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PERFORMANCE SPECIFICATION 9—SPECIFICATIONS AND TEST PROCEDURES FOR GAS CHROMATOGRAPHIC CONTINUOUS EMISSION MONITORING SYSTEMS IN STATIONARY SOURCES

1.0 Scope and Application

1.1 Applicability. These requirements apply to continuous emission monitoring systems (CEMSs) that use gas chromatography (GC) to measure gaseous organic compound emissions. The requirements include procedures intended to evaluate the acceptability of the CEMS at the time of its installation and whenever specified in regulations or permits. Quality assurance procedures for calibrating, maintaining, and operating the CEMS properly at all times are also given in this procedure.

2.0 Summary of Performance Specification

2.1 Calibration precision, calibration error, and performance audit tests are conducted to determine conformance of the CEMS with these specifications. Daily calibration and maintenance requirements are also specified.

3.0 Definitions

3.1 Gas Chromatograph (GC). That portion of the system that separates and detects organic analytes and generates an output proportional to the gas concentration. The GC must be temperature controlled.

NOTE: The term temperature controlled refers to the ability to maintain a certain temperature around the column. Temperature-programmable GC is not required for this performance specification, as long as all other requirements for precision, linearity and accuracy listed in this performance specification are met. It should be noted that temperature programming a GC will speed up peak elution, thus allowing increased sampling frequency.

3.1.1 Column. Analytical column capable of separating the analytes of interest.

3.1.2 Detector. A detection system capable of detecting and quantifying all analytes of interest.

3.1.3 Integrator. That portion of the system that quantifies the area under a particular sample peak generated by the GC.

3.1.4 Data Recorder. A strip chart recorder, computer, or digital recorder capable of recording all readings within the instrument's calibration range.

3.2 Calibration Precision. The error between triplicate injections of each calibration standard.

4.0 Interferences [Reserved]

5.0 Safety

The procedures required under this performance specification may involve hazardous materials, operations, and equipment. This performance specification does not purport to address all of the safety problems associated with these procedures. It is the responsibility of the user to establish appropriate safety problems associated with these procedures. It is the responsibility of the user to establish appropriate safety and health practices and determine the application regulatory limitations prior to performing these procedures. The CEMS user's manual and materials recommended by the reference method should be consulted for specific precautions to be taken.

6.0 Equipment and Supplies

6.1 Presurvey Sample Analysis and GC Selection. Determine the pollutants to be monitored from the applicable regulation or permit and determine the approximate concentration of each pollutant (this information can be based on past compliance test results). Select an appropriate GC configuration to measure the organic compounds. The GC components should include a heated sample injection loop (or other sample introduction systems), separatory column, temperature-controlled oven, and detector. If the source chooses dual column and/or dual detector configurations, each column/detector is considered a separate instrument for the purpose of this performance specification and thus the procedures in this performance specification shall be carried out on each system. If this method is applied in highly explosive areas, caution should be exercised in selecting the equipment and method of installation.

6.2 Sampling System. The sampling system shall be heat traced and maintained at a minimum of 120 °C with no cold spots. All system components shall be heated, including the probe, calibration valve, sample lines, sampling loop (or sample introduction system), GC oven, and the detector block (when appropriate for the type of detector being utilized, *e.g.*, flame ionization detector).

7.0 Reagents and Standards

7.1 Calibration Gases. Obtain three concentrations of calibration gases certified by the manufacturer to be accurate to within 2 percent of the value on the label. A gas dilution system may be used to prepare the calibration gases from a high concentration certified standard if the gas dilution system meets the requirements specified in Test Method 205, 40 CFR Part 51, Appendix M. The performance test specified in Test Method 205 shall be repeated quarterly, and the results of the Method 205 test shall be included in the report. The calibration gas concentration of each target analyte shall be as follows (measured concentration is based on the presurvey concentration determined in section 6.1).

NOTE: If the low level calibration gas concentration falls at or below the limit of detection for the instrument for any target pollutant, a calibration gas with a concentration at 4 to 5 times the limit

of detection for the instrument may be substituted for the low-level calibration gas listed in section 7.1.1.

7.1.1 Low-level. 40-60 percent of measured concentration.

7.1.2 Mid-level. 90-110 percent of measured concentration.

7.1.3 High-level. 140-160 percent of measured concentration, or select highest expected concentration.

7.2 Performance Audit Gas. Performance Audit Gas is an independent cylinder gas or cylinder gas mixture. A certified EPA audit gas shall be used, when possible. A gas mixture containing all the target compounds within the calibration range and certified by EPA's Traceability Protocol for Assay and Certification of Gaseous Calibration Standards may be used when EPA performance audit materials are not available. If a certified EPA audit gas or a traceability protocol gas is not available, use a gas manufacturer standard accurate to 2 percent.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Installation and Measurement Location Specifications. Install the CEMs in a location where the measurements are representative of the source emissions. Consider other factors, such as ease of access for calibration and maintenance purposes. The location should not be close to air in-leakages. The sampling location should be at least two equivalent duct diameters downstream from the nearest control device, point of pollutant generation, or other point at which a change in the pollutant concentration or emission rate occurs. The location should be at least 0.5 diameter upstream from the exhaust or control device. To calculate equivalent duct diameter, see section 12.2 of Method 1 (40 CFR Part 60, Appendix A). Sampling locations not conforming to the requirements in this section may be used if necessary upon approval of the Administrator.

8.2 Pretest Preparation Period. Using the procedures described in Method 18 (40 CFR Part 60, Appendix A), perform initial tests to determine GC conditions that provide good resolution and minimum analysis time for compounds of interest. Resolution interferences that may occur can be eliminated by appropriate GC column and detector choice or by shifting the retention times through changes in the column flow rate and the use of temperature programming.

8.3 Seven (7)-Day Calibration Error (CE) Test Period. At the beginning of each 24-hour period, set the initial instrument set points by conducting a multi-point calibration for each compound. The multi-point calibration shall meet the requirements in sections 13.1, 13.2, and 13.3. Throughout the 24-hour period, sample and analyze the stack gas at the sampling intervals prescribed in the regulation or permit. At the end of the 24-hour period, inject the calibration gases at three concentrations for each compound in triplicate and determine the average instrument response. Determine the CE for each pollutant at each concentration using Equation 9-2. Each CE shall be ≤ 10 percent. Repeat this procedure six more times for a total of 7 consecutive days.

8.4 Performance Audit Test Periods. Conduct the performance audit once during the initial 7-day CE test and quarterly thereafter. Performance Audit Tests must be conducted through the entire sampling and analyzer system. Sample and analyze the EPA audit gas(es) (or the gas mixture) three times. Calculate the average instrument response. Results from the performance audit test must meet the requirements in sections 13.3 and 13.4.

8.5 Reporting. Follow the reporting requirements of the applicable regulation or permit. If the reporting requirements include the results of this performance specification, summarize in tabular form the results of the CE tests. Include all data sheets, calculations, CEMS data records, performance audit results, and calibration gas concentrations and certifications.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization

10.1 Multi-Point Calibration. After initial startup of the GC, after routine maintenance or repair, or at least once per month, conduct a multi-point calibration of the GC for each target analyte. Calibration is performed at the instrument independent of the sample transport system. The multi-point calibration for each analyte shall meet the requirements in sections 13.1, 13.2, and 13.3.

10.2 Daily Calibration. Once every 24 hours, analyze the mid-level calibration standard for each analyte in triplicate. Calibration is performed at the instrument independent of the sample transport system. Calculate the average instrument response for each analyte. The average instrument response shall not vary by more than 10 percent from the certified concentration value of the cylinder for each analyte. If the difference between the analyzer response and the cylinder concentration for any target compound is greater than 10 percent, immediately inspect the instrument making any necessary adjustments, and conduct an initial multi-point calibration as described in section 10.1.

11.0 Analytical Procedure. Sample Collection and Analysis Are Concurrent for This Performance Specification (See section 8.0)

12.0 Calculations and Data Analysis

12.1 Nomenclature.

C_m = average instrument response, ppm.

C_a = cylinder gas value, ppm.

F = Flow rate of stack gas through sampling system, in Liters/min.

n = Number of measurement points.

r^2 = Coefficient of determination.

V = Sample system volume, in Liters, which is the volume inside the sample probe and tubing leading from the stack to the sampling loop.

x = CEMS response.

y = Actual value of calibration standard.

12.2 Coefficient of Determination. Calculate r^2 using linear regression analysis and the average concentrations obtained at three calibration points as shown in Equation 9-1.

$$r^2 = \left(\frac{n \sum x_i y_i - (\sum x_i)(\sum y_i)}{\sqrt{(n \sum y_i^2 - \sum y_i \sum y_i)(n \sum x_i^2 - \sum x_i \sum x_i)}} \right)^2 \quad \text{Eq. 9-1}$$

12.3 Calibration Error Determination. Determine the percent calibration error (CE) at each concentration for each pollutant using the following equation.

$$CE = \frac{C_m - C_a}{C_a} \times 100 \quad \text{Eq. 9-2}$$

12.4 Sampling System Time Constant (T).

$$T = \frac{F}{V} \quad \text{Eq. 9-3}$$

13.0 Method Performance

13.1 Calibration Error (CE). The CEMS must allow the determination of CE at all three calibration levels. The average CEMS calibration response must not differ by more than 10 percent of calibration gas value at each level after each 24-hour period and after any triplicate calibration response check.

13.2 Calibration Precision and Linearity. For each triplicate injection at each concentration level for each target analyte, any one injection shall not deviate more than 5 percent from the average concentration measured at that level. When the CEMS response is evaluated over three concentration levels, the linear regression curve for each organic compound shall be determined using Equation 9-1 and must have an $r^2 \geq 0.995$.

13.3 Measurement Frequency. The sample to be analyzed shall flow continuously through the sampling system. The sampling system time constant shall be ≤ 5 minutes or the sampling frequency specified in the applicable regulation, whichever is less. Use Equation 9-3 to determine T. The analytical system shall be capable of measuring the effluent stream at the frequency specified in the appropriate regulation or permit.

13.4 Performance Audit Test Error. Determine the error for each average pollutant measurement using the Equation 9-2 in section 12.3. Each error shall be less than or equal to 10 percent of the

cylinder gas certified value. Report the audit results including the average measured concentration, the error and the certified cylinder concentration of each pollutant as part of the reporting requirements in the appropriate regulation or permit.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]