State of California Air Resources Board

Method 20

Determination of Nitrogen Oxides, Sulfur Dioxide and Diluent Emissions from Stationary Gas Turbines

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Method 20 - Determination of Nitrogen Oxides, Sulfur Dioxide, and Diluent Emissions from Stationary Gas Turbines

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability. This method is applicable for the determination of nitrogen oxides (NO_x), sulfur dioxide (SO₂), and a diluent gas, either oxygen (O₂) or carbon dioxide (CO₂), emissions from stationary gas turbines. For the NO_x and diluent determinations, this method includes: (1) measurement system design criteria, (2) analyzer performance specifications and performance test procedures; and (3) procedures for emission testing.

1.2 Principle. A gas sample in continuously extracted from the exhaust stream of a stationary gas turbine; a portion of the sample stream is conveyed to instrumental analyzers for determination of NO_x and diluent content. During each NO_x and diluent determination, a separate measurement of SO_2 emissions is made, using Method 6, or its equivalent. The diluent determination is used to adjust the NO_x and SO_2 concentrations to a reference condition.

Any modification of this method beyond those expressly permitted shall be considered a major modification subject to the approval of the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board (ARB), or his or her authorized representative.

2. DEFINITIONS

2.1 Measurement System. The total equipment required for the determination of a gas concentration or a gas emission rate. The system consists of the following major subsystems:

2.1.1 Sample Interface. That portion of a system that is used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzers from the effects of the stack effluent.

2.1.2 NO_x Analyzer. That portion of the system that senses NO_x and generates an output proportional to the gas concentration.

2.1.3 O_2 Analyzer. That portion of the system that senses O_2 and generates an output proportional to the gas concentration.

2.1.4 CO₂ Analyzer. That portion of the system that senses CO_2 and generates an output proportional to the gas concentration.

2.1.5 Data Recorder. That portion of the measurement system that provides

a permanent record of the analyzer(s) output. The data recorder may include automatic data reduction capabilities.

2.2 Span Value. The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations.

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

2.4 Calibration Error. The difference between the gas concentration indicated by the measurement system and the known concentration of the calibration gas.

2.5 Zero Drift. The difference in the measurement system output readings from zero after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place and the input concentration at the time of the measurements was zero.

2.6 Calibration Drift. The difference in the measurement system output readings from the known concentration of the calibration gas after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place and the input at the time of the measurements was a high-level value.

2.7 Response Time. The amount of time required for the continuous monitoring system to display on the data output 95 percent of a step change in pollutant concentration.

2.8 Interference Response. The output response of the measurement system to a component in the sample gas other than the gas component being measured.

3. MEASUREMENT SYSTEM PERFORMANCE SPECIFICATIONS

3.1 NO₂ to NO Converter. Greater than 90 percent conversion efficiency of NO₂ to NO.

3.2 Interference Response. Less than ±2 percent of span value.

3.3 Response Time. No greater than 30 seconds.

3.4 Zero Drift. Less than ± 2 percent of span value over the period of each test run.

3.5 Calibration Drift. Less than ± 2 percent of span value over the period of each test run.

4. APPARATUS AND REAGENTS

4.1 Measurement System. Use any measurement system for NO_x and diluent that is expected to meet the specifications in this method. A schematic of an acceptable measurement system is shown in Figure 20-1. The essential components of the measurement system are described below:

4.1.1 Sample Probe. Heated stainless steel, or equivalent, open-ended, straight tube of sufficient length to traverse the sample points.

4.1.2 Sample Line. Heated (>95°C) stainless steel or Teflon tubing to transport the sample gas to the sample conditioners and analyzers.

4.1.3 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the sample conditioners and to the analyzers. The calibration valve assembly shall be capable of blocking the sample gas flow and of introducing calibration gases to the measurement system when in the calibration mode.

4.1.4 NO₂ to NO Converter. That portion of the system that converts NO₂ in the sample gas to NO. Some analyzers are designed to measure NO_x as NO₂ on a wet basis and can be used without an NO₂ to NO converter or a moisture removal trap provided the sample line to the analyzer is heated (>95°C) to the inlet of the analyzer. In addition, an NO₂ to NO converter is not necessary if the NO₂ portion of the exhaust gas is less than 5 percent of the total NO_x concentration. As a guideline, an NO₂ to NO converter is not necessary if the gas turbine is operated at 90 percent or more of peak load capacity. A converter is necessary under lower load conditions.

4.1.5 Moisture Removal Trap. A refrigerator-type condenser or other type device designed to remove continuously condensate from the sample gas while maintaining minimal contact between any condensate and the sample gas. The moisture removal trap is not necessary for analyzers that can measure NO_x concentrations on a wet basis; for these analyzers, (a) heat the sample line up to the inlet of the analyzers, (b) determine the moisture content using methods subject to the approval of the Executive Officer, and (c) correct the NO_x and diluent concentration to a dry basis.

4.1.6 Particulate Filter. An in-stack or an out-of-stack glass fiber filter, of the type specified in Method 5; however, an out-of-stack filter is recommended when the stack gas temperature exceeds 250 to 300°C.

4.1.7 Sample Pump. A nonreactive leak-free sample pump to pull the sample gas through the system at a flow rate sufficient to minimize transport delay. The pump shall be made from stainless steel or coated with Teflon, or equivalent.

4.1.8 Sample Gas Manifold. A sample gas manifold to divert portions of the sample gas stream to the analyzers. The manifold may be constructed of glass, Teflon, stainless steel, or equivalent.

4.1.9 Diluent Gas Analyzer. An analyzer to determine the percent O_2 or CO_2 concentration of the sample gas stream.

4.1.10 Nitrogen Oxides Analyzer. An analyzer to determine the ppm NO_x concentration in the sample gas stream.

4.1.11 Data Output. A strip-chart recorder, analog computer, or digital recorder for recording measurement data.

4.2 SO₂ Analysis. Method 6 apparatus and reagents.

4.3 NO_x Calibration Gases. The calibration gases for the NO_x analyzer shall be NO in N_2 . Use four calibration gas mixtures as specified below:

4.3.1 High-level Gas. A gas concentration that is equivalent to 80 to 90 percent of the span value.

4.3.2 Mid-level Gas. A gas concentration that is equivalent to 45 to 55 percent of the span value.

4.3.3 Low-level Gas. A gas concentration that is equivalent to 20 to 30 percent of the span value.

4.3.4 Zero Gas. A gas concentration of less than 0.25 percent of the span value. Ambient air may be used for the NO_x zero gas.

4.4 Diluent Calibration Gases.

4.4.1 For O_2 calibration gases, use purified air at 20.9 percent O_2 as the highlevel O_2 gas. Use a gas concentration between 11 and 15 percent O_2 in N_2 for the mid-level gas. Use purified N_2 for the zero gas.

4.4.2 For CO_2 calibraton gases, use a gas concentration between 8 and 12 percent CO_2 in air for the high-level CO_2 gas. Use a gas concentration between 2 and 5 percent CO_2 in air for the mid-level gas, and use purified air (<100 ppm CO_2) as the zero level calibration gas.

5. MEASUREMENT SYSTEM PERFORMANCE TEST PROCEDURES

Perform the following procedures before measurement of emissions (Section 6) and only once for each test program, i.e., the series of all test runs for a given gas turbine

engine.

5.1 Calibration Gas Checks. There are two alternatives for checking gases.

(a) The first is to use calibration gases that are documented traceable to National Bureau of Standards Reference Materials. Use "Traceability Protocol for Establishing True Concentrations of Gases Used for Calibrations and Audits of Continuous Source Emission Monitors" (Protocol Number 1) that is available from the Environmental Monitoring Support Laboratory, Quality Assurance Branch, Mail Drop 77, Environmental Protection Agency, Research Triangle Park, NC 27711. Obtain a certification from the gas manufacturer that the protocol was followed. These calibration gases are not to be analyzed with the Reference Methods.

(b) The second alternative is to use calibration gases not prepared according to the protocol. If this alternative is chosen, within 1 month prior to the emission test, analyze each of the calibration gas mixtures in triplicate using Method 7 or an alternative procedure approved by the United States Environmental Protection Agency for NO_x and use Method 3 for O_2 or CO_2 . Record the results on a data sheet (example is shown in Figure 20-2). For the low-level, mid-level, or high-level gas mixtures, each of the individual NO_x analytical results must be within 10 percent (or 10 ppm, whichever is greater) of the triplicate set average (O_2 or CO_2) test results must be within 0.5 percent O_2 or CO_2); otherwise, discard the entire set and repeat the triplicate analyses. If the average of the triplicate reference method test results is within 5 percent for NO_x gas or 0.5 percent O₂ or CO₂ for the O_2 or CO_2 gas of the calibration gas manufacturer's tag value, use the tag value; otherwise, conduct at least three additional reference method test analyses until the results of six individual NO_x runs (the three original plus three additional) agree within 10 percent (or 10 ppm, whichever is greater) of the average (O₂ or CO₂ test results must be within 0.5 percent O_2 or CO_2). Then use this average for the cylinder value.

5.2 Measurement System Preparation. Before the emission test, assemble the measurement system following the manufacturer's written instructions in preparing and operating the NO_2 to NO converter, the NO_x analyzer, the diluent analyzer, and other components.

5.3 Calibration Check. Conduct the calibration checks for both the NO_x and the diluent analyzers as follows:

5.3.1 After the measurement system has been prepared for use (Section 5.2), introduce zero gases and the mid-level calibration gases; set the analyzer output responses to the appropriate levels. Then introduce each of the remainder of the calibration gases described in Section 4.3 or 4.4, one at a time, to the measurement system. Record the responses on a form similar to Figure 20-3.

5.3.2 If the linear curve determined from the zero and mid-level calibration gas responses does not predict the actual response of the low-level (not applicable for the diluent analyzer) and high-level gases within ± 2 percent of the span value, the calibration shall be considered invalid. Take corrective measures on the measurement system before proceeding with the test.

5.4 Interference Response.

Introduce the gaseous components listed in Table 20-1 into the measurement system separately, or as gas mixtures. Determine the total interference output response of the system to these components in concentration units; record the values on a form similar to Figure 20-4. If the sum of the interference responses of the test gases for either the NO_x or diluent analyzer is greater than 2 percent of the applicable span value, take corrective measures on the measurement system.

Conduct an interference response test of each analyzer before its initial use in the field. Thereafter, recheck the measurement system if changes are made in the instrumentation that could alter the interference response, e.g., changes in the type of gas detector.

In lieu of conducting the interference response test, instrument vendor data, which demonstrate that for the test gases of Table 20-1 the interference performance specification is not exceeded, are acceptable.

5.5 Response Time. To determine response time, first introduce zero gas into the system at the calibration valve until all readings are stable; then, switch to monitor the stack effluent until a stable reading can be obtained. Record the upscale response time. Next, introduce high-level calibration gas into the system. Once the system has stabilized at the high-level calibration concentration, switch to monitor the stack effluent and wait until a stable value is reached. Record the downscale response time. Repeat the procedure three times. A stable value is equivalent to a change of less than 1 percent of span value for 30 seconds or less than 5 percent of the measured average concentration for 2 minutes. Record the response time data on a form similar to Figure 20-5, the readings of the upscale or downscale response time, and report the greater time as the "response time" for the analyzer. Conduct a response time test before the initial field use of the measurement system.

5.6 NO₂ to NO Conversion Efficiency.

5.6.1 Add gas from the mid-level NO in N₂ calibration gas cylinder to a clean, evacuated, leak-tight Tedlar bag. Dilute this gas approximately 1:1 with 20.9 percent O₂, purified air. Immediately attach the bag outlet to the calibration valve assembly and begin operation of the sampling system. Operate the sampling system, recording the NO_x response, for at least 30

minutes. If the NO_2 to NO conversion is 100 percent, the instrument response will be stable at the highest peak value observed. If the response at the end of 30 minutes decreases more than 2.0 percent of the highest peak value, the system is not acceptable and corrections must be made before repeating the check.

5.6.2 Alternatively, the NO₂ to NO converter check described in CFR Title 40, Part 86 Section 86.332-79, "Oxides of Nitrogen Analyzer Calibration", may be used. Other alternative procedures may be used with approval of the Executive Officer.

6. EMISSION MEASUREMENT TEST PROCEDURE

6.1 Preliminaries.

6.1.1 Selection of a Sampling Site. Select a sampling site as close as practical to the exhaust of the turbine. Turbine geometry, stack configuration, internal baffling, and point of introduction of dilution air will vary for different turbine designs. Thus, each of these factors must be given special consideration in order to obtain a representative sample. Whenever possible, the sampling site shall be located upstream of the point of introduction of dilution air into the duct. Sample ports may be located before or after the upturn elbow, in order to accommodate the configuration of the turning vanes and baffles and to permit a complete, unobstructed traverse of the stack. The sample ports shall not be located within 5 feet or 2 diameters (whichever is less) of the gas discharge to atmosphere. For supplementary-fired, combined-cycle plants, the sampling site shall be located between the gas turbine and the boiler. The diameter of the sample ports shall be sufficient to allow entry of the sample probe.

6.1.2 A preliminary O_2 or CO_2 traverse is made for the purpose of selecting sampling points of low O_2 values or high CO_2 concentrations as appropriate for the measurement system. Conduct this test at the turbine operating condition that is the lowest percentage of peak load operation included in the program. Follow the procedure below or alternative procedures subject to the approval of the Executive Officer.

6.1.2.1 Minimum Number of Points. Select a minimum number of points as follows: (1) Eight, for stacks having cross-sectional areas less than 1.5 m^2 (16.1 ft²); (2) eight plus one additional sample point for each 0.2 m² (2.2 ft²) of area, for stacks of 1.5 m^2 to 10.0 m^2 (16.1 to 107.6 ft^2) in crosssectional area; and (3) 49 sample points (48 for circular stacks) for stacks greater than 10.0 m^2 (107.6 ft²) in cross-sectional area. Note that for circular ducts, the number of sample points must be a multiple of 4, and for rectangular ducts, the number of points must be one of those listed in Table 20-2; therefore, round off the number of points (upward),

when appropriate.

6.1.2.2 Cross-sectional Layout and Location of Traverse Points. After the number of traverse points for the preliminary diluent sampling has been determined, use Method 1 to locate the traverse points.

6.1.2.3 Preliminary Diluent Measurement. While the gas turbine is operating at the lowest percent of peak load, conduct a preliminary diluent measurement as follows: Position the probe at the first traverse point and begin sampling. The minimum sampling time at each point shall be 1 minute plus the average system response time. Determine the average steady-state concentration of O_2 or CO_2 at each point and record the data on Figure 20-6.

6.1.2.4 Selection of Emission Test Sampling Points. Select the eight sampling points at which the lowest O_2 concentrations or highest CO_2 concentrations were obtained. Sample at each of these selected points during each run at the different load conditions. More than eight points may be used, if desired, providing that the points selected as described above are included.

6.2 NO_x and Diluent Measurement. This test is to be conducted at each of the specified load conditions. Three test runs at each load condition constitute a complete test.

6.2.1 At the beginning of each NO_x test run and, as applicable, during the run, record turbine data as indicated in Figure 20-7. Also, record the location and number of the traverse points on a diagram.

6.2.2 Position the probe at the first point determined in the preceding section and begin sampling. The minimum sampling time at each point shall be at least 1 minute plus the average system response time. Determine the average steady-state concentration of diluent and NO_x at each point and record the data on Figure 20-8.

6.2.3 After sampling the last point, conclude the test run by recording the final turbine operating parameters and by determining the zero and calibration drift, as follows: Immediately following the test run at each load condition, or if adjustments are necessary for the measurement system during the tests, reintroduce the zero and mid-level calibration gases as described in Sections 4.3 and 4.4, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after the drift checks are made). Record the analyzers' responses on a form similar to Figure 20-3. If the drift values exceed the specified limits, the test run preceding the check is considered invalid and will be repeated following corrections to the measurement system. Alternatively, recalibrate the

measurement system and recalculate the measurement data. Report the test results based on both the initial calibration and the recalibration data.

6.3 SO₂ Measurement.

This test is conducted only at the 100 percent peak load condition. Determine SO_2 using Method 6, or equivalent, during the test. Select a minimum of six total points from those required for the NO_x measurements; use two points for each sample run. The sample time at each point shall be at least 10 minutes. Average the diluent readings taken during the NO_x test runs at sample points corresponding to the SO₂ traverse points (see Section 6.2.2) and use this average diluent concentration to correct the integrated SO₂ concentration obtained by Method 6 to 15 percent O₂ (see equations in Section 7.3).

If the applicable regulation allows fuel sampling and analysis for fuel sulfur content to demonstrate compliance with regulatory requirements, emission sampling with Method 6 is not required, provided the fuel sulfur content meets the limits of the regulation.

7. EMISSION CALCULATIONS

7.1 Moisture Correction. Measurement data used in most of these calculations must be on a dry basis. If measurements must be corrected to dry conditions, use the following equation:

where:

Cd	=	Pollutant or diluent concentration adjusted to dry conditions, ppm or
		percent

C_w = Pollutant or diluent concentration measured under moist sample conditions, ppm or percent.

B_{ws} = Moisture content of sample gas as measured with Method 4 or another method approved by the Executive Officer, percent/100.

7.2 CO₂ Correction Factor. If pollutant concentrations are to be corrected to 15 percent O_2 and CO_2 concentration is measured in lieu of O_2 concentration measurement, a CO_2 correction factor is needed. Calculate the CO_2 correction factor as follows:

7.2.1 Calculate the fuel-specific F_0 value for the fuel burned during the test using values obtained from EPA Method 19, Section 3, and the following equation.

$$F_{\circ} = \frac{0.209 F_{d}}{F_{\circ}}$$
 Eq. 20-2

where:		
Fo	=	Fuel factor based on the ratio of oxygen volume to the
		ultimate CO ₂ volume produced by the fuel at zero percent
		excess air, dimensionless.
0.209	=	Fraction of air that is oxygen, percent/100.
F _d	=	Ratio of the volume of dry effluent gas to the gross calorific
		value of the fuel from EPA Method 19, dsm ³ /J (dscf/10 ⁶ Btu).
Fc	=	Ratio of the volume or carbon dioxide produced to the gross
		calorific value of the fuel from EPA Method 19, dsm ³ /J
		(dscf/10 ⁶ Btu).

7.2.2 Calculate the CO_2 correction factor for correcting measurement data to 15 percent oxygen, as follows:

$$X_{CO_2} = \frac{5.9}{F_0}$$
 Eq. 20-3

where:

 $X_{CO2} = CO_2$ Correction factor, percent.

 $5.9 = 20.9 \text{ percent } O_2 - 15 \text{ percent } O_2$, the defined O_2 correction value, percent.

7.3 Correction of Pollutant Concentrations to 15 percent O₂. Calculate the NO_x and SO₂ gas concentrations adjusted to 15 percent O₂ using Equation 20-4 or 20-5, as appropriate. The correction to 15 percent O₂ is very sensitive to the accuracy of the O₂ or CO₂ concentration measurement. At the level of the analyzer drift specified in Section 3, the O₂ or CO₂ correction can exceed 5 percent at the concentration levels expected in gas turbine exhaust gases. Therefore, O₂ or CO₂ analyzer stability and careful calibration are necessary.

7.3.1 Correction of Pollutant Concentration Using O₂ Concentration.

Calculate the O₂ corrected pollutant concentration, as follows:

$$C_{adj} = C_d \frac{5.9}{20.9 - \% O_2}$$
 Eq. 20-4

where:

 C_{adj} = Pollutant concentration corrected to 15 percent O₂, ppm.

 C_d = Pollutant concentration measured, dry basis, ppm.

 $O_2 =$ Measured O_2 concentration dry basis, percent.

7.3.2 Correction of Pollutant Concentration Using CO₂ Concentration. Calculate the CO₂ corrected pollutant concentration, as follows:

$$C_{adj} = C_d \frac{X_{CO_2}}{\% CO_2}$$
 Eq. 20-5

CARB Method 20 Page 10

where: $%CO_2 = Measured CO_2$ concentration, dry basis, percent.

7.4 Average Adjusted NO_x Concentration. Calculate the average adjusted NO_x concentration by summing the point values and dividing by the number of points.

7.5 NO_x and SO₂ Emission Rate Calculations. The emission rates for NO_x and SO₂ in units of pollutant mass per quantity of heat input can be calculated using the pollutant and diluent concentrations and fuel-specific F-factors based on the fuel combustion characteristics. The measured concentrations of pollutant in units of parts per million by volume (ppm) must be converted to mass per unit volume concentration units for these calculations. Use the following table for such conversions:

CONVERSION FACTORS FOR CONCENTRATION

To convert		
From	То	Multiply by
g/sm ³	ng/sm ³	10 ⁹
mg/sm ³	ng/sm³	10 ⁶
lb/scf	ng/sm ³	1.602 x 10 ¹³
ppm (SO ₂)	ng/sm ³	2.660 x 10 ⁶
ppm (NO _x)	ng/sm ³	1.912 x 10 ⁶ _
ppm (SO ₂)	lb/scf	1.660 x 10 ⁻⁷
ppm (NO _x)	lb/scf	1.194 x 10 ⁻⁷

7.5.1 Calculation of Emission Rate Using Oxygen Correction. Both the O_2 concentration and the pollutant concentration must be on a dry basis. Calculate the pollutant emission rate, as follows:

$$E = C_{d}F_{d} \frac{20.9}{20.9 - \%O_{2}} \qquad Eq. \ 20 - 6$$

where:

E = Mass emission rate of pollutant, ng/J (lb/10⁶ Btu).

7.5.2 Calculation of Emission Rate Using Carbon Dioxide Correction.

The CO_2 concentration and the pollutant concentration may be on either a dry basis or a wet basis, but both concentrations must be on the same basis for the calculations. Calculate the pollutant emission rate using Equation 20-7 or 20-8:

$$E = C_{d}F_{c} \frac{100}{\%CO_{2}}$$
 Eq. 20-7

. . .

$$E = C_w F_c \frac{100}{\% CO_{2w}}$$
 Eq. 20-8

where:

C_w = Pollutant concentration measured on a moist sample basis, ng/sm³ (lb/scf).

 $%CO_{2W} = CO_2$ concentration measured on a moist sample basis, percent.

8. **BIBLIOGRAPHY**

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- 2. EPA Method 19, Determination of Surfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxides Emission Rates, CFR40, Part 60, Appendix A
- 3. ARB Method 1, Sample and Velocity Traverses for Stationary Sources
- 4 ARB Method 3, Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight
- 5 ARB Method 4, Determination of Moisture Content in Stack Gases
- 6 ARB Method 5, Determination of Particulate Matter Emissions from Stationary Sources
- 7 ARB Method 6, Determination of Sulfur Dioxide Emissions from Stationary Sources
- 8 ARB Method 7, Determination of Nitrogen Oxide Emissions from Stationary Sources



