2

Laboratory C- Sulfur Dioxide

Cylinder/Dilution Calibration Data Sheet

Name________________________________ Date__________________________

Group no._____________________________

Concentration of SO_2 in standard cylinder, $[SO_2]$_________ ppm

Analyzer manufacturer/serial no.________________________ /____________________

Calibrator manufacturer/serial no.______________________ / ____________________

SO_2 cylinder flow Q_t (mL/min)	**Zero air flow Q_D (mL/min)**	**Concentration of SO_2, C (ppm)**	**Net Instrument Response**	
			% Scale or volts	**ppm**

$$C = \frac{Q_{co} \times [SO_2]_{std}}{Q_t}$$

Where:

C = Concentration of SO_2

Q_t = Total Flow Rate ($Q_t = Q_{SO2} + Q_D$)

Q_{SO2} = Flow rate of the gas stream from the SO_2 cylinder

Q_D = Flow rate of the diluent gas (i.e., zero air gas)

$[SO_2]_{std}$ = Cylinder gas concentration, SO_2

Chapter 4

Laboratory D

Measurement Principle and Calibration Procedure for the Continuous Measurement of Carbon Dioxide in the Atmosphere (Nondispersive Infrared Spectrometry)

Laboratory Objectives

Upon completion of this laboratory, you should be able to:

(d) Identify the operating principles of a NDIR analyzer;
(e) Verify the concentrations of calibration gases by a quality assurance procedure;
(f) Determine performance parameters for a CO NDIR analyzer. These include range, lower detectable limit, and interference equivalent (water vapor);
(g) Construct calibration curves for CO NDIR analyzers; and
(h) Prepare bag CO standard gases using a dilution system.

Introduction

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.

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:

(Eq. 4-1) $I / I_o = e^{-axC}$

where:
I = light intensity after absorption by absorbing species
I_o = 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.

Instructions

A. Multipoint Calibration

A multipoint calibration requires calibration gases with concentrations corresponding to approximately 10, 20, 40, and 80 percent of full scale or a high concentration standard gas subjected to dynamic dilution and a zero gas containing less than 0.1 mg CO/m^3 (should use NIST-traceable SRM as per EPA traceability protocol). It is further recommended that calibration gases certified to be within ± 2 percent of the stated value be purchased in high pressure cylinders with inside surfaces of a chromium-molybdenum alloy of low iron content or other appropriate linings. Store the cylinders in areas not subject to extreme temperature changes (e.g., do not expose to direct sunlight). It is recommended that CO in synthetic air be used for all calibration gases.

B. Frequency of Calibration

A multipoint calibration is required when:

1. The analyzer is first purchased,
2. The analyzer has had maintenance which could affect its response characteristics, or
3. When zero drift exceeds ± 2.5 ppm or span drift exceeds ± 15%.

C. Calibration Procedures

Follow the manufacturer’s detailed instructions when calibrating a specific analyzer. General procedures are:

1. Turn the power on and let the analyzer warm up by sampling ambient air. This usually requires several hours (as many as 24 to 48 hours) depending on the individual analyzer.

2. Record the manufacturer's name, model, and serial number of the analyzer being calibrated and the calibration apparatus.

3. Use the Calibration Data Form (at the end of the chapter) for the systematic recording of data determined during calibration of the CO analyzer. Record the requested information. This form will become the results table for your laboratory report.

4. Zero and span adjustments differ between analyzers; the manufacturer's manual should be consulted before calibration is performed.

5. Identify, by supplier and stamped cylinder number, the CO standard to be used. Record the certified concentration of the CO standard ($[CO]_{STD}$). Do not use CO standards with pressures <200 psig for calibration. It has been shown that some CO concentrations become unstable at low pressures.

Provide a record of traceability to NIST for any CO standard used in a calibration, and include the date and the name of the person or organization that conducted the analysis.

6. Record the zero and the span settings after the calibration is complete so that these settings can be used at a later date to determine changes in the instrument performance characteristics.

7. Auto-ranging analyzers should be calibrated on all ranges that are likely to be used. Select the operating range of the analyzer to be calibrated.

8. Connect diluents gas (zero gas) and CO calibration gas cylinders to the dynamic calibrator which is in turn is connected via a manifold to the analyzer.

9. Open the gas cylinder pressure valve. Adjust the secondary pressure valve until the secondary pressure gage reads the desired pressure. Refer to the dynamic calibration unit operating manual for recommended delivery pressure.

10. Connect the signal output cable(s) of the analyzer to the input terminals of the strip chart recorder(s) or DAS. Make all adjustments to the analyzer based on the appropriate analyzer responses. Analyzer responses in the procedures given herein refer to strip chart recorder or DAS responses.

11. Adjust the flow rate of the diluent air to ensure that the total air flow rate exceeds the total demand of the analyzer(s) connected to the output manifold so that no ambient air will be pulled into the manifold vent. Record the flow rate of the diluent air.

12. Allow the analyzer to sample zero air until a stable CO response is obtained. After the response has stabilized, adjust the analyzer zero control(s). (Offsetting the analyzer zero adjustments to 0.050 volts is recommended to facilitate observing any negative zero drift.)

Note: Some analyzers may not have physical zero and span knobs to adjust because their signal processing is being performed digitally by a microprocessor in the analyzer. For such analyzers, there may not be a zero or span setting that can be recorded and there may not be a means to obtain an offset analyzer response to zero air. Consult the operating manual for such an analyzer to determine whether it has this feature.

13. Adjust the flow rate from the CO standard to generate a CO concentration of approximately 80% of the URL. Measure the CO flow rate (F_{CO}) and record it on the Calibration Data Form.
    Calculate the output CO concentration [CO] using Equation 4-2.

(Eq. 4-2)

$$[CO] = \frac{F_{co} \times [CO]_{std}}{F_{co} + F_D}$$

14. Sample the generated concentration until the CO response has stabilized. Adjust the CO span control to obtain an analyzer response as determined by Equation 4-1.

15. After the zero and the 80% URL points have been set, determine two approximately evenly spaced points between zero and the 80% URL without further adjustment to the analyzer. These additional points can be generated by either increasing the dilution flow rate (F_D) or by decreasing the F_{CO}. For each concentration generated, calculate the CO concentration using Equations 4-1. Record the information for each point on the Calibration Data Form .
16. Plot the CO analyzer response (y-axis) versus the corresponding calculated concentrations [CO] (x-axis) to obtain the calibration relationship. Determine the straight line of best fit determined by the method of least squares regression. This regression can be done with a programmed calculator with this capability.

17. After determining the slope (b) and the y-intercept (a) where the regression line crosses the y-axis, draw the fitted line for each set of points. On the y-axis of the graph, locate and plot the value of a. Using the equation y = a + bx, calculate the predicted y value using the 80% URL concentration for the x-value. Plot this second point on the graph. Draw a straight line through these two points to give a best-fit line.

Quality Assurance Audit Cylinder Check (Optional)

Procedure G2: Assay and Certification of a Compressed Gas Calibration Standard Using Dilution

This procedure may be used to assay the concentration of a diluted candidate compressed gas calibration standard, based on the concentration of a diluted compressed gas reference standard of the same gas mixture. This procedure allows a specialty gas producer, a standard user, or other analytical laboratory to certify that the assayed concentration for the candidate standard is traceable to the reference standard. The procedure employs a low-concentration-range (i.e., ambient air quality level) pollutant gas analyzer to compare quantitatively diluted gas samples of both the candidate and reference standards. Dilution of the candidate and reference standards with zero gas allows greater flexibility in the range of concentrations of both the candidate and reference standards that can be assayed. Additionally, dilution allows the use of a low-concentration-range analyzer, which is more likely to have an inherently linear response than a high-concentration-range analyzer. However, the dilution technique introduces additional error into the assay which would not be present if the standards were assayed without dilution.

This additional error is measured by an accuracy check of the assay apparatus which is performed as part of the multipoint calibration. This procedure may be used for the assay of multiple candidate standards at the same time. Criteria that apply to the assay of one candidate standard apply to the assay of multiple candidate standards.

Procedure:

1. Verify that the assay apparatus is properly configured as shown in Figure 4-1 Inspect the analyzer to verify that it appears to be operating normally and that all controls are set to their expected values. Record these control values in the laboratory's records.

2. Verify that the flowmeters, if used in the assay apparatus, are properly calibrated.

3. Verify that a multipoint calibration of the analyzer has been performed within 1 month prior to the assay date and that the dilution error is not excessive.

4. Determine and establish the flow rates or concentration settings of the gas mixtures (i.e., reference standard(s), candidate standard, and zero gas) that will be used for the assay. Also check that the total flow rate coming from the mixing chamber will provide enough flow for the analyzer and sufficient excess to ensure that no ambient air will be drawn into the vent line. Changes in the sample pressure may change the calibration curve. When using the same flow rates for both candidate and reference standards, carefully set the delivery pressures of the two standards' pressure regulators to the same value so that there is no change in the flow rate when switching from one standard to the other.

   Calculate the diluted reference standards' concentration using the following equation:

   $$\text{Diluted Standard Conc.} = \frac{(\text{Undiluted Standard Conc.})\,(\text{Standard Flow Rate})}{(\text{Standard Flow Rate} + \text{Zero Gas Flow Rate})}$$

   Record the measured flow rates and the undiluted and diluted reference standard concentrations in the laboratory's records.

5. In succession, measure the zero gas, the diluted reference standard(s) and the diluted candidate standard using the analyzer. For each measurement, adjust the

flow rates, if necessary, to those determined in step 4, and allow ample time for the analyzer to achieve a stable reading.

Record the analyzer response for each measurement, using the same response units (e.g., volts, millivolts, percent of scale, etc.) as was used for the multipoint calibration. At this point, do not convert the data into concentration values using the calibration equation. Do not perform any mathematical transformations of the data. These steps will be done later. Do not make any zero control, span control, or other adjustments to the analyzer during this set of measurements. Record these analyzer responses in the laboratory's records.

6. Conduct at least two additional sets of measurements, as described in step 5 above. However, for these subsequent sets of measurements, change the order of the three measurements (e.g., measure the reference standard, zero gas, and candidate standard for the second set and measure the zero gas, candidate standard, and reference standard for the third set, etc.). Changing the order that the gas mixtures are measured helps the analyst to discover any effect that one measurement has on subsequent measurements. (The number of sets of measurements will have been determined during the analysis of the multipoint calibration data such that the 95-percent uncertainty for the regression predicted concentration of the candidate standard is #1 percent of the concentration of the reference standard.)

7. If any one or more of the measurements of a set of measurements is invalid or abnormal for any reason, discard all three measurements and repeat the set of measurements.

8. The spreadsheet (found at http://www.epa.gov/ttn/emc/news.html and provided by the course instructor) or equivalent statistical techniques must be used to calculate an estimated concentration and a 95-percent uncertainty for the candidate standard based on data from the assay measurements and from the multipoint calibration. The use of both sets of data in the statistical analysis produces an estimated concentration with smaller uncertainty while correcting for any minor calibration drift that may have occurred since the multipoint calibration.

   Record the estimated concentration and the 95-percent uncertainty in the laboratory’s records. The spreadsheet also calculates the percentage of the uncertainty that is due to the multipoint calibration. This percentage is needed for the total uncertainty calculations when two or more assays fall under the same multipoint calibration. Record this value in the laboratory’s records.

9. If the multipoint calibration data and the assay data underwent any mathematical transformations before their statistical analysis, perform the reverse transformations for the estimated concentration and the 95-percent uncertainty. Record the transformed values in the laboratory’s records.

10. Finally, the certified undiluted concentration for a candidate standard containing a unreactive gas mixture and requiring only a single assay can be calculated from the mean concentration of the diluted candidate standard as follows:

$$\text{Certified Undiluted Conc.} = \frac{(\text{Mean Diluted Conc.})\,(\text{Total Gas Flow Rate})}{(\text{Standard Flow Rate})}$$

Where: Total Gas Flow Rate = Standard Flow Rate + Zero Gas Flow Rate

For more details on this procedure see EPA-600/R-97/12, EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards (Sept. 1997).

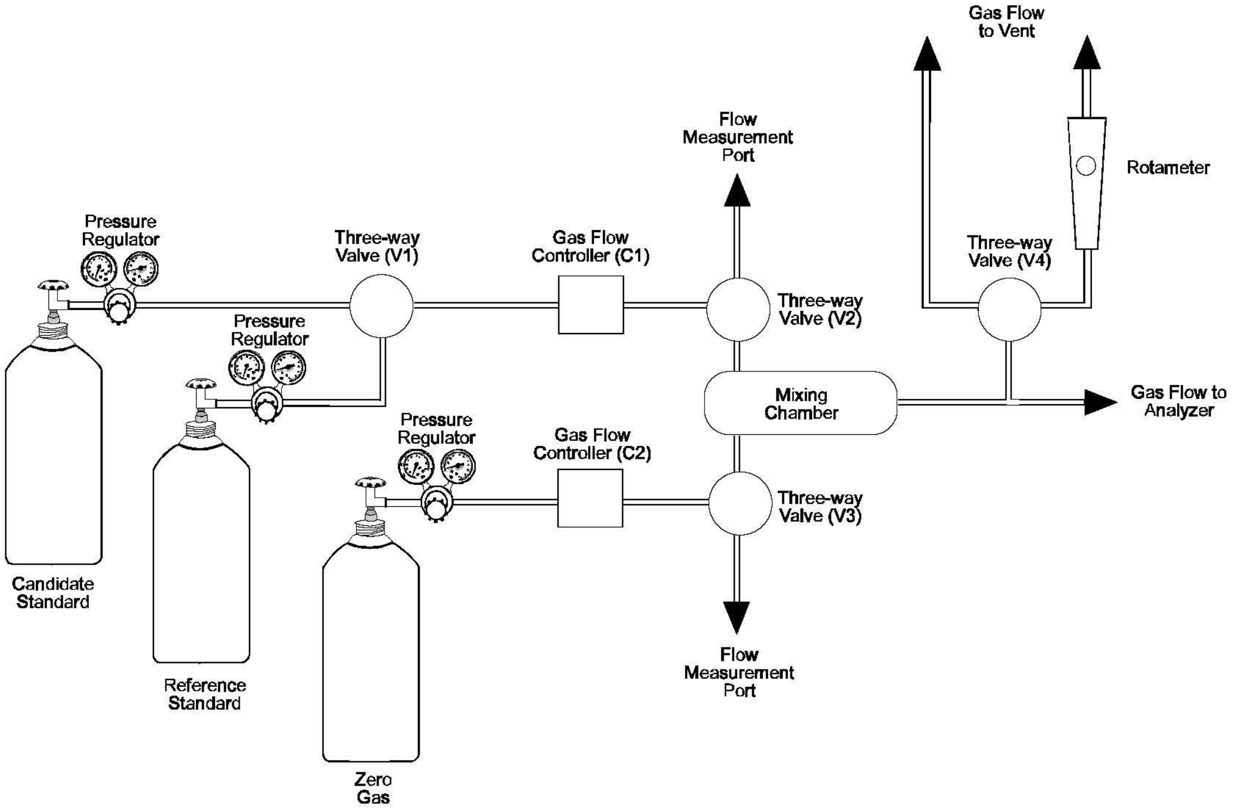


Figure 4-1. One possible design of the apparatus using flow controllers for assay of compressed gas calibration standards with dilution (Procedure G2).

Instrument Performance Parameter Specifications (Optional)

A. *Range*- See detailed instructions for Test Procedures for Determination of Instrument Performance Specifications (40 CFR 53.23). Record minimum and maximum concentration values over the range 0-50 ppm from constructed calibration curve on instrument performance parameter data sheet. (See manual appendix).

B. *Lower detectable limit*- See detailed instruction for Test Procedures for Determination of Instrument Performance Specifications (40 CFR 53.23).- Section 3. Lower Detectable Limit. Follow test procedure and record LDL as LDL = $B_L - B_Z$ on instrument performance parameter data sheet. This value, if compared to S_o (the standard deviation about the mean (noise) at zero ppm), would be about equal to 2 the noise level. (See manual Appendix A).

Laboratory D - Carbon Monoxide
Calibration Data Sheet

Name________________________________
Group no.____________________________
Date_________________________________

Analyzer Serial no.____________________
Model no.____________________________

Calibration

Data Point	Calibration gas conc. (ppm)	Net instrument response (% scale)
0	Zero	
80% URL		
60% URL		
40% URL		
20% URL		

Quality Assurance Audit Cylinder Check

Q.A. audit cylinder (#)	Net instrument response (% scale, volts)	Conc. (ppm)

Statistical Data (from spreadsheet calculation):
Estimated concentration___________________
95-percent uncertainty___________________

Laboratory D - Carbon Monoxide
Calibration Data Sheet

Name________________________________ Analyzer Serial no.____________________

Group no._____________________________ Model no.____________________________

Date_________________________________

Calibration

Data Point	**Calibration gas conc. (ppm)**	**Net instrument response (% scale)**
0	Zero	
80% URL		
60% URL		
40% URL		
20% URL		

Quality Assurance Audit Cylinder Check

Q.A. audit cylinder (#)	**Net instrument response (% scale, volts)**	**Conc. (ppm)**

Statistical Data (from spreadsheet calculation):

Estimated concentration___________________

95-percent uncertainty___________________

Laboratory D - Carbon Monoxide
Instrument Performance Data Sheet

Name________________________________

Analyzer Serial no.____________________

Group no.____________________________

Model no.____________________________

Date________________________________

Instrument Performance

Parameter	**EPA specification (ppm)**	**Actual performance (ppm)**		
Range	Minimum 0 ppm			
	Maximum 50 ppm			
Lower detectable limit	1.0 ppm	B_Z =		
		B_L=		
		LDL= B_L- B_z=		
Interference equivalent H_2O vapor	1.0 ppm		% Scale	ppm
		Saturated zero air		
		Zero air		
		Difference		

Laboratory D- Carbon Monoxide

Instrument Performance Data Sheet

Name________________________________

Analyzer Serial no.____________________

Group no.____________________________

Model no.___________________________

Date_________________________________

Instrument Performance				
Parameter	**EPA specification (ppm)**	**Actual performance (ppm)**		
Range	Minimum 0 ppm			
	Maximum 50 ppm			
Lower detectable limit	1.0 ppm	B_Z =		
		B_L=		
		LDL= B_L- B_z=		
Interference equivalent H_2O vapor	1.0 ppm		% Scale	ppm
		Saturated zero air		
		Zero air		
		Difference		