PERFORMANCE SPECIFICATION 12A

SPECIFICATIONS AND ~~TEXT~~ TEST PROCEDURES FOR TOTAL VAPOR PHASE MERCURY CONTINUOUS EMISSION MONITORING SYSTEMS IN STATIONARY SOURCES

1.0 Scope and Application

1.1 Analyte

ANALYTE	CAS NO.
Mercury (Hg)	7439-97-6

The analyte measured by these procedures and specifications to total vapor phase mercury (Hg) in the flue gas, which represents the sum of elemental Hg (Hg^0) and oxidized forms of gaseous Hg (Hg^{+2}), in concentration units of micrograms per cubic meter (µg/m^3).

1.2 Applicability

1.2.1 This specification is for evaluating the acceptability of total vapor phase Hg continuous emission monitoring systems (CEMS) installed on the exit gases from fossil fuel fired boilers at the time of or soon after installation and whenever specified in the regulations. The Hg CEMS must be capable of measuring the total concentration in µg/m^3 (regardless of speciation) of vapor phase Hg, and recording that concentration on a wet or dry basis. Particle bound Hg is not included in the measurements.

This specification is not designed to evaluate an installed CEMS's performance over an extended period of time nor does it identify specific calibration techniques and auxiliary procedures to assess the CEMS's performance. The source owner or operator, however, is responsible to calibrate, maintain, and operate the CEMS properly. The ~~Administrator~~ Director may require, under ~~Clean Air Act (CAA) section 114~~ the Georgia Rules for Air Quality Control, the operator to conduct CEMS performance evaluations at other times besides the initial test to evaluate the CEMS performance. See ~~§60.13(c)~~ Section 1.4(c) of this text.

1.2.2 Mercury monitoring approaches not entirely suited to these specifications may be approvable under the alternative monitoring or alternative test method provisions of Section 1.4(i) of this text.

2.0 Summary of Performance Specification

Procedures for measuring CEMS relative accuracy, linearity and calibration drift are outlined. CEMS installation and measurement location specifications, and data reduction procedures are included. ~~Conformance of the CEMS with the Performance Specification is determined.~~

3.0 Definitions

3.1 *Continuous Emission Monitoring System (CEMS)* means the total equipment required for the determination of a pollutant concentration. The system generally consists of the following three major subsystems: sample interface, Hg analyzer, and data recorder.

3.2 *Sample Interface* means that portion of the CEMS used for one or more of the following: sample acquisition, sample transport, sample conditioning, and protection of the monitor from the effects of the stack effluent.

3.3 *Hg Analyzer* means that portion of the Hg CEMS that measures the total vapor phase Hg mass concentration and generates a proportional output.

3.4 *Data Recorder* means that portion of the CEMS that provides a permanent electronic record of the analyzer output. The data recorder may provide automatic data reduction and CEMS control capabilities.

3.5 *Span Value* means the measurement range as specified in the applicable regulation or other requirement. If the span value is not specified in the applicable regulation or other requirement, then it must be a value approximately equivalent to two times the emission standard. Unless otherwise specified, the span value may be rounded up to the nearest multiple of 10.

3.6 *Measurement Error (ME)* means the absolute value of the difference between the concentration indicated by the Hg analyzer and the known concentration generated by a reference gas, expressed as a percentage of the span value, when the entire CEMS, including the sampling interface, is challenged.

3.7 *Measurement Error Test* means a test procedure in which the accuracy of the concentrations measured by a CEMS at three or more points over its measurement range is evaluated using reference gases. For Hg CEMS, elemental and oxidized Hg (Hg^0 and mercuric chloride, $HgCl_2$) gas standards of known concentration are used for this procedure.

3.8 *Calibration Drift (CD)* means the absolute value of the difference between the CEMS output response and either an upscale Hg reference gas or a zero-level Hg reference gas, expressed as a percentage of the span value, when the entire CEMS, including the sampling interface, is challenged after a stated period of operation during which no unscheduled maintenance or repair took place.

3.9 *Relative Accuracy Test Procedure* means a test procedure consisting of at least nine test runs, in which the accuracy of the concentrations measured by a CEMS is evaluated by comparison against concurrent measurements made with a reference method (RM). Relative accuracy tests repeated on a regular, on-going basis are referred to as relative accuracy test audits or RATAs.

3.10 *Relative Accuracy (RA)* means the absolute mean difference between the pollutant concentration~~(s)~~ determined by the CEMS and the value determined by the reference method (RM) plus the 2.5 percent error confidence coefficient of a series of tests divided by the mean of the RM tests. Alternatively, ~~for low concentration sources~~ for sources with an average RM concentration less than 5.0 micrograms per standard cubic meter (µg/scm), the RA may be expressed as the absolute value of the difference between the mean CEMS and RM values.

4.0 Interferences [Reserved]

5.0 Safety

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

6.0 Equipment and Supplies

6.1 CEMS Equipment Specifications

6.1.1 Data Recorder Scale. The Hg CEMS data recorder output range must include the full range of expected Hg concentration values in the gas stream to be sampled including zero and the span value.

6.1.2 The Hg CEMS design should also provide for the determination of calibration drift and measurement error (ME) at a zero value (zero to 20 percent of the span value) and at an upscale value (between 50 and 100 percent of the high-level value). The Hg CEMS must be constructed to permit the introduction of known concentrations of Hg and $HgCl_2$ separately into the sampling system of the CEMS immediately preceding the sample extraction filtration system such that the entire CEMS can be challenged.

6.2 Reference Gas Delivery System. The reference gas delivery system must be designed so that the flowrate exceeds the sampling system flow requirements of the CEMS and that the gas is delivered to the CEMS at atmospheric pressure.

6.3 Other equipment and supplies, as needed by the applicable reference method used for the Relative Accuracy Test Audit Procedure. See Section 8.6.2.

7.0 Reagents and Standards

7.1 Reference Gases. Reference gas standards are required for both elemental (Hg^0) and oxidized Hg (Hg and mercuric chloride, $HgCl_2$). The use of National Institute of Standards and Technology (NIST)-certified or NIST-traceable standards and reagents is required. The following gas concentrations are required.

7.1.1 Zero-level. 0 to 20 percent of the span value.

7.1.2 Mid-level. 50 to 60 percent of the span value.

7.1.3 High-level. 80 to 100 percent of the span value.

7.2 Reference gas standards may also be required for the reference methods. See Section 8.6.2.

8.0 Performance Specification (PS) Test Procedure

8.1 Installation and Measurement Location Specifications

8.1.1 CEMS Installation. Install the CEMS at an accessible location downstream of all pollution control equipment. Place the probe outlet or other sampling interface at a point or location in the stack (or vent) representative of the stack gas concentration of Hg. Since the Hg CEMS sample system normally extracts gas from a single point in the stack, use a location that has been shown to be free of stratification for Hg or, alternatively, SO_2 is recommended. ~~and NO_X through concentration measurement traverses for those gases~~. If the cause of failure to meet the RA test requirement is determined to be the measurement location and a satisfactory correction technique cannot be established, the ~~Administrator~~ Director may require the CEMS to be relocated.

Measurement locations and points or paths that are most likely to provide data that will meet the RA requirements are ~~listed~~ described in Sections 8.1.2 and 8.1.3 below.

8.1.2 Measurement Location. The measurement location should be (1) at least two equivalent diameters downstream of the nearest control device, point of pollutant generation or other point at which a change of pollutant concentration may occur, and (2) at least half an equivalent diameter upstream from the effluent exhaust. The equivalent duct diameter is calculated ~~as per 40 CFR part 60, appendix A,~~ according to Method 1 of Appendix A of this text.

8.1.3 Hg CEMS Sample Extraction Point. Use a sample extraction point (1) no less than 1.0 meter from the stack or duct wall, or (2) within the centroidal velocity traverse area of the stack or duct cross section. This does not apply to cross-stack, in-situ measurement systems.

~~8.2.1~~ 8.2 Measurement Error (ME) Test Procedure. Sequentially inject each of at least three elemental Hg reference gases (zero, mid-level, and high level, as defined in Section 7.1), three times each for a total of nine injections. Inject the gases in such a manner that the entire CEMS is challenged. Do not inject the same gas concentration twice in succession. At each reference gas concentration, determine the average of the three CEMS responses and subtract the average response from the reference gas value. Calculate the measurement error (ME) using Equation 12A-1 by expressing the absolute value of the difference between the average CEMS response (A) and the reference gas value ~~®~~ (R) as a percentage of the span (see example data sheet in Figure 12A-1). For each elemental Hg reference gas, the absolute value of the difference between the CEMS response and the reference value must not exceed 5 percent of the span value. If this specification is not met, identify and correct the problem before proceeding. Repeat the measurement error test procedure using oxidized Hg reference gases. For each oxidized Hg reference gas, the absolute value of the difference between the CEMS response and the reference value shall not exceed 10 percent of the span value. If this specification is not met, identify and correct the problem before proceeding.

$$\mathrm{ME} = \frac{|R - A|}{Span} \times 100 \qquad \text{(Equation 12A-1)}$$

8.3 ~~7~~Seven-Day Calibration Drift (CD) Test Procedure

8.3.1 CD Test Period. While the affected facility is operating ~~at more than 50 percent of normal load~~ normally, or as specified in an applicable ~~subpart~~ regulation, determine the magnitude of the ~~UD~~ CD once each day (at 24-hour intervals, to the extent practicable) for 7 consecutive unit operating days according to the procedure given in Sections 8.3.2 through 8.3.3. The 7 consecutive unit operating days need not be 7 consecutive calendar days. Use either Hg^0 or $HgCl_2$ standards for this test.

8.3.2 The purpose of the CD measurement is to verify the ability of the CEMS to conform to the established CEMS response used for determining emission concentrations or emission rates. Therefore, if periodic automatic or manual adjustments are made to the CEMS zero and upscale response settings, conduct the CD test immediately before these adjustments, or conduct it in such a way that the ~~UD~~ CD can be determined.

8.3.3 Conduct the CD test using the zero gas specified and either the mid-level or high-level gas as specified in Section 7.1 Sequentially introduce the reference gases to the CEMS at the sampling system of the CEMS immediately preceding the sample extraction filtration system. Record the CEMS response (A) for each reference gas and, using Equation 12A-2, subtract the corresponding reference value (R) from the CEMS value, and express the absolute value of the difference as a percentage of the span value (see also example data sheet in Figure 12A-2). For each reference gas, the absolute value of the difference between the CEMS response and the reference value must not exceed 5 percent of the span value. If these specifications are not met, identify and correct the problem before proceeding.

$$CD = \frac{|R - A|}{Span} \times 100 \qquad \text{(Equation 12A-2)}$$

8.4 RA Test Procedure

8.4.1 RA Test Period. Conduct the RA test according to the procedure given in Sections 8.4.2 through 8.4.6 while the affected facility is operating at normally, or as specified in an applicable ~~subpart~~ regulation. The RA test may be conducted during the CD test period.

8.4.2 Reference Methods (RM). Unless otherwise specified in an applicable ~~subpart of the~~ regulation~~s~~, use Method 29, Method 30A or Method 30B in Appendix A-~~8 to~~ of this text or American Society of Testing and Materials (ASTM) Method D 6784–02 (incorporated by reference, see ~~§60.17~~ Section 1.6 of this text) as the RM for Hg concentration. For Method 29 and ASTM Method 6784-02 only, the filterable portion of the sample need not be included when making comparisons to the CEMS results. When Method 29, Method 30B, or ASTM D6784–02 is used, conduct the RM test runs with paired or duplicate sampling systems and use the average of the vapor phase Hg concentrations measured by the two trains. When Method 30A is used, paired sampling systems are not required. If the RM and CEMS measure on a different moisture basis, data derived with Method 4 in Appendix A of this text shall also be obtained during the RA test.

8.4.3 Sampling Strategy for RM Tests. Conduct the RM tests in such a way that they will yield results representative of the emissions from the source and can be compared to the CEMS data. The RM and CEMS locations need not be immediately adjacent. Locate the RM measurement points in accordance with section 8.1.3 of Performance Specification 2 (PS2) in this Appendix. It is preferable to conduct moisture measurements (if needed) and Hg measurements simultaneously, although moisture measurements that are taken within an hour of the Hg measurements may be used to adjust the Hg concentrations to a consistent moisture basis. In order to correlate the CEMS and RM data properly, note the beginning and end of each RM test period for each paired RM run (including the exact time of day) on the CEMS chart recordings or other permanent record of output.

8.4.4 Number and length of RM Tests. Conduct a minimum of nine RM test runs. When Method 29, Method 30B, or ASTM D6784–02 is used, only test runs for which the data from the paired RM trains meet the relative deviation (RD) criteria of this performance specification (PS) shall be used in the RA calculations. In addition, for Method 29 and ASTM D 6784–02 use a minimum sample run time of 2 hours and for Method 30A and Method 30B use a minimum sample time of 30 minutes.

Note: More than nine sets of RM tests may be performed. If this option is chosen, RM test results may be excluded so long as the total number of RM test results used to determine the CEMS RA is greater than or equal to nine. However, all data must be reported, including the excluded data.

8.4.5 Correlation of RM and CEMS Data. Correlate the CEMS and the RM test data as to the time and duration by first determining from the CEMS final output (the one used for reporting) the integrated average pollutant concentration for each RM test period. Consider system response time, if important, and confirm that the results are on a consistent moisture basis with the RM test. Then, compare each integrated CEMS value against the corresponding RM value. When Method 29, Method 30B, or ASTM D6784–02 is used, compare each CEMS value against the corresponding average of the paired RM values.

8.4.6 Paired RM Outliers

8.4.6.1 When Method 29, Method 30B, or ASTM D6784–02 is used, outliers are identified through the determination of relative deviation (RD) of the paired RM tests. Data that do not meet this criteria should be flagged as a data quality problem and may not be used in the calculation of RA. The primary reason for performing paired RM sampling is to ensure the quality of the RM data. The percent RD of paired data is the parameter used to quantify data quality. Determine RD for two paired data points as follows:

$$RD = 100 \times \frac{\left|(C_a - C_b)\right|}{C_a + C_b} \qquad \textbf{Eq. 12A-1}$$

~~where~~ Where: C_a and C_b are the Hg concentration values determined from the paired samples. ~~each of the two samples respectively~~.

8.4.6.2 The minimum performance criteria for RM Hg data is that RD for any data pair must be ≤10 percent as long as the mean Hg concentration is greater than 1.0 µg/m^3. If the mean Hg concentration is less than or equal to 1.0 µg/m^3, the RD must be ≤20 percent or ≤ 0.2 µg/m^3 absolute difference. Pairs of RM data exceeding these RD criteria should be eliminated from the data set used to develop a Hg CEMS correlation or to assess CEMS RA.

8.4.7 Calculate the mean difference between the RM and CEMS values in the units of micrograms per cubic meter (µg/m^3), the standard deviation, the confidence coefficient, and the RA according to the procedures in Section 12.0.

8.5 Reporting. At a minimum (check with the permitting authority ~~the appropriate EPA Regional Office, State or local Agency~~ for additional requirements, if any), summarize in tabular form the results of the CD tests, the linearity tests and the RA tests or alternative RA procedure, as appropriate. Include all data sheets, calculations, charts (records of CEMS responses), reference gas concentration certifications, and any other information necessary to confirm that the performance of the CEMS meets the performance criteria.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

For Method 30A, sample collection and analysis are concurrent. For the other RM, post-run sample analyses are performed. Refer to the RM employed for specific analytical procedures.

12.0 Calculations and Data Analysis

Calculate and summarize the RA test results on a data sheet similar to Figure 12A-3.

12.1 Consistent Basis. All data from the RM and CEMS must be compared in units of micrograms per standard cubic meter ($\mu g/scm^3$), on a consistent and identified moisture basis. The values must be standardized to ~~(STP =~~ 20 °C, 760 millimeters (mm) Hg~~)~~.

12.1.1 Moisture Correction (as applicable). If the RM and CEMS measure Hg on a different moisture basis, they will need to be corrected to a consistent basis. U~~u~~se Equation 12A-2a to correct data from a wet basis to a dry basis. ~~to make the appropriate corrections to the Hg concentrations.~~

$$Concentration_{(dry)} = \frac{Concentration_{(wet)}}{\left(1 - B_{ws}\right)}$$

Eq. 12A-2a

~~In Equation 12A-2, B_{ws} is the moisture content of the flue gas from Method 4, expressed as a decimal fraction (e.g., for 8.0 percent H_2O, B_{ws} = 0.08).~~

Use Equations 12A-2b to correct data from a dry basis to a wet basis.

$$Concentration_{(wet)} = Concentration_{(dry)}\, x \left(1 - B_{ws}\right)$$

Eq. 12A-2b

Where: B_{ws} is the moisture content of the flue gas from Method 4 in Appendix A of this text, expressed as a decimal fraction (e.g., for 8.0 percent H_2O, B_{ws} = 0.08).

12.2 Arithmetic Mean. Calculate $\bar{d}$, the arithmetic mean of the differences, (d_i), of a data set as follows:

$$\bar{d} = \frac{1}{n}\sum_{i=1}^{n} d_i$$

Eq. 12A-3

where:

n = Number of data points; and

$\sum_{i=1}^{n} d_i$ = Algebraic summation of the individual differences, d_i.

12.3 Standard Deviation. Calculate the standard deviation, S_d, as follows:

$$S_d = \left[\frac{\sum_{i=1}^{n} d_i^2 - \frac{\left(\sum_{i=1}^{n} d_i\right)^2}{n}}{n-1}\right]^{\frac{1}{2}}$$

Eq. 12A-4

12.4 Confidence Coefficient (CC). Calculate the 2.5 percent error confidence coefficient (one-tailed), CC, as follows:

$$CC = t_{0.975}\frac{S_d}{\sqrt{n}}$$ **Eq. 12A-5**

where:

$t_{0.975}$ = t-value (see Table 12A-1)

12.5 RA. Calculate the RA of a set of data as follows:

$$RA = \frac{|\bar{d}| + |CC|}{\overline{RM}} \times 100$$ **Eq. 12A-6**

where:

$|\bar{d}|$ = Absolute value of the mean differences (from Equation 12A-3);

$|CC|$ = Absolute value of the confidence coefficient (from Equation 12A-5); and

$\overline{RM}$ = Average RM value.

13.0 Method Performance

13.1 Measurement Error (ME). ~~ME is assessed at zero-level, mid-level and high-level values as given below using standards for both Hg^0 and HgCl$_2$. The mean difference between the indicated CEMS concentration and the reference concentration value for each standard shall be no greater than 5 percent of the span value.~~ For Hg^0, the ME must not exceed 5 percent of the span value at the zero-, mid-, and high-level reference gas concentrations. For HgCl$_2$, the ME must not exceed 10 percent of the span value at the zero-, mid-, and high-level reference gas concentrations.

13.2 Calibration Drift (CD). The CD shall not exceed 5 percent of the span value on any of the 7 days of the CD test.

13.3 RA. The RA of the CEMS must be no greater than 20 percent of the mean value of the RM test data in terms of units of µg/~~m^3~~scm. Alternatively, if the mean RM is less than 5.0 µg/~~m^3~~scm, the results are acceptable if the absolute value of the difference between the mean RM and CEMS values does not exceed 1.0 µg/~~m^3~~scm.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures [Reserved]

17.0 Bibliography

17.1 40 CFR part 60*, appendix B, “Performance Specification 2—Specifications and Test Procedures for SO2 and NOX Continuous Emission Monitoring Systems in Stationary Sources.”

17.2 40 CFR part 60*, appendix A, “Method 29—Determination of Metals Emissions from Stationary Sources.”

17.3 40 CFR part 60*, appendix A, “Method 30A – Determination of total Vapor Phase Mercury Emissions From Stationary Sources (Instrumental Analyzer Procedure).

17.4 40 CFR part 60* appendix A, “Method 30B – Determination of Total Vapor Phase Mercury Emissions From Coal – Fired Combustion Sources Using Carbon Sorbent Traps.”

17.5 ASTM Method D6784–02, “Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method).”

18.0 Tables and Figures

Table 12A-1: t-Values

n[a]	$t_{0.975}$	n[a]	$t_{0.975}$	n[a]	$t_{0.975}$
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145
6	2.571	11	2.228	16	2.131

[a] The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of individual values.

Figure 12A-1: ME Determination

	Date	Time	Reference gas value ($\mu g/m^3$)	CEMS measured value ($\mu g/m^3$)	Absolute difference ($\mu g/m^3$)	ME (% of span value)
~~Low~~ Zero Level						
	Average					
Mid Level						
	Average					
High Level						
	Average					

Figure 12A-2: 7-Day Calibration Drift Determination

	Date	Time	Reference gas value (μg/m^3)	CEMS measured value (μg/m^3)	Absolute difference (μg/m^3)	CD (% of span value)
~~Low~~ Zero Level						
Upscale (Mid or High)						

Figure 12A-3: Relative Accuracy Test Data

Run No	Date	Begin time	End time	RM value (μg/m~~3~~^{3})	CEMS value (μg/m~~3~~^{3})	Difference (μg/m~~3~~^{3})	Run used? (Yes/No)	RD[1]
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
Average Values								

Arithmetic Mean Difference:
Standard Deviation:
Confidence Coefficient:
T-Value:
% Relative Accuracy:
|(RM)avg - (CEMS)avg |:

[1] Calculate the RD only if paired samples are taken using Method 30B, Method 29, or ASTM 6784–08. Express RD as a percentage or, for very low RM concentrations (≤1.0 μg/m^3), as the absolute difference between C_a and C_b.