



Designation: D6522 – 00 (Reapproved 2005)

Standard Test Method for Determination of Nitrogen Oxides, Carbon Monoxide, and Oxygen Concentrations in Emissions from Natural Gas- Fired Reciprocating Engines, Combustion Turbines, Boilers, and Process Heaters Using Portable Analyzers¹

This standard is issued under the fixed designation D6522; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of nitrogen oxides (NO and NO₂), carbon monoxide (CO), and oxygen (O₂) concentrations in controlled and uncontrolled emissions from natural gas-fired reciprocating engines, combustion turbines, boilers, and process heaters. Due to the inherent cross sensitivities of the electrochemical cells, this test method should not be applied to other pollutants or emission sources without a complete investigation of possible analytical interferences and a comparative evaluation with EPA test methods.

1.1.1 The procedures and specifications of this method were developed during laboratory and field tests funded by the Gas Research Institute (GRI).² Comparative emission tests were conducted only on natural gas-fired combustion sources.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*³

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

2.2 *EPA Methods from 40 CFR Part 60, Appendix A*⁴

¹ This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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² Gas Research Institute Topical Report, "Development of an Electrochemical Cell Emission Analyzer Test Method," GRI-96/0008, July 1997.

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

⁴ Available from Superintendent of Documents, U. S. Government Printing Office, Washington, DC 20402.

Method 3A - Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)

Method 7E - Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)

Method 10 - Determination of Carbon Monoxide Emissions from Stationary Source

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

2.3 *EPA Methods from 40 CFR Part 63, Appendix A*⁴

Method 301 - Field Validation of Pollutant Measurement Methods from Various Waste Media

2.4 *EPA Methods from 40 CFR Part 75, Appendix H*⁴
Revised Traceability Protocol No. 1: Protocol G1 and G2 Procedures

3. Terminology

3.1 For terminology relevant to this test method, see Terminology **D1356**.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *measurement system, n*—total equipment required for the determination of gas concentration. The measurement system consists of the following major subsystems:

3.2.1.1 *data recorder, n*—a strip chart recorder, computer, or digital recorder for recording measurement data.

3.2.1.2 *electrochemical cell, n*—that portion of the system that senses the gas to be measured and generates an output proportional to its concentration, or any cell that uses diffusion-limited oxidation and reduction reactions to produce an electrical potential between a sensing electrode and a counter electrode.

3.2.1.3 *external interference gas scrubber, n*—tube filled with scrubbing agent used to remove interfering compounds upstream of some electrochemical cells.

3.2.1.4 *sample interface, n*—that portion of a system used for one or more of the following: sample acquisition, sample transport, sample conditioning, or protection of the electrochemical cells from particulate matter and condensed moisture.

3.2.2 *interference check, n*—method of quantifying analytical interferences from components in the stack gas other than the analyte.

3.2.3 *initial NO cell temperature, n*—temperature of the NO cell that is recorded during the most recent pretest calibration error check.

3.2.3.1 *Discussion*—Since the NO cell can experience significant zero drift with temperature changes in some situations, the temperature must be monitored if the analyzer does not display negative concentration results.

3.2.4 *linearity check, n*—method of demonstrating the ability of a gas analyzer to respond consistently over a range of gas concentrations.

3.2.5 *nominal range, n*—range of concentrations over which each cell is operated (25 % to 125 % of span gas value).

3.2.5.1 *Discussion*—Several nominal ranges may be used for any given cell as long as the linearity and stability check results remain within specification.

3.2.6 *response time, n*—amount of time required for the measurement system to display 95 % of a step change in gas concentration on the data recorder.

3.2.7 *span gas, n*—known concentration of a gas in an appropriate diluent gas.

3.2.8 *span calibration error, n*—difference between the gas concentration exhibited by the gas analyzer and the known concentration of the span gas.

3.2.9 *stability check, n*—method of demonstrating that an electrochemical cell operated over a given nominal range provides a stable response and is not significantly affected by prolonged exposure to the analyte.

3.2.10 *stability time, n*—elapsed time from the start of the gas injection to the start of the 30-min stability check period, as determined during the stability check.

3.2.11 *zero calibration error, n*—gas concentration exhibited by the gas analyzer in response to zero-level calibration gas.

4. Summary of Test Method

4.1 A gas sample is continuously extracted from a stack and conveyed to a portable analyzer for determination of NO, NO₂, CO, and O₂ gas concentrations using electrochemical cells. Analyzer design specifications, performance specifications, and test procedures are provided to ensure reliable data. Additions to or modifications of vendor-supplied analyzers (for example, heated sample line, flow meters, and so forth) may be required to meet the design specifications of this test method.

5. Significance and Use

5.1 The results of this test method may be used to determine nitrogen oxides and carbon monoxide emissions from natural gas combustion.

5.2 This test method may also be used to monitor emissions to optimize process operation for nitrogen oxides and carbon monoxide control.

6. Interferences

6.1 NO and NO₂ can interfere with CO concentration measurements, and NO₂ can interfere with NO concentration measurements. The interference effects for the CO and NO emission measurements are quantified in 9.2 and shall not exceed 5 % of the measurement.

7. Apparatus

7.1 The minimum detectable limit depends on the nominal range of the electrochemical cell, calibration drift, and signal-to-noise ratio of the measurement system. For a well designed system, the minimum detectable limit should be less than 2 % of the nominal range.

7.2 Any measurement system that meets the performance and design specifications in Sections 9 and 10.4.11 of this test method may be used. The sampling system shall maintain the gas sample at a temperature above the dew point up to the moisture removal system. The sample conditioning system shall be designed so that there are no entrained water droplets in the gas sample when it contacts the electrochemical cells. A schematic of an acceptable measurement system is shown in Fig. 1. The essential components of the measurement system are described below:

7.3 *Sample Probe*, glass, stainless steel, or other nonreactive material, of sufficient length to traverse the sample points, and, if necessary, heated to prevent condensation.

7.4 *Heated Sample Line*, heated (sufficient to prevent condensation), nonreactive tubing, to transport the sample gas to the moisture removal system.

7.5 *Sample Transport Lines*, nonreactive tubing to transport the sample from the moisture removal system to the sample pump, sample flow rate control, and electrochemical cells.

7.6 *Calibration Assembly*, a tee-fitting to attach to the probe tip for introducing calibration gases at ambient pressure during the calibration error checks. The vented end of the tee should have a flow indicator to ensure sufficient calibration gas flow.

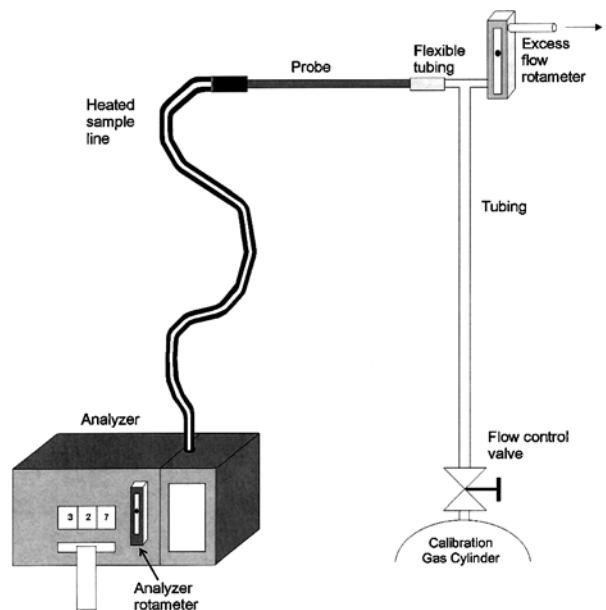


FIG. 1 Calibration System Schematic

Any other method that introduces calibration gases at the probe at atmospheric pressure may be used.

7.7 *Moisture Removal System*, a chilled condenser or similar device (for example, permeation dryer), to remove condensate continuously from the sample gas while maintaining minimal contact between the condensate and the sample gas.

7.8 *Particulate Filters*—Filters at the probe or the inlet or outlet of the moisture removal system and inlet of the analyzer may be used to prevent accumulation of particulate material in the measurement system and extend the useful life of the components. All filters shall be fabricated of materials that are nonreactive to the gas being sampled.

7.9 *Sample Pump*, a leak-free pump, to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump must be constructed of any material that is nonreactive to the gas being sampled.

7.10 *Sample Flow Rate Control*, a sample flow rate control valve and rotameter, or equivalent, to maintain a constant sampling rate within 10 % during sampling and calibration error checks. The components shall be fabricated of materials that are nonreactive to the gas being sampled.

7.11 *Gas Analyzer*, a device containing electrochemical cells to determine the NO, NO₂, CO, and O₂ concentrations in the sample gas stream and, if necessary, to correct for interference effects. The analyzer shall meet the applicable performance specifications of Section 9. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (for example, precision rotameter, pressure gage downstream of all flow controls, and so forth) shall be provided at the analyzer.

NOTE 1—Housing the analyzer in a clean, thermally-stable, vibration-free environment will minimize drift in the analyzer calibration, but this is not a requirement of the test method.

7.12 *Data Recorder*, a strip chart recorder, computer, or digital recorder, for recording measurement data. The data recorder resolution (that is, readability) shall be at least 1 ppm for CO, NO, and NO₂; 0.1 % O₂ for O₂; and 1° (C or F) for temperature. 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.

7.13 *External Interference Gas Scrubber*, used by some analyzers to remove interfering compounds upstream of a CO electrochemical cell. The scrubbing agent should be visible and should have a means of determining when the agent is exhausted (that is, color indication).

7.14 *NO Cell Temperature Indicator*, a thermocouple, thermistor, or other device must be used to monitor the temperature of the NO electrochemical cell. The temperature may be monitored at the surface or within the cell.

8. Reagents and Materials

8.1 The analytical range for each gas component is determined by the electrochemical cell design. A portion of the analytical range is selected by choosing a span gas concentration near the flue gas concentrations.

8.2 *Calibration Gases*—The calibration gases for the gas analyzer shall be CO in nitrogen or CO in nitrogen and O₂, NO in nitrogen, NO₂ in air or nitrogen, and O₂ in nitrogen.

8.2.1 For the mid-level and span cylinder gases, use calibration gases certified according to EPA Protocol G1 or G2 procedures.

8.2.2 Alternative certification techniques may be used, if approved in writing by the applicable regulatory agency.

8.3 *Span Gases*—Use these gases for calibration error, linearity, and interference checks of each nominal range of each cell. Select concentrations as follows:

8.3.1 *CO and NO Span Gases*—Choose a span gas concentration such that the average stack gas reading for each test run is greater than 25 % of the span gas concentration. Alternatively, choose the span gas such that it is not greater than twice the concentration equivalent to the emission standard. If concentration results exceed 125 % of the span gas at any time during the sampling run, then the test run for that channel is invalid.

8.3.2 *NO₂ Span Gas*—Choose a span gas concentration such that the average stack gas reading for each test run is greater than 25 % of the span gas concentration. Alternatively, choose the span gas concentration such that it is not greater than the ppm concentration value of the NO span gas. The tester should be aware that NO₂ cells are generally designed to measure much lower concentrations than NO cells and the span gas should be chosen accordingly. If concentration results exceed 125 % of the span gas at any time during the sampling run then the test run for that channel is invalid.

8.3.3 *O₂ Span Gas*—Choose a span gas concentration such that the difference between the span gas concentration and the average stack gas reading for each run is less than 10 % O₂. Where the stack oxygen is high, dry ambient air (20.9 % O₂) may be used.

8.4 *Mid-Level Gases*—Select mid-level gas concentrations that are 40 to 60 % of the span gas concentrations.

8.5 *Zero Gas*—Zero gas must have concentrations of less than 0.25 % of the span gas for each component. Ambient air may be used in a well-ventilated area.

9. Preparation of Apparatus

9.1 *Linearity Check*:

9.1.1 Conduct the linearity check once for each nominal range that is to be used on each electrochemical cell (NO, NO₂, CO, and O₂) before each field test program.

9.1.1.1 Repeat the linearity check immediately after 5 days of analyzer operation, if a field test program lasts longer than 5 days.

9.1.1.2 Repeat the linearity check whenever a cell is replaced.

9.1.2 If the analyzer uses an external interference gas scrubber with a color indicator, verify that the scrubbing agent is not depleted, following the analyzer manufacturer's recommended procedure.

9.1.3 Calibrate the analyzer with zero and span gases.

9.1.4 Inject the zero, mid-level, and span gases that are appropriate for each nominal range to be used on each cell. Gases need not be injected through the entire sample handling system.

9.1.5 Purge the analyzer, briefly with ambient air between gas injections.

9.1.6 For each gas injection, verify that the flow rate is constant and that the analyzer responses have stabilized.

9.1.7 Record all of the responses (stabilized) on a form similar to Fig. 2.

9.1.8 For the zero, mid-level, and span gases, calculate the absolute value of the difference between the gas value and the analyzer response.

9.1.9 *Linearity Specifications:*

9.1.9.1 *NO, CO and O₂ Cells*— ≤ 2.5 % of the span gas concentration.

9.1.9.2 *NO₂ Cells*— ≤ 3.0 % of the span gas concentration.

9.2 *Interference Check:*

9.2.1 Following each linearity check, determine interference responses for the CO and NO cells, using the results from the span gas injections (see 11.2 and 11.3 for calculations).

Date _____ Analyst _____

Analyzer Manufacturer/Model No. _____

Analyzer Serial Number _____

Calibration Gas Conc.	ppm NO Response	ppm NO ₂ Response	ppm CO Response	% Oxygen Response

FIG. 2 Linearity Check Data Sheet