

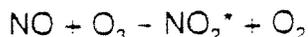
4.07 NITROGEN DIOXIDE (NO₂) BY CHEMILUMINESCENCE

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4.07.0 METHOD SUMMARY

Ambient air concentrations of nitrogen dioxide (NO₂) are indirectly photometrically measured as light intensities that result from the chemiluminescent reaction of nitric oxide (NO) with ozone (O₃) to form the activated NO₂* species according to the reaction mechanism shown below:



As the NO₂* reverts to a lower energy state, it emits broad band radiation from 500 to 3,000 nm (nanometers) with a maximum intensity at approximately 1,100 nm. Since one NO molecule reacts with one O₃ molecule to form one NO₂* molecule, the intensity of the resultant chemiluminescent radiation is linearly proportional to the NO concentration in the sample.

Ambient NO₂ is first quantitatively reduced to NO by a converter. The NO, which commonly exists in ambient air with NO₂, passes through the converter unchanged and reacts with O₃, resulting in a total nitrogen oxides (NO_x) concentration of NO + NO₂. A portion of the ambient air is also reacted with O₃ without passing through the converter, and the subsequent NO concentration is measured. The NO_x concentration minus this NO concentration yields the final NO₂ concentration.

The NO and NO + NO₂ 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 less than, or equal to, one minute.

Interference from air pollutants commonly found in the environment (ozone, sulfur dioxide, carbon monoxide, methane, and ammonia) are negligible for chemiluminescence NO₂ analyzers. The selectivity of the NO-O₃ reaction, the use of low temperature or carbon-based converters, and the selective optical filters preclude almost all possible interferences. The only possible interferences of any significance are organic nitrates, organic nitrites, peroxyacetyl nitrate (PAN), and some amines. The ambient concentrations of these compounds are usually so low as to be insignificant. However, where relatively low concentrations of low NO₂ occur simultaneously with high concentrations of PAN and other nitrogen-containing compounds (1:10 ratio), the interferences could be significant. If this situation exists, it is necessary to independently determine the interferant parameters' concentrations by gas chromatography, infrared spectroscopy, or other methods. If the interferant is determined to be significant, an equivalent method for NO₂ analysis that is not susceptible to these interferences should be selected.

The operating range for this method is 0-0.5 ppm or 0-1.0 ppm, depending upon each analyzer's "EPA Designated Reference or Equivalent Method" operating range.

Analyzers used for monitoring NO₂ in the ambient air must be USEPA-designated reference or equivalent method chemiluminescent NO_x analyzers.

The method detection limit is 2 percent of full scale (i.e., 0.01 ppm for 0-0.5 ppm range and 0.02ppm for 0-1.0ppm range).

4.07.1 SAMPLE PROBE AND SHELTER CRITERIA

4.07.1.A SITING REQUIREMENTS

The probe siting criteria as discussed below must be followed to the maximum extent possible. It is recognized that there may be situations when the probe siting criteria cannot be followed. If the siting criteria cannot be met, this must be thoroughly documented with a written request for a waiver which describes how and why the siting criteria differs. This documentation should help to avoid later questions about the data. These siting criteria are discussed in 40 CFR Part 58, Appendix E.

The spatial scales of representativeness used in this appendix (i.e., micro, middle, neighborhood, urban, and regional) are defined and discussed in 40 CFR Part 58, Appendix D. Pollutant-specific probe siting criteria generally apply to all spatial scales except where noted otherwise. Specific siting criteria that are prefaced with a "must" are defined as a requirement, and exceptions may be applied through the other provisions. However, siting criteria that are prefaced with a "should" are defined as a goal to meet for consistency, but are not a requirement.

Horizontal and Vertical Probe Placement--The height of the NO_x inlet probe must be 3 to 15 meters above the ground. The distance of the inlet probe from any supporting structures must be greater than one meter vertically or horizontally.

Spacing from Obstructions--The monitoring station must be located away from any obstacles (such as buildings, trees, etc.) that may scavenge NO_x. If obstacles are present, the distance between the obstacles (other than supporting structures) and the inlet probe must be at least twice the height that the obstacles protrude above the inlet probe. Sampling stations that are located closer to obstacles than this criteria allows should not be classified as a neighborhood scale, since the measurement from such a station would closely represent middle scale stations. Therefore, stations not meeting this criteria should be classified as middle scale.

For similar reasons, a probe inlet along a vertical wall is undesirable because air moving along that wall may be subject to possible removal mechanisms. Airflow must also be unrestricted in at least a 270 degree arc around the inlet probe, with the predominant wind direction for the season of greatest pollutant concentration included within the 270 degree arc. If the inlet probe is located on the side of a building, 180 degrees of clearance is required.

Spacing from Trees--Trees can provide surfaces for NO_x adsorption and/or reactions, and can obstruct the normal flow of wind near the monitoring station. To minimize these effects, the inlet probe should be at least 20 meters from the drip line. If tree(s)

protrude by 5 meters or more above the height of the probe, the probe must be greater than or equal to 10 meters from the drip line of the tree(s).

Spacing from Roads--It is important that the monitoring probe be removed from NO_x sources to avoid measurements being dominated by any one source, and to allow conversion of NO emissions to NO₂. Further, the effects of roadway sources must be minimized by using separation distances for neighborhood and urban scale stations found in figure 4.07-1. The minimum separation distance must also be maintained between an NO₂ probe and any other similar volume of automotive traffic such as parking lots. Sampling stations that are located closer to roads than this criteria allows should not be classified as neighborhood or urban scale stations. Such stations should generally be classified as middle scale.

MINIMUM SEPARATION DISTANCE BETWEEN NEIGHBORHOOD AND URBAN SCALE NO₂ STATIONS AND ROADWAYS (EDGE OF NEAREST TRAFFIC LANE)	
Roadway Average Daily Traffic (Vehicles per Day)	Minimum Separation Distance Between Roadways and Station (meters)
≥ 10,000	≤ 10
15,000	20
20,000	30
40,000	50
70,000	100
~ 50,000	135
≥ 110,000	≤ 250

Figure 4.07-1

4.07.1.B SAMPLE TRAIN (PROBE AND GAS LINE) MATERIALS

Sampling train (probes, gas lines, manifolds) must be constructed of borosilicate glass, stainless steel (5.5.316 or better), FEP Teflon, or equivalent material, to minimize possible reaction and degradation of the oxides of nitrogen. The use of integrating flasks on the sample manifold is strongly discouraged. Even with nonreactive gas line materials, reactive particulate matter is deposited on sample train walls over time. Therefore, the time it takes the gas to transfer from the probe inlet to the sampling device is also critical. O₃ in the presence of NO will show significant losses even in the

most inert probe material when residence times exceed 20 seconds. In addition, other sample train specifications are listed below:

Sample Probe and Gas Manifold Material--Borosilicate Glass, FEP Teflon (or equivalent), stainless steel (5.5.316 or better).

Filter--Particulate filter(s), if used, must be borosilicate glass, FEP Teflon, stainless steel (s.s. 316 or better), or equivalent material. The use of particulate filters on the sample manifold and inlet line is optional and left to the discretion of the user. Use of the filter should depend on the analyzer's susceptibility to interference, malfunction, or damage due to particulates. The user is cautioned, however, that particulate matter concentrated on a filter may cause erroneous NO₂ measurements. For this reason, filters should be changed frequently. In addition, a particulate filter may only be used in the sample line (between the gas manifold and the analyzer). Prior to routine use, it is incumbent on the user/manufacturer to prove that an in-line filter does not bias the reliability of the analyzer to measure actual concentrations of NO₂ in ambient air. These checks must be conducted at calibration, and at periodic intervals thereafter, to test the integrity of the sample introduction system. It is up to the agency operating these monitors to design and implement these checks. As with all instrument checks, documentation is a required QA activity.

Valve(s) Material--pyrex glass, FEP Teflon, or stainless steel (5.5.316 or better).

Gas Lines--Gas lines, including sample, span, and calibration lines, must be either borosilicate glass, FEP Teflon, or stainless steel (s.s.316 or better). Sample lines should be kept as short as possible to reduce sample gas residence time. All fittings must be compatible (e.g., both male and female ends either stainless steel or Teflon). Sample Train Gas Residence Time (from test gas introduced at sample inlet to first upscale analyzer response)--10 seconds preferred, 20 seconds acceptable. Demonstration of compliance may be physical testing or calculated. The residence time within the sampling line should be minimized to: 1) reduce the possibility of reactive gas interactions, and 2) to minimize NO_x adsorption on the surface of the lines.

Further information and requirements regarding probe and manifold materials and designs can be found in, "*Quality Assurance Handbook for Air Pollution Measurement Systems: Volume II. Ambient Air Specific Methods, Section 2.0.2.2.1 Design of Probes and Manifolds.*"

4.07.1.C SHELTER

The monitoring 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 within 15 to 30°C. Daily fluctuations should not exceed ±2°C (±4°F). A continuous recording thermograph should be installed at the shelter to continuously record daily fluctuations in temperature. Fluctuations greater than ±2°C may cause the electronic components of the analyzer to drift and may

introduce error into the data. For this reason, excursions outside the specifications should be flagged to indicate possible questionable data.

In addition to a temperature-controlled environment, it is highly recommended to condition all power supplied to sensitive monitoring equipment. Appropriate selection of a power conditioner for the monitoring area will minimize equipment failure and loss of data.

4.07.2 NO_x INSTRUMENT CALIBRATION

The accuracy and validity of measurement data recorded by air monitoring equipment depends on the quality assurance procedures used. The primary procedure is dynamic calibration, which determines the relationship between the observed and the actual values of the variable being measured.

In dynamic multi-point calibration, an instrument's responses are related to successive gas samples of known concentrations. A minimum of four reference points and a zero point are recommended to derive the calibration relationship. The "true" value of each NO cylinder gas or NO₂ permeation tube must be traceable to a National Institute of Standards and Technology-Standard Reference Material (NIST-SRM), Certified Reference Material (CRM), or NIST Traceable Reference Material (NTRM).

4.07.2.A STANDARD REFERENCE MATERIALS

To assure data of desired quality, the NO₂ measurement process must be under defined control limits, and any systematic errors, when combined with random variations in the measurement process, must result in a small level of uncertainty.

Good data quality requires documentation of the quality control checks and performing independent audits of the measurement process. These tasks necessitate maintaining good data recording practices and using materials, instruments, and measurement procedures traceable to reference standards of known quality. To establish traceability, multiple measurements must be made of standard reference materials (primary, secondary, and/or working standards), and process control procedures must be established. More specifically, working calibration standards must be traceable to standards of higher accuracy, such as NIST-SRM, CRM, or NTRM. Procedures for certification of an NO or NO₂ working standard against NIST-SRM, CRM, or NTRM are found in section 4.07.2.C, Certification of NO and NO₂ standards.

4.07.2.A.1 ZERO AIR

Dry zero air, verified to be free of contaminants that would cause detectable responses in the NO_x analyzer, may be purchased in high-pressure gas cylinders or generated with commercially available clean air systems. Care should be taken to ensure that an ambient concentration of carbon dioxide (CO₂), approximately 350 ppm CO₂, is maintained in any zero air source used.

4.07.2.A.2 NITRIC OXIDE (NO) CYLINDER GAS

NO Concentration Standard--NO Cylinder gas must contain a known concentration of NO in Nitrogen (N₂) with an NO₂ concentration <2 percent of the NO concentration. NO cylinder calibration gases must be traceable to either a NIST-SRM, CRM, or NTRM cylinder gas.

4.07.2.A.3 NITROGEN DIOXIDE PERMEATION DEVICES

NO₂ concentration standard--NO₂ permeation device(s) suitable for generating NO₂ concentrations at the required flowrates over the required concentration range. The NO₂ permeation device must be certified traceable to a NIST-SRM, CRM, or NTRM source.

4.07.2.B CALIBRATION PROCEDURES

Either of two NO₂ calibration methods may be used to dynamically calibrate the NO_x analyzer. These are:

Method A--Dynamic Dilution of a High Concentration NO Gas Cylinder to calibrate the NO and NO_x channels followed by Gas Phase Titration (GPT) of an NO standard with O₃ to generate NO₂ with which to calibrate the instrument's NO₂ responses.

Method B--Dynamic Dilution of a High Concentration NO Gas Cylinder to calibrate the NO and NO_x channels followed by dynamic dilution of an NO₂ permeation tube to calibrate the instrument's NO₂ responses.

Analyzers used for monitoring NO₂ in the ambient air must be USEPA-designated reference or equivalent method chemiluminescent NO_x analyzers. These chemiluminescence analyzers are nitric oxide (NO) analyzers that rely on the conversion of NO₂ to NO to measure NO₂ concentrations. To establish this relationship, the analyzer must be calibrated to both NO and NO₂, and the analyzer's converter efficiency determined. The minimum acceptable % converter efficiency is 96%.

The NO₂ analyzer will require a new calibration whenever one of the following conditions occur:

- o lapse of three months since the last calibration.
- o replacement of any major component(s) of the NO₂ analyzer and monitoring system.
- o the monitor fails a performance audit.
- o a level 1 zero/span NO/NO_x and/or NO₂ gas check is not within tolerance of the corresponding zero/span gas concentration.

NOTE: If the monitor fails a precision quality control (QC) check, the instrument response should be used only as an indicator of the analyzer's performance (no analyzer adjustment can be taken based solely on an analyzer's response to a precision gas). A level 1 zero/span QC check must be performed immediately thereafter to determine if the analyzer is within calibration tolerance.

- o the analyzer's NO₂ to NO converter efficiency falls below 96%.
- o physical relocation of the monitor.
- o an interruption of more than three days in analyzer operation.
- o any other indication such as excessive zero or span drift or malfunction of the NO₂ monitoring system.

4.07.2.B.1 CALIBRATION FREQUENCY

To ensure accurate measurements of the NO and NO₂ concentrations, calibrate the analyzer at the time of installation, and recalibrate it:

1. no later than three months after the most recent calibration or performance audit which indicated analyzer response to be acceptable; or
2. following any one of the activities listed below:
 - a. any repairs which might affect its calibration;
 - b. physical location of the analyzer; or
 - c. any other indication (including excessive zero/span drift and/or insufficient NO₂ to NO conversion) of possible significant analyzer inaccuracy.

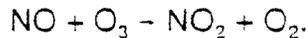
Following any of the activities listed in item 2 above, the zero and span should be checked to determine if a calibration is necessary. If the analyzer zero and span drifts do not exceed the calibration limits in figure 4.07-12 (located at the end of section 4.07.3), a calibration need not be performed. If either the zero or span drift exceeds its respective calibration limit, investigate the cause of the drift, take corrective action, and calibrate the analyzer.

An activity matrix for calibration procedures is presented in figure 4.07-9 at the end of this section.

4.07.2.B.2 CALIBRATION METHOD A

Dynamic Dilution of a High Concentration NO Gas Cylinder to calibrate the NO and NO_x channels, followed by Gas Phase Titration (GPT) of an NO standard with O₃ to generate NO₂ with which to calibrate the instrument's NO₂ responses.

The principle of GPT is based on the rapid gas phase reaction between NO and O₃, which produces stoichiometric quantities of NO₂ as shown by the following equation:



Given the NO concentration is known for this reaction, the resultant concentration of NO₂ 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 O₃, the observed decreases in NO concentration on the calibrated NO channel is equivalent to the concentration of NO₂ produced. The amount of NO₂ generated may be varied by adding varying amounts of O₃ from a stable O₃ generator.

Dynamic calibration systems based on this principle are commercially available, or may be assembled by the user. A recommended calibration system is depicted in figure 4.07-2 and detailed in USEPA 600/4-75-003 December 1975, *Technical Assistance Document (TAD) for the Chemiluminescence Measurement of Nitrogen Dioxide*. Persons desiring to assemble their own calibration systems should follow the procedures in the TAD.

Before using the assembled and purchased systems for NO₂ calibrations, your system must:

1. Use an NO standard gas traceable to an NBS-SRM. This high concentration NO gas cylinder (preferably in the range of 50 to 100 ppm with less than 1.0 ppm NO₂ impurity and the remaining balance N₂) is the primary nitric oxide (NO) calibration source from which all subsequent NO dilutions (calibration standards) are made.

Note: All regulators used in a calibration system (zero air and standard gases) should be cleaned prior to initial use to remove potential manufacturing residues that may contaminate the calibration system.

2. Have a stable O₃ source with an adjustable output.
3. Have a minimum total flow output that exceeds the analyzer flow demand by at least 10%.
4. Be capable of generating an NO concentration that is approximately 90% of the upper range limit (URL) of the NO₂ range to be calibrated.

5. Have a reaction chamber residence time of ≤ 2 min.
6. 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-O₃ reaction goes to completion (< 1 percent residual O₃) if the NO concentration in the reaction chamber (ppm) multiplied by the residence time (min) of the reactants in the chamber is ≥ 2.75 ppm-min. The theory behind the development of this equation is in the TAD.

7. For a Gas Dilution/GPT calibrator, be able to generate a series of dilute NO gas standards by diluting the NO output of the NO gas tank via a system of mass-flow-controllers that regulate both the pollutant and the dilution (zero) air to the desired NO concentration.
8. Have a Gas Dilution/GPT calibration system capable of controlling and measuring flow rates to within ± 2 percent of stated flow. All parts of the Gas Dilution/GPT calibrator in contact with the NO/NO_x/NO₂ output must be glass, Teflon, and (to a limited amount) 316 or better quality stainless steel).
9. Have dilution air (zero air) that is dry and free of interferants that would cause a detectable response in the chemiluminescent analyzer. This air may be used in generating multi-point calibrations, precision checks, and span checks. This zero air is used to establish and check the analyzer's zero base line and to dilute the NO gas to the desired concentrations. Zero air may be supplied from cylinders or from a clean air generator.

Assemble a dynamic calibration system (consult the manufacturer's manuals for proper set up and operations). See figure 4.07-2 (at the end of this method A) for a schematic diagram of a typical calibration system using a Gas Phase Titration system. Ensure that all flow meters are calibrated under conditions of use against a NIST-traceable intermediary primary standard (e.g., soap bubble meter, laminar flow element (LFE), or wet test meter). All volumetric flow rates should be corrected to 298°K (25°C, 78°F) and 760 mm (29.92 in.) Hg. Instruments using water should be corrected for the vapor pressure of water (please refer to the manufacturer's instruction manual). Precautions must be taken to remove O₂ from the NO pressure regulator and delivery system prior to the start of calibration. Failure to do so can cause significant errors in calibration. This problem may be minimized by:

1. carefully evacuating the regulator after it has been connected to the cylinder, but before opening the cylinder valve;
2. thoroughly flushing the regulator and delivery system with cylinder gas after opening the cylinder valve; and

3. not removing the regulator from the cylinder between calibrations unless absolutely necessary.

Connect the recorder and DAS output cables of the analyzer to the input cables of the strip chart recorder and DAS. All adjustments to the analyzer should be performed based on the appropriate DAS and strip chart recorder readings. References to analyzer responses in the procedures given below refer to DAS and recorder responses.

Prior to calibrating the NO_x analyzer, the DAS and strip chart recorder accuracy should be verified with a power supply and a volt meter of known accuracy. At a minimum, 80%, 20%, and 0% of analyzer full scale responses should be verified. Both chart recorder and DAS readouts should be within ±2 percent full scale volts of the analyzer output.

Calibration gases must be introduced directly to the sample inlet port of the analyzer. Ensure that calibration gases are introduced to the analyzer at atmospheric pressure.

For the GPT system, ensure the reaction chamber residence time and dynamic parameter specification are met. To determine the reaction chamber residence time and dynamic parameter specification for the desired flow conditions, perform the following GPT calibrator check procedure.

4.07.2.B.2.a Gas Phase Titration Calibrator Check Procedure

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

For calibrators that have known pre-set flow rates, use Equations 4.07-5 and 4.07-6 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 gas that has a nominal concentration in the range of 40 to 100 ppm. Determine the exact concentration ([NO]_{STD}) by referencing against an NBS-SRM.
2. Determine the volume (cm³) of the calibrator reaction chamber (V_{RC}). 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:

$$V = 4/3(\pi r^3) \text{ for a sphere, or}$$

$$V = \pi r^2 h \text{ for a cylinder}$$

(where r = radius and h = cylinder height).

The reaction chamber should not be confused with the mixing chamber where the dilution air and the generated NO₂ are mixed.

- Determine the required minimum total flow output (F_T) using Equation 4.07-1:

$$F_T = \text{analyzer flow demand (ccm)} \times (110/100) \quad \text{Eqn. 4.07-1}$$

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

- Calculate the NO concentrations ($[\text{NO}]_{\text{OUT}}$) needed to approximate the 90% upper range limit (URL) of the NO₂ analyzer to be calibrated, using Equation 4.07-2.

$$[\text{NO}]_{\text{OUT}} = \text{URL of analyzer (ppm)} \times (90/100) \quad \text{Eqn. 4.07-2}$$

- Calculate the NO flow (F_{NO} , ccm) required to generate the NO concentration ($[\text{NO}]_{\text{OUT}}$), using Equation 4.07-3.

$$F_{\text{NO}} = ([\text{NO}]_{\text{OUT}} \times F_T) / [\text{NO}]_{\text{STD}} \quad \text{Eqn. 4.07-3}$$

- Calculate the required flow through the ozone generator (F_{O_3} , ccm), using Equation 4.07-4.

$$F_{\text{O}_3} = \{([\text{NO}]_{\text{STD}} \times F_{\text{NO}} \times V_{\text{RC}}) / 2.75 \text{ ppm-min}\}^{1/2} - F_{\text{NO}} \quad \text{Eqn. 4.07-4}$$

- Verify that the residence time (t_R) in the reaction chamber is ≤ 2 min, using Equation 4.07-5.

$$t_R = F_{\text{RC}} / (F_{\text{O}} + F_{\text{NO}}) \leq 2 \text{ min} \quad \text{Eqn. 4.07-5}$$

- Verify that the dynamic parameter specification (P_R) of the calibrator's reaction chamber is ≥ 2.75 ppm-min using Equation 4.07-6.

$$P_R = [\text{NO}]_{\text{STD}} \{F_{\text{NO}} / (F_{\text{O}} + F_{\text{NO}})\} \{V_{\text{RC}} / (F_{\text{O}} + F_{\text{NO}})\} \geq 2.75 \text{ ppm-min} \quad \text{Eqn. 4.07-6}$$

NOTE: If t_R is >2 min or if P_R is < 2.75 ppm-min, then changes in flow conditions (F_T , F_{O} , F_{NO}) or 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.

- After equations 4.07-5 and 4.07-6 are satisfied, calculate the diluent air flow (F_{D}) using Equation 4.07-7.

$$F_{\text{D}} = F_T - F_{\text{NO}} \quad \text{Eqn. 4.07-7}$$

4.07.2.B.2.b Method A, Calibration Procedure for NO and NO_x

The GPT requires the use of the analyzer's NO channel to determine the amount of NO₂ generated by titration. Therefore, it is necessary to calibrate and determine the linearity of the NO channel before proceeding with the NO₂ calibration. In some analyzers it is also necessary to calibrate the NO_x channel. This can be done simultaneously with the NO calibration.

During the calibration, the analyzer must be operating in its normal sampling mode, and the test atmosphere must pass directly to the sample inlet of the analyzer.

Note: During a calibration, the analyzer's response(s) is set to equal the calibration gas concentration. Any external filters, scrubbers, conditioners, etc., may introduce bias to the measurement system. After completing the calibration, conduct a level 1 zero/span quality control check and measure the responses. Reconnect all in-line sample conditioning equipment and repeat the same level 1 zero/span quality control check. The differences between the two measured level 1 zero/span checks should be zero. If not, the in-line conditioners are introducing bias to the measurement system.

1. Record the station name and address on a calibration data form/log book. Identify individual stations by their official names and addresses. Where appropriate, station name and address should be the same as those appearing on the SAROAD or 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. The manufacturer's name, model, and serial number should be recorded.
4. Identify the calibration apparatus used. If the calibrator was purchased, record the manufacturer's name, model, and serial number. Calibrators assembled by the user should be assigned an identification number so that calibrations can be referenced to that particular apparatus.
5. Identify, by supplier and cylinder number, the reference standard to be used. Record the concentration of the calibration gas(es). Do not use cylinders with pressures < 200 psi for calibration. Provide a record of NIST traceability for any cylinder used in a calibration. Include the date, and the name of the person who conducted the referencing.
6. Select the operating range of the NO_x analyzer to be calibrated.

7. Record the zero and 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 NO₂; 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.

8. Record the shelter temperature and barometric pressure at the time of calibration.
9. Use the NO/NO_x part of calibration data form (figure 4.07-4) for the systematic recording of data determined during the systematic calibration of the NO and NO_x channels of the analyzer. Because zero and calibration adjustments differ between analyzers, the manufacturer's manual should be consulted before calibration is performed.
10. Adjust diluent air (zero air) and the O₃ generator air to obtain the flows determined in Subsection 4.07.2.B.2.a. Ensure that the total air flow exceeds the total demand of the analyzer(s) connected to the output manifold so that no ambient air will be pulled into the atmospheric dump. For safety concerns, ensure that the atmospheric dump vents to ambient air (outside the monitoring shelter). Measure the diluent and O₃ air flows using a NIST-traceable intermediate primary standard. Consult the respective manufacturer's standard operating procedures manual for specific directions. Measure and record temperature and pressure of the (in-line) diluent and O₃ air flows. Correct the actual measured air flows to standard temperature and pressure conditions (STP: i.e., T_{std} = 298°K and P_{std} = 760mmHg). Record the standardized diluent air flow (F_D) in column 1 of page 2 of figure 4.07-4.

Note: When installing an atmospheric dump, take care not to create a back pressure problem.

11. Allow the analyzer to sample zero air until a stable response is obtained (a response that does not vary by more than ±1% of full scale over a 5-minute time period); then adjust the analyzer zero control to read zero. For a strip chart recorder, offset of the analyzer zero adjustment to + 5% of the strip chart scale is recommended. This facilitates observing negative zero drift. Record the stable zero air response for the NO and NO_x channels.
12. Determine the 80% upper range limit (URL) NO cylinder gas flow (F_{NO}) by solving equation 4.07-8 for F_{NO}. Adjust the NO flow from the standard NO cylinder to generate an NO concentration of approximately 80% of the URL of the NO channel. Measure the NO flow (F_{NO}) using a NIST-traceable intermediate primary standard. Measure and record the

NO air stream (in-line) temperature and pressure. Correct the actual measured flow to STP conditions. Record F_{NO} under column 2 on the 80% URL line.

$$F_{NO} = (F_D \times [NO]_{out}) / ([NO]_{std} - [NO]_{out}) \quad \text{eqn. 4.07-8}$$

where: $[NO]_{out}$ = NO gas concentration at the output manifold

$[NO]_{std}$ = NO cylinder gas concentration

F_{NO} = flow rate of NO cylinder gas, sccm

F_D = flow rate of dilution air, sccm

13. Calculate the exact NO concentration $[NO]_{OUT}$ by solving equation 4.07-9.

$$[NO]_{OUT} = F_{NO} \times [NO]_{STD} / (F_{NO} + F_D + F_O) \quad \text{eqn. 4.07-9}$$

where: F_{O_3} = zero air flow through ozonator, sccm

Record the $[NO]_{OUT}$ under column 3 on the 80% line.

14. Calculate the exact NO_x concentration $[NO_x]_{OUT}$ by solving equation 4.07-10.

$$[NO_x]_{OUT} = F_{NO} \times ([NO]_{STD} + [NO_2]_{IMP}) / (F_{NO} + F_D + F_O) \quad \text{eqn. 4.07-10}$$

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

$[NO_x]_{OUT}$ = NO_x gas concentration at the output manifold

Record the $[NO_x]_{OUT}$ under column 5 on the 80% line.

15. Sample the generated concentration until the NO and NO_x responses have stabilized. Adjust span response for the analyzer NO and NO_x channels for a balanced output equal to the NO test gas.

NOTE: Some analyzers may have separate span controls for NO_x , NO, and NO_2 . Other analyzers may have separate span controls for only NO_x and NO. Still other analyzers may have only one span control common to all three channels. When only one span control is available, the span adjustment is made on the NO channel of the analyzer.

NOTE: If the analyzer NO and NO_x responses fail to stabilize (all flows constant) with the NO response gradually increasing and the NO_x

response gradually decreasing, check for contamination of the NO pressure regulator and delivery system.

If substantial adjustment of the NO and NO_x span control(s) is necessary, recheck the zero and span adjustments in steps 11 and 15. Record the analyzer's NO response under column 4 and the analyzer's NO_x response under column 6 on the 80% URL line.

16. Generate four more evenly spaced NO gas concentrations by decreasing F_{NO} or increasing F_{O_2} . Use equation 4.10-8 to calculate F_{NO} flows for 60% URL, 40% URL, 20% URL, and 10% URL NO gas concentrations. Measure NO and diluent flows for the 60 percent URL, 40 percent URL, 20% URL, and 10% URL NO gas concentrations as described in steps 10 and 12. Correct all flows to STP conditions. Record the calibration data for each point under the appropriate column in the NO/NO_x table of figure 4.07-4.
17. Plot the analyzer's NO and NO_x responses against the corresponding NO calibration gas concentrations. Determine the best straight line by the method of least squares. This can be done with a programmed calculator with this ability, or with the calculation data form presented in figure 4.07-5. 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 when possible.

Calculate the NO and NO_x linear regression calibration curves. Record the slope (m), y intercept (b), and correlation coefficient (r) for the corresponding NO and NO_x curves. To be considered linear, the correlation coefficient (r) must be ≥ 0.995 .

4.07.2.B.2.c Method A, Gas Phase Titration (GPT) Procedure for NO₂

Having completed the calibration of the NO and NO_x channels, the NO₂ channel may now be calibrated by GPT. Figure 4.07-4 allows for the systematic recording of the data determined during the calibration of the NO₂ channel of the analyzer. **Do not readjust zero and span knob settings for the NO and the NO_x channels.**

18. The NO₂ zero adjustment was made in step 11 of the NO/NO_x calibration and need not be repeated. Record the determined response under column 12 of the NO₂ calibration table.
19. NO₂ impurities [NO₂]_{IMP}, found in the reference standard must be recorded under column 10; if there is no impurity, disregard this column.

20. Adjust the NO flow (F_{NO}) to generate an NO concentration near 90% of the URL. Dilution air and O_3 generator air flows should be the same as used in the calculation of specified conditions in Subsection 4.07.2.B.2.a. Sample this NO concentration until the NO and NO_x responses stabilize.

Using the NO response and the NO calibration relationship obtained in step 17, calculate and record the value under column 8 on the line marked "ORIG."

Using the NO_x response and the NO_x calibration relationship obtained in step 17, calculate and record the value under column 7 [NO_x] on the line marked "ORIG."

21. Adjust the O_3 generator to produce sufficient O_3 to decrease the NO concentration from 90% to 10% of full scale. This 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 NO concentration under column 9 [NO]_{REM}. The [NO]_{ORIG} will be the same value determined in step 3.
22. Calculate the resulting NO_2 concentration [NO_2]_{OUT} using Equation 4.07-11, and record it under column 11 [NO_2]_{OUT}.

$$[NO_2]_{OUT} = [NO]_{ORIG} - [NO]_{REM} + (F_{NO} \times [NO_2]_{IMP}) / (F_{NO} + F_O + F_D) \quad \text{Eqn. 4.07-11}$$

where:

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

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

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

[NO_2]_{OUT} = concentration of NO_2 gas at the output manifold

F_{NO} = flow rate of NO cylinder gas, sccm

F_D = flow rate of dilution air, sccm

F_O = zero air flow through ozonator, sccm

If there was no NO_2 impurity in the NO reference standard, Equation 4.07-11A may be used to calculate [NO_2]_{OUT}.

$$[NO_2]_{OUT} = [NO]_{ORIG} - [NO]_{REM} \quad \text{Eqn. 4.07-11A}$$

23. Adjust the O₃ span control to obtain an NO₂ analyzer response at about the 80% URL point. Measure and record the NO₂ analyzer response under column 12.

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 NO₂. If substantial adjustment of the NO₂ span control is necessary, it may be necessary to recheck the zero and span adjustments.

24. While maintaining all other conditions, adjust the ozone generator to obtain four other concentrations of NO₂ evenly spaced between the 80% URL point and the zero point. Record the information for each point on the respective lines of the NO₂ calibration table.
25. Repeat steps 9, 10, and 11 of Calibration Procedure for NO and NO_x for the NO₂ analyzer response reading, column 12, and the corresponding calculated concentration [NO₂]_{OUT}, column 11.
26. Plot the analyzer's NO₂ response from column 12 (y-axis) versus the corresponding calculated concentration [NO₂]_{OUT} from column 11 (x-axis). Proceed as in step 17 to determine the best straight line by the method of least squares.

Calculate the NO₂ linear regression calibration curve. Record the slope (m), y intercept (b), and correlation coefficient (r) for the corresponding NO₂ curves. To be considered linear, the correlation coefficient (r) must be ≥ 0.995 .

4.07.2.B.2.d Method A, Calculation of NO₂ Converter Efficiency

Data form (figure 4.07-6) was developed for determining the converter efficiency. The following procedure is for use with this data form.

27. Values for columns 1, 2, and 3 of the converter efficiency data form are taken directly from the NO₂ table of the calibration data form.
 - a. Column 1 [NO₂]_{OUT} is from column 11 [NO₂]_{OUT} of the table (figure/form 4.07-4b).
 - 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.

28. Calculate the quantity of NO₂ converted to NO, labeled [NO₂]_{CONV}, for each point, using Equation 4.07-12.

$$[\text{NO}_2]_{\text{CONV}} = [\text{NO}_2]_{\text{OUT}} - ([\text{NO}_x]_{\text{ORIG}} - [\text{NO}_x]_{\text{REM}}) \quad \text{Eqn. 4.07-12}$$

where: [NO_x]_{ORIG} = concentration of NO_x before O₃ is added during GPT

[NO_x]_{REM} = concentration of NO after O₃ is added during GPT

[NO₂]_{OUT} = concentration of NO₂ gas at the output manifold

29. Plot [NO₂]_{CONV} (y-axis) versus [NO₂]_{OUT} (x-axis). Calculate the slope (b) of the curve using either an appropriate calculator or the calculation form (figure 4.07-5) for the method of least squares.
30. 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 and repeat the calibration.

4.07.2.B.3 CALIBRATION METHOD B

Method B: Dynamic Dilution of a High Concentration NO Gas Cylinder to calibrate the NO and NO_x channels followed by dynamic dilution of an NO₂ permeation tube to calibrate the instrument's NO₂ responses.

The principle: In a permeation device, an easily liquefiable gas such as NO₂ is condensed inside an inert container, all or part of which is constructed from a polymeric material (often Teflon). Gas from the container permeates and passes through the polymer walls at a temperature-dependent rate. The rate of gas effusion (in µg/min) at a constant temperature can be established by gravimetric determination of the weight loss of the permeation device over a known period of time. In this calibration procedure, the NO and NO_x responses of a chemiluminescence analyzer are first calibrated with an NO standard; next, accurately known concentrations of NO₂ are produced dynamically by diluting the effusion from an NO₂ permeation device with various flows of clean air to obtain a calibration for NO₂. Either the NO₂ permeation device or the NO source may be chosen as the reference standard for calibration. The remaining standard must be assayed against the reference standard for consistency.

A recommended calibration system is detailed in the USEPA document 600/4-75-003 December 1975, *Technical Assistance Document (TAD) for the Chemiluminescence Measurement of Nitrogen Dioxide*. Persons desiring to assemble their own calibration systems should follow the procedures in the TAD.

Figure 4.07-3 depicts a diagram of a typical permeation device calibration system. Such systems are also commercially available. All connections between components in

the system should be glass, Teflon, or other non-reactive material. The system consists of four functional sections:

1. A controlled-temperature section that houses the NO₂ permeation device and is flushed continuously with purified, dry zero air or nitrogen.
2. A regulated source of clean, dry zero air for dilution of the NO₂ effluent from the permeation device.
3. An NO standard and delivery system.
4. A dilution-mixing, sampling and exhaust system.

Temperature control is the primary concern in using an NO₂ permeation device as a standard NO₂ source. For example, a change in temperature of about 0.5°C effects a change in the permeation rate of the device of about 4%. For this reason, it is important that the temperature of the device be maintained at a constant value within ±0.1°C, and that it be closely monitored when the device is in use.

Generally, the NO₂ permeation device is housed in a temperature-controlled glass container that has an entrance and exit port at opposite ends; a glass thermometer accurate to ±0.05°C may be placed beside the device to monitor its temperature. A small fixed zero air or nitrogen flow (about 100 cm³/min) that is maintained at the same temperature as the permeation device flushes the NO₂ out of the device housing into a mixing chamber where the NO₂ is diluted with clean, dry zero air. A valve, e.g., a three-way stopcock, placed at the exit of the device housing may be used to divert the NO₂ stream to a vent when clean air is required at the manifold for making the necessary zero adjustments to the analyzer.

To maintain the temperature of the permeation device to within ±0.1°C of the desired value, the device and housing may be either placed physically inside a constant temperature chamber, or they can be located externally to the constant temperature chamber with the heat transfer medium circulated around the device housing. The flushing zero air or nitrogen passes through a heat exchanger, e.g., a coil of copper tubing, contained in the constant temperature chamber before passing over the device to adjust its temperature to that of the device.

The diffusion properties of NO₂ have made the construction of stable, accurate NO₂ permeation devices no easy feat. For this reason, due care must be given to their handling for reliable use. Permeation devices are available from commercial sources and from NIST as a Standard Reference Material (SRM 1629). The NIST device has a certified permeation rate of approximately 1 µg/min at about 25°C. Permeation rates of commercial devices vary according to size and recommended operating temperature. Both NIST and commercial manufacturers provide explicit instructions on the use of their respective devices, which the user should follow for accurate measurements.

Most permeation devices must equilibrate for at least 24 hours at the certified or operating temperature before the permeation rate stabilizes. Equilibration times may be longer and the permeation rate may be erratic if the device is subjected to extreme temperature variations when not in use. It was mentioned above that the flush gas over the permeation device must be extra dry. This is especially true of the NIST device and many others which have a large surface for NO₂ permeation. Some commercial devices which have a very small permeating area and are designed to operate at elevated temperatures (40 to 60°C) may not be as susceptible to trace moisture in the flush gas. Additional information regarding the use of permeation devices for calibration purposes is documented elsewhere.

If the NO₂ permeation device is to be used as the reference standard for calibration, the permeation rate of the device must be traceable to a NIST NO in N₂ standard (SRM 1683 or 1684) or NO₂ standard (SRM 1629). Otherwise, the permeation device need only be periodically assayed against the reference NO standard to assure consistency between the two working standards. Procedures for certifying the reference standard against NIST-traceable NO₂ or NO in N₂ standards and for inter-comparing the NO₂ and NO working standards are found in section 4.07.2.C.

The dynamic permeation tube dilution calibrator is required to dilute the output from the temperature-controlled permeation system to the desired concentration. All parts in contact with the NO₂ output must be glass or Teflon. The system must be capable of controlling and measuring flow rates to within ±2 percent of stated flow. A small portion of this dried zero air (approximately 100 sccm) is used as the flush gas for the permeation device.

In figure 4.07-3, the zero air stream is split to allow a small air flow to pass continuously over the permeation device. Alternatively, the flush gas could be supplied from a cylinder of pre-purified dry air or nitrogen. Whatever its source, it is extremely important that the flushing stream be extra dry so that moisture does not condense on the surface of the device. Water condensate could react with the effusing NO₂ to form an acid mist, thus changing the NO₂ concentration. A transparent drying column containing a mixture of molecular sieve (e.g., 6-16 mesh, type 4A) and indicating calcium sulfate (e.g., Drierite) has been used effectively as a moisture scrubber on the flush gas line.

Assemble a dynamic calibration system (consult the manufacturer's manuals for proper set up and operations). See figure 4.07-3 (at the end of this method B) for a schematic diagram of a typical calibration system using a dynamic dilution permeation device system. Ensure that all flow meters are calibrated under conditions of use against a NIST-traceable intermediary or primary standard (e.g., soap bubble meter, laminar flow element (LFE), or wet test meter). Correct all volumetric flow rates to 298°K (25°C, 78°F) and 760 mm Hg (29.92 in.Hg). Instruments using water should be corrected for the vapor pressure of water (Please refer to the manufacturer's instruction manual). For the permeation calibrator, ensure that the permeation chamber temperature indicator is calibrated under conditions of use to a NIST-traceable intermediary or

primary standard. Also ensure that the permeation chamber maintains a stable set point temperature within $\pm 0.1^\circ\text{C}$.

Precautions must be taken to remove O_2 from the NO pressure regulator and delivery system prior to the start of calibration. Failure to do so can cause significant errors in calibration. This problem may be minimized by:

1. carefully evacuating the regulator after it has been connected to the cylinder, but before opening the cylinder valve;
2. thoroughly flushing the regulator and delivery system with cylinder gas after opening the cylinder valve; and
3. not removing the regulator from the cylinder between calibrations unless absolutely necessary.

Connect the recorder and DAS output cables of the analyzer to the input cables of the strip chart recorder and DAS. All adjustments to the analyzer should be performed based on the appropriate DAS and strip chart recorder readings. References to analyzer responses in the procedures given below refer to DAS and recorder responses.

Prior to calibrating the NO_x analyzer, the DAS and strip chart recorder accuracy should be verified with a power supply and a volt meter of known accuracy. At a minimum, 80%, 20%, and 0% of analyzer full scale responses should be verified. Both chart recorder and DAS readouts should be within ± 2 percent full scale volts of the analyzer output.

Calibration gases must be introduced directly to the sample inlet port of the analyzer. Ensure that calibration gases are introduced to the analyzer at atmospheric pressure.

Dynamic calibration systems based upon NO gas cylinder dilution and NO_2 permeation tube dilution systems may be used to calibrate an NO_2 analyzer, provided they meet the following requirements:

1. Air flow controllers capable of maintaining constant air flows within ± 2 percent of the required flow rate.
2. Component parts in contact with NO_x gases of non-reactive and non-adsorbent material (i.e., borosilicate glass, FEP Teflon, or equivalent material).
3. Air flow indicator capable of measuring and monitoring flows with an accuracy of ± 2 percent of the measured flow rate. In addition, each flow meter must be calibrated to a NIST-traceable source (i.e., laminar flow element, soap bubble meter, or wet test meter).

4. Pressure regulators for use with NO cylinder gas have non-reactive and non-adsorptive diaphragms and internal parts. In addition, the pressure regulator must have a suitable delivery pressure.
5. Constant temperature chamber (constructed of non-reactive and non-adsorbent material) capable of housing the NO₂ permeation device(s) and maintaining its temperature to within ± 0.1 °C.
6. Temperature measuring device capable of measuring and monitoring the temperature of the NO₂ permeation chamber with an accuracy of ± 0.05 °C.
7. Drier and scrubber(s) to remove moisture and contaminants from the permeation device air system. The use of the drier is optional with NO₂ permeation devices not sensitive to moisture (refer to the supplier's instructions for use of the permeation device).
8. Valve(s) to divert the NO₂ from the permeation device when zero air or NO is required at the manifold. Valve(s) must be constructed of borosilicate glass, Teflon, or other non-reactive material.
9. Mixing chamber, designed to provide thorough mixing of reaction products and diluent air, is constructed of borosilicate glass (preferred) or other non-reactive and non-adsorbent material.
10. Output manifold constructed of borosilicate glass (preferred), Teflon, or non-reactive and non-adsorbent material. The manifold should be of sufficient diameter to insure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to ensure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

4.07.2.B.3.a Method B, Calibration Procedure for NO and NO_x

During the calibration, the analyzer must be operating in its normal sampling mode, and the test atmosphere must pass directly to the sample inlet of the analyzer.

Note: During a calibration, the analyzer's response(s) is set to equal the calibration gas concentration. Any external filters, scrubbers, conditioners, etc., may introduce bias to the measurement system. After completing the calibration, conduct a level 1 zero/span quality control check and measure the responses. Reconnect all in-line sample conditioning equipment and repeat the same level 1 zero/span quality control check. The differences between the two measured level 1 zero/span checks should be zero. If not, the in-line conditioners are introducing bias to the measurement system.

1. Record the station name and address on a calibration data form/log book. Identify individual stations by their official names and addresses. Where appropriate, station name and address should be the same as those appearing on the SAROAD or 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. The manufacturer's name, model, and serial number should be recorded.
 4. Identify the calibration apparatus used. If the calibrator was purchased, record the manufacturer's name, model, and serial number. Calibrators assembled by the user should be assigned an identification number so that calibrations can be referenced to that particular apparatus.
 5. Identify, by supplier and cylinder number, the reference standard to be used. Record the concentration of the calibration gas(es). Do not use cylinders with pressures < 200 psi for calibration. Provide a record of NIST traceability for any cylinder used in a calibration. Include the date, and name of the person who conducted the referencing.
 6. Select the operating range of the NO_x analyzer to be calibrated.
 7. Record the zero and 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 NO₂; 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.
8. Record the shelter temperature and barometric pressure at the time of calibration.
 9. Use the NO/NO_x part of calibration data form (figure 4.07-7) for the systematic recording of data determined during the systematic calibration of the NO and NO_x channels of the analyzer. Because zero and calibration adjustments differ between analyzers, the manufacturer's manual should be consulted before calibration is performed.
 10. Adjust diluent air (zero air) and the O₃ generator air to obtain the flows determined in Subsection 4.07.2.B.2.a. Ensure that the total air flow exceeds the total demand of the analyzer(s) connected to the output

manifold so that no ambient air will be pulled into the atmospheric dump. For safety concerns, ensure that the atmospheric dump vents to ambient air (outside the monitoring shelter). Measure the diluent air flow (F_D) using a NIST-traceable intermediate primary standard. Consult the respective manufacturer's standard operating procedures manual for specific directions. Measure and record temperature and pressure of the (in-line) diluent air flows. Correct the actual measured air flows to standard temperature and pressure conditions (STP: i.e., $T_{std} = 298^\circ\text{K}$ and $P_{std} = 760\text{mmHg}$). Record the standardized diluent air flow (F_D) in column 1 of figure 4.07-7b.

Note: When installing an atmospheric dump, take care not to create a back pressure problem.

11. Allow the analyzer to sample zero air until a stable response is obtained (a response that does not vary by more than $\pm 1\%$ of full scale over a 5-minute time period); then adjust the analyzer zero control to read zero. For a strip chart recorder, it is recommended to offset the analyzer zero adjustment to +5% of the strip chart scale. This facilitates observing negative zero drift. Record the stable zero air response for the NO and NO_x channels.
12. Determine the 80% upper range limit (URL) NO cylinder gas flow (F_{NO}) by solving equation 4.07-8 for F_{NO} . Adjust the NO flow from the standard NO cylinder to generate an NO concentration of approximately 80% of the URL of the NO channel. Measure the NO flow (F_{NO}) using a NIST-traceable intermediate primary standard. Measure and record the NO air stream (in-line) temperature and pressure. Correct the actual measured flow to STP conditions. Record F_{NO} in column 2 of figure 4.07-7b on the 80% URL line.

$$F_{NO} = (F_D \times [NO]_{out}) / ([NO]_{std} - [NO]_{out}) \quad \text{eqn. 4.07-8}$$

where:

$[NO]_{out}$ = NO gas concentration at the output manifold

$[NO]_{std}$ = NO cylinder gas concentration

F_{NO} = flow rate of NO cylinder gas, sccm

F_D = flow rate of dilution air, sccm

13. Calculate the exact NO concentration ($[NO]_{OUT}$) by solving equation 4.07-9.

$$[NO]_{OUT} = F_{NO} \times [NO]_{STD} / (F_{NO} + F_D + F_O) \quad \text{eqn. 4.07-9}$$

where: F_{O_3} = zero air flow through ozonator. Since Method B does not use an ozone source to generate NO_2 , F_{O_3} equals zero and equation 4.07-9 reduces to:

$$[NO]_{OUT} = F_{NO} \times [NO]_{STD} / (F_{NO} + F_D)$$

Record the $[NO]_{OUT}$ under column 3 of figure 4.07-7b on the 80% line.

14. Calculate the exact NO_x concentration ($[NO_x]_{OUT}$) by solving equation 4.07-10.

$$[NO_x]_{OUT} = F_{NO} \times ([NO]_{STD} + [NO_2]_{IMP}) / (F_{NO} + F_D + F_O) \quad \text{eqn. 4.07-10}$$

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

$[NO_x]_{OUT}$ = NO_x gas concentration at the output manifold

F_{O_3} = zero air flow through ozonator. Since Method B does not use an ozone source to generate NO_2 , F_{O_3} equals zero and equation 4.07-10 reduces to:

$$[NO_x]_{OUT} = F_{NO} \times ([NO]_{STD} + [NO_2]_{IMP}) / (F_{NO} + F_D)$$

Record the $[NO_x]_{OUT}$ under column 5 of figure 4.07-7b on the 80% line.

15. Sample the generated concentration until the NO and NO_x responses have stabilized. Adjust span response for the analyzer NO and NO_x channels for a balanced output equal to the NO test gas.

NOTE: Some analyzers may have separate span controls for NO_x , NO, and NO_2 . Other analyzers may have separate span controls for only NO_x and NO. Still other analyzers may have only one span control common to all three channels. When only one span control is available, the span adjustment is made on the NO channel of the analyzer.

NOTE: If the analyzer NO and NO_x responses fail to stabilize (all flows constant) with the NO response gradually increasing and the NO_x response gradually decreasing, check for contamination of the NO pressure regulator and delivery system.

If substantial adjustment of the NO and NO_x span control(s) is necessary, recheck the zero and span adjustments in steps 11 and 15. Record the analyzer's NO response under column 4 and the analyzer's NO_x response under column 6 of figure 4.07-7b on the 80% URL line.

16. Generate four more evenly-spaced NO gas concentrations by decreasing F_{NO} or increasing F_D . Use equation 4.10-8 to calculate F_{NO} flows for 60% URL, 40% URL, 20% URL, and 10% URL NO gas concentrations. Measure NO and diluent flows for the 60% URL, 40% URL, 20% URL, and 10% URL NO gas concentrations as described in steps 10 and 12. Correct all flows to STP conditions. Record the calibration data for each point under the appropriate column in the NO/NO_x table of figure 4.07-7b.
17. Plot the analyzer's NO and NO_x responses against the corresponding NO calibration gas concentrations. Determine the best straight line by the method of least squares. This can be done with a programmed calculator with this ability, or with the calculation data form presented in figure 4.07-5. 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 when possible.

Calculate the NO and NO_x linear regression calibration curves. Record the slope (m), y intercept (b), and correlation coefficient (r) for the corresponding NO and NO_x curves. To be considered linear, the correlation coefficient (r) must be ≥ 0.995 .

4.07.2.B.3.b Method B, NO₂ Permeation Device Procedure for NO₂

Having completed the calibration of the NO and NO_x channels, the NO₂ channel may now be calibrated by an NO₂ permeation device system. The figure 4.07-7b allows for the systematic recording of the data determined during the calibration of the NO₂ channel of the analyzer. **Do not readjust zero and span knob settings for the NO and the NO_x channels.**

18. Divert the NO flow to exhaust.
19. Select sample zero air. Adjust the diluent air flowrate (F_D) to provide zero air to the analyzer sample inlet. The total air flow must exceed the total demand of the analyzer. Allow the analyzer to sample zero air until stable response is obtained. Record the stable zero air response for the NO, NO_x, and NO₂ channels on calibration data form/figure 4.07-7b.
20. The NO₂ zero adjustment was made in step 11 of the NO/NO_x calibration and need not be repeated. Record the determined response under column 10 of data form/figure 4.07-7b.
21. Select and provide NO₂ gas to the analyzer sample inlet. Adjust F_D to generate an NO₂ concentration approximately 80% URL of the analyzer. The total air flow must exceed the total demand of the analyzer. Measure the permeation flow (F_p) and F_D using a NIST-traceable intermediate

primary standard. Measure and record the F_p and F_D air stream (in-line) temperature and pressure. Correct the actual measured flows to STP conditions.

22. Calculate the NO_2 concentration using equation 4.07-13 below:

$$[\text{NO}_2]_{\text{out}} = (P \times \text{Km}) / (F_p + F_D) \quad \text{Eqn. 4.07-13}$$

where: $[\text{NO}_2]_{\text{out}}$ = diluted NO_2 concentration supplied to the analyzer

P = permeation rate, $\mu\text{g}/\text{min}$

Km = molar constant for NO_2

$\text{Km} = 0.532$ (@ 25°C and 760 mmHg)

F_p = air flow across permeation device, sccm

F_D = diluent air flowrate, sccm

Record the 80 NIST-traceable URL value in column, $[\text{NO}_2]_{\text{OUT}}$.

23. Sample this 80 NIST-traceable URL NO_2 concentration until the analyzer's NO_x and NO_2 responses have stabilized. Record these values in columns 9 and 10.
24. Adjust F_D to generate four more evenly-spaced NO_2 gas concentrations. Use equation 4.07-13 to calculate F_D flows for 60% URL, 40% URL, 20% URL, and 10% URL NO_2 gas concentrations. Measure F_p and F_D using a NIST-traceable intermediate primary standard. Measure and record the F_p and F_D air stream (in-line) temperature and pressure. Correct the actual measured flows to STP conditions. Record the analyzer's measured ($[\text{NO}_x]_M$) and ($[\text{NO}_2]_M$) responses for each concentration. Calculate the NO_2 concentration using equation 4.07-13. Record the values in columns 9 and 10 of figure 4.07-7b.

NOTE: An equilibration time of a least fifteen minutes is recommended between concentration changes.

25. Plot the analyzer's ($[\text{NO}_2]_M$) and ($[\text{NO}_x]_M$) responses against the corresponding NO_2 calibration gas concentrations. Calculate the ($[\text{NO}_2]_M$) and ($[\text{NO}_x]_M$) linear regression calibration curves. Record the slope (m), y intercept (b), and correlation coefficient (r) for each calibration curve. The correlation coefficient for each curve must be ≥ 0.995 . If not, correct the problem and recalibrate the analyzer.

4.07.2.B.3.c Method B, Calculation of NO₂ Converter Efficiency

A data form (figure/form 4.07-8) has been developed for determining the percent converter efficiency. The following procedure is for use with this data form.

26. Calculate the quantity of NO₂ converted, labeled [NO₂]_{CONV}, for each point, using Equation 4.07-13.

$$[\text{NO}_2]_{\text{CONV}} = ([\text{NO}_2]_{\text{OUT}})/([\text{NO}_x]_{\text{M}}) \quad \text{Eqn. 4.07-13}$$

where: [NO_x]_M = analyzer's NO_x measured response to NO₂ permeation tube calibration gas

[NO₂]_{OUT} = concentration at the output manifold

27. Plot [NO_x]_M (y-axis) versus [NO₂]_{OUT} (x-axis) and draw or calculate the slope (b) of the curve using either an appropriate calculator or the calculation form (figure 4.07-5) for the method of least squares.
28. 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 and repeat the calibration.

4.07.2.C CERTIFICATION OF NO AND NO₂ WORKING STANDARDS

NIST-SRM or CRM Nitric Oxide (NO) in N₂ gas cylinders are typically certified for 18 months. After the certification date has expired, the standard in question must be recertified against currently certified NO or NO₂ NIST-SRM or CRM. The following procedures may be used to recertify working NO or NO₂ standards.

4.07.2.C.1 Certification of NO working standard against a NIST-traceable NO or NO₂ standard

The NO content of the NO working standard must be periodically assayed against NIST-traceable NO or NO₂ standards. Any NO₂ impurity in the cylinder must also be assayed. Certification of the NO working standard should be made on a quarterly basis, or more frequently, if required. Procedures are outlined below for certification against either an NO or NO₂ NIST-traceable standard. The simplest and most straightforward procedure is to certify against an NO standard.

NOTE: If the assayed NO₂ impurity concentration, [NO₂]_{IMP}, is greater than 1 ppm, make certain that the NO delivery system is not the source of contamination before discarding the NO standard.

4.07.2.C.1.a Certification of NO working standard against a NIST-traceable NO standard

Use a NIST-traceable standard and the GPT calibration procedure to calibrate the NO, NO_x, and NO₂ responses of the analyzer. Also determine the converter efficiency of the analyzer. Refer to the calibration procedure for exact details; ignore the recommended zero offset adjustments.

Generate several NO concentrations by dilution of the NO working standard. Use the nominal NO concentration of the working standard, [NO]_{NOM}, to calculate the diluted concentrations. Plot the analyzer NO response (in ppm) versus the nominal diluted NO concentration and determine the slope, S_{NOM}. Calculate the NO concentration of the working standard, [NO]_{STD}, from equation 4.07-15.

$$[\text{NO}]_{\text{STD}} = [\text{NO}]_{\text{NOM}} \times S_{\text{NOM}} \quad \text{Eqn. 4.07-15}$$

where: [NO]_{NOM} = expected concentration of the NO cylinder to be certified

If the nominal NO concentration of the working standard is unknown, generate several NO concentrations to give on-scale NO responses. Measure and record F_{NO} and F_T for each NO concentration generated. Plot the analyzer NO response versus F_{NO}/F_T and determine the slope which gives [NO]_{STD} directly.

The analyzer NO_x responses to the generated NO concentrations reflect any NO₂ impurity in the NO working standard. Plot the difference between the analyzer NO_x and NO responses versus F_{NO}/F_T. The slope of this plot is [NO₂]_{IMPURITY}.

In the procedure above, it is possible to assay the NO content of the working standard without first calibrating the NO and NO_x responses of the analyzer. This is done by simply comparing relative NO responses of the working NO standard to the NIST-traceable NO standard. The NO₂ impurity can be determined from the analyzer NO_x responses, provided the converter efficiency is known.

4.07.2.C.1.b Certification of NO Working Standard Against a NIST-traceable NO₂ Standard

Use the NO working standard and the GPT calibration procedure to "calibrate" the NO/NO_x and NO₂ responses of the chemiluminescence analyzer. Refer to the calibration procedure for exact details. Ignore the recommended zero offset adjustments. For this pseudo-calibration, use the nominal NO cylinder value of the working standard and assume that no NO₂ impurity is in the cylinder. For an analyzer with dual detectors, the NO_x span adjustment must be made by diverting the sample flow around the converter and routing it directly to the NO_x detector. This operation electronically balances the two detectors.

From the GPT data, plot the analyzer NO₂ response versus the NO₂ concentration generated by GPT. Determine the slope, S_{NOM}, and the x-intercept of the curve. Generate several NO₂ concentrations by dilution of the NIST-traceable NO₂ standard.

Plot the analyzer NO₂ response versus the slope, S_{NIST}. Calculate the NO concentration of the working standard, [NO]_{STD}, from equation 4.07-16.

$$[\text{NO}]_{\text{STD}} = [\text{NO}]_{\text{NOM}} \times S_{\text{NOM}}/S_{\text{NIST}} \quad \text{Eqn. 4.07-16}$$

where: [NO]_{NOM} = expected concentration of the NO cylinder to be certified

Calculate the NO₂ impurity from equation 4.07-17.

$$[\text{NO}_2]_{\text{IMP}} = ((\text{X-intercept}) (F_T/F_{\text{NO}}))(S_{\text{NOM}}/S_{\text{NIST}}) \quad \text{Eqn. 4.07-17}$$

4.07.2.C.2 Certification of NO or NO₂ Working Standard Against a NIST-traceable NO₂ Standard

Either the NO₂ permeation device or the NO source may be chosen as the reference standard for calibration. The reference standard must be certified against a NIST-traceable standard. The remaining standard must then be assayed against the reference standard for consistency. To show consistency, the NO₂ generated by a permeation device is compared to the NO₂ generated by gas phase titration of the NO standard. Certifications and intercomparisons should be done quarterly or more frequently, as required.

Certification of an NO₂ standard against NBS-traceable standards and the intercomparison of the NO and NO₂ standards are discussed below.

4.07.2.C.2.a CERTIFICATION OF NO₂ WORKING STANDARD AGAINST A NIST-TRACEABLE NO₂ STANDARD

The NO₂ chemiluminescence analyzer need not be in calibration for these measurements. Generate several NO₂ concentrations by dilution of the NIST-traceable NO₂ standard. Plot the analyzer NO₂ response versus the NO₂ concentration and determine the slope, S_{NIST}. Generate several NO₂ concentrations by dilution of the working NO₂ standard to give on-scale NO₂ responses. Measure the total flow at the manifold, F_T, for each NO₂ concentration generated. Plot the analyzer NO₂ response versus 1/F_T and determine the slope, S_{STD}. Calculate the permeation rate, P, from equation 4.07-18:

$$P = S_{\text{STD}}/(K_m \times S_{\text{NIST}}) \quad \text{Eqn. 4.07-18}$$

where: K_m = (0.532 μl NO₂)/(μg NO₂) at 25 deg C and 760 mmHg

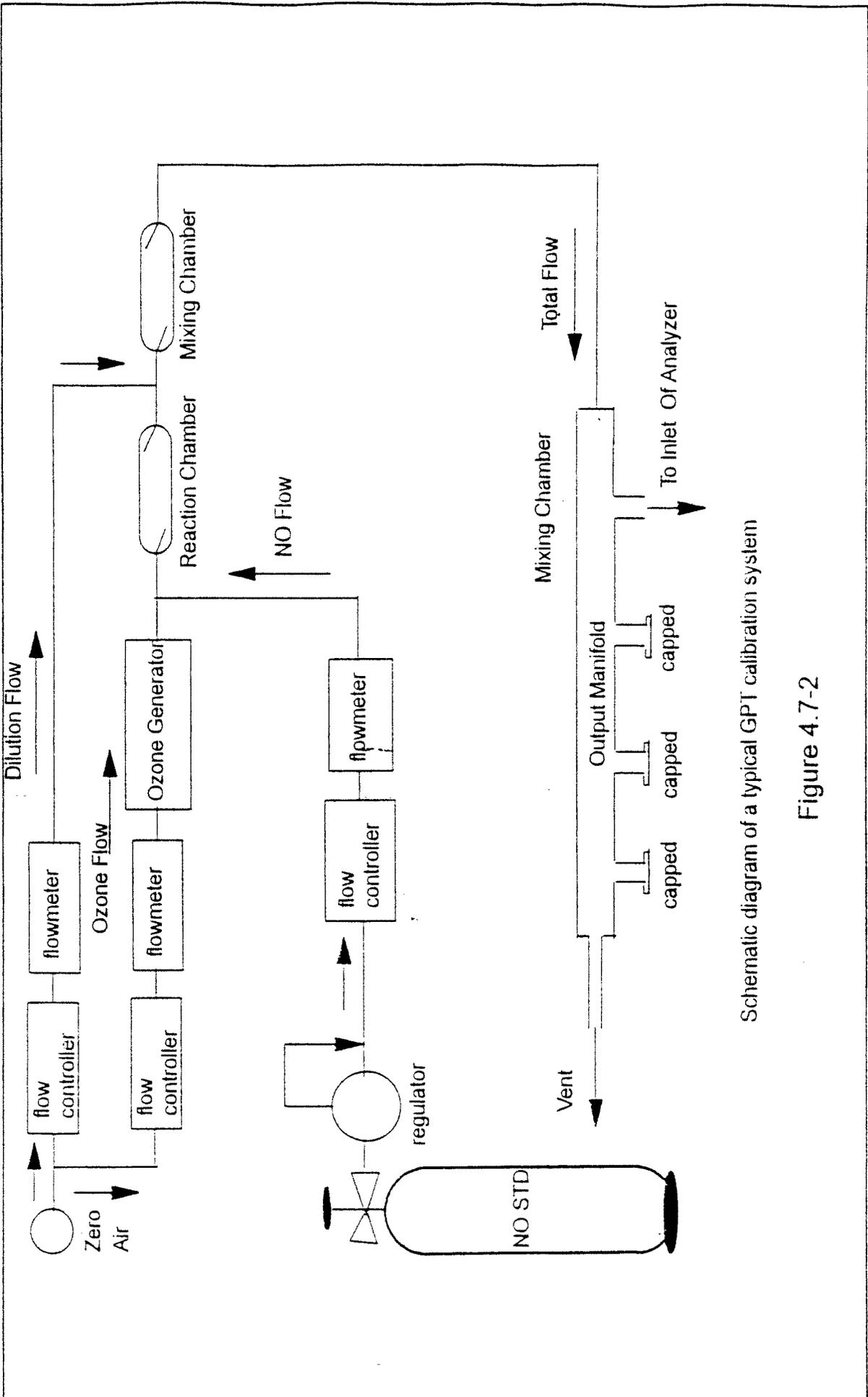
4.07.2.C.2.b CERTIFICATION OF NO₂ WORKING STANDARD AGAINST A NIST-TRACEABLE NO STANDARD

Use the NIST-traceable NO standard and the GPT calibration procedure to calibrate the NO, NO_x, and NO₂ responses of a chemiluminescence analyzer. Refer to the GPT calibration procedure (section 4.07.2.B.2) for exact details; ignore the recommended zero offset adjustments. Generate several NO₂ concentrations by dilution of the working NO₂ standard to give on-scale NO₂ responses. Measure the total flow at the manifold, F_T, for each NO₂ concentration generated. Plot the analyzer NO₂ response versus 1/F_T, and determine the slope, S_{STD}. Calculate the permeation rate, P, from equation 4.07-19:

$$P = S_{STD}/K_m \quad \text{Eqn. 4.07-19}$$

4.07.2.C.2.c INTERCOMPARISON OF NO₂ AND NO WORKING STANDARDS

To compare the working NO₂ standard to a certified NO working standard, follow the same procedure as outlined above for "certifying an NO₂ working standard against a NIST-traceable NO standard." The NO₂ and NO_x span adjustments must take into account any NO₂ impurity in the NO working standard. To make comparison between a working NO standard and a certified NO₂ standard, follow the same procedure as described for certifying a working NO standard against a NIST-traceable NO₂ standard (see subsection 4.07.2.C.1.b).



Schematic diagram of a typical GPT calibration system

Figure 4.7-2

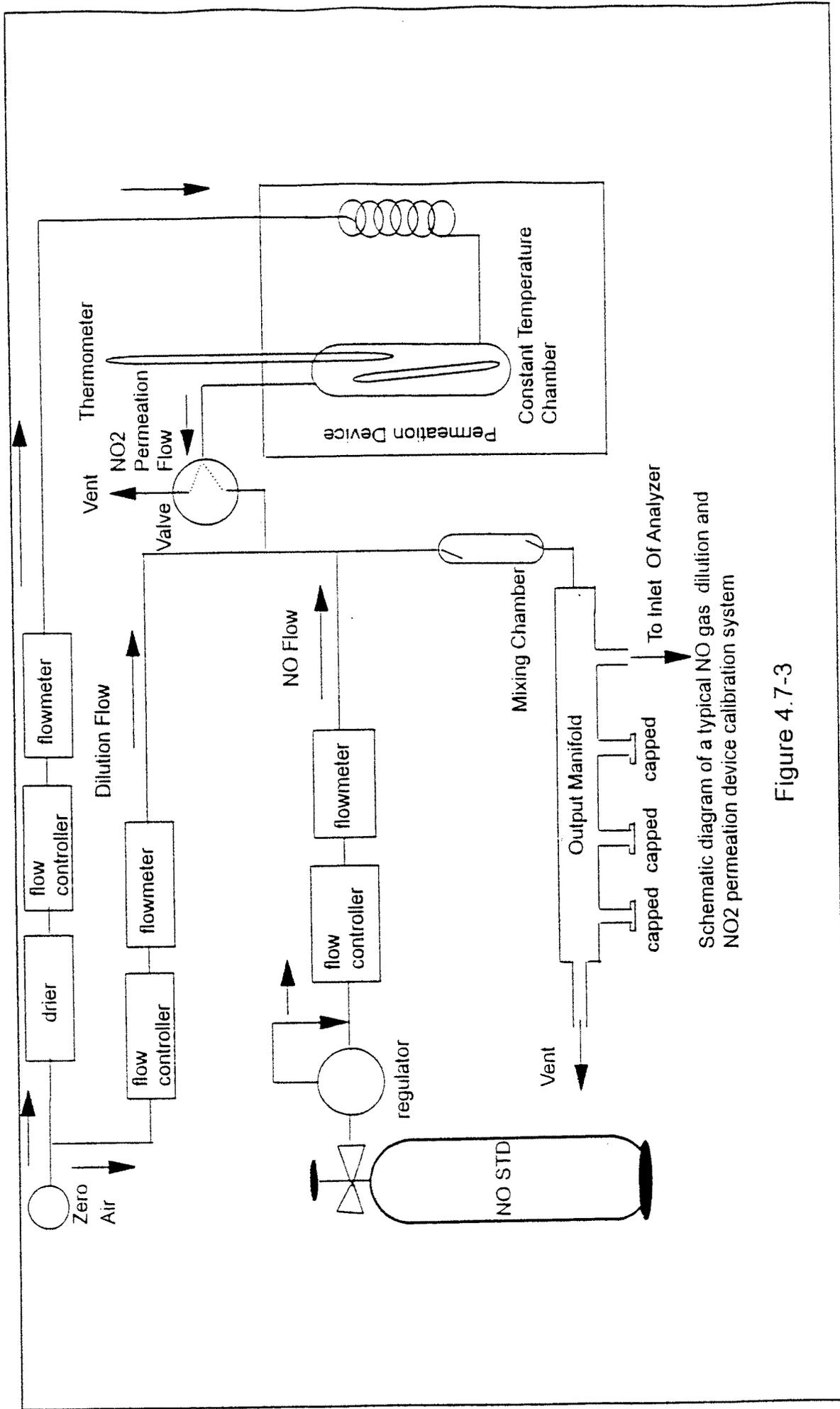


Figure 4.7-3
 Schematic diagram of a typical NO gas dilution and NO2 permeation device calibration system

NO₂ CALIBRATION DATA FORM BY GPT
(front side)

1. Station _____

2. Calibrated by _____ Date _____

3. Analyzer Mfr. _____ 4. Calibrator Mfr. _____
 Model _____ Model _____
 S/N _____ S/N _____

5. NO Reference Standard
 Supplier _____ Cylinder Number _____
 Concentration [NO]_{STD} _____ Cylinder Pressure _____
 NO₂ Impurity, [NO₂]_{IMP} _____
 Reference to NBS-SRM _____

By _____ Barometric Pressure _____

	NO	NO _x	NO ₂
6. Zero Knob Setting	_____	_____	_____
Span Knob Setting	_____	_____	_____

7. Temperature _____ Barometric Pressure _____

Equations Used for NO/NO_x/NO₂ Calibration

Equation 4.07-9

$$[NO]_{OUT} = F_{NO} \times [NO]_{STD} / (F_{NO} + F_O + F_D)$$

F_{NO} = flow rate of NO standard, sccm

Equation 4.07-10

$$[NO_x]_{OUT} = F_{NO} \times ([NO]_{STD} + [NO_2]_{IMP}) / (F_{NO} + F_O + F_D)$$

F_{O₃} = flow rate of air through O₃ generator, sccm

F_D = flow rate of dilution air, sccm

Equation 4.07-11

$$[NO_2]_{OUT} = [NO]_{ORIG} - [NO]_{REM} + (F_{NO} \times [NO_2]_{IMP} / (F_{NO} + F_O + F_D))$$

If [NO₂]_{IMP} = 0, use Equation 4.07-11A

[NO]_{OUT}, [NO_x]_{OUT} = concentration at the output manifold

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

Equation 4.07-11A

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

[NO₂]_{IMP} = concentration of NO₂ impurity in the standard NO cylinder

Equation 4.07-12

$$[NO_2]_{CCNV} = [NO_2]_{OUT} - ([NO_x]_{ORIG} - [NO_x]_{REM})$$

[NO]_{ORIG} = concentration of NO before O₃ is added during GPT
 [NO]_{REM} = concentration of NO after O₃ is added during GPT
 [NO₂]_{OUT} = concentration of NO₂ after O₃ is added to NO during GPT

URL = upper range limit

[NO]_{ORIG} = concentration of NO before O₃ is added during GPT

[NO]_{REM} = concentration of NO after O₃ is added during GPT

[NO₂]_{CCNV} = measure of analyzer's efficiency to convert NO₂ to NO by ratio of NO₂ generated vs. total NO_x

Figure 4.07-4A

NO₂ CALIBRATION DATA FORM BY GPT
(back side)

NO/NO_x CALIBRATION AND LINEARITY CHECK

Calibrations Points NO/NO _x	1 F _O + F _{O₃} , sccm	2 F _{NO} , sccm	3 [NO] _{OUT} , ppm	4 NO recorder reading	5 [NO _x] _{OUT} , ppm	6 NO _x , recorder reading
Zero						
80% URL						
60% URL						
40% URL						
20% URL						
10% URL						

NO CALIBRATION BY GPT

Calibration Points NO/NO _x	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 recorder, reading
Zero						
80% URL						
60% URL						
40% URL						
20% URL						
10% URL						

Figure 4.07-4B

CALCULATION FORM FOR THE METHOD OF LEAST SQUARES

Calibration Point	Concentration, ppm x	x ²	Recorder reading y	y ²	xy
Zero					
80% URL					
60% URL					
40% URL					
20% URL					
10% URL					

$\Sigma x = \underline{\hspace{2cm}}$, $\Sigma x^2 = \underline{\hspace{2cm}}$, $\Sigma y = \underline{\hspace{2cm}}$, $\Sigma y^2 = \underline{\hspace{2cm}}$, $\Sigma xy = \underline{\hspace{2cm}}$

$x_{avg.} = \Sigma x/n = \underline{\hspace{2cm}}$, $y_{avg.} = \Sigma y/n = \underline{\hspace{2cm}}$, and

n = number of calibration points

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

$$Y = y_{avg.} + b(x - x_{avg.}) = (y_{avg.} - bx_{avg.}) + bx = a + bx,$$

where Y = predicted mean response for corresponding x,

b = slope of the fitted line, and

a = intercept where the line crosses the y-axis.

$$b = \frac{\{\Sigma xy - [(\Sigma x)(\Sigma y)]/n\}}{[\Sigma x^2 - (\Sigma x)^2/n]}$$

$$a = y_{avg.} - bx_{avg.}$$

Figure 4.07-5

**CONVERTER EFFICIENCY DATA FORM
BY METHOD OF GPT**

Calibration Point	1 [NO ₂] _{OUT} (x)	2 [NO _x] _{ORIG}	3 [NO _x] _{REM}	4 [NO ₂] _{CONV} (y)
Zero Set Point				
80% URL				
60% URL				
40% URL				
20% URL				
10% URL				

$$[\text{NO}_2]_{\text{CONV}} = [\text{NO}_2]_{\text{OUT}} - ([\text{NO}_x]_{\text{ORIG}} - [\text{NO}_x]_{\text{REM}})$$

Eqn. 4.07-12

where:

[NO_x]_{ORIG} = concentration of NO_x before O₃ is added during GPT

[NO_x]_{REM} = concentration of NO after O₃ is added during GPT

[NO₂]_{OUT} = concentration of NO₂ gas at the output manifold

Figure 4.07-6

NO₂ CALIBRATION DATA FORM BY PERMEATION DEVICE
(front side)

1. Station _____

2. Calibrated by _____ Date _____

3. Analyzer Mfr. _____ 4. Calibrator Mfr. _____
 Model _____ Model _____
 S/N _____ S/N _____

5. NO Reference Standard
 Supplier _____ Cylinder Number _____
 Concentration [NO]_{STD} _____ Cylinder Pressure _____
 NO₂ Impurity, [NO₂]_{IMP} _____
 Reference to NIST-SRM _____
 By _____

6. NO₂ Reference Standard
 Supplier _____ Permeation Tube Number _____
 NO₂ Permeation Rate at _____ °K P = _____ ng/min.
 Reference to NIST-SRM _____ By: _____
 Date of Certification _____

	NO	NO _x	NO ₂
7. Analyzer Zero/Span Setting	_____	_____	_____
Zero Knob Setting	_____	_____	_____
Span Knob Setting	_____	_____	_____

8. _____ Barometric Pressure _____

Equations Used for NO/NO_x/NO₂ Calibration

Equation 4.07-9

F_{NO} = flow rate of NO standard, sccm

$$[NO]_{OUT} = F_{NO} \times [NO]_{STD} / (F_{NO} + F_D)$$

Equation 4.07-10

$$[NO]_{OUT} = F_{NO} \times ([NO]_{STD} + [NO_2]_{IMP}) / (F_{NO} + F_D)$$

F_D = flow rate of dilution air, sccm

F_P = air flow across permeation device, sccm

Equation 4.07-13

$$[NO_2]_{OUT} = (P \times Km) / (F_P + F_D)$$

Km = molar constant for NO₂ = 0.532

Equation 4.07-14

$$[NO_2]_{CONV} = ([NO_2]) / ([NO]_{DM})$$

P = Permeation rate @ known °C, mmHg

[NO_x]_{DM}, [NO₂]_{DM} = Analyzer Measured Response to NO₂ Calibration by NO₂ Permeation Tube Method

Equation 4.07-15

$$\% [NO_2]_{CONV} = (\text{slope}[NO]_{DM}) / (\text{slope}[NO_2]_{OUT}) \times 100$$

[NO]_{OUT}, [NO_x]_{OUT}, [NO₂]_{OUT} = (slope [NO₂]_{OUT}) X 100 concentration at the output manifold

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

[NO₂]_{CONV} = measure of analyzer's efficiency to convert NO₂ to NO by ratio of NO₂ generated to total NO₂

URL = upper range limit

Figure 4.07-7A

NO₂ CALIBRATION DATA FORM BY PERMEATION DEVICE
(back side)

NO/NO_x CALIBRATION AND LINEARITY CHECK

Calibrations Points NO/NO _x	1 F _O + F _{O₃} sccm	2 F _{NO} sccm	3 [NO] _{OUT}	4 NO recorder ppm	5 [NO _x] _{OUT}	6 NO _x recorder ppm
Zero						
80% URL						
60% URL						
40% URL						
20% URL						
10% URL						

NO₂ CALIBRATION BY PERMEATION DEVICE

Calibration Points NO/NO _x	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] _M ppm
Zero						
ORIG						
80% URL						
60% URL						
40% URL						
20% URL						
10% URL						

Figure 4.07-7B

CONVERTER EFFICIENCY DATA FORM

Calibration Point	1 [NO ₂] _{OUT} (x)	2 [NO _x] _M (y)	3 [NO ₂] _{CONV}
Zero Set Point			
80% URL			
60% URL			
40% URL			
20% URL			
10% URL			

$$[\text{NO}_2]_{\text{CONV}} = ([\text{NO}_2]_{\text{OUT}}) / ([\text{NO}_x]_{\text{M}})$$

Eqn. 4.07-13

where:

[NO_x]_M = analyzer's NO_x measured response to NO₂ permeation tube calibration gas

[NO₂]_{OUT} = concentration at the output manifold

Figure 4.07-8

ACTIVITY MATRIX FOR CALIBRATION PROCEDURES			
Calibration Activities	Acceptance Limits	Frequency and Method of Measurement	Action if Requirements Are Not Met
Calibration gases	U.S. EPA QA Handbook for Air Pollution Measurement Systems, Sec. 2.0.7, Subsec. 7.1.	Assayed against a NIST-SRM quarterly Method 4.07.2.C also U.S. EPA QA Handbook for Air Pollution Measurement Systems, Sec. 2.0.7	Working gas standard is unstable and/or measurement method is out of control; take corrective action such as obtaining new calibration gas
Dilution gas	Dry zero air, free of contaminants; TAD and U.S. EPA QA Handbook for Air Pollution Measurement Systems, Sec. 2.0.7, Subsec. 7.1.	See TAD	Return to supplier, or take appropriate corrective action with generation system
Multi-point calibration (GPT)	<ol style="list-style-type: none"> $t_a \leq 2$ min PR ≥ 2.75 ppm-min Use calibration procedure in Subsec. 4.07.2.B.2; also TAD and the <u>Federal Register</u>. Converter efficiency $\geq 96\%$ 	<u>Method</u> <ol style="list-style-type: none"> 4.07.2.B.2.a 4.07.2.B.2.b, TAD, <u>Federal Register</u> 4.07.2.B.2.c 	<ol style="list-style-type: none"> Adjust flow conditions and/or reaction chamber; volume to meet suggested limits Repeat the calibration Replace converter & calibrate the analyzer

Figure 4.07-9

4.07.3 NITROGEN DIOXIDE EQUIPMENT STANDARD OPERATING PROCEDURES

Essential to quality assurance (QA) are scheduled quality control (QC) checks for verifying the operational status of the monitoring system. The operator should visit the site at least once per week. Every two weeks a level 1 zero/span QC check must be conducted on the analyzer. In between the level 1 zero/span checks, level 2 zero/span QC checks must be conducted on the analyzer at a frequency desired by the user. Both level 1 and level 2 zero/span checks must be conducted at a level between 70% and 90% of the analyzer's operating NO/NO_x measurement range.

NOTE: It is strongly encouraged that an automatic system for the remote-controlled activation and recording of level 1 zero/span checks be installed so that more frequent (e.g., daily) systematic zero/span checks could be conducted. Acceptable checks could then be used to bracket acceptable time blocks of data to limit invalidating larger time blocks of data when the instrumentation malfunctions.

In addition, an independent precision check between 0.08 and 0.10 ppm NO₂ must be carried out at least once every two weeks. Figure 4.07-10, at the end of this section, summarizes the QA activities for routine operations. Each activity is discussed in the following subsections.

To provide for documentation and accountability of activities, it is recommended that a checklist must be compiled and then filled out by the field operator as each activity is completed. The completed checklist can then be filed with other site operational information (e.g., calibrations, maintenance, etc.) to provide complete documentation for the site. An example checklist is Figure 4.07-11 at the end of this section.

4.07.3.A EQUIPMENT

4.07.3.A.1 MONITORING SHELTER

See section 4.07.1.C for monitoring shelter description and recommendations.

4.07.3.A.2 SAMPLE INTRODUCTION SYSTEM

The sample introduction system consists of:

- an intake port;
- particulate and moisture traps;
- a sampling manifold;
- a sampling blower; and
- a sampling line to the analyzer.

Recommended guidance for design, installation, and maintenance of a sample introduction system can be found in, *USEPA /600/4-77-027a December 1986 Quality Assurance Handbook for Air Pollution Measurement Systems: Volume II. Ambient Air Specific Methods, Section 2.02 Sampling Considerations.*

As part of the QA program, the field operator should inspect the above components on a predetermined schedule for:

- breakage;
- leaks;
- particulates or foreign matter;
- moisture deposition in sample line or manifold; and
- connection of sample line to sample manifold.

Any component of the sample introduction system that is not within tolerance is either cleaned or replaced immediately.

4.07.3.A.3 ANALYZER INSPECTION

On each site visitation the field operator should inspect the following external operating parameters of the analyzer. These will vary from instrument to instrument, but in general they will include the following:

- correct settings of flow meters and regulators;
- cycling of temperature control indicators;
- temperature level, if equipped with a pyrometer;
- analyzer vacuum pump pressure;
- verification that the analyzer is in the sampling mode rather than the zero or the calibration mode; and
- verification that the zero and span potentiometers are locked and set at the proper values.

4.07.3.A.4 CHART RECORDER

During each visit to the monitoring site, the field operator should check the recorder against the following list:

- legibility of the ink trace;
- ink supply in the reservoir;
- chart paper supply;
- chart speed control setting;
- signal input range switch; and
- time synchronization (mark chart with correct time, date, and operator's signature)

At least once per week, the operator must note the exact pen position on the chart paper with a tick mark. Place the time, date, and the operator's initials beside the mark. Due to the variety of strip chart recorders available, specific operator instructions for these recorders are not incorporated in this document. Consult the respective manual(s) for each recorder model used.

4.07.3.A.5 SIGNAL AVERAGER

The signal averager time should be checked during each site visit (at least weekly). Document, sign, and date these observations in the station log book.

After a power outage, the signal averager must be cleared and reset on the hour. The average for the previous hour will be lost, so that average must be manually averaged from the strip chart. Any changes to the signal averager must be documented in the station log book and on the corresponding section of the chart recorder paper.

Correct any problems so that normal routine operations are reestablished. Sign, date and document the problems/corrections in the station log book.

NOTE: If an electronic data logger is used in conjunction with a strip chart recorder, a signal averager may not be desirable.

For operational procedures of specific signal averages, please consult the manufacturer's manual.

4.07.3.A.6 DATA ACQUISITION SYSTEM (DAS)

The DAS should be checked during each site visit (at least weekly) for the following:

- correct synchronization of time
- correct synchronization of date
- any error-indicator messages
- DAS is in normal operating mode

Note observations in the site log book and on the corresponding section of the chart recorder. Sign and date these observations.

Correct any problems so that normal routine operations are reestablished. Sign, date, and document the problems/corrections in the station log book.

For operational procedures of a specific DAS, please consult the manufacturer's manual.

4.07.3.A.7 ZERO AIR

During each site visit, visually inspect the zero air system and service as needed.

4.07.3.A.8 GAS CYLINDER PRESSURE

Once per week, note and record the span and precision NO gas tank pressures in the station log book. If the pressure for either the span NO gas tank or precision NO gas tank is below 300 psi, it should be replaced with an NO gas tank of higher pressure. A new NO gas tank should be ordered when the pressure falls to 500 psi. When an NO span gas tank is changed, the new NO span gas concentration must be checked with the analyzer's calibrated output (DAS, chart recorder) for verification of the specified NO span gas concentration.

4.07.3.B QUALITY CONTROL (QC) PERFORMANCE CHECKS

Zero, NO, and NO₂ span checks are required to document within-control conditions. The purpose of the zero and span QC checks are to provide interim checks on the response of the instrument to known concentrations. If an analyzer's response falls outside the prescribed limits, the analyzer is out of control, and the cause must be determined and corrected. Maintenance of a quality control chart is highly recommended to provide a visual check to determine:

1. if the analyzer is within control conditions.
2. the trend of the analyzer's bias so corrections can be planned and made to improve precision control over the NO₂ measurement process before an out-of-limits situation occurs. Please refer to *EPA-600/9-76-005 QA Handbook for Air Pollution Measurement Systems: Volume 1. Principles, Appendix H, Control Charts* for specifics on the use of control charts.

Every two weeks, a level 1 zero/span check must be made on the analyzer. Level 2 zero/span checks should be conducted between the level 1 zero/span checks at a frequency desired by the user.

Standard(s) used for multi-point calibration may be used for conducting span checks.

It is essential that the same NO and NO₂ gases be used each time a zero/span check is conducted. This provides a means to track the analyzer's reliability to measure the same gas over a long period.

Figure 4.07-12 (NO and NO₂ Zero/Span Drift Control Limits) summarizes the required quality control actions for the use of zero and span checks to determine NO₂ analyzer calibration control. This figure is at the end of this section.

4.07.3.B.1 LEVEL 1 ZERO/SPAN QC CHECKS

A level 1 NO and NO₂ zero/span check must be conducted every two weeks. An NO and NO₂ gas used for the multi-point calibration may be used to conduct a level 1

zero/span check. The NO/NO₂ span gas must be a NIST-traceable certified NO/NO₂ standard within the 70% to 90% URL of the analyzer.

The analyzer should be operating in its normal sampling mode with the test concentrations passing through as much of the inlet and sample conditioning system as is practicable. Wet or dirty inlet lines can cause changes in the NO₂ pollutant concentrations. Efforts should be made to introduce the span gas into as much of the sample train as possible. **The span gas must pass through all sample conditioning components used in the sample train.** The calibration response can then be compared to the response when the span concentration is introduced at the analyzer, downstream of the sample inlet components, as a check of the entire sample inlet system.

NO span gas and NO₂ span gas must be separately introduced into the NO₂ measurement system. These gas concentrations must be within 70% to 90% of the analyzer's measurement range. **No adjustment(s) to the analyzer may be made immediately prior to, or during, the zero and span calibration. Analyzer response readings must be obtained "as is" before any adjustments are made to the analyzer.** These unadjusted zero and span readings provide valuable information for:

- confirming the validity (or invalidating) the measurements obtained immediately preceding the calibration.
- monitoring the analyzer's calibration drift.
- determining the frequency of recalibration.

To conduct a level 1 zero and span check, perform the following:

1. Disconnect the analyzer's inlet from the ambient sample probe at the junction of the probe manifold and the sample line, and connect it to the NO span gas tank (or if a gas dilution calibration system is used, the NO gas dilution calibration system). Leave the analyzer in its normal sampling mode. Make no other adjustments to the analyzer.
2. Sample and measure the span test concentration and record the unadjusted, stable ("as is") span response reading in the station log book, on the strip chart recorder, span check data form/figure 4.07-13 (at the end of this section), and on an X-S control chart used for recording level 1 zero/span checks.

NOTE: All analyzer response readings must be recorded in the analyzer's normal output units (e.g., millivolts, percent of scale, etc.—the same units used for the calibration curve). If these units are concentration units, they should be identified as "indicated" or "uncorrected" to differentiate them from the "actual" concentration units that are used for reporting the reference span gas concentration measurements.

3. Sample and measure the zero test concentration standard and record the unadjusted, stable zero reading in the station log book, on the strip chart recorder, and on an X-S control chart used for recording level 1 zero/span checks.
4. Repeat steps 1 through 3 using NO₂ span gas.
5. Perform any needed analyzer adjustments (flow, pressure, etc.) or analyzer maintenance.
6. If adjustment of the zero is needed, or if any adjustments have been made to the analyzer, adjust the zero to the desired zero reading. Offsetting the zero reading (e.g., to 5% of scale) may help to observe any negative drift that may occur. Record the adjusted, stable zero reading in the station log book, on the strip chart recorder, and on an X-S control chart used for recording level 1 zero/span checks.
7. Sample and measure the span test concentration. If span adjustment is needed, adjust the span response to the desired value, allowing for any zero offset used in the previous step. Record the final adjusted, stable span reading in the station log book, on the strip chart recorder, and on an X-S control chart used for recording level 1 zero/span checks.
8. If any adjustments were made to the zero, span, or other parameters, or if the analyzer maintenance was carried out, allow the analyzer to restabilize at the new settings, then recheck the zero and span readings. Record the new zero/span settings as well as the actual zero and span readings on the chart recorder, on the X-S control chart, and in the station log book.

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

- a. Lack of preventive maintenance
- b. Fluctuations in the electrical power supply
- c. Fluctuations in flow
- d. Changes in zero air source
- e. Change in span gas concentration
- f. Degradation of photomultiplier tube

- g. Electronic and physical components not within manufacturer's specifications
- h. NO₂ converter is converting insufficient NO₂ to NO.

For specific and detailed corrective actions to be taken, please consult the manufacturer's instruction/operations manual.

4.07.3.B.2 LEVEL 2 ZERO/SPAN CHECK

A level 2 zero/span check is an unofficial quality control check of an analyzer's response. Level 2 zero/span checks should be conducted on a more frequent and pre-determined schedule between level 1 zero/span checks. 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 a multi-point) calibration should be conducted before any corrective action is taken.

If a level 2 zero and span check is to be used in the quality control program, a reference response for the check must be obtained immediately following a zero and span (or multi-point) calibration while the analyzer's calibration relationship is accurately known. Subsequent level 2 check responses are compared to the most recent reference response to determine if a change in response has occurred. Like level 1 zero/span checks, all level 2 zero and span checks are recorded/plotted on a zero/span check form (figure/form 4.07-13) and on an X-S quality control chart.

NOTE: Keep in mind that any level 2 check that involves only part of the analyzer's measurement system cannot provide information about the portions of the system not checked and, therefore, cannot be used as a verification of the overall analyzer's calibrated measurement system.

Conduct level 2 zero/span checks as level 1 zero/span checks, except make no adjustments to the analyzer's calibration without verification by a level 1 zero and span or multi-point calibration. It is further recommended that level 2 zero/span checks be automated to remotely activate every 24 hours.

DAILY ACTIVITY MATRIX			
Characteristics	Acceptance Limits	Frequency and Method of Measurement	Action if Requirements Are Not Met
Shelter temperature	Mean temperature between 15 to 30°C, daily fluctuations not greater than ±2°C (4°F)	Edit thermograph chart daily for variations greater than ±2°C (4°F)	<ol style="list-style-type: none"> 1. Mark strip chart for the affected time period 2. Repair of adjusted 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
Recorder	<ol style="list-style-type: none"> 1. Adequate ink supply and chart paper 2. Legible ink traces 3. Correct settings of chart speed and range switches 4. Correct time 	Weekly visual inspection	<ol style="list-style-type: none"> 1. Replenish ink and chart paper supply 2. Adjust recorder time to agree with clock; note on chart
Analyzer operational settings	<ol style="list-style-type: none"> 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/span and NO ₂ converter efficiency checks within tolerance limits as described in Subsec 4.07.3.B.1	Level 1 zero/span and one point converter efficiency checks every 2 weeks; Level 2 between Level 1 checks at frequency desired by user.	<ol style="list-style-type: none"> 1. Isolate source of error, and repair 2. After corrective action, recalibrate analyzer
Precision check	Assess precision as described in Sec. 4.07.7.A	Every 2 weeks, Subsec 4.07.3.9.2.	Calculate, report precision, U.S. EPA QA Handbook for Air Pollution Measurement Systems, Sec 2.0.8

Figure 4.07-10

OPERATIONAL CHECKLIST

Site ID _____ Date _____

Site Location _____ Technician _____

Site Address _____

1. Inspect thermograph for temperature variations greater than $\pm 2^{\circ}\text{C}$ (4°F). Identify time frame of any temperature level out of tolerance.

Comments: _____

2. Inspect sample introduction system for moisture, particulate buildup, foreign objects, breakage, leaks.

Comments: _____

3. Is sample line connected to manifold?

Comments: _____

4. Inspect data recording system.

	OK	Corrective Action Taken
o Legibility of trace	_____	_____
o Ink supply	_____	_____
o Paper supply	_____	_____
o Chart speed selector	_____	_____
o Signal range switch	_____	_____
o Time synchronization	_____	_____

Comments: _____

Figure 4.07-11 A

OPERATIONAL CHECKLIST (continued)

5. Inspect analyzer operational parameters.

	OK	Corrective Action Taken
o Sample flow rate	_____	_____
o Oven temperature light flashing	_____	_____
o Analyzer in sample mode	_____	_____
o Zero and span potentiometers locked at correct setting	_____	_____

Comments: _____

6. Zero the analyzer.

7. Is unadjusted zero within tolerance?

Comments: _____

8. Span the analyzer

9. Is unadjusted span within tolerance?

Comments: _____

10. Enter zero and span values on span check data form.

11. Return to sample mode.

12. Record cylinder pressure of zero and span tanks.

Zero air _____
Span air _____

13. Close valve on zero and span tanks.

Signature _____ Date _____

Figure 4.07-11 B

NO and NO₂ ZERO/SPAN DRIFT CALIBRATION LIMITS

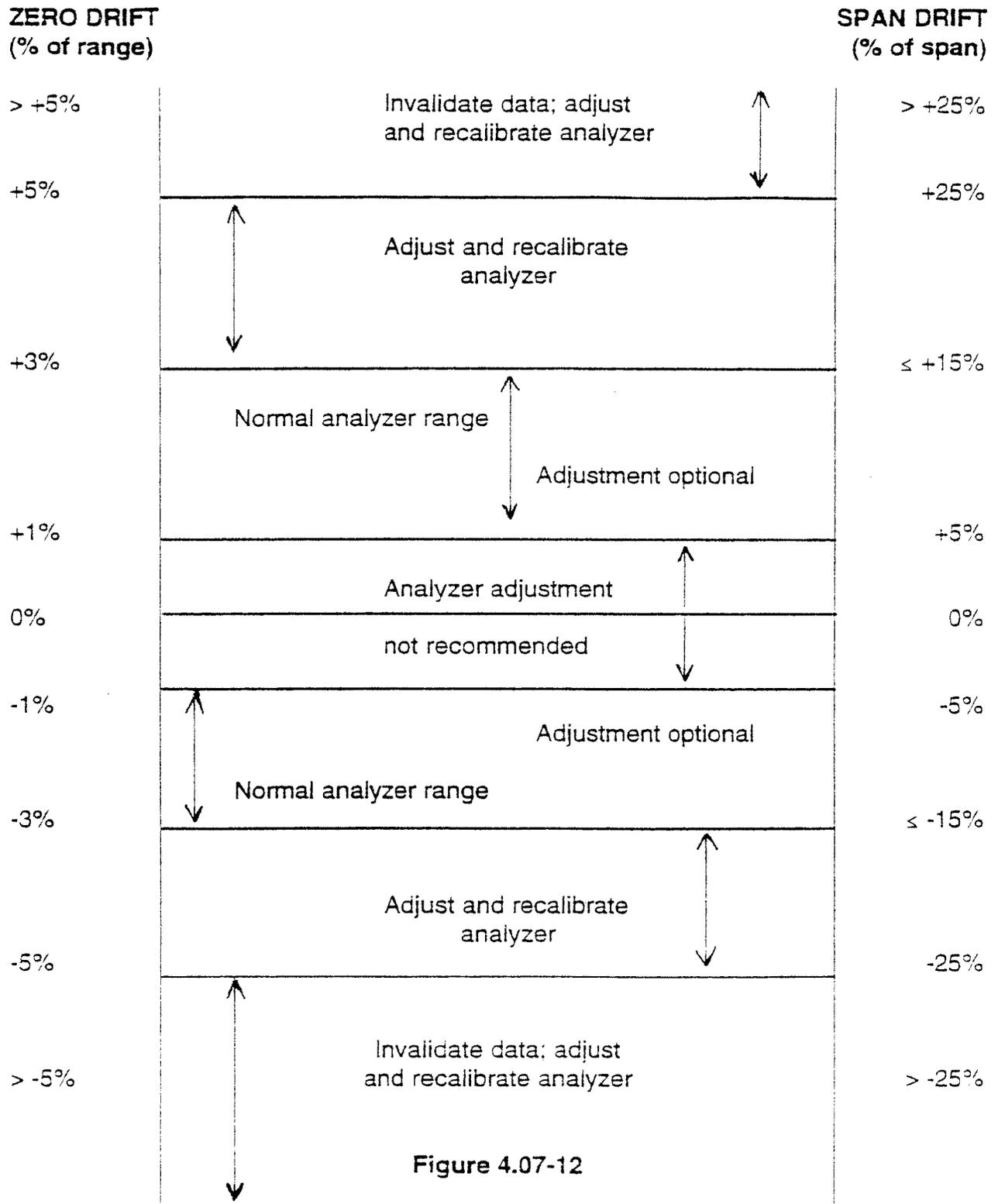


Figure 4.07-12

4.07.5 **AUDIT PROCEDURES**

The quarterly audit is the responsibility of the agency conducting the monitoring program. At any time, ADEC may choose to conduct oversight audits of a monitoring project. Chapter 5 of the *Alaska Quality Assurance Manual for Ambient Air Quality Monitoring* is devoted to this subject.

An audit is an independent assessment of the accuracy of data generated by an ambient air analyzer or a network of analyzers. Independence is achieved by having the NO₂ audit performed by an operator (trained and experienced in the NO₂ method he/she will be auditing) other than the operator (or anyone else directly associated with conducting the routine field measurements, calibrations, data validation, data reporting, etc.), and by using audit standards, reference materials, and equipment different from those routinely used in monitoring.

Note: To establish independence and comparability of audits, it is recommended to have one audit per monitoring network per year performed by an outside company or agency.

The audit is an assessment of the measurement process under normal operations--that is, without any special preparation or adjustment of the system. Routine quality assurance checks conducted by the operator are necessary for obtaining and reporting good quality data, but they are not part of the auditing process.

Proper implementation of an auditing program will ensure the integrity of the data and assess the accuracy of the data.

4.07.6 **DATA ACQUISITION, PROCESSING, AND REPORTING**

Nitrogen Dioxide data is acquired from analyzers by data acquisition systems (DAS) or by strip chart recorders. **If a DAS is used, a strip chart recorder must also be employed to capture the same data.** Additionally, if the DAS is to be used as the primary data record, 7% of reduced strip chart data must be compared against the corresponding DAS-acquired data. Processed raw data is forwarded to the agency program or project manager from their station manager(s).

Program and project managers are responsible for:

1. acquiring all processed raw data;
2. processing the data (and all other relevant SAROAD/AIRS site information) in SAROAD/AIRS report format;
3. certifying the integrity and validity of the reported data, including a report on reasons for missing or invalid data; and

4. reporting the data on a quarterly basis to the ADEC Air Program Data Base Manager. The data is to be provided on magnetic media to avoid additional data entry errors. Independent projects in support of a permit application may not be required to submit quarterly reports.

4.07.6.A DATA VALIDATION

Monitoring data of poor quality may be worse than no data. Data validation is one activity of a QA program to screen data for possible errors or anomalies. The following data validity checks should be applied to identify gross data anomalies:

4.07.6.A.1 SPAN DRIFT CHECK

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 zero and span checks be used as the first level of data validation for accepting data. This means that up to two weeks of monitoring data may be invalidated if the span drift for a level 1 zero and span check is equal to or greater than 25%. For this reason it is recommended that level 1 zero and span checks be conducted more frequently than the bi-weekly requirement.

4.07.6.A.2 HOURLY AVERAGE

Hourly Average--A minimum of 45 minutes of valid data is required to report an hourly average concentration. Figure 4.07-16, Data Form for Recording Hourly Averages, may be found at the end of this section.

NOTE: If a power outage occurs that lasts for one hour or more, the hour the system came back on may need to be voided to allow sufficient time for the analyzer to achieve recommended operating temperature.

4.07.6.A.3 EDIT OF STRIP CHART

The station operator has the primary responsibility for distinguishing valid measurements from indications caused by malfunctioning instruments or source interferences.

Data editing will be greatly enhanced if the station operator is conscious of several aids in chart review. These are listed below:

- a. Familiarity with typical diurnal, daily, seasonal, or wind direction specific concentration variations (e.g., the times maximum concentrations occur).
- b. Familiarity with the type of instrument malfunctions which cause characteristic trace irregularities.

- c. Cyclical or repetitive variations (at the same time each day or at periodic intervals during the day) may be caused by excessive line voltage or temperature variations. Nearby source activity can also cause erroneous or non-representative measurements.
- d. Traces showing little or no activity often indicate a loss of sensitivity, flow problems, or sample line leaks.
- e. A wide, solid trace indicating excessive noise or spikes that are sharper than is possible with the normal instrument response time and are indicative of erratic behavior. Noisy outputs usually result when analyzers are exposed to vibration sources.
- f. A long, steady increase or decrease in deflection.
- g. A trace that drops below the zero baseline during certain periods; this may indicate a larger-than-normal drop in the ambient room temperature or the power line voltage. This may also indicate contaminant(s) in the zero air.
- h. Enter meaningful notes on the charts. **The more information that can be provided, the more valuable the strip charts will be.** Draw an arrow from each note to the area of the chart discussed. For example, notes should include:
 1. the causes of, or comment on, irregularities in the trace,; e.g., changes in zero from day to day, sudden changes in the trace, flow errors, or corrective actions.
 2. checks and/or adjustments to the analyzer(s).
 3. span drift equal to or greater than 25% of the chart.

NOTE: Data must be flagged or voided for any time interval in which a malfunction of the sampling system is detected.

4.07.6.B DATA REDUCTION

Data can be reduced either manually or automatically. Automatic data reduction is done by DAS that are programmed at the time of the analyzer's multi-point calibration.

4.07.6.B.1 WITH SIGNAL AVERAGER

Hourly average concentrations from a strip chart recorder with a signal averager may be obtained by the following procedure:

- a. Use of a signal averager is recommended to facilitate data reduction. The signal averager provides an average, for each hour, that is recorded by the chart recorder and data logger. The average shown by the signal averager always indicates the output of the analyzer, including any zero, span, or precision checks. The hourly average concentration may be obtained from the strip chart by the method explained in 2 of this section.
- b. All hours in which a precision check was performed must be manually averaged to exclude the period precision gas was sampled as the precision gas is sampled through the ambient port of the analyzer.

NOTE: Use of the term "signal averager" refers solely to a stand-alone unit such as the Monitor Lab's 8640.

- c. The hours in which a zero-span was performed by the operator may have to be edited manually to exclude the zero span period from the sample average. There must be 45 minutes of sample time to form a valid hourly average.

NOTE: Complete data reduction documentation must be maintained on the strip chart recorder. The analyst's name and the date the data reduction took place must be included.

- d. Fill in the identification data called for at the top of the SAROAD/AIRS hourly data form (Figure/Form 4.07-16).
- e. Read the hourly signal averaged deflection (% chart) for all of the hourly intervals for which data have not been marked invalid, and record all values on the hourly averaged data form in the column headed, "Reading--Original (Orig)." Ignore the columns marked "Zero Baseline," "Difference," and "y, add + 5."
- f. Convert "Reading--Orig," values (% chart) to concentrations (ppm) by using the most recent NO₂ calibration curve, and record the concentrations in the last column of the SAROAD/AIRS hourly data form.

4.07.6.B.2 WITHOUT USE OF SIGNAL AVERAGER

Hourly average concentrations from a strip chart record may be obtained by the following procedure:

- a. Make sure the strip chart record has a zero trace at the beginning and end of the sampling period.
- b. Fill in the identification data called for at the top of the SAROAD/AIRS hourly data form.

- c. 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 by using a straight edge.
- d. Read the zero baseline (% chart) at the midpoint of each hourly interval, and record the value on the data form.
- e. Determine the hourly averages by placing a transparent straight edge parallel to the horizontal chart division lines. Adjust the straight edge between the lowest and highest points of the trace in the interval between two vertical hour lines of interest so that the area above the straight edge and bounded by the trace and the hour lines is approximately equal to the area below the straight edge and bounded by the trace and hour lines.

Read the deflection (% chart) for all of the hourly intervals for which data have not been marked invalid, and record all values on the hourly average data form in the column headed "Reading--Original (Orig.)."
- f. Subtract the zero baseline value from the reading value, and record the difference.
- g. Add the percentage of zero offset, if applicable, to each difference.
- h. Convert reading values (% chart) to concentrations (ppm) by using the most recent NO₂ calibration curve, and record the concentrations in the last column of the SAROAD/AIRS hourly data form.
- i. An alternative method of converting % chart to ppm is to eliminate steps f and h and to use equation 4.07-20:

$$\text{ppm} = (y - y_z)/\text{slope} \qquad \text{eqn. 4.07-20}$$

where:

y = recorder reading in % scale (from step 5)

y_z = zero baseline in % scale (from step 4)

slope = slope of the calibration relationship (from section 4.07.2.B)

4.07.6.C DATA QUALITY CONTROL

To ensure that only reliable, accurate, complete, representative, and comparable data is reported to the ADEC Air Program Data Base Manager, the following quality control (QC) activities will be performed on each set of reported data:

- 1. Check 7% of the data for transcription error. If a transcription error is found, correct the problem. Recheck all data in the respective data batch

for transcription correctness. Document the problem(s) and the appropriate corrective action(s) taken to report reliable data.

2. Randomly recalculate 7% of all data. Recalculations must agree within a round-off error of the original sample calculation. If not, recalculate all data in the respective data batch. Correct any error(s). Document the problem(s) and the appropriate corrective action(s) taken to report reliable data.
3. Conduct a level 1 zero/span NO and NO₂ check at a minimum of once every two weeks (see section 4.07.3.B.1 for specifics on conducting level 1 zero/span NO and NO₂ checks). The analyzer's response to the level 1 zero/span check concentration must be within $\pm 15\%$ of the NO and NO₂ span check standard concentrations, and zero must be within $\pm 3\%$ of measurement range. In addition, the NO₂ to NO converter efficiency must be $>96\%$. If the level 1 zero/span check fails any of the above requirements:
 - a. identify the problem;
 - b. correct the problem;
 - c. recalibrate the NO₂ analyzer as soon as possible. If, however, the level 1 zero/span check result is outside $\pm 25.0\%$ of the NO/NO₂ span checks, or zero drift is $> \pm 5\%$ of the analyzer full scale range, then all data must be invalidated to the last acceptable span check or multi-point calibration. The NO₂ analyzer must also be recalibrated before being used to collect data; and
 - d. document the problem(s) and the corrective action(s) taken to return the NO₂ analyzer to acceptable routine operations.
4. Conduct a precision check at a minimum of once every two weeks. The analyzer's response to the precision check NO₂ concentration must be within $\pm 15\%$ of the NO₂ precision check standard concentration. If the precision check fails the above requirement, conduct a level 1 zero/span check to substantiate the problem and take the necessary corrective action(s) to return the NO₂ analyzer to acceptable routine operations. (See Figure 4.07-12 for NO and NO₂ zero/span Drift Calibration Limits).
5. Visually inspect all sample information data/documentation sheets. Ensure all necessary information is recorded and complete.

4.07.6.D STATISTICAL TRACKING

All equipment must be maintained with current up-to-date maintenance log books. All repairs, maintenance, calibrations, etc., must be recorded, signed, and dated.

The program or project manager will ensure that the following X-S charts are maintained and up-to-date:

- Level 1 NO and NO₂ zero/span checks
- Level 2 NO and NO₂ zero/span checks
- NO and NO₂ precision checks

NOTE: Please refer to *EPA-600/9-76-005 QA Handbook for Air Pollution Measurement Systems: Volume 1. Principles, Appendix H, Control Charts* for directions on establishing and maintaining control charts.

4.07.6.E DATA REPORTING

NO₂ information and hourly averages data is transcribed from the hourly averages form 4.07-41 to a SAROAD/AIRS hourly data form. (See *EPA-600/9-76-005 QA Handbook for Air Pollution Measurement Systems: Volume 2.0.3*, for details and basic instructions for filling out the SAROAD.)

NO₂ information and hourly averages from data acquisition systems may also be polled and processed into SAROAD/AIRS format by computer with the appropriate computer software. However, data reduced and reported in this manner must be verified against a 7% random strip chart data reduction check. Also, any NO₂ concentration anomalies reported by the DAS must be compared against the strip chart recorder reduced data. Differences between reported DAS collected/reduced data and strip chart recorder collected/reduced data must agree within 4% of the analyzer's calibrated full-scale range (e.g., .02ppm for a 0-0.5ppm range). If obvious differences are noted between the two collection/reporting systems, all data back to the last acceptable level 1 zero/span check must be examined by both systems. The reason(s) for the difference(s) must be investigated, corrected, and documented. The appropriate sections of collected data that do not meet data validation requirements must be invalidated. Other questionable data should be flagged and reported to the local agency data base manager. It is incumbent upon the local and/or ADEC data base manager to decide whether to include the flagged data in ADEC's air monitoring data base.

Quarterly data reports submitted to the Department must include (but not be limited to) the following QA documentation:

1. All valid or flagged one-hour averages (from all channels used to calculate and report NO₂ data);
2. Minimum and maximum one-hour averages and other summary statistics for all reported parameters;
3. Data which has exceeded the full-scale range of the analyzer, shall be flagged and manually verified against strip chart recorder output. Copies of verified strip chart(s) shall be made available to the Department upon request;
4. Reasons for each hour of missing/invalid/flagged data shall be identified and explained;
5. Details of all maintenance activities and any changes to instrument and standard operating procedures;
6. Results of all pre-calibration checks and unadjusted zero/span checks;
7. Results of all analyzer calibrations;
8. Results of all NO₂ converter efficiency checks;
9. Copies of calibration and equipment standards used for calibrations, calibration checks, and audits;
10. Results of all calibration flow checks; and
11. All final analyzer potentiometer (and other instrument) settings for all calibrations and zero/span checks.

4.07.7 ASSESSMENT OF MONITORING DATA FOR PRECISION AND ACCURACY

4.07.7.A PRECISION

4.07.3.B.3 NO₂ PRECISION CHECKS

For continuous analyzers, a periodic check is used to assess the data for precision. A one-point precision check must be conducted at least once every two weeks on each analyzer at a concentration between 16% and 20% of the analyzer's upper range limit (URL). The analyzer must be operated in its normal sampling mode. The precision test gas must pass through all filters, scrubbers, conditioners, and other components used during normal ambient sampling. The precision check gas standard must be traceable to a NIST-SRM- or NIST/EPA-approved CRM. **The precision check standard should be independent from that used for calibration.**

The precision check procedure follows:

1. Connect the analyzer to a calibration system to generate an NO₂ precision gas that has a concentration between 16% and 20% of the analyzer's URL (between 0.08 and 0.10 ppm for a 0.5 ppm URL). The NO₂ gas may be generated by either a GPT or an NO₂ permeation tube gas calibrator. **If a precision check is made in conjunction with a zero/span check, it must be made prior to any zero or span adjustment(s).**
2. Allow the analyzer to sample the precision gas until a stable response is obtained (at least 5 minutes).
3. Record this value on the precision check form (see figure/form 4.07-14 at the end of this section) on an X-S quality control chart, and on the chart recorder paper as "unadjusted precision check."

The difference between the concentration indicated by the analyzer and the actual concentration of the precision check gas is used to assess the precision of the monitoring data (see *EPA-600/9-76-005 QA Handbook for Air Pollution Measurement Systems; Volume 2.0.8 Calculations to Assess Monitoring Data for Precision and Accuracy for SLAMS and PSD Automated Analyzers and Manual Methods*).

Use the same control criteria to evaluate acceptable NO₂ precision checks as used to evaluate acceptable level 1 span checks (see figure 4.07-12). These bi-weekly precision check values will be used to determine single instrument precision as described in 40 CFR 58, Appendices A and B.

It is essential that the same NO and NO₂ gases be used each time a precision check is conducted. This allows a means to track the NO₂ analyzer's calibration stability. All

precision check results must be documented. It is strongly recommended that ongoing quality control (QC) X-S charts be maintained to document precision check result trends for the NO₂ analyzer. For more information on QC charts, please refer to *EPA QA Handbook for Air Pollution Measurement Systems: Volume 1. Principles. Section .H Control Chart*.

The NO₂ precision test gas may be generated either by method of gas phase titration (GPT) or permeation device.

4.07.7.A.1 NO₂ PRECISION CHECKS BY GPT METHOD

To conduct NO₂ precision checks by GPT, follow the procedures used in subsection 4.07.2.B.2. However, instead of generating multiple NO₂ gas concentrations for a multi-point calibration, generate one level of NO₂ between 16% and 20% of analyzer full range.

4.07.7.A.2 NO₂ PRECISION CHECKS BY PERMEATION DEVICE METHOD

To conduct NO₂ precision checks by permeation tube method, follow the procedures used in subsection 4.07.2.B.3. However, instead of generating multiple NO₂ gas concentrations for a multi-point calibration, generate one level of NO₂ between 16% and 20% of analyzer full range.

4.07.7.B ACCURACY

The accuracy of the NO₂ analyzer is assessed by auditing the performance of the analyzer as described previously in section 4.07.5. The audit gas values and the corresponding analyzer-measured values are reported. The percentage differences between these values are used to calculate accuracy as described in 40 CFR 58, Appendices A and B.

4.07.8 DATA QUALIFICATION

Quarterly data reports must be ≥75% complete. Data reports <75% complete must be accompanied by a missing data report. The missing data reports will identify:

- specific and comprehensive reasons for missing data, and
- the appropriate corrective action(s) that were taken to return data reporting to acceptable levels of completeness.

4.07.9 DATA SUBMISSION

NO₂ data will be reported on a quarterly basis. The data will be reported on magnetic media with a hard copy backup. Quarterly reports will be submitted within a time period specified by the data base manager, but no later than one month following the end of

the respective quarter. Independent projects performed in support of a permit application may not be required to submit quarterly reports.

NO₂ information and hourly averages from data acquisition systems may also be polled and processed into SAROAD/AIRS format by computer with the appropriate computer software. However, data reduced and reported in this manner must be verified against a 7% random strip chart data reduction check. Also, any NO₂ concentration anomalies reported by the DAS must be compared against the strip chart recorder reduced data. Differences between reported DAS collected/reduced data and strip chart recorder collected/reduced data must agree within 4% of the analyzer's calibrated full scale range (e.g., 0.02ppm for a 0-0.5ppm range). If obvious differences are noted between the two collection/reporting systems, all data back to the last acceptable level 1 zero/span check must be examined by both systems. The reason(s) for the difference(s) must be investigated, corrected, and documented. The appropriate sections of collected data that do not meet data validation requirements must be invalidated. Other questionable data should be flagged and reported to the local agency data base manager. It is incumbent upon the local and/or ADEC data base manager to decide whether to include the flagged data in ADEC's air monitoring data base.

Quarterly data reports submitted to the Department must include (but not be limited to) the following QA documentation:

1. All valid or flagged one-hour averages (from all channels used to calculate and report NO₂ data);
2. Minimum and maximum one-hour averages and other summary statistics for all reported parameters;
3. Data which has exceeded the full scale range of the analyzer shall be flagged and manually verified against strip chart recorder output. Copies of verified strip chart(s) shall be made available to the Department upon request;
4. Reasons for each hour of missing/invalid/flagged data shall be identified and explained;
5. Details of all maintenance activities and any changes to instrument and standard operating procedures;
6. Results of all pre-calibration checks and unadjusted zero/span checks;
7. Results of all analyzer calibrations;
8. Results of all NO₂ converter efficiency checks;

9. Copies of calibration and equipment standards used for calibrations, calibration checks, and audits;
10. Results of all calibration flow checks; and
11. All final analyzer potentiometer (and other instrument) settings for all calibrations and zero/span checks.

4.07.10 EQUIPMENT DE-INSTALLATION

When an NO₂ monitoring site is to be shut down, the functions listed below are highly recommended. If the site is to be permanently shut down, a final performance and systems audit is to be performed. If the site is to be a seasonal shutdown only, a performance audit should be performed prior to the shutdown, but certainly within the final calendar quarter of instrument operation.

1. Conduct a final level 1 zero/span and precision check to validate the last portion of collected data.
2. Log the date, time, zero/span values, zero and span potentiometer values, and any other pertinent information, on the operator logsheet.
3. Turn off and unplug the NO₂ analyzer (consult the respective manufacturer's operating manual).
4. Turn off and shut down the permeation device gas calibrator (consult the respective manufacturer's operating manual).
5. Turn off and shut down the GPT calibrator (consult the respective manufacturer's operating manual).
6. Turn off and shut down the data logger (consult the respective manufacturer's operating manual).
7. Turn off and shut down the signal averager and chart recorder (consult the respective manufacturer's operating manuals).
8. Turn off and shut down the zero air system (consult the respective manufacturer's operating manual).
9. Turn off and shut down the power conditioning system (consult the respective manufacturer's operating manual).
10. Close gas tank valves for precision gas tank, span gas tank, zero air tank (if applicable), and calibration gas tank. Remove pressure regulators and replace with twist caps for safety transportation.

4.07.11 SAFETY PROCEDURES

The following basic precautions should be taken while working with NO₂ instrumentation:

1. Operate all monitoring instruments with the available grounding plug (3-wire plug).
2. Exhaust the analyzer safely, especially when calibrating the unit with high NO_x concentrations.
3. When working/troubleshooting/repairing any electrical instrument, the power should usually be turned off and the power line disconnected.
4. Take normal precautions for shock protection/prevention when working inside of any electrical instrument with the power connected.
5. Ensure that all high-pressure gas tanks are securely chained or otherwise attached to something solid so that the tanks remain in an upright and secure position at all times.

