

## **OTM-39 Method for Determination of Oxygen, Carbon Monoxide and Nitrogen Oxides from Stationary Sources using Portable Gas Analyzers Equipped with Electrochemical Sensors**

This method was submitted by Innovative Environmental Solutions, Inc. under contract to the Pipeline Research Council International (PRCI) on behalf of the PRCI member companies to EPA's Office of Air Quality, Planning and Standards, Air Quality Assessment Division, Measurement Technology Group (MTG) for (1) inclusion into the Other Test Method (OTM) category on EPA's Air Emission Measurement Center (EMC) website at: <https://www.epa.gov/emc/emc-other-test-methods> and (2) consideration as a broadly applicable alternative test method. OTM-39 has now been approved for use at (1) Industrial/Commercial/Institutional Steam Generating Units subject to 40 CFR Part 60, Subpart Db<sup>1</sup>, (2) stationary spark ignition internal combustion engines subject to 40 CFR Part 60, Subpart JJJJ<sup>2</sup>, and (3) Reciprocating Internal Combustion Engines subject to 40 CFR Part 63, Subpart ZZZZ<sup>3</sup>, see <https://www.epa.gov/sites/production/files/2018-05/documents/alt138.pdf>.

Supporting data for this OTM were provided by PRCI can be found at the links below:

- 1) Considerations for Developing a New Electrochemical Cell Portable Analyzer Test Method, Innovative Environmental Solutions, Inc., for the Pipeline Research Council International, Inc., Catalog PR-312-14206-R01, May 2015

<https://www.prci.org/Research/CompressorPumpStation/CPSProjects/CPS-11-6/3235/15171/15170.aspx>

- 2) Portable Analyzer Test Method Update for Common Analyzers Phase 2 Report, Innovative Environmental Solutions, Inc., for the Pipeline Research Council International, Inc., Catalog PR-312-17204-R01, August 2017

<https://www.prci.org/Research/CompressorPumpStation/CPSProjects/CPS-11-6A/3241/141821/125629.aspx>

- 3) Portable Analyzer Test Method Update for Common Analyzers Phase 3 Report, Innovative Environmental Solutions, Inc., for the Pipeline Research Council International, Inc., Catalog PR-312-17204-R01, October 2017

<https://www.prci.org/Research/CompressorPumpStation/CPSProjects/CPS-11-6A/3241/136252/125634.aspx>

**The posting of a test method on the OTM portion of the EMC website is neither an endorsement by EPA regarding the validity of the test method nor a regulatory approval of the test method.** The

purpose of the OTM portion of the EMC website is to promote discussion of developing emission measurement methodologies and to provide regulatory agencies, the regulated community, and the public at large with potentially helpful tools.

**Other Test Methods** are test methods which have not yet been subject to Federal rulemaking. Each of these methods, as well as the available technical documentation supporting them, have been reviewed by the EMC staff and have been found to be potentially useful to the emission measurement community. The types of technical information reviewed include field and laboratory validation studies; results of collaborative testing; articles from peer-reviewed journals; peer-review comments; and quality assurance (QA) and quality control (QC) procedures in the method itself. A table summarizing the

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<sup>1</sup>Oxygen Measurements

<sup>2</sup>Nitrogen Oxides, Carbon Monoxide, and Oxygen Measurements

<sup>3</sup>Carbon Monoxide, and Oxygen Measurements

available technical information for each method can be found at the link below. As noted above, the EPA strongly encourages the submission of additional supporting field and laboratory data as well as comments in regard to these methods. These methods may be considered for use in federally enforceable State and local programs (e.g., Title V permits, State Implementation Plans (SIP)) provided they are subject to an EPA Regional SIP approval process or permit veto opportunity and public notice with the opportunity for comment. The methods may also be considered to be candidates to be alternative methods to OTM-40 2 meet Federal requirements under 40 CFR Parts 60, 61, and 63; **however, they must be approved as alternatives through a separate action under §§60.8(b), 61.13(h), or 63.7(f) before a source may use them for this purpose.** Consideration of the applicability of an OTM for a particular purpose should be based on the stated applicability, the supporting technical information outlined in the table, or regulatory actions including approval as an alternative test method or inclusion in a SIP.

These methods are available for application without EPA oversight for other non-EPA program uses including state permitting programs and scientific and engineering applications. As many of these methods are submitted by parties outside the Agency, the EPA staff may not necessarily be the technical experts on these methods. Therefore, technical support from EPA for these methods is limited, but the table contains contact information for the developers so that you may contact them directly. Also, be aware that these methods are subject to change based on the review of additional validation studies or on public comment as a part of adoption as a Federal test method, the Title V permitting process, or inclusion in a SIP.

#### Method History

Initial Posting – 08/24/2020

EPA advises all potential users to review the method and all appendices carefully before application of this method.

## OTM-39 Method for Determination of Oxygen, Carbon Monoxide and Nitrogen Oxides from Stationary Sources using Portable Gas Analyzers Equipped with Electrochemical Sensors

### 1.0 *Scope and Application*

This test method is a procedure for measuring nitrogen oxides (NO and NO<sub>2</sub>), carbon monoxide (CO), and oxygen (O<sub>2</sub>) concentrations in controlled and uncontrolled emissions from reciprocating engines, combustion turbines, boilers, and process heaters firing natural gas using portable gas analyzers with electrochemical sensors. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known and acceptable quality for each testing program. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need, but instead refers to other test methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional methods which are found in 40 CFR Part 60, Appendices A-1 and A-3:

- (a) Method 1—Sample and Velocity Traverses for Stationary Sources.
- (b) Method 4—Determination of Moisture Content in Stack Gases.
- (c) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

### 1.1 *Analytes*

This method measures the concentrations of nitrogen oxides (NO and NO<sub>2</sub>), carbon monoxide (CO), and oxygen (O<sub>2</sub>) as determined using an electrochemical portable analyzer.

Table 1-1 Analyte list

Analyte	CAS No	Sensitivity (minimum detectable limit)
Nitric oxide (NO)	10102-43-9	< 2% of calibration gas value
Nitrogen dioxide (NO <sub>2</sub> )	10102-44-0	< 2% of calibration gas value
Carbon Monoxide (CO)	630-08-0	< 2% of calibration gas value
Oxygen (O <sub>2</sub> )	7782-44-7	< 2% of calibration gas value

### 1.2 *Applicability*

This method is intended for the measurement of nitrogen oxides (NO and NO<sub>2</sub>), carbon monoxide (CO), and/or oxygen (O<sub>2</sub>) in stationary source emissions for the purposes of conducting performance tests to demonstrate compliance with an applicable emissions standard. The use of this method for performance tests used to demonstrate compliance with federal emissions standards or monitoring requirements must be approved by the EPA Administrator. This method is available for application without Federal oversight for other non-federal program uses including state permitting programs and engineering applications.

### 1.3 *Data Quality Objectives (DQO)*

This method is designed to provide high-quality data for the determinations described above. In these and other applications, the principal objective is to ensure data accuracy at the emission levels that are at or below the emissions target. To meet this objective, the use of EPA traceability protocol calibration gases and measurement

system performance tests are required.

#### 1.4 *Data Quality Assessment for Low Emitters.*

This test method includes specific considerations for “low” emission testing where measured emissions of NO are expected to be 20 ppmv or less. Emissions greater than 20 ppmv are considered and noted as “general” emissions levels in this method. This includes sensor resolution, calibration gas concentration and thermal stability requirements.

#### 2.0 *Summary of Method*

A gas sample is continuously extracted from an emission source exhaust duct and conveyed to a portable gas analyzer for determination of O<sub>2</sub>, and NO, NO<sub>2</sub>, and/or CO gas concentrations using electrochemical gas sensors. Portable gas analyzer design specifications, performance specifications, and test procedures are provided to ensure reliable performance. Electrochemical gas sensors are designed to detect and quantify the concentration of a specific gas by measuring the flow of current resulting from the electrochemical reaction of that gas on an electrode surface. The sensor is comprised of two electrodes, the sensing electrode and the counter electrode, that are held at a precisely chosen constant relative potential. By selecting the flow rate and sensor design such that every molecule that reaches the electrode surface is oxidized, the current response curve is predictable. This type of design is known as “mass transport limited” or “diffusion controlled.” The electrochemical sensor range is determined by the sensor manufacturer.

*Note: This method incorporates technology specific characteristics of electrochemical portable gas analyzers and is not technology neutral.*

Table 2 – 1 Instrument Technology Requirements

<b>Instrumentation</b>	<b>Technology</b>	<b>Requirement</b>
Portable Gas Analyzer	Sensing Technology	Electrochemical Sensors
	Temperature Monitoring	Sensor Temperature Display
	Zero-Calibration	Automatic
	Maintenance	Annual by Authorized Service or Manufacturer

#### 3.0 *Definitions*

3.1 *Ambient air rinse means* the gas analyzer sample stream is ambient air. This occurs for a set amount of time between measurements. It is also referred to as purging, breathing, or rinsing. It is required between the introduction of each analyte calibration gas during system verification and between sample runs for emissions tests.

*Note: Ambient rinses should be at least 5 minutes in length unless otherwise stated in the method. The duration of the ambient air rinse must be sufficient to refresh the surface of the electrodes inside the sensor. Without an ambient air rinse, electrochemical sensors will become "saturated" and the output will drift. The amount of time for the ambient air rinse is generally dependent upon the gas concentration and the time of exposure.*

3.2 *Calibration error means* the percentage difference between the gas concentration measured by the gas analyzer and the known concentration of the calibration gas.

3.3 *Calibration gas means* a gas mixture containing an analyte at a known concentration and produced and

certified in accordance with “EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards,” September 1997, as amended August 25, 1999, EPA-600/R-97/121 or more recent updates. The system verification tests require the use of calibration gas prepared according to this protocol.

- 3.3.1 *Daily calibration gas* means the calibration gas ranges listed in Table 7-1 of this method.
- 3.3.2 *Span calibration gas* means the known concentration of a gas in an appropriate diluent gas according to Table 3-1.
- 3.3.3 *Mid-level calibration gas* means a known concentration of a gas in an appropriate diluent gas according to Table 3-1.
- 3.3.4 *Low-level calibration gas* means a NO calibration gas of between the concentration of 5 – 25 ppmv.
- 3.3.5 *Zero calibration gas* means a calibration gas which meets requirements under the definition for “zero air material” in 40 CFR 72.2.

Table 3-1. Linearity Gas Concentrations (As Certified)

Analyte	Mid-level calibration gas concentration (ppmv)	Span calibration gas concentration (ppmv)
CO	100	2000
CO <sub>low</sub>	100	300
NO	100	500
NO <sub>low</sub>	100	200
NO <sub>2</sub>	100	300
O <sub>2</sub>	15%	20.9%

- 3.4 *Interference check* means the procedure for quantifying cross-sensitivities from components in the stack gas other than the target analyte.
- 3.5 *Linearity check* means a periodic check of a gas analyzer to verify the linear response of the electrochemical sensors in a gas analyzer over a range of gas concentrations. Linearity checks must be performed at least every calendar quarter for each analyte or whenever an electrochemical sensor is replaced.
- 3.6 *Low emitters* means sources (e.g., turbines) in which the concentration of NO does not exceed 20 ppmv.
- 3.7 *Measurement range* means the portable gas analyzer manufacturer-determined range of concentration within which the sensor will operate with the specified accuracy and excess of this range is considered overload.

*Note: A sensor manufacturer may recommend a nominal range of 0 – 4000 ppm with an overload level of 5000 ppm. The portable gas analyzer manufacturer using this sensor may conservatively recommend a measurement range of 0 – 4000 ppm. Post checks must be performed whenever a gas analyzer reading is above 80% of the measurement range. For the analyzer described above, a post check would be required when readings are observed in excess of 3,200 ppm (80% of 4000 ppm).*

3.8 *Measurement system* means the total equipment required for the determination of gas concentration. The measurement system consists of the following major subsystems:

- (a) *data recorder* – a computer or digital recorder for recording measurement data.
- (b) *electrochemical sensor* – that portion of the system that senses the gas to be measured and generates an output proportional to its concentration, or any sensor that uses diffusion-limited oxidation and reduction reactions to produce an electron flow or current between a sensing electrode and a counter electrode. Referred to as “sensor”.
- (c) *external interference gas scrubber* – device filled with scrubbing agent used to remove interfering compounds upstream of some electrochemical sensors.

(d) *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 electrochemical sensors from particulate matter and condensed moisture.

(e) *temperature device* – temperature measurement device(s) installed 1) immediately next to an electrochemical sensor to measure and record the temperature within the analyzer ( $T_s$ ) and 2) mounted on the external surface of the portable gas analyzer to measure and record the temperature of the ambient environment ( $T_a$ ).

3.9 *Response time* means the amount of time, as measured on the data recorder, required for the measurement system to display 90 % of the concentration of the calibration gas.

3.10 *Sample run* means the event of collecting and measuring the emissions from a single location from the stack or duct. A test normally consists of a specific number of sample runs.

3.11 *Test* means a series of sample runs required by the applicable regulation.

3.12 *Sensor stability time* means the elapsed time from the start of the response time to the time when the sensor stability criteria of less than 1.0% per minute change is achieved.

3.13 *Stability check* means the procedure for demonstrating that an electrochemical sensor response to the calibration gas provides a stable output. Defined as less than 1.0% per minute change in measured concentration during minutes 4 to 5 in the time period immediately following the 2 minutes allotted for the response time.

3.14 *Thermal check* means calculation of change in temperature with respect to time to demonstrate that the portable gas analyzer system has sufficiently equilibrated to the test environment. This is a measurement of thermal stability and defined as a temperature change of less than 1.1°C (2°F) in 15 minutes.

3.15 *Thermal stability* means calculation of the change in ambient temperature,  $T_A$ , or sensor temperature,  $T_s$ , during the system performance tests, sample collection test or post-check system verification.

#### 4.0 *Interferences*

4.1 *Analytical Interferences.* NO and NO<sub>2</sub> can interfere with CO concentration measurements from electrochemical sensors, and NO<sub>2</sub> can interfere with NO concentration measurements from electrochemical sensors. To mitigate any interference concerns, the use of gas scrubbers immediately prior to an electrochemical sensor is acceptable and to eliminate any confounding effects calibration criteria must be met using calibration gases prepared as a single analyte standard balanced in nitrogen or synthetic air.

4.2 *Sampling Interface Interferences.* Sampling interface interferences prevent the transport of target analytes to the instrumentation or have the potential to damage the measurement system components (water condensation and moisture, for example). You must adhere to the manufacturer's recommended procedures and specific provisions and performance criteria included in this method to eliminate sampling interface interferences.

#### 5.0 *Safety*

This method may require you to work with hazardous materials and in hazardous conditions. We encourage you to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning cylinder and noxious gases may apply. NO and NO<sub>2</sub> are toxic and dangerous gases. Nitric oxide is immediately converted to NO<sub>2</sub> upon reaction with air and NO<sub>2</sub> is a highly poisonous and insidious gas. Inflammation of the lungs from exposure may cause only slight pain or pass unnoticed, but the resulting edema several days later may cause death. A concentration of 100 ppm is dangerous for even a short exposure, and 200 ppm may be fatal. All calibration gases must be handled with utmost care and with adequate ventilation.

#### 6.0 *Equipment and Supplies*

6.1 This section presents an example of key equipment and supplies designed for this application. Any electrochemical measurement system that meets the performance and design specifications in this test method may be used.

6.2 *Sample Transport and Conditioning System.* The sample transport and conditioning system shall be designed and operated to preclude water condensation that can affect the accuracy of the readings and to prevent moisture contact with the electrochemical sensors. The essential components are described below.

6.2.1 *Sample Probe.* Glass, stainless steel, or other non-reactive material of sufficient length to traverse the sample points in the source exhaust duct. Probe assembly is to minimize condensation and scrubbing of NO<sub>2</sub> or other water miscible gas species.

6.2.2 *Particulate Filters.* Filters at the probe, the inlet, or outlet of the *moisture removal system*, and/or at the inlet or within the body of the gas analyzer are recommended to prevent accumulation of particulate material in the *measurement system* and extend the useful life of the components. Filters shall be fabricated of materials that are nonreactive with the sample gas.

6.2.3 *Sample Line.* The sample line from the probe to the conditioning system/sample pump should be made of Teflon or other material that does not absorb or otherwise alter the sample gas. For NO<sub>x</sub> testing, heated or proven design which prevents scrubbing of NO<sub>2</sub> or other water miscible gas species is required.

6.2.4 *Moisture Removal System.* A device to dry the sample to prevent scrubbing of NO<sub>2</sub> or other water miscible gas species.

6.2.5 *Sample Pump.* A device to pull the sample gas through the system at a consistent *flow rate*. The pump wetted surfaces should be constructed of material that is nonreactive with the sample gas.

*Note: An aged or weak sample pump will result in a low flow rate. An inadequate flow rate will result in low bias and false negative readings. Pumps must be included in annual gas analyzer maintenance. Flow rate must be visibly monitored either by an intrinsic flow rate meter or by placing a flow rate control valve upstream of the gas analyzer during system verification and at the exhaust (to measure flow) of the gas analyzer during source testing.*

6.2.6 *System Verification Assembly.* A tee-fitting to attach to the probe tip for introducing *calibration gases* at ambient pressure during the system verification. The vented end of the tee should have a flow indicator to ensure sufficient *calibration gas* flow. A schematic of an acceptable calibration assembly is shown in Figure 17-1. Any other similar method, such as a demand flow regulator, that introduces *calibration gases* at the probe at atmospheric pressure may be used.

6.2.7 *Gas Flow Rate Control.* A gas flow rate control valve and rotameter, or equivalent, to maintain a constant sampling rate during system performance tests and to measure and record the flow rate during source testing. The flow during the system verification and source testing must be within 10 % of each other. The rate control components shall be fabricated of materials that are non-reactive with the sample gas.

6.2.8 *Interference Gas Scrubber.* A device used to remove interfering compounds upstream of a CO electrochemical sensor. The *measurement system* must 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).

6.2.9 *Sensor Temperature Indicator.* A thermocouple, thermistor, or other device must be used to monitor and display the sensor temperature. The temperature may be monitored at the surface or within the sensor. Sensor temperature must be monitored, recorded, and visibly displayed.

6.2.10 *Ambient Temperature Indicator.* A thermocouple, thermistor, or other device must be used to monitor the *ambient temperature* of the portable gas analyzer. The temperature should be monitored at the surface of the gas analyzer. Instrument *ambient temperature* must be monitored, recorded, and visibly displayed.

6.3 *Portable Gas Analyzer.* An instrument containing electrochemical sensors to determine the NO, NO<sub>2</sub>,

CO, and O<sub>2</sub> concentrations in the sample gas stream. These analyzers must be operated per manufacturer instructions in addition to the following requirements:

- (a) The gas analyzer shall contain electrochemical sensors with a minimum resolution of 1.0 ppm for “general” range emission testing or 0.1 ppm for “low” emitter testing (i.e., < 20 ppm).
- (b) The gas analyzer must be adequately charged prior to operation. Analyzers which have not been operated within the last 30 calendar days, or have no battery charge remaining, must be fully charged per the manufacturer’s specifications to ensure 100% bias on the NO sensor.

*Note: NO sensors operate with an electrical bias, if no charge or not enough charge remains then the bias on the NO sensor will be inadequate. Only when the analyzer is fully charged will the NO sensor electrical bias will be restored. If this sensor operates with an inadequate bias, it could be biased low and may not stabilize at the concentration of the calibration gas.*

- (c) The manufacturer’s maintenance procedures should be followed, and any required or suggested calibration and annual maintenance must be performed. This can be completed by the manufacturer, the operator, or a third party, although a record of this maintenance shall be maintained and provided to the applicable authority upon request.

6.4 *Data Recorder.* A computer, or digital recorder, for recording measurement data. The data recorder resolution (that is, readability) must be at least 1 ppmv for CO, NO, and NO<sub>2</sub> for general testing; at least 0.1 ppmv for CO, NO, and NO<sub>2</sub> for low emitter testing (i.e., < 20 ppm); at least 0.1% O<sub>2</sub> for oxygen measurements; and 0.1° C (0.2°F) for temperature. Alternatively, a digital or analog meter that complies with these resolution specifications may be used to obtain the gas analyzer responses and the readings may be recorded manually. The data recorder must be capable of reading at a minimum of 10 second intervals.

## 7.0 *Reagents and Standards*

7.1 *Measurement Range.* The measurement range for each analyte is determined by the electrochemical sensor design and specified by the portable gas analyzer manufacturer.

7.2 *Calibration Gases.* The calibration gases for the gas analyzer shall be CO in nitrogen or CO in synthetic air, NO in nitrogen, NO<sub>2</sub> in synthetic air or nitrogen, and O<sub>2</sub> in nitrogen. Each *calibration gas* must be certified (or recertified) within an uncertainty of 2.0 percent in accordance with “EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards” September 1997, as amended August 25, 1999, EPA-600/R-97/12. Zero gas must meet the requirements under the definition for “zero air material” in 40 CFR 72.2. The calibration gas must be used before its expiration date and the cylinder gas pressure must be greater than the minimum pressure of use. It is acceptable to prepare calibration gas mixtures from EPA Traceability Protocol gases in accordance with Method 205 in appendix M to 40 CFR Part 51, however blended gases which contain multiple analytes are not permitted.

7.3 *Calibration Gas Concentrations.* Use the appropriate calibration gas for the calibration check of each sensor. Select the appropriate low-level or high-level calibration gas listed in Table 7-1 for each analyte to be measured. The calibration gas concentration may not exceed the measurement range of the analyzer and/or electrochemical sensor. If the expected gas concentration is greater than the high-level calibration gas concentrations, the high-level concentration must be selected.

Table 7-1. Calibration gas concentrations (as certified)

Analyte	Low-level calibration gas concentration range (ppmv)	High-level calibration gas concentration range (ppmv)
CO	95 - 105	1900 - 2100
NO	95 - 105	475 - 525
NO <sub>2</sub>	95 - 105	95 - 105



O <sub>2</sub>	Dry ambient air (20.9% O <sub>2</sub> )	Dry ambient air (20.9% O <sub>2</sub> )
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*Example 1: If the expected gas concentration is 200 ppm CO, the selection of low-level or high-level calibration gas will be based upon the measurement range of the sensor. In most cases, the installed sensor will be a low CO sensor with an upper limit of around 500 ppm measurement range, and therefore, low-level calibration gas will be selected to not overrange the sensor.*

*Example 2: If the expected gas concentration is 2500 ppm CO, this is in excess of the high-level calibration gas of 1900 - 2100 ppm and therefore, the high-level calibrations gas must be selected.*

7.4 *Linearity Check.* Instrument preventative maintenance must be carried out and documented on an annual basis. It is required that analyzer manufacturer's maintenance procedures be followed, and an annual calibration and maintenance be performed. This can be completed by the manufacturer, the operator, or a third party. The linearity check must challenge the instrument through the entire measurement range with at least a span calibration gas, mid-level calibration gas, and zero gas as listed in Table 3-1. The absolute value of the difference between the gas value and the analyzer response shall not be greater than 2.5% of the span gas value. If you choose to challenge at additional ranges, the difference between the gas value and the analyzer response shall not be greater than 2.5% of the span calibration gas value for each range.

#### 8.0 *Sample Collection, Preservation and Storage*

Emission Test Procedure: Since you are allowed to choose different options to comply with some of the performance criteria, it is your responsibility to identify the specific options you have chosen and to document that the performance criteria for that option have been met.

8.1 *Sampling Location.* Select a sampling site following EPA Method 1 or 1A (40 CFR Part 60, Appendix A).

8.2 *Stratification Tests.* Perform stratification testing according to procedures found in Section 8.1.2 of EPA Method 7E (40 CFR Part 60, Appendix A), unless otherwise specified by the applicable subpart or rule.

8.3 *Initial Measurement System Performance Tests.* Before measuring emissions, you must perform the procedures:

- (a) *Calibration Gas Verification*
- (b) *Linearity Verification*
- (c) *Equipment Verification*
- (d) *System Warm-up*
- (e) *Leak Check*
- (f) *Zero Calibration Error*
- (g) *System Verification*
- (h) *Low-emitter Verification (if applicable)*

8.4 *Calibration Gas Verification.* Obtain a certificate from the gas manufacturer documenting the quality of the gas. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gas certifications have not expired. This documentation should be available on-site (i.e., test location) for inspection.

8.5 *Linearity Verification.* At least once per calendar quarter in which the gas analyzer is in use or whenever a sensor is replaced, perform the linearity check on the system after the system verification process by challenging each sensor with a span calibration gas, a mid-level calibration gas, and a zero calibration gas per the requirement in Section 7.4. The absolute value of the difference between the gas value and the analyzer response shall not be greater than 2.5% of the span gas value. This documentation should be available on-site for inspection and must be reported.

8.6 *Equipment Verification.* Assemble the sampling system by following the manufacturer's recommended procedures; verify through visual, electronic, or other suitable method that the gas scrubbing agent is not depleted; inspect the particulate filter(s) through visual, electronic, or other suitable method; and record all observations on an appropriate form.

8.7 *System Warm-up and Thermal Check.* Power the gas analyzer, and with the pump running, record the time, and the ambient and sensor temperatures (T<sub>A</sub>, T<sub>S</sub>). Allow the gas analyzer and sample interface to warm-up

according to manufacturer's recommendations. After the recommended warm-up and the gas analyzer is stable, record the time, and ambient and sensor temperatures ( $T_A, T_S$ ) again and calculate the thermal response ( $TC_A, TC_S$ ) according to Equation OTM-39-1 or OTM-39-2. When the system warm-up is complete, zero the analyzer according to the manufacturers recommendation prior to the leak check, zero calibration error, and system verification.

*Note: The gas analyzer is stable when either  $T_A$  or  $T_S$  changes less than  $1.1^\circ\text{C}$  ( $2^\circ\text{F}$ ) in 15 minutes.*

8.8 *Leak Check.* With the pump running, perform a leak check by plugging the sample line and observing that the gas flow rate is less than 0.03 l/min, or alternatively, by injecting an oxygen free gas through the sampling probe tip and verifying that the  $\text{O}_2$  reading is less than or equal to 0.2%; record the result of the check.

8.9 *Zero Calibration Error.* Introduce the zero calibration gas at the probe tip using the calibration assembly. During the zero calibration error, make no adjustments to the system except those necessary to achieve the correct calibration gas flow rate through the gas analyzer. Allow the electrochemical sensors' responses to stabilize for at least 30 seconds before recording the results and calculate the zero calibration error according to Equation OTM-39-3. The requirement for the zero calibration error is that the CO, NO, and  $\text{NO}_2$  response must be  $\leq 3.0\%$  of the value of the calibration gas used, while the  $\text{O}_2$  response must be  $\leq 0.3\%$   $\text{O}_2$ . If the method specifications are not met, take corrective actions and repeat the zero calibration error.

8.10 *System Verification: Pretest Response Time, Stability, and Calibration Error.* The following procedure is prescriptive and designed to evaluate the health and accuracy of the electrochemical sensors used in the portable gas analyzers. Figure 17-2 (CO and NO) and Figure 17-3 ( $\text{NO}_2$ ) present an example of the portable gas analyzer response during the system verification cycle. Conduct the system verification at the facility being tested immediately prior to the start of a sample collections test. Keep the gas analyzer in the same location until the post-test calibration error is conducted. The system verification must be completed for each test or series of tests located at the same location.

#### 8.10.1 *Response Time.*

8.10.1.1 Turn the pump on and introduce the CO calibration gas to the sample line through the probe, or tubing as appropriate, per Figure 17-1 and ensure that the calibration gas flows through all parts of the sample interface. Check the calibration gas flow rate on the instrument monitor or an excess flow rotameter (if applicable), record the flow rate (e.g., lpm, cfm), and then perform an ambient rinse.

8.10.1.2 Stop the ambient rinse and reconnect the sample line, as needed, and observe the display for a reading of CO. The first detection of CO is time zero (Time 0) for the response time. Recheck and record the flow rate. Record the time in seconds (i.e., *response time*) it takes to achieve 90% of the full *calibration gas* value. If the response time is greater than 2 minutes, this indicates a thermal stability or sensor integrity issue and requires corrective action prior to testing. Stop the system verification, troubleshoot, and repeat the response time.

Example 1 – 100 ppmv calibration gas, must read  $\geq 0.9 \times 100 = 90$  ppm within 2 minutes.

Example 2 – 2,000 ppmv calibration gas, must read  $\geq 0.9 \times 2000 = 1800$  ppm within 2 minutes.

8.10.2 *Stability Check.* After the response time has been determined, continue to flow the CO calibration gas for 240 seconds (4 minutes) from the start of the response test and record the CO, NO, and  $\text{NO}_2$  concentrations. Record data every 10 seconds. Allow for the calibration gas to continue to flow for an additional minute and record the CO concentration at 300 seconds (5 minutes) from the start of the response time. The difference in the recorded CO concentrations at 300 and 240 seconds must be less than one percent of the CO *calibration gas* concentration.

$$|ppm(300 \text{ sec}) - ppm(240 \text{ sec})| \leq 0.01 * \text{calibration gas concentration}$$

Example 1 – 100 ppmv calibration gas,  $| (ppm_{5min} - ppm_{4min}) | \leq 0.01 * 100 \leq 1 \text{ ppm}$

$$\text{Example 2} - 2,000 \text{ ppmv calibration gas, } |(ppm_{5min} - ppm_{4min})| \leq 0.01 * 2000 \leq 20 \text{ ppm}$$

8.10.3 *Calibration Error.* Average the measured values of the CO response observed (every 10 seconds) during the stability check. This value must be within 5.0% of the calibration gas value.

$$\text{Example 1} - 100 \text{ ppmv calibration gas, } 95 \leq (\text{average of readings minute 4 to 5}) \leq 105$$

$$\text{Example 2} - 2,000 \text{ ppmv calibration gas, } 1900 \leq (\text{average of readings minute 4 to 5}) \leq 2,100$$

8.10.4 If the gas analyzer CO measurement passes the specifications in Sections 8.10.1, 8.10.2 and 8.10.3, record the NO and NO<sub>2</sub> concentrations measured and calculate the percent interference according to Equation OTM 39-5. This value must be 5.0% or less. If the gas analyzer CO measurement does not pass the response time, stability check, calibration error, and/or interference checks, corrective actions are required. Stop the system verification, troubleshoot, and repeat the system verification starting from the response time test.

8.10.5 Disconnect the *sample line* from the gas analyzer, as needed, and perform an ambient air rinse for 5 minutes; record time and T<sub>A</sub> and T<sub>S</sub> and then turn off the sample pump.

8.10.6 Repeat Sections 8.10.1 through 8.10.5 for NO. If the analyzer NO measurement passes these specifications, record the NO<sub>2</sub> concentration measured during the calibration error check to calculate interference (according to Equation OTM 39-6).

8.10.7 *NO<sub>2</sub> System Verification.* Introduce the NO<sub>2</sub> calibration gas to the sample line through the probe, or tubing as appropriate, per Figure 17-1, and ensure that the calibration gas flows through all parts of the sample interface. Check the flow rate on the instrument monitor or excess flow rotameter (if applicable). Connect the sample line to the gas analyzer, as needed, turn on the pump, and run the NO<sub>2</sub> calibration gas for 10 minutes to pre-condition the system. Disconnect the sample line from the gas analyzer, as needed, and perform an ambient air rinse for 5 minutes.

8.10.8 Repeat Sections 8.10.1 through 8.10.5 for NO<sub>2</sub>, there are no interferences to record for NO<sub>2</sub>.

8.10.9 Repeat sections 8.10.1 through 8.10.5 for O<sub>2</sub>.

8.10.10 *Low-emitter Verification Calibration.* If the NO measurements are expected to be < 20 ppm, you must challenge the instrument with a low-level calibration gas and the NO response must be within 5.0% of the calibration gas value. If the analyzer NO measurement does not pass this specification, you may not use this analyzer for low emitters.

## 8.11 *Sample Collection Method.*

8.11.1 Position the sampling probe at the first or only measurement traverse point and begin sampling at the same flow rate used during the system verification. You must maintain the sampling flow rate within 10% of the gas analyzer flow rate value used during the system verification during the entire sample run.

8.11.2 Allow the sample gas to flow through the sampling system for at least 5 minutes before recording any data. Sample for an equal period of time at each traverse point for the required run time. Record concentration values every 15 seconds and T<sub>S</sub> and T<sub>A</sub> at least once every 10 minutes. If an electrochemical sensor is exposed to gas concentrations greater than 80 % of the measurement range during any sample run, you must perform the post test system verification check.

At least once every 3 hours of clock time, perform an instrument zero calibration check where ambient air is introduced and the CO, NO and NO<sub>2</sub> are allowed to stabilize. Additionally, you must recalibrate the analyzer with air at the zero level on each occasion when the sampling location changes.

*Note: The actual procedure for performing the instrument zero calibration check will be per the instrument manufacturer's instructions. For many portable analyzers, this is automatic upon "power up" of the analyzer.*

8.11.3 At the conclusion of each sample run perform the ambient air rinse for a minimum of 5 minutes and the CO, NO and NO<sub>2</sub> responses are ≤3.0% of the concentration measured during the previous run. A

conservative estimate for the period of time required is shown in Table 8-1

Table 8-1. Ambient Air Rinse

Gas	Concentration (ppm)	Rinse time (min)
NO	< 200	5
	200-1000	10
	1001 – 2000	20
	3000+	30
NO <sub>LOW</sub>	< 50	5
	51- 200	10
	201 – 300	20
NO <sub>2</sub>	<50	5
	51- 200	10
	201 – 300	20
CO	<100	5
	101 – 1000	10
	1001-2000	15
	2001-4000	30
	4001-8000	45
	8000-10000	60
CO <sub>LOW</sub>	< 20	5
	21 – 100	10
	101 – 200	15
	201-500	20

## 8.12 Post Test requirements

8.12.1 After each test or series of tests, conduct the post-test system verification per the requirements in Section 8.10. Make no changes to the measurement system or gas analyzer calibration until all of the calibration error tests have been completed and results have been recorded.

8.12.2 If the response time, stability check, calibration error, or low-emitter verification exceeds the performance specifications in Section 8.10, all measurements since the previous acceptable checks are invalid. You may also choose to perform zero or calibration error tests after each test run

## 9.0 Quality Assurance and Quality Control

Table 9-1 summarizes the QA/QC performance criteria.

Table 9-1. Quality Assurance/Quality Control Criteria

Section	QA/QC test or specification	Acceptance Criteria	Frequency	Corrective action if not met
6.2	Sample Transport and Conditioning System	See requirements in Section 6.2.1 – 6.2.11	Each test	Do not test unless these criteria are met.
6.3	Portable Gas Analyzer (performance and maintenance)	See requirements in Section 6.3. Maintenance must be carried out and documented by an authorized service organization or appropriately trained operator.	Annually	Do not test unless these criteria are met.

6.3	Portable Gas Analyzer (battery charge).	If the gas analyzer has not been operated within the last 30 calendar days or when no battery charge remaining, then it must be fully charged per the manufacturer's specifications. System performance checks may not be performed until charged.	At least every 30 days or when no battery charge remaining	Do not test unless this criterion is met.
7.2	Calibration Gas	Certified using EPA Traceability Protocol	Each test	Do not test unless this criterion is met.
7.3	Calibration Gas Concentration Range(s)	Meet the Low-Range and High-Range (as appropriate) in Table 7-1	Each test	Do not test unless these criteria are met.
7.4	Linearity Check	2.5% of the span gas in Table 3-1	Each Calendar Quarter when in operation	Repeat Linearity Check.
8.1	Sampling Location	According to EPA Method 1 or 1A	Each test	Use an alternative sampling location that meets the acceptance criteria.
8.2	Stratification Test	$\pm 5.0\%$ of mean for 1-point sampling; $\pm 10\%$ of mean for 3-point sampling; alternatively, all points within: $\pm 0.5$ ppm of mean for 1-point sampling; $\pm 1.0$ ppm of mean for 3-point sampling	Each test	Sample at 12 traverse points or Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line.
8.6	Gas Scrubber Sufficient	Verify	Equipment start-up	Replace gas scrubber.
8.7	Thermal Check	$T_A$ or $T_S$ changes less than $1.1^\circ\text{C}$ ( $2^\circ\text{F}$ ) in 15 minutes.	Equipment start-up	Do not test unless this criterion is met.
8.8	Leak Check	With plugged sample line, flow rate is less than 0.3 l/min, or alternatively, inject oxygen free gas and verify oxygen $\leq 0.2\%$	Equipment start-up	Do not test unless this criterion is met.
8.9	Zero Calibration Error	CO, NO, NO <sub>2</sub> response must be $\leq 3.0\%$ of calibration gas for each analyte, oxygen must be $\leq 0.3\%$ O <sub>2</sub>	Prior to each test	Do not test unless these criteria are met.
8.10.1	System Verification – Response Time	$\leq 2$ minutes (for each analyte)	Each test	Troubleshoot, and repeat response time.
8.10.2	System Verification – Stability Check	% difference in the recorded concentrations at 5 and 4 minutes must be less than 1.0% of the calibration gas value, for each analyte when applicable	Each test	Repeat System Verification.
8.10.3	System Verification – Calibration	$< 5.0\%$ of the calibration gas value	Each test	Repeat System Verification.

8.10.4	System Verification - Interference	Interference may not exceed 5.0%	Calculate interference responses for NO ( $I_{NO}$ ) and CO ( $I_{CO}$ ) using the equations in Section 12 and the system performance check calibration results and average emission concentrations for the test	Repeat System Verification.
8.10.10	System Verification – Low Emitter Verification	< 5.0% of the calibration gas value using a calibration gas between 5 and 25 ppmv	Each test when values are expected to be below 20 ppmv	Repeat System Verification.
8.11.1	Sample Collection – Flow Rate	Flow rates during system verification and source testing must be within 10 % of each other	Each run	Invalidate the test and repeat.
8.11.3	Sample Collection – Zero Calibration Check	CO, NO, NO <sub>2</sub> response must be ≤ 3.0% of calibration gas for each analyte	At least every 3 hours and after a sampling location changes	Do not test unless this criterion is met.
8.11.4	Sample Collection – Ambient Air Rinse	CO, NO and NO <sub>2</sub> responses are ≤3.0% of the calibration gas used	After each test run	Do not test unless these criteria is met.
8.12.1	Post-test System Verification – Response Time	≤2 minutes (for each analyte)	Each test	Invalidate data since previous System Verification.
8.12.1	Post-test System Verification – Stability Check	% difference in the recorded concentrations at 5 and 4 minutes must be less than 1.0% of the calibration gas concentration, for each analyte when applicable	Each test.	Invalidate data since previous System Verification.
8.12.1	Post-test System Verification – Calibration	< 5.0% of the calibration value	Each Test	Invalidate data since previous System Verification.
8.12.1	Post-test System Verification – Low Emitter Verification	< 5.0% of the calibration gas value using a calibration gas between 5 and 25 ppmv	Each test when values are below 20 ppmv	Invalidate data since previous System Verification.

## 10.0 Calibration and Standardization

10.1 You must operate the instrument per the manufacturer's recommendations and as described in Section 8. The system verification described in Section 8.10 is required and must meet the specifications in Section 13 before you start the test. Then, after the test commences, you must perform the ambient air rinse after each run and recalibrate as specified in Section 8.11. Finally, you must perform the post-test System Verification in Section 8.12 as defined.

10.2 You must include a copy of the manufacturer's certification of the calibration gases used in the testing as part of the test report. This certification must include the 13 documentation requirements in the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999. When Method 205 is used to produce diluted calibration gases, you must document that the specifications

for the gas dilution system are met for the test. You must also include the date of the most recent dilution system calibration against flow standards and the name of the person or manufacturer who carried out the calibration in the test report.

### 11.0 Analytical Procedures

Because sample collection and analysis are performed together (see Section 8), additional discussion of the analytical procedure is not necessary.

### 12.0 Calculations and Data Analysis

#### 12.1 Nomenclature.

Where as:

C = concentration measured, ppm or %  
 C<sub>S</sub> = concentration of calibration gas, ppm or %  
 CE = calibration error, %  
 C<sub>NOG</sub> = concentration of NO span gas, ppm NO,  
 C<sub>NOS</sub> = concentration of NO in stack gas, ppm NO,  
 C<sub>COS</sub> = concentration of CO in stack gas, ppm CO,  
 C<sub>COG</sub> = concentration of CO span gas, ppm NO<sub>2</sub>,  
 C<sub>NO2S</sub> = concentration of NO<sub>2</sub> in stack gas, ppm NO<sub>2</sub>, and  
 C<sub>NO2G</sub> = concentration of NO<sub>2</sub> span gas, ppm NO<sub>2</sub>, and  
 C<sub>NOxS</sub> = concentration of NO<sub>x</sub> in stack gas, ppm NO<sub>x</sub>.  
 I<sub>CO</sub> = CO interference response, %,  
 I<sub>NO</sub> = NO interference response, %,  
 R<sub>CO-NO</sub> = CO response to NO span gas, ppm CO,  
 R<sub>CO-NO2</sub> = CO response to NO<sub>2</sub> span gas, ppm CO,  
 R<sub>NO-NO2</sub> = NO response to NO<sub>2</sub> span gas, ppm NO,  
 TC<sub>A</sub> = Thermal check ambient temperature  
 TC<sub>S</sub> = Thermal check sensor temperature  
 T<sub>AF</sub> = Ambient temperature (final)  
 T<sub>AI</sub> = Ambient temperature (initial)  
 T<sub>SF</sub> = Sensor Temperature (final)  
 T<sub>SI</sub> = Sensor Temperature (initial)  
 ZCE = Zero calibration error

#### 12.2 Thermal Check.

$$\text{Equation OTM 39-1} \quad TC_S = T_{SF} - T_{SI}$$

$$\text{Equation OTM 39-2} \quad TC_A = T_{AF} - T_{AI}$$

#### 12.3 Calibration Error.

$$\text{Equation OTM 39-3} \quad CE = \frac{C_s - C}{C_s} \times 100$$

$$\text{Equation OTM 39-4} \quad ZCE = \frac{C}{C_s} \times 100$$

#### 12.4 Interference Response.

$$\text{Equation OTM 38-5} \quad I_{CO} = \left[ \left( \frac{R_{CO-NO}}{C_{NOG}} \times \frac{C_{NOS}}{C_{COS}} \right) + \left( \frac{R_{CO-NO2}}{C_{NO2G}} \times \frac{C_{NO2S}}{C_{COS}} \right) \right] \times 100$$

$$\text{Equation OTM 38-6} \quad I_{NO} = \left( \frac{R_{NO-NO2}}{C_{NO2G}} \times \frac{C_{NO2S}}{C_{NOxS}} \right) \times 100$$

### 13.0 Method Performance

13.1 Zero Calibration Error. The requirement for the zero-calibration error is that the CO, NO, and NO<sub>2</sub>

response must be  $\leq 3.0\%$  of the calibration gas. The O<sub>2</sub> response must be  $\leq 0.3\%$  O<sub>2</sub>.

13.2 *Linearity Verification.* For the zero, mid-level, and span gases; the absolute value of the difference between the gas value and the analyzer response shall not be greater than 2.5% of the span gas.

13.3 *System Verification.*

13.3.1 *Response Time.* The time in seconds it takes to achieve 90% of the full calibration gas value shall be no greater than 2 minutes.

13.3.2 *Stability Check.* The difference in the recorded pollutant or diluent concentrations at 300 and 240 seconds must be less than one percent of the calibration gas concentration.

13.3.3 *Calibration.* The measured values of the pollutant response observed (every 10 seconds) during the stability check. This value must be within 5.0% of the calibration gas value.

13.3.4 *Low-emitter Verification.* If the NO measurements are expected to be  $< 20$  ppm, the NO response must be within 5.0% of the low-level calibration gas value.

14.0 *Pollution Prevention*

*(reserved)*

15.0 *Waste Management*

*(reserved)*

16.0 *References*

16.1 Pipeline Research Council International (PRCI) PR-312-14206-R01, "Technical Considerations for Developing a New Electrochemical Cell Portable Analyzer Test Method,"

16.2 Table 10.1 Testo 350 Combustion & Emission Analyzer Instruction manual, p. 104, 105 0970 3519 en 02 V01.00 en\_US

16.3 *EPA Methods from 40 CFR Part 60, Appendix A*

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

16.4 *EPA Methods from 40 CFR Part 63, Appendix A:*

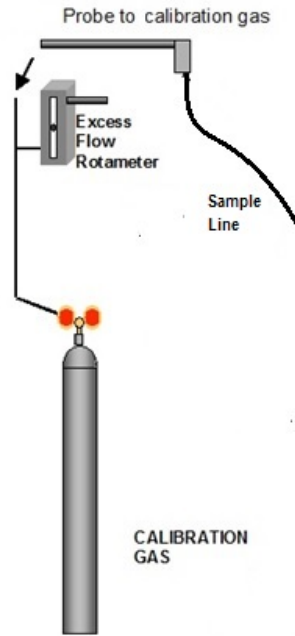
Method 301 – Field Validation of Pollutant Measurement Methods from Various Waste Media

16.5 *EPA Methods from 40 CFR Part 75, Appendix H:*

Revised Traceability Protocol No. 1: Protocol G1 and G2 Procedures

17.0 *Tables Diagrams Flowcharts and Validation Data*





**Figure 17-1 System Verification Assembly.**

**Figure 17-2. Example system performance -test checks cycle CO, NO.**

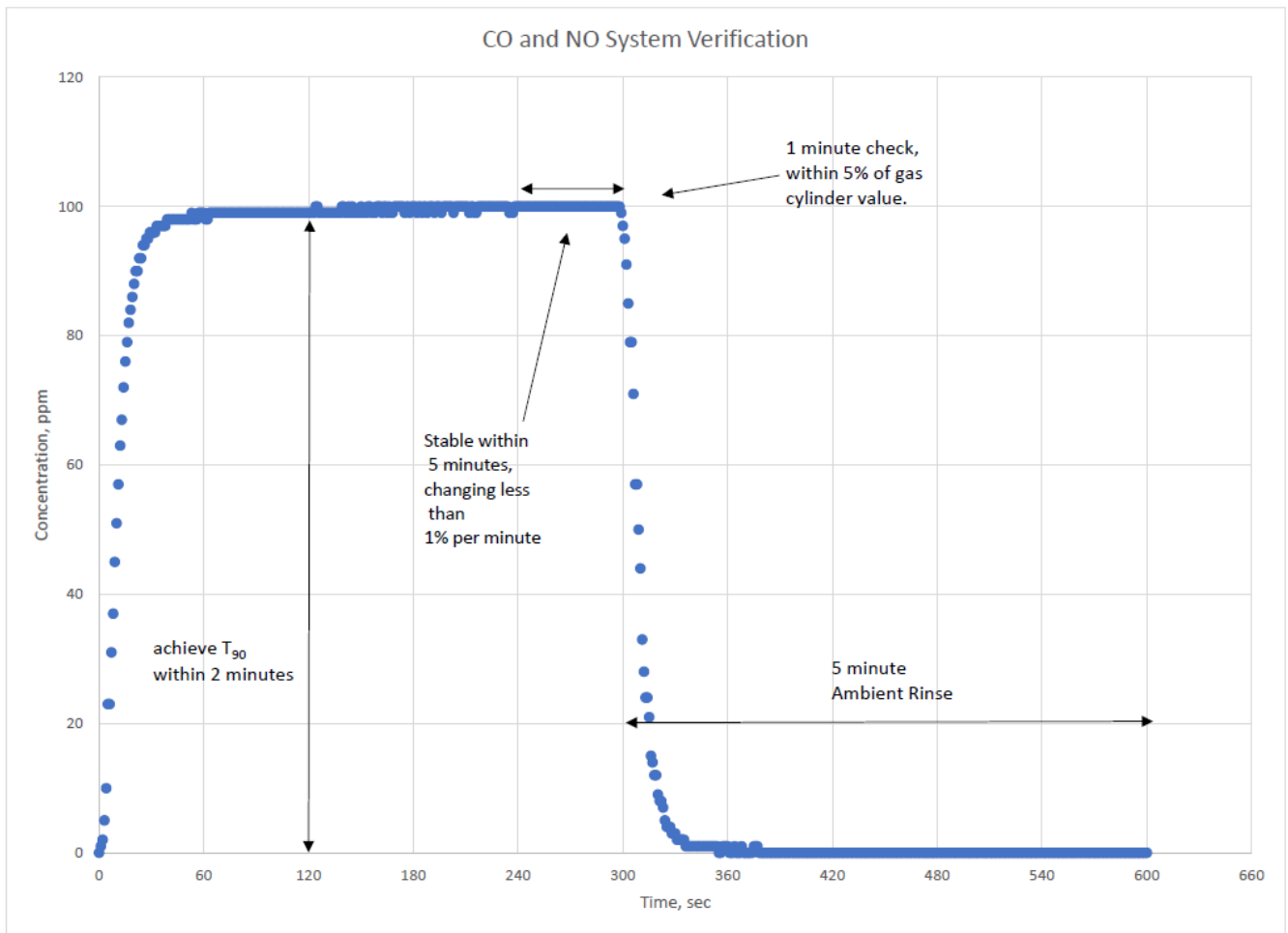


Figure 17-3. Sequence for Electrochemical Sensor and Gas Analyzer System Performance Check for NO<sub>2</sub>

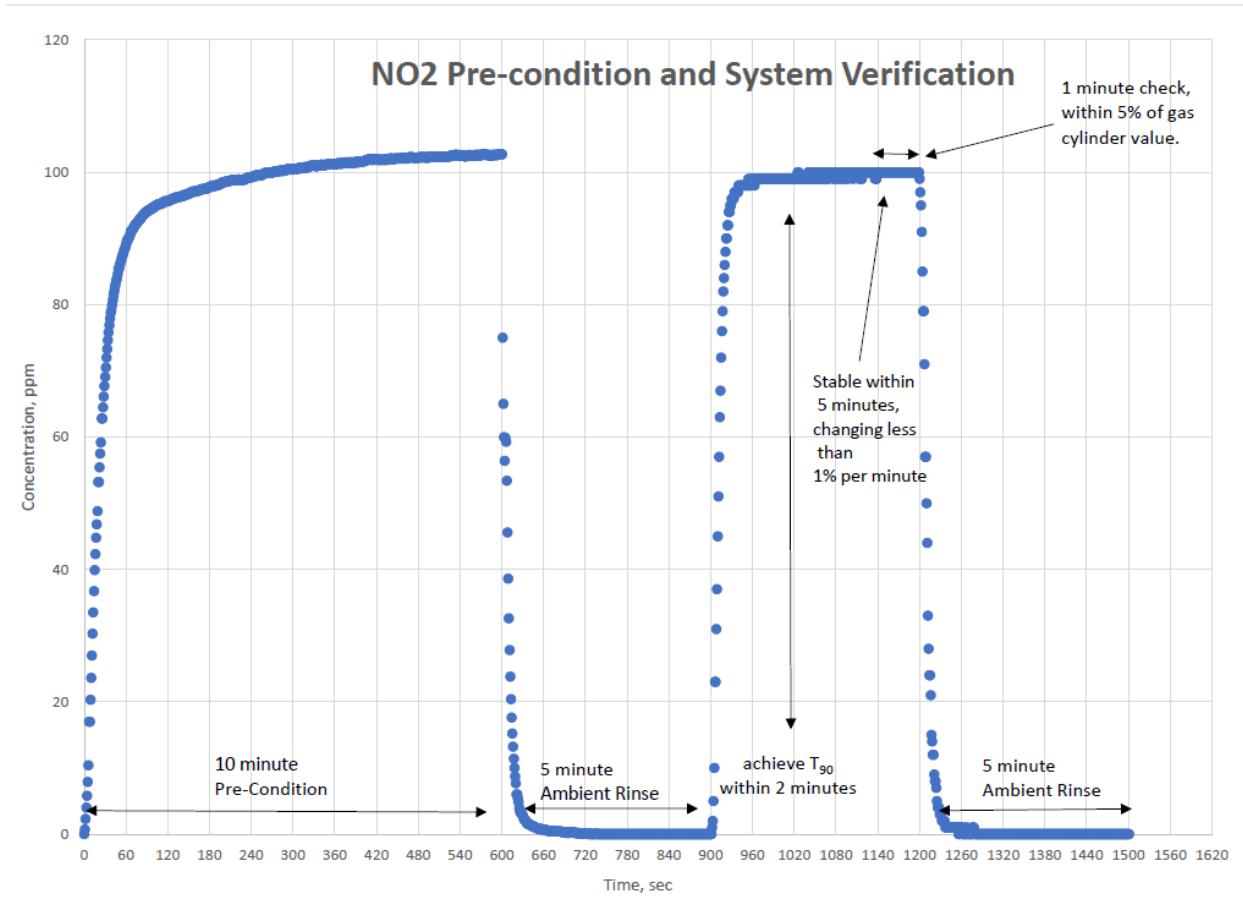


Figure 17-4 Example Data Sheet – Equipment Verification

Today's Date		Portable Analyzer Identifier			Analyte			
		A	B	C	NO	NO <sub>2</sub>	CO	O <sub>2</sub>
Date		Date of Last Annual Maintenance	Date of Last Use	Battery Charge	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Check	less than 1 year	Less than 30 days	Battery Charge to full	Lot #				
	More than 1 year Stop Test	More than 30 days		Balance Gas	N <sub>2</sub> <input type="checkbox"/>	N <sub>2</sub> <input type="checkbox"/> Air <input type="checkbox"/>	N <sub>2</sub> <input type="checkbox"/> Air <input type="checkbox"/>	N <sub>2</sub> <input type="checkbox"/>
				Test Gas ppm				
				Expiration Date				
				Cylinder Pressure Check				
				Sensor				
				NO	NO <sub>2</sub>	CO	O <sub>2</sub>	
				Portable Analyzer Measurement Range				
				Detection Limit: Resolution				
				Detection Limit: Minimum <2% of cal gas concentration				
				Zero Calibration Check				
				NO	NO <sub>2</sub>	CO	O <sub>2</sub>	

Figure 17-5 Example Data Sheet - System warm-up, leak check, and filter/scrubber checks

	Start time	time		T <sub>s</sub>		T <sub>A</sub>	
	Turn on Analyzer with Pump Running	After warm-up		Sensor Temperature		Instrument Ambient Temperature	
Record Time			Record Temperature				
Thermal Check	Calculate using time, T <sub>s</sub> , T <sub>A</sub>	T <sub>A</sub> or T <sub>s</sub> changes less than 1.1°C (2°F) in 15 minutes				Results:	
ReZero	<input type="checkbox"/>						
Leak Test	Select One	Plug Sample Line <input type="checkbox"/>	Sample Flow Rate:	< 0.03 l/min	Pass	<input type="checkbox"/>	
		Oxygen Free Gas <input type="checkbox"/>	O <sub>2</sub> reading:	≤ 0.2%	Pass	<input type="checkbox"/>	
Gas Scrubber Check		Visual <input type="checkbox"/>	Electronic <input type="checkbox"/>	Other <input type="checkbox"/>			
Particulate Filter check		Visual <input type="checkbox"/>	Electronic <input type="checkbox"/>	Other <input type="checkbox"/>			

Figure 17-6 Example Data Sheet - System Verification

CO	Time, sec	Record Flow Rate	Reading for T90, ppm	Reading for Stability/ Calibration, ppm	Interference, ppm		T <sub>s</sub> (deg)	T <sub>A</sub> (deg)
Rinse <input type="checkbox"/>	0							
	30							
	60							
	90							
	120							
	180							
	240							
	300				NO	NO <sub>2</sub>		
Pass/Fail			T90	Stability	Calibration	Interference	Thermal	
Rinse <input type="checkbox"/>	5 min							

