Guidance for Portable Electrochemical Analyzer Testing Used for Compliance Monitoring

Section I. Introduction

DEQ’s Air Quality Division administers the provisions of 40 CFR Part 70 as well as the minor source permitting program, and issues Part 70 source permits, minor source permits and applicability determinations. The permits issued by DEQ impose emission limitations and restrictions on operations to ensure that the National Ambient Air Quality Standards (NAAQS) are not violated. All Part 70 permits and most other permits require periodic source compliance monitoring tests to assure continuing compliance with the emissions limitations. Portable electrochemical (EC) analyzer testing has been used to comply with these monitoring requirements. Pursuant to Air Quality rules at Oklahoma Administrative Code (OAC) 252:100-43-2, “[a]ll testing and monitoring shall be conducted in accordance with the methods described in this Subchapter.” This guidance was developed to ensure consistency in performing emissions testing and to provide a minimum level of quality assurance in determining results. It is not intended to replace the reference methods of 40 CFR Part 60, Appendix A, but rather to facilitate the measurement of emissions from sources that require periodic emission tests as part of their monitoring schedules. DEQ reserves the right to withdraw or modify this guidance without advance notice.

This guidance is applicable to the determination of oxides of nitrogen (NO and NO₂), carbon monoxide (CO), and oxygen (O₂) concentrations in controlled and uncontrolled emissions from combustion sources using fuels such as natural gas, propane, butane and fuel oils. A gas sample is extracted from a stack and is conveyed to an EC analyzer to determine the NO, NO₂, CO and O₂ gas concentrations. Additions to, or modifications of, vendor supplied EC analyzers (e.g., heated sample lines, thermocouples, flow meters, etc.) may be required to meet the specifications indicated in this guidance. The instrument and EC cell design determine the analytical range (span) for each gas component. The minimum detectable limit depends on the span and resolution of the EC cell and the signal to noise ratio of the measurement system.

Section II. EC Analyzer Apparatus

A. Any measurement system that meets the performance and design specifications of this guidance can be used. The sampling system should maintain the gas sample at conditions that limit condensation in the lines or when it contacts the EC cells. A diagram of an acceptable measurement system is shown in Figure 1. Some of the components of the measurement system are described below.
B. The sample probe and sample line should be made of glass, stainless steel, or other non-reactive material and should be designed to limit condensation.

C. The calibration assembly should introduce calibration gases to the sample probe at ambient pressure during calibration checks. The assembly should be designed such that only the calibration gases are processed and the calibration gases flow through all the filters in the sampling line.

D. The moisture removal system should be used to remove condensate from the sample gas while maintaining minimal contact between the condensate and the sample gases.

E. Particulate filters should be utilized before the inlet of the EC analyzer to prevent accumulation of particulate material in the measurement system and to extend the useful life of the EC analyzer. All filters should be made of materials that are non-reactive to the gases being sampled.

F. The sample pump should be a leak-free pump that will transport the sample gas to the system at a flow rate sufficient to minimize the response time of the measurement system. If the pump is upstream of the EC cells, the pump should be constructed of material that is non-reactive to the gases being sampled.

G. The sample flow rate should not vary by more than 10% throughout the calibration, testing, and drift check.

H. Interference gas scrubbers should be checked and replenished in accordance with the manufacturer’s recommendations. EC analyzers should have a means to determine when the agent is depleted.

I. A data recorder should be used for recording the EC analyzer data.

Section III. EC Analyzer Calibration and Testing Specifications

A. Except for an initial compliance test, all combustion equipment shall be tested “as-found.” No tuning or maintenance for the purpose of lowering tested emissions is allowed within 24 hours prior to testing. If tests are conducted before and after maintenance, the test results should be recorded and made available for review.

B. Each EC analyzer should be certified by the manufacturer at least once per year unless waived by DEQ. Assemble the measurement system by following the manufacturer’s recommended procedures for preparing and preconditioning the EC analyzer. Ensure the system has no leaks and verify that the gas-scrubbing agent is not depleted. When an EC cell is replaced, the EC analyzer should be re-calibrated.

C. Calibration of the EC analyzer should be done using certified calibration gases (EPA Protocol gases). Fresh air, free from ambient CO and NOx, is permitted for O2 calibration (20.9% O2), and as a zero gas
for CO and NO\textsubscript{x}. Calibration gases for NO, NO\textsubscript{2}, and CO should be chosen so that the concentration of the calibration gas is between 20\% and 125\% of the range of concentrations of the EC analyzer cell for each pollutant. Alternatively, calibration gases should not exceed 200\% of the anticipated concentration expected from the emission unit being tested. If the measured concentration exceeds 125\% of the span of the EC analyzer, at any time during the sampling run, that test run should be considered invalid. For NO\textsubscript{2} concentrations below 10\% of the total NO\textsubscript{x} concentration, NO\textsubscript{2} does not have to be measured directly, and calibration of the EC analyzer for NO\textsubscript{2} is not required.

\textbf{D.} Individually inject each calibration gas into the EC analyzer and record the start time, response time (the time it takes for the EC analyzer to get a steady response from a calibration gas after injecting the calibration gas into the measurement system), and concentrations. Gases should be injected through the entire sample handling system. All EC analyzer output responses should be recorded at least once per minute. Actual measurements should not be averaged until after the response time of the measurement system. After each calibration gas run, the EC analyzer should be refreshed with fresh air, free from CO, NO\textsubscript{x}, and other pollutants. Repeat these steps for each calibration gas.

\textbf{E.} For the EC analyzer O\textsubscript{2} cell calibration, the minimum detectable limit should be 0.3\%. For the EC analyzer NO\textsubscript{x} and CO cells, the minimum detectable limit should be 2\% of the calibration gas or 2 parts per million (ppm), whichever is less restrictive. If an invalid calibration is exhibited, corrective action should be taken, and the EC analyzer calibration check should be repeated until an acceptable EC analyzer performance is achieved.

\textbf{F.} Calculate the mean of the readings from the EC analyzer for each calibration gas. The average calculated EC analyzer response error for each calibration gas should not exceed ±5\% of the calibration gas concentration. The maximum allowable deviation of any single reading, after the response time and prior to the refresh period, should not exceed ±2\% of the average calculated EC analyzer response.

For example, for a calibration gas with a concentration of 100 ppm, the calibration gas check should be considered valid only if 1) the average of the measured concentrations for that calibration gas are within 5 ppm of 100 ppm, i.e., 95 to 105 ppm, and 2) the maximum deviation of any single measurement comprising that average is less than 2\% or approximately 2 ppm.

\textbf{G.} During calibration an interference check should be performed. During the calibration check of a single gas species (e.g., NO & NO\textsubscript{2}), record the response displayed by the other EC cells (i.e., CO & NO). Record the interference response for each EC cell to each calibration gas. The CO, NO, and NO\textsubscript{2} interference response should not exceed 5\% of the calibration gas concentration. EC analyzers that have been verified for interference response using an interference scrubber are considered to be in compliance with this interference check specification when the interference scrubber is replenished per the manufacturer’s specifications. The potential for interference from other flue gas constituents should be reviewed with the EC analyzer manufacturer based on site-specific data.

\textbf{H.} A post-test calibration check should be performed in the same manner as the pre-test calibration after each emission unit test. If the post-test calibration checks do not meet the required specifications, all test data for that emission unit should be considered invalid and re-calibration and re-testing should be conducted. To prevent loss of data, the drift of the analyzer should be determined after each measurement cycle. This should be done by performing a calibration check after each measurement cycle and determining the drift to ensure that it is still within the limit of ±5\%. No
changes to the sampling system or EC analyzer calibration should be made until all of the post-test calibration checks have been recorded. The difference (% Drift) between the pre-test calibration and the post-test calibration should not exceed 5% for each pollutant.

Section IV. Emissions Measurements

A. Field testing should be conducted by personnel trained in the use of the specific EC analyzer used for the testing. Samples of pollutant concentrations should be taken from sample ports in the stack or using a “Shepard’s hook” from a location in the stack such that a representative concentration is measured and bias (e.g., air leakage at weep holes) is prevented. A single sampling location near the center of the duct may be selected.

B. Prior to sample collection, ensure that the pre-test calibration was performed. Zero the EC analyzer with fresh air, free from ambient CO and NO\textsubscript{x} or other combustion gases. Each test for an emission unit should consist of at least three 15-minute measurement cycles. Position the probe at the sampling point and begin the measurement cycle at the same flow rate used during the calibration check. Measurements should not be recorded and averaged until the measurement system response time has passed. The EC analyzer should be “refreshed,” the analyzer drift should be determined, and the moisture collection system emptied after each sampling cycle. Use the measurement data to calculate the mean effluent concentration. Record the average gas sample concentration for each pollutant from the cycle on a form similar to the one provided.

C. Conduct the post-test calibration check after testing of each emission unit. If the sampling system is disassembled or if the EC analyzer calibration is adjusted, the EC analyzer should be recalibrated before conducting the next emission unit test.

D. The emissions testing should produce at least three sets of concentration data for each pollutant of concern. Results from each test represent a quasi-steady-state measurement of pollutant concentration and the measured pollutant concentrations should be calculated as the mean gas concentration using the emissions data collected during the three test runs. Data from additional tests may be included in the calculation so long as other operational parameters remain relatively unchanged.

E. The measured pollutant concentrations should then be corrected to give actual values using the pre-test calibration and post-test calibration results. The following equation should be used.

\[
C_{\text{ACTUAL}} = (C_{\text{MEAS}} - C_{\text{CZ}}) \times \frac{(C_{\text{CAL}} - C_{\text{CZ}})}{(C_{\text{CM}} - C_{\text{CZ}})}
\]

Where:

- \(C_{\text{ACTUAL}}\) = actual pollutant concentration, parts per million dry volume (ppmdv)
- \(C_{\text{MEAS}}\) = measured pollutant concentration, ppmdv
- \(C_{\text{CAL}}\) = concentration of the calibration gas, parts per million by volume (ppmv)
- \(C_{\text{CZ}}\) = average of pre-test and post-test calibration zero checks, ppmdv
- \(C_{\text{CM}}\) = average of pre-test and post-test measured concentrations of the calibration gas measurement checks, ppmdv

Section V. Operational Parameter Measurements

Emissions testing results, i.e., NO\textsubscript{x}, CO, and O\textsubscript{2} concentrations (ppmv), are typically used in conjunction with stack flow to determine compliance with a permitted emission limit (lb/hr). Other specific parameters may also need to be documented. The results of any
measurements or calculated parameters should also be recorded on a form similar to the one provided in Appendix A.

A. During the emissions testing of the emission unit, the following operational parameters should be measured or determined:
   1. engine/turbine load and speed (RPM) or power (HP);
   2. fuel BTU content (BTU/SCF); and
   3. fuel consumption (SCFH).

B. Sampling of the fuel, that is representative of the fuel combusted in the emission unit, should be performed. The fuel sampling should be conducted within a calendar quarter of the testing. The sampling should determine the C1 to C6+ composition and BTU content. The sample should be taken from the inlet gas line downstream from any inlet separator, and obtained using a manifold to remove entrained liquids from the sample and a probe to collect the sample from the center of the gas line. GPA standard method 2166 (or similar method) should be used. Emission units utilizing “commercial-grade natural gas” are exempt from the fuel sampling requirements.

C. During emissions testing, the stack velocity (or flow) shall be measured or determined using one of the following methods:
   1. EPA Reference Method 2;
   2. EPA Reference Method 19; or
   3. an equivalent method, as approved by DEQ.

Section VI. Calculations

As mentioned previously, emissions testing results, i.e., NOₓ, CO, and O₂ concentrations, are typically used in conjunction with other measured parameters to determine compliance with a permitted emission limit. The following issues should be considered in documenting compliance with the various criteria.

A. Calculation of the emissions (lb/hr) to show compliance with the permitted emission limits should be calculated as the corrected mean concentration multiplied by the stack flow corrected to zero percent oxygen.

\[
E_{\text{MEAS}} = C_{\text{ACTUAL}} \times Q_{\text{STACK}} \times \left( \frac{\text{MWp}}{385.4} \right) \times 1 \times 10^{-6}
\]

Where:
- \(E_{\text{MEAS}}\) = the measured emissions from the emission unit at standard conditions and 0% O₂, lb/hr;
- \(C_{\text{ACTUAL}}\) = average actual pollutant concentration, ppmdv;
- \(Q_{\text{STACK}}\) = stack flow of the emission unit, DSCFH @ 0% O₂;
- \(\text{MWp}\) = molecular weight of the pollutant, lb/lb-mole:
  - = 46 lb/lb-mole for NOₓ (as NO₂);
  - = 28 lb/lb-mole for CO.

For an Ideal Gas at EPA standard conditions: 20 °C (68 °F) and 1 atm (760 mm); there are 385.4 SCF/lb-mole. The factor of (1E-6) is used to convert ppmvd to a fraction.

B. Calculation of the flow (QSTACK, DSCFH) from the emission unit using the calculations provided in Reference Method 19 is shown below. The stack flow should be corrected to zero percent oxygen.

\[
Q_{\text{STACK}} = Q_{\text{FUEL}} \times F_{\text{BTU}} \times F_{D} \times \left( \frac{20.9\% - %O_{\text{2MEAS}}}{100} \right) \times 1 \times 10^{-6}
\]

Where:
- \(Q_{\text{STACK}}\) = stack flow of the emission unit, DSCFH @ 0% O₂;
- \(Q_{\text{FUEL}}\) = flow of the fuel to the emission unit, SCFH;
- \(F_{\text{BTU}}\) = gas heating value, HHV, (from fuel analysis), BTU/SCF;
- \(F_{D}\) = stack flow per unit of heat input, SCF/MMBTU;
- %O₂MEAS = measured oxygen concentration, % dry basis.

20.9% is the concentration of O₂ in the air. The factor of (1E-6) is used to convert BTU to MMBTU.
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Section VII. Recordkeeping Requirements

A. Each company performing portable EC analyzer analyses shall develop and maintain a testing protocol. These protocols shall be made available for review by DEQ. Each protocol should also contain the following elements:

1. information regarding the EC analyzer including, but not limited to, a copy of the make, model, serial number, and manufacturer’s EC analyzer specifications,
2. EC analyzer certification documentation,
3. documentation of the EC analyzer operator’s training, experience, and other qualifications.

B. A report of each test shall be prepared. Each report should contain the following items:

1. date, place, and time of test, company or entity performing the test, and signature of person conducting the test,
2. manufacturer, model, serial number, and emission unit ID (as listed in an applicable permit) of the emission unit tested,
3. emission unit rating (horsepower and RPM) and control device utilized, if applicable,
4. applicable permit emissions limitations, e.g., lb/hr,
5. EC analyzer calibration records: start times, response times, end times, measured concentrations, interference responses, calibration gas concentrations, percent error, and minimum detectable limit,
6. the testing records: start times, end times, duration test runs, measured concentrations, average concentrations, and corrected concentrations,
7. emission unit load (service power) and speed or power during testing. The method of determining the service power for engines and turbines should be described or shown,
8. emission unit fuel consumption, fuel BTU analysis, and stack flow,
9. copies of the strip chart recording or computer or digital recording of actual measurements taken during the calibration and testing,
10. calculated emissions on a lb/hr basis for the emission unit.

C. All testing records shall be maintained for a period of five years for major sources and a period of two years for all other sources, unless an applicable permit specifies a longer period.

Section VIII. Reporting Requirements

A. The person performing emissions testing should promptly report the results of such tests to the permittee so that any notifications required by an applicable regulation or permit condition can be submitted in a timely manner.

B. Testing results that show emissions exceeding those allowed in an applicable permit shall be reported as provided in the permit, and in accordance with OAC 252:100-9, Excess Emission Reporting Requirements.

C. A copy of the testing protocol shall be submitted to DEQ and updated as necessary.

Section IX. References


## Appendix A

Emission Unit Test Results

Company: _____________________________ Facility: _____________________________

Source Tested: ________________________ Date: ________________________________

Source Manufacturer/Model #:_____________ Source Serial #:____________________

Site Rated Horsepower:__________________ Load During Test: ____________________

Analyst: :______________________________ Type of Control: ______________________

Analyzer Manufacturer/Model #:___________ Analyzer Serial #:_____________________

### Calibration Measurements

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<th>Post-Test Calibration</th>
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<td>CO</td>
<td>NO</td>
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<tr>
<td>Run #1</td>
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<tr>
<td>Zero Resp., ppmdv/%</td>
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<tr>
<td>Interference Resp., ppmdv/%</td>
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<td>Min. Det. Resp., ppmdv/%</td>
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<td>Start Time</td>
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<td>Response Time</td>
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<td>End Time</td>
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<tr>
<td>Avg. Conc., ppmdv/%</td>
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<tr>
<td>Cal. Gas Conc., ppmdv</td>
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<tr>
<td>Conc. Difference, ppmdv</td>
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<tr>
<td>Calibration Error, %</td>
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<tr>
<td>% Interference, %</td>
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<tr>
<td>Diff. Pre &amp; Post Test, ppmdv</td>
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<tr>
<td>%Drift, %</td>
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Interference Response should only be recorded as required for NO and NO2 interference for CO and NO2 for NO.
### Emission Measurements

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<td><strong>End Time</strong></td>
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<tr>
<td><strong>Run Duration</strong></td>
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<tr>
<td><strong>Avg. Conc., ppmvd/%</strong></td>
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<td><strong>Cal. Drift Check, ppmvd/%</strong></td>
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<td><strong>%Drift</strong></td>
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<td><strong>Run Duration</strong></td>
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<td><strong>Avg. Conc., ppmvd/%</strong></td>
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### Testing Results

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<tr>
<th></th>
<th>CO</th>
<th>NO</th>
<th>NO2</th>
<th>% O2</th>
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<tr>
<td>Average Conc., ppmvd/%</td>
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<td>Cal. Conc. Diff., ppmvd</td>
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<tr>
<td>Corrected Conc., ppmvd</td>
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### Engine Parameters

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<tr>
<td><strong>Eng. Speed/Power, rpm/hp</strong></td>
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<tr>
<td><strong>Fuel Flow, SCFH</strong></td>
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<td><strong>Fuel BTU Content, BTU/SCF</strong></td>
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<td><strong>Fd, SCF/MMBTU</strong></td>
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<td><strong>Calc. Stack Flow, SCFH</strong></td>
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<td><strong>Avg. % O2, %</strong></td>
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<td><strong>Stack Flow at 0% O2, SCFH</strong></td>
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### Calculated Emissions and Limits

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<td><strong>Stack Flow, SCFH</strong></td>
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<td>46</td>
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<td><strong>Calc. Emissions, lb/hr</strong></td>
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<tr>
<td><strong>Permit Limits, lb/hr</strong></td>
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**CERTIFICATION:** Based on information and belief formed after reasonable inquiry, I certify that the statements and information contained in this report are true, accurate, complete and representative of the emissions from this source.

Print Name
Signature
Date
Title