

**Measurement and Reporting of Vapor Phase Mercury Emissions,
Using a Sorbent Trap Monitoring System
(DRAFT 9/25/08)**

1. Scope and Application

The purpose of this protocol is to establish procedures for the performance-based monitoring of vapor-phase mercury (Hg) emissions in combustion flue gas streams, using a sorbent trap monitoring system. Guidelines are also provided for reporting Hg emissions data from sorbent trap systems and for using the data to demonstrate compliance with applicable Hg emission limits. The performance-based approach 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 protocol should have a thorough working knowledge of Methods 1, 2, 3, 4 and 5 in appendices A-1 through A-3 to 40 CFR Part 60, 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 (µg/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 steam generators. 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 protocol and the sorbent media capture ability must not be exceeded. The sampling rate must be maintained at a constant proportion to the total stack flow rate to ensure that a representative sample is collected. Failure to achieve certain performance criteria will result in invalid Hg emissions monitoring data.

2. Principle

Known volumes of flue gas are continuously 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. For quality-assurance purposes, a section of each sorbent trap is spiked with Hg⁰ prior to sampling. This section is analyzed separately and a specified percentage of the spike must be recovered.

3. 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. 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 protocol 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. 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. A certified stack gas volumetric flow monitor is also required to ensure that the sample flow rate is maintained proportional to the stack gas flow rate. If an applicable regulation requires the Hg concentration data obtained with the sorbent trap monitoring system to be used to calculate Hg mass emissions (e.g., lb Hg), the moisture content of the stack gas must also be determined (see Section 7.2.4 of this protocol). Further, if the Hg emissions are to be expressed on a heat input basis (e.g., lb/TBtu), or if a certain percentage reduction of Hg must be demonstrated, a method of quantifying unit heat input is required. One acceptable way of measuring heat input is to use data from a certified diluent gas (CO₂ or O₂) monitor together with data from the flow monitor, moisture data (if needed), and an appropriate F-factor. If Hg emissions are to be expressed in terms of electrical output (e.g., lb/GW-hr), measurements of hourly electrical load and unit operating time are required (see Section 11.8 of this protocol).

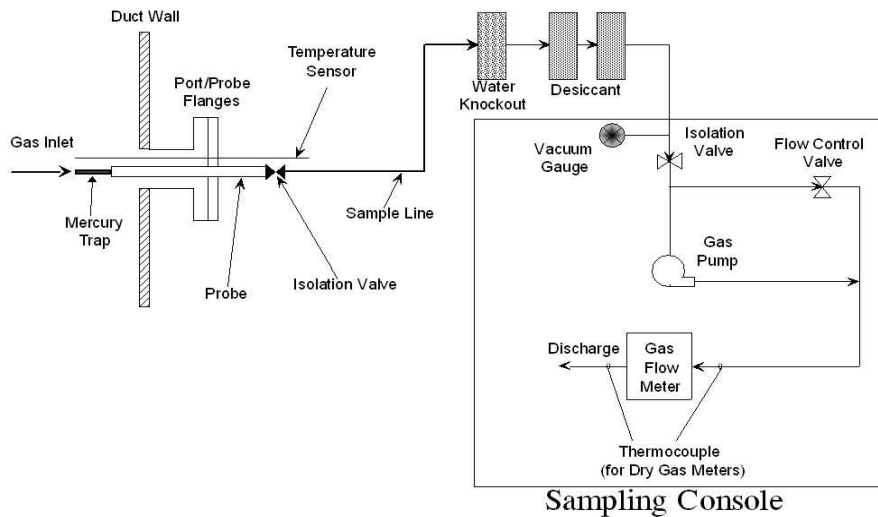


Figure 1. Typical Sorbent Trap Monitoring System

5.1 Sorbent Trap Monitoring System

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

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 protocol 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's 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 40 CFR Part 60.

5.1.8 Barometer

Same as section 6.1.2 of Method 5 in appendix A-3 to 40 CFR Part 60.

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, gas generators or tanks that are certified by the National Institute of Standards and Technology (NIST) or traceable to NIST 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 Table 1 in Section 8 of this protocol. 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. 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 protocol.

7. Sample Collection and Transport

7.1 *Pre-Test Procedures*

7.1.1 Installation and Measurement Location

7.1.1.1 Sorbent Trap Monitoring System.

Select a monitoring location that is representative of the Hg emissions from the source, where the sorbent trap monitoring system is likely to pass the relative accuracy test audit (RATA) e.g., a location that: (a) conforms to the guidelines in section 8.1.1 of Performance Specification 2 in appendix B to 40 CFR Part 60; and/or (b) is shown to be free of stratification or minimally stratified through measurement traverses for Hg or other gases such as SO₂ and NO_x. If the monitoring system is unable to pass the RATA and the measurement location is determined to be the cause, relocate the probe.

7.1.1.2 Auxiliary Monitors

For auxiliary monitors that are needed for flow-proportional sampling or to convert Hg concentrations to the desired units of measure (i.e., flow monitors, CO₂ or O₂ monitors, and/or moisture monitors, as applicable), follow the installation and measurement location guidelines in section 1 of appendix A to 40 CFR Part 75.

7.1.2 Estimate of Hg Concentration in the Flue Gas

An estimate 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.

7.1.3 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 protocol). 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 protocol. 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 (μg), 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.

7.1.4 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.

7.1.5 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 gas flow 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 7.1.2 of this protocol. 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 within ± 25 percent of the reference ratio from the first hour of the data collection period (see Section 11.2 of this protocol). 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

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 that is certified according to 40 CFR Part 75. Alternatively, the owner or operator may use the appropriate fuel-specific moisture default value provided in 40 CFR 75.11(b).

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 7.1.4 of this protocol. 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" 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" shall be followed for all samples (including field samples and blanks).

8. Quality Assurance and Quality Control (QA/QC)

Table 1, below, summarizes the QA/QC performance criteria that are used to validate the Hg emissions data from sorbent trap monitoring systems. Failure to achieve these performance criteria will result in invalidation of Hg emissions data, except where otherwise noted. Section 8.1 below provides specific instructions pertaining to the

TABLE 1. QA/QC 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	Invalidate the data from the paired traps or, if certain conditions are met, report adjusted data from a single trap (see Section 11.7.1.3)
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 ± 25%.	Every hour throughout data collection period.	Invalidate the data from the paired traps or, if certain conditions are met, report adjusted data from a single trap (see Section 11.7.1.3)
Sorbent trap section 2 breakthrough	≤5% of section 1 Hg mass	Every sample	Invalidate the data from the paired traps or, if certain conditions are met, report adjusted data from a single trap (see Section 11.7.1.3)
Paired sorbent trap agreement.	<p>≤10% Relative Deviation (RD) if the average concentration is > 1.0 µg/m³</p> <p>≤ 20% RD if the average concentration is ≤ 1.0 µg/m³.</p> <p>Results also acceptable if absolute difference between concentrations from paired traps is ≤ 0.03 µg/m³</p>	Every sample	Either invalidate the data from the paired traps or, if certain conditions are met, report the results from the trap with the higher Hg concentration (see Section 11.7.1.3).
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 shall not be analyzed until the percent recovery criterion has been met.
Multipoint analyzer calibration	Each analyzer reading within ± 10% of true value and r ² ≥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	Invalidate the data from the paired traps or, if certain conditions are met, report adjusted data from a single trap (see Section 11.7.1.3)
RATA	RA ≤ 20.0% <u>or</u> Mean difference ≤ 1.0 µg/dscm, when the mean RM value is < 5.0 µg/scm	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 ± 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 ± 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.

relative accuracy test audit (RATA) requirements for sorbent trap monitoring systems. Section 8.2 provides general QA/QC guidelines for auxiliary monitoring systems that are needed to convert Hg concentration data from a sorbent trap system to various units of measure. Section 8.3 describes the QA/QC program that must be developed and implemented for the monitoring systems.

8.1 *Sorbent Trap System RATAs.*

For the initial certification of a sorbent trap monitoring system, a RATA is required. For on-going QA purposes, the RATA must be repeated annually¹. The RATA grace period provisions in section 2.3.3 of appendix B to 40 CFR Part 75 apply to the sorbent trap monitoring system. Perform each RATA according to the general procedures for gas monitoring system RATAs described in sections 6.5 through 6.5.8 of appendix A to 40 CFR Part 75, supplemented by the special instructions in Sections 8.1.1 through 8.1.4 of this protocol.

8.1.1 Reference Methods.

Acceptable Hg reference methods for the RATA of a sorbent trap system include ASTM D6784-02 (the Ontario Hydro Method), Method 30-A in appendix A-8 to 40 CFR Part 60, and Method 30-B in appendix A-8 to 40 CFR Part 60. If Method 30-B is used, the sorbent material used in the reference method traps does not have to be the same type of sorbent that is used in the monitoring system. When the Ontario Hydro Method is used, paired sampling trains are required. To validate an Ontario Hydro test run, the relative deviation (RD), calculated using Equation 6 in Section 11.6 of this protocol², must not exceed 10 percent, when the average concentration is greater than 1.0 µg/dscm. If the average concentration is ≤ 1.0 µg/dscm, the RD must not exceed 20 percent. The RD results are also acceptable if the absolute difference between the Hg concentrations measured by the paired trains does not exceed 0.03 µg/dscm. If the RD criterion is met, the run is valid. For each valid run, average the Hg concentrations measured by the two trains arithmetically (vapor phase Hg, only).

8.1.2 Special Considerations.

The RATA must be done at normal load (as defined in section 6.5.2.1 of appendix A to 40 CFR Part 75), while combusting coal. Locate the reference method (RM) sampling points according to section 6.5.6(b) in appendix A to 40 CFR Part 75. If stratification testing is deemed necessary to justify using fewer RM sample points or alternative RM point locations, follow the applicable procedures in sections 8.1.3 through 8.1.3.5 of Method 30-A in appendix A-8 to 40 CFR Part 60. A minimum of 9 valid runs are required for each RATA. If more than 9 runs are performed, a maximum of three runs may be discarded. Install a new pair of sorbent traps prior to each test run. The type

¹ “Annually” means once every four QA operating quarters. A “QA operating quarter” is a calendar quarter with at least 168 unit or stack operating hours (see 40 CFR 72.2).

² When using Equation 6 in section 11.6 for paired Ontario Hydro samples, “RD” is the relative deviation between samples “a” and “b”, and “C_a” and “C_b” are the Hg concentrations of samples “a” and “b”.

of sorbent material used by the traps during the RATA must be the same as for daily operation of the monitoring system; however, the size of the traps used for the RATA 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 7.1.3 of this protocol. The time per run must be long enough to collect a sufficient mass of Hg to analyze. For each run, the sorbent trap data shall be validated according to the quality assurance criteria in Table 1.

8.1.3 Calculation of Relative Accuracy

Calculate the relative accuracy (RA) of the monitoring system, on a $\mu\text{g}/\text{scm}$ basis, according to section 7.3 in appendix A to 40 CFR Part 75. For a unit that qualifies as a low emitter of Hg (i.e., the mean reference method (RM) concentration during the RATA is $< 5 \mu\text{g}/\text{scm}$), if the calculated RA exceeds 20.0%, the results of the RATA are still acceptable if the absolute difference between the mean RM and monitoring system concentrations does not exceed $1.0 \mu\text{g}/\text{scm}$. All comparisons of RM and monitoring system data must be made on a consistent moisture basis (dry or wet).

8.1.4 Bias Adjustment

8.1.4.1 Sorbent Trap Monitoring System

To ensure that Hg concentration is not under-reported, the bias test described in section 7.6.4 of Appendix A to 40 CFR Part 75 shall be performed each time that a RATA of the sorbent trap monitoring system is done. If the bias test is failed, a bias adjustment factor (BAF) must be calculated in accordance with section 7.6.5(a) of Appendix A to 40 CFR Part 75, and applied to the hourly data from the sorbent trap system, beginning with the hour after the RATA is completed. For low emitting sources (mean RM concentration during the RATA $< 5 \mu\text{g}/\text{scm}$), if the calculated BAF exceeds 1.250, a BAF of 1.250 may be used for reporting purposes.

8.1.4.2 Auxiliary Monitoring Systems

For a flow monitor that is certified and quality-assured according to 40 CFR Part 75, bias adjustment is mandatory, in accordance with sections 7.6.4 and 7.6.5 in appendix A to 40 CFR Part 75. Bias adjustment is not required for diluent gas monitors or moisture monitoring systems.

8.2 *Certification and QA of Auxiliary Monitoring Systems.*

Auxiliary monitoring systems that are used to measure stack gas volumetric flow rate and/or diluent gas concentration and/or moisture must be certified. Periodic QA testing of these monitoring systems is also required. The certification test procedures and performance specifications for these systems are found in 40 CFR §75.20(c), and in sections 3 and 6 of appendix A to 40 CFR Part 75. The QA test requirements, acceptance criteria, and data validation provisions are found in appendix B to 40 CFR Part 75.

8.3 *QA/QC Program for Sorbent Trap & Auxiliary Monitoring Systems*

The owner or operator shall develop and implement a quality assurance/quality control (QA/QC) program for the sorbent trap monitoring system and (if applicable) for the auxiliary monitoring systems used to convert Hg concentration data from the sorbent trap system to the appropriate units of measure. At a minimum, include in the QA/QC program a written plan that describes in detail (or that refers to separate documents containing) complete, step-by-step procedures and operations for the following activities. Electronic storage of the QA/QC plan is permissible, provided that the information can be made available in hard copy to auditors and inspectors.

8.3.1 Requirements for All Monitoring Systems

8.3.1.1 Preventive Maintenance

Keep a written record of procedures needed to maintain the monitoring system in proper operating condition and a schedule for those procedures. This shall, at a minimum, include procedures specified by the manufacturers of the equipment and, if applicable, additional or alternate procedures developed for the equipment.

8.3.1.2 Record Keeping and Reporting

Keep a written record describing procedures that will be used to implement the recordkeeping and reporting requirements of the applicable regulation.

8.3.1.3 Maintenance Records

Keep a record of all testing, maintenance, or repair activities performed on any monitoring system in a location and format suitable for inspection. A maintenance log may be used for this purpose. The following records should be maintained: date, time, and description of any testing, adjustment, repair, replacement, or preventive maintenance action performed on any monitoring system and records of any corrective actions associated with a monitor outage period. Additionally, any adjustment that recharacterizes a system's ability to record and report emissions data must be recorded (e.g., changing of flow monitor or moisture monitoring system polynomial coefficients, K factors or mathematical algorithms, changing of temperature and pressure coefficients and dilution ratio settings), and a written explanation of the procedures used to make the adjustment(s) shall be kept.

8.3.2 Specific Requirements for Sorbent Trap Monitoring Systems

8.3.2.1 Sorbent Trap Identification and Tracking

Include procedures for inscribing or otherwise permanently marking a unique identification number on each sorbent trap, for tracking purposes. Keep records of the ID of the monitoring system in which each sorbent trap is used, and the dates and hours of each Hg collection period.

8.3.2.2 Monitoring System Integrity and Data Quality

Explain the procedures used to perform the leak checks when a sorbent trap is placed in service and removed from service. Also explain the other QA procedures used to ensure system integrity and data quality, including, but not limited to, gas flow meter calibrations, verification of moisture removal, and ensuring air-tight pump operation. In addition, the QA plan must include the data acceptance and quality control criteria in Section 8 of this protocol. All reference meters used to calibrate the gas flow meters (e.g., wet test meters) shall be periodically recalibrated. Annual, or more frequent, recalibration is recommended. If a NIST–traceable calibration device is used as a reference flow meter, the QA plan must include a protocol for on-going maintenance and periodic recalibration to maintain the accuracy and NIST–traceability of the calibrator.

8.3.2.3 Hg Analysis

Explain the chain of custody employed in packing, transporting, and analyzing the sorbent traps (see Sections 7.2.8 and 7.2.9 of this protocol). Keep records of all Hg analyses. The analyses shall be performed in accordance with the procedures described in Section 10 of this protocol.

8.3.2.4 Laboratory Certification

It is recommended that any laboratory performing analyses of carbon sorbent traps be certified by the International Organization for Standardization (ISO) to have a proficiency that meets the requirements of ISO 17025. However, if the laboratory performs the spike recovery study described in Section 10.3 of this protocol and repeats that procedure annually, ISO certification is not necessary.

8.3.2.5 Data Collection Period

State, and provide the rationale for, the minimum acceptable data collection period (e.g., one day, one week, etc.) for the size of sorbent trap selected for the monitoring. Include in the discussion such factors as the Hg concentration in the stack gas, the capacity of the sorbent trap, and the minimum mass of Hg required for the analysis.

8.3.2.6 Relative Accuracy Test Audit Procedures

Keep records of the procedures and details peculiar to the sorbent trap monitoring systems that are to be followed for relative accuracy test audits, such as trap size, reference methods used, sampling and analysis methods used, etc.

8.3.3 Specific Requirements for Auxiliary Monitoring Systems

8.3.3.1 Daily Calibrations and Linearity Checks

Keep a written record of the procedures used for daily calibrations of all auxiliary monitoring systems. If a CO₂ or O₂ monitor is used, also keep records of the procedures used to perform linearity checks. Explain how the test results are calculated and

evaluated.

8.3.3.2 Monitoring System Adjustments

Explain how each component of the continuous emission monitoring system will be adjusted to provide correct responses to calibration gases or reference signals after routine maintenance, repairs, or corrective actions.

8.3.3.3 Relative Accuracy Test Audits

Keep a written record of procedures used for RATAs of the monitoring systems. Indicate the reference methods used and explain how the test results are calculated and evaluated.

8.3.3.4 Verification of Emission Controls Performance

For units and common stack configurations that have FGD systems or add-on Hg emission controls, if parametric data are used to verify proper control device operation during missing data periods (see Section 11.8.5, below), the QA plan shall identify the parameters that are monitored and the acceptable range of values for each parameter. If data from a certified SO₂ CEMS are used to verify proper FGD operation, the SO₂ monitoring system must be included in the QA plan.

8.4 *Recertification*

Whenever the owner or operator makes a replacement, modification, or change in a certified sorbent trap monitoring system or auxiliary monitoring system that may significantly affect the ability of the system to accurately measure or record the Hg concentration, stack gas volumetric flow rate, CO₂ concentration, O₂ concentration, or percent moisture, the owner or operator shall recertify the monitoring system. Furthermore, whenever the owner or operator makes a replacement, modification, or change to the flue gas handling system or the unit operation that may significantly change the flow or concentration profile, the owner or operator shall recertify the monitoring system. The same tests performed for the initial certification of the monitoring system shall be repeated for recertification, unless otherwise specified in the applicable regulation. The conditional data validation provisions in 40 CFR 75.20(b)(3) may be used for recertification events. Examples of changes that require recertification include: (a) replacement of a gas analyzer; (b) change in the type of sorbent material used in the sorbent traps; and (c) change in location or orientation of the sampling probe.

9. 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 protocol.

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 40 CFR Part 60 or the procedures in section 16 of Method 5 in appendix A-3 to 40 CFR Part 60. 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: (a) A wet test meter calibrated according to section 10.3.1 of Method 5 in appendix A-3 to 40 CFR Part 60; (b) a gas flow metering device calibrated at multiple flow rates using the procedures in section 16 of Method 5 in appendix A-3 to 40 CFR Part 60; or (c) 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_i at each tested flow rate from Section 9.2.2.1 or 9.2.2.2 of this protocol (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 protocol, 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 reporting purposes. 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 protocol. 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 protocol. 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 40 CFR Part 60 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 protocol.

10. 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 protocol.

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 protocol, 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 x 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 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 10.1 of this protocol. 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. Calculations, Data Reduction, 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 $\mu\text{g}/\text{m}^3$, a target sample rate of 0.30 L/min, and a sample duration of 5 days:

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

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

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:

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

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 (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 2:

$$R_h = \frac{KQ_h}{F_h} \quad (\text{Equation 2})$$

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 (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:

$$\%R = \frac{M_3}{M_s} \times 100 \quad (\text{Equation 3})$$

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 7.1.3 of this protocol, (μg)

11.4 Calculation of Breakthrough.

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

$$\%B = \frac{M_2}{M_1} \times 100 \quad (\text{Equation 4})$$

Where:

%B = Percent breakthrough

M₂ = Mass of Hg recovered from section 2 of the sorbent trap, (µg)

M₁ = Mass of Hg recovered from section 1 of the sorbent trap, (µg)

11.5 Calculation of Hg Concentration.

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

$$C = \frac{M^*}{V_t} \quad (\text{Equation 5})$$

Where:

C = Concentration of Hg for the collection period, (µg/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).

(Note: For the purposes of this protocol, standard temperature and pressure are defined as 20°C and 760 mm Hg, respectively).

11.6 Calculation of Paired Trap Agreement.

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

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

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" (µg/dscm)

C_b = Concentration of Hg for the collection period, for sorbent trap "b" (µg/dscm)

11.7 *Data Reduction.*

11.7.1 Sorbent Trap Monitoring Systems.

Typical data collection periods for normal, day-to-day operation of a sorbent trap monitoring system range from about 24 hours to 168 hours. For the required RATAs of the system, smaller sorbent traps are often used, and the data collection time per run is considerably shorter (e.g., 1 hour or less). Generally speaking, the acceptance criteria for the following five QA specifications in Table 1 above must be met to validate a data collection period: (a) the post-test 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.

11.7.1.1 When both traps meet the acceptance criteria for all five QA specifications, the two measured Hg concentrations shall be averaged arithmetically and the average value shall be applied to each hour of the data collection period.

11.7.1.2 To validate a RATA run, both traps must meet the acceptance criteria for all five QA specifications. However, as discussed in Section 11.7.1.3 below, for normal day-to-day operation of the monitoring system, a data collection period may, in certain instances, be validated based on the results from one trap.

11.7.1.3 For the routine, day-to-day operation of the monitoring system, when one of the traps either: (a) fails the post-test 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, provided that the other trap meets the acceptance criteria for all four of these QA specifications, the Hg concentration measured by the valid trap may multiplied by a factor of 1.111 and used for reporting purposes. Further, if both traps meet the acceptance criteria for all four of these QA specifications, but the acceptance (RD) 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.

11.7.1.4 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, use missing data substitution, according to Section 11.8.5 of this protocol.

11.7.2 Auxiliary Monitoring Systems

Reduce the data from the auxiliary monitoring systems to hourly averages, in accordance with 40 CFR 75.10(d).

11.8 *Calculation of Hg Mass Emissions, Emission Rates, and Percentage Reduction.*

When an applicable regulation requires a particular Hg emission limit to be met or a certain percentage reduction of Hg to be achieved, use the calculation methods in Sections 11.8.1 through 11.8.4 below to demonstrate compliance with these requirements unless other methods are specified in the regulation. To ensure that the methods in

Sections 11.8.1 through 11.8.4 are applied correctly, the missing data substitution provisions of Section 11.8.5 must be taken into account.

11.8.1 Hg Mass Emissions

11.8.1.1 Calculate the Hg mass emissions for each hour in each sorbent trap data collection period, using the following equation:

$$M_h = K C_h Q_h t_h (1 - B_{ws}) \quad (\text{Equation 7})$$

Where:

M_h = Hg mass emissions for the hour (lb)

K = Units conversion constant, 6.236×10^{-11} lb-scm/ μ g-scf,

C_h = Flow-proportional average Hg concentration for the data collection period, dry basis, as measured by the paired³ sorbent traps, adjusted for bias, if necessary (μ g/dscm).

Q_h = Stack gas volumetric flow rate for the hour, adjusted for bias, if necessary (scfh)

t_h = Unit or stack operating time⁴, fraction of the hour, expressed as a decimal (e.g., 1.00 for a full operating hour, 0.5 for 30 minutes of operation, 0.00 for a non-operating hour⁵, etc.)

B_{ws} = Moisture fraction of the stack gas, expressed as a decimal (equal to % H₂O/100)

11.8.1.2 If the applicable regulation specifies a limit on Hg mass emissions over a given time period (e.g., day, month, year, 12-month rolling period), use Equation 8 to calculate the cumulative Hg mass emissions:

$$M_t = \sum_{h=1}^n M_h \quad (\text{Equation 8})$$

Where:

M_t = Cumulative Hg mass emissions over the specified time period (lb)

M_h = Hg mass emissions for hour “h” in the specified time period, from Equation 7 (lb)

n = Number of hours in the specified time period

11.8.2 Heat Input-Based Hg Emission Rates.

11.8.2.1 Use Equation 9 to calculate the Hg emission rate in units of pounds per trillion Btu (lb/TBtu), for each unit or stack operating hour⁶ in each sorbent trap data collection

³ C_h may be the Hg concentration measured by a single trap in some instances (see section 11.7.1).

⁴ “Unit operating time and “stack operating time” are defined in 40 CFR 72.2.

⁵ When using Equation 7, calculate the hourly Hg mass emissions on a clock hour basis. For non-operating hours, the Hg mass emissions will, of course, be zero.

⁶ “Unit operating hour” and “stack operating hour” are defined in 40 CFR 72.2

period:

$$E_{hm} = \frac{M_h}{(HI)_h(t_h)} \times 10^6 \quad (\text{Equation 9})$$

Where:

E_{hm} = Hg emission rate for the hour (lb/TBtu)

M_h = Hg mass emissions for the hour, from Equation 7 (lb)

$(HI)_h$ = Heat input rate from coal combustion for the hour, calculated from measurements of stack gas flow rate, diluent gas concentration, and moisture (if needed), or appropriate substitute data values for these parameters, together with a fuel-specific F-factor and an appropriate equation from section 5.2 of appendix F to 40 CFR Part 75 (mmBtu/hr)

t_h = Unit or stack operating time, fraction of the hour, expressed as a decimal (e.g., 1.00 for a full operating hour, 0.5 for 30 minutes of operation, etc.)

10^6 = Conversion factor from mmBtu to TBtu

11.8.2.2 If the applicable regulation requires a heat input-based Hg emission rate limit to be met over a specified averaging period (e.g., day, month, year, rolling 12-month period), use Equation 10 to calculate the average emission rate.

$$\bar{E}_{hm} = \frac{\sum_{h=1}^n E_{hm}}{n} \quad (\text{Equation 10})$$

Where:

\bar{E}_{hm} = Hg emission rate for the specified averaging period (lb/TBtu)

E_{hm} = Hg emission rate for unit or stack operating hour “h” in the averaging period, from Equation 9 (lb/TBtu)

n = Number of unit or stack operating hours in the averaging period

(Note: Do not include non-operating hours with zero emission rates in the average).

11.8.3 Electrical Output-Based Emission Rates.

11.8.3.1 Use Equation 11 to calculate the Hg emission rate in units of pounds per gigawatt hour for each unit or stack operating hour in each sorbent trap data collection period (lb/GW-hr):

$$E_{ho} = \frac{M_h}{(MW)_h(t_h)} \times 10^3 \quad (\text{Equation 11})$$

Where:

E_{ho} = Electrical output-based Hg emission rate (lb/GW-hr)

M_h = Hg mass emissions for the hour, from Equation 7 (lb)

$(MW)_h$ = Electrical load for the hour, in megawatts (MW)

t_h = Unit or stack operating time, fraction of the hour, expressed as a decimal (e.g., 1.00 for a full operating hour, 0.5 for 30 minutes of operation, etc.)

10^3 = Conversion factor from megawatts to gigawatts

11.8.3.2 If the applicable regulation requires an electrical output-based Hg emission rate limit to be met over a specified averaging period (e.g., day, month, year, 12-month rolling period), use Equation 12 to calculate the average emission rate:

$$\bar{E}_o = \frac{\sum_{h=1}^n E_{ho}}{n} \quad (\text{Equation 12})$$

Where:

\bar{E}_o = Hg emission rate for the specified averaging period (lb/GW-hr)

E_{ho} = Electrical output-based hourly Hg emission rate for unit or stack operating hour “h” in the averaging period, from Equation 11 (lb/GW-hr)

n = Number of unit or stack operating hours in the averaging period

(Note: Do not include non-operating hours with zero emission rates in the average).

11.8.4 Percentage Reduction of Hg

If the applicable regulation requires a certain percentage reduction of Hg to be achieved over a specified period of time (e.g., day, month, year, 12-month rolling period), follow the applicable procedures in Sections 11.8.4.1 through 11.8.4.4, below.

11.8.4.1 Fuel sampling and analysis is required to determine either the “inlet” Hg content of the coal or the gross calorific value (GCV) of the coal. Coal sampling is required on each day that the unit operates. Collect the coal samples from feeders or other representative locations, according to ASTM Method D 2234-00, using Type I increment collection, Conditions A, B, or C, with systematic spacing. Alternatively, samples may be collected according to 40 CFR 63.7521(c). Use ASTM D 2013-04 to prepare the samples for analysis. Determine the Hg content of the coal using ASTM D 6722-01, ASTM D 6414-01, or ASTM D 3684-01. Determine the GCV using ASTM D 5865-04 or ASTM D 3176-02. More recent versions of any of these ASTM methods may be used.

11.8.4.2 When multiple values of Hg content or GCV are obtained over a specified time period (e.g., a 12-month period), use the arithmetic average of all valid sample results and substitute data values in the calculations.

11.8.4.3 Percentage Reduction (Mass Basis)

11.8.4.3.1 Coal Consumption.

Use Equation 13 to determine the amount of coal combusted during the specified time period:

$$(Coal)_p = \frac{\sum_{h=1}^n (HI)_h (t_h)}{GCV} \times 10^6 \quad (\text{Equation 13})$$

Where:

$(Coal)_p$ = Mass of coal combusted during the specified time period (lb)

$(HI)_h$ = Heat input rate from coal combustion for hour “h” in the specified time period, calculated from measurements of stack gas flow rate, diluent gas concentration, and moisture (if needed), or appropriate substitute data values for these parameters, together with a fuel-specific F-factor and an appropriate equation from section 5.2 of appendix F to 40 CFR Part 75 (mmBtu/hr)

t_h = Unit or stack operating time for hour “h” in the specified time period, fraction of the hour, expressed as a decimal (e.g., 1.00 for a full operating hour, 0.5 for 30 minutes of operation, 0.00 for a non-operating hour, etc.)

GCV = Gross calorific value of the coal for the specified time period (Btu/lb)

10^6 = Conversion factor from mmBtu to Btu

n = Number of clock hours⁷ in the specified time period

11.8.4.3.2 Inlet Hg Mass

Use Equation 14 to calculate the “inlet Hg mass”, i.e., the mass of Hg in the coal combusted during the specified time period:

$$(Mass)_{Hg-coal} = (C_{Hg-coal})(Coal)_p \times 10^{-6} \quad (\text{Equation 14})$$

Where:

$(Mass)_{Hg-coal}$ = Total mass of Hg in the coal combusted during the specified time period (lb)

$C_{Hg-coal}$ = Measured Hg content of the coal combusted during the specified time period (ppm, mass basis)

$(Coal)_p$ = Mass of coal combusted during the specified time period, from Equation 13 (lb)

10^{-6} = Conversion factor, ppm to lb

11.8.4.3.3 Calculation of Percentage Reduction

Use Equation 15 to calculate the percentage reduction of Hg achieved in the specified time period:

⁷ Calculate $(Coal)_p$ on a clock hour basis. For non-operating hours, $(HI)_h$, t_h , and $(Coal)_p$ will all be zero.

$$(\%R)_{mass} = \frac{(Mass)_{Hg-coal} - M_t}{(Mass)_{Hg-coal}} \times 100 \quad (\text{Equation 15})$$

Where:

$(\%R)_{mass}$ = Percentage reduction of Hg achieved in the specified time period, mass basis (percent)

$(Mass)_{Hg-coal}$ = Total mass of Hg in the coal combusted during the specified time period, from Equation 14 (lb)

M_t = Cumulative Hg mass emissions over the specified time period, from Equation 8 (lb)

11.8.4.4 Percentage Reduction (Emission Rate Basis)

11.8.4.4.1 Inlet Hg Emission Rate

Use Equation 16 to calculate the “inlet Hg emission rate” for the specified time period, in units of lb/TBtu:

$$E_r = \frac{(Mass)_{Hg-coal}}{\sum_{h=1}^n (HI)_h t_h} \times 10^6 \quad (\text{Equation 16})$$

Where:

E_r = Inlet Hg emission rate for the specified specified time period (lb/TBtu)

$(Mass)_{Hg-coal}$ = Total mass of Hg in the coal combusted during the specified time period, from Equation 14 (lb)

$(HI)_h$ = Heat input rate from coal combustion for hour “h” in the specified time period, calculated from measurements of stack gas flow rate, diluent gas concentration, and moisture (if needed), or appropriate substitute data values for these parameters, together with a fuel-specific F-factor and an appropriate equation from section 5.2 of appendix F to 40 CFR Part 75 (mmBtu/hr)

t_h = Unit or stack operating time for hour “h” in the specified time period, fraction of the hour, expressed as a decimal (e.g., 1.00 for a full operating hour, 0.5 for 30 minutes of operation, 0.00 for a non-operating hour, etc.)

10^6 = Conversion factor from mmBtu to TBtu

n = Number of clock hours in the specified time period

11.8.4.4.2 Calculation of Percentage Reduction

Use Equation 17 to calculate the percentage reduction of Hg achieved in the specified time period:

$$(\%R)_{rate} = \frac{E_r - \bar{E}_{hm}}{E_r} \times 100 \quad (\text{Equation 17})$$

Where:

$(\%R)_{\text{rate}}$ = Percentage reduction of Hg achieved in the specified time period, emission rate basis (percent)

E_r = Inlet Hg emission rate for the specified time period, from Equation 16 (lb/TBtu)

\overline{E}_{hm} = Outlet Hg emission rate for the specified time period, from Equation 10 (lb/TBtu)

11.8.5 Missing Data Provisions

Missing data substitution is required whenever a measured value of a parameter that is needed to calculate the hourly Hg mass emissions, Hg emission rate, or percentage reduction is not available. Use the following procedures, as applicable, to provide substitute data values when essential data from sorbent trap monitoring systems, auxiliary monitoring systems, certified backup monitoring systems, reference methods, or coal sampling and analysis are unavailable.

11.8.5.1 Sorbent Trap Monitoring Systems.

11.8.5.1.1 Definition of Missing Data Periods

For a certified sorbent trap monitoring system, a missing data period occurs in the following circumstances, unless quality-assured Hg concentration data from a certified backup Hg monitoring system or Hg reference method are available: (a) whenever a gas sample is not extracted from the stack during unit operation (e.g., during a monitoring system malfunction or when the system undergoes maintenance); and (b) when the results of the Hg analysis for a pair of sorbent traps are missing or invalid, as described in Table 1 of this protocol. When the analytical results from a pair of sorbent traps are missing or invalid, the missing data period begins with the first hour in which those traps were brought into service and ends at the first hour in which valid Hg concentration data are obtained with another pair of sorbent traps (i.e., the hour at which this pair of traps is placed in service).

11.8.5.1.2 Initial Missing Data Procedures.

Immediately following the initial certification of a sorbent trap monitoring system, apply the initial missing data algorithms in 40 CFR 75.31(b) for Hg concentration⁸, until 720 hours of quality-assured Hg concentration data have been collected. Calculate, and update hourly, the percent monitor data availability (PMA) for Hg concentration, in accordance with 40 CFR 75.32.

11.8.5.1.3 Standard Missing Data Procedures.

Once 720 quality-assured hours of Hg concentration data have been obtained following initial certification, the owner or operator shall provide substitute data for Hg concentration in accordance with the standard missing data procedures in 40 CFR

⁸ These missing data procedures, which apply to SO₂ concentration, CO₂ concentration, and moisture, are equally suitable for Hg concentration.

75.33(b)(1) through (b)(4), except that the term “Hg concentration” shall apply rather than “SO₂ concentration”, the term “sorbent trap monitoring system” shall apply rather than “SO₂ pollutant concentration monitor”, the term “maximum potential Hg concentration” shall apply, rather than “maximum potential SO₂ concentration”, and the 95.0, 90.0, and 80.0 percent monitor data availability trigger conditions prescribed 40 CFR 75.33(b)(1) through (b)(4) shall be replaced, respectively, with 90.0, 80.0, and 70.0 percent (see Table 2, below).

11.8.5.1.4 Special Considerations for Units With Emission Controls

For a unit equipped with a flue gas desulfurization (FGD) system that significantly reduces the concentration of Hg emitted to the atmosphere (including circulating fluidized bed units that use limestone injection), or for a unit equipped with add-on Hg emission controls (e.g., carbon injection), the standard missing data procedures in Section 11.8.5.1.3 of this protocol may only be used for hours in which the SO₂ or Hg emission controls are documented to be operating properly, based on parametric data recorded during the missing data period⁹. For any hour(s) in the missing data period for which this documentation is unavailable, the owner or operator must report the maximum potential Hg concentration (MPC), as defined in Section 11.8.5.1.5 of this protocol.

Table 2: Standard Missing Data Procedures for Hg Concentration

Trigger Conditions		Calculation Routines	
Percent Monitor Data Availability (PMA)	Duration (N) of Monitor Outage (Hours)	Method	Lookback Period
90 or more	$N \leq 24$	Average of.....	HB and HA ¹
	$N > 24$	The greater of: Average of..... 90th percentile.....	HB and HA 720 hours*
80 or more, but below 90	$N \leq 8$	Average of.....	HB and HA
	$N > 8$	The greater of: Average of..... 95th percentile.....	HB and HA 720 hours*
70 or more, but below 80	$N > 0$	Maximum value.....	720 hours*
Below 70	$N > 0$	Maximum potential concentration.....	None

¹ HB and HA = Quality-assured Hg concentrations in the hour before and hour after the monitor outage.

* Quality-assured monitor operating hours, during unit operation

However, when the PMA is less than 80.0 percent, but greater than or equal to 70.0 percent, and a missing data period occurs, the owner or operator may report the maximum controlled Hg concentration in the previous 720 hours of quality-assured data, in lieu of reporting the maximum value in the 720-hour lookback, for each missing data

⁹ Note: hourly SO₂ concentration data from a certified CEMS may be used to demonstrate that a FGD system is working properly.

hour in which the FGD or Hg emission controls are documented to be operating properly. Further, when the PMA is less than 70.0 percent and a missing data period occurs, the owner or operator may report the greater of: (a) the maximum expected Hg concentration (MEC); or (b) 1.25 times the maximum controlled Hg concentration recorded in the previous 720 quality-assured hours of data, for each missing data hour in which the FGD or Hg emission controls are documented to be operating properly. The MEC shall be determined in accordance with Section 11.8.5.1.6 of this protocol.

11.8.5.1.5 Maximum Potential Concentration

For the purposes of this protocol, there are two options for determining the maximum potential Hg concentration: (a) use one of the following default values: 9 $\mu\text{g}/\text{scm}$ for bituminous coal; 10 $\mu\text{g}/\text{scm}$ for sub-bituminous coal; 16 $\mu\text{g}/\text{scm}$ for lignite, and 1 $\mu\text{g}/\text{scm}$ for waste coal, i.e., anthracite culm or bituminous gob. If different coals are blended, use the highest MPC for any fuel in the blend; or (b) base the MPC on the results of site-specific emission testing using the one of the Hg reference methods in Section 8.1.1 of this protocol. Option (b) may only be used if the unit does not have add-on Hg emission controls or a flue gas desulfurization system, or if testing is performed upstream of all emission control devices. A minimum of 3 test runs are required, at the normal operating load. Use the highest total Hg concentration obtained in any of the tests as the MPC.

11.8.5.1.6 Maximum Expected Concentration

For units with FGD systems that significantly reduce Hg emissions (including fluidized bed units that use limestone injection) and for units equipped with add-on Hg emission controls (e.g., carbon injection), determine the maximum expected Hg concentration (MEC) during normal, stable operation of the unit and emission controls. To calculate the MEC, substitute the MPC value from Section 11.8.5.1.5 of this protocol into Equation A-2 in section 2.1.1.2 of appendix A to 40 CFR Part 75. For units with add-on Hg emission controls, base the percent removal efficiency on design engineering calculations. For units with FGD systems, use the best available estimate of the Hg removal efficiency of the FGD system.

11.8.5.2 Auxiliary Monitoring Systems.

For the auxiliary monitoring systems (flow rate, diluent gas, and moisture), follow the applicable missing data procedures in Subpart D of 40 CFR Part 75.

11.8.5.3 Coal Sampling and Analysis

If the results of the analysis of a daily coal sample are either invalid or unavailable, use a substitute data value for that day. The substitute data value shall either be: (a) the average Hg content or average GCV (as applicable) from the previous 30 valid daily samples; or (b) the average of all Hg content or GCV values (as applicable) obtained to date if the fewer than 30 valid historical sample results are available. If no valid historical Hg content or GCV data are available, apply the results of the first valid sample retrospectively to all missing data days.

11.8.5.4 Data Availability

Every effort should be made to obtain valid data and to minimize the use of missing data substitution. Data availability of at least 90 percent for all parameters is believed to be both reasonable and achievable.

12. Reporting Guidelines

Quarterly electronic reporting of data from sorbent trap monitoring systems and (if applicable) auxiliary monitoring systems is recommended, unless otherwise specified in an applicable regulation or policy. If electronic reporting is implemented, supporting information must also be provided to enable comprehensive electronic auditing of the emissions data. At a minimum, the following data elements should be reported electronically:

12.1 *Unit Information*

Report unit information, including, but not limited to, the unit ID number, the maximum rated heat input capacity, the operating range (in terms of load), the normal operating load(s), the type(s) of fuel combusted, and the type(s) of emission controls.

12.2 *Stack Information*

For units that share a monitored common stack or for units with monitored multiple stack exhaust configurations, report the stack ID number(s) and show the unit/stack relationships.

12.3 *Monitoring System Information*

Report information for each monitoring system, including, but not limited to, system location, parameter monitored, system and component ID numbers, and component data (e.g., component type, manufacturer, model, serial number, installation date, etc.).

12.4 *Span and Range Information*

If auxiliary monitoring systems are used, report span and range information for these systems.

12.5 *Formulas*

Report, as applicable, the mathematical formulas that are used to calculate hourly Hg mass emissions and Hg emission rates.

12.6 *Operating Data*

Report hourly unit operating data including, but not limited to, date and hour, unit (or stack) operating time, unit load, and fuel code.

12.7 *Emissions Data*

12.7.1 *Hourly Data*

Report hourly Hg concentration data from the sorbent trap monitoring system and (if applicable) hourly data from the auxiliary monitoring systems that are used to calculate Hg mass emissions and Hg emission rates. For the sorbent trap system, a single Hg concentration value (derived from the analysis of the paired traps) is reported for each operating hour in each data collection period. Where bias adjustment is required, report both the unadjusted and bias-adjusted values. Report the hour-by-hour percent monitor data availability (PMA) for all monitored parameters. Indicate which hourly values of each monitored parameter are quality-assured and which ones are substitute data values. Also report, if applicable, the calculated hourly Hg mass emissions and/or Hg emission rates.

12.7.2 *Cumulative and Average Values*

Report, as applicable, the cumulative Hg mass emissions and/or average Hg emission rates (e.g., quarterly and year-to-date totals or averages).

12.8 *Supplementary Information*

For each data collection period of the sorbent trap monitoring system, report supplementary data, including: starting and ending dates and times; ID numbers for the monitoring system, sorbent trap, and gas flow meter; sorbent trap serial numbers; Hg catch in sections 1 and 2 of each trap; mass of Hg in each third section spike and the mass of Hg recovered; total sample volume; gas flow meter readings; sampling rates; ratio of stack flow rate to sample flow rate; leak check results; and use of single trap adjustment factor (if applicable).

12.9 *QA Test Data and Results*

Report, as applicable, detailed quality assurance test data and summarized results, for the following QA tests: (a) calibration error tests, linearity checks, and RATAs of the auxiliary monitoring systems; and (b) and gas flow meter calibrations, for the sorbent trap monitoring system. Also, if applicable, report the results of all coal analyses for Hg content and GCV.

13. 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 µg/dscm to 100 µg/dscm.