

**Other Test Method 47 (OTM-47) Measurement of Ethylene Oxide Emissions from Stationary Sources by Cavity Ring-Down Spectroscopy****Background on OTM-47**

This method was submitted by CleanAir Engineering to the EPA's Office of Air Quality, Planning and Standards, Air Quality Assessment Division, Measurement Technology Group (MTG) for 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>. **The posting of a test method on the Other Test Methods 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 Other Test Methods portion of the EMC website is to promote discussion of developing emission measurement methodologies and to provide potentially helpful tools to regulatory agencies, the regulated community, and the public at large.

The method was submitted to the EPA as part of a site-specific alternative test method request to conduct performance testing at a commercial sterilizer subject to 40 CFR Part 63, Subpart O using a Cavity Ring-Down Spectroscopy (CRDS) Instrument. The alternative test method request also included a Method 301 (40 CFR Part 63, Appendix A) evaluation, per the requirements in §63.7(f)(2), demonstrating equivalence with an existing reference approach for this rule, and the results of this evaluation are summarized in Section 17 of this method. EPA does not have enough information on the performance of this method to approve its use broadly at this time, however, will consider its use on a site-specific basis. To use this method for any relevant NSPS or NESHAP standard, you must submit the request to the Group Leader, Measurement Technology Group, U.S. Environmental Protection Agency, E143-02, Research Triangle Park, NC 27711. EPA has developed a guideline for those seeking these approvals which can be found at <https://www.epa.gov/system/files/documents/2022-09/gd-022r5.pdf>.

OTM 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. OTMs may also be used to collect data for the purposes of developing or assisting in the development of national standards of performance and national emission standards for hazardous pollutants under sections 111 and/or 112, respectively, of the Clean Air Act as specified in the applicable Information Collection Requests(s) and can be considered for use as alternative methods to meet Federal requirements under 40 CFR Parts 60, 61, and 63. These methods are available for application without EPA oversight for other non-EPA program uses including state permitting programs and scientific and engineering applications. 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 – 03/23/2023

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

## **Other Test Method 47 (OTM-47) Measurement of Ethylene Oxide Emissions from Stationary Sources by Cavity Ring-Down Spectroscopy (CRDS)**

### *1.0 Scope and Application.*

1.1 *Scope.* OTM-47 is a performance-based method for measuring vapor phase emissions from stationary sources using a cavity ring-down spectroscopy (CRDS) analyzer. Quality assurance (QA) and quality control (QC) requirements are included to assure that data generated by this method is of known quality. Requirements to ensure consistent QA/QC for equipment, supplies, sample collection, as well as calculations and data analysis are included within this method

This method requires knowledge of the following EPA test methods, found in 40 CFR Part 60, Appendix A:

- a) Method 1 – Sample and Velocity Traverses for Stationary Sources
- b) Method 7E – Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)
- c) Method 25A – Determination of Total Gaseous Organic Concentration using a Flame Ionization Analyzer

1.2 *Application.* This method is used to quantify ethylene oxide concentrations within a stationary source gas matrix to evaluate compliance with applicable emissions standards or to conduct performance testing of a Ethylene Oxide Continuous Emission Monitoring System (CEMS). Measurements are generated via CRDS analysis using specific wavelengths of interest in the infrared (IR) spectroscopic region. Samples are collected and analyzed by instrumentation software for measurement and the assessment of data quality.

1.2.1 *Analytes.* Target analytes are specific to the instrument that collects the measurements. The instrumentation analyzes defined wavelength regions in the IR for each analyte of interest. Performance metrics within this method must be met to validate the test results.

1.2.2 *Method Range and Sensitivity.* The analytical range and sensitivity of measurements are dependent on analyte absorptivity, instrument configuration, data collection parameters, and the gas matrix. Instrument factors include ring-down times, absorption path length, laser signal, among others, and additional metrics which may be specific to each instrument's make and model.

1.2.3 *Data Quality Objectives (DQO).* OTM-47 is designed to provide data of known quality for determining compliance with applicable emission standards and for relative accuracy test audits (RATAs) of facility CEMS. The principal objective is to ensure the accuracy of the data at the actual emission levels encountered. To meet this objective, the use of EPA traceability protocol calibration gases and measurement system performance tests are required.

2.0 *Summary of Method.* A sample from the effluent is continuously extracted and directed to the CRDS analyzer for measuring the concentration of the target analyte(s). Method

performance requirements, including site-specific detection limit (SADL) determination, must be met to validate test data.

### 3.0 *Definitions*

3.1 *Analyte or Target Analyte.* Primary component of interest in the CRDS analysis.

3.2 *Analyzer Calibration Error.* For non-dilution systems, this is the difference between the manufacturer-certified concentration of calibration gas and the measured concentration of the same gas which has been introduced to the analyzer in direct calibration mode.

3.3 *Calibration Curve.* The relationship between an analyzer's measured response and the actual concentrations of those gases.

3.4 *Calibration Gas.* A gas mixture containing the primary target analyte at a known concentration and produced and certified in accordance with "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards," May 2012 or most recent update. The tests for analyzer calibration error, drift, and system bias require the use of calibration gases prepared according to this protocol, if available. If a zero gas is used for the low-level gas, it must meet the requirements under the definition of "zero air material" in 40 CFR 72.2 in place of being prepared by the traceability protocol.

3.4.1 *Low-Level Gas.* A calibration gas less than 20 percent of the calibration span and may be a zero gas.

3.4.2 *Mid-Level Gas.* A calibration gas which is 40 to 60 percent of the calibration span.

3.4.3 *High-Level Gas.* A calibration gas which is equal to the calibration span.

3.4.4 *Upscale Gas.* A calibration gas, either the mid- or high-level, which is used during system bias checks.

3.5 *Calibration Span.* Calibration Span means the upper limit of the analyzer's calibration that is set by the choice of high-level calibration gas. No valid run average concentration may exceed the calibration span. To the extent practicable, the measured emissions should be between 20 to 100 percent of the selected calibration span. This may not be practicable in some cases of low concentration measurements or testing for compliance with an emission limit when emissions are substantially less than the limit. In such cases, calibration spans that are practicable to achieving the data quality objectives without being excessively high should be chosen.

3.6 *Cavity / Cavity Cell.* Cavity within the CRDS analyzer that is maintained at a specific pressure and temperature with optical components to allow the laser to pass through the sample to the detector.

3.7 *Centroidal Area.* The central area of the source which is no greater than 1 percent of the source cross section. This area has the same geometric shape as the source.

- 3.8 *CRDS Gas Analyzer.* Instrument that uses the CRDS gas measurement technique to analyze the sample and generate an output proportional to its concentration.
- 3.9 *Data Recorder.* Equipment that permanently records the concentrations reported by the analyzer. This may be analyzer-specific software that accompanies the instrument or a data acquisition system (DAS).
- 3.10 *Dilution Factor (DF).* The ratio of the standard addition (SA) calibration gas flow rate ( $Q_{\text{spike}}$ ) to the CRDS system sampling rate ( $Q_{\text{total}}$ ) expressed as a percentage.
- 3.11 *Direct Calibration Mode.* Mode where calibration gases are directly introduced into the analyzer (or into the assembled measurement system at a point downstream of all sample conditioning equipment) according to the manufacturer's recommended calibration procedure. This mode of calibration applies to non-dilution-type measurement systems.
- 3.12 *Drift.* The difference between pre- and post-test system bias (or calibration error) results at a specific calibration gas concentration level (i.e., low-, mid-, or high-).
- 3.13 *Effective Spike Dilution (ESA).* This is the expected increase in the measured concentration of the target analyte as a result of standard addition (SA) gas injections to the CRDS sampling system.
- 3.14 *Independent Measurement(s).* An independent measurement requires separation of at least two times the response time (RT) between valid readings.
- 3.15 *Interference Check.* The test to detect analyzer responses to compounds other than the compound of interest, usually a gas present in the measured stream, which is not adequately accounted for in the calibration procedure and may cause measurement bias.
- 3.16 *Limit of Detection (LOD).* The lowest level of the target analyte's concentration which the analyzer can detect in the presence of the sample gas matrix interferences with 99 percent confidence.
- 3.17 *Measurement System.* All the equipment used to determine the target analyte's concentration. The measurement system is comprised of the following major subsystems: sample acquisition, sample transport, sample conditioning (optional), calibration gas manifold, CRDS analyzer, and data recorder.
- 3.18 *Minimum Detection Limit (MDL).* The lower limit of detection for the CRDS analyzer and is generally calculated as three times the standard deviation of at least eight points at the averaging interval of the measurements.
- 3.19 *Native, or Native Concentration.* The un-spiked concentration of the target analyte within the source gas matrix.

3.20 *Response Time*. The time necessary for the measurement system to respond to a change in gas concentration at the sampling point when the system is operating normally and at the target sample flow rate or dilution ratio.

3.21 *Run*. A pre-determined time during which a series of gas samples are taken from the source.

3.22 *Sample Analysis*. Process of interpreting sample to obtain analyte concentrations. This must be automated using a software routine and verified through the calibration procedures outlined in this method.

3.23 *Sample Interval*. Defined as the programmed reporting interval of the DAS which collates CRDS measurement averages for reporting.

3.24 *Stable value*. The measure of two or more values which are statistically the same and the absence of measurement system drift.

3.25 *Standard Addition (SA)*. Also referred to as dynamic spiking, this is the addition of known amounts of the target analyte (either statistically or dynamically) to the actual measurement path or measured sample matrix to assess the performance of the measurement system in the presence of potential interference from the sample gas matrix.

3.26 *Standard Addition Detection Level (SADL)*. Also referred as the site-specific detection limit is the in-stack detection limit as determined using the standard addition response (SAR) procedure.

3.27 *Standard Addition Response (SAR)*. This is the detected, or measured, amount of the target analyte addition to the sampling system.

3.28 *System Bias*. The difference between a calibration gas measured in direct calibration mode and system calibration mode. System bias is determined before and after each run at the low- (or zero gas) and either the mid- or high-concentration levels. For dilution-type systems, pre- and post-run system calibration error is measured rather than system bias.

3.29 *System Calibration Error*. Applies to dilution-type systems and is the difference between the measured concentration of low-, mid-, or high-level calibration gas and the certified concentration for each gas when introduced in system calibration mode. For dilution-type systems, a 3-point system calibration error test is conducted instead of the analyzer calibration error test, and 2-point system calibration error tests are conducted instead of system bias tests.

3.30 *System Calibration Mode*. Introduction of the calibration gases into the measurement system at the probe (upstream of the filter and all sample conditioning components).

3.31 *Test*. A series of runs.

#### 4.0 Interferences

Interferences may vary among instruments and instrument-specific interferences must be evaluated through the interference test procedures. Primary interferences are divided into two classifications: analytical and sampling.

4.1 *Analytical Interferences.* An analytical interference complicates or prevents the analysis of a target analyte. Analytical interferences may vary from instrument to instrument and pre-test performance validation must be completed along with instrument-specific interference tests. Common interferences may include water vapor and carbon dioxide since both compounds have strong IR absorption relative to other analytes within the gas matrix. The overall impact of interferences includes interferant concentrations, target concentrations, and potential spectral overlap. An analytical interference complicates or prevents the analysis of a target analyte. Analytical interferences may vary from instrument to instrument and pre-test performance validation must be completed along with instrument-specific interference tests. Common interferences may include water vapor and carbon dioxide since both compounds have strong IR absorption relative to other analytes within the gas matrix. The overall impact of interferences includes interferant concentrations, target concentrations, and potential spectral overlap.

4.2 *Sampling System Interferences.* Interferences within the sampling system prevent or impair target analytes from reaching the instrument. Analyte spiking is designed to measure potential sampling system interferences. Common interferences include sample temperature, reactive analytes, sample materials, and moisture.

4.2.1 *Sample Temperature.* A temperature below the dewpoint of the sample gas causes condensation of analytes and/or water vapor. Therefore, the temperature of the source and sampling system materials are evaluated to ensure the proper transport of samples from the source to the instrument.

4.2.2 *Reactive Analytes.* Analyte-specific reactions may occur within the sampling system due to polymerization, adsorption/desorption effects, or gas matrix interferences.

4.2.3 *Sample Materials.* Probe and sample line materials must be evaluated for the target analyte. For example, HF reacts with glass components.

4.2.4 *Moisture.* While moisture is an analytical interference, it can also act as a sampling system interference as condensed moisture removes soluble compounds.

## 5.0 Safety

This method may require work with hazardous materials and in hazardous conditions, like those associated with other stack sampling methods and procedures. It is encouraged for the user to establish safety procedures before using this method. Among other precautions, the tester should become familiar with the safety recommendations in the gas analyzer's user manual. Leak checks of the sampling system, proper exhaust ventilation, and safe gas cylinder handling are only a few ways to mitigate exposure to harmful compounds.

Exposure to suspected carcinogens or other compounds with serious health risks should be avoided in all circumstances. Refer to the safety data sheet (SDS) of each specific compound for safe handling instructions.

This method does not address all potential safety risks associated with its operation. All individuals performing this method must follow safety and health practices consistent with applicable legal requirements and prudent practices for each application.

## 6.0 *Equipment and Supplies*

6.1 *Sample Probe.* An appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes, and transport analytes to the CRDS analyzer. Special materials or configurations may be required in some applications. For example, high sample temperatures may require cooling probes while high moisture or analyte concentrations may require a sample dilution system.

6.2 *Particulate Filter.* A filter shall be connected to the outlet of the heated probe within a heated volume, as needed. The filter should be rated for 99 percent removal efficiency at 1-micron. Filter material should be selected based on the gas matrix and target analyte.

6.3 *Sample Line.* A sample line of sufficient length and material shall be connected to the exit of the heated filter and connected to the CRDS analyzer or gas manifold. The sample line must be heated to prevent condensation or polymerization of materials within the line and should be constructed of a material that is inert to and does not adsorb the target analyte(s).

6.4 *Heating System.* The heating system for the probe, filter, sample line, and potential ancillary system components shall be capable of heating the sample to prevent condensation within the line during sample transport.

6.5 *Gas Distribution Manifold.* A heated gas distribution manifold, if necessary, should allow the operator to control the flow of gas standards or samples directly to the CRDS analyzer or sampling system.

6.6 *Calibration Assembly.* A calibration assembly must be in place upstream of the heated filter to introduce direct gas cylinder challenges or dynamic spikes through the sampling system.

6.7 *Dilution Manifold.* In some cases, a dilution system may be necessary due to high source concentrations.

6.8 *Mass Flow Meter (MFM) or Mass Flow Controller (MFC).* All mass flow meters, or mass flow controllers shall be calibrated in the appropriate range of use and be accurate to at least  $\pm 2$  percent of the flow meter span.

6.9 *Gas Cylinder Regulators and Tubing.* The gas cylinder regulator and tubing to transport the gas to the CRDS system should be appropriate for the individual gas standards utilized.

6.10 *Rotameter.* Rotameters may be used to send calibration gases through the sampling system. Ranges may be 0-1 LPM, 0-5 LPM, 0-10 LPM, or another appropriate range. This

meter need not be calibrated.

6.11 *CRDS Analytical System.* All the equipment used, including a CRDS analyzer, to continuously measure the target analyte(s) from the proposed gas matrix within the required detection limit. The measurement system comprises six major subsystems: Sample acquisition, sample transport, calibration gas manifold, gas analyzer, and data recorder. All subsystems which come into contact with the sample gas must be operated at sufficiently high temperatures to avoid condensation prior to the CRDS gas analyzer.

6.12 *CRDS Cavity Pump.* Must be of sufficient rating to maintain system vacuum and flow rates.

6.13 *Absolute Pressure Gauge.* A pressure gauge must be included within the analyzer to measure the pressure of the cavity.

6.14 *Temperature Gauge.* Capable of measuring the cavity temperatures to within  $\pm 2^{\circ}\text{C}$ .

## 7.0 *Reagents and Standards*

### 7.1 *Calibration Gas.*

7.1.1 *High-Level Gas.* A calibration gas concentration that is equal to the instrument's calibration span value. To the extent practical, this gas should be selected to achieve the upper limit of the expected highest concentration or 2.5 times the emission limit (concentration equivalent).

7.1.2 *Mid-Level Gas.* A calibration gas concentration that is 40 to 60 percent of the calibration span.

7.1.3 *Low-Level Gas.* A calibration gas concentration which is less than 20 percent of the calibration span. This may be a zero gas.

7.1.4 *Standard Addition Gas.* Note that this gas may be the high- or mid-level gas used for bias checks and/or SADL determination tests. The target analyte concentration should allow for a dynamic spike addition of 50 to 150 percent of the anticipated source concentration or the applicable standard while diluting the sample by no more than 20% ( $DF \leq 20\%$ ). At a minimum, the spike gas shall introduce at least 3 times the system LOD for recovery evaluations. Appropriate mass flow controllers or a predefined tracer gas may be used to determine the dynamic spike dilution factor.

7.2 *Interference Check Gases.* Interference checks are performed to identify gases in the sample gas that can potentially interfere with the measurement. The interference gas(es) used in the check may be selected based on the process or by the instrument manufacturer. At a minimum, water vapor interference tests must be conducted to bracket known sample conditions and additional interference gases may include carbon dioxide and methane.

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



## 8.1 *Sample Site & Point Selection*

8.1.1 Unless otherwise specified in an applicable regulation or by the Administrator, when this method is used to determine compliance with an emission standard, a stratification test must be conducted per Section 8.1.2 to determine the sample traverse points used for the test. For CEMS performance testing, follow the sampling site selection and traverse point layout procedures described in the appropriate performance specification or applicable regulation.

8.1.2 *Stratification Test.* A stratification test must be performed at each site prior to the start of a test to determine the appropriate number of sample points. If multiple pollutants or diluents are tested concurrently at the same site, the analysis of a single pollutant or diluent will satisfy this requirement. A stratification test is not required for stacks less than 4 inches in diameter.

A probe of sufficient length must be used to measure concentrations from either:

- a) 12 points located according to Table 1-1 or Table 1-2 of EPA Method 1 (40 CFR Part 60, Appendix A), or
- b) 3 points along a line passing through the centroidal area at 16.7, 50.0, and 83.3 percent of the measurement line length.

Sample for a minimum of twice the system response time (see Section 8.2.6) at each traverse point and calculate individual point and mean concentrations of the stratification compound. If the concentrations at each point differ from the mean concentration by no more than  $\pm 5.0$  percent of the mean or  $\pm 0.5$  ppm (whichever is less restrictive), the gas stream is considered unstratified, and the tester may collect samples from a single point that most closely matches the mean. If this criterion is not met but the concentration at each point differs from the mean for all points by  $\pm 10$  percent of the mean or  $\pm 1.0$  ppm (whichever is less restrictive), the gas stream is considered minimally stratified, and the tester may collect samples from three points at 16.7, 50.0 and 83.3 percent of the source diameter along the measurement line. If the gas stream is found to be stratified, locate 12 traverse points for the test in accordance with Table 1-1 or Table 1-2 of EPA Method 1 (40 CFR Part 60, Appendix A).

## 8.2 *Pre-Test Measurement System Performance*

8.2.1 *Calibration Gas Verification.* Obtain a certificate from the gas manufacturer to document the quality of the gas. Confirm this certification is complete and current (not expired). This documentation should be available on-site for inspection upon request.

8.2.2 *Measurement System Preparation.* Assemble, prepare, and precondition the measurement system according to standard operating procedures and analyzer specifications. Adjust the system to achieve the correct sampling rate or dilution ratio, if applicable.

8.2.3 *Calibration Error Test.* Conduct a 3-point calibration error test, before the first run and again after any failed drift or bias tests, or a failed 2-point system calibration error test for dilution systems. Introduce the low-, mid-, and high-level calibration gases sequentially. For non-dilution systems, gases are introduced in direct calibration mode. For dilution-type measurement systems, the gases are introduced in system calibration mode.

8.2.3.1 For non-dilution systems, the tester may adjust the system to maintain the correct flow rate at the analyzer during the test, but the tester may not make adjustments for any other purpose.

For dilution-type systems, the tester must operate the measurement system at the appropriate dilution ratio during all system calibration error checks and may make only the adjustments necessary to maintain this ratio.

8.2.3.2 Record the analyzer response to each calibration gas in tabular format to evaluate the certified value, measured value, absolute difference, and error. The error is calculated per Equation 47-1 in Section 12.2 or the system calibration error using Equation 47-3 in Section 12.4, if applicable. The calibration error specification from Section 13.1 must be met for low-, mid-, and high-level gases. If the calibration error specification is not met, take corrective action and repeat this process until an acceptable calibration error is achieved. Low-, mid- and high-level direct checks and system checks must meet QA/QC requirements without any corrections or the direct calibration procedures must be repeated until satisfactory results are obtained.

8.2.4 *Dynamic Spiking.* Prior to, during or after sampling begins, you must verify the measurement approach is appropriate for the source type by completing a series of dynamic spikes, following the procedure and requirements in Section 13.5 of this method.

8.2.5 *System Bias Check.* Before sampling begins, determine whether the mid- or high-level calibration gas best matches the approximate emissions and select this as the upscale gas.

8.2.5.1 Introduce the upscale gas at the probe, upstream of all sample conditioning components, in system calibration mode. Record the time it takes for the measured concentration to reach a value that is at least 95 percent of the expected value or  $\pm 0.25$  ppm (whichever is less restrictive) of a stable response for both the low-level and upscale gases. Continue to observe the gas concentration until it has reached a final, stable value and record the response.

*Note: Operate the measurement system at the normal sampling rate during all system bias checks and only make adjustments necessary to achieve proper calibration gas flow rates at the analyzer.*

8.2.5.2 Introduce the low-level gas in system calibration mode and record the elapsed time for the concentration response to decrease to a value within 5.0 percent or 0.25 ppm (whichever is less restrictive) of the certified low-range gas concentration. Identical to the upscale concentration, continue to observe the low-level concentration until it has reached a final, stable value and record the response.

8.2.5.3 From the recorded data, calculate the measurement system response time (Section 8.2.6) and calculate the initial system bias per Equation 47-2 in Section 12.3. For dilution systems, calculate the system calibration error in lieu of the system bias using Equation 47-3 in Section 12.4. See Section 13.2 for acceptable performance criteria regarding system bias and system calibration error. If the initial system bias (or system calibration error) specification is not met,

take corrective action and repeat the applicable calibration error or bias tests until acceptable results are achieved, after which sampling may begin.

*Note: For dilution systems, data from the 3-point system calibration error test described in Section 8.2.3 may be used to meet the initial 2-point system calibration error test requirements of this section, if the calibration gases were injected as described in this section, and if the response time data were recorded.*

**8.2.6 System Response Time Test.** This is determined during the initial system bias (or 2-point system calibration error) check by observing the time required to achieve 95 percent of a stable response for both the low-level and upscale gases. The longer interval between the two gas responses is the system response time.

**8.2.7 Interference Check.** Conduct an interference check of the CRDS analyzer prior to its initial use in the field. If there are multiple analyzers of the same make and model, the tester need only perform this alternative interference check on one analyzer. Interference check requirements may also be met if the instrument manufacturer performs this check in a controlled environment or a similar check on an analyzer of the same make and model provided that the results are sufficiently documented. In lieu of analyzer interference checks, a standard addition dynamic spike may be performed at each source to evaluate system performance in the presence of gas matrix interferences.

**8.2.7.1** Appropriate interference test gases which are potentially encountered during a test may be introduced into the analyzer separately or as mixtures. Test the analyzer with the interference gas alone at the highest concentration at a test source and again with the addition of the target analyte at a representative concentration, or series of concentrations. Record all data and document the total interference response during each condition. The specification in Section 13.4 must be met.

**8.2.7.2** A copy of this data, including the date completed with a signed certification, must be available for inspection at the test site and included with the test report. This interference test is valid for the life of the instrument unless major analytical components (e.g., the detector) are replaced with different model parts. If major components are replaced, the interference gas check must be repeated before returning the analyzer to service. The tester must ensure that any specific technology, equipment, or procedures that are intended to remove interference effects are operating properly during testing.

**8.3 Dilution-Type Systems – Special Considerations.** When a dilution-type measurement system is used, three important considerations must be considered to ensure quality emission data.

**8.3.1** First, the critical orifice size and dilution ratio must be properly selected so that the sample dew point will be below the sample line and analyzer temperatures.

8.3.2 Second, a high-quality, accurate probe controller must be used to maintain the dilution ratio during the test. The probe controller should be capable of monitoring the dilution air pressure, eductor vacuum, and sample flow rates.

8.3.3 Third, differences between the molecular weight of calibration gas mixtures and the stack gas must be addressed as these can affect the dilution ratio and introduce measurement bias.

#### 8.4 *Sample Collection*

8.4.1 Position the probe at the first sampling point and purge the system for at least two times the response time before recording any test data. Next, traverse all required sampling points at equal durations and appropriate flow rates (or dilution ratios, as applicable).

8.4.2 Each time the probe is removed from the stack and replaced the tester must recondition the sampling system for at least two times the system response time prior to the next recording. If the average of any run exceeds the calibration span value, that run is invalid.

8.4.3 The tester may satisfy the multipoint traverse requirement by sampling sequentially using a single-hole probe or a multi-hole probe designed to sample at the prescribed points with a flow within 10 percent of the mean flow rate. Notwithstanding, for applications under Part 75 of this chapter, the use of multi-hole probes is subject to the approval of the Administrator.

#### 8.5 *Post-Test QA/QC – Bias & Drift Assessment*

8.5.1 *Post-Run Bias.* After each run, repeat the system bias check (or 2-point system calibration error check for dilution systems) to validate the run. Do not adjust the measurement system (other than to maintain the target sampling rate or dilution ratio) between the end of the run and the completion of the post-run system bias or system calibration error check. Note that for all post-run system bias or 2-point system calibration error checks, the tester may inject the low-level gas first and upscale gas last, or vice-versa. If conducting a relative accuracy test or relative accuracy test audit consisting of nine runs or more, the tester may sample for up to three runs before performing the post-run bias or system calibration error check provided the test passes at the conclusion of the group of three runs. A failed post-run bias or system calibration error check, in this case, will invalidate all runs conducted after the last passed check. When conducting a performance or compliance test, the tester should perform a post-run system bias or system calibration error check after each test run unless dynamic spiking is elected.

8.5.2 *Drift.* After each run, evaluate the low-level and upscale drift using Equation 47-4 in Section 12.5. If the post-run low- and upscale bias (or 2-point system calibration error) checks are passed, but the low- or upscale drift exceeds the specification in Section 13.3, the run data are valid. However, if the low or upscale drift exceeds the specification, a 3-point calibration error test and a system bias (or 2-point system calibration error) check must be performed and passed before any more runs are conducted.

8.5.3 *Dilution Systems.* For dilution systems, data from a 3-point system calibration error test may be used to meet the pre-run 2-point system calibration error requirement for the first run in a

test sequence. Also, the post-run bias (or 2-point calibration error) check data may be used as the pre-run data for the next run in the test sequence at the discretion of the tester.

8.6 *Moisture Correction.* For CRDS systems that measure a wet sample, the measured content of the target analyte may need to be corrected to a dry basis if required by the applicable emissions limit or CEMS. Conversely, for CRDS systems that measure a dry sample, the measured content may need to be corrected to a wet basis if required by the applicable emissions limit or CEMS. If the moisture content is not measured directly by the CRDS analyzer, EPA Method 4 or other appropriate methods, subject to the approval of the Administrator, must be followed for correction calculations. Moisture correction is also required if the unit conversion from the applicable standard and moisture basis of the CRDS analyzer is different from the moisture basis of the diluent analyzer, if applicable.

8.7 *Limit of Detection (LOD) Determination.* An LOD determination test must be performed on each analyzer utilized for source testing with LOD details supplied in the final test report.

8.7.1 Collect a minimum of seven consecutive measurements separated by twice the RT.

8.7.2 Calculate the standard deviation of the measured values.

8.7.3 Define LOD as three times the standard deviation of these measurements.

8.8 *Site Specific Detection Level Determination.* All instruments must undergo a site-specific Detection Level utilizing the SADL procedures of Section 13.5. All run averages below the site-specific value must be reported as less than (<) the site-specific DL value. Any SA test must be performed as a dynamic spike by passing the spiked gas through all filters, scrubbers, conditioners, and any other monitoring system components used during normal sampling, and as much of the sampling probe as practical.

8.8.1 First, ensure LOD has been completed for the analyzer make and model. If not, perform this test in a controlled environment ( *See Section 8.7*).

8.8.2 Select a SA value, or desired DF for the SADL test.

8.8.3 Calculate the SAR from Equation 47-9.

8.8.4 Calculate ESA from Equation 47-10.

8.8.5 If ESA is greater than or equal to LOD, the ESA is the site-specific detection level.

## 9.0 *Quality Control*

The summary table beginning below includes QA/QC measures along with the associated frequency and acceptance criteria. All the QC data, along with the sample run data, must be documented and included in the test report.

**Summary Table of QA/QC**

Process	Specification	Criteria	Frequency
Identify Data User	--	Regulatory Agency or another primary end user of data	Pre-Test.
Analyzer Design	Resolution or sensitivity	<2.0% of the full-scale CRDS range or <1/2 of the applicable standard	Manufacturer design.
Calibration Gases	Traceability Protocol (G1, G2)	Valid certificate required; $\pm 2.0\%$ or best commercially available. Zero air material must meet requirements found in 40 CFR 72.2.	
	High-level gas	Equal to calibration span.	Each test.
	Mid-level gas	40 to 60% of calibration span.	Each test.
	Low-level gas	Zero air material.	Each test.
Data Recorder (if applicable)	Resolution	<2.0% of full-scale CRDS range or <1/2 of applicable standard	Manufacturer design.
	Frequency	$\leq 1$ -minute average	During run.
Sample Extraction	Probe material	An appropriate material of sufficient length and physical integrity	Each test.
	Probe, filter, and sample line temperature	Always keep sample above dew point (by heating or dilution).	Each run.
	Calibration valve material	Inert to target analyte and gas matrix.	Each test.
	Sample pump material	Inert to target analyte and gas matrix.	Each test.
	Manifold material	Inert to target analyte and gas matrix.	Each Test.
Particulate Removal (if applicable)	Filter material	Pass system bias checks or pre- and post-test analyte spiking	Each test.
Calibration Span	Set-point	Upper limit of the expected highest measured concentration or 2.5 times emission limit (concentration equivalent)	Each Test
Analyzer & Calibration Gas Performance	Analyzer calibration error (or 3-point system calibration error for dilution systems).	Within $\pm 2.0\%$ of the calibration span of the analyzer for the low-, mid-, and high-level calibration gases or an absolute difference of $\leq 0.05$ ppmv.	Pre-test and after a failed system bias test, drift test, or dynamic spike.
System Performance	System bias (or pre- and post-run 2-point system calibration error for dilution systems)	Within $\pm 5.0\%$ of the analyzer calibration span for low-scale and upscale calibration gases. Alternatively, $\leq 0.10$ ppmv absolute difference.	Before and after each run.
	Standard Addition (SA)	Performed dynamically	Once per Source
		Within $\pm 20\%$ or $\pm 0.05$ ppmv of expected concentration.	
		Calculate using Equation 47-2.	
	SADL Validation	Must be greater than or equal to instrument's LOD value.	Once per Source Type
	System Response Time	Determines minimum sampling time per point	Pre-Test.
	Drift	$\leq 3.0\%$ of calibration span for low-level and mid-or high-level gases	Before and after each run.
		Alternative specification: $\leq 0.15$ ppmv absolute difference.	
		Calculate using Equation 47-4.	
	Spike Dilution Factor	$\leq 20\%$ of system volumetric flow rate	Pre-test.

	Targeted Spiking Level	As practical, 50 to 150 percent of applicable standard but above native target analyte value	Pre-test.
	Purge Time	$\geq 2$ times system response time	Before starting the first run and after any event where the probe is removed from the source.
	Minimum Sample Time	Defined as two times the system response time	Each sample point.
	Stable sample flow rate or CRDS pressure (surrogate for maintaining system response time)	Within 10% of flow rate or CRDS pressure established during system response time check.	Each run.
Sample Point Selection	Stratification Test	All points within:	Prior to first run.
		$\pm 5\%$ of mean for 1-point sampling	
		$\pm 10\%$ of mean for 3-point sampling	
	Stratification Test	Alternatively, all points within:	
		$\pm 0.25$ ppmv of mean for 1-point sampling	
		$\pm 0.50$ ppmv of mean for 3-point sampling	
Data Parameters	Average run concentration	Run average $\leq$ calibration span.	Each run.

## 10.0 Calibration and Standardization

10.1 *Calibration.* The initial 3-point calibration error test as described in Section 8.2.3 and the system bias (or system calibration error) checks described in Section 8.2.4 are required and must meet the specifications in Section 13 before starting the test. Make all necessary adjustments to calibrate the gas analyzer and data recorder. Then, after the test commences, the system bias (or system calibration error) checks described in Section 8.2.4 are required before and after each run. The analyzer must be calibrated for the target analyte.

10.2 *Standardization.* A copy of the manufacturer's certification of the calibration gases used in the testing is required 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 on August 25, 1999. When EPA Method 205 is used to produce diluted calibration gases, the tester must document that the specifications for the gas dilution system are met for the test. The report 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 Procedure

As sample collection and analysis are conducted simultaneously, additional discussion of the analytical procedure is not necessary.

## 12.0 Data Analysis and Calculations

The following procedures for calculations and analysis are listed in this section.

12.1 *Nomenclature. The terms used throughout the equations are defined as follows:*

$ACE$  = Analyzer calibration error, percent of calibration span.

$B_{WS}$  = Moisture content of sample gas, percent/100.

$C_{Avg}$  = Average unadjusted gas concentration indicated by data recorder for the run, ppmv.

$C_D$  = Analyte concentration on a dry basis, ppmv.

$C_{Dir}$  = Measured calibration gas concentration (low, mid, or high) as introduced in direct calibration mode, ppmv.

$C_{Gas}$  = Average gas concentration adjusted for bias, ppmv.

$C_M$  = Average of initial and final system calibration bias (or 2-point system calibration error) check responses for the upscale calibration gas, ppmv.

$C_{MA}$  = Actual concentration of the upscale calibration gas, ppmv.

$C_{Native}$  = Native target analyte concentration in the gas stream, ppmv.

$C_O$  = Average of the initial and final system calibration bias (or 2-point system calibration error) check responses from the low-level (or zero) calibration gas, ppmv.

$C_{OA}$  = Actual concentration of the low-level calibration gas, ppmv.

$C_S$  = Measured concentration of a calibration gas (low, mid, or high) when introduced in system calibration mode, ppmv.

$C_{Spike}$  = Measured concentration of target analyte in spiked sample, ppmv.

$C_{Exp}$  = Expected concentration of target analyte in the spike gas diluted in the sample, ppmv.

$C_V$  = Certified concentration of a calibration gas (low, mid, or high), ppmv.

$C_W$  = Analyte concentration on a wet basis, ppmv.

$CS$  = Calibration span, ppmv.

$D$  = Drift assessment, percent of calibration span.

$DF$  = Dilution factor of dilution system or spike gas, dimensionless.

$Q_{Spike}$  = Flow rate of spike gas introduced in system calibration mode, LPM.

$Q_{Total}$  = Total sample flow rate during the spike test, LPM.

$R$  = Spike recovery, percent.

$SB$  = System bias, percent of calibration span.

$SB_i$  = Pre-run system bias, percent of calibration span.

$SB_{final}$  = Post-run system bias, percent of calibration span.

$SCE$  = System calibration error, percent of calibration span.



$SCE_i$  = Pre-run system calibration error, percent of calibration span.

$SCE_{final}$  = Post-run system calibration error, percent of calibration span.

12.2 *Analyzer Calibration Error.* For non-dilution systems, Use Equation 47-1 to calculate the analyzer calibration error for the low-, mid-, and high-level calibration gases.

$$ACE = \frac{C_{Dir} - C_V}{CS} \times 100\% \quad \text{Eq. 47-1}$$

12.3 *System Bias.* For non-dilution systems, use Equation 47-2 to calculate the system bias separately for both the low-level and upscale calibration gases. No adjustments to the data are made for bias corrections. Results are invalid if system bias exceeds 5 percent of the zero or upscale calibration gas checks.

$$SB = \frac{C_S - C_{Dir}}{CS} \times 100\% \quad \text{Eq. 47-2}$$

12.4 *System Calibration Error.* Use Equation 47-3 to calculate the system calibration error for dilution systems. Equation 47-3 applies to both the initial and 3-point system calibration error test and the subsequent 2-point calibration error checks between test runs. In this equation, the term  $C_s$  refers to the diluted calibration gas concentration measured by the analyzer.

$$SCE = \frac{(C_S \times DF) - C_V}{CS} \times 100\% \quad \text{Eq. 47-3}$$

12.5 *Drift Assessment.* Use Equation 47-4 to separately calculate the low-level and upscale drift over each test run. For dilution systems, replace  $SB_{final}$  and  $SB_i$  with  $SCE_{final}$  and  $SCE_i$ , respectively, to calculate and evaluate system drift. No adjustments to the data are made for drift corrections. Results are invalid if drift test bias exceeds 3 percent of the zero or upscale calibration gas checks.

$$D = |SB_{final} - SB_i| \quad \text{Eq. 47-4}$$

12.6 *Moisture Correction (optional).* Use equation 47-5 to convert concentrations from a wet-basis to a dry-basis.

$$C_D = \frac{C_W}{1 - B_{WS}} \quad \text{Eq. 47-5}$$

12.7 *Target Analyte Concentration.* For each test run, calculate,  $C_{avg}$ , the arithmetic average of all valid analyte concentration values (e.g., 1-minute averages).

12.8 *Standard Addition %Recovery (R).* Expected spike calculation and recovery for the dynamic spiking event is outlined in Section 13.5. First, the dilution factor during the spike must remain below 20 percent and be calculated per Equation 47-6. Next, the expected spike concentration ( $C_{Exp}$ ) is calculated per Equation 47-7 to evaluate the spike recovery (R) of

Equation 47-8. Spike recovery must be within 20% of the expected concentration to proceed.

$$DF = \frac{Q_{Spike}}{Q_{Total}} < 20\% \quad \text{Eq. 47-6}$$

$$C_{Exp} = (C_{V_{spike}} \times DF) + (1 - DF)(C_{Native}) \quad \text{Eq. 47-7}$$

$$R = \frac{C_{Spike}}{C_{Exp}}, 0.80 \leq R \leq 1.20 \quad \text{Eq. 47-8}$$

12.9 *Standard Addition Response (SAR)*. This is determined by evaluating the measured concentration of the spiked target analyte along with the native concentration of the target analyte and the dilution factor in the equation below.

$$SAR = C_{Spike} - (1 - DF) * C_{Native} \quad \text{Eq. 47-9}$$

12.10 *Effective Spike Addition (ESA)*. This is the expected increase in the measured concentration as a result of a dynamic spike injection. ESA is calculated by the equation below:

$$ESA = DF * (C_{Spike} - C_{Native}) \quad \text{Eq. 47-10}$$

### 13.0 *Method Performance*

13.1 *Calibration Error*. This specification is applicable to both the analyzer calibration error and the 3-point system calibration error tests described in Section 8.2.3. At each calibration gas level (low, mid, and high) the calibration error must be within  $\pm 2.0$  percent of the calibration span or  $\pm 0.05$  ppmv of the expected concentration, whichever is less stringent.

13.2 *System Bias*. This specification is applicable to both the system bias and 2-point system calibration error tests described in Section 8.2.4. The pre- and post-run system bias (or system calibration error) must be within  $\pm 5.0$  percent of the calibration span or  $\pm 0.10$  ppmv of the expected concentration, whichever is less stringent.

13.3 *Drift*. For each run, the low-level and upscale drifts must be less than or equal to 3.0 percent of the calibration span. The drift is also acceptable if the pre- and post-run bias (or the pre- and post-run system calibration error) responses do not differ by more than 0.15 ppmv at each concentration level, whichever is less stringent. Note that the drift may be conducted before and after the test provided the drift assessment meets criteria.

13.4 *Interference*. The total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.5 percent of the calibration span for the analyzer tested. In summing the interferences, use the larger of the absolute values obtained for the interferent tested with and without the pollutant present. The results are also acceptable if the sum of the responses does not exceed 0.25 ppmv for a calibration span of 5 to 10 ppmv, or 0.15 ppmv for a calibration span  $< 5$  ppmv, whichever is less stringent.

13.5 *Standard Addition Procedure.* Note that due to intermittent processes, or batch processes, it is not always possible to conduct standard addition testing while process units are in operation. In those cases, spikes may be performed in an ambient air matrix, if specified in the test protocol. In lieu of the instrument-specific interference tests, dynamic spiking may be performed. Recoveries must be within  $100 \pm 20$  percent or have an absolute difference between the measured and expected concentrations less than or equal to 0.05 ppmv, whichever is more restrictive, for the requirements of the standard addition spiking procedure to be satisfied.

13.5.5 Each standard addition, also known as a dynamic spike, consists of measurement of the source emissions concentration of the target analyte with and without the addition of the target analyte. With a single instrument, the tester must alternate measurement of the native and spiked samples so that each measurement of spiked samples is immediately preceded and followed by native gas measurement.

13.5.6 Introduce SA in such a manner that the entire system is challenged.

13.5.7 Unless otherwise specified by an applicable standard or rule, the SA must not exceed 100% of the instrument span when the SA and Native concentrations are combined.

13.5.8 When introducing the SA, note the volumetric flow rate of the addition if a tracer gas is not included. The SA volumetric flow rate must not exceed 20 percent of the sampling system flow rate. The DF is determined as a ratio of spiked flow to total flow.

13.5.9 First collect a minimum of two unspiked sample measurements for the pre-spike background. Measurements should agree within 5.0 percent of 3x the LOD to avoid bias. Collect 2 independent native measurements of the target analyte.

13.5.10 Introduce the SA to the probe tip, documenting flow rates and calibration reference values.

13.5.11 Maintain flow for a minimum of 2x RT and verify the spiked values agree within 5.0 percent. Collect 2 independent spiked measurements of the target analyte.

13.5.12 Calculate SAR & ESA to evaluate SADL. Repeat before proceeding with sampling if necessary.

#### 14.0 *Pollution Prevention*

To minimize pollution associated with system calibrations, select the lowest concentration of required calibration gases as acceptable by emission standards and operating permits. In cases where expected concentrations are above permissible exposure limits, dynamic spike requirements should replace direct calibration requirements to limit personnel exposure to target analytes.

#### 15.0 *Waste Management*

All materials should be handled and disposed of according to the applicable SDS instructions. Exhaust gases should be filtered or routed back to the process when possible. All surplus materials should be properly handled and disposed.

#### 16.0 *References*

- 1) “ERA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards” May 2012 as amended, EPA/600/R-12/53
- 2) “Method 1 – Sample and Velocity Traverses for Stationary Sources,” 40 CFR Part 60, Appendix A.
- 3) “Method 7E – Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure),” 40 CFR Part 60, Appendix A.
- 4) “Method 301 – Field Validation of Pollutant Measurement Methods from Various Waste Media,” 40 CFR Part 63, Appendix A.
- 5) “CRDS Validation and OTM Development Specific to Ethylene Oxide,” Childers, J., Schmid V., et al., A&WMA Air Quality Measurement Methods and Technology, 2022.

#### 17.0 *Tables, Diagrams, Flowcharts, and Validation Data*

Figure 47-1: Testing Flow Chart

Table 47-1: CRDS Target Analytes (EXAMPLE)

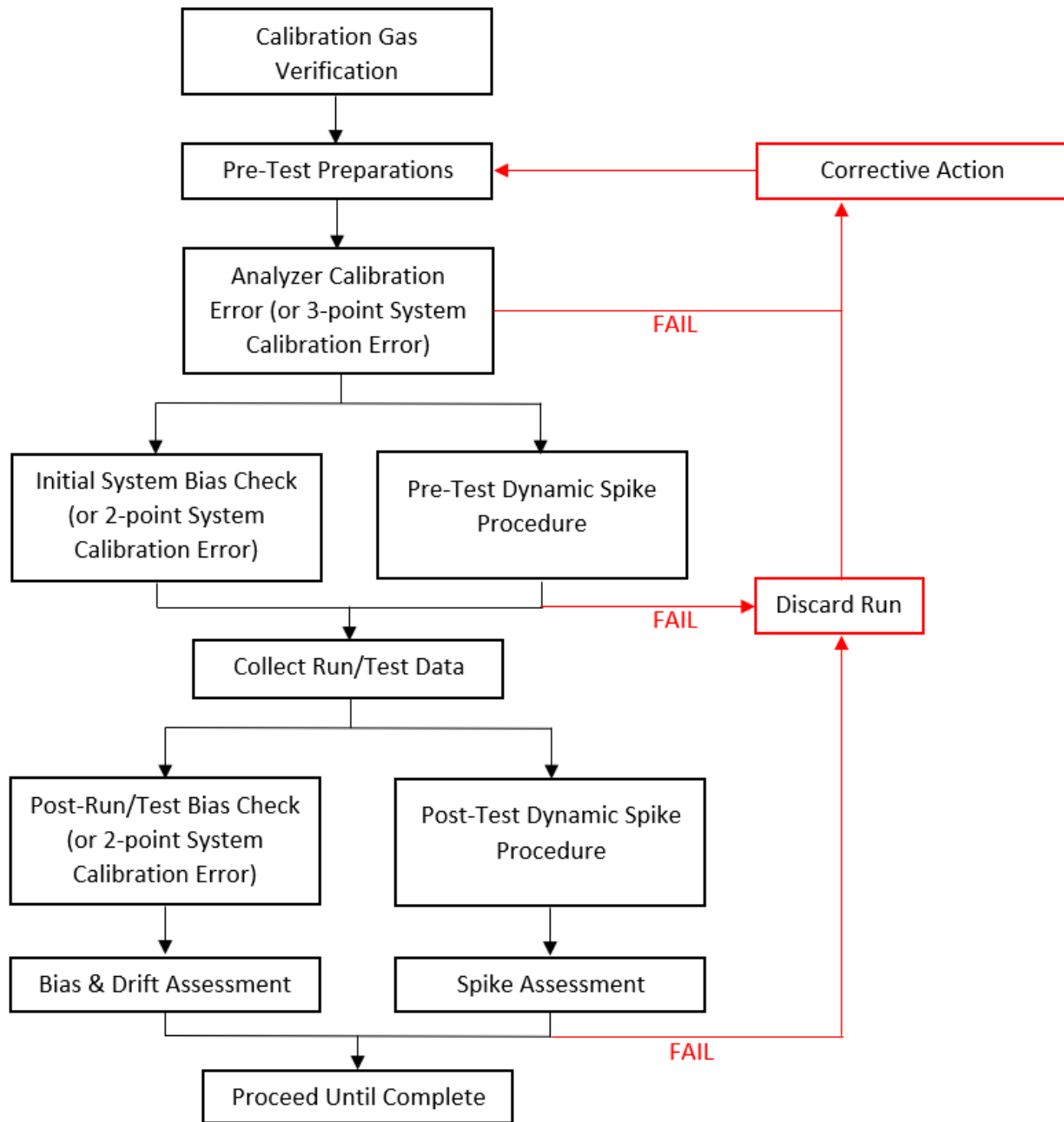
Figure 47-2: Method 301 Validation Summary

Table 47-2: Method 301 Results Summary

Figure 47-3: Method 301 Bias Analysis

Table 47-3: Test Results

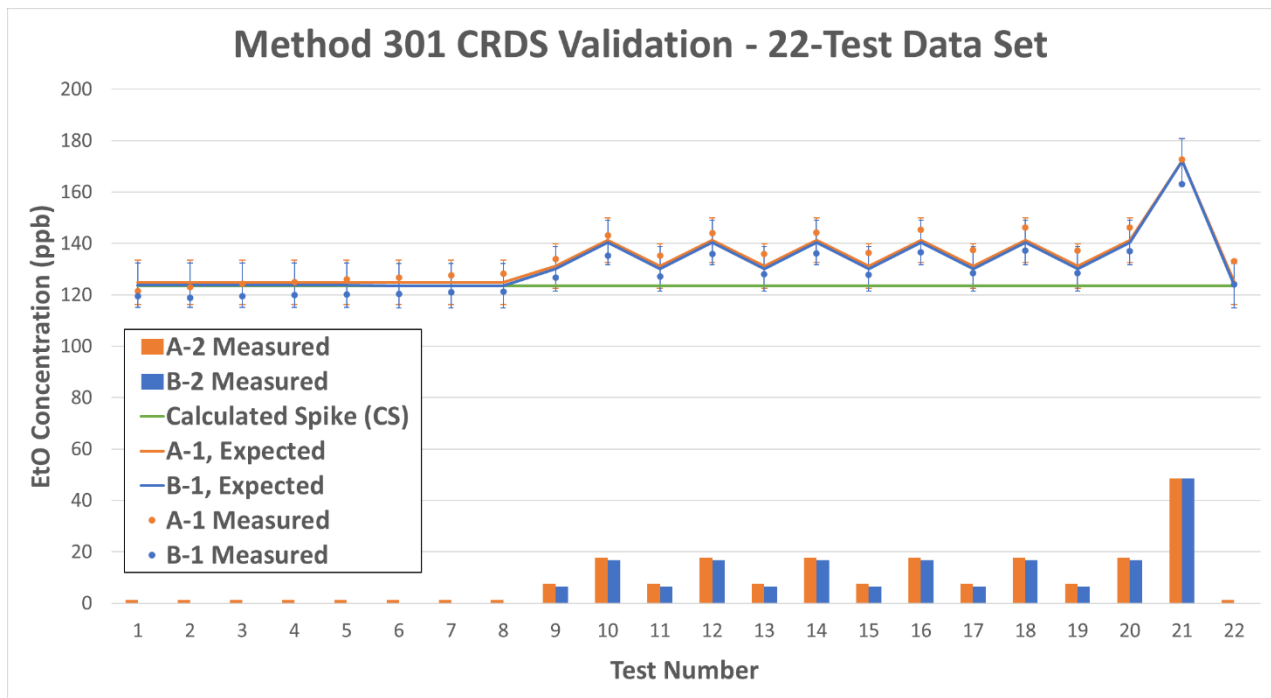
Figure 47-1: Testing Flow Chart



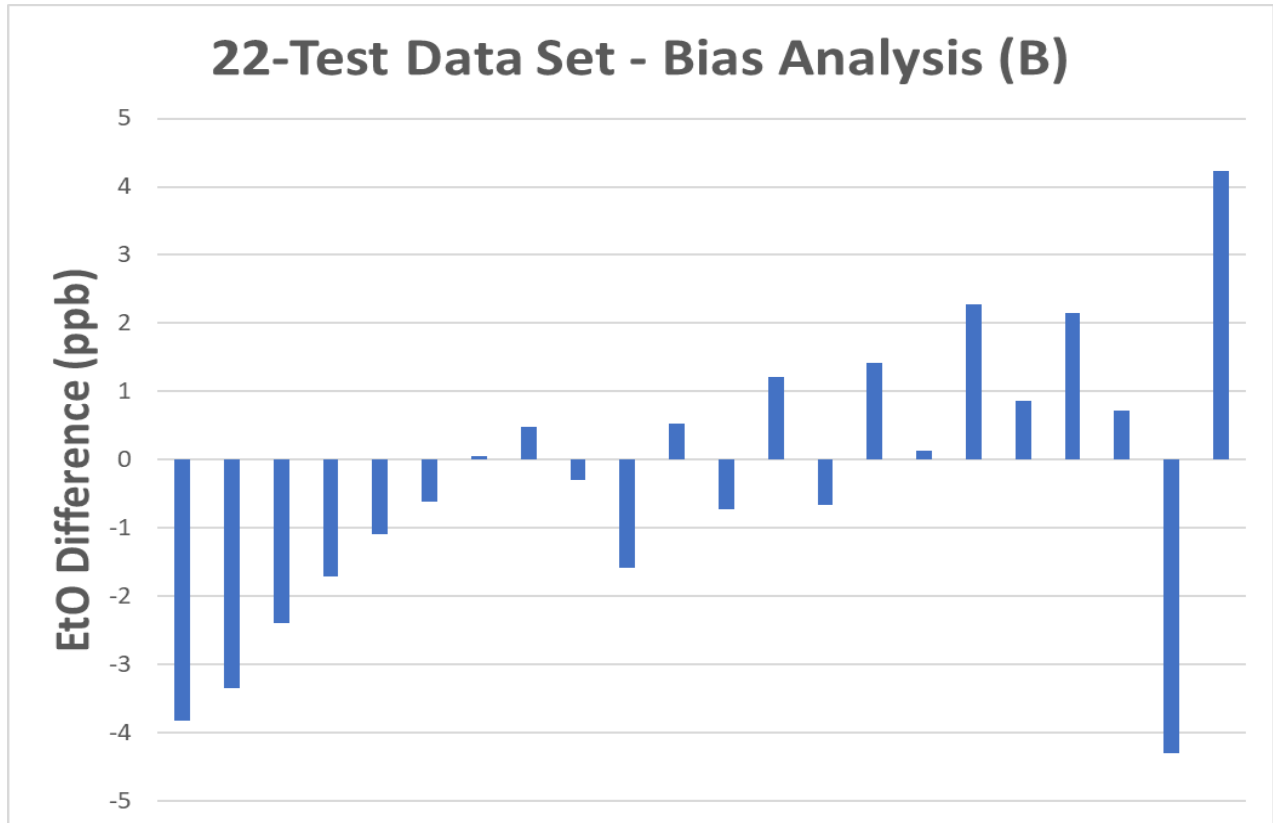
**Table 47-1: CRDS Target Analytes (EXAMPLE)**

Analyte	CAS Registry Number	Analyte	CAS Registry Number
Acetylene	74-86-2	Formaldehyde	50-00-0
Ammonia	7664-41-7	Hydrogen Chloride	7647-01-0
Carbon Dioxide	124-38-9	Hydrogen Fluoride	7664-39-3
Carbon Monoxide	630-08-0	Hydrogen Peroxide	7722-84-1
Ethane	74-84-0	Hydrogen Sulfide	7783-06-4
Ethylene	74-85-1	Methane	74-82-8
Ethylene Oxide	75-21-8	Nitrous Oxide	10024-97-2

**Figure 47-2: Method 301 Validation Summary**



**Figure 47-3: Method 301 Bias Analysis**



**Table 47-2: Method 301 Results Summary**

ITEM	RESULT	CRITERIA	PASS/FAIL
<b>Validation Technique</b>	Quadruplicate (2 spiked, 2 unspiked)	N/A	
<b>Number of Tests</b>	22	Minimum of 6	
<b>Bias</b>	-0.298 ppb	N/A	
<b>T-Test</b>	0.678	< t-critical, t-critical = 2.080	PASS
<b>Relative Bias</b>	0.24%	≤10%	PASS
<b>Correction Factor (CF)</b>	1.002	0.70 ≤ CF ≤ 1.30	PASS
<b>RSD</b>	1.69%	RSD < 20%	PASS

**Table 47-3: Test Results**

Count	A-1	B-1	B-2	A-2	d-A	d-B	(di-dm)^2
22					-6.554		89.173
1	121	120	0.152	1.28	-3.82		12.41
2	123	119	0.034	1.16	-3.35		9.34
3	124	119	0.050	1.17	-2.40		4.43
4	125	120	0.034	1.15	-1.72		2.02
5	126	120	0.033	1.14	-1.10		0.641
6	127	120	0.016	1.18	-0.620		0.103
7	128	121	-0.003	1.15	0.046		0.118
8	128	121	-0.013	1.19	0.474		0.596
9	134	127	6.51	7.56	-0.299		0.000
10	143	135	16.8	17.6	-1.58		1.65
11	135	127	6.56	7.61	0.521		0.670
12	144	136	16.8	17.6	-0.732		0.188
13	136	128	6.54	7.61	1.21		2.27
14	144	136	16.8	17.6	-0.659		0.131
15	136	128	6.56	7.62	1.42		2.95
16	145	137	16.8	17.6	0.126		0.180
17	137	128	6.55	7.59	2.28		6.63
18	146	137	16.8	17.6	0.867		1.36
19	137	129	6.57	7.62	2.15		5.97
20	146	137	16.8	17.6	0.721		1.04
21	173	163	48.5	48.6	-4.30		16.01
22	133	124	0.007	1.33	4.23		20.47
t-critical	2.080						
t-test	0.678					t-test < t-critical	
Bias	-0.298	ppb					
Rel. Bias	0.241	%			$B_R \leq 10\%$		
CF	1.002				$0.70 \leq CF \leq 1.30$		
RSD	1.688	%			RSD < 20%		