

Chapter 9

Oxides of Nitrogen Measurement Principle and Calibration Procedures

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

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

The beginning of this chapter will discuss the nitrogen dioxide (NO_2) measurement principle and calibration procedures for use with traditional ambient monitors. The latter sections of this chapter will focus on high sensitivity (NO_y) precursor gas monitoring instrumentation,

their calibration and related sampling issues. The (NO_y) precursor gas analyzers are very similar to the traditional analyzers used to monitor for NO₂. They share the measurement principle of the chemiluminescent reaction of nitric oxide and ozone (NO-O₃) and utilize essentially the same calibration procedure.

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

Nitrogen Dioxide (NO₂) Measurement Principle

The basis of the measurement principle for NO₂ is the same as that for ozone. The only difference between the two principles is the chemiluminescent reaction involved, and the indirect determination (as opposed to direct for ozone) of the NO₂ concentration.

When nitric oxide reacts with ozone, some electronically activated nitrogen dioxide is formed. In order to lose its energy of activation, the activated nitrogen dioxide emits a quantum of light. This released light energy has a characteristic band of 600 to 2400 nm with a strong peak at 1200 nm. This light emission spectrum is unique to the NO-O₃ reaction. The light intensity released from the chemiluminescent reaction is proportional to the reactant concentration of NO, and, therefore, can be used to measure NO concentrations. As in the ozone measurement method, a photomultiplier tube is used to convert the light-energy emitted from the reaction to an electrical impulse (Clough and Thrush 1967) (Fontijn, Sabadell, and Ronco 1970).

In order to utilize the NO-O₃ chemiluminescent reaction for the measurement of NO₂, it is necessary to reduce NO₂ to NO so that it can react with ozone. NO₂ analyzers employ a converter which reduces all NO₂ present in the air sample to NO. Two basic types of converters are used: a thermal reduction converter, or a chemical reduction converter. Both types of converters reduce only NO₂, while allowing NO to pass through the converter unchanged. Chemical reduction is the preferred method in modern ambient air monitoring instruments since the reduction of NO₂ to NO can occur at a lower temperature.

In the NO₂ measurement process, the sampled air is first passed directly into the chemiluminescent reaction chamber, and the concentration of NO is measured. The NO concentration is then stored electronically for later use. The analyzer then passes a sample of air through the converter, thereby transforming NO₂ to NO but leaving the original NO content unchanged. This sample is then measured and the resultant concentration is stored as total oxides of nitrogen ([NO₂] + [NO]) or, as it is sometimes termed, [NO_x]. The analyzer electronically subtracts the original NO concentration (which was stored) from the NO_x concentration to yield the concentration of NO₂. This [NO] – [NO_x] determination sequence is sometimes reversed, depending on the instrument's design.

Chemistry

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



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



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

Equipment

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

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

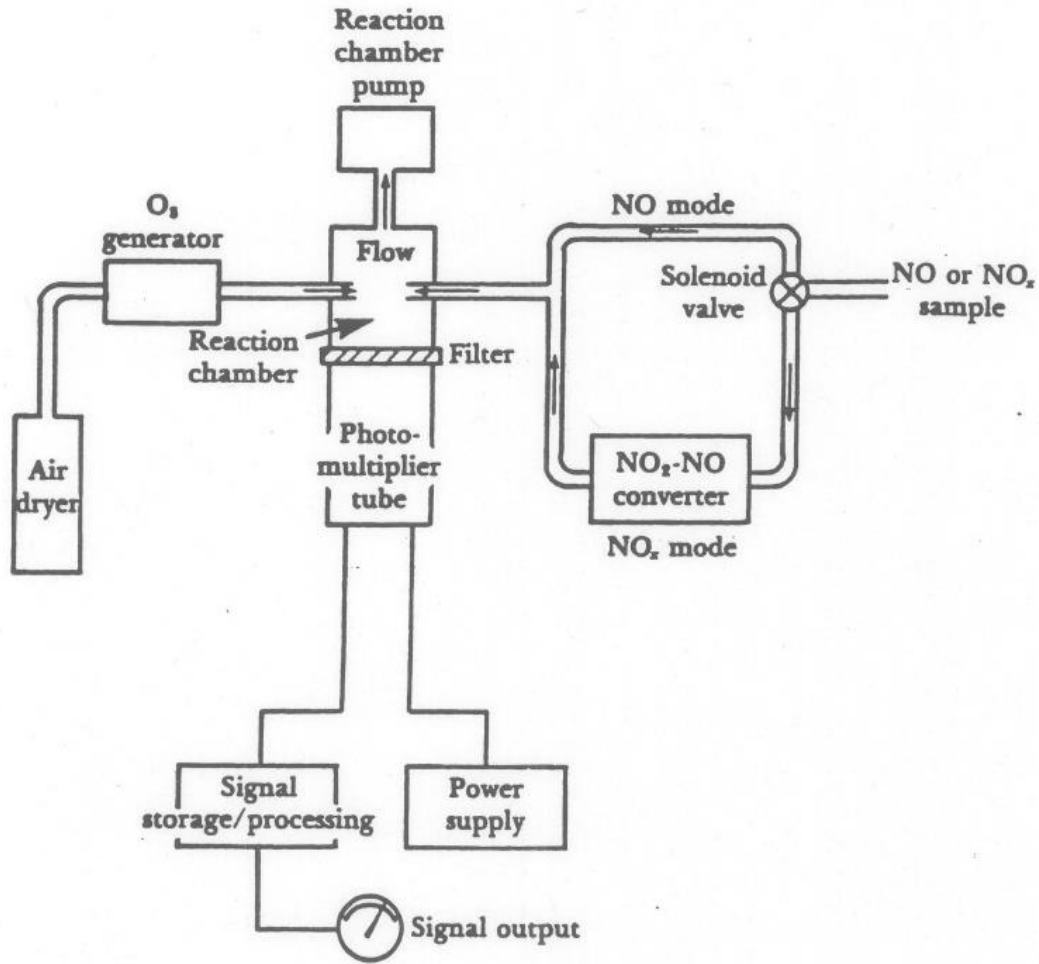


Figure 9-1. Chemiluminescent NO₂ analyzer.

The use of a solenoid or a sample separation tee depends on the method employed by the manufacturer to separate the air sample for the NO and NO₂ determinations. NO₂ analyzers can employ one of two basic configurations, dual or cyclic, for the NO and NO_x measurements. In dual-type analyzers, the air sample is divided at the analyzer inlet and half passes continuously through a converter to one reaction chamber (NO_x) while the other half passes continuously (though an equivalent converter volume) to a second reaction chamber (NO). The NO and NO_x concentrations are measured continuously with either a single detector time shared between the two reaction cells or a pair of matched detectors (one for each reaction cell).

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

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

As discussed earlier, chemical reduction converters are the preferred over thermal converters and are made from a variety of materials: pure metals such as gold, tungsten, platinum or molybdenum; various alloys; or carbon-based compounds such as nonabsorptive charcoals or carbon impregnated with various metals. Although their compositions differ, chemical converters reduce NO₂ to NO by forming an oxide of the converter material. In the case of carbon-based converters, reduction occurs as follows:



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

Ozone and sample flow control is an important consideration in the proper use of an NO₂ analyzer due to the stoichiometric properties of the chemiluminescent reaction. For the instrument's response to remain stable, it is essential that constant flow rates be maintained. This is achieved by the use of capillaries and pressure regulators. The use of these flow controllers results in a constant flow to the reaction chamber over a wide range of sample source pressures and flow rates.

A schematic representation of an NO₂ analyzer's reaction chamber is shown in Figure 9-2. The reaction chamber is a light-tight container of a size which is sufficient to allow the total chemiluminescent reaction to take place. The two reactant gases (O₃ + NO) are metered into the chamber, mixed, and the resultant light energy is passed to the photomultiplier tube via a “window” at one end of the chamber. To facilitate proper mixing and flow through the chamber, a vacuum pump maintains a partial vacuum within the chamber of about 200-300 mm Hg. A red, sharp-cut optical filter, which absorbs any light emissions below 600 nm, is placed between the reaction chamber and the photomultiplier tube. This filter is required to eliminate interfering emissions of shorter wavelengths which are emitted from the chemiluminescent reaction of ozone with certain unsaturated hydrocarbons.

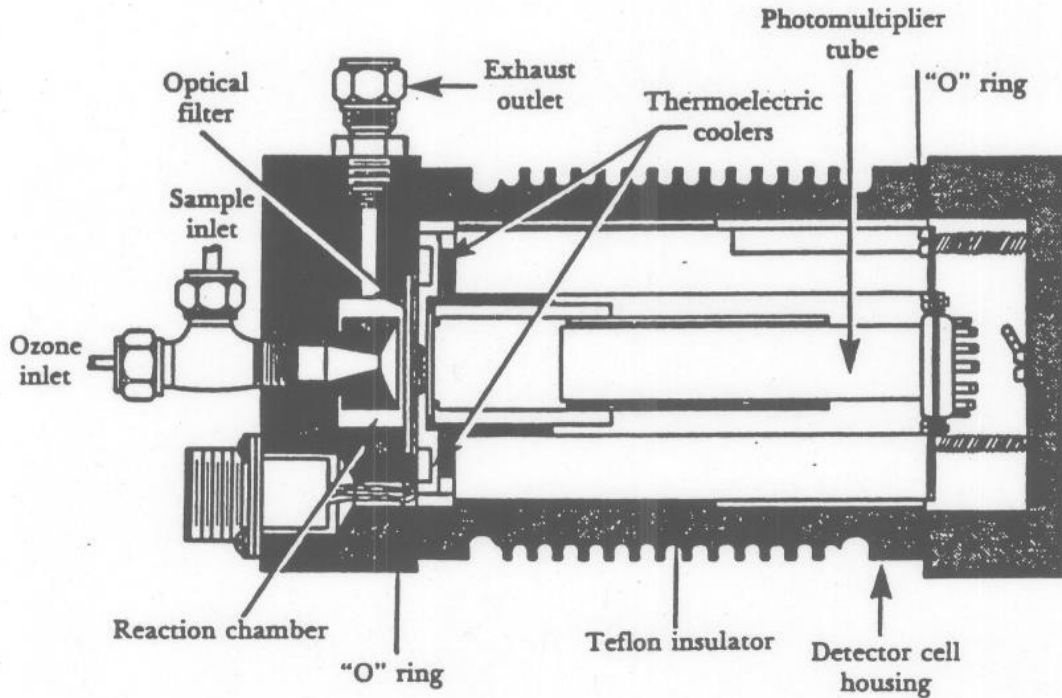


Figure 9-2. Reaction chamber/photomultiplier assembly.

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

As explained previously, the signal processing components of an NO₂ analyzer operate in conjunction with the sample cycling valves. This is accomplished by independent timer controls which alternate the NO-NO₂ measurement cycles every 5 to 30 seconds. Each mode's PMT signal is fed to a corresponding analog circuit where that signal is stored. At the end of the double cycle (NO-NO₂ measurement), the two modes' output signals are subtracted by an electronic subtraction circuit and the NO₂ concentration is registered by readout circuitry.

Calculations

Most NO₂ ambient analyzers have direct readout capability, indicating NO₂ concentration in ppm. If it is necessary to record NO₂ data in concentrations of µg/std m³ the following conversion factor is used:

$$(Eq. 9-3) \quad \frac{\mu\text{g NO}_2}{\text{std m}^3} = \text{ppm NO}_2 \times 1880$$

Calibration Procedures

EPA allows either of two different methods for the calibration of NO₂ analyzers: gas phase titration (GPT) or, alternatively, calibration with an NO₂ permeation tube/dilution system (for further details see 40 CFR 50 Appendix F). Both of these calibration methods essentially satisfy the two requirements for NO₂ analyzer calibration which are:

1. calibration of NO and NO_x responses of the analyzer using an NO standard, and
2. calibration of NO₂ response of the analyzer with NO₂, generated directly, or indirectly, from an NO₂ standard.

Gas Phase Titration (GPT) Method

This calibration technique is based on the rapid gas phase reaction of NO and O₃ to produce stoichiometric quantities of NO₂. The reaction proceeds according to the following reaction (Hodgeson et al. 1972):



The quantitative nature of the reaction is used in a manner such that, once the concentration of reacted NO is known, the concentration of NO₂ is determined. Ozone is added to excess NO in a dynamic calibration system, and the previously calibrated NO channel of the analyzer is used to measure changes in NO concentration. Upon the addition of O₃, the decrease in NO concentration observed by the calibrated NO channel is equivalent to the concentration of NO₂ produced. The amount of NO₂ generated is varied by changing the concentration of O₃ added.

Figure 9-3 shows the recommended configuration of a typical GPT calibration system. Dynamic calibration systems utilizing this basic configuration are available commercially or can be assembled using Figure 9-3 as a guide. However, before either a commercial or self-assembled GPT/NO₂ calibrator is used, the following conditions must be met:

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

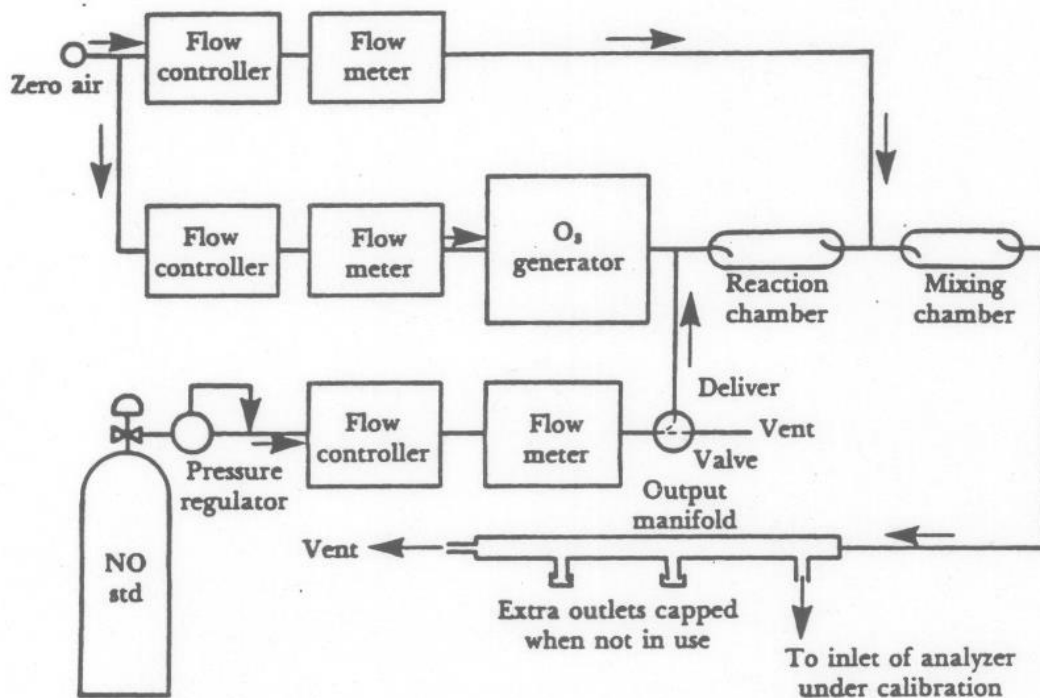


Figure 9-3. Schematic diagram of a typical GPT calibration system.

In addition to the requirements listed above, there are some other items which are important in performing a valid NO₂ calibration. Pressurized cylinders of NO in nitrogen (N₂) at levels between 50 to 100 ppm are recommended for use in the GPT system. Care should be taken to use only cylinders containing NO in oxygen-free N₂, and assayed to contain no more than 1.0 ppm NO₂ as impurity. It is preferable to have no NO₂ impurity. Some agencies will reject a cylinder of NO with any NO₂ impurity. To assure that the cylinder's concentration is as stated, it should be certified against a National Institute of Standards and Technology's (NIST) Standard Reference Material (SRM) for NO. It is important to select a cylinder pressure regulator of a non-reactive material, such as stainless steel to avoid oxidation of the NO. Additionally, the pressure regulator and as much of the connecting non-reactive connecting tubing (e.g., glass, teflon™) should be properly purged to remove contaminants which may react with the NO. A slow and steady decline in instrument response during challenge with a span concentration may be a result of an improperly purged regulator and sample line.

Only a clean, dry source of oxygen should be used for ozonation by the ozone generator. In addition, it is very important that the flow of oxygen to the ozone generator be regulated so as to allow no variation in the resulting O₃ concentration.

As mentioned before, gas phase titration requires the use of the NO channel of the analyzer to determine the amount of NO₂ generated by titration. Therefore, it is necessary to calibrate and determine the linearity of the NO channel before proceeding with the NO₂

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

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

After calibrating the NO-NO_x channels, the ozone generator is activated on the dynamic multi-gas calibrator/GPT system and NO₂ is generated for calibrating the instrument's NO₂ response. Again, to determine the NO₂ concentration the analyzer's NO channel is used to measure the initial NO concentration and then the resultant NO concentrations as the ozone output is changed. Generally, six separate NO₂ concentrations are generated by adjusting the concentration of ozone (see Chapter 6, "Ozone Generator"). These concentrations should cover the entire NO₂ response range chosen. A calibration curve reflecting instrument response vs. NO₂ concentration (calculated from NO response) is plotted for future use.

The accuracy of the NO₂ calibration is dependent on the analyzer's converter efficiency. Therefore, a determination of converter efficiency is a required part of the calibration procedures. To determine the converter efficiency, the total NO₂ concentration generated during the GPT calibration is calculated:

$$(Eq. 9-5) \quad [NO_2]_{out} = [NO]_{orig} - [NO]_{rem} + NO_2 \text{ impurity}$$

Where:

- $[NO_2]_{out}$ = the total NO₂ concentration generated
- $[NO]_{orig}$ = the original NO concentration at 90% of NO range (taken from NO calibration curve)
- $[NO]_{rem}$ = the NO concentration at 80% of NO₂ range-ozone generator on (taken from NO calibration curve)
- $NO_2 \text{ impurity}$ = NO₂ concentration resulting from NO₂ present in the NO cylinder, if any.

The total NO₂ concentration converted to NO in the analyzer's converter is calculated:

$$(Eq. 9-6) \quad [NO_2]_{conv} = [NO_2]_{out} - ([NO_x]_{orig} - [NO_x]_{rem})$$

Where: $[NO_2]_{conv}$ = total NO₂ concentration converted to NO

The slope of a plot of $[\text{NO}_2]_{\text{conv}}$ vs. $[\text{NO}_2]_{\text{out}}$ is the average converter efficiency of the analyzer. A converter efficiency of less than 96% is considered unacceptable.

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

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

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

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

NO_2 Permeation Tube Method

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

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

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

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

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

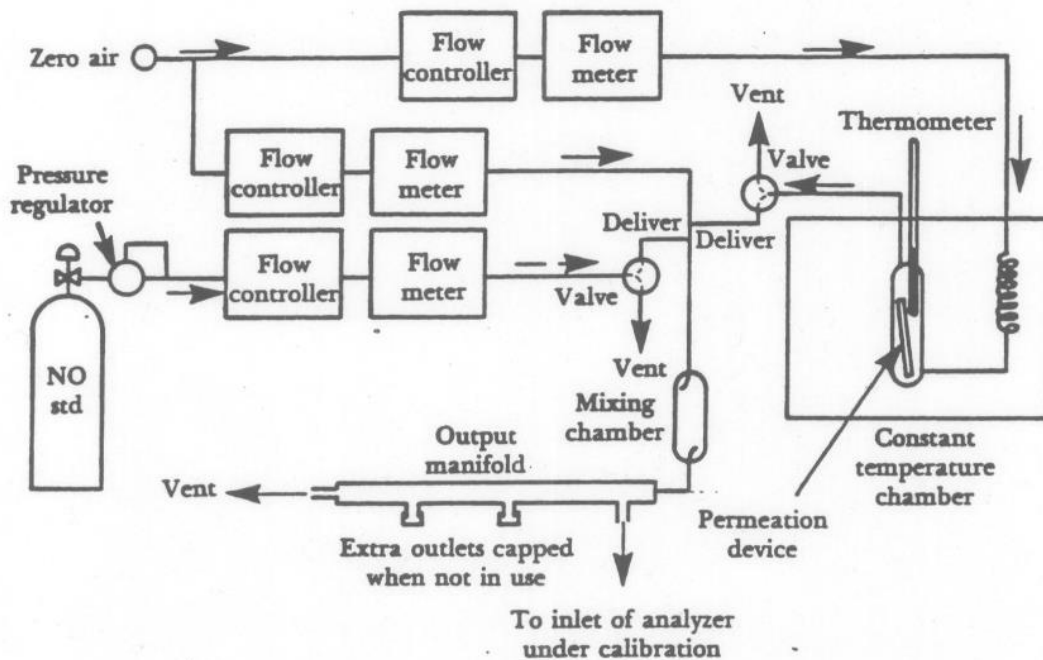


Figure 9-4. Schematic diagram of a typical calibration apparatus using an NO₂ permeation tube.

An essential element of the NO₂ permeation calibrator is the maintenance of the permeation tube at a constant temperature. In order for the calibration to be accurate and valid, a constant temperature with $\pm 0.1^\circ\text{C}$ must be maintained and monitored while the calibrator is in use. This requires that the permeation tube be contained in a temperature controllable, constant temperature chamber.

In addition to maintaining the permeation tube at a constant temperature, it is also necessary to maintain the purge gas at the same temperature. The purge gas is a small, fixed zero air or nitrogen flow that carries the NO₂ out of the permeation area into a mixing chamber where the NO₂ is diluted with clean, dry zero air. To maintain the purge gas's temperature, it is necessary to pass the air (or nitrogen) through a heat exchanger (e.g., a coil of copper tubing), contained in the constant temperature chamber. The gas is then passed over the permeation tube.

Once the permeation tube calibration system has been assembled, is operative, and the NO cylinder and NO₂ permeation tube have been intercompared with respect to certified standards, the actual calibration of an NO₂ chemiluminescence analyzer is straight forward. The object of the calibration is to determine NO, NO₂, and NO_x response of the analyzer as a function of known NO and NO₂ concentrations. Also, it is an important part of the calibration to determine the converter efficiency of the instrument.

The NO and NO_x channels of the analyzer are calibrated from NO concentrations generated by dilutions of the NO cylinder's contents. The procedure used in the GPT method for

these two channels is applicable. The instrument's span and zero controls are adjusted to reflect these concentrations. Also, calibration curves are prepared.

The NO₂ channels is calibrated by generating several (usually six) concentrations of NO₂. This is done by diluting the effluent from the permeation tube. The instrument's controls are set based on the span concentration (approximately 80% of the upper range limit), and a calibration curve is prepared for the NO₂ response.

Converter efficiency is determined using the same basic procedure as in the GPT method. The total NO₂ concentration generated, $[\text{NO}_2]_{\text{out}}$, is calculated from the permeation rate and the total flow (dilution gas + purge gas) of the system. The amount of NO₂ converted to NO ($[\text{NO}_2]_{\text{conv}}$) by the analyzer is determined by the instrument's NO_x response to the generated NO₂ concentrations. $[\text{NO}_2]_{\text{conv}}$ (y-axis), is plotted versus $[\text{NO}_2]_{\text{out}}$ (x-axis), to give the converter efficiency curve. The slope of this curve multiplied by one hundred gives the converter's efficiency in percent. In modern instruments the converter efficiency is determined by the instrument's software and displayed digitally. If efficiency is less than 96%, the converter should be replaced or recharged.

The publications cited in the gas phase titration section also contain pertinent information concerning the NO₂ permeation tube method. These publications should be consulted before performing the calibration of the NO₂ chemiluminescence by means of the permeation tube method.

Reference Measurement Principle - Characteristics and Capabilities

Advantages

Chemiluminescence NO₂ analyzers have a relatively fast response time, due to the mechanism of the gas phase reaction of ozone and nitric oxide. They also tend to be reliable and easy to operate, requiring little in the way of ancillary equipment.

Interferences

Interference from air pollutants commonly found in the environment- ozone, sulfur dioxide, carbon monoxide, methane, and ammonia- are negligible for chemiluminescence NO₂ analyzers. The selectivity of the NO-O₃ reaction, the use of low temperature catalytic converters, and selective optical filters, preclude almost all possible interferences. The only possible interferences of any significance are organic nitrates, organic nitrites, and PAN. The ambient concentrations of these compounds are usually so low in most areas of the country that this interference can be disregarded. However, for highly quantitative ambient air studies, under circumstances where relatively low concentrations of NO₂ occur

simultaneously with high concentrations of PAN and other nitrogen-containing compounds (1:10 ratio), the results of these particular interferences could be significant. If this situation exists, then it may be necessary to determine independently the concentrations of the interfering species by gas chromatography, infrared spectroscopy, or other methods. Upon determining their concentrations, corrections to the chemiluminescent NO₂ determinations can be made. Further discussion is included in the latter section of this chapter specifically regarding interferences on high sensitivity precursor gas monitoring.

Range and Sensitivity

Most chemiluminescence NO₂ analyzers are equipped to measure several different concentration ranges. Typically, the lowest range is up to 0.05 ppm NO₂, with the largest range being up to 100 ppm NO₂. It is possible to select several ranges between these two cited, but a range of 0 to 0.5 ppm is the usual range used in most ambient air monitoring applications. It is typical for modern analyzers to be equipped with an auto-ranging feature.

Normal minimum sensitivity (Lower Detectable Limit – LDL) for the determination of NO, NO_x, NO₂ is reported as 0.4 ppb (0.0004 ppm).

Problems, Precautions, Troubleshooting

Problems and precautions regarding the use of chemiluminescent NO₂ instruments for ambient monitoring have been discussed at various points within this chapter. These precautions mainly involve the NO₂-NO converter's design/operation, ozone generator design/operation, and calibration procedures. The operating manual of any NO₂ analyzer contains specific instructions in these areas. A thorough maintenance and calibration program will assure that problems will be kept at a minimum.

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

Table 9-1. Typical NO_x monitor problems

Observation	Problem Cause	Remedy
<p>NO Mode</p> <p>NO sample result too low or zero</p>	<ol style="list-style-type: none"> 1. Sample line clogged or closed 2. Ozonizer inoperative 3. Photomultiplier tube failure 4. Signal amplifier open 5. Vacuum pump inoperative 	<ol style="list-style-type: none"> 1. Check inlet line and flow meter 2. Check O₃ supply and ozonizer lamp 3. Check photomultiplier tube 4. Check all circuits 5. Check pump
<p>NO sample results too high</p>	<ol style="list-style-type: none"> 1. Photomultiplier tube too sensitive 2. Sample too large 	<ol style="list-style-type: none"> 1. Check photomultiplier tube and amplifier circuits 2. Check inlet flow meter
<p>NO₂ Mode</p> <p>NO₂ sample results too low</p>	<ol style="list-style-type: none"> 1. Sample line clogged or closed 2. Ozonizer inoperative 3. Photomultiplier tube failure 4. Signal amplifier open 5. Vacuum pump inoperative 6. NO₂ converter ineffective 	<ol style="list-style-type: none"> 1. Check inlet line and flow meter 2. Check O₂ supply and ozonizer lamp 3. Check photomultiplier tube 4. Check all circuits 5. Check pump 6. Check converter heater, or replace catalyst
<p>Interference</p> <p>All sampling results too low or high</p>	<ol style="list-style-type: none"> 1. NH₃ or PAN 2. Photomultiplier tube may be failing 	<ol style="list-style-type: none"> 1. Monitor for NH₃/PAN 2. Check photomultiplier tube and amplifier circuits against manufacturer's specifications

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

Quality Assurance

To assure that the data obtained from a chemiluminescence NO₂ monitor is valid, a conscientious quality assurance program should be carried out on various aspects of the ambient monitoring/data production process. Five general areas of concern for an NO₂ monitoring quality assurance program are:

1. calibration;

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

Calibration

The details of performing an NO₂ analyzer calibration are contained in preceding sections. However, after the calibration procedures have been performed there is still a tendency for the instrument to drift from the set calibration responses. A one point span check performed at least once per week using a GPT or perm tube system, will determine if the instrument's precision is being maintained. The accuracy of the instrument is determined by a check of three different NO₂ concentrations. This should be performed at least once each quarter. If either of these audit processes shows a deviation from the original calibration, a full recalibration should be performed.

Operation

An essential part of the quality assurance program is scheduled series of checks for the purpose of verifying the operational status of the monitoring system. The operator should visit the site at least once per week, noting such items as: temperature inside the monitoring shelter, condition of the sample introduction system (i.e., water in lines, conditions of prefilters, leaks/breaks in lines, etc.), status of the recorder or data acquisition system (i.e., proper ink level and trace, adequate paper supply, chart drive working), and the condition of the NO₂ analyzer (i.e., flow controls at proper settings, temperature indicators at proper levels, span and zero stable).

Data Reduction

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

Performance Audits

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

For an NO₂ monitoring system, two performance audits are recommended: a multipoint calibration audit and a data audit. The multipoint calibration audit consists of challenging the analyzer with three different, known concentrations of NO₂ covering the analyzer's range. The difference between these known concentrations and the analyzer's response is used to calculate the accuracy of the analyzer. This multipoint calibration audit should be carried out at least once per quarter.

Data reduction audit involves reading a strip chart record, calculating an average, and transcribing or recording the results on the AIRS data form. This independent check of the

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

The data processing check is made by calculating the accuracy:

$$A = [\text{NO}_2]_R - [\text{NO}_2]_{\text{CHECK}}$$

where

A = the difference in measured and check values

$[\text{NO}_2]_R$ = the recorded analyzer response, ppm

$[\text{NO}_2]_{\text{CHECK}}$ = the data processing NO_2 concentration, ppm.

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

System Audit

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

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

Measurement Quality Objectives

Table 9-2: An example (prepared by USEPA) of measurement quality objectives (MQO) for the ambient measurement of NO₂ by chemiluminescence.

Measurement Quality Objectives - Parameter NO ₂ (Chemiluminescence)				
Requirement	Freq.	Acceptance Criteria	Reference	Information/Action
Standard Reporting Units	All data	ppm	40 CFR, Pt 50.11	
Shelter Temp. Temp. range	Daily	20 to 30°C	40 CFR, Pt. 53.20	Instruments designated as reference or equivalent has been tested over this temp. range. Maintain shelter temp. above sample dewpoint. Shelter should have a 24- hour temp. recorder. Flag all data for which temp. range or fluctuations are outside acceptance criteria.
Temp. control	Daily	±2°C	Vol II, S 7.1 ^{1/} Vol II, MS 2.32	
Equipment NO ₂ analyzer	Purchase Specs	Reference or equivalent method	40 CFR, Pt 53.9	
Air flow controllers	“	Flow rate regulated to ±2%	40 CFR, Pt 50, App F, S22	
Flowmeters		Accuracy ±2%	EPA-600/4-75-003	
Detection Noise	Purchase specs	0.005 ppm	40 CFR, Pt 53.20 & 23	Instruments designated as reference or equivalent have been determined to meet these acceptance criteria
Lower Detection level		0.01 ppm	“	
Completeness Hourly Data	Quarterly	75%	40 CFR, Pt 50.11	
Compressed Gases Dilution gas (zero air)	Purchase specs	Free of contaminants	EPA-600/4-75-003	Return cylinder to supplier.
Gaseous standards	“	NIST Traceable (e.g. EPA Protocol Gas)	40 CFR, Pt 50, App F, S1.3 EPA-600/R-97/121	Nitric oxide in nitrogen EPA Protocol Gases have a 24-month certification period and must be recertified to extend the certification.

Measurement Quality Objectives - Parameter NO ₂ (Chemiluminescence)				
Requirement	Freq.	Acceptance Criteria	Reference	Information/Action
Calibration Multipoint calibration (at least 5 points) Converter efficiency Zero/span check—level 1 Flowmeters	> 1/6 months, after failure of QC check or after maintenance During multipoint calibration 1/2 weeks 1/3 months	Res. time < 2 min Dynam. parameter > 275 ppm-min All points w/in $\pm 2\%$ of full scale of best-fit straight line 96 % Zero drift ± 20 -30 ppb Span drift ± 20 to 25 % Zero drift ± 10 to 15 ppb Span drift $\pm 15\%$ Accuracy $\pm 2\%$	40 CFR, Pt 50, App F, S 1 Vol II, S 126 Vol II, MS 232 40 CFR, Pt. 50, App F Vol II, MS 232 Vol II, MS 232 Vol II, S 126 Vol II, S 126 Vol II, MS 232 Vol II, App 12	Zero gas and at least four upscale calibration points. Points outside acceptance criterion are repeated. If still outside consult manufacturer's manual and invalidate data to last acceptable multipoint calibration or zero/span check. Replace or service converter. If calibration factors are updated after each zero/span , invalidate data to last acceptable zero/span check, adjust analyzer, and perform multipoint calibration. If fixed calibration factors are used to calculate data , invalidate data to last acceptable zero/span check, adjust analyzer, and perform multipoint calibration. Flowmeter calibration should be traceable to NIST standards.
Performance Evaluation (NPAP) State audits	1/year at selected sites 1/year	Mean absolute difference 15% State requirements	NPAP QAPP Vol II, App 15, S 3	Use information to inform reporting agency for corrective action and technical systems audits.
Precision Single analyzer Reporting organization	1/2 weeks 1/3 months	None 95% Confidence Interval $\pm 15\%$	40 CFR, Pt 58, App A EPA-600/4-83-023 Vol II, App 15, S 6	Concentration. = 0.08-0.10 ppm.
Accuracy Single analyzer Reporting organization	25% of sites quarterly (all sites yearly)	None 95% Confidence Interval $\pm 20\%$	40 CFR, Pt 58, App A EPA-600/4-83-023 Vol II, App 15, S 3	Four concentration ranges. If failure, recalibrate analyzer and reanalyze samples. Repeated failure requires corrective action.

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

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

High Sensitivity Total Reactive Nitrogen Oxides (NO_y) Measurements

Introduction

Measurement of ambient nitrogen oxides differs from measurement of CO or SO₂ in that the target air pollutant is not a single chemical but a group of chemicals of differing properties, and is not a criteria air pollutant. Nitrogen oxides released from emission sources are primarily nitric oxide (NO) with lesser amounts of nitrogen dioxide (NO₂), which collectively are termed NO_x (i.e., NO_x = NO + NO₂). These primary emitted species are converted by atmospheric processes to numerous other inorganic and organic nitrogen oxides, which collectively are called NO_z, and the total of all reactive gaseous nitrogen species present in ambient air is called NO_y (i.e., NO_y = NO_x + NO_z).

Precursor gas monitoring in the NCore network builds upon capabilities of EPA's Photochemical Assessment Measurement Stations (PAMS) network and Southern Oxidants Study to measure ozone precursors, including total reactive oxides of nitrogen (NO_y). Measuring NO_y is a valuable adjunct to NO and NO_x monitoring because the individual species comprising NO_z include numerous organic and inorganic nitrogen oxide compounds, that are difficult to measure individually, but collectively contribute to a more complete and conservative measure of nitrogen oxides. Determining NO_y concentrations is useful in establishing nitrogen oxide emission patterns and temporal trends, and in assessing the photochemical age and reactivity of air masses. NO_y measurements are a critical tool in accounting for progress in large-scale nitrogen emission reduction programs, providing input for a variety of source apportionment and observation based models, and assisting in the evaluation of air quality models.

Properties of NO_y

NO_y includes all of the nitrogen oxide compounds that reacts or is formed in the lower atmosphere and that contribute to the photochemical formation of O₃ and the transport and ultimate fate of nitrogen oxides. NO_y compounds include NO_x (NO + NO₂) and NO_z, which include nitrogen acids [nitric acid (HNO₃) and nitrous acid (HONO)], organic nitrates [e.g., peroxy acetyl nitrate (PAN), methyl peroxy acetyl nitrate (MPAN), and peroxy propionyl nitrate (PPN)], other organic nitrogen oxides, particulate nitrates, nitrate radical (NO₃), nitrogen trioxide (N₂O₃), nitrogen pentoxide (N₂O₅) and halogen-nitrogen species (e.g., ClONO₂ and BrONO₂). In typical urban environments, the principal NO_y compounds include NO, NO₂, HNO₃, and PAN, and in some cases particulate nitrate.

In terms of precursor monitoring in NCore, a key factor is that the numerous species making up the total NO_y differ widely in their physical properties and chemical reactivity. For example, some species, such as NO₂ and HONO, are readily photolyzed, whereas others, such as PAN, decompose rapidly at moderate temperatures. NO and NO₂ are chemically reactive, but have relatively low solubility in water, whereas the key product species HNO₃ is highly soluble and relatively unreactive. Consequently, physical removal of HNO₃ from the atmosphere is a key removal process for NO_y. Organic nitrogen oxides can

vary widely in volatility and stability, and HNO_3 is known to be highly “sticky”; that is, adsorptive on surfaces. In addition, particulate ammonium nitrate (NH_4NO_3) is volatile under certain ambient conditions, and can decompose to release HNO_3 and ammonia (NH_3) into the gas phase. These factors make accurate sampling and measurement of atmospheric NO_y much more challenging than determination of CO or SO_2 . A discussion of sampling and measurement issues that must be addressed in order to make more useful measurements of NO_y is provided in the following sections.

Sources of NO_y

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

Historical Overview of NO_y Measurement Method

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

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

used to monitor NO_x except that, in the NO_y methodology, the converter has been moved to the sample inlet to avoid line losses of adsorbent NO_y species like HNO_3 , and additional calibration procedures recommended for adequate measurement of the various NO_z species.

Summary of NO_y Measurement by Chemiluminescence Method

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

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

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

As shown in Figure 9-5, separate sample transfer lines downstream of the sample inlet point are used for the NO_y and NO measurement channels, and a third transfer line is used to deliver calibration and converter efficiency assessment standards from the gas phase titration (GPT) calibration system to the sample inlet. Because of the remote location of the converter relative to the analyzer itself, these transfer lines may be of considerable length (i.e., up to 20 m). The length of the sample transfer line presents no problem in the NO_y measurement mode of the NO_y instrument, since all NO_y species are converted to NO in the heated converter, and since that same converter destroys any ozone present in the sample air. However, in the instrument's NO mode, the ambient air drawn down the sample transfer line contains both ambient NO and ambient O₃. These two species can react to decrease the NO reaching the chemiluminescence detector, resulting in an under-estimation of the ambient NO level.

This effect can be substantial: assuming 100 ppbv of O₃, loss of 10 percent of the NO can occur within a few seconds. One way to counteract this effect, is for sample air to be drawn rapidly through the sample transfer line. For example, at a sample flow rate of 6 L/min, a sampling line with an inner diameter of 4 mm and a length of 15 m (50 feet) would result in a residence time of less than 2 seconds. Rapid transport of the sample can best be accomplished using an auxiliary sampling pump (not shown in Figure 4-1) to draw sample down the transfer line to a "T" fitting at the back panel of the NO_y analyzer. The sample flow to the chemiluminescence detector is then drawn from that "T" by the analyzer's internal sample pump. If implemented, it is recommended that this approach be implemented on both the NO and NO_y sample lines, to achieve consistent residence times in the two lines. However, implementing rapid sample transport through the Mo converter in this way may reduce converter efficiency and/or lifetime.

Consequently, a preferable approach may be to reduce sample transport time in both the NO and NO_y flow paths by reducing the gas pressure.

Recommendations for NCore

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

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

Recommended Method Performance Criteria

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

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

Precision

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

Bias

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

Representativeness

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

Completeness

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

Comparability

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

Method Detection Limit

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

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

Lower Detectable Limit

The LDL is the minimum pollutant concentration that produces a signal of twice the noise level. To estimate the LDL, zero air is sampled and the noise level of the readings is determined according to 40 CFR 53.23(b). The vendor-specified LDL for the most sensitive

range of high sensitivity NO_y analyzers should be 0.10 ppb or lower, over an averaging time of no more than 5 minutes.

Linear Range

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

Zero/Span Drift

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

Recommended Analyzer Features for High Sensitivity Ambient NO_y Measurements

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

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

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

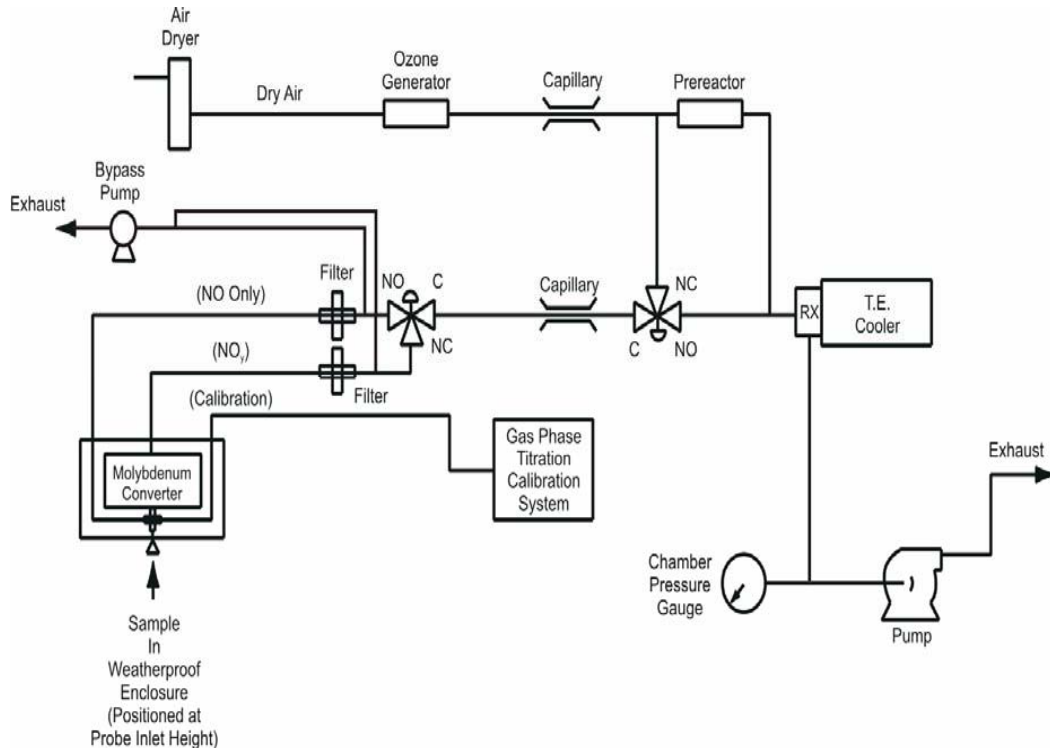


Figure 9-5. General schematic of a typical chemiluminescence NO_y instrument.

1. Locate the sample inlet at 10 meters to avoid the physical removal of HNO_3 . The inlet should face the prevailing wind direction, be as short as possible, and be constructed of PFA Teflon®. Half of a Teflon® filter holder with the filter support used as a “bug screen” should have a negligible effect on NO_y measurements, and provides a practical solution to ward off larger insects.
2. Locate the site in an area that is not obstructed by nearby trees and obstacles.
3. Ensure that the sample residence time in the NO sample transfer line is less than 2 seconds to address the O_3/NO reaction and subsequent loss of NO in the line, and protect the sample transfer lines from light through the use of opaque conduit normally provided by the vendor.
4. A heated molybdenum converter rather than a heated gold/reactant converter is recommended, since the latter requires a supply of either a toxic reductant gas (CO) or a flammable reductant gas (H_2), and provides no clear advantage in determining total NO_y in urban and suburban air.
5. The temperature of the molybdenum converter should be maintained at $350\text{ }^\circ\text{C}$. Higher temperatures than recommended may result in converting significant amounts of non- NO_y species such as ammonia, organic amines, or particulate ammonium. If a manufacturer recommends a converter temperature above $350\text{ }^\circ\text{C}$, he should show evidence that such non- NO_y species are not converted. It is equally important that the converter not be operated below $350\text{ }^\circ\text{C}$ to ensure optimal conversion of NO_y species.

6. Automatic over-range capabilities are used to track the rapid changes that may occur in ambient NO_y levels. High sensitivity analyzers often have an analog output range limited to 200 ppb full scale; digital ranges of up to 400 ppb may be needed to track peak concentrations in urban areas.

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

Sampling Issues

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

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

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

Potential Problems and Solutions

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

Interferences

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

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

Converter Efficiency

Overview

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

As noted in the discussion of interferences, non- NO_y species such as ammonia, particulate ammonium, or hydrogen cyanide can also be oxidized to NO, although this conversion can be minimized (to a few percent or less) by maintaining the converter temperature at 350 °C. At sub-ppb NO_y concentrations, interference from such compounds can be substantial, and even at higher levels the potential for interferences must be kept in mind. Sampling near a

large source of ammonia, for example, could produce erroneously high NO_y readings, even though the conversion efficiency for ammonia is much less than that for NO_2 or the various NO_z compounds. In general, the efficiency of a converter system at sub-ppb levels may vary depending on the mix of NO_y species present, the age and condition of the converter, the converter temperature, ambient humidity, or ozone levels and cannot be entirely predicted even from the behavior of a similar system. For these reasons, converter efficiency must be evaluated.

Challenge Species for Converter Efficiency Checks

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

Conversion efficiency testing with NPN is in addition to, not in place of, routine calibration with NO and NO_2 . Changes in pollutant levels and meteorological conditions over time can significantly alter the instrument's conversion efficiency. Thus, NO_y monitoring requires routine NPN converter efficiency checks and consistent procedures to maintain or repair the converter when its efficiency falls below acceptable levels. A single-point conversion efficiency check with NPN is recommended every month in continuous NO_y monitoring. An NPN conversion efficiency of 95 percent or greater is considered acceptable for NO_y monitoring, converters falling below 95 percent efficiency should be replaced. Note that a new converter should be allowed to "burn in" over one to three days of use before performance of an NPN test. Also, the NPN standard may not be certified to better than $\pm 5\%$, so it is recommended to track conversion over time and use 95% of the original efficiency as the performance cutoff.

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

Equipment and Supplies

Calibration Equipment

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

Calibration Standard and Standard Delivery System

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

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

Zero Air Source/Generator

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

Reagents and Standards

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

Calibration Standards

The primary NO standards must be certified commercially-prepared compressed gas standards of NO in N₂, with a certified accuracy of no worse than ± 2 percent. NO gas standards of 5 to 20 ppm (with less than 1 ppm NO₂) are conveniently diluted with a MFC calibrator down to working concentrations of 10 ppb or less. The commercially-prepared standard may contain only NO, or may be a mixed component standard that also contains known concentrations of other non-reactive precursor gases (e.g., CO, SO₂). This standard

must be traceable to a NIST NO in N₂ Standard Reference Material (SRM 1683 or SRM 1684), NIST NO₂ Standard Reference Material (SRM 1629), or a NIST/EPA-approved commercially available Certified Reference Material (CRM). Section 2.0.7 of EPA's Quality Assurance Handbook gives a recommended protocol for certifying NO gas cylinders against either a NO SRM or CRM. Commercial gas standards for NO₂ and NPN should be obtained with a certified accuracy no worse than ±2 percent, and ±5 percent, respectively.

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

Zero Air

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

Quality Control

Site Visit Checklists and Remote Diagnostic Checks

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

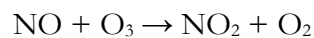
Multipoint Calibrations

Calibration procedures for high sensitivity NO_y analyzers are more complicated than for other high sensitivity precursor gas analyzers (i.e., for CO and SO₂), in that they include calibration with NO and NO₂, as well as checks of the converter efficiency for NO_x species

and potential interferents. A basic requirement is for a multipoint NO calibration that includes a minimum of four points (three spaced over the expected range and a zero point), generated by the calibration system. Although more points may be preferable, current high sensitivity analyzers typically provide linear response over their entire operating range; therefore, four points should be sufficient. Multipoint calibrations must be done prior to the high sensitivity NO_y analyzer being put into service and at least quarterly thereafter. An analyzer should be calibrated (or recalibrated) if any of the following conditions occur:

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

The analyzers should be calibrated in-situ without disturbing the normal sampling inlet system to the degree possible. A second requirement is for multipoint calibration with NO₂, as a check of the conversion efficiency of the molybdenum converter for NO₂. This calibration is conducted by gas phase titration of NO with O₃. MFC calibration systems in common use at ambient monitoring sites have GPT capability. The multipoint NO₂ calibration should be done at approximately the same three concentration levels as the NO calibration noted above. The major equipment/components required for the GPT NO₂ calibration are: a stable O₃ generator, a data acquisition and display device, and the NO concentration standard used for the multipoint NO calibration. The principle of this calibration technique is the rapid gas phase reaction of NO with O₃ to produce equal stoichiometric quantities of NO₂ in accordance with the following equation:



This is the same overall reaction detailed earlier in this chapter for the GPT calibration procedure for the traditional NO_x ambient analyzers. For calibration purposes, ozone is added to a stable and excess concentration of NO in a dynamic calibration system, and the NO reading of the chemiluminescence NO_y instrument is used as an indicator of changes in NO concentration. The NO standard is diluted sufficiently to produce an upscale NO reading on the measurement range of interest, and upon addition of O₃ the decrease in NO reading observed is equivalent to the concentration of NO₂ produced. The amount of NO₂ generated may be varied by adding variable amounts of O₃ from a stable O₃ generator, which is a component of the GPT system of the calibrator. Comparison of the NO and NO_y responses of the analyzer then allows determination of the ratio of NO₂ response to NO₂ generated, which indicates the converter efficiency for NO₂. Maintenance or replacement of

the converter should be undertaken whenever the NO₂ conversion efficiency falls below 96 percent.

Level 1 Zero/Span Checks

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

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

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

Precision Checks

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

Preventive Maintenance and Troubleshooting

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

Preventive Maintenance

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

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

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

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

Item	Schedule
Maintain air dryer	As needed
Replace particle filter	Weekly
Perform pneumatic system leak check	At least quarterly
Inspect internal, external tubing; replace if necessary	Inlet, weekly; other, quarterly
Clean optical bench	As needed
Replace PMT	As needed
Monitor NO ₂ conversion efficiency	At least every 6 months
Monitor NPN conversion efficiency	At least every month

Troubleshooting

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

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

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

Problem	Possible Cause	Possible Solution
Noisy output	Defective DC power supply	Replace power supply
	Dirty reaction cell	Clean cell
	PMT failure	Replace PMT
High positive zero drift	Defective bandpass filter	Replace filter
	PMT failure	Replace PMT
High Prereactor zero reading	Moisture in PMT housing	Allow PMT housing to warm up; purge with dry gas, reassemble
No response to span gas	PMT failure	Replace PMT
	Voltage failure	Replace high voltage source

Problem	Possible Cause	Possible Solution
	No O ₃ supply	Clean or replace O ₃ generator
Low or declining response to span gas	O ₃ source failing	Clean or replace O ₃ generator
	Dirty reaction cell window	Clean window
Zero output at ambient levels	Pump failure	Check pump
	PMT failure	Replace PMT
Low NO ₂ or NPN efficiency	Aging or dirty converter	Replace converter
No flow through analyzer	Pump failure	Replace/ rebuild pump head

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