

## **Chapter 5**

### **Continuous Monitoring of Oxides of Nitrogen**



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## **1.0 Introduction**

This chapter outlines the requirements for the ambient air monitoring of oxides of nitrogen (NO, NO<sub>2</sub>, and NO<sub>x</sub>) and total reactive oxides of nitrogen (NO<sub>y</sub>). The requirements stated in this chapter are to be followed by all organizations (e.g. State, local, industrial, and consultant) that conduct ambient air monitoring in Indiana and report data to the Air Quality System (AQS).

This chapter does not replace the analyzer's operation manual. The analyzer's operation manual should be read before any analyzer calibration, audit, or maintenance is performed. The operation manual should be available at the monitoring station as a reference guide.

## **2.0 Probe Siting Criteria**

For specific probe siting and spatial scales of representation, refer to the Code of Federal Regulations (CFR) 40, Part 58, Appendix E. In general, probe siting must meet the following requirements:

### **2.1 Horizontal and Vertical Probe Placement**

1. The probe inlet (sample inlet) must be at a height of 2 to 15 meters above ground level.
2. The probe inlet must be more than 1 meter vertically and horizontally away from any supporting structure.
3. For NO<sub>y</sub>, the catalytic converter must be positioned at a program specific height above ground level approximately 10 meters as required for enhanced ozone monitoring programs.

### **2.2 Spacing from Obstructions**

1. The distance between an obstacle and the inlet probe must be at least twice the height that the obstacle protrudes above the inlet probe (2x rule).
2. Inlet probe placement extending out from a vertical wall is undesirable because air moving along that wall may be subject to removal mechanisms of NO<sub>2</sub>.
3. Airflow must be unrestricted in an arc of 270° around the inlet probe. The predominant wind direction must be included within the 270° arc of inlet probe airflow.

### **2.3 Spacing from Roads**

1. The probe inlet should be placed far enough away from any NO<sub>2</sub> sources which could dominate (bias) the data (see Table 1 for separation distances).

## 2.4 Spacing from Trees

1. The sample probe, inlet, or at least 90 percent of the monitoring path must be at least 10 meters from the drip line of trees which are located in the predominant seasonal wind direction. Ideally, the probe should be at least 20 meters from the drip line of trees in all directions.

**Table 1**  
**Minimum Separation Distance Between Neighborhood**  
**and Urban Scale Oxides of Nitrogen Monitoring Station and Roadways**  
**(Edge of Nearest Traffic Lane)**

Roadway average daily traffic (vehicles/day)	Minimum separation distance between roadways and stations (meters)
$\leq 10,000$	*10
15,000	20
20,000	30
40,000	50
70,000	100
$\geq 110,000$	250

\* Distances should be interpolated based on traffic flow.

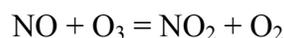
## 3.0 Monitoring Methodology

All methods used to monitor NO<sub>2</sub> must be an EPA reference or equivalent method as described in 40 CFR Part 50.1. Continuous ambient NO<sub>2</sub> analyzers must have an EPA reference method number posted on the analyzer or listed in the instrument manual. At present, EPA does not have a reference or equivalency requirement for NO<sub>y</sub>.

### 3.1 Chemiluminescent Measurement Method of NO<sub>2</sub>

The chemiluminescence measurement method is based on the reaction of ozone (O<sub>3</sub>) with nitric oxide (NO) to form nitrogen dioxide (NO<sub>2</sub>) (see Equation 5-1).

**Equation 5-1**



A typical ambient NO<sub>2</sub> analyzer determines concentrations of NO<sub>2</sub> by measuring NO and NO<sub>x</sub> concentrations. NO<sub>x</sub> is defined as the sum of the NO<sub>2</sub> and NO analyzer measurements. The analyzer never directly measures NO<sub>2</sub>.

**Equation 5-2**



**OR**

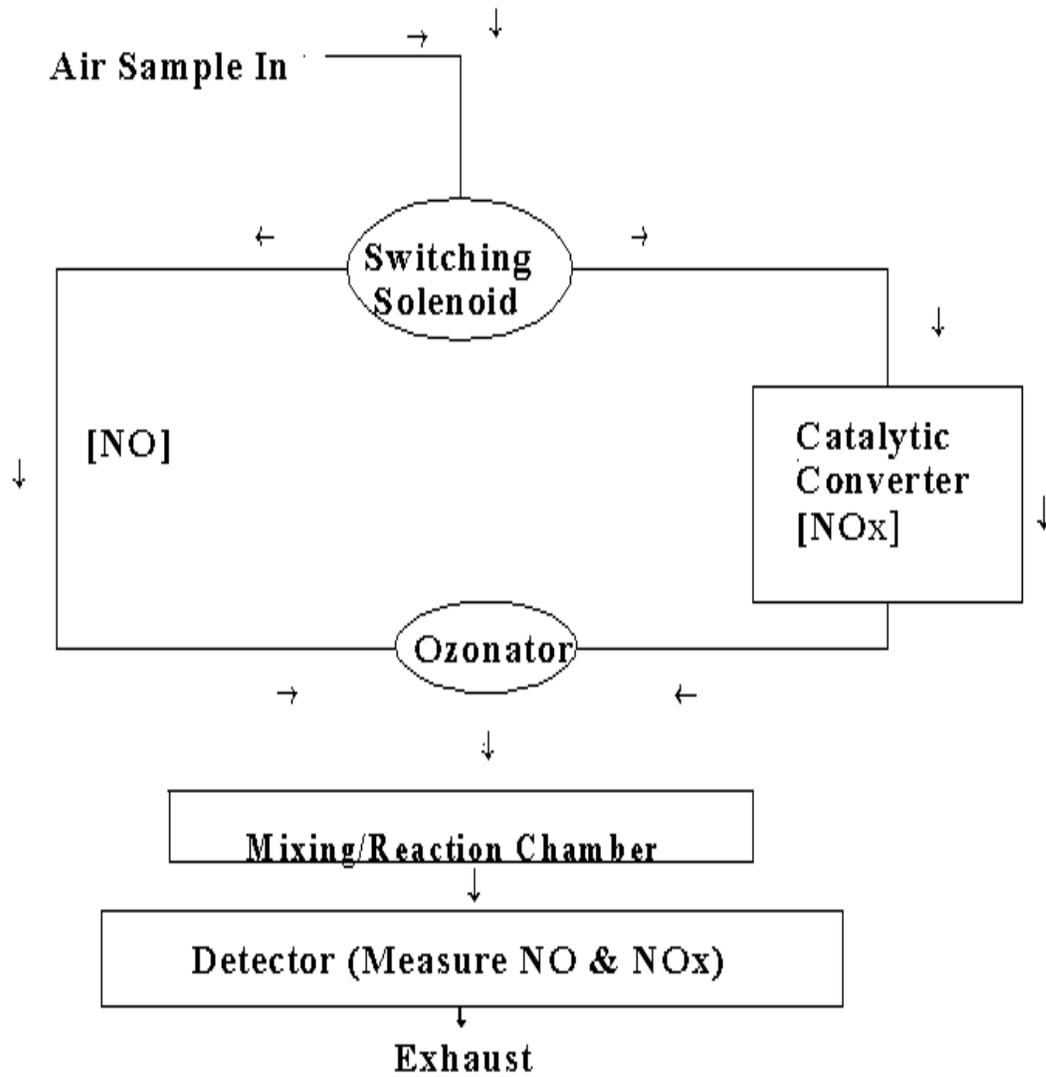


The analyzer ozonates an incoming ambient air sample (containing NO) to produce electronically excited NO<sub>2</sub> molecules. These molecules immediately decay to a lower energy level by emitting light (chemiluminescence) in the 600 nm to 2400 nm wavelength range. The intensity of the light generated is directly proportional to the concentration of NO in the ambient air sample. **The NO concentration of Equation 5-2 has now been measured.**

NO<sub>x</sub> is measured by passing the air sample for part of the measurement cycle through a catalytic converter. Any NO<sub>2</sub> in the air sample is first reduced by the converter to NO. Any NO already in the air sample is not affected by the converter. The reduced NO<sub>2</sub> and NO is then ozonated by the analyzer to produce the electronically excited (light emitting-chemiluminescent) NO<sub>2</sub> molecule. The intensity of light is measured by the analyzer and is reported as a NO<sub>x</sub> concentration. **The NO<sub>x</sub> concentration of Equation 5-2 has now been measured.**

Using Equation 5-2 the analyzer derives the concentration of NO<sub>2</sub> by subtracting the NO concentration from the NO<sub>x</sub> concentration. Figure 1 shows the basic flow pattern of a typical NO/NO<sub>2</sub>/NO<sub>x</sub> analyzer.

**Figure 1**  
**Analyzer Flow Diagram**



### **3.2 Chemiluminescent Measurement Method of NO<sub>y</sub>**

The same principle used for the measurement of NO, NO<sub>2</sub>, and NO<sub>x</sub> is used for the total reactive oxides measurement by the NO/NO<sub>2</sub>/NO<sub>x</sub> analyzer. The NO and NO<sub>y</sub> concentrations are determined by photo chemically measuring the light intensity at wavelengths greater than 600 nanometers from the chemiluminescent reaction of nitric oxide with ozone (see Equation 5-1). The primary differences between the configuration of the NO<sub>y</sub> instrument and the EPA approved NO<sub>2</sub> instrument are the locations of the catalytic converter, particulate filter(s), flow control capillary, and the 3-way solenoid valve used for mode control.

To measure NO<sub>y</sub>, sample air is passed through a probe-mounted catalytic converter. The nitroxyl compounds present are reduced to NO. The NO already in the air sample is not affected by the converter. The NO resulting from the reduction of these nitroxyl compounds, plus any native NO is reactive with ozone. The resulting chemiluminescent light is measured as the total NO<sub>y</sub> concentration. To measure NO separately and specifically, sample air is by-passed around the catalytic converter so that no reduction of the nitroxyl compounds to NO occurs.

The NO is reactive with the ozone and the resulting chemiluminescent light is measured as the NO concentration.

### **4.0 Calibration Methodology**

The calibration method for a NO/NO<sub>2</sub>/NO<sub>x</sub> analyzer is based on the gas phase titration (GPT) between O<sub>3</sub> and excess NO to produce NO<sub>2</sub>.

A high concentration cylinder of NO gas (approximately 50 parts per million, or ppm) is diluted with measured flows of zero (clean) air.

Zero air is defined as dilution air which is free of moisture and the pollutants being measured by the analyzer. For the NO/NO<sub>2</sub>/NO<sub>x</sub> calibration method, dilution air is cleaned or scrubbed of NO, NO<sub>2</sub>, and O<sub>3</sub> with the following: a drying column of silica gel, an oxidizing catalyst column or ultra violet lamp to convert NO to NO<sub>2</sub>, and a charcoal column for NO<sub>2</sub> and O<sub>3</sub> removal. This scrubbing method will remove NO, NO<sub>2</sub>, and O<sub>3</sub> below the minimum detectable limits of the analyzer.

A known concentration of the diluted NO gas is titrated with concentrations of O<sub>3</sub> in order to produce NO<sub>2</sub> concentrations. When titrating NO with O<sub>3</sub>, the changes in the calibrated NO channel are used to determine NO<sub>2</sub> concentrations (Equation 5-1). The example calibration (Figure 2, page 27) shows the changes in the NO channel and the produced NO<sub>2</sub> concentrations.

The calibration method for NO<sub>y</sub> is similar to the calibration method of NO/NO<sub>2</sub>/NO<sub>x</sub> instruments. It uses the gas phase titration of an NO standard with O<sub>3</sub>. When the NO concentration is known, the concentration of NO<sub>2</sub> can be determined. Ozone is added to excess NO in a dynamic calibration system, and the NO channel of the chemiluminescence NO<sub>y</sub> instrument is used as an indicator of changes in NO concentration. Upon the addition of O<sub>3</sub>, the

decrease in NO concentration observed on the calibration NO channel is equivalent to the concentration of NO<sub>2</sub> produced. The amount of NO<sub>2</sub> generated may be varied by adding variable amounts of O<sub>3</sub> from a stable O<sub>3</sub> generator. The NO<sub>y</sub> catalytic converter is probe-mounted between the zero air sample and the instrument.

#### 4.1 Permeation System (NO<sub>2</sub>)

NO<sub>2</sub> can also be produced using a permeation system. The permeation system is used to produce concentrations of NO<sub>2</sub> using a vial of NO<sub>2</sub> (with a known permeation rate) that is contained in a chamber or oven heated to a constant temperature. A flow of zero air is passed through this chamber and varying amounts of dilution air are then added in order to produce different concentrations of NO<sub>2</sub>. The vial is under high pressure so the NO<sub>2</sub> is in a liquid state. Total flow through system is measured and used in Formula A to determine NO<sub>2</sub> concentration.

#### Formula A

$$\frac{\text{Perm Rate} \times 0.532}{\text{Total Flow}}$$

An NO<sub>2</sub> permeation system can be used for daily zero and span checks. (see Section 10.3).

An NO<sub>2</sub> permeation system **cannot** be used for data validation audits, biweekly precision checks, or for accuracy audits (see Section 8.0). The Code of Federal Regulations (40 CFR Part 58 Appendix A) require a residual amount of NO when precision checks, and audits are performed (see Section 8.0). This will determine the analyzer's ability to differentiate between NO and NO<sub>x</sub> measuring capabilities. An NO<sub>2</sub> permeation system does not have the capability to provide this residual NO. However, it may help determine when a problem has occurred with the analyzer, thus reducing the amount of data that could be invalidated.

An NO<sub>2</sub> permeation system is also of limited use for calibrations since it cannot be used to calibrate the NO channel of the analyzer. The preferred system for calibration and auditing is the GPT blending/dilution system.

#### 4.2 Blending and Dilution Systems (GPT)

A GPT system consists of a cylinder of NO (in an oxygen-free gas, usually nitrogen), an ozonator, and a dilution/blending system. Specific components of the GPT system are:

1. An air flow controller capable of maintaining and measuring constant air flows within  $\pm 2.0\%$  of the standard flow. The flow controller may be a mass flow controller, rotameter, capillary, or pressure regulator (snubber) type.
2. An NO flow controller (made of nonreactive material, i.e. stainless steel) capable of maintaining and measuring constant flows within  $\pm 2\%$  of the standard flow. The flow

controller may be a mass flow controller, rotameter, capillary, or snubber type.

3. A pressure regulator for the cylinder of the NO standard gas which must be made of nonreactive materials (i.e. stainless steel, Teflon). The regulator must be able to deliver NO at a suitable pressure. The regulator must have a CGA 660 cylinder connection fitting.
4. An ozone generator capable of generating sufficient, stable levels of O<sub>3</sub> for the GPT reaction with NO concentrations.
5. A shutoff valve (of nonreactive material) to stop the NO flow when zero air is required.
6. A reaction chamber (nonreactive material) for the quantitative reaction of O<sub>3</sub> with excess NO with sufficient volume to meet the residence requirements of 40 CFR Part 50, Appendix F, Section 1.4.
7. A mixing chamber (nonreactive material) designed to provide thorough mixing of the GPT reaction products and dilution air. The inlet and outlet should be of sufficient diameter so that the chamber is at atmospheric pressure under normal operation and sufficient turbulence must be created in the chamber to facilitate thorough mixing. Chamber volumes in the range of 150 to 250 cm<sup>3</sup> are sufficient.

**NOTE: MOST COMMERCIALY MADE GPT BLENDING & DILUTION SYSTEMS HAVE A COMBINED REACTION AND MIXING CHAMBER. THE RESIDENCE REQUIRED HAS BEEN CALCULATED AND SHOULD BE LISTED IN THE OPERATION MANUAL.**

8. An output manifold (nonreactive material) to provide a vented sample to the analyzer.
9. A cylinder of NO gas with less than 1 ppm NO<sub>2</sub> impurity certified by the Indiana Department of Environmental Management, Office of Air Quality, Quality Assurance Section (IDEM, OAQ, QAS).

See Chapter 6 of this manual, "Certification Methods for Transfer Standards".

The NO cylinder valve must be compatible with a CGA 660 regulator fitting.

10. A zero (clean) air system which is free of the contaminants of NO, NO<sub>2</sub>, and O<sub>3</sub> (see Section 4.0).

### 4.3 Certification Requirements

Portable blending systems (GPT) used for audits and calibrations must be certified by the IDEM/OAQ/QAS at least every 6 months. Stationary blending systems must be certified by the QA Lab annually.

For blending systems with mass flow meters/controllers, this certification includes certifying the flow meters prior to the NO gas certification.

System recertification must be done immediately if any of the following conditions occur:

1. Major maintenance on the blending system (e.g. mass flow meter replacement)
2. Any unexplained problems with calibrations or audits that make calibrator output concentrations questionable
3. Replacement of the certified NO gas cylinder with a new cylinder

### 5.0 Analyzer Calibrations

#### 5.1 Analyzer Calibration Procedures for Automated Systems

Leading Environmental Analysis and Display System (LEADS) is an automated near real-time data acquisition system. See LEADS Manual chapters 2, 3, and 4 for Automated Calibration Procedures.

#### 5.2 Analyzer Calibration Procedures for non-Automated Systems

The calibration of one NO/NO<sub>2</sub>/NO<sub>x</sub> analyzer actually involves performing three calibrations; one calibration for each of the analyzer's three channels (see Form 1). While the NO and NO<sub>x</sub> channels can be calibrated simultaneously, a typical GPT calibration may take 3 to 4 hours to complete. Because the principle, apparatus, and procedures used to calibrate the NO<sub>y</sub> instrument are similar to the NO/NO<sub>2</sub>/NO<sub>x</sub> instruments, it may be possible to calibrate both types of instruments simultaneously. Since the procedures for the calibration of the NO/NO<sub>2</sub>/NO<sub>y</sub> analyzer are the same as the NO/NO<sub>2</sub>/NO<sub>x</sub> analyzer, the NO<sub>x</sub> response is replaced with the NO<sub>y</sub> response when referring to the NO/NO<sub>2</sub>/NO<sub>y</sub> analyzer calibration (see Forms 1 and 2).

The calibrated NO and NO<sub>x</sub> channels of the analyzer indirectly determine NO<sub>2</sub> concentrations (see Equation 5-2).

**NOTE: NO<sub>2</sub> IS NEVER DIRECTLY MEASURED. IN ORDER TO ACCURATELY MEASURE NO<sub>2</sub>, THE NO AND NO<sub>x</sub> CHANNELS MUST FIRST BE CALIBRATED ACCURATELY.**

A data validation audit should be conducted prior to any routine recalibration. This one point audit must be conducted prior to any analyzer adjustments. The purpose of the audit is to determine the validity of the data from the last audit or calibration to the present date. See Section 8.0 for the audit procedure.

### 5.3 NO and NO<sub>x</sub> (NO<sub>y</sub>) Calibration Procedures

GPT techniques require the use of the NO channel of the analyzer and determine the amount of NO<sub>2</sub> generated through titration. When titrating NO with O<sub>3</sub>, the changes in the calibrated NO channel determine the NO<sub>2</sub> concentrations.

It is necessary to calibrate and determine the linearity of the NO and NO<sub>x</sub> (NO<sub>y</sub>) channels before proceeding with the NO<sub>2</sub> calibration. The calibrated NO and NO<sub>x</sub> (NO<sub>y</sub>) channels of the analyzer will then indirectly determine NO<sub>2</sub> concentrations using Equation 5-2.

During the calibration, the analyzer must be operating in its normal sampling mode. The calibration gas must pass through all filters, scrubbers, conditioners, and other components used during the normal ambient sampling mode. All operational adjustments to the analyzer (i.e. sample flow, PMT voltages, converter replacement, etc.) should be completed prior to the calibration.

Record all pertinent information on the calibration forms (i.e. see Forms 1 & 2).

**NOTE: All NO/NO<sub>2</sub>/NO<sub>x</sub> and NO/NO<sub>2</sub>/NO<sub>y</sub> analyzers must be routinely calibrated at least once every six (6) months.**

1. Record the station name and the AQS (Air Quality System) site identification number on the calibration form.
2. Identify the person performing the calibration (initials) and record the date of the calibration.
3. Record the analyzer's manufacturer name (brand), model number, and serial number.
4. Record the analyzer's initial settings: flows, vacuum, etc.
5. Record the GPT system (calibrator) manufacturer name, model number, and serial number.
6. Record the NO calibration gas cylinder number, the certified concentration, and the certification date.

**NOTE: DO NOT USE CYLINDERS WITH PRESSURES < 200 PSIG (POUNDS PER SQUARE INCH GAUGE).**

**GASES MAY BECOME UNSTABLE AT LOW PRESSURES AND CAUSE CALIBRATION ERRORS.**

All calibration and audit cylinders must be traceable to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM). See Chapter 6 of this manual for traceability/certification procedures.

7. Record the initial zero and span potentiometer (pot) settings prior to any adjustments. Analyzer controls will vary with each manufacturer's brand and model. Some analyzers will have only one zero or span pot; while other brands may have zero and span pots for each of the NO, NO<sub>2</sub>, and NO<sub>x</sub> (NO<sub>y</sub>) channels.

Some analyzers are microprocessor controlled and have no potentiometers at all, but they will have readings which correspond to the zero and span pot settings.

Because calibration adjustments will differ between analyzer models, consult the manufacturer's manual before performing the calibration.

8. Use the NO/NO<sub>x</sub> (NO<sub>y</sub>) Calibration Data sections of the calibration forms (Forms 1 & 2) to record the information.
9. Select and record the operating range of the analyzer to be calibrated.





**NOTE:** Select a range for which the analyzer has been designated as an EPA reference method.

Most analyzers are calibrated in the 0 to 0.5 ppm range. Refer to the analyzer's manual for designated ranges. The NO<sub>y</sub> analyzer can be run at any range that it is capable of and that meets your monitoring needs.

10. Confirm that the analyzer is connected to a recording device such as a data acquisition system (DAS), a strip chart recorder, and/or a digital voltmeter. Since the analyzer will have three output voltage connections (for NO, NO<sub>2</sub>, and NO<sub>x</sub> (NO<sub>y</sub>)), label or be able to differentiate between the three outputs.
11. Adjust the flow of the diluent air (zero air) on the calibrator so that its total output flow exceeds the total demand of the analyzer(s) by at least 25%.

**For Example:** If the analyzer flow demand is 1.00 liters per minute (l/min), the total output flow from the calibrator should be no less than 1.25 l/min.

The excess flow from the calibrator is necessary to ensure that the analyzer has a sufficient amount of sample. If not, the analyzer could draw air from other than the desired sample stream.

12. Connect the analyzer's "sample in" port to the "sample out" port of the calibrator using a vented nonreactive (TFE Teflon) sample line/manifold. For the NO<sub>y</sub> hookup, one line is connected to the converter while a second line bypasses the converter.

**NOTE: Logon and annotate all data recording devices (data acquisition system, strip chart recorder, etc.) with the audit starting date, site, parameter, initials, and time.**

**WARNING: THE SAMPLE GAS MUST BE DELIVERED TO THE ANALYZER AT ATMOSPHERIC PRESSURE. A MANIFOLD OR TEE VENT MUST BE USED FROM THE CALIBRATOR SO THAT EXCESS SAMPLE FLOW CAN BE BLED OFF. FOR THE NO<sub>y</sub> CALIBRATION HOOKUP, NO MANIFOLD OR TEE VENT IS USED.**

**AN UNVENTED SAMPLE GAS COULD PRESSURIZE & DAMAGE THE ANALYZER.**

13. Allow the analyzer to sample zero air until NO, NO<sub>x</sub> (NO<sub>y</sub>), and NO<sub>2</sub> responses have stabilized (usually 10 to 20 minutes). After the responses have stabilized, adjust the analyzer zero control(s) to the desired zero offset. Offsetting the analyzer zero to +1% of scale (i.e. 0.005 ppm on a 0.5 ppm range) is recommended to facilitate observing any negative zero drift. A +5% offset of the data recording device(s) (i.e. strip chart recorder) would also be acceptable.
14. Record the stable zero air analyzer response for NO, NO<sub>x</sub> (NO<sub>y</sub>), and NO<sub>2</sub> on the calibration form.

15. Attach a stainless steel regulator to the NO gas calibration cylinder. Refer to Section 7.0 for the regulator purge procedure.

**NOTE: THE REGULATOR MUST BE PURGED OF ALL AIR BEFORE PROCEEDING WITH THE CALIBRATION (SEE SECTION 7.0 FOR THE REGULATOR PURGE PROCEDURE).**

**ATMOSPHERIC O<sub>2</sub> IN THE REGULATOR WILL REACT WITH THE NO AND FORM UNWANTED NO<sub>2</sub> IN THE GAS STREAM.**

16. Adjust the NO flow from the GPT dilution system (or calibrator) to generate a concentration of approximately 90% of the upper range limit (URL) of the NO channel.

**For Example:** For an analyzer set on a 0.5 ppm range 90% of the URL would be 0.450 ppm.

17. Calculate the exact NO concentration  $[\text{NO}]_{\text{out}}$  using Equation 5-3.

**NOTE: BRACKETS [ ] DENOTE A CONCENTRATION (PARTS PER MILLION, ppm) WHILE AN 'F' WITH A SUBSCRIPT DENOTES A FLOW.**

**Equation 5-3:**

$$[\text{NO}]_{\text{out}} = \frac{F_{\text{NO}} \times [\text{NO}]_{\text{std}}}{F_{\text{NO}} + F_{\text{d}} + F_{\text{o}}}$$

Where:

$[\text{NO}]_{\text{out}}$	=	output concentration of NO in ppm
$F_{\text{NO}}$	=	flow of the NO GPT blending system gas in cc/min
$[\text{NO}]_{\text{std}}$	=	concentration in ppm of the NO gas cylinder
$F_{\text{d}}$	=	flow of the dilution gas (zero air) in cc/min
$F_{\text{o}}$	=	flow through the ozonator

**NOTE: MOST MASS FLOW CONTROLLED CALIBRATORS INDICATE THE  $F_{\text{d}}$  FLOW IN LITERS PER MINUTE (l/min). CONVERT l/min TO cc/min BY MULTIPLYING cc/min x 1000 (cc/min = l/min x 1000).**

**NOTE: ON MOST CALIBRATORS, THE FLOW THROUGH THE OZONATOR IS FIXED AND ALREADY INCORPORATED INTO THE  $F_{\text{d}}$  FACTOR. THEREFORE, THE  $F_{\text{o}}$  CAN BE DROPPED FROM THE EQUATION. CHECK THE CALIBRATOR MANUAL FOR THE EXACT FLOW CONFIGURATIONS.**

Example calculation using Equation 5-3:

Assume  $F_o$  is already incorporated into the  $F_d$  flow,

$$F_{NO} = 45.0 \text{ cc/min}$$

$$F_d = 4,955.0 \text{ cc/min}$$

$$[NO]_{std} = 50.0 \text{ ppm}$$

$$[NO]_{out} = \frac{45.0 \text{ cc/min} \times 50.0 \text{ ppm}}{45.0 \text{ cc/min} + 4,955.0 \text{ cc/min}}$$

$$[NO]_{out} = \frac{2,250.0 \text{ cc/min} \times \text{ppm}}{5,000.0 \text{ cc/min}} = 0.450 \text{ ppm}$$

**NOTE: BECAUSE DATA IS REPORTED TO THREE SIGNIFICANT DIGITS, ROUND THE CONCENTRATION TO THE NEAREST THOUSANDS PPM (.XXX).**

18. Calculate the exact  $NO_x$  ( $NO_y$ ) concentration  $[NO_x]_{out}$  ( $[NO_y]_{out}$ ) using Equation 5-4.

**Equation 5-4:**

$$[NO_y]_{out} \text{ or } [NO_x]_{out} = \frac{F_{NO} \times ([NO]_{std} + [NO]_{imp})}{F_{NO} + F_d + F_o}$$

Where:  $[NO_2]_{imp}$  = the concentration in ppm of the  $NO_2$  impurity in the NO gas cylinder,  $[NO]_{std}$

**NOTE: IF  $[NO_2]_{IMP} = 0$  OR IS LESS THAN 1% OF THE NO GAS CYLINDER CONCENTRATION, THEN THE  $[NO_x]_{OUT}$  CALCULATION IS THE SAME AS THE  $[NO]_{OUT}$  CALCULATION.**

**THE  $NO_2$  IMPURITY IS INDICATED ON THE MANUFACTURER'S LABEL OR CERTIFICATION STICKER ON THE NO GAS CYLINDER  $[NO]_{STD}$**

19. Record the  $[NO]_{out}$  and  $[NO_x]_{out}$  ( $[NO_y]_{out}$ ) concentrations on the calibration form.
20. The analyzer should sample the generated concentration until the NO and  $NO_x$  ( $NO_y$ ) responses stabilize (usually 10 to 20 minutes). Adjust the NO (and  $NO_x$  ( $NO_y$ ) if present) span control to obtain a recorder response as determined by Equation 5-5.

**NOTE: IF THE MONITOR RESPONSE EXHIBITS A VERY SLOW RESPONSE TO THE FIRST NO CONCENTRATION, THERE MAY STILL BE SOME RESIDUAL O<sub>2</sub> CONTAMINATION IN THE NO REGULATOR. REPURGE THE REGULATOR (SEE SECTION 7.0).**

**Equation 5-5:**

$$\text{Desired Recorder Response (\% of scale)} = \frac{([\text{NO}]_{\text{out}} \times 100)}{\text{URL}} + Z_{\text{NO}}$$

Where: URL = upper range limit of the NO channel  
Z<sub>NO</sub> = recorder response of the NO channel

Example calculation using Equation 5-5:

$$\text{Desired Recorder Response (\% of scale)} = \frac{(0.450 \text{ ppm} \times 100)}{0.5 \text{ ppm}} + 5\% = 95.0\%$$

21. After setting the zero and approximately 90% URL NO/NO<sub>x</sub> (NO<sub>y</sub>) (span) concentrations, determine at least three more evenly spaced concentrations between the zero and span concentrations. Run this concentration without any further adjustments to the analyzer.

For example, a typical NO/NO<sub>x</sub> (NO<sub>y</sub>) calibration with a URL of 0.5 ppm would consist of (listed in order that they should be run):

- a. 0.000 ppm (zero)
- b. 0.400 to 0.450 ppm (span)
- c. 0.250 to 0.300 ppm
- d. 0.150 to 0.200 ppm
- e. 0.080 to 0.100 ppm (mid-level)

The additional concentrations can be generated by either increasing the calibration dilution flow (F<sub>d</sub>) or by decreasing the NO cylinder gas flow (F<sub>NO</sub>). For each concentration generated, calculate the exact NO and NO<sub>x</sub> (NO<sub>y</sub>) concentrations using Equations 5-3 and 5-4. Record the required information on the NO/NO<sub>x</sub> (NO<sub>y</sub>) calibration data section on the calibration form.

22. Use a calculator or a linear regression (least squares) computer program to calculate the slope and intercept for the NO channel. Include the upscale calculated concentrations plus the zero to determine the slope and intercept. See Table 2 for example calculations.

**OR**

23. Adjust the analyzer's NO (and NO<sub>x</sub> (NO<sub>y</sub>)) span pot(s) or other electronic adjustments so

that the slope is a fixed value (i.e., for a 0.5 ppm range: a 0.5 slope for a 1 volt output; a 0.005 slope for a 100 millivolt or strip chart output; a 0.0005 slope for a 1000 millivolt output). This method will allow the same slope to be used for data reduction for the entire network. The other calibration concentrations must be within  $\pm 2\%$  of the range of the analyzer for each of the standard concentrations (e.g., if 0.5 ppm range, all measured concentrations must be within 0.010 ppm of their respective standard concentrations).

24. Use Equation 5-6 to calculate the observed (or measured) concentration for all upscale analyzer responses. Use Equation 5-7 to calculate the difference between the standard and observed concentrations.

The standard concentration is defined as  $[\text{NO}]_{\text{out}}$  calculated from Equation 5-3. The observed concentration is defined by the following equation:

**Equation 5-6:**

$$\text{obsv. response} = (\text{mon. response} - \text{mon. zero response}) \times \text{slope}$$

**NOTE: Please make note of the following abbreviations which will be used throughout the rest of this chapter:**

observed concentration	=	obsv. conc.
standard concentration	=	std. conc.
monitor response	=	mon. resp.
monitor zero response	=	mon. zero resp.
percent difference	=	% diff.

**NOTE: BECAUSE PRECISION AND ACCURACY DATA IS REPORTED TO THE NEAREST TENTH, THE % DIFF. MAY BE ROUNDED TO THE NEAREST TENTH OF A PERCENT (X.X).**

25. All observed concentrations for NO, NO<sub>x</sub> (NO<sub>y</sub>), and NO<sub>2</sub> channel calibrations must be within the standard concentration by  $\pm 2\%$  of the range of the analyzer (0.010 ppm).

**Table 2**  
**Example Data for Linear Regression**

(Y) Concentration [NO] <sub>out</sub> (ppm)	(X) Monitor Response (volts)	(*) Observed Concentration (ppm)	(**) Observed Concentration (ppm)	(***) Relative Diff.
0.450	0.907	0.450	0.450	0.000
0.326	0.654	0.323	0.324	0.002
0.205	0.427	0.209	0.210	0.005
0.124	0.262	0.126	0.128	0.004
0.000	0.007	-0.002	0.000	0.000

\* All five points (X & Y) are regressed (Section 5.3 step 22):

**Slope: 0.50267**

**Intercept: -0.00591**

**NOTE:** Observed concentration is abbreviated as obsv. conc. monitor response is abbreviated as mon. resp.

$$\text{obsv. conc.} = (\text{mon. resp.} \times \text{slope}) + \text{intercept}$$

\*\* Fixed value for the slope (Section 5.3 step 23):

Slope: 0.500

Zero: 0.007

$$\text{obsv. conc.} = (\text{mon. resp.} - \text{zero mon. resp.}) \times \text{slope}$$

Where:

mon. resp.	=	0.427 v (volt)
mon. zero resp.	=	0.007 v
slope	=	0.500
obsv. conc.	=	(0.427 - 0.007) x 0.500
obsv. conc.	=	0.210 ppm

**Equation 5-7:**

$$\% \text{ diff.} = \frac{\text{obsv. conc.} - \text{std. conc.}}{\text{std. conc.}} \times 100$$

Where:     std. conc.       =     0.205 ppm  
          obsv. conc.       =     0.210 ppm

**Example calculation:**

diff. = 0.210 - 0.205 ppm  
diff. = 0.005 ppm

Analyzers which cannot routinely meet the calibration limit (0.010 ppm) may be in need of maintenance.

26. Repeat steps 22 to 25 of Section 5.3 for the NO<sub>x</sub> (NO<sub>y</sub>) channel calculations.
27. Record all information/data on the GPT Calibration Form (Form 1 or 2).
28. Perform and then record any analyzer diagnostic test results. These tests provide baseline data for future troubleshooting.
29. The NO<sub>2</sub> channel is now ready for calibration.

**5.4 NO<sub>2</sub> Calibration Procedures for NO/NO<sub>2</sub>/NO<sub>x</sub> or NO/NO<sub>2</sub>/NO<sub>y</sub> Analyzers**

After calibrating the NO and NO<sub>x</sub> (NO<sub>y</sub>) channels, the NO<sub>2</sub> channel is calibrated using the Gas Phase Titration (GPT) technique. Ozone (O<sub>3</sub>) is used to titrate against an excess amount of NO gas in order to produce NO<sub>2</sub> concentrations.

The NO<sub>2</sub> channel calibration procedure is as follows:

1. Rerun the zero air and record the analyzer response for the NO, NO<sub>x</sub> (NO<sub>y</sub>), and NO<sub>2</sub> channels.
2. Adjust the NO flow from the GPT blending system (calibrator) to generate a concentration of approximately 90% of the URL of the NO channel (see 16 to 18 of Section 5.4 for the exact procedures and calculations).
3. After the analyzer has stabilized, record the channel responses as [NO]<sub>orig</sub> and [NO<sub>x</sub>] ([NO<sub>y</sub>]) on the NO<sub>2</sub> section of the calibration form. Convert the responses to ppm concentrations using the slope and analyzer zero response for each respective NO and NO<sub>x</sub> (NO<sub>y</sub>) channel.

[NO]<sub>orig</sub> (original NO) is defined as the concentration of NO before the titration with O<sub>3</sub>.

**Example calculation:**

	<u>Slope</u>	<u>Zero Response</u>	<u>Monitor Response*</u>
NO	0.500	0.007 v	0.897 v
NO <sub>x</sub> (NO <sub>y</sub> )	0.500	0.007 v	0.899 v

\*assume a 0 to 1.0 volt dc analyzer output range

Using Equation 5-6:

$$[\text{NO}]_{\text{orig}} = (0.897 \text{ v} - 0.007 \text{ v}) \times 0.500 = 0.445 \text{ ppm}$$

$$[\text{NO}_x]_{\text{orig}} ([\text{NO}_y]_{\text{orig}}) = (0.899 \text{ v} - 0.007 \text{ v}) \times 0.500 = 0.466 \text{ ppm}$$

- Adjust the O<sub>3</sub> generator on the calibrator to produce an NO<sub>2</sub> analyzer response of approximately 80% of scale.

**To prevent calibration errors, be sure to allow at least .050 ppm of NO to remain ([NO]<sub>rem</sub>).**

**Example calculation:**

80% of a 0.5 ppm range = 0.400 ppm

**NOTE:** It is helpful during the titration to have each of the analyzer's three outputs (NO, NO<sub>2</sub>, NO<sub>x</sub> (NO<sub>y</sub>)) connected to a strip chart recorder. When the calibrator's ozone generator is turned on, the analyzer will respond as follows: the NO response will decrease; the NO<sub>2</sub> response will increase; the NO<sub>x</sub> (NO<sub>y</sub>) response will not change or the response may decrease slightly.

- After the analyzer's responses have stabilized (usually 15 to 25 minutes) record the analyzer responses for [NO]<sub>rem</sub>, [NO<sub>x</sub>]([NO<sub>y</sub>]), and [NO<sub>2</sub>]<sub>meas</sub> in mv, v, or % chart. Refer to the NO<sub>2</sub> section of the calibration form, Form 1 or 2.

[NO]<sub>rem</sub> (remaining NO) is defined as the concentration of remaining NO after titration with O<sub>3</sub>.

[NO<sub>2</sub>]<sub>meas</sub> (measured or observed NO<sub>2</sub>) is defined as the concentration calculated from the analyzer's response for the NO<sub>2</sub> channel.

- Calculate the concentration of NO<sub>2</sub> produced which is indicated as [NO<sub>2</sub>]<sub>out</sub> by using Equation 5-8.

**NOTE:** The [NO<sub>2</sub>]<sub>out</sub> is also called the standard NO<sub>2</sub> concentration.

**Equation 5-8:**

$$[\text{NO}_2]_{\text{out}} = [\text{NO}]_{\text{orig}} - [\text{NO}]_{\text{rem}}$$

Where:  $[\text{NO}]_{\text{orig}} = 0.445 \text{ ppm}$   
 $[\text{NO}]_{\text{rem}} = 0.080 \text{ ppm}$

**Example calculation:**

$$[\text{NO}_2]_{\text{out}} = 0.445 \text{ ppm} - 0.080 \text{ ppm} = 0.365 \text{ ppm}$$

7. One of the steps to be followed next will depend on the brand and model of the analyzer.
  - a. For an analyzer with a  $\text{NO}_2$  span potentiometer, adjust the span pot. until the analyzer's output corresponds to the calculated  $[\text{NO}_2]_{\text{out}}$  concentration. Always refer to the analyzer's manual for specific instructions.
  - b. For a microprocessor controlled analyzer (i.e., TECO 42i), refer to the manual and adjust the  $\text{NO}_2$  output until it agrees with the calculated  $[\text{NO}_2]_{\text{out}}$  concentration.
  - c. For an analyzer without an  $\text{NO}_2$  span potentiometer (i.e., CSI 1600), record the analyzer's output for the  $\text{NO}_2$  channel. Since no adjustment can be made to this channel it is extremely important to have first accurately calibrated the  $\text{NO}$  and  $\text{NO}_x$  channels.
8. Titrate at least one additional  $\text{NO}_2$  concentration,  $[\text{NO}_2]_{\text{out}}$ , by changing the ozonator output on the GPT blending system (calibrator). For each concentration calculate and record the following:
  - a. Analyzer response for the  $\text{NO}$  channel and calculated  $[\text{NO}]_{\text{rem}}$  concentration
  - b. Analyzer response for the  $\text{NO}_x$  ( $\text{NO}_y$ ) channel and the calculated  $[\text{NO}_x]([\text{NO}_y])$  concentration
  - c. Analyzer response for the  $\text{NO}_2$  channel and the calculated  $[\text{NO}_2]_{\text{out}}$  concentration

A typical  $\text{NO}_2$  calibration will have a zero and at least four upscale points. The upscale points will be at these approximate concentrations:

1. 0.0 ppm (zero)
2. 0.400 ppm
3. 0.300 ppm
4. .200 ppm
5. .090 ppm

9. Use a calculator or a computer with a linear regression (least squares) program in order to

calculate the slope and intercept for the NO<sub>2</sub> channel. Include the four upscale NO<sub>2</sub> concentrations [NO<sub>2</sub>]<sub>out</sub>, plus the monitor response for zero air in the linear regression. See Table 2 for an example calibration.

**OR**

10. Adjust the analyzer's NO<sub>2</sub> span potentiometer (pot) so that the slope is a fixed value (i.e. for a 0.5 ppm range: a 0.5 slope for a 1 volt output; a 0.005 slope for a 100 millivolt or strip chart output; a 0.0005 slope for a 1000 millivolt output).

For analyzers with no NO<sub>2</sub> adjustment, assume a constant slope (see Table 2).

11. For all NO<sub>2</sub> upscale points, calculate the observed concentration, [NO<sub>2</sub>]<sub>meas</sub>, and the percent difference between the standard, [NO<sub>2</sub>]<sub>out</sub>, and the observed, [NO<sub>2</sub>]<sub>meas</sub>. Use Equations 5-6 and 5-7.
12. All observed concentrations for NO<sub>2</sub> must be within the corresponding standard concentrations by ±2% of the analyzer range. If any observed concentration is found to be greater than ±2% of the analyzer range, then recalculate and/or rerun that concentration.

**NOTE: If the percent difference is greater than ±2%, the NO and/or the NO<sub>x</sub> channels may have drifted. If this is the case then the entire calibration, starting with the NO/NO<sub>x</sub> calibration, may have to be repeated.**

13. The Code of Federal Regulations requires that all NO/NO<sub>2</sub>/NO<sub>x</sub> analyzers have a converter efficiency of at least 96%. Data from analyzers with a converter efficiency of less than 96% is considered invalid.

Converter efficiency is defined as the percent of NO<sub>2</sub> which is converted to NO so that the NO<sub>x</sub> (NO<sub>y</sub>) component can be measured by the analyzer.

See Figure 1 for an analyzer diagram. Inefficient converters (< 96%) do not convert all of the NO<sub>2</sub> to NO which results in a NO<sub>x</sub> (NO<sub>y</sub>) concentration biased low.

If the converter efficiency falls below 96%, then the converter must be replaced. The analyzer must then be recalibrated.

For most analyzers, converter efficiency must be calculated at the time of each calibration. Section 6.1 outlines this procedure.

For microprocessor controlled analyzers (i.e. TECO 42i), the converter efficiency is automatically calculated. The procedures of Section 6.0 would then not have to be followed for the TECO 42i. Check the analyzer's manual to determine if the converter efficiency has to be manually calculated.

14. After finishing an on-site calibration, complete the following steps:

- a. Reconnect the analyzer to the sample manifold
- b. Ensure that the analyzer is in the monitor mode
- c. Ensure that the analyzer is connected to all data recording devices and that all strip charts have been annotated

**NOTE:** All strip charts should be annotated with the following information: site name, date, chart speed, calibration starting time, initials of the person performing the calibration, all responses with the applicable standard concentrations and the parameter, the initial and final zero, and the calibration ending time.

In addition, record and post the following:

- d. Record all pertinent information in the site logbook
- e. Post a copy of the calibration at the site

**NOTE:** Residual NO and NO<sub>2</sub> trapped in a calibrator can cause stability problems during the next calibration. Purge the calibrator with zero air after each calibration is completed.

## 6.0 Converter Efficiency Calculations

The converter efficiency is calculated from data generated from the upscale concentrations titrated during the NO<sub>2</sub> part of the analyzer calibration (see Equation 5-9).

### Equation 5-9:

$$[\text{NO}_2]_{\text{converted}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_x]_{\text{orig}} - [\text{NO}_x]_{\text{rem}})$$

**OR**

$$[\text{NO}_2]_{\text{converted}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_y]_{\text{orig}} - [\text{NO}_y]_{\text{rem}})$$

Where:

$[\text{NO}_2]_{\text{converted}}$	=	the concentration (ppm) of NO <sub>2</sub> converted by the analyzer's catalytic converter
$[\text{NO}_2]_{\text{out}}$	=	the standard concentration (ppm) of NO <sub>2</sub> produced by the GPT blending system
$[\text{NO}_x]_{\text{orig}}$	=	the concentration (ppm) of NO <sub>x</sub> (original) before titration
$[\text{NO}_x]_{\text{rem}}$	=	the concentration (ppm) of NO <sub>x</sub> (remaining) concentration after titration
$[\text{NO}_y]_{\text{orig}}$	=	the concentration (ppm) of NO <sub>y</sub> (original) before titration
$[\text{NO}_y]_{\text{rem}}$	=	the concentration (ppm) of NO <sub>y</sub> (remaining) concentration after titration

**Example calculation:** See Figure 2 for an example calculation for NO/NO<sub>2</sub>/NO<sub>x</sub>.

The required data for a converter efficiency calculation are: the [NO<sub>x</sub>]<sub>orig</sub> ([NO<sub>y</sub>]<sub>orig</sub>) concentration (prior to O<sub>3</sub> titration), the [NO<sub>x</sub>]<sub>rem</sub> ([NO<sub>y</sub>]) concentrations (after O<sub>3</sub> titration) and the [NO<sub>2</sub>]<sub>out</sub> concentrations. See Forms 1 and 2 for the GPT calibration and Forms 4 and 5 for an example converter efficiency calculation.

### 6.1 Calculation Procedure for Converter Efficiency

1. Transfer the concentrations of [NO<sub>2</sub>]<sub>out</sub>, [NO<sub>x</sub>]<sub>orig</sub> ([NO<sub>y</sub>]<sub>orig</sub>), and [NO<sub>x</sub>]<sub>rem</sub> ([NO<sub>y</sub>]) from the NO<sub>2</sub> GPT data table (Form 1) to the Converter Efficiency data table (Form 3). Also include zero points ([NO<sub>2</sub>]<sub>out</sub> = 0 and [NO<sub>2</sub>]<sub>conv</sub> = 0) in the data table. For NO<sub>y</sub>, the concentrations will be transferred from Form 2 to Form 4.
2. Using a calculator or a computer with a linear regression (least squares) program, enter the [NO<sub>2</sub>]<sub>out</sub> on the x-axis and the [NO<sub>2</sub>]<sub>conv</sub> on the y-axis.
3. Use the upscale data sets plus the zero value to determine a slope.
4. Percent converter efficiency is defined by Equation 5-10.

#### Equation 5-10:

$$\text{Percent Converter Efficiency} = \text{Slope} \times 100$$

5. Converter efficiency must be 96% or greater. Since this efficiency is derived from several calculated data points, it is possible for the efficiency to be greater than 100%.

**Converter Efficiency NO/NO<sub>2</sub>/NO<sub>x</sub>**

Point	(X) [NO <sub>2</sub> ] <sub>out</sub> (ppm)	[NO <sub>x</sub> ] <sub>orig</sub> (ppm)	[NO <sub>x</sub> ] <sub>rem</sub> (ppm)	(Y) [NO <sub>2</sub> ] <sub>conv</sub> (ppm)
<b>1</b>				
<b>2</b>				
<b>3</b>				
<b>4</b>				
<b>5</b>				

$$[\text{NO}_2]_{\text{conv}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_x]_{\text{orig}} - [\text{NO}_x]_{\text{rem}})$$

Converter Efficiency = Slope x 100

Slope: \_\_\_\_\_

Converter Efficiency: \_\_\_\_\_ %

Comments: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

**Form 4**  
**Converter Efficiency NO/NO<sub>2</sub>/NO<sub>y</sub>**

<b>Point</b>	<b>(X) [NO<sub>2</sub>]<sub>out</sub> (ppm)</b>	<b>[NO<sub>y</sub>]<sub>orig</sub> (ppm)</b>	<b>[NO<sub>y</sub>]<sub>rem</sub> (ppm)</b>	<b>(Y) [NO<sub>2</sub>]<sub>conv</sub> (ppm)</b>
<b>1</b>				
<b>2</b>				
<b>3</b>				
<b>4</b>				
<b>5</b>				

$$[\text{NO}_2]_{\text{conv}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_y]_{\text{orig}} - [\text{NO}_y]_{\text{rem}})$$

$$\text{Converter Efficiency} = \text{Slope} \times 100$$

Slope: \_\_\_\_\_

Converter Efficiency: \_\_\_\_\_%

Comments:

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**Figure 2**  
**Converter Efficiency**

<b>Point</b>	<b>(X) [NO<sub>2</sub>]<sub>out</sub> (ppm)</b>	<b>[NO<sub>x</sub>]<sub>orig</sub> (ppm)</b>	<b>[NO<sub>x</sub>]<sub>rem</sub> (ppm)</b>	<b>(Y) [NO<sub>2</sub>]<sub>conv</sub> (ppm)</b>
<b>1</b>	<b>0.000</b>	<b>0.451</b>	<b>0.451</b>	<b>0.000</b>
<b>2</b>	<b>0.398</b>	<b>0.451</b>	<b>0.451</b>	<b>0.398</b>
<b>3</b>	<b>0.298</b>	<b>0.451</b>	<b>0.451</b>	<b>0.298</b>
<b>4</b>	<b>0.199</b>	<b>0.451</b>	<b>0.453</b>	<b>0.201</b>
<b>5</b>	<b>0.101</b>	<b>0.451</b>	<b>0.452</b>	<b>0.102</b>

$$[\text{NO}_2]_{\text{conv}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_x]_{\text{orig}} - [\text{NO}_x]_{\text{rem}})$$

$$\text{Converter Efficiency} = \text{Slope} \times 100$$

**Slope:** 0.99900

**Converter Efficiency:** 99.9%

**Comments:** Diagnostic tests were performed before and after the calibration with the following results:

<b>Test</b>	<b>Initial</b>	<b>Final</b>	<b>Unit</b>
Time Constant	60	60	sec
Cooler Temperature	-3.7	-3.7	°C
Converter Temperature	329	329	°C
Reaction Chamber Temp.	49.8	49.9	°C
NO Zero Background	5.7	6.2	
NO <sub>x</sub> Zero Background	6.6	8.5	
Analog Offset %	0.0	0.0	
Dip #1 to #8 status	2,3,6	2,3,6	on
T Program	4205tP	4205tP	
Internal Temperature	31.9	36.8	°C

## 7.0 Regulator Purge Procedure

NO gas is very reactive with atmospheric oxygen. NO will react with oxygen in air to form unwanted NO<sub>2</sub> in the regulator and gas delivery line. Therefore, it is necessary to purge and evacuate the regulator and gas delivery line of air in order to avoid this NO<sub>2</sub> formation.

The regulator and gas delivery line can be evacuated of air by using an electric pump or a hand operated vacuum pump. The procedure is as follows:

1. Attach a stainless steel regulator (CGA 660 fitting) to the NO gas cylinder.

A single or dual stage regulator can be used. The regulator should be equipped with an output shutoff valve made of a nonreactive material.

Attach the gas delivery line to the regulator (attach to the output shutoff valve). An 1/8" outside diameter (1/8" OD) Teflon gas delivery line is recommended.

A male quick connect type shutoff fitting should be attached to the end of the gas delivery line. This fitting will allow the vacuum to be maintained in the gas delivery line.

2. Attach the vacuum pump (equipped with a female quick connect type fitting) to the gas delivery line. Evacuate the regulator and gas delivery line of air with the vacuum pump (hand vacuum or electric pump).
3. Disconnect the vacuum pump and then open the cylinder valve to fill the regulator and gas delivery line with NO.
4. Close the cylinder shutoff valve and reconnect the vacuum pump to the gas delivery line. Immediately start the evacuation of the regulator and gas delivery line.

If an electric pump is used, evacuate for at least 15 seconds. If a hand vacuum pump is used, draw as much of a vacuum as the hand vacuum will allow.

5. Repeat steps 3 and 4 of 7.0 at least 3 times. It is important to evacuate as much air as possible from the regulator and lines. Flushing the system several times will minimize problems with the calibration.
6. If the analyzer responds slowly to the first upscale NO concentration or the analyzer's NO<sub>2</sub> channel is indicating an upscale concentration of NO<sub>2</sub>, the regulator purge procedure should be repeated.

## **8.0 Quality Assurance Audits**

Quality assurance audits are performed to ensure the validity of the data submitted to the National AQS Data Bank. Results of these audits are also used to estimate the Precision and Accuracy (P&A) of the monitoring network's data. Reports of the P&A statewide are submitted quarterly by IDEM/OAQ/QAS to the USEPA. See Chapter 13, Quality Assessment and Statistical Analysis of Air Monitoring Data, of this manual for detailed information on P&A.

### **8.1 Calibrator Audits and Certifications for Automated Systems**

Leading Environmental Analysis and Display System (LEADS) is an automated near real-time data acquisition system. See Chapter 1 of the Quality Assurance Manual for introductory LEADS information.

### **8.2 Calibrator Audit and Certification Procedures for Automated Systems**

See the following SOPs for API-Teledyne Calibrator Audit and Certification Procedures: API 401 Ozone Calibrator Photometer Setup, Certification, and Operation; API 403 Ozone Calibrator Photometer Field (1-day) Certification; API 700 Mass Flow Calibrator Certification; API 700 Mass Flow Controller (MFC) Calibration; API 703 Ozone Calibrator Photometer Setup, Certification, and Operation; API 703E Ozone Calibrator Photometer Setup, Certification, and Operation; and LEADS Calibrator Audit. Also, see the LEADS Manual.

### **8.3 Data Validation and Precision Audits for non-Automated Systems**

Routine audits are performed every two weeks (biweekly) in order to assess the validity and precision of the NO<sub>2</sub> data. The biweekly audit consists of running two upscale NO<sub>2</sub> concentrations from a GPT blending system (audit device) with a certified NO standard gas cylinder. The audit device must meet the same criteria as that of the GPT blending system used for the calibration (Section 4.2). The audit device must be certified by the IDEM-QAS (Section 4.2 and Chapter 6).

The first biweekly audit point consists of an NO<sub>2</sub> concentration of approximately 80% URL (0.350 ppm to 0.420 ppm). This concentration is used to validate data back to the most recent audit or calibration. See Chapter 11, Valid Data Requirements, in this manual for the details of data validation.

The second biweekly audit point consists of an NO<sub>2</sub> concentration in the required range of 0.08 ppm to 0.10 ppm. This second audit point is used to assess the precision of the data based on a quarterly calculation.

The same GPT blending system used to calibrate the analyzer may be used to perform the biweekly audit on the analyzer. It is suggested (but not required) that the auditor be different from the person who performed the calibration.

Table 3 (page 38) shows the required ranges for NO<sub>2</sub> precision and accuracy audit concentrations.

Record all information below on the NO<sub>2</sub> audit form or equivalent. See Form 5.

**NOTE: MAKE NO ADJUSTMENTS TO THE ANALYZER PRIOR TO THE AUDIT.**

**Form 5**  
**NO<sub>x</sub> Audit Form**

Site Name \_\_\_\_\_ Site \_\_\_\_\_  
AQS# \_\_\_\_\_ Auditor \_\_\_\_\_ Date \_\_\_\_\_

Last Audit \_\_\_\_\_ Temp \_\_\_\_\_ °C  
Audit Start Time \_\_\_\_\_ Audit End Time \_\_\_\_\_  
Analyzer Brand/Model/SN \_\_\_\_\_  
Cal. Date \_\_\_\_\_ Range \_\_\_\_\_  
TECO: C.E. \_\_\_\_\_ S.F. \_\_\_\_\_ B.F. \_\_\_\_\_ VAC: \_\_\_\_\_

Primary Recorder/Range \_\_\_\_\_ Secondary Recorder/Range \_\_\_\_\_  
DVM/Range \_\_\_\_\_

Audit Std. Brand/Model/SN \_\_\_\_\_ Cert Date \_\_\_\_\_  
Flow Meter Cert. Date \_\_\_\_\_ Cyl. SN \_\_\_\_\_ Cyl. Conc. \_\_\_\_\_ Cyl. PSI \_\_\_\_\_

Zero Response(s) NO<sub>2</sub> Prim \_\_\_\_\_ Sec \_\_\_\_\_ DVM \_\_\_\_\_  
NO Prim \_\_\_\_\_ DVM \_\_\_\_\_ NO<sub>x</sub> Prim \_\_\_\_\_ DVM \_\_\_\_\_

Validation Point Std. NO Conc. \_\_\_\_\_  
Response(s) NO Prim \_\_\_\_\_ DVM \_\_\_\_\_ Meas. NO Conc. \_\_\_\_\_ NO % Diff \_\_\_\_\_  
NO<sub>x</sub> Prim \_\_\_\_\_ DVM \_\_\_\_\_ Meas. NO<sub>x</sub> Conc. \_\_\_\_\_ NO<sub>x</sub> % Diff \_\_\_\_\_

O<sub>3</sub> Setting \_\_\_\_\_ NO<sub>2</sub> GPT Response Prim. \_\_\_\_\_ Sec. \_\_\_\_\_ DVM \_\_\_\_\_  
NO GPT Remaining Prim. \_\_\_\_\_ DVM \_\_\_\_\_ Conc.(.08-.12) \_\_\_\_\_  
Meas. NO<sub>2</sub> Conc. \_\_\_\_\_ Std. NO<sub>2</sub> Conc. (.35-.45) \_\_\_\_\_ NO<sub>2</sub> % Diff \_\_\_\_\_

Precision Point Std. NO Conc. \_\_\_\_\_  
Response(s) NO Prim \_\_\_\_\_ DVM \_\_\_\_\_ Meas NO Conc. \_\_\_\_\_ NO %  
Diff \_\_\_\_\_  
NO<sub>x</sub> Prim. \_\_\_\_\_ DVM \_\_\_\_\_ Meas NO<sub>x</sub> Conc. \_\_\_\_\_ NO<sub>x</sub> % Diff \_\_\_\_\_

O<sub>3</sub> Setting \_\_\_\_\_ NO<sub>2</sub> GPT Response Prim. \_\_\_\_\_ Sec. \_\_\_\_\_ DVM \_\_\_\_\_  
NO GPT Remaining Prim. \_\_\_\_\_ DVM \_\_\_\_\_ Conc.(.08-.12) \_\_\_\_\_  
Meas NO<sub>2</sub> Conc. \_\_\_\_\_ Std. NO<sub>2</sub> Conc.(.08-.10) \_\_\_\_\_ NO<sub>2</sub> % Diff \_\_\_\_\_

Remarks: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

The field audit procedure is as follows:

1. Record the station name and the AQS site identification number on the NO<sub>2</sub> audit form.
2. Identify the person performing the audit (initials), and record the audit date.
3. Record the analyzer's operational period (date and time). The operational period is defined as the period of time starting from the last audit or calibration (date and time) to the current audit (date and time).
4. Record the analyzer's manufacturer name, model number, and serial number.
5. Record the analyzer's settings: range, flows, vacuum, etc.

**NOTE:** It is a good idea to inspect the analyzer before the start of the field audit. For example: Check to see that the analyzer is in the monitor mode; the sample line is connected to the sample manifold or outside sample line; the analyzer is connected to the data recording device(s); and if there are any other conditions that could affect the data or the field audit results.

6. Record the analyzer's last calibration date. Analyzers must be calibrated at least every six months.
7. Record the audit device manufacturer name, model number, and serial number.
8. Record the NO audit gas cylinder number, certified concentration, and certification date.

**NOTE: DO NOT USE CYLINDERS WITH PRESSURES < 200 PSIG.**

**GASES MAY BECOME UNSTABLE AT LOW PRESSURES AND CAUSE AUDIT ERRORS.**

**BE SURE THAT THE AUDIT GPT BLENDER AND GAS HAVE A CURRENT CERTIFICATION BEFORE PROCEEDING.**

9. Record the zero and span potentiometer settings. Analyzer controls will vary with each manufacturer's brand and model. Some analyzers will have only one zero or span potentiometer while other brands may have zero and span potentiometers for each of the NO, NO<sub>2</sub>, and NO<sub>x</sub> (NO<sub>y</sub>) channels. Microprocessor controlled analyzers have no potentiometers but will have readings which correspond to the zero and span pot settings.
10. Indicate the analyzer's primary and secondary recording device. If a digital voltmeter (DVM) is to be used during the audit then indicate this on the audit form.
11. Confirm that the analyzer is connected to a recording device such as: a data acquisition

system (DAS), a strip chart recorder, and/or a digital voltmeter. Since the analyzer will have three output voltage connections (for NO, NO<sub>2</sub>, and NO<sub>x</sub> (NO<sub>y</sub>)), label or be able to differentiate between the three outputs.

12. Adjust the flow of the diluent air (zero air) on the audit device so that its total output flow exceeds the total demand of the analyzer by at least 25%.

See Section 5.3 for example calculations.

13. Connect the analyzer's "sample in" port to the "sample out" port of the audit device using a vented nonreactive (TFE Teflon) sample line/manifold. For the NO<sub>y</sub> hookup, one line goes to the converter while one bypasses the converter.

**NOTE: Logon and annotate all data recording devices (data acquisition system, strip chart recorder, etc.) with the audit starting date, site, parameter, initials, and time.**

**WARNING: THE SAMPLE GAS MUST BE DELIVERED TO THE ANALYZER AT ATMOSPHERIC PRESSURE. A MANIFOLD OR TEE VENT MUST BE USED FROM THE AUDIT DEVICE SO THAT EXCESS SAMPLE FLOW CAN BE BLED OFF. AN UNVENTED SAMPLE GAS COULD PRESSURIZE & DAMAGE THE ANALYZER. FOR THE NO<sub>y</sub> AUDIT HOOKUP, NO MANIFOLD OR TEE VENT IS USED.**

14. Allow the analyzer to sample zero air until NO, NO<sub>2</sub>, and NO<sub>x</sub>, and responses stabilize (usually 10 to 20 minutes). Record the analyzer responses to zero air on the audit form.
15. Attach a stainless steel regulator to the NO audit cylinder. Refer to Section 7.0 for the regulator purge procedure.

**NOTE: THE REGULATOR MUST BE PURGED OF ALL AIR BEFORE PROCEEDING WITH THE AUDIT. ATMOSPHERIC O<sub>2</sub> IN THE REGULATOR WILL REACT WITH THE NO AND FORM UNWANTED NO<sub>2</sub> IN THE GAS STREAM.**

16. For the data validation concentration, adjust the NO flow from the audit GPT blending system to generate a concentration of approximately 90% of the upper range limit (URL) of the NO channel. An NO concentration in the 0.430 ppm to 0.470 ppm range is suggested; however, this point should be within the calibration curve of the analyzer.
17. Calculate the exact NO concentration [NO]<sub>out</sub> using Equation 5-3. Record this concentration under Std. NO Conc. on the audit form. Also record the audit setting, gas flow, and total flow.

See Section 5.3 for Equation 5-3 and example calculations.

18. After the analyzer responses have stabilized, record the responses as Response NO, Primary/DVM and Response NO<sub>x</sub> (NO<sub>y</sub>), Primary/DVM on the audit form.

19. Using the analyzer's respective NO/NO<sub>x</sub> (NO<sub>y</sub>) current calibration slopes and zero responses with Equation 5-6, convert the Response NO, Primary and Response NO<sub>x</sub>, Primary to concentrations (ppm).

Record the respective concentrations as Meas. NO Conc. and Meas. NO<sub>x</sub> Conc.

See Section 5.3 for Equation 5-6 and example calculations.

**NOTE:** The standard concentration (NO Std. Conc.) is defined as [NO]<sub>out</sub> calculated from Equation 5-3. The observed concentration (obsv. conc. or meas. conc.) is defined by Equation 5-6.

**NOTE: IF THE MONITOR RESPONSE EXHIBITS A VERY SLOW RESPONSE TO THE FIRST NO CONCENTRATION, THERE MAY STILL BE SOME RESIDUAL O<sub>2</sub> CONTAMINATION IN THE NO REGULATOR. REPURGE THE REGULATOR, SEE SECTION 7.0.**

20. Calculate and record the percent difference (% diff.) between the standard concentration (Std. Conc.) and observed concentration (Meas. Conc.) for the NO and NO<sub>x</sub> (NO<sub>y</sub>) channels. See Equation 5-7 for the % diff. calculation.
21. The results of the NO and NO<sub>x</sub> (NO<sub>y</sub>) channel audits will determine one of following outcomes:
  - a. If the percent difference for the NO and NO<sub>x</sub> (NO<sub>y</sub>) validation audit is within ±10%, the collected data is valid.
  - b. If the percent difference for the NO and NO<sub>x</sub> (NO<sub>y</sub>) validation audit is greater than ±10%, then the network operator must be informed that the analyzer is out of calibration. The data collected since the last audit or calibration may be invalid based on further investigation but a recalibration must be done as soon as possible. The NO<sub>2</sub> part of the audit should still be performed.
21. For the NO<sub>2</sub> data validation concentration, adjust the O<sub>3</sub> generator on the audit GPT blending system to produce a NO remaining [NO]<sub>rem</sub> in the 0.08 to 0.12 ppm range. NO concentrations substantially higher than 0.08 ppm may lead to evaluation errors in chemiluminescence analyzers due to inevitable minor NO-NO<sub>x</sub> channel imbalance. These errors may be minimized by modifying the GPT technique to lower the NO remaining in the NO<sub>2</sub> audit gas to levels closer to typical ambient NO concentrations at the site.

An NO<sub>2</sub> analyzer response of approximately 80% of the URL should be produced.

**NOTE: THE CODE OF FEDERAL REGULATIONS (40 CFR 58 APPENDIX A) REQUIRES A RESIDUAL NO CONCENTRATION, [NO]<sub>REM</sub>, DURING THE**

**TITRATION OF ALL NO<sub>2</sub> AUDIT CONCENTRATIONS. THIS RESIDUAL MUST BE IN THE RANGE OF 0.08 ppm TO 0.12 ppm.**

23. After the analyzer responses have stabilized, record the NO REMAINING and NO<sub>2</sub> RESPONSE readings from the primary, secondary, and DVM recording devices. Also, record the O<sub>3</sub> SETTING on the audit device.
24. Calculate and record the standard NO<sub>2</sub> concentration [NO<sub>2</sub>]<sub>STD</sub> using Equation 5-11.

**Equation 5-11:**

$$[\text{NO}_2]_{\text{std}} = \frac{(\text{NO}_{\text{orig}} \text{ response} - \text{NO}_{\text{rem}} \text{ response}) \times [\text{NO}]_{\text{orig}}}{\text{NO}_{\text{orig}} \text{ response} - \text{NO zero response}}$$

Where: NO<sub>orig</sub> = the monitor response in % chart, millivolts or volts before O<sub>3</sub> titration  
NO<sub>rem</sub> = the monitor response in % chart, millivolts or volts after O<sub>3</sub> titration  
[NO]<sub>orig</sub> = the original NO concentration (ppm) before O<sub>3</sub> titration

**Example calculation using Equation 5-11:**

Where: NO<sub>orig</sub> = 0.947 volt  
NO<sub>rem</sub> = 0.171 volt  
NO zero response = 0.007 volt  
[NO]<sub>orig</sub> = 0.472 ppm  
[NO<sub>2</sub>]<sub>std</sub> =  $\frac{(0.947 \text{ volt} - 0.171 \text{ volt}) \times 0.472 \text{ ppm}}{0.947 \text{ volt} - 0.007 \text{ volt}}$   
[NO<sub>2</sub>]<sub>std</sub> =  $\frac{0.776 \text{ volt} \times 0.472 \text{ ppm}}{0.940 \text{ volt}} = 0.390 \text{ ppm}$

25. Calculate the observed or measured concentration (obsv. conc./meas. conc.) of NO<sub>2</sub> and the analyzer's current slope for the NO<sub>2</sub> channel. Use Equation 5-6 (Page 17). Record the analyzer's NO<sub>2</sub> response and the analyzer's NO<sub>2</sub> zero response on Form 5.

**Example calculation:**

Where: NO<sub>2</sub> response = 0.776 volt  
NO<sub>2</sub> zero response = 0.006 volt  
NO<sub>2</sub> calibration slope = 0.5  
obsv. conc. = (0.776 volt - 0.006 volt) x 0.5  
obsv. conc. = 0.770 volt x 0.5 = 0.385 ppm

26. Calculate and record the percent difference (% diff.) between the [NO<sub>2</sub>] observed concentration (obsv. conc.) and the [NO<sub>2</sub>] standard concentration (std. conc.). Use

Equation 5-7.

**NOTE: BECAUSE P&A DATA IS REPORTED TO THE NEAREST TENTH OF A PERCENT, THE % DIFF. SHOULD BE ROUNDED TO THE NEAREST TENTH OF A PERCENT (X.X).**

27. The results of the NO<sub>2</sub> channel audit will determine one of the following outcomes:
- If the percent difference for the NO<sub>2</sub> validation audit is within  $\pm 10\%$ , the collected data is valid.
  - If the percent difference for the NO<sub>2</sub> validation audit is greater than  $\pm 10\%$ , then the network operator must be informed that the analyzer is out of calibration. The data collected since the last audit or calibration may be invalid based on further investigation but a recalibration must be done as soon as possible. The NO<sub>2</sub> quality control (precision) audit should still be performed
28. For the NO<sub>2</sub> precision point, adjust NO flow on the audit GPT blending system to obtain an NO concentration ( $[\text{NO}]_{\text{orig}}$ ) in the range of 0.17 ppm to 0.20 ppm. This NO concentration will allow the titration of an NO<sub>2</sub> concentration in the 0.08 ppm to 0.10 ppm range.

See Table 4 for a list of NO and NO<sub>2</sub> titration ranges.

See Section 5.3 for NO flow equations and calculation examples.

Remember, during titration a residual of 0.08 to 0.12 ppm of NO is required.

Before performing a field audit with a particular audit GPT blending system, it is a good idea (and time saver) to know the general flow and ozonator settings for each audit concentration.

29. After the NO response has stabilized, titrate an NO<sub>2</sub> concentration in the 0.08 ppm to 0.10 ppm range.

Repeat steps in Section 8.3, Steps 23 to 26 to complete the audit.

30. The results of the NO<sub>2</sub> channel audit will determine one of the following outcomes:
- If the percent difference for the NO/NO<sub>x</sub> and NO<sub>2</sub> precision audit is within  $\pm 15\%$ , the collected data is valid.
  - If the percent difference for the NO/NO<sub>x</sub> and NO<sub>2</sub> precision audit is greater than  $\pm 15\%$ , then the network operator must be informed that the analyzer is out of calibration. The data collected since the last audit or calibration may be invalid based on further investigation but a recalibration must be done as soon as possible.

31. After the audit has been completed (biweekly or accuracy), perform the following:
- Reconnect the analyzer's sample line to the outside sample line or manifold.
  - Ensure that the analyzer is in the monitor mode and has its normal flow.
  - Ensure that the data recording devices are connected to the analyzer and are registering a signal.
  - Logoff and annotate all data recording devices with the ending time of the audit, the initials of the auditor, and the results of the audit (% diff.).
  - For a strip chart recorder be sure to indicate on the chart: site name, audit starting and ending date/time, zero response, upscale responses for standard concentrations, the parameter, and the auditor's initials.
  - Record all applicable information in the site logbook: include at least the audit date, the initials of the auditor, the type of audit (validation/precision and/or accuracy), and the results of the audit (% diff.).

**NOTE:** Residual NO and NO<sub>2</sub> trapped in a calibrator can cause stability problems during the next audit. It is a good idea to purge the audit device with zero air for a few minutes after each audit is completed.

#### **8.4 Accuracy Audits**

Accuracy audits must be performed on at least 25% of the network's analyzers each calendar quarter. At the end of the year, all analyzers must have had an accuracy audit. Networks which have 4 or fewer analyzers must conduct accuracy audits so that all analyzers have had an accuracy audit by the end of the year. Accuracy would then be calculated in the 2nd and 4th quarters of the year. Since this is a statistical assessment of the data's accuracy, it is suggested that accuracy audits be conducted more often than once per quarter (i.e., monthly). This ensures a larger and more representative database for the accuracy calculations.

The Federal Register requires that a different audit GPT blender and gas standard from that of the calibrator used for the calibration be used to perform the accuracy audit. The auditor should also be different from that of the person who performed the calibration.

The analyzer must be collecting valid data on all channels (NO, NO<sub>2</sub>, or NO<sub>x</sub> (NO<sub>y</sub>) ≤ ±15% for the data validation concentration) in order to conduct an accuracy audit.

**Table 3**  
**Required (Code of Federal Regulations) Concentrations for Precision and Accuracy**

Level	NO <sub>2</sub> Accuracy Audit Concentrations (ppm)
1	0.0003 to 0.0029
2	0.0030 to 0.0049
3	0.0050 to 0.0079
4	0.0080 to 0.0199
5	0.0200 to 0.0499
6	0.0500 to 0.0999
7	0.1000 to 0.2999
8	0.3000 to 0.4999
9	0.5000 to 0.7999
10	0.8000 to 1.0000

NO<sub>2</sub> precision range: 0.0800 to 0.1000 ppm

**NOTE: IF ANY CHANNEL (NO, NO<sub>x</sub> (NO<sub>y</sub>) OR NO<sub>2</sub>) HAS A DATA VALIDATION % DIFF. > 15%, DO NOT CONDUCT THE ACCURACY AUDIT.**

Follow steps 1 to 26 and 30 of Section 8.3 for the accuracy audit.

## **9.0 Data Reduction and Reporting**

The annual primary standard is met when the annual average concentration in a calendar year is less than or equal to 0.0530 ppm, as determined in accordance with 40 CFR Part 50 Appendix S for the annual primary standard.

The 1-hour primary standard is met when the three-year average of the annual 98th percentile of the daily maximum 1-hour average concentration is less than or equal to 0.1000 ppm, as determined in accordance with 40 CFR Part 50 appendix S for the 1-hour primary standard.

The secondary standard is attained when the annual arithmetic mean concentration in a calendar year is less than or equal to 0.0530 ppm, rounded to three decimal places (fractional parts equal to or greater than 0.0005 ppm must be rounded up). To demonstrate attainment, an annual mean must be based upon hourly data that are at least 75 percent complete or upon data derived from manual methods that are at least 75 percent complete for the scheduled sampling days in each calendar quarter.

The continuous data produced for entry into the National Air Quality System (AQS) data bank must be reduced to 24 1-hour averages per day. This reduction must follow the guidelines and requirements set forth in Chapter 12 of this manual.

Although not specified as criteria pollutants, NO and NO<sub>x</sub> (NO<sub>y</sub>) data should also be submitted to IDEM. NO and NO<sub>x</sub> (NO<sub>y</sub>) data may be validated through biweekly audits but precision and accuracy audits are not required for this data.

Data should be submitted to the IDEM Ambient Monitoring Section within 60 days after the end of the quarter. This will allow sufficient time for review before AQS submittal deadlines of 90 days after the end of each reporting calendar quarter, although AQS data submittal of less than 60 days is encouraged.

## **10.0 Routine Station Operations**

Essential to a good quality assurance program are scheduled checks for verifying the operation of the monitoring system. At least once per week, an operator should visit each site in order to evaluate operating conditions and to perform routine maintenance.

Conducting routine site/analyzer checks and taking prompt corrective actions for any problems will minimize the loss of data. The results of any of the checks below can directly affect the validity of the data.

### **10.1 Station Checks**

All sites should have a bound logbook in which site checks, analyzer maintenance/checks, and audit information can be recorded.

1. The average shelter temperature should range from 20 °C to 30 °C (68 °F to 86 °F). A certified thermograph or other temperature recording device must be installed to continuously monitor the site temperature fluctuations as per 40 CFR Part 53.31(1). Data may be invalidated by the IDEM-QAS any time the shelter temperature is out of the 15 °C to 33 °C (59.0 °F to 91.4 °F) range.
2. The sample manifold/blower or lines should be inspected weekly for cleanliness, leaks, and obstructions.
3. The exterior sample line, candy cane, and funnel should be inspected weekly for cleanliness, breaks, and obstructions.
4. All data recording devices should be inspected for ink trace or printout legibility, paper supply, and correct time (or time synchronization).

For those counties in Indiana which change time in the spring and in the fall, do not change the time on the data recording devices. **All data recording devices remain on the same time year-round (standard time).**

5. Record all station activities/checks in the site logbook.

## 10.2 Analyzer Checks

1. All analyzers must be equipped with an inlet particulate filter assembly. Check the analyzer's manual for the recommended filter pore size. Usually a 5 micron pore size, 47 millimeter diameter, nonreactive round filter is used.

The inlet particulate filter must be changed at least every three weeks. A clean filter will minimize the reaction and loss of the NO<sub>2</sub> in the sample air with particulate matter on the filter. After installing a clean filter, be sure to tightly reassemble the inlet filter holder in order to prevent leaks.

2. NO/NO<sub>2</sub>/NO<sub>x</sub> or NO/NO<sub>2</sub>/NO<sub>y</sub> analyzers use desiccant columns for the drying of the air drawn into the analyzer's ozonator.

Two desiccant columns connected in series must be used on each analyzer. An indicating (color change) type desiccant is used in the columns. This indicating desiccant can consist of either silica gel or anhydrous CaSO<sub>4</sub> (drierite).

The desiccant columns should be inspected weekly for any color change. The first column (farthest from the analyzer) should be changed whenever the desiccant has changed color (color change indicates that the column is no longer removing moisture).

Humid conditions, especially in the summer months, will require more frequent changing of the columns.

**NOTE: ALWAYS USE TWO COLUMNS IN SERIES AND NEVER LET THE INNER COLUMN BECOME EXPENDED.**

**EXPENDED DRYER COLUMNS WILL CAUSE THE ANALYZER TO BE OUT OF CALIBRATION.**

**EXPENDED DRYER COLUMNS CAN CAUSE AS MUCH AS A 25% CALIBRATION ERROR, RESULTING IN LOW NO<sub>2</sub> VALUES.**

3. Check weekly and record, in the site log, analyzer flow rates and vacuum readings. Readings should correspond to those from the last calibration.
4. Check weekly and record, in the site log, the zero and span potentiometer settings. Readings should correspond to those from the last calibration.

5. Verify that the analyzer is in the monitor mode and that it is connected to and providing a signal to the primary and secondary data recording devices.
6. Some analyzer models have extensive diagnostic tests and some of these tests may need to be conducted weekly. Check the site logbook and conduct any indicated tests.
7. Routine maintenance must also be performed on all analyzers. Consult the analyzer's equipment manual for specific requirements and frequencies that indicate what maintenance must be performed and how often. A schedule of routine maintenance should be made and followed. Some maintenance items common to most analyzers are:
  - a. sample pump
  - b. catalytic converter
  - c. interior filters/screens (cleaning or replacement)
  - d. cooling fan (cleaning and lubrication)
  - e. charcoal scrubber column (replacement)

**NOTE: VENT ALL ANALYZER EXHAUST GAS TO THE OUTSIDE.**

Some analyzers produce high levels of ozone which first must be scrubbed with an activated charcoal column and then vented to the outside.

### **10.3 Zero/Span/One-Point Quality Control Check**

1. Daily zero and span checks are ran. These checks are used to catch analyzer drift and to help determine data validation. These quality control measures are intended to further ensure high quality monitoring data and to prevent unnecessary data loss. Once a week, a one-point quality control check (precision audit) is done along with the daily zero and span check. Currently, all continuous NO/NO<sub>2</sub>/NO<sub>x</sub> analyzers are routinely audited remotely through the LEADS. The zero, span and precision one-point quality control check are scheduled by the OAQ/AMS/LEADS Administrator and are set to run at midnight when ambient NO<sub>2</sub> levels could be expected to be at a low. The span concentration is .400 ppm NO<sub>2</sub> and the precision level check is .090 ppm NO<sub>2</sub>. For data validation, the span check must be  $\leq \pm 10\%$ , and the precision one-point quality control check must be  $\leq \pm 15\%$ ; if not, determine if maintenance is needed and then run a multi-point calibration. Zero drift should be  $\leq \pm 3.0$  ppb for a 24 hour period and  $\leq \pm 5.0$  ppb if greater than 24 hours up to 14 days.

On-site manual precision audits may be conducted by IDEM quality assurance staff on an as needed basis such as:

- LEADS communication malfunction

- Unstable or failing remote audit results.

Zero air and an NO<sub>2</sub> concentration that is 70% to 90% of the analyzer's range should be run each day. Those equipped with zero/span options can be set up to automatically cycle through the zero/span check each day.

For analyzers which are equipped with a daily zero and span device, check and record, in the site logbook, the most recent zero and span. Compare the most recent readings with the log entries for any zero or span drift. Dramatic shifts in zero and/or spans may require a recalibration of the analyzer.

**NOTE: VENT ALL GPT BLENDERS (CALIBRATORS) AND ZERO/SPAN DEVICES TO THE OUTSIDE. UNVENTED UNITS CAN CAUSE THE BUILDUP OF UNHEALTHY CONCENTRATIONS OF NO/NO<sub>2</sub> AT THE SITE.**

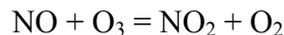
Exhaust gases must be run first through an activated charcoal column before venting to the outside.

2. For analyzers not equipped with a daily zero and span device, perform a zero check at least once every two weeks.

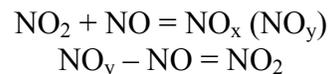
An activated charcoal column with an NO catalyst can be used to produce the zero air. Because charcoal will not remove NO, a catalyst such as Purafil is required to convert NO to NO<sub>2</sub>. The charcoal will then remove the NO<sub>2</sub>.

## 11.0 Equations

### Equation 5-1 - Chemiluminescent & Titration Method:



### Equation 5-2 - Analyzer Measurement Principle:



### Equation 5-3 - NO Concentration from the Calibrator:

$$[\text{NO}]_{\text{out}} = \frac{F_{\text{NO}} \times [\text{NO}]_{\text{std}}}{F_{\text{NO}} + F_{\text{d}} + F_{\text{o}}}$$

**Equation 5-4 - NO<sub>x</sub> Concentration from the Calibrator:**

$$[\text{NO}_x]_{\text{out}} = \frac{F_{\text{NO}} \times [\text{NO}]_{\text{std}}}{F_{\text{NO}} + F_d + F_o}$$

**Equation 5-5 - Desired Recorder Response:**

$$\text{Desired Recorder Response (\% of scale)} = \frac{([\text{NO}]_{\text{out}} \times 100) + Z_{\text{NO}}}{\text{URL}}$$

**Equation 5-6 - Observed (Measured) Concentration from the Calibration Curve (Slope):**

$$\text{obsv. conc.} = (\text{mon. res.} - \text{mon. zero resp.}) \times \text{slope}$$

**Equation 5-7 - Percent Difference between the observed and standard concentrations:**

$$\% \text{ diff.} = \frac{\text{obsv. conc.} - \text{std. conc.}}{\text{std. conc.}} \times 100$$

**Equation 5-8 - Standard Concentration of NO<sub>2</sub> from the Calibrator:**

$$[\text{NO}_2]_{\text{out}} = [\text{NO}]_{\text{orig}} - [\text{NO}]_{\text{rem}}$$

**Equation 5-9 - Concentration of NO<sub>2</sub> Converted:**

$$[\text{NO}_2]_{\text{converted}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_y]_{\text{orig}} - [\text{NO}_y]_{\text{rem}})$$

**OR**

$$[\text{NO}_2]_{\text{converted}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_x]_{\text{orig}} - [\text{NO}_x]_{\text{rem}})$$

**Equation 5-10 - Percent Converter Efficiency:**

$$\text{Percent Converter Efficiency} = \text{slope} \times 100$$

**Equation 5-11 - Standard Audit NO<sub>2</sub> Concentration:**

$$[\text{NO}_2]_{\text{std}} = \frac{(\text{NO}_{\text{orig}} \text{ response} - \text{NO}_{\text{rem}} \text{ response}) \times [\text{NO}]_{\text{orig}}}{\text{NO}_{\text{orig}} \text{ response} - \text{NO zero response}}$$

**12.0 Requirements and Definitions**

1. Analyzers must be recalibrated at least once every 6 months. A minimum of 4 upscale concentrations plus a zero is required for a valid calibration.

2. A valid calibration requires all calibrations points to be within  $\pm 2\%$  of the full range of the analyzer (e.g., if the range is 0.5 ppm, then the measured values must be within  $\pm 0.010$  ppm of the standard. Therefore, if the standard value introduced into the analyzer is 0.400 ppm, the measured value must be between 0.390 and 0.410 ppm).
3. The analyzer converter efficiency must be  $\geq 96\%$ .
4. GPT portable gas blenders and NO gas cylinders must be certified by IDEM-QAS at least once every 6 months. Stationary blending systems must be certified by the QA Lab annually. This includes the certification of any mass flow meters used with the calibration or auditing device.
5. Data validation and precision audits are conducted at a minimum on each analyzer once every two weeks (biweekly).

The data validation audit concentration should be between 70% and 90% of the analyzer's range. The precision audit concentration must be in the range of 0.08 ppm to 0.10 ppm.

6. The percent difference data validation limits for the accuracy audit are:
  - a.  $< \pm 7.5\%$  --- The analyzer is in calibration and data is valid.
  - b.  $\leq \pm 15\%$  and  $\geq \pm 7.5\%$  --- The analyzer is out of calibration but data is valid.
  - c.  $> \pm 15\%$  --- The analyzer is out of calibration and data is invalid.
  - d. Audit levels 1&2 allow  $\pm 1.5$  ppb difference or  $\pm 15\%$ .
7. The percent difference for the validation(span) is  $\pm 10\%$  and the precision point is  $\pm 15\%$ .
8. The drift limits are  $\leq \pm 3.0$  ppb (24 hr) and  $\leq +5.0$  ppb (>24 hr-14 day) for the zero and  $\leq \pm 10\%$  for the span.

During the NO<sub>2</sub> upscale audit values, residual NO in the range of 0.08 ppm to 0.12 ppm is required for non-LEADS. For LEADS, a residual NO of 0.07 ppm is acceptable. See page 8-14 of the LEADS Manual.

9. Accuracy audits must be performed on at least 25% of the analyzers in the network for each calendar quarter. For networks with four or fewer analyzers, an accuracy audit must be performed on each analyzer so that by the end of the year all analyzers have received one accuracy audit. Accuracy would then be calculated and reported in the 2nd and 4th quarters of the year. The QA section recommends that one accuracy audit on each analyzer be conducted every quarter. The accuracy audit will include NO<sub>2</sub> concentrations in the following ranges:
  - a. 0.0500 to 0.0999 ppm (Level 6)

- b. 0.1000 to 0.2999 ppm (Level 7)
- c. 0.3000 to 0.4999 ppm (Level 8)