

METHOD 324 - DETERMINATION OF VAPOR PHASE FLUE GAS MERCURY
EMISSIONS FROM STATIONARY SOURCES USING DRY SORBENT TRAP SAMPLING

1.0 Introduction.

This method describes sampling criteria and procedures for the continuous sampling of mercury (Hg) emissions in combustion flue gas streams using sorbent traps. Analysis of each trap can be by cold vapor atomic fluorescence spectrometry (AF) which is described in this method, or by cold vapor atomic absorption spectrometry (AA). Only the AF analytical method is detailed in this method, with reference being made to other published methods for the AA analytical procedure. The Electric Power Research Institute has investigated the AF analytical procedure in the field with the support of ADA-ES and Frontier Geosciences, Inc. The AF procedure is based on EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. Persons using this method should have a thorough working knowledge of Methods 1, 2, 3, 4 and 5 of 40 CFR Part 60, Appendix A.

1.1 Scope and Application.

1.1.1 Analytes. The analyte measured by this method is total vapor-phase Hg, which represents the sum of elemental (CAS Number 7439-97-6) and oxidized forms of Hg, mass concentration (micrograms/dscm) in flue gas samples.

1.1.2 Applicability. This method is applicable to the determination of vapor-phase Hg concentrations ranging from 0.03

µg/dncm to 100 µg/dncm in low-dust applications, including controlled and uncontrolled emissions from stationary sources, only when specified within the regulations. When employed to demonstrate compliance with an emission regulation, paired sampling is to be performed as part of the method quality control procedure. The method is appropriate for flue gas Hg measurements from combustion sources. Very low Hg concentrations will require greater sample volumes. The method can be used over any period from 30 minutes to several days in duration, provided appropriate sample volumes are collected and all the quality control criteria in Section 9.0 are met. When sampling for periods greater than 12 hours, the sample rate is required to be maintained at a constant proportion to the total stack flowrate, ±25% to ensure representativeness of the sample collected.

2.0 Summary of Method.

Known volumes of flue gas are extracted from a duct through a single or paired sorbent traps with a nominal flow rate of 0.2 to 0.6 liters per minute through each trap. Each trap is then acid leached and the resulting leachate is analyzed by cold vapor atomic fluorescence spectrometry (CVAFS) detection. The AF analytical procedure is described in detail in EPA Method 1631. Analysis by AA can be performed by existing recognized procedures, such as that contained in ASTM Method D6784-02 or EPA Method 29.

3.0 Definitions. (Reserved).

4.0 Clean Handling and Contamination.

During preparation of the sorbent traps, as well as transport, field handling, sampling, recovery, and laboratory analysis, special attention must be paid to cleanliness procedures. This is to avoid Hg contamination of the samples, which generally contain very small amounts of Hg. For specifics on how to avoid contamination, Section 4 of Method 1631 should be well understood.

5.0 Safety.

5.1 Site hazards must be prepared for in advance of applying this method in the field. Suitable clothing to protect against site hazards is required, and requires advance coordination with the site 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.

5.2 Laboratory safety policies are to minimize risk of chemical exposure and to properly handle waste disposal. Personnel will don appropriate laboratory attire according to a Chemical Hygiene Plan established by the laboratory. This includes, but is not limited to, laboratory coat, safety goggles, and nitrile gloves under clean gloves.

5.3 The toxicity or carcinogenicity of reagents used in this method has not been fully established. The procedures required in this method may involve hazardous materials,

operations, and equipment. This method may not address all of the safety problems associated with these procedures. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performing these procedures. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized. Chemists should refer to the MSDS for each chemical with which they are working.

5.4 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.

6.0 Equipment and Supplies.

6.1 Hg Sampling Train. A Schematic of a single trap sampling train used for this method is shown in Figure 324-1. Where this method is used to collect data to demonstrate compliance with a regulation, it must be performed with paired sorbent trap equipment.

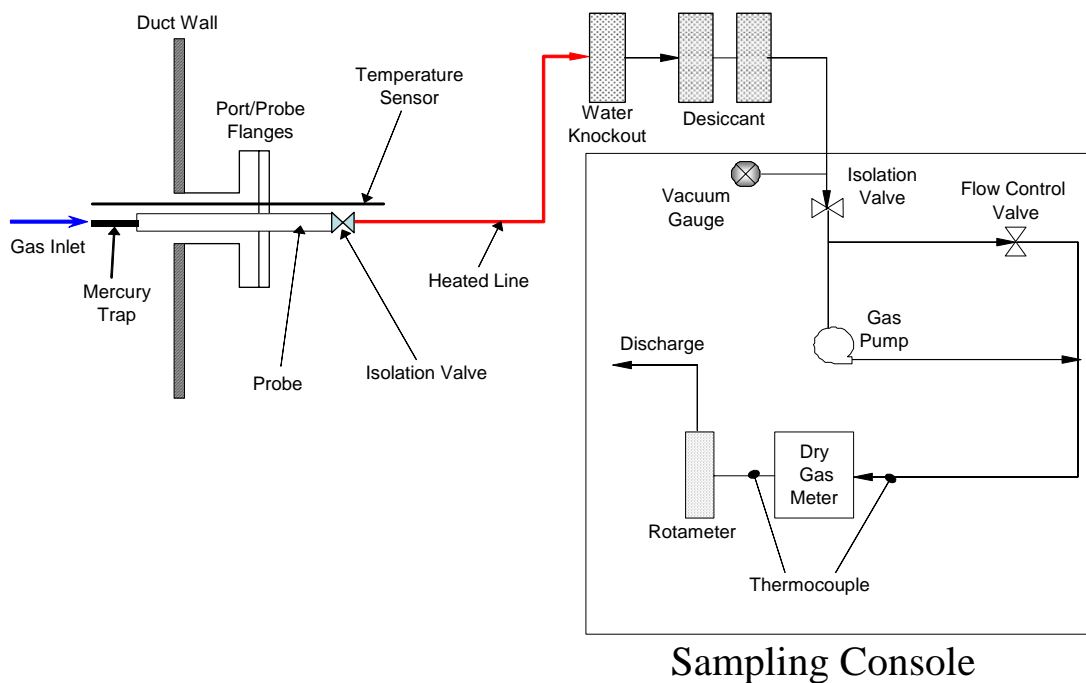


Figure 324-1. Hg Sampling Train illustrating Single Trap.

6.1.1 Sorbent Trap. Use sorbent traps with separate main and backup sections in series for collection of Hg. Selection of the sorbent trap shall be based on: 1) achievement of the performance criteria of this method and 2) data is available to demonstrate the method can pass the criteria in EPA Method 301 when used in this method and when the results are compared with those from EPA Method 29, EPA Method 101A or ASTM Method 6784-02 for the measurement of vapor-phase Hg in a similar flue gas matrix. Appropriate traps are referred to as "sorbent trap" throughout this method. The method requires the analysis of Hg in both main and backup portions of the sorbent within each trap. The sorbent trap should be obtained from a reliable source that

has clean handling procedures in place for ultra low-level Hg analysis. This will help assure the low Hg environment required to manufacture sorbent traps with low blank levels of Hg. Sorbent trap sampling requirements or needed characteristics are shown in Table 324-1. Blank/cleanliness and other requirements are described in Table 324-2. The sorbent trap is supported on a probe and inserted directly into the flue gas stream, as shown on Figure 324-1. The sampled sorbent trap is the entire Hg sample.

6.1.2 Sampling Probe. The probe assembly shall have a leak-free attachment to the sorbent trap. For duct temperatures from 200 to 375°F, no heating is required. For duct temperatures less than 200°F, the sorbent tube must be heated to at least 200°F or higher to avoid liquid condensation in the sorbent trap by using a heated probe. For duct temperatures greater than 375°F a large sorbent trap must be used, as shown in Table 324-1, and no heating is required. A thermocouple is used to monitor stack temperature.

6.1.3 Umbilical Vacuum Line. A 250°F heated umbilical line shall be used to convey to the moisture knockout the sampled gas that has passed through the sorbent trap and probe assembly.

6.1.4 Moisture Knockout. Impingers and desiccant can be combined to dry the sample gas prior to entering the dry gas meter. Alternative sample drying methods are acceptable as long as they do not affect sample volume measurement.

6.1.5 Vacuum Pump. A leak tight vacuum pump capable of

delivering a controlled extraction flow rate between 0.1 to 0.8 liters per minute.

6.1.6 Dry Gas Meter. Use a dry gas meter that is calibrated according to the procedures in 40 CFR Part 60, Appendix A Method 5, to measure the total sample volume collected. The dry gas meter must be sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor capable of measuring typical meter temperatures accurately to within 3°C (5.4°F).

6.2 Sample Analysis Equipment. Laboratory equipment as described in Method 1631, Sections 6.3 to 6.7 is required for analysis by AF. For analysis by AA, refer to Method 29 or ASTM Method 6784-02.

Table 324-1. Sorbent Trap and Sampling Requirements.

| Item to be determined | Small Sorbent Trap | Large Sorbent Trap |
|--|---|--|
| Sampling Target: Hg Loading Range, ug | Minimum = 0.025 µg/trap Maximum = 150 µg/trap | Minimum = 0.10 µg/trap Maximum = 1800 µg/trap |
| Sampling Duration Required: limits on sample times | Minimum = 30 minutes Maximum = 24 hours | Minimum = 24 hours Maximum = 10 days |
| Sampling Temperature Required | 200 to 375°F | 200 to 425°F |
| Sampling Rate Required | 0.2 to 0.6 L/min; start at 0.4 L/min Must be constant proportion within +/- 25% if greater than 12 hours; constant rate within +/-25% if less than 12 hours. | 0.2 to 0.6 L/min; start at 0.4 L/min Must be constant proportion of stack flowrate within +/-25% |

7.0 Analysis by AF, Reagents and Standards.

For analysis by AF, use Method 1631, Sections 7.1 - 7.3 and 7.5 - 7.12 for laboratory reagents and standards. Refer to Method 29 or ASTM Method 6784-02 for analysis by AA.

7.1 Reagent Water. Same as Method 1631, Section 7.1.

7.2 Air. Same as Method 1631, Section 7.2.

7.3 Hydrochloric Acid. Same as Method 1631, Section 7.3.

7.4 Stannous Chloride. Same as Method 1631, Section 7.5.

7.5 Bromine Monochloride (BrCl, .01N). Same as Method 1631, Section 7.6.

7.6 Hg Standards. Same as Method 1631, Sections 7.7 to 7.11.

7.7 Nitric Acid. Reagent grade, low Hg.

7.8 Sulfuric Acid. Reagent grade, low Hg.

7.9 Nitrogen. Same as Method 1631, Section 7.12.

7.10 Argon. Same as Method 1631, Section 7.13.

8.0 Sample Collection and Transport.

8.1 Pre-Test.

8.1.1 Site information should be obtained in accordance with Method 1 (40 CFR Part 60, Appendix A). Identify a location that has been shown to be free of stratification for SO₂ and NO_x through concentration measurement traverses for those gases. An estimation of the expected Hg concentration is required to establish minimum sample volumes. Based on estimated minimum sample volume and normal sample rates for each size trap used,

determine sampling duration with the data provided in Table 324-1.

8.1.2 Sorbent traps must be obtained from a reliable source such that high quality control and trace cleanliness are maintained. Method detection limits will be adversely affected if adequate cleanliness is not maintained. Sorbent traps should be handled only with powder-free low Hg gloves (vinyl, latex or nitrile are acceptable) that have not touched any other surface. The sorbent traps should not be removed from their clean storage containers until after the preliminary leak check has been completed. Field efforts at clean handling of the Sorbent traps are key to the success of this method.

8.1.3 Assemble the sample train according to Figure 324-1, except omit the sorbent trap.

8.1.4 Preliminary Leak Check: Perform system leak check without the single or dual sorbent traps in place. This entails plugging the end of the probe to which each sorbent trap will be affixed, and using the vacuum pump to draw a vacuum in each sample train. Adjust the vacuum in the sample train to 15" Hg. A rotameter on the dry gas meter will indicate the leakage rate. The leakage rate must be less than 2 percent of the planned sampling rate.

8.1.5 Release the vacuum in the sample train, turn off the pump, and affix the Sorbent trap to the end of the probe, using clean handling procedures. Leave the flue gas end of the sorbent

trap plugged.

8.1.6 Pre-test leak check: Perform a leak check with the Sorbent trap in place. Use the sampling vacuum pump to draw a vacuum in the sample train. Adjust the vacuum in the sample train to 15 inches Hg. A rotameter on the dry gas meter will indicate the leakage rate. Record the leakage rate. The leakage rate must be less than 2 percent of the planned sampling rate. Once the leak check passes this criterion, carefully release the vacuum in the sample train (the sorbent trap must not be exposed to abrupt changes in pressure or to backflow), then re-cap the flue gas end of the sorbent trap until the probe is ready for insertion. The sorbent trap packing beds must be undisturbed by the leak test to prevent gas channeling through the media during sampling.

8.1.7 Use temperature controllers to heat the portions of the trains that require it. The sorbent trap must be maintained between 200 and 375 °F during sampling.

8.1.8 Gas temperature and static pressure must be considered prior to sampling in order to maintain proper safety precautions during sampling.

8.2 Sample Collection.

8.2.1 Remove the plug from the end of a sorbent trap and store it in a clean sorbent trap storage container. Remove the sample duct port cap and insert the probe. Secure the probe and ensure that no leakage occurs between the duct and environment.

8.2.2 Record initial data including the start time, starting dry gas meter readings, and the name of the field tester(s). Set the initial sample flow rate to 0.4 L/min (+/- 25%).

8.2.3 For constant-flow sampling (samples less than 12 hours in duration): Every 10-15 minutes during the sampling period: record the time, the sample flow rate, the gas meter readings, the duct temperature, the flow meter temperatures, temperatures of heated equipment such as the vacuum lines and the probes (if heated), and the sampling vacuum reading. Adjust the sample rate as needed, maintaining constant sampling within +/- 25% of the initial reading.

8.2.4 For constant proportion sampling (samples 12 hours or greater in duration): Every hour during the sampling period: record the time, the sample flow rate, the gas meter readings, the duct temperature, the flow meter temperatures, temperatures of heated equipment such as the vacuum lines and the probes (if heated), and the sampling vacuum readings. Also record the stack flow rate reading, whether provided as a CEM flow monitor signal, a pitot probe or other direct flow indication, or a plant input signal. Adjust the sampling rate to maintain proportional sampling within +/- 25% relative to the total stack flowrate.

8.2.5 Obtain and record operating data for the facility during the test period, including total stack flowrate and the oxygen concentration at the flue gas test location. Barometric

pressure must be obtained for correcting sample volume to standard conditions.

8.2.6 Post Test Leak Check: When sampling is completed, turn off the sample pump, remove the probe from the port and carefully re-plug the end of the sorbent trap. Perform leak check by turning on the sampling vacuum pumps with the plug in place. The rotameter on the dry gas meters will indicate the leakage rates. Record the leakage rate and vacuum. The leakage rate must be less than 2 percent of the actual sampling rate. Following the leak check, carefully release the vacuum in the sample train.

8.2.7 Sample Recovery: Recover each sampled sorbent trap by removing it from the probe, plugging both ends with the clean caps provided with the sorbent trap, and then wiping any dirt off the outside of the sorbent trap. Place the sorbent trap into the clean sample storage container in which it was provided, along with the data sheet that includes the post-test leak check, final volume, and test end time.

8.3 Quality Control Samples and Requirements.

8.3.1 Field blanks. Refer to Table 324-2.

8.3.2 Duplicate (paired or side by side) samples. Refer to Section 8.6.6 of Performance Specification 12A of 40 CFR Part 60, Appendix B for this criteria.

8.3.3 Breakthrough performance data ("B" bed in each trap, or second traps behind). Refer to Table 324-2.

8.3.4 Field spikes (sorbent traps spiked with Hg in the lab and periodically sampled in the field to determine overall accuracy). Refer to Table 324-2.

8.3.5 Laboratory matrix and matrix spike duplicates. Refer to Table 324-2.

9.0 Quality Control.

Table 324-2 summarizes the major quantifiable QC components.

Table 324-2. Quality Control for Samples

| QA/QC Specification | Acceptance Criteria | Frequency | Corrective Action |
|--|--|--|--|
| Leak-check | <2% of sampling rate | Pre and post-sampling | Pre-sampling: repair leak. Post-sampling: Flag data and repeat run if for regulatory compliance. |
| Sample Flow Rate for samples less than 12 hours in duration | 0.4 L/min initially and +/- 25% of initial rate throughout run | Throughout run every 10-15 minutes | Adjust when data is recorded. |
| Sample Flow Rate for samples greater than 12 hours in duration | 0.4 L/min initially and maintain +/-25% of ratio to flue gas flow rate throughout sampling | Throughout run every hour | Adjust when data is recorded |
| Sorbent trap laboratory blank (same lot as samples) | <5 ng/trap and a standard deviation of <1.0 ng/trap (n=3) | 3 per analysis set of 20 sorbent traps | |
| Sorbent trap field blank (same lot as samples) | <5 ng/trap and a standard deviation of <1.0 ng/trap (n=3) OR <5% of average sample collected | 1 per every 10 field samples collected | |
| B-Trap Bed Analysis | <2% of A-Trap Bed Value OR < 5 ng/trap | Every sample | |
| Paired Train Results | Same as Section 8.6.6 of PS-12A of 40CFR Par60, Appendix B | | |
| Field Spikes | 80 % to 120% recovery | For long-term regulatory monitoring, 1 per every 3 | If the first 4 field spikes do not meet the +/-20% criteria, take |

| | | | |
|---|----------------------|--|---|
| | | samples for the first 12 samples | corrective sampling and laboratory measures and repeat at the 1 per every 3 sample rate until the +/-20% criteria is met. |
| Laboratory matrix and matrix spike duplicates | 85% to 115% recovery | 1 per every 10 or 20 samples- to be determined | |

10.0 Calibration and Standards.

Same as Sections 10.1, 10.2 and 10.4 of Method 1631.

10.1 Calibration and Standardization. Same as Sections 10.1 and 10.4 of Method 1631.

10.2 Bubbler System. Same as Section 10.2 of M1631.

10.3 Flow-Injection System. Not applicable.

11.0 Analytical Procedures.

11.1 Preparation Step. The sorbent traps are received and processed in a low-Hg environment (class-100 laminar-flow hood and gaseous Hg air concentrations below 20 ng/m³) following clean-handling procedures. Any dirt or particulate present on the exterior of the trap must be removed to avoid contamination of the sample. The sorbent traps are then opened and the sorbent bed(s) transferred to an appropriate sized trace-clean vessel. It is recommended that the height of the trace-clean vessel be at least 3 times the diameter to facilitate a refluxing action.

11.2 Leaching Step. The sorbent trap is then subjected to a hot-acid leach using a 70:30 ratio mixture of concentrated HNO₃ / H₂SO₄. The acid volume must be 40% of the expected end volume of the digest after dilution. The HNO₃ / H₂SO₄ acid to carbon

should be approximately 35:1. The leachate is then heated to a temperature of 50-60 °C for 1.5-2.0 hours in the finger-tight capped vessels. This process may generate significant quantities of noxious and corrosive gasses and must only be performed in a well-ventilated fume hood. Care must be taken to prevent excessive heated leaching of the samples as this will begin to break down the charcoal material.

11.3 Dilution Step. After the leached samples have been removed from the hot plate and allowed to cool to room temperature, they are brought to volume with a 5% (v/v) solution of 0.01 N BrCl. As the leaching digest contains a substantial amount of dissolved gasses, add the BrCl slowly, especially if the samples are still warm. As before, this procedure must be performed in a properly functioning fume hood. The sample is now ready for analysis.

11.4 Hg Reduction and Purging. (ref Section 11.2 of M1631 except: NH_2OH is not used)

11.4.1 Bubbler System. Pipette an aliquot of the digested sample into the bubbler containing pre-blanked reagent water and a soda lime trap connected to the exhaust port. Add stannous chloride (SnCl_2) to reduce the aliquot and then seal the bubbler. Connect gold sample traps to the end of the soda lime trap as shown in Figures 1 and 2 of Method 1631. Finally, connect the N_2 lines and purge for 20 minutes. The sample trap can then be added into the analytical train. M1631, Section 11.2.1.

11.4.2 Flow Injection System. If required.

11.5 Desorption of Hg from the gold trap, and peak evaluation. Use Section 11.3 and 11.4 in M1631.

11.6 Instrument Calibration. Analyze the standards by AA or AF following the guidelines specified by the instrument manufacturer. Construct a calibration curve by plotting the absorbances of the standards versus $\mu\text{g/l}$ Hg. The R^2 for the calibration curve should be 0.999 or better. If the curve does not have an R^2 value equal to or better than 0.999 then the curve should be rerun. If the curve still does not meet this criteria then new standards should be prepared and the instrument recalibrated. All calibration points contained in the curve must be within 10% of the calibration value when the calibration curve is applied to the calibration standards.

11.7 Sample Analysis. Analyze the samples in duplicate following the same procedures used for instrument calibration. From the calibration curve, determine sample Hg concentrations. To determine total Hg mass in each sample fraction, refer to calculations in Section 15. Record all sample dilutions

11.8 Continued Calibration Performance. To verify continued calibration performance, a continuing calibration check standard should be run every 10 samples. The measured mercury concentration of the continuing calibration check standard must be within 10 % of the expected value.

11.9 Measurement Precision. The QA/QC for the analytical

portion of this method is that every sample, after it has been prepared, is to be analyzed in duplicate with every tenth sample analyzed in triplicate. These results must be within 10% of each other. If this is not the case, then the instrument must be recalibrated and the samples reanalyzed.

11.10 Measurement Accuracy. Following calibration, an independently prepared standard (not from same calibration stock solution) should be analyzed. In addition, after every ten samples, a known spike sample (standard addition) must be analyzed. The measured mercury content of the spiked samples must be within 10 % of the expected value.

11.11 Independent QA/QC Checks. It is suggested that the QA/QC procedures developed for a test program include submitting, on occasion, spiked mercury samples to the analytical laboratory by either the prime contractor, if different from the laboratory, or an independent organization. The measured mercury content of reference samples must be within 15 % of the expected value. If this limit is exceeded, corrective action (e.g. re-calibration) must be taken and the samples re-analyzed.

11.12 Quality Assurance/Quality Control. For this method, it is important that both the sampling team and analytical people be very well trained in the procedures. This is a complicated method that requires a high-level of sampling and analytical experience. For the sampling portion of the QA /QC procedure, both solution and field blanks are required. It

should be noted that if high-quality reagents are used and care is taken in their preparation and in the train assembly, there should be little, if any, Hg measured in either the solution or field blanks.

11.13 Solution Blanks. Solution blanks must be taken and analyzed every time a new batch of solution is prepared. If Hg is detected in these solution blanks, the concentration is subtracted from the measured sample results. The maximum amount that can be subtracted is 10% of the measured result or 10 times the detection limit of the instrument whichever is lower. If the solution blanks are greater than 10% the data must be flagged as suspect.

11.14 Field Blanks. A field blank is performed by assembling a sample train, transporting it to the sampling location during the sampling period, and recovering it as a regular sample. These data are used to ensure that there is no contamination as a result of the sampling activities. A minimum of one field blank at each sampling location must be completed for each test site. Any Hg detected in the field blanks cannot be subtracted from the results. Whether or not the Hg detected in the field blanks is significant is determined based on the QA/QC procedures established prior to the testing. At a minimum, if field blanks exceed 30% of the measured value at the corresponding location, the data must be flagged as suspect.

12.0 Calculations and Data Analysis.

Use Section 12 in M1631.

13.0 Constant Proportion Sampling

Calculate the Sample Rate/Stack Flow = "x". "X" must be maintained within .75"x" to 1.25"x" for sampling times in excess of 12 hours. For mass emission rate calculations, use the flow CEM total measured flow corresponding to the sorbent trap sample time period.

14.0 Sampling and Data Summary Calculations.

Refer to 40 CFR 60, Appendix A, Methods 2, 4, and 5 for example calculations.

15.0 Pollution Prevention.

Refer to Section 13 in Method 1631.

16.0 Waste Management.

Refer to Section 14 in Method 1631.

17.0 Bibliography.

17.1 EPA Method 1631, Revision E "Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry," August 2002.

17.2 "Comparison of Sampling Methods to Determine Total and Speciated Mercury in Flue Gas," CRADA F00-038 Final Report, DOE/NETL-2001/1147, January 4, 2001.

17.3 40 CFR Part 60, Appendix A, "Method 29 - Determination of Metals Emissions from Stationary Sources".

17.4 40 CFR Part 60, Appendix B, "Performance Specification 12A, Specification and Test Procedures for Total Vapor Phase

Mercury Continuous Emission Monitoring Systems in Stationary Sources".

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