

performance specifications for both the lower and upper concentration boundaries of the range, and should be verified and specified for each sensor as provided by the sensor manufacturer. Specifications for this purpose are suggested in Sections 4.6.1 and 4.6.2.

2.3 Special Requirements.

2.3.1 Baseline Drift and Filter Degassing. If a sensor's baseline is higher than 1 ppm equivalent, or if an interference rejection filter is used and it is not certain that the filter does not absorb/adsorb a portion of the desired gas, then it will be necessary to use a means for maintaining the filter and sensor electrode temperature below 30 degrees centigrade. This requirement is to prevent excessive baseline drifts, which may be caused either by changes in the sensor's baseline, or by degassing of the filter. Such drift may increase very rapidly with increasing temperature, following Arrhenius' Law, approximately. Under these conditions an electronic compensation technique to correct apparent baseline drift is not acceptable, because the apparent baseline shift with temperature depends both on the state of the sensor's baseline, and the history of exposure of the degassing filter to the gas to be measured. Both factors can change in an unpredictable manner. Therefore, as a demonstration that proper filter/sensor temperature is maintained during each run, it is necessary to keep a record of the filter/sensor temperature during each run.

2.3.2 Electrode Activity Reserve. Electrode activity reserve is the ratio of the reaction rate at the electrode surface to the rate of diffusion of the gas entering the sensor. Since electrochemical sensors should be operated under diffusion control to insure stable and responsive performance, adequate electrode activity reserve should be available to insure proper analyzer performance.

3.0 Definitions.

3.1 Measurement System. The total equipment required for the determination of NO and NO₂ gas concentrations. The measurement system consists of the following major subsystems:

3.1.1 Sample Interface. That portion of a system used for one or more of the following: sample acquisition, sample transport, sample conditioning, or protection of the analyzer from the deleterious effects of the stack effluent.

3.1.2 Electrochemical Analyzer. A device that uses electrochemical sensors to measure both NO and NO₂ separately and adds the result to yield oxides of nitrogen (NO_x). The analyzer must include provision for maintaining the filter/sensor temperature below 30 degrees

centigrade, and must provide a means for generating a record of said temperature during the test run.

3.1.3 Data Recorder. A strip chart device, digital computer or printer for recording sample gas measurements and filter/sensor temperature data from the analyzer.

3.2 Calibration Gas. A known concentration of gas in an appropriate diluent gas.

3.3 Analyzer Calibration Error. The difference between the gas concentration exhibited by the gas analyzer and the known concentration of the calibration gas when the calibration gas is introduced directly to the analyzer.

3.4 Sampling System Bias. The difference between the gas concentrations exhibited by the measurement system when a known concentration gas is introduced at the inlet of the sampling probe and when the same gas is introduced directly to the analyzer.

3.5. Zero Drift. The difference in the measurement system output reading from the initial calibration response at the zero concentration level and after a stated period of operation during which no unscheduled maintenance, repair or adjustment took place.

3.6 Calibration Drift. The difference in the measurement system output reading from the initial calibration response at a mid-range calibration value and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.7 Response Time. The amount of time required for the measurement system to display 95 percent of a step change in total gas concentration of a mixture consisting of approximately equal concentrations of NO and NO₂ upper range gases on the data recorder.

3.8 Interference Check. A method for detecting and quantifying analytical interferences through either direct recording or auto-instrumental indication of the analyzer response to an interfering gas.

3.9 Sensor Sensitivity Range. The measurement range in ppm for each sensor. This value should be specified by the sensor manufacturer to allow sufficient reactive capacity, baseline stability, and output signal strength so that the performance standards of Section 4.0 are met on a consistent and reproducible basis. An acceptable sensor sensitivity range should be specified by the sensor manufacturer to meet the lower and upper boundary performance specifications, as defined below.

3.9.1 Sensor Baseline. An electrochemical sensor's baseline is the difference in electrochemical current measured at 20 degrees centigrade between the sensing and reference electrodes when exposed to zero gas. The output signal may either be expressed in microamps or in ppm equivalents. Gas desorption by an inline filter may increase the sensor's apparent baseline, considerably. Sensor baseline is small at low temperatures (below 25 degrees centigrade), but can change in an unpredictable manner and increase exponentially with increasing temperature (following Arrhenius' law, approximately).

3.9.2 Sensor Baseline PPM Equivalents. The sensor's baseline should be specified by the sensor manufacturer, and should be expressed in microamps, divided by the sensor's sensitivity expressed in microamps/ppm.

3.9.3 NO Sensor Lower Concentration Boundary, PPM. An NO sensor's lower concentration boundary in ppm, which should be specified by the sensor manufacturer. A sensor's performance at low sensitivity depends on three factors: baseline drift and filter degassing (both of which give rise to exponentially increasing sensor drift with increasing temperature), and instrument signal to noise ratio. The sensor's lower concentration boundary in ppm should be no lower than 50 times the sensor's baseline in ppm at 20 degrees centigrade, unless the baseline is less than 2 ppm equivalent, in which case the lower concentration boundary should be no less than 20 times the sensor's baseline.

3.9.4 NO Sensor Upper Concentration Boundary, PPM. An NO sensor's upper concentration boundary in ppm, which should be specified by the sensor manufacturer. The upper concentration boundary in ppm should be specified in consideration of the requirement that the sensor calibration drift should be less than 2 percent of the calibration gas value after one hour of continuous exposure to NO span gas having a concentration of between 90 and 100 percent of the upper boundary of the sensor's sensitivity range.

3.9.5 NO₂ Lower and Upper Concentration Boundaries, PPM. The lower concentration boundary should be specified by the sensor manufacturer so that the NO₂ sensor has a baseline of less than 0.1 microamp at 20 degrees centigrade. For the upper concentration boundary, the sensor's manufacturer should specify this value in such a manner that the sensor's drift following a one hour continuous exposure at 90 to 100 percent of the sensor's upper boundary should be less than 2 percent.

3.10 Interference Rejection Filter. A filter that is designed to remove one or more interfering gases, thereby increasing

electrochemical sensor specificity.

3.10.1 Filter Desorption (Degassing). Gas retained by the filter by an absorption/adsorption mechanism will desorb gradually over a period of time, resulting in a false instrument zero. The rate of desorption is a function of both temperature and the amount of gas adsorbed by the filter during previous exposures, and will decrease with time as the absorbed/adsorbed gas is depleted.

3.10.2 Filter Adsorption. A mechanism by which a portion of the desired gas is retained on the surface of the filter particles, resulting in an gradual increase in sensor response as equilibrium conditions are approached.

4.0 Measurement System Performance Specifications.

4.1 Measurement System Calibration Error. Less than +/- 2 percent of the high-range calibration gases for the zero, mid-range and high-range calibration gases.

4.2 Sampling System Bias. Less than +/- 5 percent of the high-range calibration gases for the zero, and mid-range, or high-range calibration gases.

4.3 Zero Drift. Less than +/- 3 percent of the high-range calibration gases over the period of each run.

4.4 Calibration Drift. Less than +/- 3 percent of the high-range calibration gases over the period of each run, with the exception that if the gas concentration is less than 100 ppm, then the absolute value of the difference between the system's response value and the reference value shall be less than, or equal to 5 ppm.

4.5 Interference Checks.

4.5.1 Initial Interference Response Check. Conduct an initial interference response check of the analyzer prior to its first use in the field, as described in Section 6.4.1. Repeat if changes are made in the instrumentation, such as sensor replacement. The sum of the responses for the initial interference response check for each sensor shall be less than 2 percent of the high-range calibration gases, or 5 ppm, whichever is greater.

4.5.2 Regular Interference Performance Check. Conduct before and after each test run, or after changing an interference rejection filter. Conduct an interference performance test as described in Section 6.4.2. The sum of the responses for the interference performance test for each sensor shall be less than 2 percent of the

high-range calibration gases, or 5 ppm, whichever is greater.

4.6 Sensitivity Range. A sensor's sensitivity range should be specified by the sensor manufacturer to meet the upper and lower concentration boundary performance specifications detailed below.

4.6.1 NO Lower Concentration Boundary. The lower concentration boundary of the NO sensor in ppm should be no lower than fifty times the sensor's ppm equivalent baseline at 20 degrees centigrade, unless the baseline is less than 2 ppm equivalent, in which case the lower concentration boundary should be no less than twenty times the baseline.

4.6.2 NO Upper Concentration Boundary. The NO sensor should be exposed to NO calibration gas of between 90 and 100 percent of the sensor manufacturer's stated upper concentration boundary. After a period of fifteen minutes, readings should be recorded every five minutes for a period of one hour, with no interruption or purging. All readings of drift should be less than +/- 2 percent of the calibration gas value, unless the concentration of the calibration gas is less than 100 ppm, in which case drift should not exceed +/- 5 percent.

4.6.3 NO₂ Range. The sensor's manufacturer should certify that the sensor's baseline is less than 0.1 microamps at 20 degrees centigrade and that its drift following a one hour continuous exposure at 90 to 100 percent of the sensor's upper boundary is less than +/- 2 percent.

5.0 Apparatus and Reagents.

5.1 Measurement System. Any measurement system for nitrogen oxides that meets the performance specifications of this method. The essential components of the measurement system are described below.

5.1.1 Sample Probe. Glass, stainless steel, inconel, hastelloy x, or equivalent; of sufficient length to traverse the sample points. The sampling probe shall be designed to prevent condensation.

5.1.2 Sample Transport Line. Stainless steel, teflon, or viton tubing; either heated to prevent condensation or located after the condensation removal system; to transport the sample gas to the analyzer.

5.1.3 Moisture Removal System. Any system such as a permeation drier or refrigeration device that will remove the water vapor on a continuous basis without removing a significant amount of the following gases: NO, NO₂, CO₂, SO₂ and O₂.

5.1.4 Particulate Filter. An in-stack or an out-of-stack heated filter. The filter shall be stainless steel, Hastelloy X, Teflon, or glass fiber mat with a fluorocarbon binder. All filters shall be fabricated of materials that neither react with, nor retain the gas being sampled.

5.1.5 NO_x Analyzer. An analyzer that includes both an electrochemical NO sensor and an electrochemical NO₂ sensor; to determine continuously the total NO_x concentration in the sample gas stream. The analyzer shall meet the applicable performance specifications of Section 4.

5.1.6 Sample Flow Rate Control. A sample flow rate control mechanism and rotameter, or equivalent, to maintain a constant sampling rate within +/- 10 percent of the flow rate should be specified by the instrument manufacturer.

5.1.7 Sample Gas Manifold. A manifold to divert a portion of the sample gas stream to the inlet probe of the analyzer and the remainder to the by-pass discharge vent. It should be constructed of materials that are not reactive to the gas being sampled.

5.1.8 Data Recorder. A strip chart recorder, digital computer or printer, or memory storage device; for recording measurement data. The data recorder resolution shall be 0.25 percent of the sensor sensitivity upper range, or 1 ppm, whichever is higher. The recorder may be an integral part of the analyzer. Alternatively, a digital or analog meter having the same resolution may be used to obtain the analyzer responses and the readings may be recorded manually.

5.2 NO_x Calibration Gases. The calibration gases for the NO_x analyzer shall be NO in nitrogen, and NO₂ in nitrogen or air.

5.2.1 High-range. For the NO and NO₂ sensors, choose concentrations such that the average stack gas measurements for each run are greater than 25 percent of these values.

5.2.2 Mid-range. For the NO and NO₂ sensors, gas concentrations equivalent to between 40 and 60 percent of the high-range gases.

5.2.3 Zero Gas. Concentration of less than 0.25 percent of the high-range calibration gases, or 1 ppm, whichever is higher. Purified ambient air may be used for zero gas after first passing it through a charcoal filter.

6.0 Pre-Test Measurement System Performance Test Procedures.

6.1 Calibration Gas Concentration Verification. Use one of the following two alternatives for establishing the concentrations of calibration gases.

6.1.1 Alternative Number 1. Use calibration gases that are analyzed following the Environmental Protection Agency traceability Protocol Number 1. Obtain a certification from the gas manufacturer that Protocol Number 1 was followed.

6.1.2 Alternative Number 2. Obtain gas mixtures with the gas manufacturer's tolerance not to exceed +/- 2 percent of the tag value. For NO gas mixtures, the tag date of analysis of the cylinder contents shall not be over one year old. For NO₂ mixtures, the tag date shall not be over six months old. Verify each new gas cylinder by first calibrating the analyzer with the previously used cylinder, and then check the analyzer response by analyzing the new cylinder. The latter analyzer reading shall not differ from the new cylinder's tag value by more than 10 percent, or 10 ppm, whichever is greater. If the analyzer's readings differ by more than 10 percent, recheck the new cylinder with Protocol 1 gas. If they agree within 10 percent, then use the analyzed value of the new cylinder in place of the tagged value for subsequent analyzer calibrations.

6.2 Measurement System Preparation. Assemble the measurement system by following the manufacturer's written instructions for preparing and preconditioning the gas analyzer and the other system components. Introduce the calibration gases in sequence and make all necessary adjustments to calibrate the measurement system. Use a sample gas manifold or a demand regulator assembly to feed the calibration gases to the measurement system.

6.2.1 Response Time. Use one of the two following alternatives to determine the system's oxides of nitrogen response time prior to its initial use in the field.

6.2.1.1 Alternative Number 1. Use rotameters to inject into the system's sample probe equal flow rates of a mixture of the upper range NO oxide calibration gas and the NO₂ calibration gas having a concentration that is 50 percent (+/-10 percent) of the NO calibration gas, or 500 ppm, whichever is lower. Use the rotameters to monitor the calibration gas mixture ratio, and set the total flow to correspond to the instrument's flow rate. Determine the system's NO_x response time by observing the time required to achieve a stable total NO_x response. Once stabilized, remove the probe, and while sampling purified ambient air (zero gas), observe the time required to read a value of zero for total NO_x. Note and record the longer of the two times as the response time.

6.2.1.2 Alternative Number 2. If the response time of the system to NO₂ as defined by the instrument manufacturer's specification is longer than five times the response of the system to NO gas, introduce the upper range NO₂ calibration gas to the system's sampling probe. Record the time required for the NO₂ display to reach 85 percent of its stable response. Then introduce zero gas and repeat the procedure. Note and record the longer of the two times as the NO_x response time.

6.3 Measurement System Calibration Error Check. Conduct the measurement system calibration check by introducing calibration gases at the inlet of the system's sampling probe as follows: After the measurement system has been prepared for use, introduce the zero, mid range, and high range NO gases to the system. During this check make no adjustments to the system. Allow an time interval equal to the systems response time, then record the system's responses to each calibration gas. The measurement system's calibration error check shall be considered invalid if the gas concentration displayed by the system exceeds +/- 2 percent of the NO high-range calibration gases, or 5 ppm, whichever is higher, for any of the calibration gases. If an invalid calibration is exhibited, take corrective action, and repeat the system calibration error check until acceptable performance is achieved. Record the analyzer responses on a form similar to Figure 1. Repeat the procedure, using zero, mid range and high range NO₂ calibration gases. The measurement system's calibration error check shall be considered invalid if the gas concentration displayed by the system exceeds +/- 2 percent of the NO₂ high-range calibration gases, or 5 ppm, whichever is higher, for any of the calibration gases.

6.4 Interference Response Checks.

6.4.1 Primary Check. Before initial use of the instrument, or after changing a sensor, conduct an interference response check as follows: Check the response to possible interfering gases of the NO and NO₂ sensors separately. Introduce the gaseous components listed below into the analyzer directly. Feed the gas to the instrument, and record the sensor response at the end of a period corresponding to two times the NO_x response time of the system. Determine the total interference output response to these components in concentration units, and record the values for the NO and the NO₂ sensors separately. The sum of the interference responses for each sensor shall be less than 5 percent of the high-range calibration gas value, or 5 ppm, whichever is greater. Use the following gases to test for interferences:

6.4.1.1 NO Sensor.

CO: 500 ppm +/-10 percent.

NO₂: 90-100 percent of the NO₂ sensor's upper concentration boundary; balance air.

SO₂/NO mixture: 50 percent 200 ppm SO₂+/-10 percent;
50 percent 200 ppm NO +/- 10 percent; balance nitrogen.

CO₂: 10 percent +/- 1 percent; balance air

Note: At the sensor's electrodes NO is oxidized to NO₂, which then reacts with SO₂ to produce additional NO, thus resulting in a false reading. Interference to SO₂ shall be measured in the presence of NO gas.

6.4.1.2 NO₂ Sensor.

CO: 500 ppm +/-10 percent.

NO: 90 percent to 100 percent of the NO sensor's sensitivity range, up to 1000 ppm.

SO₂: 200 ppm +/-10 percent.

CO₂: 10 percent +/- 1 percent; balance air.

6.4.2 Field Use. Before and after each series of tests (up to three consecutive test sets) either manually or using an automatic instrumental interference check as described in Section 6.6, record the response of the NO sensor to NO₂ and SO₂ calibration gases as listed in Section 6.4.1.1. Record the response of the NO₂ sensor to NO and SO₂ calibration gases listed in Section 6.4.1.2. Interference responses for each sensor to each gas shall be less than 6 percent of calibration gas value. Depending upon approach, use a form similar to Figure 2 or Figure 4. For natural gas applications, or where SO₂ expected values are less than 10 ppm, SO₂ interference gas tests are not required.

6.5 Sampling System Bias Check. Conduct the sampling system bias check prior to its initial use in the field. Thereafter recheck the

measurement system before each test by introducing calibration gases at the inlet of the sampling probe.

6.5.1 NO. Introduce the upper range NO calibration gas to the inlet of the sample probe. Allow an interval equal to the system's response time and record the analyzer reading. Introduce the calibration gas directly to the analyzer and record the reading. The sampling system bias check shall be considered invalid if the difference between the two readings exceeds 5 percent of the NO calibration gas value, or 5 ppm, whichever is greater.

6.5.2 NO₂. Introduce the upper range NO₂ calibration gas to the inlet of the sample probe. Allow an interval equal to three times the system's response time and record the analyzer reading. Introduce the calibration gas directly to the analyzer and record the reading. The sampling system bias check shall be considered invalid if the difference between the two readings exceeds 10 percent of the NO₂ calibration gas value (equivalent to 5 percent of the NO calibration gas value), or 5 ppm, whichever is greater.

6.6 Calibration Certification Protocol. Obtain a record to confirm proper sensor and interference rejection filter performance, and to meet the requirements of Section 6.4 before and after each test. Use high range gases for NO, NO₂, and SO₂ to determine possible cross interferences. See Figure 4.

7.0 Emission Test Procedure.

7.1 Selection of Sampling Site and Sampling Points. Select a measurement site and sampling points using the same criteria that are applicable to Method 1.

7.2 Sample Collection. Position the sampling probe at the measurement point and begin sampling at the same rate as used in Section 5.1.6. The sampling time per run shall be at least three times the system's NO_x response time. Do not extrapolate the instrument's calibrations beyond 125 percent of the high-range calibration gas values.

7.2.1 Temperature Considerations. In order to assure reproducible performance during each testing procedure, ensure that filter and sensor electrodes do not exceed 30 degrees centigrade, or change by more than 5 degrees centigrade.

7.3 Zero and Calibration Drift Tests. Immediately preceding and following each series of runs (up to three consecutive runs), repeat the sampling system bias check procedure described in Section 6.5. (Make no adjustments to the measurement system until after the drift tests are completed). After waiting each time for a period equal to two NO_x response times, record the analyzer's responses on a form similar to Figure 3.

7.3.1 Acceptable Performance. If either the zero or high range calibration value exceeds the sampling system bias specification, then the run is considered invalid. Repeat both the analyzer calibration error check procedure and the sampling system bias check procedure before repeating the run.

7.3.2 Adjustments. If both the zero and high range calibration

values are within the sampling system bias specification, then use the average of the initial and final bias check values to calculate the gas concentration for the run.

7.4 Interference Test. Perform the interference test as described in Section 6.4.

8.0 Emissions Calculations.

The tester may choose to correct the emissions data for a test run using a correction factor determined from the initial and final calibration error checks. The average emissions concentration may be computed by averaging all measurements recorded at equal time intervals during the entire duration of a run. For sampling run durations of less than 1 hour, perform measurements at 1 minute intervals, or a minimum of 20 measurements, whichever is less restrictive, For sampling run durations greater than 1 hour, perform measurements at 2 minute intervals, or a minimum of 96 measurements, whichever is less restrictive.

Figure 1

Analyzer Linearity Data

Date: _____ Tester: _____

Source Identification: _____

Analyzer Model # _____

Analyzer Serial # _____ Sampling System # _____

Sensitivity Range: NO Sensor: _____ (ppm); NO₂ Sensor: _____ (ppm)

High-range Calibration Gases: NO: _____ (ppm); NO₂: _____ (ppm)
NO Sensor # _____ NO₂ Sensor # _____

NO Filter Module # _____

NO Linearity

NO Calibration Gas	Gas Conc.	Anal. Response	Percent High-Range Gas
Zero/low-range:			
Mid-range:			
High-range:			

NO₂ Linearity

NO ₂ Calibration Gas	Gas Conc.	Anal. Response	Percent High-Range Gas
Zero/low-range:			
Mid-range:			
High-range:			

Figure 2

Interference Response Data

Date: _____ Tester: _____
Analyzer Model # _____
Analyzer Serial # _____ Sampling System # _____
Sensitivity Range: NO Sensor: _____ (ppm); NO₂ Sensor: _____ (ppm)
High-range Calibration Gases: NO: _____ (ppm); NO₂: _____ (ppm)
NO Sensor # _____ NO₂ Sensor # _____
NO Filter Module # _____

NO Interference Test

Test Gas	Gas Conc.	Anal. Response	Percent High-Range Gas
CO	ppm		
NO ₂	ppm		
SO ₂	ppm		
CO ₂	percent		

NO₂ Interference Test

Test Gas	Gas Conc.	Anal. Response	Percent High-range Gas
CO	ppm		
NO	ppm		
SO ₂	ppm		
CO ₂	percent		

Figure 3

Calibration Error Data

Date: _____ Tester: _____

Source Type: _____ Source ID: _____

Analyzer Model # _____

Analyzer Serial # _____ Sampling System # _____

Sensitivity Range: NO Sensor: _____ (ppm); NO₂ Sensor: _____ (ppm)

High-range Calibration Gases: NO: _____ (ppm); NO₂: _____ (ppm)
 NO Sensor # _____ NO₂ Sensor # _____

NO Filter Module # _____ System Response Time: _____ min.

Test #: _____ Start Time: _____ Stop Time: _____

Pretest Calibration Check:

Analyzer Channel	Zero Gas Conc.	Zero Response	Zero Error: Percent High-Range Gas	Span Gas Conc.	Span Response	Span Error: Percent High-Range Gas
NO						
NO ₂						

Post-Test Calibration Check:

Analyzer Channel	Zero Gas Conc.	Zero Response	Zero Error: Percent High-Range Gas	Span Gas Conc.	Span Response	Span Error: Percent High-Range Gas
NO						

NO ₂						
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Figure 4

Calibration Certification Protocol

time: xx:xx:xx

date: xx/xx/xx

NO₂ Span Gas: xxx ppm *

[sensor performance message]

[optional second sensor performance message]

[interference filter performance message]

[optional second interference filter message]

* Note: Repeat for NO.