

**Determination of Nitrogen Oxides, Carbon Monoxide, and Oxygen
Emissions from Natural Gas-Fired Engines, Boilers and Process Heaters
Using Portable Analyzers**

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability. This method is applicable to 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 method should not be applied to other pollutants or emission sources without a complete investigation of possible analytical interferences and a comparative evaluation with other EPA test methods.

1.2 Principle. 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 (e.g. heated sample line, flow meters, etc.) may be required to meet the design specifications of this test method.

2. RANGE AND SENSITIVITY

2.1 Analytical Range. 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.

2.1.1 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 percent 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 percent of the span gas at any time during the sampling run then the test run for that channel is invalid.

2.1.2 NO₂ Span Gas. Choose a span gas concentration such that the average stack gas reading for each test run is greater than 25 percent 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 percent of the span gas at any time during the sampling run then the test run for that channel is invalid.

2.1.3 O₂ Span Gas. The difference between the span gas concentration and the average stack gas reading for each run shall be less than 10% O₂. Where the stack oxygen is high, dry ambient air (20.9% O₂) may be used.

2.2 Sensitivity. 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 percent of the nominal range.

3. DEFINITIONS

3.1 Measurement System. The total equipment required for the determination of gas concentration. The measurement system consists of the following major subsystems:

3.1.1 Sample Interface. That portion of a system used for one or more of the following: sample acquisition, sample transport, sample conditioning, or protection of the electrochemical cells from particulate matter and condensed moisture.

3.1.2 External Interference Gas Scrubber. A tube filled with scrubbing agent used to remove interfering compounds upstream of some electrochemical cells.

3.1.3 Electrochemical Cell. That portion of the system that senses the gas to be measured and generates an output proportional to its concentration. Any cell that uses diffusion-limited oxidation and reduction reactions to produce an electrical potential between a sensing electrode and a counter electrode.

3.1.4 Data Recorder. A strip chart recorder, computer, or digital recorder for recording measurement data.

3.2 Nominal Range. The range of concentrations over which each cell is operated (25% to 125% of span gas value). Several nominal ranges may be used for any given cell as long as the linearity and stability check results remain within specification.

3.3 Span Gas. A known concentration of a gas in an appropriate diluent gas.

3.4 Zero Calibration Error. The gas concentration exhibited by the gas analyzer in response to zero-level calibration gas.

3.5 Span Calibration Error. The difference between the gas concentration exhibited by the gas analyzer and the known concentration of the span gas.

3.6 Response Time. The amount of time required for the measurement system to display 95 percent of a step change in gas concentration on the data recorder.

3.7 Interference Check. A method of quantifying analytical interferences from components in the stack gas other than the analyte.

3.8 Linearity Check. A method of demonstrating the ability of a gas analyzer to respond consistently over a range of gas concentrations.

3.9 Stability Check. A 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.

3.10 Stability Time. As determined during the Stability check; the elapsed time from the start of the gas injection to the start of the 30-minute stability check period.

3.11 Initial NO Cell Temperature. The temperature of the NO cell that is recorded during the most recent pretest calibration error check. 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.

4. MEASUREMENT SYSTEM PERFORMANCE SPECIFICATIONS

4.1 Zero Calibration Error. Less than or equal to ± 3 percent of the span gas value for NO, NO₂, and CO channels and less than or equal to $\pm 0.3\%$ O₂ for the O₂ channel.

4.2 Span Calibration Error. Less than $\pm 5\%$ of the span gas value for NO, NO₂, and CO channels and less than or equal to $\pm 0.5\%$ O₂ for the O₂ channel.

4.3 Interference Response. The CO and NO interference responses must be less than or equal to ± 5 percent of the average stack concentration for each test run.

4.4 Linearity. 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

concentration for NO, CO and O₂ cells and not greater than 3.0% of the span gas for NO₂ cells.

4.5 Stability Check Response. The analyzer responses to CO, NO, and NO₂ span gases shall not vary more than 2.0% of span gas value over a 30-minute period or more than 1.0 % of the span gas value over a 15-minute period.

5. APPARATUS AND REAGENTS

5.1 Measurement System. Use any measurement system that meets the performance and design specifications in Sections 4 and 5 of this method. 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 Figure 1. The essential components of the measurement system are described below:

5.1.1 Sample Probe. Glass, stainless steel, or other nonreactive material, of sufficient length to traverse the sample points. If necessary to prevent condensation, the sampling probe shall be heated.

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

5.1.3 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.

5.1.4 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. Alternatively use any other method that introduces calibration gases at the probe at atmospheric pressure.

5.1.5 Moisture Removal System. A chilled condenser or similar device (e.g., permeation dryer), to remove condensate continuously from the sample gas while maintaining minimal contact between the condensate and the sample gas.

5.1.6 Particulate Filter. 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.

5.1.7 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 may be constructed of any material that is nonreactive to the gas being sampled.

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

5.1.9 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 4. A means of controlling the analyzer flow rate and a device for determining proper sample flow rate (e.g., precision rotameter, pressure gauge downstream of all flow controls, etc.) shall be provided at the analyzer. (Note: 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 method.)

5.1.10 Data Recorder. A strip chart recorder, computer, or digital recorder, for recording measurement data. The data recorder resolution (i.e., readability) shall be at least 1 ppm for CO, NO, and NO₂; 0.1% O₂ for O₂; and one degree (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.

5.1.11 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 (i.e. color indication).

5.1.12 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.

5.2 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.

5.3.1 Span Gases. Used for calibration error, linearity, and interference checks of each nominal range of each cell. Select concentrations according to procedures in Section 2.1.

5.3.2 Mid-Level Gases. Select concentrations that are 40-60% of the span gas concentrations.

5.3.3 Zero Gas. Concentration of less than 0.25 percent of the span gas for each component. Ambient air may be used in a well ventilated area.

6. MEASUREMENT SYSTEM PERFORMANCE CHECK PROCEDURES

Perform the following procedures before measurement of emissions (Section 7).

6.1 Calibration Gas Concentration Verification. For the mid-level and span cylinder gases, use calibration gases certified according to EPA Protocol G1 or G2 procedures (see Bibliography). Alternative

certification techniques may be used if they are approved in writing by the applicable regulatory agency.

6.2 Linearity Check. Conduct the following procedure once for each nominal range that is to be used on each electrochemical cell (NO, NO₂, CO, and O₂) before each field test program. If a field test program lasts longer than five days, the linearity check shall be repeated before each five days of analyzer operation. Repeat the linearity check if a cell is replaced.

6.2.1 Linearity Check Gases. For each cell obtain the following gases: zero (0-0.25% of nominal range), mid-level (40-60% of span gas concentration), and span gas (selected according to Section 2.1).

6.2.2 Procedure. If the analyzer uses an external interference gas scrubber with a color indicator, using the analyzer manufacturer's recommended procedure, verify that the scrubbing agent is not depleted. After calibrating the analyzer with zero and span gases, 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. Purge the analyzer briefly with ambient air between gas injections. For each gas injection, verify that the flow rate is constant and that the analyzer responses have stabilized before recording all of the responses on a form similar to Figure 2.

6.3 Interference Check. Following each linearity check, use the results from the span gas injections to determine interference responses for the CO and NO cells.

6.3.1 CO Interference Response.

$$I_{CO} = [(R_{CO-NO} / C_{NOG} \times C_{NOS} / C_{COS}) + (R_{CO-NO2} / C_{NO2G} \times C_{NO2S} / C_{COS})] \times 100$$

where: I_{CO} = CO interference response (percent)
 R_{CO-NO} = CO response to NO span gas (ppm CO)

C_{NOG} = concentration of NO span gas (ppm NO)
 C_{NOS} = concentration of NO in stack gas (ppm NO)
 C_{COS} = concentration of CO in stack gas (ppm CO)
 $R_{\text{CO-NO}_2}$ = CO response to NO₂ span gas (ppm CO)
 $C_{\text{NO}_2\text{G}}$ = concentration of NO₂ span gas (ppm NO₂)
 $C_{\text{NO}_2\text{S}}$ = concentration of NO₂ in stack gas (ppm NO₂)

6.3.2 NO Interference Response.

$$I_{NO} = (R_{NO-NO_2} / C_{NO_2G}) \times (C_{NO_2S} / C_{NO_xS}) \times 100$$

where:

- I_{NO} = NO interference response (percent)
- R_{NO-NO_2} = NO response to NO_2 span gas (ppm NO)
- C_{NO_2G} = concentration of NO_2 span gas (ppm NO_2)
- C_{NO_2S} = concentration of NO_2 in stack gas (ppm NO_2)
- C_{NO_xS} = concentration of NO_x in stack gas (ppm NO_x)

6.4 Stability Check. Conduct the following procedure once for each nominal range that is to be used on each pollutant electrochemical cell (NO, NO_2 , and CO) before each field test program. If a field test program lasts longer than five days, the stability check shall be repeated before each five days of analyzer operation. Repeat the stability check if a cell is replaced or if a cell is exposed to gas concentrations greater than 125 percent of the highest span gas concentration.

6.4.1 Procedure. Inject the span 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. After the analyzer response has stabilized, continue to flow the span gas for at least 30 minutes. Make no adjustments to the analyzer during the test except to maintain constant flow. Record the stability time as the number of minutes elapsed between the start of the gas injection and the start of the 30-minute stability check period. If the concentration reaches a peak value within five minutes, you may choose to record the data for at least 15 minutes following the peak.

6.4.2 Calculations. Determine the highest and lowest concentrations recorded during the 30-minute period and record the results on a form similar to Figure 3. The absolute value of the difference between the maximum and minimum values recorded during the 30-minute period must be less than 2.0% of the span gas concentration. Alternatively, record stability check data in the same manner for the 15-minute

period following the peak concentration. The difference between the maximum and minimum values for the 15-minute check must be less than 1.0% of the span gas concentration.

7. EMISSION TEST PROCEDURE

7.1 Selection of Sampling Site and Sampling Points.

7.1.1 Reciprocating Engines. Select a sampling site located at least five stack diameters downstream of any turbocharger exhaust, crossover junction, or recirculation take-offs and upstream of any dilution air inlet. Locate the sampling site no closer than one meter or three stack diameters (whichever is less) upstream of the gas discharge to the atmosphere. Use a minimum of three sampling points located at positions of 16.7, 50, and 83.3 percent of the stack diameter. Alternatively, the tester may choose an alternative sampling location and/or sample from a single point in the center of the duct if previous test data demonstrate that the stack gas concentration does not vary significantly across the duct diameter.

7.1.2 Combustion Turbines. Select a sampling site and sample points according to the procedures in 40 CFR, Part 60, Appendix A, Method 20. Alternatively, the tester may choose an alternative sampling location and/or sample from a single point in the center of the duct if previous test data demonstrate that the stack gas concentrations of CO, NO_x, and O₂ does not vary significantly across the duct diameter.

7.2 Warm Up Period. Assemble the sampling system and allow the analyzer and sample interface to warm up and adjust to ambient temperature at the location where the stack measurements will take place.

7.3 Pretest Calibration Error Check. Conduct the calibration error check at the sampling location (near the sampling port) just prior to the start of an emissions test or test run. Keep the analyzer in the

same location until the post test calibration error check is conducted.

7.3.1 For analyzers that use an external interference gas scrubber tube, inspect the condition of the scrubbing agent and ensure that it will not be exhausted during sampling.

7.3.2 Inject the zero and span calibration gases at the probe tip using the calibration assembly. Ensure that the calibration gases flow through all parts of the sample interface (including any exhaust lines). During this check, make no adjustments to the system except those necessary to achieve the correct calibration gas flow rate at the analyzer. Set the analyzer flow rate to the value recommended by the analyzer manufacturer. Allow each reading to stabilize before recording the result on a form similar to Figure 4. The time allowed for the span gas to stabilize shall be no less than the stability time noted during the stability check. After achieving a stable response, disconnect the gas and briefly purge with ambient air.

7.3.3 Determine the NO and CO response times by observing the time required to respond to 95% of a step change in the analyzer response for both the zero and span gases. Note the longer of the two times as the response time. For NO₂ span gas record the time required to respond to 90% of a step change.

7.3.4 Calibrate all electrochemical cells in the analyzer if the analyzer uses an internal calculation method to compensate for interferences.

7.3.5 If the zero and span calibration error test results are not within the specifications in Section 4, take corrective action and repeat the calibration error check until acceptable performance is achieved.

7.4 NO Cell Temperature Monitoring. Record the initial NO cell temperature during the pretest calibration error check and monitor

and record the temperature regularly (at least once each 5 minutes) during the sample collection period. If at any time during sampling the NO cell temperature is 85_F or greater and has increased or decreased by more than 5_F since the pretest calibration, stop sampling immediately and conduct a post test calibration error check per Section 7.6, re-zero the analyzer, and then conduct another pretest calibration error check before continuing.

7.5 Sample Collection. Position the sampling probe at the first measurement point and begin sampling at the same rate used during the calibration error check. Maintain constant rate sampling (i.e. ± 10 percent of the analyzer flow rate value used in section 7.3.2) during the entire test run. Sample for an equal period of time at each test point. Sample the stack gas for at least twice the response time or the period of the stability time, whichever is greater, before collecting test data at each point. If recording emission data manually, record concentration values at least once each minute. If a computer or the analyzer record data automatically, the concentration data must be recorded either (1) at least once each minute, or (2) as a block average for the test run using values sampled at least once each minute. Do not break any seals in the sample handling system until after the post test calibration error test (this includes opening the moisture removal system to drain condensate).

7.6 Post Test Calibration Error Check. Immediately after the test run or set of test runs conduct span and zero calibration error checks using the procedure in Section 7.3. Conduct the calibration error check at the sampling location. Make no changes to the sampling system or analyzer calibration until all of the calibration error test results have been recorded. If the zero or span calibration error exceeds the specifications in Section 4 then all test data collected since the previous calibration error check are invalid. If the sampling system is disassembled or the analyzer calibration is adjusted, repeat the calibration error check before conducting the next test or test run.

7.7 Interference Verification. The tester shall review the results of the post test calibrations and compare them to the results of the most recent interference test. Use the post test calibration results and average emission concentrations for the test to calculate interference responses (I_{NO} and I_{CO}) using the procedure in section 6.3. If an interference response exceeds 5%, all emission test results since the last successful interference test for that compound are invalid.

7.8 Re-Zero. At least once every three hours or each time the analyzer sampling location changes, recalibrate the analyzer at the zero level according to the manufacturer*s instructions and conduct a pretest calibration error test before resuming sampling. If the analyzer is capable of reporting negative concentration data (at least 5% of the span gas below zero), then the tester is not required to re-zero the analyzer.

8. CALIBRATION CORRECTIONS

8.1 The tester may choose to correct the emissions data for a test run using the pretest and post test calibration error results. Use the following formula to make the corrections:

$$C_{GAS} = (C_R - C_o) \frac{C_{MA}}{C_M - C_o}$$

where:

C_{GAS}	=	corrected flue gas concentration
C_R	=	flue gas concentration indicated by gas analyzer
C_o	=	average of initial and final zero checks
C_M	=	average of initial and final span checks
C_{MA}	=	actual concentration of span gas

9. BIBLIOGRAPHY

1. "Appendix H to Part 75 - Revised Traceability Protocol No. 1," Federal Register, Vol. 58, No. 6, January 11, 1993, pp. 3750-3757.

FIGURE 1.
CALIBRATION SYSTEM SCHEMATIC

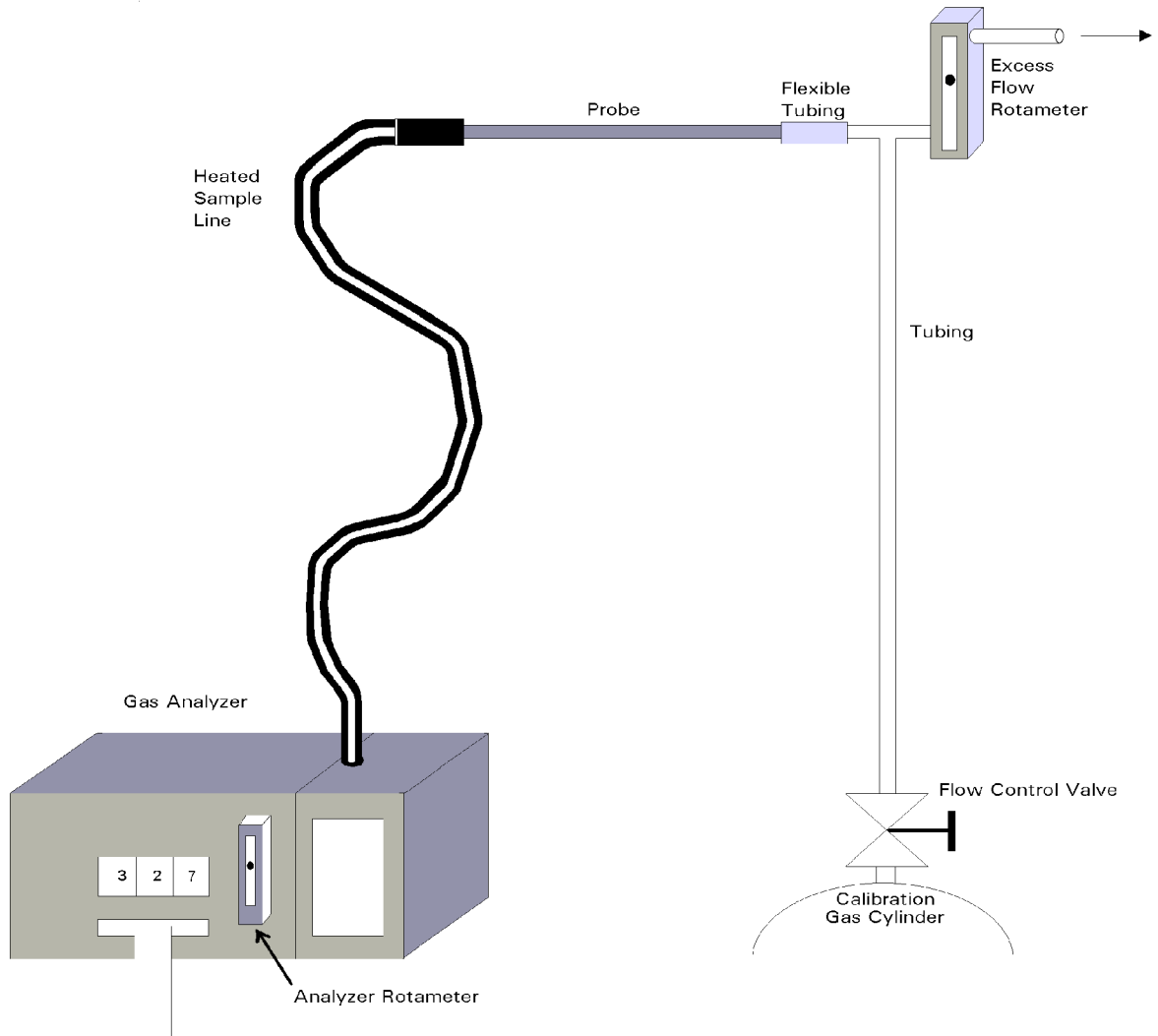


FIGURE 3.
STABILITY CHECK DATA SHEET

Date _____ Analyst _____

Analyzer Manufacturer/Model No. _____

Analyzer Serial Number _____

Pollutant Channel _____ Span Gas Concentration _____

Elapsed Time (Minutes)	Analyzer Response	Elapsed Time (Cont.)	Analyzer Response	Elapsed Time (Cont.)	Analyzer Response
1		17		33	
2		18		34	
3		19		35	
4		20		36	
5		21		37	
6		22		38	
7		23		39	
8		24		40	
9		25		41	
10		26		42	
11		27		43	
12		28		44	
13		29		45	
14		30		46	
15		31		47	
16		32		48	

For 30-minute stability period: _____ maximum _____ minimum

For 15-minute stability period: _____ maximum _____ minimum

Maximum Deviation = $100 \times (\text{max.} - \text{min.}) / \text{span gas conc.} =$ _____

Stability Time _____

FIGURE 4.
CALIBRATION ERROR CHECK DATA SHEET

Emission Source _____

Emission Test Run Number(s) _____ Start Test Period _____

Stop Test Period _____

Date _____

Analyst _____

Analyzer Manufacturer/Model No. _____

Analyzer Serial Number _____

Pretest Calibration Error Check Results:

Initial NO cell temperature _____

Channel	Zero Gas Conc.	Zero Response	Zero Error (%)	Span Gas Conc.	Span Response	Span Error (%)
NO						
NO ₂						
CO						
O ₂						

Post Test Calibration Error Check Results:

Final NO cell temperature _____

Channel	Zero Gas Conc.	Zero Response	Zero Error (%)	Span Gas Conc.	Span Response	Span Error (%)
NO						
NO ₂						
CO						
O ₂						