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Quality Assurance Guidance Document 2.3

Reference Method for the Determination of Nitrogen Dioxide in the Atmosphere (Chemiluminescence)

Outline

Introduction

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

The NO and the NO plus NO_2 measurements may be made either concurrently with a dual channel detection system or cyclically with a single channel system as long as the cycle time is not greater than 1 minute.

The U.S. Environmental Protection Agency (EPA) reference method for the determination of nitrogen dioxide in the atmosphere (EPA 1997c) and the technical assistance document (TAD) for this method (Ellis 1976) were used extensively for the method description. The EPA quality assurance requirements for state and local air monitoring stations (EPA 1994b) was used in the development of effective quality assurance procedures.

Method Highlights

In this quality assurance guidance document for the NO_2 reference method, the procedures are designed to serve as guidelines for the development of agency quality assurance programs. Because recordkeeping is a critical part of quality assurance activities, several data forms are included to aid in the documentation of necessary data. Partially filled-in forms are interspersed throughout the text of the method description to illustrate their uses. Activity matrices at the end of pertinent sections can be used for quick review of the material covered in the text sections. Following is a brief summary of the material covered in this NO_2 method description.

1. Procurement of Equipment

Section 1.0 gives the specifications, criteria, and design features of the equipment and material required for the operation and quality assurance of a chemiluminescent NO_X analyzer. The selection of the correct equipment and supplies is a prerequisite to a quality assurance program. This section is designed to provide a guide for the procurement and initial check of equipment and supplies.

2. Calibration of Equipment

Section 2.0 provides procedures and forms to be used in selecting and checking calibration equipment, performing a multipoint calibration, and evaluating calibration data. Sections 2.1, 2.2, and 2.3 primarily address minimum acceptable requirements for equipment and standards to be used in the generation of NO_2 concentrations. Detailed procedures for the acceptance of gas-phase titration (GPT) calibrators are also given. Section 2.4 provides a step-by-step description of the recommended calibration procedures for a chemiluminescent NO_X analyzer along with example calculations. The data form (Figure 2.2 of Section 2.4.2) is to be used for documenting calibration data. The primary element of quality control is dynamic instrument calibration.

3. Operation and Procedure

Section 3.0 outlines the protocol to be followed by the operator during each site visit. Checks should include visual inspection of the shelter, sample introduction system, analyzer, and recorder. In addition, analyzer performance checks consisting of zero, span, and precision points are to be made. To provide for documentation and accountability of activities, a checklist similar to the example provided in Figure 3.1 of Section 3.0 should be compiled and then filled out by the field operator as each activity is completed. Analyzer Level 1 zero and span checks must be carried out at least once every 2 weeks. Level 2 zero and span checks should be conducted in between the Level l checks at a frequency desired by the user. Span concentrations for both levels should be between 70 and 90% of the measurement range. A one-point precision check is to be done every 2 weeks at an NO_2 concentration between 0.08 and 0.10 ppm. Data forms similar to Figures 3.2 and 3.3 of Section 3.0 are to be used in documenting the analyzer performance checks. An essential part of the quality assurance program is a scheduled series of checks for the purpose of verifying the operational status of the monitoring system.

4. Data Reduction

Section 4.0 describes procedures to be used for editing of strip charts and for manual data reduction. Data collected on strip charts serve no useful function until converted into meaningful units (parts per million [ppm] or micrograms per cubic meter [$\mu g/m^3$]) by hourly averaging and application of a calibration relationship. These data must then be transcribed into a format that is appropriate for input into EPA's Aerometric Information Retrieval System Air Quality System (AIRS AQS). Information about the format is contained in the AIRS user's guide for air quality data coding (EPA 1995). Updates about the format may be found on the AIRS World Wide Web site (www.epa.gov/ttn/airs/).

5. Maintenance

Section 5.0 addresses recordkeeping and scheduled activities pertinent to preventive and corrective maintenance. An example operation checklist and maintenance record appears in Figure 3.1 of Section 3.0. Preventive and corrective maintenance are necessary to minimize loss of air quality data due to analyzer malfunctions and out-of-control conditions.

6. Assessment of Data for Accuracy and Precision

Section 6.0 discusses system and performance audits along with audit procedures and forms. Accuracy of data is assessed by performing an independent audit.

Multipoint performance audits used to assess the accuracy of the data collection are discussed in Section 6.1. Examples of an audit summary form and audit calculation forms are presented in Figures 6.1 through 6.3. A data reduction audit is discussed in Section 6.2, and a systems audit in Section 6.3. Figure 6.4 presents an example checklist that may be used by the auditor.

Section 7.0 describes the techniques for assessment of monitoring data for accuracy and precision.

7. Reference Information

Section 8.0 discusses the traceability of measurements to established standards of higher accuracy, a necessary prerequisite for obtaining accurate data.

Section 9.0 contains pertinent references.

1.0 Procurement of Equipment and Supplies

The measurement of NO_2 in ambient air requires basic sampling equipment and other supplies. These include, but are not limited to, the following:

1. Chemiluminescent NO_X analyzer conforming to EPA specifications (see Section 1.1 for a World Wide Web address for obtaining an up-to-date list of analyzers)
2. Strip chart recorder or data acquisition system (DAS)
3. Sampling lines
4. Sampling manifold
5. Calibration equipment
6. National Institute of Standards and Technology Standard Reference Material® (NIST-SRM)
7. Gaseous calibration standard (compressed gas mixture or permeation tube) traceable to NIST
8. Zero air
9. Spare parts
10. Record forms
11. Independent performance audit equipment.

Purchases of these supplies should be recorded in a log book to provide a reference for future procurement needs and for future fiscal planning. An example of this log is Figure 1.1. Quality assurance activities for procurement of apparatus and supplies are summarized in Table 1-1.

Item	**Description**	**Qty**	**PO #**	**Vendor**	**Date**		**Cost**	**Initials**	**Accept/ Reject**	**Comments**
					Ord.	**Rec'd**				
ONA-2	Oxides of nitrogen analyzer	1	01579	ACME	3-27-00	5-13-00	$10,000	ABC	Accept	None

Figure 1.1. Example of a procurement log.

TABLE 1-1. ACTIVITY MATRIX FOR PROCUREMENT OF EQUIPMENT AND SUPPLIES

Equipment/Supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Chemiluminescent NO_x analyzer	Meets performance specifications of EPA regulations for reference and equivalent methods	Manufacturer should provide a report of the specific analyzer's performance; reverify performance specifications at initial calibration	Manufacturer should make proper adjustments and rerun the performance check
Data acquisition system	Input voltage range compatible with output signal for analyzer, input resolution $\geq$1024, sampling date $\leq$1 minute	Check upon receipt	Return equipment to supplier
Sample lines and manifold	Constructed of Teflon® or glass	Check upon receipt	Return equipment to supplier
Calibration equipment	Meets guidelines of EPA 1997c and Sec. 2.3.2	Check upon receipt	Return equipment/ supplies to supplier
Working standard NO cylinder gas or NO_2 permeation tube	Traceable to NIST; meets limits in EPA traceability protocol for accuracy and stability	Certified concentration verified using EPA traceability protocol	Obtain new working standard and check for traceability
Record forms	Develop standard forms	Not applicable	Revise forms as appropriate
Audit equipment	Must not be the same as that used for calibration	System must be checked out against known standards	Locate problem and correct or return to supplier

1.1 Chemiluminescent NO_X Analyzer

Chemiluminescent NO_X analyzers currently available for the measurement of NO_2 in ambient air are competitively priced. However, price differences do become apparent when options are ordered. Available options range from automatic zero and span functions to complete telemetry systems that transmit daily zero and span checks and real-time data from the site to a central location. Although these options have advantages, their absence from the basic monitor will not detract from performance. The necessity and desirability of options will be dictated by field personnel availability, site accessibility, and budget limitations.

Only analyzers designated by EPA as a reference or an equivalent method should be purchased. When purchasing, the buyer should request that the manufacturer supply documented proof that the analyzer does conform to EPA specifications. In addition, the user should reverify these performance characteristics either during the initial calibration or by using abbreviated forms of the test procedures provided in EPA regulations for reference and equivalent methods (EPA 1997a). Acceptance of the analyzer should be based on results from these performance tests. Once accepted, reference and equivalent analyzers are warranted by the manufacturer to operate within the required performance specifications for 1 year.

An up-to-date list of analyzers designated by EPA as reference or equivalent methods for NO_2 is available at an EPA World Wide Web site (www.epa.gov/ttn/amtic/criteria.html).

1.2 Data Acquisition System and Strip Chart Recorder

Electronic DASs are widely used and, as shown below, have many advantages over strip chart recorders.

- Accuracy. A properly operating DAS usually collects data at rates of several times per second. The 1-second values are calculated and stored until the end of the hour when the hourly NO_2 value is computed automatically. These hourly averages are more accurate than those from a strip chart because no human interpretation is involved.
- Data collection options. Instantaneous, short-term, and hourly data are collected and stored.
- Data flags. Data review parameters, such as maximum and minimum values, can be written into the software code to screen and flag suspect data.
- Long-term storage. Data can be stored indefinitely to provide a long-term storage device for many years of data.
- Spreadsheet capability. Newer systems allow calling up several parameters at one time to compare factors such as meteorological conditions by using a spreadsheet type of presentation.
- Calibration control. A DAS can control calibration equipment and record calibration data as they are being collected, making an excellent tool for use in remote locations.

Strip chart recorders are commercially available in a wide variety of prices and specifications. Factors to be considered when purchasing a recorder are:

- Compatibility with the output signal of the analyzer
- Chart width (a minimum of 15 cm [6 in.]) is recommended for the desired accuracy in data reduction
- Chart speed (at least 2.5 cm [1 in.]/h)
- Response time
- Precision and reliability
- Flexibility of operating variables (speed, range)
- Maintenance requirements.

1.3 Sampling Lines and Manifold

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

1.4 Calibration Equipment

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

1. No later than 3 months after the most recent calibration or performance audit that indicated analyzer response to be acceptable; or
2. Following any one of the activities listed below:

   - An interruption of more than a few days in analyzer operation
   - Any repairs that might affect its calibration
   - Physical relocation of the analyzer or
   - Any other indication (including excessive zero or span drift) of possible significant inaccuracy of the analyzer.

Following any of the other activities listed under Item 2 above, a Level l zero and span check should be made to determine if a calibration is necessary. If the analyzer zero and span drifts do not exceed the acceptance limits, a calibration need not be performed. See Section 12 (“Instrument Calibration and Frequency”) in Volume II, Part 1, of EPA's *Quality Assurance Handbook for Air Pollution Measurement Systems* (EPA 1998; subsequently referred to as “this handbook”). If either the zero or span drift exceed their respective acceptance limit, investigate the cause of the drift, take corrective action and calibrate the analyzer.

When purchasing or designing a calibration system, be sure that the calibration system meets the guidelines outlined in the reference method (EPA 1997c). Calibration procedures are also detailed in the TAD (Ellis 1976).

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

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

Only the first method is discussed in this document. Those wishing to use the second method should read Section 2 of the TAD. The first method requires four major components. They are:

1. NO compressed gas calibration standard
2. Stable O_3 generator
3. Source of zero air
4. GPT system.

The NO standard must be traceable to an NIST-SRM. The specific NO SRMs available from NIST are listed in the NIST-SRM catalog (NIST 1998). An acceptable protocol to demonstrate the traceability of a commercially produced NO standard to an NIST-SRM is described in the EPA traceability protocol for gaseous calibration standards (EPA 1997b).

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

The equipment needed to carry out the calibration is commercially available, or it can be assembled by the user. When purchasing a calibrator or its components, certain factors must be considered.

- Traceability of the NO standard to an NIST-SRM
- Accuracy of the flow-measuring device (e.g., rotometer, mass flowmeter, piston or soap bubble flowmeter)
- Maximum and minimum flow rates of dilution air and NO standard
- Stability of the O_3 generator
- Ease of transporting the calibrator from site to site.

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

1.5 Spare Parts and Expendable Supplies

In addition to the basic equipment discussed above, it is necessary to maintain an inventory of spare parts and expendable supplies. The manufacturer's manual contains a section describing the parts that require periodic replacement and the frequency of replacement. Based on these requirements, the management of the monitoring network can determine which parts and the quantity of each that should be available at all times. A general list of spare parts and expendable supplies is provided below (for specific requirements, refer to the manufacturer’s manual):

- Particulate filters
- Sampling lines
- Pump diaphragms
- Dryer columns
- Activated charcoal
- Recorder chart paper
- Recorder ink or pen
- NO standard
- Record forms
- Spare fittings and glassware assortment.

1.6 Reanalysis of Compressed Gas Calibration Standards

All NO standards used for calibration purposes should be reanalyzed by the user or the specialty gas producer at least once every 2 years. The EPA traceability protocol (EPA 1997b) describes the procedures for analysis and for reanalysis of cylinder gases. Flow-measuring devices should be recalibrated by following the procedures and schedules in Appendix 12 ("Calibration of Primary and Secondary Standards for Flow Measurement") in Volume II, Part 1, this handbook (EPA 1998).

1.7 Record Forms

Record keeping is a critical part of all quality assurance programs. Standard forms similar to those that appear in this manual should be developed for individual programs. Three things to consider in the development of record forms are:

1. Does the form serve a necessary function?
2. Is the documentation complete?
3. Will the forms be filed in such a manner that they can be retrieved easily when needed?

1.8 Audit Equipment

Personnel, equipment, and NO standards used in conducting audits must be independent from those normally used in calibrations and operations.

Known concentrations of NO_2 can be generated by the GPT of NO with O_3 to produce NO_2 or by the use of an NO_2 permeation tube and a dynamic dilution system. All audit gas standards must be traceable to NIST-SRMs as described by the EPA traceability protocol. All flow rates should be measured using a calibrated piston or soap bubble flowmeter or an equivalently accurate flowmeter.

2.0 Calibration of Equipment

The accuracy and precision of data derived from air monitoring instrumentation depend on the quality control procedures used, primarily the dynamic instrument calibration. Calibration determines the relationship between the observed and the true values of the variable being measured. See Section 12 ("Instrument Calibration and Frequency") in Volume II, Part 1, of this handbook for a general discussion of calibration procedures.

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

Most present-day monitoring instrument systems are subject to drift and variation in internal parameters and cannot be expected to maintain stable calibration over long periods of time. Therefore, it is necessary to dynamically check the calibration relationship on a predetermined schedule. Precision is determined by a one-point check at least once every 2 weeks. Accuracy is determined by a three-point audit once each quarter. Zero and span checks must be used to document within-control conditions, these checks are also used in data reduction and validation. Table 2-1 at the end of this section summarizes the quality assurance activities for calibration.

2.1 Gaseous Calibration Standards

2.1.1 Compressed Gas Calibration Standards

The NIST-SRMs provide references against which all NO standards must be compared. The steps required to compare the concentration of a commercially produced standard to an NIST-SRM are described in the EPA traceability protocol.

2.1.2 NO_2 Permeation Tubes

The steps required to compare the permeation rate of a commercially produced permeation to an NIST-SRM or to an NIST-traceable mass reference standard are described in the EPA traceability protocol.

2.2 Dilution Gases

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

2.3 Dynamic Multipoint Calibration Principles

Two methods for dynamic multipoint calibration of NO_2 are specified in the reference method (EPA 1997c).

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

Both methods provide reliable results when correct calibration procedures are followed. Experience has shown, however, that NO_2 permeation tubes may become unreliable if not handled properly. Furthermore, the conditions that contribute to the degradation of the tubes are not well understood at this time, so care should be exercised by those using the second method for calibrating NO_2 analyzers. Analyzers that require calibration of NO or NO_X channels must use an NO standard and a dynamic dilution system to generate known concentrations. Both methods require the use of an NO calibration gas to determine the efficiency of the analyzer's NO_2 to NO converter. Only the first method (GPT) is discussed in this document; those using the second method (NO_2 permeation tube) should refer to the TAD.

2.3.1 Gas-Phase Titration (GPT)

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

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

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

Dynamic calibration systems based on this GPT principle are commercially available, or may be assembled by the user. A recommended calibration system is described in the reference method and detailed in the TAD. Persons desiring to assemble their own calibration systems should follow the procedures in the TAD. Figure 2.1 shows a diagram of the GPT apparatus.

Both the assembled and the purchased calibration systems must meet the following conditions before being used for NO_2 calibrations.

- Use an NO standard traceable to an NIST-SRM.

- Have a stable O_3 source with an adjustable output.

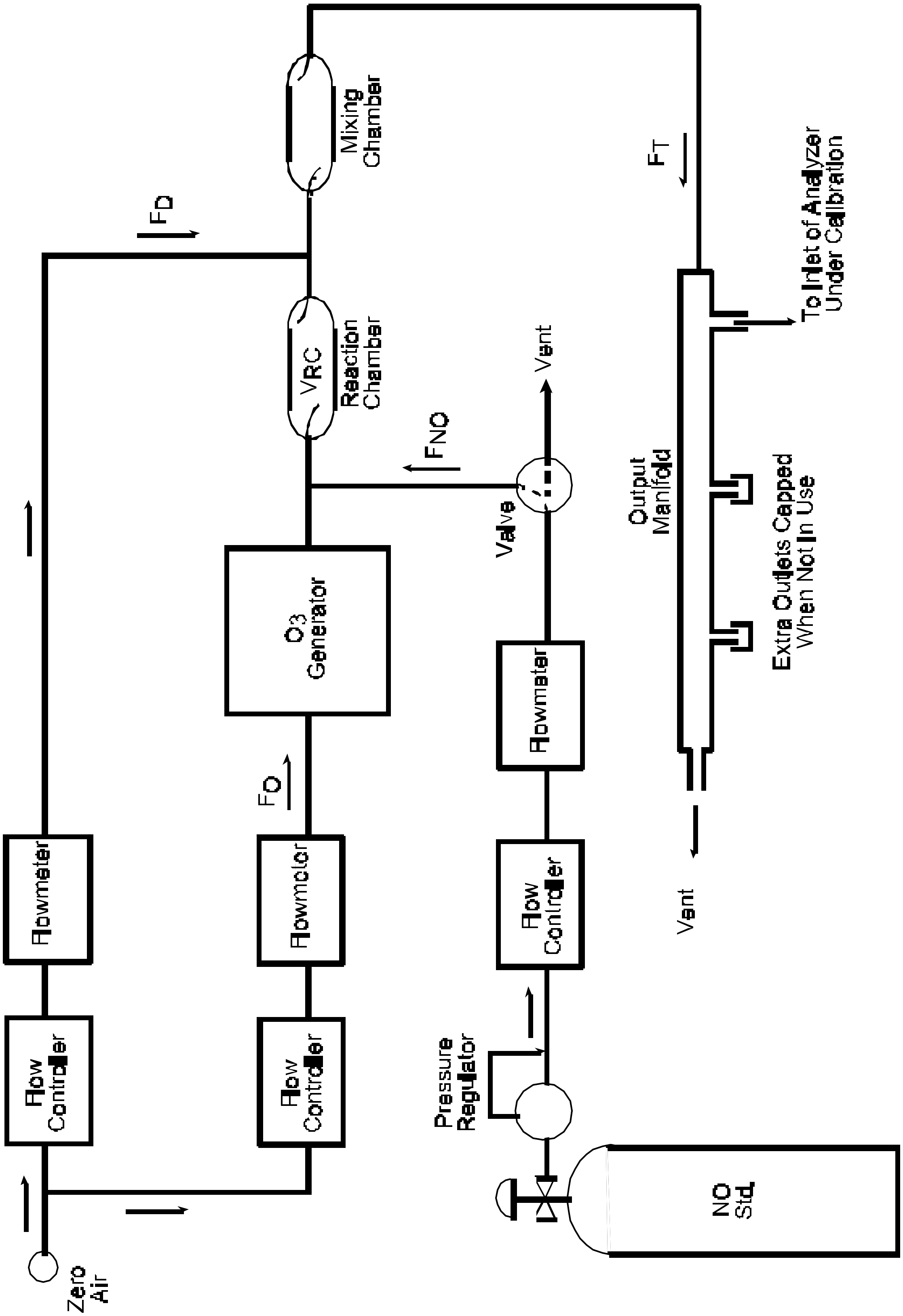

Figure 2.1. Schematic diagram of a typical GPT calibration system.

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

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

2.3.2 GPT Calibrator Check Procedure

The following procedures and equations should be used to determine whether an existing GPT calibration system will meet required conditions for a specific calibration.

For calibrators that have known preset flow rates, use Equations 2-5 and 2-6 of Steps 7 and 8 to verify the required conditions. If the calibrator does not meet specifications, follow the complete procedure to determine what flow modifications must be made.

1. Select an NO standard that has a nominal concentration in the range of 50 to 100 ppm. Determine the concentration of the NO standard, $[NO]_{STD}$* by referencing against an NIST-SRM, as discussed in the EPA traceability protocol.

2. Determine the volume of the calibrator reaction chamber (V_{RC}) in cubic centimeters. If the actual volume is not known, estimate the volume by measuring the approximate dimensions of the chamber and using an appropriate formula such as $V = (4/3)Br^3$ for a sphere or $V = Br^2 1$ for a cylinder. The reaction chamber should not be confused with the mixing chamber where the dilution air and the generated NO_2 are mixed.

3. Determine the required minimum total flow rate output (F_T) using Equation 2-l.

$$F_T = \text{analyzer flow rate demand } (\text{cm}^3/\text{min}) \times \frac{110}{100} \tag{2-1}$$

   If more than one analyzer is to be calibrated at the same time, multiply F_T by the number of analyzers.

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*Throughout this method description, the notation [NO] will denote the concentration of NO; similarly for $[NO_2]$ and $[NO_X]$.

4. Calculate the NO concentration ($[NO]_{OUT}$) needed to approximate 90% of the URL of the NO_2 analyzer to be calibrated using Equation 2-2.

$$[NO]_{OUT} = \text{URL of analyzer (ppm)} \times \frac{90}{100} \tag{2-2}$$

5. Calculate the NO flow rate (F_{NO}) required to generate the NO concentration $[NO]_{OUT}$ using Equation 2-3.

$$F_{NO} = \frac{[NO]_{OUT} \times F_T}{[NO]_{STD}} \tag{2-3}$$

6. Calculate the required flow rate through the ozone generator (F_O) using Equation 2-4.

$$F_O = \sqrt{\frac{[NO]_{STD} \times F_{NO} \times V_{RC}}{2.75 \text{ ppm-min}}} - F_{NO} \tag{2-4}$$

7. Verify that the residence time (t_R) in the reaction chamber is #2 min using Equation 2-5.

$$t_R = \frac{V_{RC}}{F_O + F_{NO}} \leq 2 \text{ min} \tag{2-5}$$

8. Verify that the dynamic parameter specification (P_R) of the calibrator's reaction chamber is $2.75 ppm-min using Equation 2-6.

$$P_R = [NO]_{STD} \left(\frac{F_{NO}}{F_O + F_{NO}} \right) \left(\frac{V_{RC}}{F_O + F_{NO}} \right) \tag{2-6}$$

Note: If t_R is >2 min or if P_R is <2.75 ppm-min, changes in flow rates (F_T, F_O, F_{NO}), in the reaction chamber volume (V_{RC}), or both will have to be made, and t_R and P_R will have to be recalculated.

9. After Equations 2-5 and 2-6 are satisfied, calculate the diluent air flow rate (F_D) using Equation 2-7.

$$F_D = F_T - F_O - F_{NO} \tag{2-7}$$

2.3.3 Example Calculation

Following is an example calculation that can be used to determine whether an existing GPT calibrator will meet the required conditions for a specific calibration. For this example, it is assumed that only the volume of the reaction chamber, V_{RC}, and the concentration of the NO standard, $[NO]_{STD}$, are known. All flow rates (F_{NO}, F_O, F_T, and F_D) will be calculated. In many uses, these flow rates are known and need only to be substituted in Equations 2-5 and 2-6 to verify the required conditions. Before doing any calculations, the URL and flow rate demand of the analyzer being calibrated must be known. Operating parameters are determined from the operations manual:

$$\text{URL} = 0.5\ \text{ppm}$$
$$\text{Analyzer flow rate demand} = 2500\ \text{cm}^3/\text{min}$$

The volume of the calibrator reaction chamber is determined by physical measurement.

$$V_{RC} = 180\ \text{cm}^3$$

The concentration of the NO standard to be used is determined by reference against an NIST-SRM.

$$[\text{NO}]_{STD} = 50.5\ \text{ppm}$$

1. Determine the minimum total flow (F_T) required at the output manifold using Equation 2-l.

$$F_T = 2500\ \text{cm}^3/\text{min}\left(\frac{110}{100}\right) = 2750\ \text{cm}^3/\text{min}$$

   Because low flow rates are difficult to control and measure, it is often advantageous to set a higher total flow rate than needed.

2. Determine the highest NO concentration, $[\text{NO}]_{OUT}$, required at the output manifold using Equation 2-2.

$$[\text{NO}]_{OUT} = 0.5\ \text{ppm}\left(\frac{90}{100}\right) = 0.45\ \text{ppm}$$

3. Calculate the NO flow rate (F_{NO}) required to generate the NO concentration $[\text{NO}]_{OUT}$ using Equation 2-3.

$$F_{NO} = \frac{0.45\ \text{ppm} \times 2750\ \text{cm}^3/\text{min}}{50.5\ \text{ppm}} = 24.5\ \text{cm}^3/\text{min}$$

4. Calculate the required flow rate of the ozone generator (F_O) using Equation 2-4.

$$F_O = \frac{\sqrt{50.5\ \text{ppm} \times 24.5\ \text{cm}^3/\text{min} \times 180\ \text{cm}^3}}{2.75\ \text{ppm-min}} - 24.5\ \text{cm}^3/\text{min}$$

$$= \sqrt{80984\ \text{cm}^6/\text{min}^2} - 24.5\ \text{cm}^3/\text{min} = 260.08\ \text{cm}^3/\text{min}$$

5. Verify that the residence time (t_R) in the reaction chamber is #2 min using Equation 2-5.

$$t_R = \frac{180\ \mathrm{cm}^3}{260.08\ \mathrm{cm}^3/\mathrm{min} + 24.5\ \mathrm{cm}^3/\mathrm{min}} = 0.63\ \mathrm{min}$$

6. Verify the dynamic parameter specification (P_R) of the calibrator reaction chamber using Equation 2-6 and previously determined values.

$$P_R = 50.5\ \mathrm{ppm} \times \frac{24.5\ \mathrm{cm}^3/\mathrm{min}}{260.08\ \mathrm{cm}^3/\mathrm{min} + 24.5\ \mathrm{cm}^3/\mathrm{min}}$$
$$\times \frac{180\ \mathrm{cm}^3}{260.08\ \mathrm{cm}^3/\mathrm{min} + 24.5\ \mathrm{cm}^3/\mathrm{min}}$$
$$= 2.75\ \mathrm{ppm{-}min}$$

7. Calculate the diluent air flow rate (F_D) required at the mixing chamber using Equation 2-7.

$$F_D = 2750\ \mathrm{cm}^3/\mathrm{min} - 260.08\ \mathrm{cm}^3/\mathrm{min} - 24.5\ \mathrm{cm}^3/\mathrm{min} = 2465\ \mathrm{cm}^3/\mathrm{min}$$

2.4 Calibration Procedures

The procedures for multipoint calibration of a chemiluminescent NO_X analyzer by GPT of an NO standard with O_3 are specified in the reference method. To facilitate these procedures, operational and calculation data forms have been developed. These forms will aid in conducting a calibration and in providing for the quality assurance checks. Detailed descriptions of the calibration theory and procedures for GPT are in the reference method and TAD.

Documentation of all data on the station, instrument, calibrator, NO standard, and calibration procedures are of prime importance since the validity of the data collected by the instrument is dependent on its calibration.

2.4.1 General Calibration Recommendations

Calibration must be performed with a calibrator that meets all conditions specified in Section 2.3.2. Flow settings (with the exception of the NO flow rate, F_{NO}) and the concentration of the NO standard, $[NO]_{STD,}$ used in the GPT calibration for NO_2 must be the same as those used in the calculations of specified conditions.

The user should be sure that all flowmeters are calibrated under the conditions of use against a reliable standard such as a piston or soap bubble flowmeter or wet test meter. All volumetric flow rates should be corrected to standard temperature and pressure (STP) of 25 °C (77 °F) and 760 mm (29.92 in.)

Hg. Calibrations of flowmeters are discussed in Appendix 12 (“Calibration of Primary and Secondary Standards for Flow Measurements”) in Volume II, Part 1, of this handbook.

Precautions must be taken to purge O_2 and other contaminants from the NO standard’s pressure regulator and the delivery system prior to the start of calibration to avoid any premature conversion of the NO to NO_2. Failure to do so can cause significant errors in calibration. This problem may be minimized by:

- Carefully evacuating the pressure regulator, when possible, after it has been connected to the NO standard and before opening the cylinder hand valve
- Thoroughly flushing the regulator and the delivery system with NO after opening the cylinder valve
- Not removing the regulator from the cylinder between calibrations unless absolutely necessary.

Further discussion of these procedures is given in the TAD.

2.4.2 Calibration Procedure for NO and NO_x

The GPT requires the use of the NO channel of the analyzer to determine the amount of NO_2 generated by titration. Therefore, it is necessary to calibrate and determine the linearity of the NO channel before proceeding with the NO_2 calibration. In some analyzers, it is also necessary to calibrate the NO_X channel. This can be done simultaneously with the NO calibration. The following procedure uses the calibration data form, Figure 2.2, to aid in the collection and documentation of calibration data. During the calibration, the analyzer should be operating in its normal sampling mode, and the test atmosphere should pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling and as much of the ambient air inlet system as is practicable. All operational adjustments to the analyzer should be completed prior to the calibration.

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

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

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

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

1. Station Redbank
417 Redbank Road
Millsville, Ohio
2. Calibrated by Joe Smith Date 3-2-00
3. Analyzer mfgr. ACME
Model $NO/NO_2/NO_X$ (No. 9876)
S/N 14782
4. Calibrator mfgr. State Agency
Model GPT
S/N 2A
5. NO reference standard
Supplier Gas Supplier
Concentration $[NO]_{STD}$ 50.5
NO_2 impurity, $[NO_2]_{IMP}$ 0
Traceable to NIST-SRM No. 1683d
Cylinder number 6783
Cylinder pressure 1500 psig
Cylinder No. AL-9323517

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

7. Temperature 25°C Barometric pressure 760 mm Hg

NO/NO_X Calibration and Linearity Check

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

NO_2 Calibration by GPT

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

Figure 2.2. Example of a calibration data form (front side).

Equations used for NO/NO_X/NO_2 calibration

Equation 2-8

$$[NO]_{OUT} = \frac{F_{NO} \text{ x } [NO]_{STD}}{F_{NO} + F_O + F_D}$$

Equation 2-9

$$[NO]_{OUT} = \frac{F_{NO} \text{ x } ([NO]_{STD} + NO_2]_{IMP})}{F_{NO} + F_O + F_D}$$

Equation 2-10

$$\text{Response (volts)} = \frac{[NO]_{OUT}}{URL} 100 + Z_{NO}$$

For NO_2 substitute $[NO_2]_{OUT}$ and Z_{NO_2}

For NO_X substitute $[NO_X]_{OUT}$ and Z_{NO_X}

Equation 2-11

$$[NO_2]_{OUT} = [NO]_{ORIG} - [NO]_{REM} + \frac{F_{NO} \text{ x } [NO_2]_{IMP}}{F_{NO} + F_O + F_D}$$

If $[NO_2]_{IMP} = 0$ use Equation 2 – 11A

Equation 2-11A

$[NO_2]_{OUT} = [NO]_{ORIG} - [NO]_{REM}$

F_{NO} = flow rate of NO standard

F_O = flow rate of air through O_3 generator

F_D = flow rate of dilution air

$[NO]_{OUT}$, $[NO_X]_{OUT}$, $[NO_2]_{OUT}$ = concentration at the output manifold

$[NO]_{STD}$ = concentration of the undiluted NO standard

$[NO_2]_{IMP}$ = concentration of NO_2 impurity in the standard NO cylinder

URL = upper range limit

$[NO]_{ORIG}$ = concentration of NO before O_3 is added during GPT

$[NO]_{REM}$= concentration of NO after O_3 is added during GPT

Z_{NO}, Z_{NO_X}, Z_{NO2} = analyzer response to zero air

Figure 2.2a. Example of a calibration data form (back side).

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

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

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

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

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

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

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

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

   c. Adjust the flow rate of the diluent air and the O_3 generator air to obtain the flow rates determined in Section 2.3.2. Be sure that the total air flow rate exceeds the total demand of the analyzer(s) connected to the output manifold so that no ambient air will be pulled into the manifold vent. Record the sum of the flow rates of diluent air (F_D) and O_3 generator air (F_O) in Column 1 of Figure 2.2.

   d. Allow the analyzer to sample zero air until stable NO, NO_X, and NO_2 responses are obtained. After the responses have stabilized, adjust the analyzer zero control(s). (Offsetting the analyzer zero adjustments to 0.050 volts is recommended to facilitate observing any negative zero drift.) Record the stable zero air responses (Z_{NO} and Z_{NO_x}) under Column 4 of Figure 2-2 for NO and under Column 6 for NO_X. Record the NO_2 zero air response (Z_{NO_2})in Column 12.

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

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

$$[NO]_{OUT} = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_{O} + F_{D}} \tag{2-8}$$

Calculate the output NO_X concentration $[NO_X]_{OUT}$ using Equation 2-9.

$$[NO_x]_{OUT} = \frac{F_{NO} + ([NO]_{STD} + [NO_2]_{IMP})}{F_{NO} + F_{O} + F_{D}} \tag{2-9}$$

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

g. Sample the generated concentration until the NO and the NO_X responses have stabilized. Adjust the NO span control to obtain an analyzer response as determined by Equation 2-10.

$$\text{Analyzer response} = \left(\frac{[NO]_{OUT}}{URL} \times 100 \right) + Z_{NO} \tag{2-10}$$

where URL = nominal upper range limit of the NO channel being calibrated in parts per million.

Note: Some analyzers may have separate span controls for NO, NO_X, and NO_2; others may have separate span controls only for NO and NO_X; while still others may have only one span control common to all three channels. If only one span control is available, make the span adjustment on the NO channel. When adjusting the analyzer's NO_X span control, substitute the $[NO_X]_{OUT}$ and the Z_{NO_x} in Equation 2-10 to determine the analyzer response. If substantial adjustments of the span controls are necessary, recheck the zero span adjustments by repeating Steps 8f and 8g. Record the NO analyzer response under Column 4 and the NO_X analyzer response under Column 6 on the 80% URL line.

h. After the zero and the 80% URL points have been set, determine two approximately evenly spaced points between zero and the 80% URL without further adjustment to the analyzer. These additional points can be generated by either increasing the dilution flow rate (F_D) or by decreasing the F_{NO}. For each concentration generated, calculate the NO and NO_X concentrations using Equations 2-8 and 2-9. Record the required information for each point under the appropriate column in the NO/NO_X table in Figure 2.2.

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

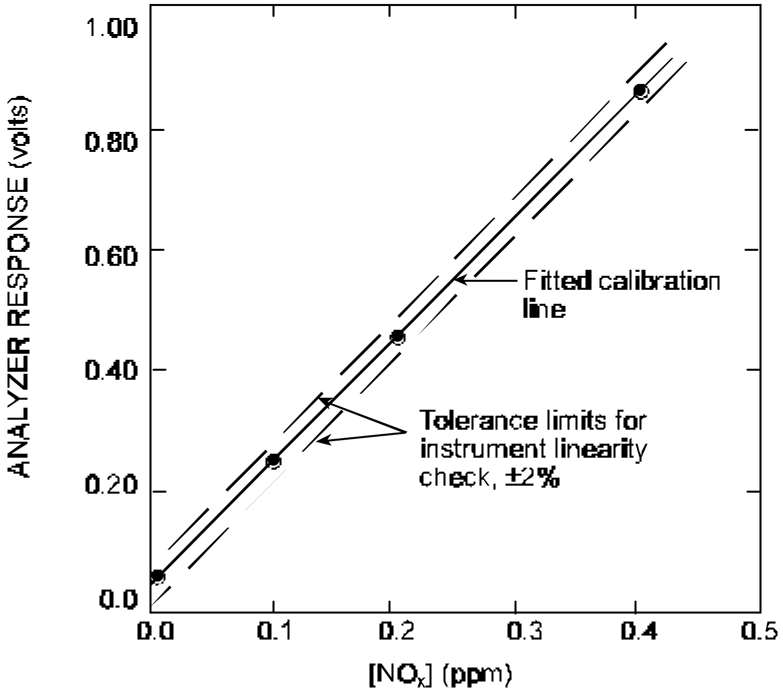

Figure 2.3. Example of an NO_X calibration relationship.

form presented in Figure 2.4. Because the time required to perform the calculation manually using the data form is considerably longer than that using a programmed calculator, it is suggested that the latter be used.

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

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

Calibration point	**Concentration (ppm) x**	**x^2**	**Analyzer response (volts) y**	**y^2**	**xy**
Zero	0.00	0.00	0.050	0.0025	0.0000
80% URL	0.40	0.16	0.850	0.7225	0.3400
1	0.20	0.04	0.450	0.2025	0.0900
2	0.10	0.01	0.250	0.0625	0.0250

$\cdot x = \underline{0.70}$, $\cdot x^2 = \underline{0.21}$, $\cdot y = 1.600$, $\cdot y^2 = \underline{0.9900}$, $\cdot xy = \underline{0.4550}$

$\bar{x} = \cdot x/n = \underline{0.175}$, $\bar{y} = \cdot y/n = \underline{0.400}$, and

n = number of calibration points = 4

The equation of the line fitted to the data is written as:

$$\hat{y} = \bar{y} + b(x - \bar{x}) = (\bar{y} - b\bar{x}) + bx = a + bx$$

where $\hat{y}$ = predicted mean response for corresponding x

b = slope of the fitted line

a = intercept where the line crosses the y-axis

$$b = \frac{\sum xy - \frac{(\sum x)(\sum y)}{n}}{\sum x^2 - \frac{(\sum x)^2}{n}} = \frac{0.1750}{0.0875} = \underline{2.000}$$

$$a = \bar{y} - b\bar{x} = \underline{0.050}$$

Figure 2.4. Calculation form for the method of least squares.

to eliminate calibration errors; if the repeated points still fall outside the limits, consult the manufacturer's manual on how to correct the nonlinearity.

2.4.3 Gas-Phase Titration Procedure for NO_2

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

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

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

3. Adjust the NO flow rate (F_{NO}) to generate an NO concentration near 90% of the URL. Dilution air and O_3 generator air flow rates should be the same as that used in the calculation of specified conditions in Section 2.3.2. Sample this NO concentration until the NO and NO_X responses stabilize. Using the NO calibration relationship determined in Step 10 in Section 2.4.2, measure and record the NO concentration under Column 8, $[NO]_{ORIG}$. Using the NO_X calibration relationship obtained in Step 10, measure and record the NO_X concentration under Column 7, $[NO_X]$. Record both values on the line marked “ORIG.”

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

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

$$[NO_2]_{OUT} = [NO]_{ORIG} - [NO]_{REM} + \frac{F_{NO} \times [NO_2]_{IMP}}{F_{NO} + F_O + F_D} \qquad (2\text{-}11)$$

If there was no NO_2 impurity in the NO reference standard, Equation 2-11A may be used to calculate $[NO_2]_{OUT}$.

$$[NO_2]_{OUT} = [NO]_{ORIG} - [NO]_{REM} \qquad (2\text{-}11A)$$

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

$$\text{Analyzer response} = \left(\frac{[NO_2]_{OUT}}{URL} \text{ x DAS range}\right) + Z_{NO_2} \qquad (2\text{-}10A)$$

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

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

8. Repeat Steps 9, 10, and 11 of Section 2.4.2 for the NO_2 analyzer response, Column 12, and the corresponding calculated concentration $[NO_2]_{OUT,}$ Column 11.

2.4.4 Example NO and NO_2 Calibration

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

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

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

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

5. Adjust the diluent air flow rate (F_D) and the O_3 generator air flow rate (F_O) to obtain the flow rates close to those determined in Section 2.3.2. Remeasure these flows for each calibration:

$$F_D = 2460 \text{ cm}^3\text{/min at STP}$$
$$F_O = 260 \text{ cm}^3\text{/min at STP}$$

   Record the sum of F_D and F_O under Column 1.

$$F_D + F_O = 2720 \text{ cm}^3\text{/min at STP}$$

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

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

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

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

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

   Record this value on the 80% URL line of Column 3. Calculate the exact NO_X concentration $[NO_X]_{OUT}$ using Equation 2-9.

$$[NO_x]_{OUT} = \frac{21.8 \times (50.5 + 0)}{2720 + 21.8} + 0.405 \text{ ppm}$$

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

9. Sample the generated concentration until the NO and NO_X analyzer responses have stabilized. Calculate the expected analyzer response for this concentration using Equation 2-10.

$$\text{Analyzer response} = \left(\frac{0.405}{0.500} \times 200\right) + 0.050 = 0.860 \text{ volts}$$

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

   Substitute the NO_X values in Equation 2-10; an analyzer response of 0.860 volts is determined. Adjust the NO_X span control and record this response under Column 6.

10. Generate two approximately evenly spaced points between zero and the 80% URL by changing either F_{NO} or F_D. In this example, F_{NO} was changed. Allow the analyzer response to stabilize before moving to the next calibration point. When the response has stabilized, record it in the appropriate column of the NO/NO_X calibration table.

11. Plot the analyzer response from Column 4 (y-axis) versus the corresponding calculated concentration $[NO]_{OUT}$ from Column 3 (x-axis). A straight line of best fit is now calculated by the method of least squares. For this example, the slope (b) is 2.00 with a y-intercept of 0.050 volts. Plot the calibration relationship as in Figure 2.3. To check linearity, draw the +2% and -2% URL lines parallel to this calibration line. In this example, the analyzer response is linear.

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

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

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

14. The resulting NO_2 concentration is now calculated. Because there were no NO_2 impurities present in the NO standard, Equation 2-11A may be used.

$$[NO_2]_{OUT} = 0.450 - 0.050 = 0.400 \text{ ppm } NO_2$$

15. Calculate the required recorder response using Equation 2-10.

$$\text{Analyzer response} = \left(\frac{0.400}{0.500} \times 2.00 \right) + 0.050 = 0.850 \text{ volts}$$

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

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

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

2.5 Determination of NO_2 to NO Converter Efficiency

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

A data form (Figure 2.5) has been developed for determining the converter efficiency. The following procedure is for use with this data form.

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

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

Slope (b) = 0.97

Converter efficiency = 100 x b = 97%

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

Figure 2.5. Converter efficiency data form.

a. Column l, $[NO_2]_{OUT}$, is from Column 11, $[NO_2]_{OUT}$, of the table from Figure 2.2.

b. Column 2, $[NO_X]_{ORIG}$, is from the line marked “ORIG” of Column 7, $[NO_X]$, of the table; this value will be the same for all lines of Column 2.

c. Column 3, $[NO_X]_{REM}$, is from the appropriate calibration points of Column 7 of the table.

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

$$[NO]_{CONV} = [NO_2]_{OUT} - ([NO_X]_{ORIG} - [NO_X]_{REM}) \qquad (2\text{-}12)$$

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

3. Plot $[NO_2]_{CONV}$ (y-axis) versus $[NO_2]_{OUT}$ (x-axis), and the converter efficiency curve (Figure 2.6), and then calculate the slope (b) of the curve using either an appropriate calculator or the calculation form (Figure 2.4) using the method of least squares regression.

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

2.6 Calibration Frequency

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

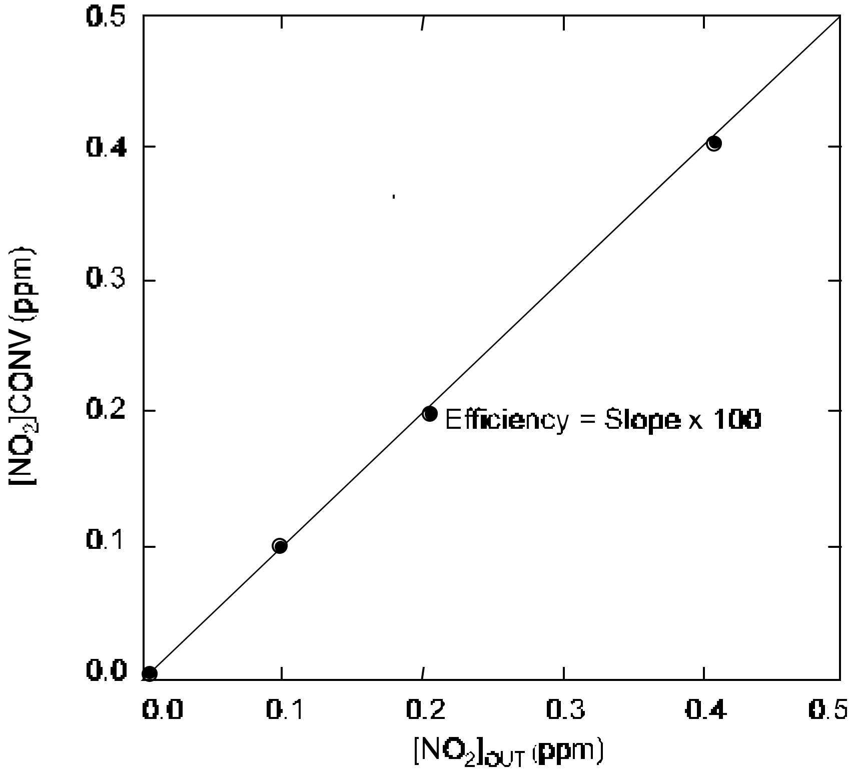

Figure 2.6. Converter efficiency relationship.

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

2. Following any one of the activities listed below:

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

b. Any repairs that might affect its calibration;

c. Physical relocation of the analyzer; or

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

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

TABLE 2-1. ACTIVITY MATRIX FOR CALIBRATION PROCUREMENT

Calibration activities	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Calibration gases	Traceable to NIST via the EPA traceability protocol 50 to 100 ppm NO in N_2 with less than 1 ppm in NO_2	Recertified every 2 years using the EPA traceability protocol	Working gas standard is unstable and/or measurement method is out of control; take corrective action such as obtaining new calibration gas
Dilution gas	Zero air, free of contaminants; see the TAD	See the TAD	Return to supplier, or take appropriate corrective action with generation system
Multipoint calibration (GPT)	1. $t_R \leq 2$ min $P_R \geq 2.75$ ppm-min	1. Sec. 2.3.2	1. Adjust flow conditions and/or reaction chamber volume to meet suggested limits
	2. Use calibration procedure in Sec. 2.4; also the TAD; EPA 1997c	2. Sec. 2.4; the TAD; EPA 1997c; and Figure 2.2; see Sec. 2.1 for frequency	2. Repeat the calibration
	3. Converter efficiency $\geq$96%	3. Sec. 2.5 and Figures 2.5 and 2.6	3. Replace or service the converter

3.0 Operation and Procedure

Scheduled checks are essential to quality assurance for verifying the operational status of the monitoring system. The operator should visit the site at least once each week. Every 2 weeks a Level 1 zero and span check must be made on the analyzer. Level 2 zero and span checks should be conducted at a frequency desired by the user.

In addition, an independent precision check between 0.08 and 0.10 ppm must be carried out at least once every 2 weeks. Table 3-1 at the end of this section summarizes the quality assurance activities for routine operations. A discussion of each activity appears in the following sections.

To provide for documentation and accountability of activities, a checklist should be compiled and then filled out by the field operator as each activity is completed. Figure 3.1 presents an example operations checklist and maintenance record.

In Sections 3.1 and 3.2, reference is made to the sampling shelter and the sample introduction system. The design and construction of these components of the sample introduction system are not within the scope of this document. For guidance, consult Section 7 ("Sampling Methods") in Volume II, Part 1, of this handbook.

3.1 Shelter

The shelter's role in quality assurance is to provide a temperature-controlled environment in which the sampling equipment can operate at optimum performance. The mean shelter temperature should be between 22 and 28 °C (72 and 82 °F). A thermograph should be installed at the shelter to continuously record daily fluctuations in temperature. Fluctuations greater than ±2 °C (±4 °F) may cause the electronic components of the analyzer to drift and may introduce error into the data; thus the fluctuations outside of the specifications should be identified, and the data for the affected time period should be flagged to indicate possible discrepancies.

3.2 Sample Introduction System

The sample introduction system consists of an intake port, the particulate and moisture traps, the sampling manifold and blower, and the sampling line to the analyzer. The field operator, as part of the quality assurance program, should inspect each of these components for breakage, leaks, and buildup of particulate matter or other foreign objects; check for moisture deposition in the sample line or manifold; see that the sample line is connected to the manifold; and see that any component of the sample introduction system that is not within tolerance is either cleaned or replaced immediately. See Section 7 ("Sampling Methods") in Volume II, Part 1, of this handbook.

Operations Checklist and Maintenance Record
Nitrogen Dioxide Analyzer

Station Name Municipal Incinerator
Month/Year September 2000
Station ID Number 001
Technician C. Jones
Instrument Make/Model ACME ONA-2
Serial No. NO_2-7723

Date	Sample Flow	Ozone Flow	Reaction Chamber Temp.	PMT Temp.	Zero Setting	Span Setting	PMT Voltage	Chamber Pressure	Change Filter
9/4	531	120	49.2	-2.6	002	107	1015	193	NO

Operation Instructions

Daily Checks:	Sample and ozone flow rates, data acquisition system power, chart traces, shelter temperature and voltage, shelter security, surrounding area
Weekly Checks:	Filter change, reaction chamber and photomultiplier tube (PMT) temperature, PMT voltage, reaction chamber pressure, sample introduction system, converter temperature
Monthly Checks:	Electronic zero and span, check desiccant, zero gas and span gas cylinder pressures
Quarterly Checks:	Multipoint calibration, Date of last calibration: 7/3/00
Semiannual Checks:	Clean fan/fan filter Inspect capillary tube Replace external ozone scrubber
Annual Checks:	Inspect internal and external tubing
Biannual Checks:	Rebuild or replace pump

Comments

9/4—Excessive span drift (>5%)—checked resistance at test points J1 and J10 on temperature control board—card found to be defective and was replaced—temp fell within limits with new card

Figure 3.1. Example of an operations checklist and maintenance record.

3.3 Strip Chart Recorder

During each weekly visit to the monitoring site, the field operator should use the following list to check the strip chart recorder for proper operation:

- Ink trace for visibility
- Ink level in reservoir
- Chart paper for supply

- Chart speed control setting
- Signal input range switch
- Time synchronization.

Any operational parameter that is not within tolerance must be corrected immediately.

3.4 Chemiluminescent NO_X Analyzer

Specific instructions in the manufacturer's manual should be read thoroughly before attempting to operate the analyzer. As part of the quality assurance program, each site visitation should include a visual inspection of the external operation of the analyzer, the zero and span checks, and a biweekly precision point check.

3.4.1 Visual Inspection

During the visual inspection, the field operator should inspect the external operating parameters of the analyzer. The parameters of concern will vary among analyzers, but in general they will include the following:

- Correct setting of flowmeters and pressure regulators
- Cycling of temperature control indicators
- Temperature level if equipped with a pyrometer
- Verification that the analyzer is in the sampling mode rather than the zero or the calibration mode
- Zero and span potentiometers locked and set at proper values.

3.4.2 Zero and Span Checks

Zero and span checks must be used to document within-control conditions. The purpose is to provide interim checks on the response of the analyzer to known concentrations. If a response falls outside of the acceptance limits, the analyzer is considered out of control, and the cause must be determined and corrected. A quality control chart can be used to provide a visual check to determine if the analyzer is within acceptance limits. A zero check should be conducted at the same time that the span check is performed.

A Level 1 zero and span check is a simplified, two-point analyzer calibration used when analyzer linearity does not need to be checked or verified. Sometimes when no adjustments are made to the analyzer, the Level 1 calibration may be called a zero/span check, in which case it must not be confused with a Level 2 zero/span check. Because most analyzers have a reliably linear or near-linear output response with concentration, they can be adequately calibrated with only two concentration standards (two-point calibration). Although lacking the advantages of the multipoint calibration, the two-point zero and span calibration–because of its simplicity–should be carried out much more frequently. Also, two-point calibrations are easily automated. Frequent checks or updating of the calibration relationship with a two-point zero and span calibration improves the quality of the monitoring data by helping to keep the calibration relationship more closely matched to any changes (drift) in the analyzer response.

A Level 2 zero and span check is an “unofficial” check of an analyzer’s response. It may include dynamic checks made with uncertified test concentrations, artificial stimulation of the analyzer’s detector, electronic or other types of checks of a portion of the analyzer, etc. Level 2 zero and span checks are not to be used as a basis for analyzer zero or span adjustments, calibration updates, or adjustment of ambient data. They are intended as quick, convenient checks to be used between zero and span calibrations to check for possible analyzer malfunction or calibration drift. Whenever a Level 2 zero and span check indicates a possible calibration problem, a Level 1 zero and span (or multipoint) calibration should be carried out before any corrective action is taken.

A system of Level 1 and Level 2 zero span checks is recommended. These checks must be conducted in accordance with the specific guidance given in Section 12 (“Instrument Calibration and Frequency”) in Volume II, Part 1, of this handbook. Level 1 zero and span checks must be conducted every two weeks. Level 2 checks should be conducted in between the Level 1 checks at a frequency desired by the user. Span concentrations for both levels should be between 70 and 90% of the measurement range. The data should be recorded on the zero span check form, Figure 3.2.

Site ID 001
Location Municipal Incinerator
Address 3336 Jefferson Avenue

Pollutant NO_2
Analyzer ACME Chemiluminizer
Serial Number NO2-7723

Date	Technician	Unadjusted zero gas response (volts)	Span concentration (ppm)	Unadjusted span gas response (volts)
3-1-00	C.J.	0.050	0.40	0.855
3-15-00	C.J.	0.050	0.40	0.850
3-29-00	C.J.	0.050	0.40	0.860

Figure 3.2. Example of a Level 1 zero and span check data form.

Zero and span data are to be used to:

- Provide data to allow analyzer adjustment for zero and span drift
- Provide a decision point on when to calibrate the analyzer
- Provide a decision point on invalidation of monitoring data.

When the response from a span check is outside the acceptance limits, the cause for the extreme drift should be determined, and corrective action should be taken. Some of the causes for drift are listed below:

- Lack of preventive maintenance
- Fluctuations in electrical power supply
- Fluctuations in flow
- Change in zero air source
- Change in concentration of the NO standard
- Degradation of photomultiplier tube
- Electronic and physical components not within manufacturer's specifications.

Corrective actions for the above can be found in the manufacturer's instruction/operations manual.

3.4.3 Precision Check

For continuous analyzers, a periodic check is used to assess the data for precision. A one-point precision check must be carried out at least once every 2 weeks on each analyzer at an NO_2 concentration between 0.08 and 0.10 ppm. The analyzer must be operated in its normal sampling mode, and the precision test gas must pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling. The NO standards from which precision check test concentrations are obtained must be traceable to an NIST-SRM. Those standards that are used for either calibration or auditing may be used for the precision check.

3.4.3.1 Precision Check Procedure

1. Connect the analyzer to a precision gas that has a NO_2 concentration between 0.08 and 0.10 ppm. A precision gas may be generated by either the GPT or a NO_2 permeation tube. If a precision check is made in conjunction with a zero/span check, it must be made prior to any zero or span adjustments.

2. Allow the analyzer to sample the precision gas for at least 5 minutes or until a stable analyzer response is obtained.

3. Record this value on the precision check data form (Figure 3.3), and mark the chart as “unadjusted precision check.” The NO and NO_X precision checks should also be made if data are being reported. Information from the check procedure is used to assess the precision of the monitoring

data. For information regarding procedures to calculate and report precision, see the EPA guideline on the meaning and use of precision and accuracy data (Rhodes 1983).

Calibrator Used State Agency
GPT No. 6
By Bill Brown

Standard Used NO cylinder 14782
Concentration 50.0 ppm
Verified Against NBS-SRM NO cylinder 2789
Date 6-18-00

Precision check by	**Date**	**Station location**	**Analyzer ID**	**Precision test gas concentration (ppm)**	**Analyzer response (ppm)**	**Difference (ppm)**
C. Jones	7-11-00	Redbank	ACME SN 14782	0.085	0.080	-0.005
C. Jones	7-11-00	Downtown	ACME SN 14784	0.090	0.085	-0.005
C. Jones	7-11-00	Uptown	ACME SN 14786	0.080	0.085	0.005

Figure 3.3. Example of precision check form.

TABLE 3-1. DAILY ACTIVITY MATRIX

Characteristic	**Acceptance limits**	**Frequency and method of measurement**	**Action if requirements are not met**
Shelter temperature	Mean temperature between 22 and 28 °C (72 and 82 °F), daily fluctuations not greater than +2 °C (4 °F)	Examine thermograph chart daily for variations greater than +2 °C (4 °F)	1. Mark strip chart for the affected time period 2. Repair or adjust temperature control system
Sample introduction system	No moisture, foreign material, leaks, obstructions; sample line connected to manifold	Weekly visual inspection	Clean, repair, or replace as needed
Data acquisition system	System powered up and collecting data, data downloaded on command or schedule	Daily visual inspection	Adjust or repair as needed
Analyzer operational settings	1. Flow and regulator indicators at proper settings 2. Temperature indicators cycling or at proper levels 3. Analyzer set in sample mode 4. Zero and span controls locked	Weekly visual inspection	Adjust or repair as needed
Analyzer operational check	Zero and span within acceptance limits as described in Sec. 12, Vol. II, Part 1, of this handbook	Level 1 zero and span every 2 weeks; Level 2 between Level 1 checks at frequency desired by user	1. Isolate source of error and repair 2. After corrective action, recalibrate analyzer
Precision check	Assess precision as described in the EPA guideline on the meaning and use of precision and accuracy data	Every 2 weeks, Sec. 3.4.3	Calculate and report precision

4.0 Data Reduction, Validation, and Reporting

Quality assurance activities for manual data reduction, validation, and reporting are summarized in Table 4-1 at the end of this section. For additional information, see Section 17 (“Data Review, Verification, and Validation”) in Volume II, Part 1, of this handbook.

4.1 Data Validation

Monitoring data of poor quality may be worse than no data. Data validation is one activity of a quality assurance program to screen data for possible errors or anomalies. Sections 4.1.1 and 4.1.2 recommend two data validation checks.

4.1.1 Span Check Drift

The first level of data validation should be to accept or reject monitoring data based upon routine periodic analyzer checks. It is recommended that results from the Level 1 span checks discussed in Section 3.4.2 be used as the first level of data validation for accepting data. This means up to 2 weeks of monitoring data may be invalidated if the span drift for a Level 1 span check is greater than or equal to 25%. For this reason, it may be desirable to perform Level 1 checks more often than the minimum recommended frequency of every 2 weeks.

4.1.2 Edit of Strip Chart

The strip chart should be edited to detect signs of the monitoring system's malfunctions that result in traces on the chart that do not represent atmospheric concentrations. When reviewing a strip chart, typical indicators of malfunctions to watch for are:

- A straight trace (other than minimum detectable) for several hours
- Excessive noise indicated by a wide solid trace, or erratic behavior such as spikes that are sharper than is possible with the normal instrument response time. Noisy outputs may occur when analyzers are exposed to vibrations.
- A long steady increase or decrease in deflection
- A cyclic trace pattern with a definite time period indicating a sensitivity to changes in temperature or parameters other than NO_2 concentration
- A trace below the zero baseline that may indicate a larger than normal drop in ambient room temperature or power line voltage
- Span drift equal to or greater than 25%.

Void data for any time interval for which a malfunction of the sample introduction system is detected.

4.2 Data Reduction

To obtain hourly average concentrations from a strip chart record, the following procedure may be used.

1. Be sure the strip chart record for the sampling period has a zero trace at the beginning and end of the sampling period.
2. Fill in the identification data called for at the top of the hourly average data form.
3. Use a straight edge to draw a line from the zero baseline at the start of the sampling period to the zero baseline at the end of the sampling period. This line represents the zero baseline to be used for the sampling period.
4. Read the zero baseline in percentage of the chart at the midpoint of each hour interval, and record the value on the data form.
5. Determine the hourly averages for the interval of interest between two vertical hour lines by placing a transparent straight edge parallel to the horizontal chart division lines and by adjusting the straight edge between the lowest and highest points of the trace in that interval so that the area above the straight edge and bounded by the trace and the hour lines is estimated to equal the area below the straight edge and bounded by the trace and hour lines, as shown in Figure 4.1.

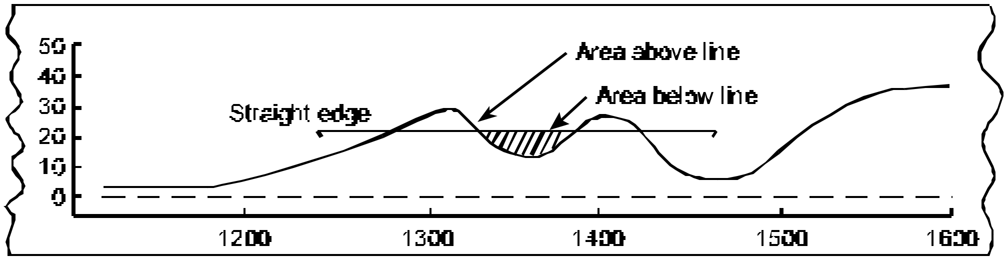

Figure 4.1. Technique for determining hourly averages from a strip chart trace using a straight edge.

Read and record the percentage of chart deflection on the hourly average data form. Repeat the procedure for all the hour intervals sampled that have not been marked invalid. Record all values on the hourly average data form.

6. Subtract the zero baseline value from the reading value and record the difference on the hourly averages form.
7. Add the percentage of zero offset, +5, to the difference on the hourly averages form.

8. Convert the percentage of chart values to NO_2 concentrations in parts per million using the most recent calibration curve. Record the parts per million NO_2 values on the hourly averages form.

An alternative method for converting percentage of chart to parts per million is to use Equation 4-1 and thus to eliminate Steps 6, 7, and 8 of the above procedure.

$$\text{ppm} = \frac{y - y_z}{\text{slope}} \qquad (4\text{-}1)$$

where

y = recorder reading in percentage of scale, from Step 5
y_z = zero baseline in percentage of scale, from Step 4
slope = slope of the calibration relationship, as determined in Section 2.3.2

4.2.1 Data Reporting

Transcribe information and data from the hourly averages form into a format that is appropriate for input into AIRS AQS. Information about the format is contained in the AIRS user's guide for air quality data coding (EPA 1995). Updates about the format may be found at the AIRS World Wide Web site (www.epa.gov/ttn/airs/).

TABLE 4-1. ACTIVITY MATRIX FOR DATA REDUCTION

Activity	Acceptance limits	Frequency and method of measurement	Action if requirements are no met
Span check drift	Level 1 span check <25%	Perform Level 1 check at least every 2 weeks, but more frequent checks may be desirable	Invalidate data; take corrective action; increase frequency of Level 1 checks until data are acceptable
Review output of data acquisition system	Check for missing data due to power losses and for any unusual baseline excursions	Every time the data are downloaded	Flag any suspicious data for later validation during data reduction
Data reduction	Stepwise procedure for data reduction (Sec. 4.2)	For each strip chart, follow the method given in Sec. 4.2	Review the reduction procedure
Data reporting	Follow AIRS AQS guide for air quality data coding (EPA 1995)	Perform visual check	Review the data transcription procedure

5.0 Maintenance

5.1 Preventive Maintenance

Preventive maintenance should prevent down-time and data loss. Management and field operators should jointly develop their preventive maintenance program. A program designed by persons unfamiliar with analyzer operations may include unnecessary items or omit mandatory ones. Table 5-1 illustrates items that monitoring agencies should include in their NO_2 preventive maintenance program.

TABLE 5-1. EXAMPLE OF A PREVENTIVE MAINTENANCE SCHEDULE FOR NO_2 MONITORING

Item	Schedule
Replace particle filter and perform QC checks	Weekly
Perform Level I zero and span check[a]	Weekly
Perform electronic parameter checks (Level 2 zero and span check)	Weekly
Replace ozone generator desiccant	Monthly
Perform multipoint calibration	Quarterly
Replace external ozone scrubber	Semiannually
Clean fan/fan filter	Semiannually
Inspect capillary tubes	Semiannually
Inspect internal, external tubing; replace if necessary	Annually
Replace photomultiplier tube (PMT)	As needed
Rebuild or replace pump	Every 2 years

[a] Weekly Level I zero and span checks should be performed only if nightly automated Level I zero and span checks are not performed.

In addition to a schedule, the preventive maintenance plan should also include more detailed task descriptions, such as those illustrated below:

- Because the analyzer pneumatic system requires so much preventive maintenance, the tubing, solenoids, and pump should be inspected regularly. Cracked tubing or loose fittings can cause the instrument to analyze room air rather than ambient air and lead to the invalidation of data. A faulty pump or rotometer can also cause problems with pneumatic systems. When variations in the rotometer reading force the operator to adjust the rotometer setting frequently, the pump is failing and should be either repaired or replaced.

- Check the instrument for vibration. When pumps get old, they sometimes will vibrate more than is normal. If this occurs, it can cause cracks if the internal tubing is touching another surface.

- Always operate the NO_X analyzer with a permeation dryer. Water vapor can interfere and cause malfunctions as well. Some analyzers come equipped with permeation dryers installed and these do not need servicing. Older models usually require a canister filled with desiccant that should be changed often. Most desiccants change color, which indicates that it is no longer able to dry the air effectively. It is recommended that two clear canisters be used so the outermost canister can be changed without allowing moist air to enter into the analyzer. The two-canister setup can also be a safeguard against possible breakthrough if one canister leaks. If the operator suspects that the permeation dryer is overloaded or not operating correctly, check the analyzer with Level I span gas. If it responds slowly and does not reach its normal response, the cause may be the permeation dryer.

- Fitting the exhaust port of the instrument with an ozone scrubber is recommended. The ozone generator within the instrument produces ozone concentrations of 1-3 ppm. Most of this ozone does not react with the NO in the reaction chamber and is vented out the exhaust port. To avoid exposing operators to high levels of ozone, it is highly recommended that a scrubber be fitted on the exhaust port of this instrument. If a charcoal canister is fitted on the exhaust port, it should be recognized that ozone will react with all of the charcoal and breakthrough will eventually occur. Replacing the canister or its contents at least every 6 months is recommended.

Consult the analyzer operations manual for complete details on operation and maintenance.

5.2 Corrective Maintenance

Corrective maintenance is defined as nonscheduled maintenance activities that become necessary because of system malfunctions. A few examples of corrective maintenance are: replacing a damaged pump diaphragm, cleaning a clogged sample line, and replacing a NO_2 converter. The need for corrective maintenance becomes apparent as the operator performs the operations described in Section 3.0. When corrective maintenance is needed, the operator should refer to the analyzer operations manual for trouble-shooting procedures. A detailed maintenance record of corrective activities should be kept on file for each analyzer at the site to identify recurring malfunctions. An example operations checklist and maintenance record appears in Figure 3.1.

6.0 Auditing Procedure

An audit is an independent assessment of data accuracy. Independence is achieved by having the audit done by a different operator than the one conducting the routine field measurements and by using audit standards and equipment different from those used in routine monitoring. The audit should be a true assessment of the measurement process under normal operations without any special preparation or adjustment of the system. Routine quality control checks (such as zero and span checks in Section 2.3.3) conducted by the operator are necessary for obtaining and reporting good quality data, but they are not considered part of the auditing procedure. For additional information, see Section 15 ("Assessment and Corrective Action") in Volume II, Part 1, of this handbook.

Three different types of audits are recommended: a performance audit, a data reduction audit, and a systems audit. Performance audits are described in Section 6.1 and data reduction audits are described in Sections 6.2 and 6.3, respectively. These audits are summarized in Table 6.1 at the end of this section.

Proper implementation of an auditing program will serve a twofold purpose: (1) to ensure the integrity of the data and (2) to assess the data for accuracy. The technique for estimating the accuracy of the data is given in the EPA guideline on the meaning and use of precision and accuracy data (Rhodes 1983).

6.1 Performance Audit

A performance audit consists of challenging the chemiluminescent NO_X analyzer with audit gas mixtures containing known concentrations of NO_2 within the measurement range of the analyzer. The difference between the known concentration and the analyzer response is obtained, and an estimate of the analyzer's accuracy is determined.

6.1.1 Equipment

Personnel, equipment, and NO standards used in conducting audits must be independent from those normally used in calibrations and in span checks.

Audit gas mixtures containing known concentrations of NO_2 can be generated by the GPT of NO with O_3 to produce NO_2 or by the use of an NO_2 permeation tube and a dynamic dilution system. The NO and NO_X channels should be audited by dilution of the NO standard with zero air. All audit standards must be traceable to NIST-SRMs as described in the EPA traceability protocol. All flow rates should be measured using a calibrated piston or soap bubble flowmeter or an equivalently accurate flowmeter.

Procedures used to generate NO, NO_X, and NO_2 concentrations, although not identical, are somewhat similar to the procedures described in Section 2.3.2. If, during a performance audit, the differences recorded for most analyzers are either negatively or positively biased, a check of the calibrator used in routine calibrations of the analyzers may be advisable.

6.1.2 Audit Schedule

The recommended audit schedule depends upon the purpose for which the monitoring data are being collected. For example, EPA's quality assurance requirements for state and local air monitoring stations (SLAMS) specify that each SLAMS analyzer be audited at least once per year (EPA 1994b). Each agency must audit 25% of the reference or equivalent analyzers each quarter. If an agency operates less than four reference or equivalent analyzers, it must randomly select analyzers for reauditing so that one analyzer will be audited each calendar quarter and each analyzer will be audited at least once a year.

EPA's quality assurance requirements for prevention of significant deterioration (PSD) air monitoring (EPA 1994a) specify that each PSD reference or equivalent analyzer be audited at least once a sampling quarter. Results of these audits are used to estimate the accuracy of ambient air data.

6.1.3 Audit Procedures for NO, NO_X, and NO_2

Audits should be conducted by challenging the analyzer with at least one audit gas mixture of known concentration from each of the following ranges within the measurement range of the analyzer being audited:

Audit Point	Concentration Range, ppm NO_2
1	0.03 to 0.08
2	0.15 to 0.20
3	0.35 to 0.45
4	0.80 to 0.90

The differences in concentrations (parts per million) between the audit values and the measured analyzer responses are used to calculate accuracy, as described in the EPA guideline on the meaning and use of precision and accuracy data.

Information on the station, analyzer, audit device, audit standards, and audit procedures is of prime importance because the validity of audit results depends on accurate documentation. The following procedures and audit report forms (Figures 6.1, 6.2, 6.2a, and 6.3) have been developed to aid in conducting the audit.

6.1.3.1 Procedure for an NO Audit

1. Record the station name, address, analyzer manufacturer, model, and serial number on the audit summary report.

2. Identify the person(s) performing the audit and the date that the audit is performed.

3. Record the type of audit device used. If the audit device was purchased, record the manufacturer's name, model, and serial number. If the audit device was assembled by the

1. Station Red Bank — Analyzer ACME
Red Bank Road — NO/NO_2/NO_X
Millsville, Ohio — SN 14782
2. Audit performed by Bill Brown — Date 5-15-00
3. Audit device used State Agency
GPT No. 6
4. NO standard used Cylinder 14782 — Concentration 50.0 ppm
Verified against NBS-SRM SRM # 1683b (50 ppm)
By Bill Brown — Date 5-4-00
5. Flow measured with Acme Bubble Meter

6. Analyzer response to zero air
NO zero = 0.050 volts
NO_2 zero = 0.050 volts
NO_X zero = 0.050 volts

AUDIT SUMMARY

Analyzer channel	**Audit value (ppm)**	**Analyzer response (volts)**	**Analyzer response (ppm)**	**Percent difference (Equation 4)**
NO	0.000	0.050	0.000	—
	0.450	0.960	0.455	+1.1
	0.200	0.455	0.203	+1.5
	0.050	0.150	0.050	0.0
NO_2	0.000	0.050	0.000	—
	0.361	0.800	0.375	+3.9
	0.178	0.422	0.186	+4.5
	0.047	0.148	0.049	+4.3
NO_X	0.000	0.050	0.000	—
	0.450	0.985	0.460	+2.2
	0.200	0.472	0.208	+3.8
	0.050	0.158	0.053	+6.2

Figure 6.1. Example of an audit summary form.

Zero air: $[NO_2]_R$ = 0.050 volts, 0.000 ppm (see Equation 1, Figure 6.2a)
$[NO]_A$ = 0.000 ppm

Audit point: $[NO]_R$ = 0.960 volts, 0.455 ppm (see Equation 1, Figure 6-2a)
$[NO]_A$ = 0.450 ppm (Equation 3 above)

Flow measurements	**t (min)**	**t_{avg} (min)**	**V (cm^3)**	**F_T (cm^3/min) (Equation 2)**
Total flow (F_T)	0.250 0.240 0.260	0.250	1,000	4,000
NO flow (F_{NO})	0.276 0.279 0.279	0.278	10	36.0

Audit point: $[NO]_R$ = 0.455 volts, 0.203 ppm (Equation 1, Figure 6-2a)
$[NO]_A$ = 0.200 ppm (Equation 3, Figure 6-2a)

Flow measurements	**t (min)**	**t_{avg} (min)**	**V (cm^3)**	**F_T (cm^3/min) (Equation 2)**
Total flow (F_T)	0.260 0.250 0.240	0.250	1,000	4,000
NO flow (F_{NO})	0.625 0.624 0.626	0.625	10	16.0

Audit point: $[NO]_R$ = 0.150 volts, 0.5 ppm (Equation 1)

$[NO]_A$ = 0.050 ppm (Equation 3)

Flow measurements	**t (min)**	**t_{avg} (min)**	**V (cm^3)**	**F_T (cm^3/min) (Equation 2)**
Total flow (F_T)	0.250 0.250 0.250	0.250	1,000	4,000
NO flow (F_{NO})	2.510 2.500 2.490	2.500	10	4.0

NO audit calibration equation (y = b x + a)

NO audit concentration (x) vs. analyzer response in volts (y)

Slope (b) = 2.0235

Intercept (a) = 4.964

Correlation coefficient (r) = 1.000

Figure 6.2. Example of an NO audit calculation form (front side).

Equation 1

$$\text{ppm} = \frac{y - a}{b}$$

Equation 2

$$F_T = \frac{V}{t_{avg}} \text{ or } F_{NO} = \frac{V}{t_{avg}}$$

Equation 3

$$[NO]_A = \frac{[NO]_{STD} \times F_{NO}}{F_T}$$

Equation 4

$$\% \text{ difference} = \frac{[NO]_R - [NO]_A}{[NO]_A} \times 100$$

For NO_2, substitute $[NO_2]_R$ and $[NO]_A$
For NO_X, substitute $[NO_X]_R$ and $[NO_X]_A$

Equation 5

$[NO_2]_A = [NO]_{ORIG} - [NO]_{REM}$

Equation 6

$$t_{avg} = \frac{t_1 + t_2 + t_3}{3}$$

y = analyzer response, volts
b = slope of the calibration line
a = intercept of the calibration line
F_T = total flow rate, cm^3/min
F_{NO} = flow rate of NO_{STD}, cm^3/min
V = volume measured with soap bubble flowmeter
t_{avg} = average time in minutes
$[NO]_{STD}$ = concentration of NO standard used, ppm
$[NO]_A$ = NO audit concentration, ppm
$[NO]_R$ = analyzer NO response, ppm
$[NO_2]_A$ = NO_2 audit concentration after titration of NO with O_3, ppm
$[NO]_{ORIG}$ = NO concentration before titration of NO with O_3, ppm
$[NO]_{REM}$ = NO concentration remaining after titration with O_3, ppm

Figure 6.2a. Example of an NO audit calculation form (back side).

	1		**2**		**3**	**4**	
	$[NO]_{ORIG}$[a]		**$[NO]_{REM}$[a]**		**$[NO_2]_A$ (Equation 5)**	**$[NO_2]_R$[b]**	
Audit point	**volts**	**ppm**	**volts**	**ppm**	**ppm**	**volts**	**ppm**
1	0.990	0.465	0.260	0.104	0.361	0.800	0.375
2	0.610	0.277	0.250	0.099	0.178	0.422	0.186
3	0.350	0.148	0.255	0.101	0.047	0.148	0.049

[a] Calculated from NO audit calibration equation.
[b] Calculated from NO_2 station calibration equation.

Figure 6.3. Example of an NO_2 audit calculation form.

user, assign it an identification number so that audits can be referenced to that particular apparatus.

4. Identify the NO standard and the NIST-SRM to which the standard is traceable. Reanalyze the NO standard every 2 years, following the EPA traceability protocol.

5. Identify the device used to measure the flow rates.

6. Attach the appropriate pressure regulator to the NO standard, and carefully flush the pressure regulator.

7. Connect the outlet of the pressure regulator to the GPT calibration system using 1/8-in. Teflon® tubing of minimum length.

8. Adjust the flow rates in the GPT system according to the relationships in Equations 6-1, 6-2, and 6-3:

$$P_R = [\mathrm{NO}]_{RC} \text{ x } t_R \ \$2.75 \text{ ppm-min} \qquad (6\text{-}1)$$

where

$$[\mathrm{NO}]_{RC} = [\mathrm{NO}]_{STD} \text{ x } \frac{F_{NO}}{F_O + F_{NO}} \qquad (6\text{-}2)$$

and

$$t_R = \frac{V_{RC}}{F_O + F_{NO}} \leq 2 \text{ min} \qquad (6\text{-}3)$$

where

P_R = dynamic parameter specification, determined empirically, to ensure complete reaction of the available O_3, ppm-min
$[\mathrm{NO}]_{RC}$ = NO concentration in the reaction chamber, ppm
t_R = residence time in the reaction chamber, min
$[\mathrm{NO}]_{STD}$ = concentration of the NO standard, ppm
F_{NO} = NO flow rate, standard cm^3/min
F_O = O_3 generator flow rate, standard cm^3/min
V_{RC} = volume of the reaction chamber, cm^3.

The flow conditions to be used are selected according to the following sequence:

a. Determine F_T, the total flow rate required at the output manifold (F_T = analyzer(s) demand plus 10 to 50% excess).

b. Determine F_{NO}, the flow rate of NO required to generate the lowest NO concentration required at the output manifold during the GPT (approximately 0.15 ppm).

$$F_{NO} = \frac{0.15 \times F_T}{[NO]_{STD}} \qquad (6\text{-}4)$$

c. Measure V_{RC}, the system's reaction chamber volume; this must be in the range of approximately 100 to 500 cm^3.

d. Compute F_O, the ozone generator flow rate, using Equation 6-5.

$$F_O = \sqrt{\frac{[NO]_{STD} \times F_{NO} \times V_{RC}}{2.75}} - F_{NO} \qquad (6\text{-}5)$$

e. Compute t_R, the reaction chamber residence time, using Equation 6-3; verify that t_R # 2 min.

f. Compute F_D, the diluent air flow rate, using Equation 6-6.

$$F_D = F_T - F_O - F_{NO} \qquad (6\text{-}6)$$

Adjust F_O to the value determined above. F_O should not be further adjusted during the NO-NO_X or NO_2 audit procedures; only F_{NO} (or F_D) and the O_3 generator settings are adjusted during the course of the audit.

9. Connect the analyzer sample line to the glass manifold of the audit device. The audit gas mixture must pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling and as much of the sample introduction system as is practical.

10. Allow the analyzer to sample zero air until stable responses are obtained. Record the analyzer zero values for all channels audited in the appropriate spaces of the audit form, Figure 6.1.

11. Generate the first audit gas mixture by adding the NO standard gas to the zero air, making sure the concentration is within one of the required concentration ranges.

12. After a stable analyzer response is obtained, record the analyzer NO response, $[NO]_R$, on the NO calculation form, Figure 6.2. Calculate the $[NO]_R$ in parts per million using Equation 1 of Figure 6.2a, where b and a are the slope and intercept of the analyzer's calibration line, respectively.

13. Attach the piston or soap bubble flowmeter to the audit device outlet line, and determine the total flow rate (F_T). Do not adjust the audit device settings. Record the value in Figure 6.2 and calculate the total flow rate using Equation 2 of Figure 6.2a.

14. Disconnect the NO flow line at the audit device reaction chamber. Connect the piston or soap bubble flowmeter to the line; determine the NO flow rate (F_{NO}) using Equation 2; and record the value on the calculation form.

15. Calculate the NO audit concentration $[NO]_A$ for the first audit gas mixture using Equation 3 of Figure 6.2a, and record the results.

16. Repeat Steps 11 through 15 for the remaining audit gas mixtures. A minimum of three audit gas mixtures is recommended.

17. Transfer the NO audit concentrations and the analyzer NO responses to the summary form, Figure 6.1.

18. Calculate the percentage difference for each audit point using Equation 4 of Figure 6.2a, and record each value on Figure 6.1.

19. Prepare an audit calibration equation for the NO channel by using least squares regression. Include the zero air point. (The audit concentration is the x-variable; the analyzer response is the y-variable.) The NO calibration curve will be used to determine the actual audit concentrations during the generation of the NO_2 audit gas mixtures. Record the slope, intercept, and correlation coefficient of the audit calibration equation on the calculation form.

6.1.3.2 Procedure for NO_2 Audit Using Gas-Phase Titration (GPT)

1. Generate an audit gas mixture containing an NO concentration that is approximately 0.08 to 0.12 ppm higher than the NO_2 audit concentration required. Allow the analyzer to sample this audit gas mixture until a stable analyzer response is obtained. Determine the NO concentration, $[NO]_{ORIG}$, from the NO audit calibration relationship. Record this value for the first audit gas mixture in Column 1 of the NO_2 calculation form, Figure 6.3.

2. Add O_3 to reduce the NO concentration by an amount equivalent to the NO_2 audit concentration required. After the analyzer response stabilizes, determine the NO concentration remaining, $[NO]_{REM}$, from the NO audit calibration relationship. Record this value for the first gas mixture in Column 2 of the calculation form, Figure 6.3.

3. Calculate the NO_2 audit concentration, $[NO_2]_A$, using Equation 5 of Figure 6.2a and record the value in Column 3 of the calculation form, Figure 6.3.

4. Record the analyzer NO_2 response, $[NO_2]_R$, in Column 4.

5. Repeat Steps 1 through 4 for the remaining audit gas mixtures.

6. Transfer the NO_2 audit concentrations and the analyzer NO_2 responses to the summary form, Figure 6.1.

7. Determine the percentage difference for each point, using Equation 4 of Figure 6.2a.

6.1.3.3 Procedure for NO_X Audit

The NO_X channel may be audited by the same method used to audit the NO channel and by determining converter efficiency using data from the NO_X and NO_2 audit.

Use Figure 6.1 to report the audit concentration, the analyzer response, and the percentage difference. Record the information on Figures 6.1, 6.2, and 6.3. Mark the strip chart record with the following information:

- Person conducting the audit
- Time and date of audit
- Concentrations of the audit gas mixtures
- The stable analyzer response for each audit gas mixture.

6.1.4 Interpretation of Audit Results

Results of the audit will be used to estimate the accuracy of the ambient air quality data. Calculation of accuracy is described in the EPA guideline on the meaning and use of precision and accuracy data.

6.2 Data Reduction Audit

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

The data processing check is made by calculating the accuracy:

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

where

$A =$ the difference in measured and check values

$[NO_2]_R =$ the recorded analyzer response, ppm

$[NO_2]_{CHECK} =$ the data processing NO_2 concentration, ppm.

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

6.3 Systems 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 this handbook.

Conduct the systems audit at the startup of a new monitoring system and periodically (as appropriate) as significant changes in system operations occur.

A checklist for a systems audit is Figure 6.4. Questions in this checklist should be reviewed for applicability to the particular local, state, or federal agency.

SYSTEMS AUDIT CHECKLIST

Station ______________________________ Analyzer ______________________________

______________________________ ______________________________

______________________________ ______________________________

Audit performed by: ______________________ Date ______________________________

Yes	No		
________	________	1.	Zero, span, and precision checks performed weekly or biweekly
________	________	2.	Voltage and temperature variations monitored
________	________	3.	Flowmeters routinely calibrated to ±2% accuracy against a reliable standard such as a soap bubble flowmeter or wet test meter
________	________	4.	Flowrates monitored routinely
________	________	5.	Excessive noise minimized
________	________	6.	Data processing checks performed
________	________	7.	Multipoint calibrations performed routinely and a record of these calibrations maintained
________	________	8.	Quality control charts maintained for zero and span checks
________	________	9.	Maintenance routinely performed on pertinent components as per manufacturer's manual
________	________	10.	Calibration gases traceable to NIST via EPA traceability protocol, certification not expired
________	________	11.	Sample introduction system check made weekly
________	________	12.	Particulate filter (if used) changed frequently
________	________	13.	Recording system checked and serviced before each sampling period
________	________	14.	Recorded data checked for signs of system malfunctions
________	________	15.	Data quality records maintained—completeness, accuracy, precision, and representativeness

Figure 6.4. Checklist for use by auditor (measurement of continuous NO_2 in ambient air).

TABLE 6-1. ACTIVITY MATRIX FOR AUDIT PROCEDURE

Activity	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Performance audit	The difference in concentrations between the measured values and the audit values is used as a measure of accuracy	At least once per quarter; Sec. 6.1.3 for procedure	Recalibrate the analyzer
Data reduction audit	Adhere to stepwise procedure for data reduction, Sec. 4.0; no difference exceeding ±0.02 ppm	Perform independent data processing check on a sample of the recorded data e.g., check data 1 day out of every 2 weeks, 2 hours for each day	Check all remaining data if one or more data reduction checks, exceed ±0.02 ppm
Systems audit	Method as described in this section of this handbook	At the startup of a new monitoring system, and periodically as appropriate; observation and checklist (Figure 6.4)	Initiate improved methods and/or training programs

7.0 Assessment of Monitoring Data for Precision and Accuracy

For continuous analyzers, perform a check every 2 weeks to assess data precision. Use these data to estimate single instrument precision as described in the EPA guideline on the meaning and use of precision and accuracy data. The precision check procedures described in Section 3.0 are consistent with those given in EPA quality assurance requirements for SLAMS and EPA quality assurance requirements for PSD air monitoring.

Estimates of single instrument accuracy for ambient air quality measurements from continuous methods are calculated according to the procedure in the EPA guideline. The performance of the audit is described in Section 6.0.

8.0 Recommended Standards for Establishing Traceability

To assure data of desired quality, two considerations are essential: (1) the measurement process must be in statistical control at the time of the measurement, and (2) the systematic errors, when combined with the random variation in the measurement process, must result in a suitably small uncertainty.

Evidence of good quality data includes documentation of the quality control checks and the independent audits of the measurement process by recording data on specific forms or on a quality control chart and by using materials, instruments, and measurement procedures that can be traced to appropriate standards of reference. To establish traceability, data must be obtained routinely by repeated measurements of standard reference samples (primary, secondary, and/or working standards), and a condition of process control must be established. More specifically. working calibration standards should be traceable to standards of higher accuracy, such as those listed in Table 8-1 (NIST 1998).

TABLE 8-1. NIST-SRMs AVAILABLE FOR TRACEABILITY OF CALIBRATION AND AUDIT GAS STANDARDS

NIST-SRM No.	Type	Size, liters at STP	Nominal concentration (ppm)
1683b	Nitric oxide in N_2	870	50
1684b	Nitric oxide in N_2	870	100
1685b	Nitric oxide in N_2	870	250
2627a	Nitric oxide in N_2	870	5
2628a	Nitric oxide in N_2	870	10
2629a	Nitric oxide in N_2	870	20

9.0 References

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