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## PERFORMANCE SPECIFICATION 12B—SPECIFICATIONS AND TEST PROCEDURES FOR MONITORING TOTAL VAPOR PHASE MERCURY EMISSIONS FROM STATIONARY SOURCES USING A SORBENT TRAP MONITORING SYSTEM

### *1.0 Scope and Application*

The purpose of Performance Specification 12B (PS 12B) is to establish performance benchmarks for, and to evaluate the acceptability of, sorbent trap monitoring systems used to monitor total vapor-phase mercury (Hg) emissions in stationary source flue gas streams. These monitoring systems involve continuous repetitive in-stack sampling using paired sorbent media traps with periodic analysis of the time-integrated samples. Persons using PS 12B should have a thorough working knowledge of Methods 1, 2, 3, 4, 5 and 30B in appendices A-1 through A-3 and A-8 to this part.

1.1 Analyte. The analyte measured by these procedures and specifications is total vapor phase Hg in the flue gas, which represents the sum of elemental Hg (Hg<sup>0</sup>, CAS Number 7439-97-6) and gaseous forms of oxidized Hg (*i.e.*, Hg<sup>+2</sup>) in mass concentration units of micrograms per dry standard cubic meter (µg/dscm).

### *1.2 Applicability*

1.2.1 These procedures are only intended for use under relatively low particulate conditions (e.g., monitoring after all pollution control devices). This specification is for evaluating the acceptability of total vapor phase Hg sorbent trap monitoring systems installed at stationary sources at the time of, or soon after, installation and whenever specified in the regulations. The Hg monitoring system must be capable of measuring the total concentration of vapor phase Hg (regardless of speciation), in units of µg/dscm.

1.2.2 This specification contains routine procedures and specifications designed to evaluate an installed sorbent trap monitoring system's performance over time; Procedure 5 of appendix F to this part contains additional procedures and specifications which may be required for long term operation. In addition, the source owner or operator is responsible to calibrate, maintain, and operate the monitoring system properly. The Administrator may require the owner or operator, under section 114 of the Clean Air Act, to conduct performance evaluations at other times besides the initial test to evaluate the CEMS performance. *See* §60.13(c) and 63.8(e)(1).

### *2.0 Principle*

Known volumes of flue gas are continuously extracted from a stack or duct through paired, in-stack, pre-spiked sorbent media traps at appropriate nominal flow rates. The sorbent traps in the sampling system are periodically exchanged with new ones, prepared for analysis as needed, and analyzed by any technique that can meet the performance criteria. For quality-assurance

purposes, a section of each sorbent trap is spiked with Hg<sup>0</sup> prior to sampling. Following sampling, this section is analyzed separately and a specified minimum percentage of the spike must be recovered. Paired train sampling is required to determine method precision.

### *3.0 Definitions*

*3.1 Sorbent Trap Monitoring System* means the total equipment required for the collection of gaseous Hg samples using paired three-partition sorbent traps.

*3.2 Relative Accuracy Test Procedure* means a test procedure consisting of at least nine runs, in which the accuracy of the total vapor phase Hg concentrations measured by the sorbent trap monitoring system 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.

*3.3 Relative Accuracy (RA)* means the absolute mean difference between the pollutant (Hg) concentrations determined by the sorbent trap monitoring system and the values 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, the RA may be expressed as the absolute value of the difference between the mean sorbent trap monitoring system and RM values.

*3.4 Relative Deviation (RD)* means the absolute difference of the Hg concentration values obtained with a pair of sorbent traps divided by the sum of those concentrations, expressed as a percentage. RD is used to assess the precision of the sorbent trap monitoring system.

*3.5 Spike Recovery* means the mass of Hg recovered from the spiked trap section, expressed as a percentage of the amount spiked. Spike recovery is used to assess sample matrix interference.

### *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.

### *6.0 Equipment and Supplies*

#### *6.1 Sorbent Trap Monitoring System Equipment Specifications.*

*6.1.1 Monitoring System.* The equipment described in Method 30B in appendix A-8 to this part must be used to continuously sample for Hg emissions, with the substitution of three-section traps in place of two-section traps, as described below. A typical sorbent trap monitoring system is shown in Figure 12B-1.

6.1.2 Three-Section Sorbent Traps. The sorbent media used to collect Hg must be configured in traps with three distinct and identical segments or sections, connected in series, to be separately analyzed. section 1 is designated for primary capture of gaseous Hg. section 2 is designated as a backup section for determination of vapor-phase Hg breakthrough. section 3 is designated for quality assurance/quality control (QA/QC) purposes. section 3 must be spiked with a known amount of gaseous Hg<sup>0</sup> prior to sampling and later analyzed to determine the spike (and hence sample) recovery efficiency.

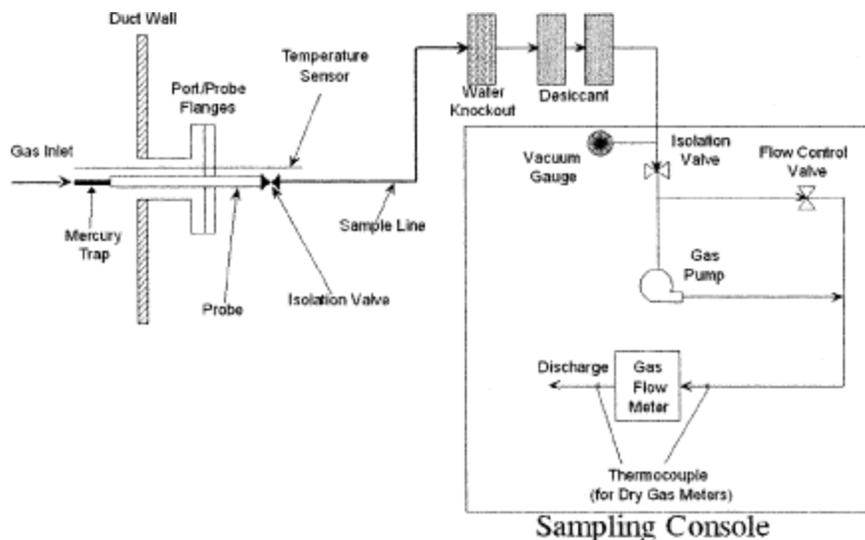


Figure 12B-1. Typical Sorbent Trap Monitoring System (only one trap and associated sampling system is illustrated).

6.1.3 Gaseous Hg<sup>0</sup> Sorbent Trap Spiking System. A known mass of gaseous Hg<sup>0</sup> must be spiked onto section 3 of each sorbent trap prior to sampling. Any approach capable of quantitatively delivering known masses of Hg<sup>0</sup> onto sorbent traps is acceptable. Several technologies or devices are available to meet this objective. Their practicality is a function of Hg mass spike levels. For low levels, NIST-certified or NIST-traceable gas generators or tanks may be suitable, but will likely require long preparation times. A more practical, alternative system, capable of delivering almost any mass required, employs NIST-certified or NIST-traceable Hg salt solutions (e.g., Hg(NO<sub>3</sub>)<sub>2</sub>). With this system, an aliquot of known volume and concentration is added to a reaction vessel containing a reducing agent (e.g., stannous chloride); the Hg salt solution is reduced to Hg<sup>0</sup> and purged onto section 3 of the sorbent trap by using an impinger sparging system.

6.1.4 Sample Analysis Equipment. Any analytical system capable of quantitatively recovering and quantifying total gaseous Hg from sorbent media is acceptable provided that the analysis can meet the performance criteria in Table 12B-1 in section 9 of this performance specification. Candidate recovery techniques include leaching, digestion, and thermal desorption. Candidate analytical techniques include ultraviolet atomic fluorescence (UV AF); ultraviolet atomic absorption (UV AA), with and without gold trapping; and in-situ X-ray fluorescence (XRF).

## 7.0 Reagents and Standards

Only NIST-certified or NIST-traceable calibration gas standards and reagents must be used for the tests and procedures required under this performance specification. The sorbent media may be any collection material (e.g., carbon, chemically treated filter, *etc.*) capable of quantitatively capturing and recovering for subsequent analysis, all gaseous forms of Hg in the emissions from the intended application. Selection of the sorbent media must be based on the material's ability to achieve the performance criteria contained in this method as well as the sorbent's vapor phase Hg capture efficiency for the emissions matrix and the expected sampling duration at the test site.

## 8.0 Performance Specification Test Procedure

### 8.1 Installation and Measurement Location Specifications.

8.1.1 Selection of Monitoring Site. Sampling site information should be obtained in accordance with Method 1 in appendix A-1 to this part. Place the probe inlet at a point or location in the stack (or vent) downstream of all pollution control equipment and representative of the stack gas concentration of Hg. A location that has been shown to be free of stratification for Hg or, alternatively, SO<sub>2</sub> is recommended. An estimation of the expected stack Hg concentration is required to establish a target sample flow rate, total gas sample volume, and the mass of Hg<sup>0</sup> to be spiked onto section 3 of each sorbent trap.

8.1.2 Pre-sampling Spiking of Sorbent Traps. Based on the estimated Hg concentration in the stack, the target sample rate and the target sampling duration, calculate the expected mass loading for section 1 of each sorbent trap (*see* section 12.1 of this performance specification). The pre-sampling spike to be added to section 3 of each sorbent trap must be within  $\pm 50$  percent of the expected section 1 mass loading. Spike section 3 of each sorbent trap at this level, as described in section 6.1.3 of this performance specification. For each sorbent trap, keep a record of the mass of Hg<sup>0</sup> added to section 3. This record must include, at a minimum, the identification number of the trap, the date and time of the spike, the name of the analyst performing the procedure, the method of spiking, the mass of Hg<sup>0</sup> added to section 3 of the trap ( $\mu\text{g}$ ), and the supporting calculations.

8.1.3 Pre-monitoring Leak Check. Perform a leak check with the sorbent traps in place in the sampling system. Draw a vacuum in each sample train. Adjust the vacuum in each sample train to  $\sim 15$ " Hg. Use the gas flow meter to determine leak rate. The leakage rate must not exceed 4 percent of the target sampling rate. Once the leak check passes this criterion, carefully release the vacuum in the sample train, then seal the sorbent trap inlet until the probe is ready for insertion into the stack or duct.

8.1.4 Determination of Flue Gas Characteristics. Determine or measure the flue gas measurement environment characteristics (gas temperature, static pressure, gas velocity, stack moisture, *etc.*) in order to determine ancillary requirements such as probe heating requirements (if any), sampling rate, proportional sampling conditions, moisture management, *etc.*

### 8.2 Monitoring.

8.2.1 System Preparation and Initial Data Recording. Remove the plug from the end of each sorbent trap and store each plug in a clean sorbent trap storage container. Remove the stack or duct port cap and insert the probe(s) with the inlet(s) aligned perpendicular to the stack gas flow. Secure the probe(s) and ensure that no leakage occurs between the duct and environment. Record initial data including the sorbent trap ID, start time, starting gas flow meter readings, initial temperatures, set points, and any other appropriate information.

8.2.2 Flow Rate Control. Set the initial sample flow rate at the target value from section 8.1.1 of this performance specification. Then, for every operating hour during the sampling period, record the date and time, the sample flow rate, the gas flow meter reading, the stack temperature (if needed), the flow meter temperatures (if needed), temperatures of heated equipment such as the vacuum lines and the probes (if heated), and the sampling system vacuum readings. Also, record the stack gas flow rate and the ratio of the stack gas flow rate to the sample flow rate. Adjust the sampling flow rate to maintain proportional sampling, *i.e.*, keep the ratio of the stack gas flow rate to sample flow rate within  $\pm 25$  percent of the reference ratio from the first hour of the data collection period (*see* section 12.2 of this performance specification). The sample flow rate through a sorbent trap monitoring system during any hour (or portion of an hour) that the unit is not operating must be zero.

8.2.3 Stack Gas Moisture Determination. If data from the sorbent trap monitoring system will be used to calculate Hg mass emissions, determine the stack gas moisture content using a continuous moisture monitoring system or other means acceptable to the Administrator, such as the ones described in §75.11(b) of this chapter. Alternatively, for combustion of coal, wood, or natural gas in boilers only, a default moisture percentage from §75.11(b) of this chapter may be used.

8.2.4 Essential Operating Data. Obtain and record any essential operating data for the facility during the test period, e.g., the barometric pressure for correcting the sample volume measured by a dry gas meter to standard conditions. At the end of the data collection period, record the final gas flow meter reading and the final values of all other essential parameters.

8.2.5 Post-monitoring Leak Check. When the monitoring period is completed, turn off the sample pump, remove the probe/sorbent trap from the port and carefully re-plug the end of each sorbent trap. Perform a leak check with the sorbent traps in place, at the maximum vacuum reached during the monitoring period. Use the same general approach described in section 8.1.3 of this performance specification. Record the leakage rate and vacuum. The leakage rate must not exceed 4 percent of the average sampling rate for the monitoring period. Following the leak check, carefully release the vacuum in the sample train.

8.2.6 Sample Recovery. Recover each sampled sorbent trap by removing it from the probe and seal both ends. Wipe any deposited material from the outside of the sorbent trap. Place the sorbent trap into an appropriate sample storage container and store/preserve it in an appropriate manner.

8.2.7 Sample Preservation, Storage, and Transport. While the performance criteria of this approach provide for verification of appropriate sample handling, it is still important that the user

consider, determine, and plan for suitable sample preservation, storage, transport, and holding times for these measurements. Therefore, procedures in recognized voluntary consensus standards such as those in ASTM D6911-03 “Standard Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis” should be followed for all samples.

8.2.8 Sample Custody. Proper procedures and documentation for sample chain of custody are critical to ensuring data integrity. Chain of custody procedures in recognized voluntary consensus standards such as those in ASTM D4840-99 “Standard Guide for Sample Chain-of-Custody Procedures” should be followed for all samples (including field samples and blanks).

### 8.3 Relative Accuracy (RA) Test Procedure

8.3.1 For the initial certification of a sorbent trap monitoring system, a RA Test is required. Follow the basic RA test procedures and calculation methodology described in sections 8.4.1 through 8.4.7 and 12.4 of PS 12A in this appendix, replacing the term “CEMS” with “sorbent trap monitoring system”.

8.3.2 Special Considerations. The type of sorbent material used in the traps must be the same as that used for daily operation of the monitoring system; however, the size of the traps used for the RA test may be smaller than the traps used for daily operation of the system. Spike the third section of each sorbent trap with elemental Hg, as described in section 8.1.2 of this performance specification. Install a new pair of sorbent traps prior to each test run. For each run, the sorbent trap data must be validated according to the quality assurance criteria in Table 12B-1 in section 9.0, below.

8.3.3 Acceptance Criteria. The RA of the sorbent trap monitoring system must be no greater than 20 percent of the mean value of the RM test data in terms of units of  $\mu\text{g}/\text{scm}$ . Alternatively, if the RM concentration is less than or equal to  $5.0 \mu\text{g}/\text{scm}$ , then the RA results are acceptable if the absolute difference between the means of the RM and sorbent trap monitoring system values does not exceed  $1.0 \mu\text{g}/\text{scm}$ .

### 9.0 Quality Assurance and Quality Control (QA/QC)

Table 12B-1 summarizes the QA/QC performance criteria that are used to validate the Hg emissions data from a sorbent trap monitoring system. Failure to achieve these performance criteria will result in invalidation of Hg emissions data, except where otherwise noted.

**TABLE 12B-1—QA/QC CRITERIA FOR SORBENT TRAP MONITORING SYSTEMS**

| <b>QA/QC test or specification</b> | <b>Acceptance criteria</b>          | <b>Frequency</b>    | <b>Consequences if not met</b>                               |
|------------------------------------|-------------------------------------|---------------------|--|
| Pre-test leak check                | $\leq 4\%$ of target sampling rate  | Prior to monitoring | Monitoring must not commence until the leak check is passed. |
| Post-test leak                     | $\leq 4\%$ of average sampling rate | After monitoring    | Invalidate the data from                                     |

|  |  |  |  |
|--|--|--|--|
| check  |  |  | the paired traps or, if certain conditions are met, report adjusted data from a single trap (see Section 12.8.3).                          |
| Ratio of stack gas flow rate to sample flow rate | No more than 5% of the hourly ratios or 5 hourly ratios (whichever is less restrictive) may deviate from the reference ratio by more than $\pm 25\%$                                   | Every hour throughout monitoring period                                | Invalidate the data from the paired traps or, if certain conditions are met, report adjusted data from a single trap (see Section 12.8.3). |
| Sorbent trap section 2 breakthrough              | $\leq 5\%$ of Section 1 Hg mass<br>$\leq 10\%$ of Section 1 Hg mass if average Hg concentration is $\leq 0.5 \mu\text{g}/\text{scm}$   | Every sample   | Invalidate the data from the paired traps or, if certain conditions are met, report adjusted data from a single trap (see Section 12.8.3). |
|  | No criterion when Hg concentration for trap less than 10% of the applicable emission limit (must meet all other QA/QC specifications)  |  |  |
| Paired sorbent trap agreement                    | $\leq 10\%$ Relative Deviation (RD) if the average concentration is $> 1.0 \mu\text{g}/\text{m}^3$<br>$\leq 20\%$ RD if the average concentration is $\leq 1.0 \mu\text{g}/\text{m}^3$ | Every sample   | Either invalidate the data from the paired traps or report the results from the trap with the higher Hg concentration.                     |
|  | Results also acceptable if absolute difference between concentrations from paired traps is $\leq 0.03 \mu\text{g}/\text{m}^3$  |  |  |
| Spike Recovery Study                             | Average recovery between 85% and 115% for each of the 3 spike concentration levels   | Prior to analyzing field samples and prior to use of new sorbent media | Field samples must not be analyzed until the percent recovery criteria have been met.  |
| Multipoint analyzer calibration                  | Each analyzer reading within $\pm 10\%$ of true value and $r^2 \geq 0.99$  | On the day of analysis, before analyzing any samples                   | Recalibrate until successful.  |
| Analysis of independent calibration              | Within $\pm 10\%$ of true value  | Following daily calibration, prior to analyzing field                  | Recalibrate and repeat independent standard analysis until successful.   |

| standard  |  | samples   |  |
|---|--|---|--|
| Spike recovery from section 3 of both sorbent traps | 75-125% of spike amount  | Every sample  | Invalidate the data from the paired traps or, if certain conditions are met, report adjusted data from a single trap (see Section 12.8.3). |
| Relative Accuracy                                   | RA $\leq$ 20.0% of RM mean value; or if RM mean value $\leq$ 5.0 $\mu\text{g}/\text{scm}$ , absolute difference between RM and sorbent trap monitoring system mean values $\leq$ 1.0 $\mu\text{g}/\text{scm}$  | RA specification must be met for initial certification                              | Data from the system are invalid until a RA test is passed.  |
| Gas flow meter calibration                          | An initial calibration factor (Y) has been determined at 3 settings; for mass flow meters, initial calibration with stack gas has been performed. For subsequent calibrations, Y within $\pm$ 5% of average value from the most recent 3-point calibration | At 3 settings prior to initial use and at least quarterly at one setting thereafter | Recalibrate meter at 3 settings to determine a new value of Y.   |
| Temperature sensor calibration                      | Absolute temperature measured by sensor within $\pm$ 1.5% of a reference sensor  | Prior to initial use and at least quarterly thereafter                              | Recalibrate; sensor may not be used until specification is met.  |
| Barometer calibration                               | Absolute pressure measured by instrument within $\pm$ 10 mm Hg of reading with a NIST-traceable barometer  | Prior to initial use and at least quarterly thereafter                              | Recalibrate; instrument may not be used until specification is met.  |

## 10.0 Calibration and Standardization

10.1 Gaseous and Liquid Standards. Only NIST certified or NIST-traceable calibration standards (*i.e.*, calibration gases, solutions, *etc.*) must be used for the spiking and analytical procedures in this performance specification.

10.2 Gas Flow Meter Calibration. The manufacturer or supplier of the gas flow meter should perform all necessary set-up, testing, programming, *etc.*, and should provide the end user with any necessary instructions, to ensure that the meter will give an accurate readout of dry gas volume in standard cubic meters for the particular field application.

10.2.1 Initial Calibration. Prior to its initial use, a calibration of the flow meter must be performed. The initial calibration may be done by the manufacturer, by the equipment supplier, or by the end user. If the flow meter is volumetric in nature (e.g., a dry gas meter), the manufacturer, equipment supplier, or end user may perform a direct volumetric calibration using

any gas. For a mass flow meter, the manufacturer, equipment supplier, or end user may calibrate the meter using a bottled gas mixture containing  $12 \pm 0.5\%$  CO<sub>2</sub>,  $7 \pm 0.5\%$  O<sub>2</sub>, and balance N<sub>2</sub>, or these same gases in proportions more representative of the expected stack gas composition. Mass flow meters may also be initially calibrated on-site, using actual stack gas.

10.2.1.1 Initial Calibration Procedures. Determine an average calibration factor (Y) for the gas flow meter, by calibrating it at three sample flow rate settings covering the range of sample flow rates at which the sorbent trap monitoring system typically operates. Either the procedures in section 10.3.1 of Method 5 in appendix A-3 to this part or the procedures in section 16 of Method 5 in appendix A-3 to this part may be followed. If a dry gas meter is being calibrated, use at least five revolutions of the meter at each flow rate.

10.2.1.2 Alternative Initial Calibration Procedures. Alternatively, the initial calibration of the gas flow meter may be performed using a reference gas flow meter (RGFM). The RGFM may be either: (1) A wet test meter calibrated according to section 10.3.1 of Method 5 in appendix A-3 to this part; (2) A gas flow metering device calibrated at multiple flow rates using the procedures in section 16 of Method 5 in appendix A-3 to this part; or (3) A NIST-traceable calibration device capable of measuring volumetric flow to an accuracy of 1 percent. To calibrate the gas flow meter using the RGFM, proceed as follows: While the sorbent trap monitoring system is sampling the actual stack gas or a compressed gas mixture that simulates the stack gas composition (as applicable), connect the RGFM to the discharge of the system. Care should be taken to minimize the dead volume between the sample flow meter being tested and the RGFM. Concurrently measure dry gas volume with the RGFM and the flow meter being calibrated for a minimum of 10 minutes at each of three flow rates covering the typical range of operation of the sorbent trap monitoring system. For each 10-minute (or longer) data collection period, record the total sample volume, in units of dry standard cubic meters (dscm), measured by the RGFM and the gas flow meter being tested.

10.2.1.3 Initial Calibration Factor. Calculate an individual calibration factor  $Y_i$  at each tested flow rate from section 10.2.1.1 or 10.2.1.2 of this performance specification (as applicable), by taking the ratio of the reference sample volume to the sample volume recorded by the gas flow meter. Average the three  $Y_i$  values, to determine Y, the calibration factor for the flow meter. Each of the three individual values of  $Y_i$  must be within  $\pm 0.02$  of Y. Except as otherwise provided in sections 10.2.1.4 and 10.2.1.5 of this performance specification, use the average Y value from the three level calibration to adjust all subsequent gas volume measurements made with the gas flow meter.

10.2.2 Initial On-Site Calibration Check. For a mass flow meter that was initially calibrated using a compressed gas mixture, an on-site calibration check must be performed before using the flow meter to provide data. While sampling stack gas, check the calibration of the flow meter at one intermediate flow rate typical of normal operation of the monitoring system. Follow the basic procedures in section 10.2.1.1 or 10.2.1.2 of this performance specification. If the onsite calibration check shows that the value of  $Y_i$ , the calibration factor at the tested flow rate, differs by more than 5 percent from the value of Y obtained in the initial calibration of the meter, repeat the full 3-level calibration of the meter using stack gas to determine a new value of Y, and apply the new Y value to all subsequent gas volume measurements made with the gas flow meter.

10.2.3 Ongoing Quality Control. Recalibrate the gas flow meter quarterly at one intermediate flow rate setting representative of normal operation of the monitoring system. Follow the basic procedures in section 10.2.1.1 or 10.2.1.2 of this performance specification. If a quarterly recalibration shows that the value of  $Y_i$ , the calibration factor at the tested flow rate, differs from the current value of  $Y$  by more than 5 percent, repeat the full 3-level calibration of the meter to determine a new value of  $Y$ , and apply the new  $Y$  value to all subsequent gas volume measurements made with the gas flow meter.

10.3 Calibration of Thermocouples and Other Temperature Sensors. Use the procedures and criteria in section 10.3 of Method 2 in appendix A-1 to this part to calibrate in-stack temperature sensors and thermocouples. Calibrations must be performed prior to initial use and at least quarterly thereafter. At each calibration point, the absolute temperature measured by the temperature sensor must agree to within  $\pm 1.5$  percent of the temperature measured with the reference sensor, otherwise the sensor may not continue to be used.

10.4 Barometer Calibration. Calibrate the barometer against another barometer that has a NIST-traceable calibration. This calibration must be performed prior to initial use and at least quarterly thereafter. At each calibration point, the absolute pressure measured by the barometer must agree to within  $\pm 10$  mm Hg of the pressure measured by the NIST-traceable barometer, otherwise the barometer may not continue to be used.

10.5 Calibration of Other Sensors and Gauges. Calibrate all other sensors and gauges according to the procedures specified by the instrument manufacturer(s).

10.6 Analytical System Calibration. *See* section 11.1 of this performance specification.

### *11.0 Analytical Procedures*

The analysis of the Hg samples may be conducted using any instrument or technology capable of quantifying total Hg from the sorbent media and meeting the performance criteria in section 9 of this performance specification.

11.1 Analyzer System Calibration. Perform a multipoint calibration of the analyzer at three or more upscale points over the desired quantitative range (multiple calibration ranges must be calibrated, if necessary). The field samples analyzed must fall within a calibrated, quantitative range and meet the necessary performance criteria. For samples that are suitable for aliquotting, a series of dilutions may be needed to ensure that the samples fall within a calibrated range. However, for sorbent media samples that are consumed during analysis (e.g., thermal desorption techniques), extra care must be taken to ensure that the analytical system is appropriately calibrated prior to sample analysis. The calibration curve range(s) should be determined based on the anticipated level of Hg mass on the sorbent media. Knowledge of estimated stack Hg concentrations and total sample volume may be required prior to analysis. The calibration curve for use with the various analytical techniques (e.g., UV AA, UV AF, and XRF) can be generated by directly introducing standard solutions into the analyzer or by spiking the standards onto the sorbent media and then introducing into the analyzer after preparing the sorbent/standard according to the particular analytical technique. For each calibration curve, the value of the

square of the linear correlation coefficient, *i.e.*,  $r^2$ , must be  $\geq 0.99$ , and the analyzer response must be within  $\pm 10$  percent of reference value at each upscale calibration point. Calibrations must be performed on the day of the analysis, before analyzing any of the samples. Following calibration, an independently prepared standard (not from same calibration stock solution) must be analyzed. The measured value of the independently prepared standard must be within  $\pm 10$  percent of the expected value.

11.2 Sample Preparation. Carefully separate the three sections of each sorbent trap. Combine for analysis all materials associated with each section, *i.e.*, any supporting substrate that the sample gas passes through prior to entering a media section (e.g., glass wool, polyurethane foam, *etc.*) must be analyzed with that segment.

11.3 Spike Recovery Study. Before analyzing any field samples, the laboratory must demonstrate the ability to recover and quantify Hg from the sorbent media by performing the following spike recovery study for sorbent media traps spiked with elemental mercury. Using the procedures described in sections 6.2 and 12.1 of this performance specification, spike the third section of nine sorbent traps with gaseous  $\text{Hg}^0$ , *i.e.*, three traps at each of three different mass loadings, representing the range of masses anticipated in the field samples. This will yield a  $3 \times 3$  sample matrix. Prepare and analyze the third section of each spiked trap, using the techniques that will be used to prepare and analyze the field samples. The average recovery for each spike concentration must be between 85 and 115 percent. If multiple types of sorbent media are to be analyzed, a separate spike recovery study is required for each sorbent material. If multiple ranges are calibrated, a separate spike recovery study is required for each range.

11.4 Field Sample Analyses. Analyze the sorbent trap samples following the same procedures that were used for conducting the spike recovery study. The three sections of each sorbent trap must be analyzed separately (*i.e.*, section 1, then section 2, then section 3). Quantify the total mass of Hg for each section based on analytical system response and the calibration curve from section 11.1 of this performance specification. Determine the spike recovery from sorbent trap section 3. The spike recovery must be no less than 75 percent and no greater than 125 percent. To report the final Hg mass for each trap, add together the Hg masses collected in trap sections 1 and 2.

## 12.0 Calculations, Data Reduction, and Data Analysis

12.1 Calculation of Pre-Sampling Spiking Level. Determine sorbent trap section 3 spiking level using estimates of the stack Hg concentration, the target sample flow rate, and the expected monitoring period. Calculate  $M_{exp}$ , the expected Hg mass that will be collected in section 1 of the trap, using Equation 12B-1. The pre-sampling spike must be within  $\pm 50$  percent of this mass.

$$M_{exp} = [Q_s t_s C_{est}] \times 10^{-3} \quad (\text{Equation 12B-1})$$

Where:

$M_{exp}$  = Expected sample mass ( $\mu\text{g}$ )

$Q_s$  = Sample flow rate (L/min)

$t_s$  = Expected monitoring period (min)

$C_{est}$  = Estimated Hg concentration in stack gas ( $\mu\text{g}/\text{m}^3$ )

$10^{-3}$  = Conversion factor ( $\text{m}^3/\text{L}$ )

*Example calculation:* For an estimated stack Hg concentration of  $5 \mu\text{g}/\text{m}^3$ , a target sample rate of 0.30 L/min, and a monitoring period of 5 days:

$$M_{exp} = (0.30 \text{ L/min})(1440 \text{ min/day})(5 \text{ days})(10^{-3} \text{ m}^3/\text{L})(5 \mu\text{g}/\text{m}^3) = 10.8 \mu\text{g}$$

A pre-sampling spike of  $10.8 \mu\text{g} \pm 50$  percent is, therefore, appropriate.

12.2 Calculations for Flow-Proportional Sampling. For the first hour of the data collection period, determine the reference ratio of the stack gas volumetric flow rate to the sample flow rate, as follows:

$$R_{ref} = \frac{KQ_{ref}}{F_{ref}} \quad (\text{Equation 12B-1})$$

Where:

$R_{ref}$  = Reference ratio of hourly stack gas flow rate to hourly sample flow rate

$Q_{ref}$  = Average stack gas volumetric flow rate for first hour of collection period (scfh)

$F_{ref}$  = Average sample flow rate for first hour of the collection period, in appropriate units (e.g., liters/min, cc/min, dscm/min)

$K$  = Power of ten multiplier, to keep the value of  $R_{ref}$  between 1 and 100. The appropriate  $K$  value will depend on the selected units of measure for the sample flow rate.

Then, for each subsequent hour of the data collection period, calculate ratio of the stack gas flow rate to the sample flow rate using Equation 12B-3:

$$R_h = \frac{KQ_h}{F_h} \quad (\text{Equation 12B-3})$$

Where:

$R_h$  = Ratio of hourly stack gas flow rate to hourly sample flow rate

$Q_h$  = Average stack gas volumetric flow rate for the hour (scfh)

$F_h$  = Average sample flow rate for the hour, in appropriate units (e.g., liters/min, cc/min, dscm/min)

$K$  = Power of ten multiplier, to keep the value of  $R_h$  between 1 and 100. The appropriate  $K$  value will depend on the selected units of measure for the sample flow rate and the range of expected stack gas flow rates.

Maintain the value of  $R_h$  within  $\pm 25$  percent of  $R_{ref}$  throughout the data collection period.

12.3 Calculation of Spike Recovery. Calculate the percent recovery of each section 3 spike, as follows:

$$\%R = \frac{M_3}{M_s} \times 100 \quad (\text{Equation 12B-4})$$

Where:

$\%R$  = Percentage recovery of the pre-sampling spike

$M_3$  = Mass of Hg recovered from section 3 of the sorbent trap, ( $\mu\text{g}$ )

$M_s$  = Calculated Hg mass of the pre-sampling spike, from section 8.1.2 of this performance specification, ( $\mu\text{g}$ )

12.4 Calculation of Breakthrough. Calculate the percent breakthrough to the second section of the sorbent trap, as follows:

$$\%B = \frac{M_2}{M_1} \times 100 \quad (\text{Equation 12B-5})$$

Where:

$\%B$  = Percent breakthrough

$M_2$  = Mass of Hg recovered from section 2 of the sorbent trap, ( $\mu\text{g}$ )

$M_1$  = Mass of Hg recovered from section 1 of the sorbent trap, ( $\mu\text{g}$ )

12.5 Calculation of Hg Concentration. Calculate the Hg concentration for each sorbent trap, using the following equation:

$$C = \frac{M^*}{V_t} \quad (\text{Equation 12B-6})$$

Where:

$C$  = Concentration of Hg for the collection period, ( $\mu\text{g}/\text{dscm}$ )

$M^*$  = Total mass of Hg recovered from sections 1 and 2 of the sorbent trap, ( $\mu\text{g}$ )

$V_t$  = Total volume of dry gas metered during the collection period, (dscm). For the purposes of this performance specification, standard temperature and pressure are defined as  $20^\circ\text{C}$  and  $760\text{ mm Hg}$ , respectively.

12.6 Calculation of Paired Trap Agreement. Calculate the relative deviation (RD) between the Hg concentrations measured with the paired sorbent traps:

$$RD = \frac{|C_a - C_b|}{C_a + C_b} \times 100 \quad (\text{Equation 12B-7})$$

Where:

RD = Relative deviation between the Hg concentrations from traps “a” and “b” (percent)

C<sub>a</sub> = Concentration of Hg for the collection period, for sorbent trap “a” (µg/dscm)

C<sub>b</sub> = Concentration of Hg for the collection period, for sorbent trap “b” (µg/dscm)

12.7 Calculation of Relative Accuracy. Calculate the relative accuracy as described in section 12.4 of PS 12A in this appendix.

12.8 Data Reduction. Typical monitoring periods for normal, day-to-day operation of a sorbent trap monitoring system range from about 24 hours to 168 hours. For the required RA tests of the system, smaller sorbent traps are often used, and the “monitoring period” or time per run is considerably shorter (e.g., 1 hour or less). Generally speaking, to validate sorbent trap monitoring system data, the acceptance criteria for the following five QC specifications in Table 12B-1 above must be met for both traps: (a) the post-monitoring leak check; (b) the ratio of stack gas flow rate to sample flow rate; (c) section 2 breakthrough; (d) paired trap agreement; and (e) section 3 spike recovery.

12.8.1 For routine day-to-day operation of a sorbent trap monitoring system, when both traps meet the acceptance criteria for all five QC specifications, the two measured Hg concentrations must be averaged arithmetically and the average value must be applied to each hour of the data collection period.

12.8.2 To validate a RA test run, both traps must meet the acceptance criteria for all five QC specifications. However, as specified in section 12.8.3 below, for routine day-to-day operation of the monitoring system, a monitoring period may, in certain instances, be validated based on the results from one trap.

12.8.3 For the routine, day-to-day operation of the monitoring system, when one of the two sorbent trap samples or sampling systems either: (a) Fails the post-monitoring leak check; or (b) has excessive section 2 breakthrough; or (c) fails to maintain the proper stack flow-to-sample flow ratio; or (d) fails to achieve the required section 3 spike recovery; or (e) is lost, broken, or damaged, provided that the other trap meets the acceptance criteria for all four of these QC specifications, the Hg concentration measured by the valid trap may be multiplied by a factor of 1.111 and then used for reporting purposes. Further, if both traps meet the acceptance criteria for all four of these QC specifications, but the acceptance criterion for paired trap agreement is not met, the owner or operator may report the higher of the two Hg concentrations measured by the traps, in lieu of invalidating the data from the paired traps.

12.8.4 Whenever the data from a pair of sorbent traps must be invalidated and no quality-assured data from a certified backup Hg monitoring system or Hg reference method are available to cover the hours in the data collection period, treat those hours in the manner specified in the applicable regulation (*i.e.*, use missing data substitution procedures or count the hours as monitoring system down time, as appropriate).

### *13.0 Monitoring System Performance*

These monitoring criteria and procedures have been successfully applied to coal-fired utility boilers (including units with post-combustion emission controls), having vapor-phase Hg concentrations ranging from 0.03 µg/dscm to approximately 100 µg/dscm.

### *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 SO<sub>2</sub> and NO<sub>x</sub>Continuous Emission Monitoring Systems in Stationary Sources.”

17.2 40 CFR Part 60, Appendix B, “Performance Specification 12A—Specifications and Test Procedures for Total Vapor Phase Mercury Continuous Emission Monitoring Systems in Stationary Sources.”