



Designation: ~~D6522-00 (Reapproved 2005)~~ Designation: **D6522 – 11**

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 using portable analyzers with electrochemical sensors. 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 originally 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 Comparative emission tests were conducted only on natural gas-fired combustion sources. Subsequently, the United States Environmental Protection Agency (EPA) sponsored Environmental Technology Verification (ETV) program conducted further evaluations of electrochemical cell analyzers, which included laboratory tests and field tests on natural gas and diesel-fueled generators. The EPA has reviewed the ETV test results, published additional information, and provided technical input that has been considered in the update of this method.³~~

1.2 This test method contains notes that are explanatory and are not part of the mandatory requirements of the standard.

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

1.4 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:⁴

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

2.2 EPA Methods from 40 CFR Part 60, Appendix A⁵

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-A}:

Method 301-Field—Field Validation of Pollutant Measurement Methods from Various Waste Media⁵

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.

Current edition approved Oct-Dec. 1, 2005-2011. Published January 2006-February 2012. Originally approved in 2000. Last previous edition approved in 2000/2005 as D6522 - 00(2005). DOI: 10.1520/D6522-00R05.10.1520/D6522-11.

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 "Evaluation of Portable Analyzers for Use in Quality Assuring Predictive Emission Monitoring Systems for NOx" EPA Contract No. 68-W-03-033, September 2004.

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

⁴ 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.

⁵ Available from Superintendent of Documents, U. G. Government Printing Office, Washington, DC 20402.

2.4 *EPA Methods from 40 CFR Part 75, Appendix H⁶H:*
Revised Traceability Protocol No. 1: Protocol G1 and G2 Procedures⁶

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~~ device 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.~~ 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. Nitric oxide cell temperature monitoring is not required if the analyzer can display negative concentrations. Drift due to temperature changes will be identified in the post calibration check for analyzers that show can display negative concentrations.

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

3.2.4.1 *Discussion*—Linearity checks are not required for analyzers where the electrochemical sensor manufacturer has published data demonstrating linearity through the sensor range.

3.2.5 *nominal range, n*—range of concentrations over which each cell is operated (25 % to 125 % of span upscale calibration 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* upscale calibration gas, n—known concentration of a gas in an appropriate diluent gas.

3.2.8 *span calibration error* upscale calibration error, n—difference between the gas concentration exhibited by the gas analyzer and the known concentration of the span upscale calibration 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 15-min or 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 duct 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.

4.2 Additions to or modifications of some vendor-supplied analyzers (for example, heated sample line, flow meters, and so forth) may be required necessary 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 emission concentrations from natural gas combustion at stationary sources.

⁶ EPA-600/R-97/121, EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999. Available from: <http://www.epa.gov/ttn/emc/news.html>.

5.2 This test method may also be used to monitor emissions during short-term emission tests or periodically in order 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. 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.

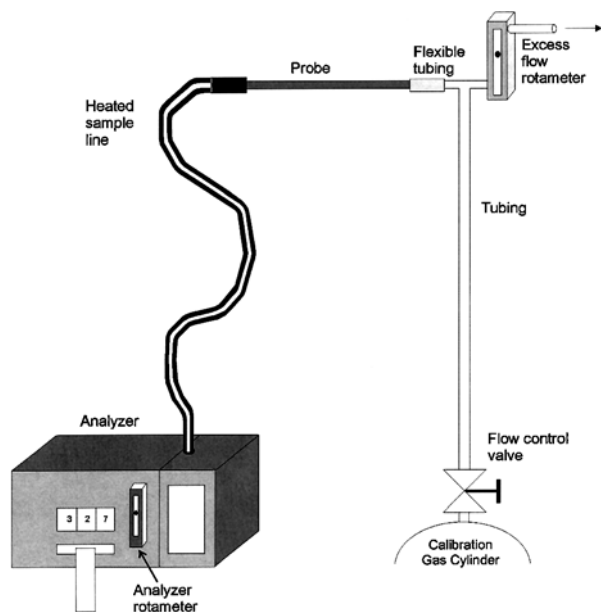


FIG. 1 Calibration System Schematic

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.~~

7.11.1 A means of controlling the analyzer flow rate and a device for determining proper sample flow rate shall be provided at the analyzer. For example, a needle valve and precision rotameter, or pressure gauge downstream of all flow controls, or equivalent can be used.

7.11.2 The electrochemical cell analyzer should have a minimum upscale calibration level appropriate to the stack gas concentration being measured. For example, if the stack gas NO_x concentration is less than 10 ppm, the analyzer should have the capability to analyze a 10-ppm (or less) upscale calibration gas for the NO and NO₂ cells.

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 1—Housing the analyzer in a clean, thermally-stable, vibration-free environment will minimize drift in the analyzer calibration.~~

NOTE 2—If the NO_x analyzer resolution is 0.1 ppm, it will be more likely to pass the performance specifications when testing at sources with low stack gas concentrations.

NOTE 3—It is recommended that analyzer manufacturer's maintenance procedures be followed.

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.

NOTE 4—Some analyzers incorporate a digital data logger. Such a recorder may be used provided it meets the resolution requirements of 7.12.

~~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), a device used by some analyzers to remove interfering compounds upstream of a CO electrochemical cell. The measurement system should provide the operator with a means of determining when the scrubbing agent is exhausted (that is, visible color change indication, or electronic ppm hour counter, or equivalent).~~

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. This is not required if the analyzer is capable of displaying negative concentrations.

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~~ an upscale calibration gas concentration near approximating 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 air~~, NO in nitrogen, NO₂ in nitrogen, NO_x in air, and O₂ in air or nitrogen, and O₂ in nitrogen.

8.2.1 For the mid-level and ~~span~~ cylinder upscale calibration 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~~ Upscale Calibration 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-Upscale Calibration Gases*—Choose a ~~span~~ an upscale calibration gas concentration such that the average stack gas reading for each test run is greater than 25 % of the ~~span~~ upscale calibration gas concentration. Alternatively, choose the ~~span~~ upscale calibration gas such that it is not greater than twice the concentration equivalent to the emission standard. If concentration results exceed 125 % of the ~~span~~ upscale calibration gas at any time during the sampling run, then the test run for that channel is ~~invalid~~ not valid.

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

8.3.3 *O₂ Span-Upscale Calibration Gas*—Choose a ~~span~~ an upscale calibration gas concentration such that the difference between the ~~span~~ upscale calibration 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.~~ Where the stack oxygen is high, dry ambient air having a dew point less than 20°C may be used and assumed to have a concentration of 20.9 % O₂.

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

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

9. Preparation of Apparatus

9.1 *Linearity Check*:—The procedures in this subsection are not required if the manufacturer of the sensors used in the particular analyzer has published information clearly demonstrating the linearity of the sensor throughout the sensor range, and explicitly states the minimum and maximum measurement ranges for which the sensor can be shown to exhibit a linear response meeting or exceeding the requirements of this method. It is the responsibility of the person performing this method to acquire such information from the sensor manufacturer or portable analyzer manufacturer and have this prior to performing the test. If this information is not available from the manufacturer at the time of the test, the following procedures in this section shall be conducted.

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 or other depletion 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-upscaled calibration gases.

9.1.4 Inject the zero, mid-level, and spanupscale calibration 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 spanupscale calibration 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. —≤2.5 % of the upscale calibration gas concentration, or <1 ppm difference from the upscale calibration gas concentration, whichever is less restrictive.

9.1.9.2 *NO₂ Cells*—≤3.0% of the span gas concentration. —≤3.0 % of the upscale calibration gas concentration or <1 ppm difference from the upscale calibration gas concentration, whichever is less restrictive.

9.2 *Interference Check*:

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

9.2.2 *Interference Specifications* —CO and NO interference responses—≤5% of the average stack concentration for each test run. —CO and NO interference responses—≤5 %.

9.3 *Stability Check*:

9.3.1 ~~Conduct the stability check once for each nominal range that is to be used on each pollutant electrochemical cell (NO, NO₂, and CO) before each field test program.~~ Conduct the stability check once for each nominal range that is to be used on each pollutant electrochemical cell (NO, NO₂, and CO) before each field test program. The analyzer should be purged with ambient air between gas injections. Otherwise, the cells will be exposed to high NO and NO₂ concentrations for an extended time which can cause a cell's performance to degrade (this is the so-called "O₂-starved exposure").

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

9.3.1.2 Repeat the stability check if a cell is replaced or if a cell is exposed to gas concentrations greater than 125 % of the highest spanupscale calibration gas concentration.

9.3.2 Inject the span-upscaled calibration gas into the analyzer and record the analyzer response at least once per minute until the conclusion of the test. One-minute average values may be used instead of instantaneous readings.

9.3.3 After the analyzer response has stabilized, continue to flow the span-upscaled calibration gas for at least 30 minutes.

9.3.3.1 ~~Alternatively, if the concentration reaches a peak maximum value within 5 minutes, the data may be recorded for at least 15 minutes (rather than 30 minutes) following the peak.~~

9.3.3.2 ~~If the 15-min test period is used, a initial maximum value.~~

9.3.3.2 The more stringent specification shall be met (see in 9.3.8)—shall apply when the 15-minute test period is used.

9.3.4 Make no adjustments to the analyzer during the test except to maintain constant flow.

9.3.5 Record the stabilitystabilization time as the number of minutes elapsed between the start of the gas injection and the start of the 30-min (or 15-min) stability check period.

9.3.6 Determine the highest and lowest concentrations recorded during the 30-min (or 15-min) period and record the results on a form similar to Fig. 3.

9.3.7 Calculate the absolute value of the difference between the maximum and minimum values recorded during the 30-min period (or the 15-min period) for the CO, NO, and NO₂ span-gases—upscale calibration gases.

9.3.8 *Stability Specifications*:

9.3.8.1 ~~Thirty-minute period—≤2.0% of the span gas concentration.~~

