

Quality Assurance and Operating Procedures for Sorbent Trap Monitoring Systems

1.0 Scope and Application

This appendix specifies sampling, and analytical, and quality-assurance criteria and procedures for the performance-based monitoring of vapor-phase mercury (Hg) emissions in combustion flue gas streams, using a sorbent trap monitoring system (as defined in §72.2 of this chapter). The principle employed is continuous sampling using in-stack sorbent media coupled with analysis of the integrated samples. The performance-based approach of this appendix allows for use of various suitable sampling and analytical technologies while maintaining a specified and documented level of data quality through performance criteria. Persons using this appendix should have a thorough working knowledge of Methods 1, 2, 3, 4 and 5 in appendices A–1 through A–3 to part 60 of this chapter, as well as the determinative technique selected for analysis.

1.1 Analytes.

The analyte measured by these procedures and specifications is total vapor-phase Hg in the flue gas, which represents the sum of elemental Hg (Hg⁰, CAS Number 7439–97–6) and oxidized forms of Hg, in mass concentration units of micrograms per dry standard cubic meter (µgm/dscm).

1.2 Applicability.

These performance criteria and procedures are applicable to monitoring of vapor-phase Hg emissions under relatively low-dust conditions (*i.e.* , sampling in the stack after all pollution control devices), from coal-fired electric utility steam generators which are subject to subpart I of this part. Individual sample collection times can range from 30 minutes to several days in duration, depending on the Hg concentration in the stack. The monitoring system must achieve the performance criteria specified in Section 8 of this appendix and the sorbent media capture ability must not be exceeded. The sampling rate must be maintained at a constant proportion to the total stack flowrate to ensure representativeness of the sample collected. Failure to achieve certain performance criteria will result in invalid Hg emissions monitoring data.

2.0 Principle.

Known volumes of flue gas are extracted from a stack or duct through paired, in-stack, pre-spiked sorbent media traps at an appropriate nominal flow rate. Collection of Hg on the sorbent media in the stack mitigates potential loss of Hg during transport through a probe/sample line. Paired train sampling is required to determine measurement precision and verify acceptability of the measured emissions data.

The sorbent traps are recovered from the sampling system, prepared for analysis, as needed, and analyzed by any suitable determinative technique that can meet the performance criteria. A section of each sorbent trap is spiked with Hg⁰ prior to sampling. This section is analyzed separately and the recovery value is used to correct the individual Hg sample for measurement bias.

3.0 Clean Handling and Contamination.

To avoid Hg contamination of the samples, special attention should be paid to cleanliness during transport, field handling, sampling, recovery, and laboratory analysis, as well as during preparation of the sorbent cartridges. Collection and analysis of blank samples (field, trip, lab) is useful in verifying the absence of contaminant Hg.

4.0 Safety.

4.1 Site hazards.

Site hazards must be thoroughly considered in advance of applying these procedures/specifications in the field; advance coordination with the site is critical to understand the conditions and applicable safety policies. At a minimum, portions of the sampling system will be hot, requiring appropriate gloves, long sleeves, and caution in handling this equipment.

4.2 Laboratory safety policies.

Laboratory safety policies should be in place to minimize risk of chemical exposure and to properly handle waste disposal. Personnel shall wear appropriate laboratory attire according to a Chemical Hygiene Plan established by the laboratory.

4.3 Toxicity or carcinogenicity.

The toxicity or carcinogenicity of any reagents used must be considered. Depending upon the sampling and analytical technologies selected, this measurement may involve hazardous materials, operations, and equipment and this appendix does not address all of the safety problems associated with implementing this approach. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performance. Any chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized. Chemists should refer to the Material Safety Data Sheet (MSDS) for each chemical used.

4.4 Wastes.

Any wastes generated by this procedure must be disposed of according to a hazardous materials management plan that details and tracks various waste streams and disposal procedures.

5.0 Equipment and Supplies.

The following list is presented as an example of key equipment and supplies likely required to perform vapor-phase Hg monitoring using a sorbent trap monitoring system. It is recognized that additional equipment and supplies may be needed. Collection of paired samples is required. Also required are a certified stack gas volumetric flow monitor that meets the requirements of §75.10 and an acceptable means of correcting for the stack gas moisture content, *i.e.*, either by using data from a certified continuous moisture monitoring system or by using an approved default moisture value (see §§75.11(b)).

5.1 Sorbent Trap Monitoring System.

A typical sorbent trap monitoring system is shown in Figure K-1. The monitoring system shall include the following components:

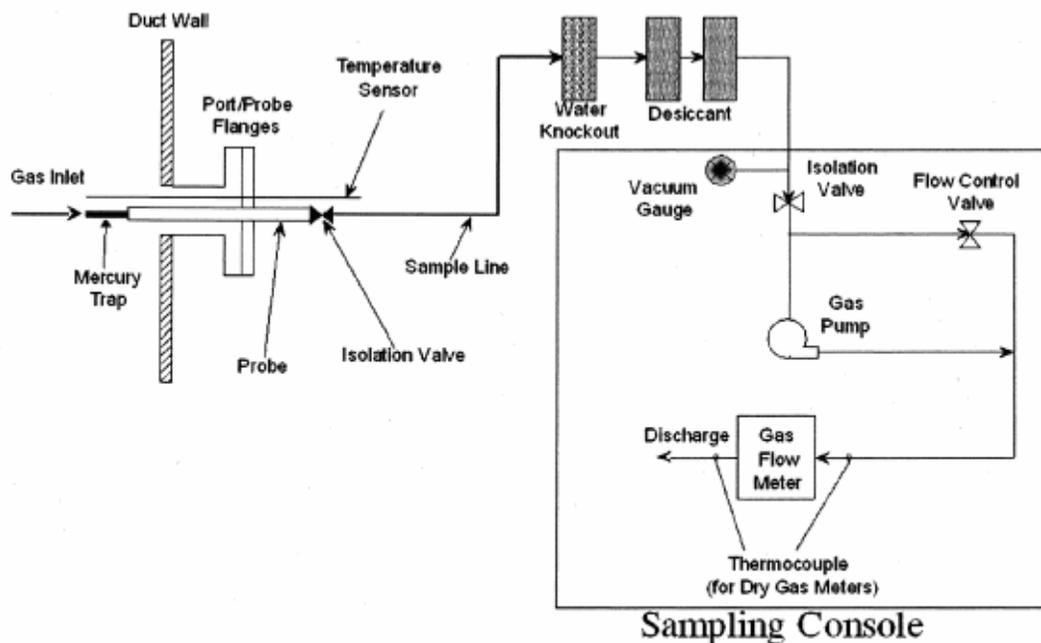


Figure K-1. Typical Sorbent Trap Monitoring System

5.1.1 Sorbent Traps.

The sorbent media used to collect Hg must be configured in a trap with three distinct and identical segments or sections, connected in series, that are amenable to separate analyses. 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 QA/QC purposes where this section shall be spiked with a known amount of gaseous Hg⁰ prior to sampling and later analyzed to determine recovery efficiency. 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 for the intended application. Selection of the sorbent media shall be based on the material's ability to achieve the performance criteria contained in Section 8 of this appendix as well as the sorbent's vapor-phase Hg capture efficiency for the emissions matrix and the expected sampling duration at the test site. The sorbent media must be obtained from a source that can demonstrate the quality assurance and control necessary to ensure consistent reliability. The paired sorbent traps are supported on a probe (or probes) and inserted directly into the flue gas stream.

5.1.2 Sampling Probe Assembly.

Each probe assembly shall have a leak-free attachment to the sorbent trap(s). Each sorbent trap must be mounted at the entrance of or within the probe such that the gas sampled enters the trap directly. Each probe/sorbent trap assembly must be heated to a temperature sufficient to prevent liquid condensation in the sorbent trap(s). Auxiliary heating is required only where the stack temperature is too low to prevent condensation. Use a calibrated thermocouple to monitor the stack temperature. A single probe capable of operating the paired sorbent traps may be used. Alternatively, individual probe/sorbent trap assemblies may be used, provided that the individual sorbent traps are co-located to ensure representative Hg monitoring and are sufficiently separated to prevent aerodynamic interference.

5.1.3 Moisture Removal Device

A robust moisture removal device or system, suitable for continuous duty (such as a Peltier cooler), shall be used to remove water vapor from the gas stream prior to entering the gas flow meter.

5.1.4 Vacuum Pump.

Use a leak-tight, vacuum pump capable of operating within the candidate system's flow range.

5.1.5 Gas Flow Meter

A gas flow meter (such as a dry gas meter, thermal mass flow meter, or other suitable measurement device) shall be used to determine the total sample volume on a dry basis, in units of standard cubic meters. The meter must be sufficiently accurate to measure the total sample volume to within 2 percent and must be calibrated at selected flow rates across the range of sample flow rates at which the sorbent trap monitoring system typically operates. The gas flow meter shall be equipped with any necessary auxiliary measurement devices (e.g., temperature sensors, pressure measurement devices) needed to correct the sample volume to standard conditions.

5.1.6 Sample Flow Rate Meter and Controller.

Use a flow rate indicator and controller for maintaining necessary sampling flow rates.

5.1.7 Temperature Sensor.

Same as Section 6.1.1.7 of Method 5 in appendix A–3 to part 60 of this chapter.

5.1.8 Barometer.

Same as Section 6.1.2 of Method 5 in appendix A–3 to part 60 of this chapter.

5.1.9 Data Logger (Optional).

Device for recording associated and necessary ancillary information (e.g. , temperatures, pressures, flow, time, etc.).

5.2 Gaseous Hg⁰ Sorbent Trap Spiking System.

A known mass of gaseous Hg⁰ must be spiked onto section 3 of each sorbent trap prior to sampling. Any approach capable of quantitatively delivering known masses of Hg⁰ 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, makes use of NIST-certified or NIST-traceable Hg salt solutions (e.g. , Hg(NO₃)₂). 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 Hg⁰ and purged onto section 3 of the sorbent trap using an impinger sparging system.

5.3 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 Section 8 of this procedure. 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) analysis.

6.0 Reagents and Standards.

Only NIST-certified or NIST-traceable calibration gas standards and reagents shall be used for the tests and procedures required under this appendix.

7.0 Sample Collection and Transport.

7.1 Pre-Test Procedures.

7.1.1 Selection of Sampling Site.

Sampling site information should be obtained in accordance with Method 1 in appendix A–1 to part 60 of this chapter. Identify a monitoring location representative of source Hg emissions. Locations shown to be free of stratification through measurement traverses for gases such as SO₂ and NO_x may be one such approach. 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 Hg⁰ to be spiked onto section 3 of each sorbent trap.

7.1.2 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 (for an example calculation, see section 11.1 of this appendix). The pre-sampling spike to be added to section 3 of each sorbent trap shall be within ±50 percent of the expected section 1 mass loading. Spike section 3 of each sorbent trap at this level, as described in section 5.2 of this appendix. For each sorbent trap, keep an official record of the mass of Hg⁰ added to section 3. This record shall include, at a minimum, the ID number of the trap, the date and time of the spike, the name of the analyst performing the procedure, the mass of Hg⁰ added to section 3 of the trap (µgm), and the supporting calculations. This record shall be maintained in a format suitable for inspection and audit and shall be made available to the regulatory agencies upon request.

7.1.3 Pre-test Leak Check

Perform a leak check with the sorbent traps in place. Draw a vacuum in each sample train. Adjust the vacuum in the sample train to □15" Hg. Using the gas flow meter, 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.

7.1.4 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), initial sample rate, proportional sampling conditions, moisture management, etc.

7.2 Sample Collection.

7.2.1 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). Secure the probe(s) and ensure that no leakage occurs between the duct and environment.

7.2.2 Record initial data including the sorbent trap ID, start time, starting dry gas meter readings, initial temperatures, set-points, and any other appropriate information.

7.2.3 Flow Rate Control

Set the initial sample flow rate at the target value from section 7.1.1 of this appendix. Record the initial gas flow meter reading, stack temperature (if needed to convert to standard conditions), meter temperatures (if needed), etc. 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, as measured by the certified flow monitor, 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 constant, to within ± 25 percent of the reference ratio from the first hour of the data collection period (see section 11 of this appendix). The sample flow rate through a sorbent trap monitoring system during any hour (or portion of an hour) in which the unit is not operating shall be zero.

7.2.4 Stack Gas Moisture Determination.

Determine stack gas moisture using a continuous moisture monitoring system, as described in §75.11(b). Alternatively, the owner or operator may use the appropriate fuel-specific moisture default value provided in §75.11, or a site-specific moisture default value approved by petition under §75.66.

7.2.5 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.

7.2.6 Post Test Leak Check.

When sampling 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 sampling period. Use the same general approach described in section 7.1.3 of this appendix. Record the leakage rate and vacuum. The leakage rate must not exceed 4 percent of the average sampling rate for the data collection period. Following the leak check, carefully release the vacuum in the sample train.

7.2.7 Sample Recovery.

Recover each sampled sorbent trap by removing it from the probe, sealing 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 in appropriate manner.

7.2.8 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 ASTM D6911-03 "Standard Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis" (incorporated by reference, see §75.6) shall be followed for all samples.

7.2.9 Sample Custody.

Proper procedures and documentation for sample chain of custody are critical to ensuring data integrity. The chain of custody procedures in ASTM D4840-99 (reapproved 2004) "Standard Guide for Sample Chain-of-Custody Procedures" (incorporated by reference, see §75.6) shall be followed for all samples (including field samples and blanks).

8.0 Quality Assurance and Quality Control.

Table K-1 summarizes the QA/QC performance criteria that are used to validate the Hg emissions data from sorbent trap monitoring systems, including the relative accuracy test audit (RATA) requirement (see §75.20(c)(9), section 6.5.7 of appendix A to this part, and section 2.3 of appendix B to this part). Except as provided in §75.15(h) and as otherwise indicated in Table K-1, failure to achieve these performance criteria will result in invalidation of Hg emissions data.

Table K-1.—Quality Assurance/Quality Control Criteria for Sorbent Trap Monitoring Systems

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Pre-test leak check	≤4% of target sampling rate	Prior to sampling	Sampling shall not commence until the leak check is passed.
Post-test leak check	≤4% of average sampling rate	After sampling	** See <i>Note</i> , below.
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 ± 25%	Every hour throughout data collection period	** See <i>Note</i> , below.
Sorbent trap section 2 break-through	≤5% of Section 1 Hg mass	Every sample	** See <i>Note</i> , below.
Paired sorbent trap agreement	≤10% Relative Deviation (RD) if the average concentration is > 1.0 µg/m ³ ≤ 20% RD if the average concentration is ≤ 1.0 µg/m ³ Results are also acceptable if absolute difference between concentrations from paired traps is ≤ 0.03 µg/m ³	Every sample	Either invalidate the data from the paired traps or report the results from the trap with the higher Hg concentration.
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 shall not be analyzed until the percent recovery criteria has been met
Multipoint analyzer calibration	Each analyzer reading within ± 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 standard	Within ± 10% of true value	Following daily calibration, prior to analyzing field samples	Recalibrate and repeat independent standard analysis until successful.
Spike recovery from section 3 of sorbent trap	75–125% of spike amount	Every sample	** See <i>Note</i> , below.
RATA	RA ≤ 20.0% <i>or</i> Mean difference ≤ 1.0 µg/dscm for low emitters	For initial certification and annually thereafter	Data from the system are invalidated until a RATA is passed.

Gas flow meter calibration	Calibration factor (Y) within $\pm 5\%$ of average value from the most recent 3-point calibration	At three settings prior to initial use and at least quarterly at one setting thereafter. For mass flow meters, initial calibration with stack gas is required	Recalibrate the meter at three orifice 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 ± 10 mm Hg of reading with a mercury barometer	Prior to initial use and at least quarterly thereafter	Recalibrate. Instrument may not be used until specification is met.

****Note:** If both traps fail to meet the acceptance criteria, the data from the pair of traps are invalidated. However, if only one of the paired traps fails to meet this particular acceptance criterion and the other sample meets all of the applicable QA criteria, the results of the valid trap may be used for reporting under this part, provided that the measured Hg concentration is multiplied by a factor of 1.111. When the data from both traps are invalidated and quality-assured data from a certified backup monitoring system, reference method, or approved alternative monitoring system are unavailable, missing data substitution must be used.

9.0 Calibration and Standardization.

9.1 Only NIST-certified and NIST-traceable calibration standards (i.e., calibration gases, solutions, etc.) shall be used for the spiking and analytical procedures in this appendix.

9.2 Gas Flow Meter Calibration

9.2.1 Preliminaries. 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.

9.2.2 Initial Calibration. Prior to its initial use, a calibration of the flow meter shall 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 $12 \pm 0.5\%$ CO₂, $7 \pm 0.5\%$ O₂, and balance N₂, 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.

9.2.2.1 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. You may either follow the procedures in section 10.3.1 of Method 5 in appendix A–3 to part 60 of this chapter or the procedures in section 16 of Method 5 in appendix A–3 to part 60 of this chapter. If a dry gas meter is being calibrated, use at least five revolutions of the meter at each flow rate.

9.2.2.2 Alternative Initial Calibration Procedures. Alternatively, you may perform the initial calibration of the gas flow meter using a reference gas flow meter (RGFM). The RGFM may either be: (1) A wet test meter calibrated according to section 10.3.1 of Method 5 in appendix A–3 to part 60; (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 part 60; 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.

9.2.2.3 Initial Calibration Factor. Calculate an individual calibration factor Y_{iat} at each tested flow rate from section 9.2.2.1 or 9.2.2.2 of this appendix (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 ± 0.02 of Y. Except as otherwise provided in sections 9.2.2.4 and 9.2.2.5 of this appendix, use the average Y value from the three level calibration to adjust all subsequent gas volume measurements made with the gas flow meter.

9.2.2.4 Initial On-Site Calibration Check. For a mass flow meter that was initially calibrated using a compressed gas mixture, an on-site calibration check shall be performed before using the flow meter to provide data for this part. 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 9.2.2.1 or 9.2.2.2 of this appendix. If the on-site 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.

9.2.2.5 Ongoing Quality Assurance. 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 9.2.2.1 or 9.2.2.2 of this appendix. 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.

9.3 Thermocouples and Other Temperature Sensors.

Use the procedures and criteria in Section 10.3 of Method 2 in appendix A-1 to part 60 of this chapter to calibrate in-stack temperature sensors and thermocouples. Dial thermometers shall be calibrated against mercury-in-glass thermometers. 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 ± 1.5 percent of the temperature measured with the reference sensor, otherwise the sensor may not continue to be used.

9.4 Barometer.

Calibrate against a mercury barometer. 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 ± 10 mm Hg of the pressure measured by the mercury barometer, otherwise the barometer may not continue to be used.

9.5 Other Sensors and Gauges.

Calibrate all other sensors and gauges according to the procedures specified by the instrument manufacturer(s).

9.6 Analytical System Calibration.

See section 10.1 of this appendix.

10.0 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 8 of this appendix.

10.1 Analyzer System Calibration.

Perform a multipoint calibration of the analyzer at three or more upscale points over the desired quantitative range (multiple calibration ranges shall 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 ≥ 0.99 , and the analyzer response must be within ± 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) shall be analyzed. The measured value of the independently prepared standard must be within ± 10 percent of the expected value.

10.2 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.

10.3 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 5.2 and 11.1 of this appendix, spike the third section of nine sorbent traps with gaseous Hg⁰, *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 × 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.

10.4 Field Sample Analysis

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 10.1 of this appendix. 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.

11.0 Calculations and Data Analysis.

11.1 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 sample duration. First, calculate the expected Hg mass that will be collected in section 1 of the trap. The pre-sampling spike must be within ±50 percent of this mass. Example calculation: For an estimated stack Hg concentration of 5 µgm/m³, a target sample rate of 0.30 L/min, and a sample duration of 5 days:

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

A pre-sampling spike of 10.8 µgm ±50 percent is, therefore, appropriate.

11.2 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:

$$R_{\text{ref}} = \frac{KQ_{\text{ref}}}{F_{\text{ref}}} \quad (\text{Eq. K-1})$$

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, adjusted for bias, if necessary, according to section 7.6.5 of appendix A to this part, (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 the equation K-2:

$$R_k = \frac{KQ_k}{F_k} \quad (\text{Eq. K-2})$$

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, adjusted for bias, if necessary, according to section 7.6.5 of appendix A to this part, (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 ± 25 percent of R_{ref} throughout the data collection period.

11.3 Calculation of Spike Recovery.

Calculate the percent recovery of each section 3 spike, as follows:

$$\%R = \frac{M_3}{M_s} \times 100 \quad (\text{Eq. K-3})$$

Where:

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

M_3 = Mass of Hg recovered from section 3 of the sorbent trap, (μg)

M_s = Calculated Hg mass of the pre-sampling spike, from section 7.1.2 of this appendix, (μg)

11.4 Calculation of Breakthrough.

Calculate the percent breakthrough to the second section of the sorbent trap, as follows:

$$\%B = \frac{M_2}{M_1} \times 100 \quad (\text{Eq. K-4})$$

Where:

$\%B$ = Percent breakthrough

M_2 = Mass of Hg recovered from section 2 of the sorbent trap, (μg)

M_1 = Mass of Hg recovered from section 1 of the sorbent trap, (μg)

11.5 [Reserved]

11.6 Calculation of Hg Concentration

Calculate the Hg concentration for each sorbent trap, using the following equation:

$$C = \frac{M^*}{V_t} \quad (\text{Eq. K-5})$$

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, (μg)

V_t = Total volume of dry gas metered during the collection period, (dscm). For the purposes of this appendix, standard temperature and pressure are defined as 20 °C and 760 mm Hg, respectively.

11.7 Calculation of Paired Trap Agreement

Calculate the relative deviation (RD) between the Hg concentrations measured with the paired sorbent traps:

$$\text{RD} = \frac{|C_a - C_b|}{C_a + C_b} \times 100 \quad (\text{Eq. K-6})$$

Where:

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

C_a = Concentration of Hg for the collection period, for sorbent trap “a” ($\mu\text{g}/\text{dscm}$)

C_b = Concentration of Hg for the collection period, for sorbent trap “b” ($\mu\text{g}/\text{dscm}$)

11.8 Calculation of Hg Mass Emissions.

To calculate Hg mass emissions, follow the procedures in section 9.1.2 of appendix F to this part. Use the average of the two Hg concentrations from the paired traps in the calculations, except as provided in §75.15(h) or in Table K–1.

12.0 Method Performance.

These monitoring criteria and procedures have been applied to coal-fired utility boilers (including units with post-combustion emission controls), having vapor-phase Hg concentrations ranging from 0.03 $\mu\text{g}/\text{dscm}$ to 100 $\mu\text{g}/\text{dscm}$.

[70 FR 28695, May 18, 2005, as amended at 72 FR 51528, Sept. 7, 2007; 73 FR 4376, Jan. 24, 2008]

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