**Designation: D 6784 – 02**

# Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)[1]

This standard is issued under the fixed designation D 6784; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This method applies to the determination of elemental, oxidized, particle-bound, and total mercury emissions from coal-fired stationary sources.

1.2 This method is applicable to elemental, oxidized, particle-bound, and total mercury concentrations ranging from approximately 0.5 to 100 μg/$Nm^3$.

1.3 This method describes equipment and procedures for obtaining samples from effluent ducts and stacks, equipment and procedures for laboratory analysis, and procedures for calculating results.

1.4 This method is applicable for sampling elemental, oxidized, and particle-bound mercury in flue gases of coal-fired stationary sources. It may not be suitable at all measurement locations, particularly those with high particulate loadings, as explained in Section 16.

1.5 Method applicability is limited to flue gas stream temperatures within the thermal stability range of the sampling probe and filter components.

1.6 The values stated in SI units are to be regarded as the standard. The values in parentheses are for information only.

1.7 This standard assumes users are familiar with EPA stack-gas sampling procedures as stated in EPA Methods 1–4, Method 5, and Method 17.

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[3]

D 2986 Practice for Evaluation of Air-Assay Media by the Monodisperse DOP (Dioctyl Phthalate) Smoke Test[3]

D 3154 Test Method for Average Velocity in a Duct (Pitot Tube Method)[3]

D 3685 Test Methods for Sampling and Determination of Particulate Matter in Stack Gases[3]

E 1 Specification for ASTM Thermometers[4]

2.2 *Other Standards:*[5]

EPA Method 1 Sample and Velocity Traverses for Stationary Sources

EPA Method 2 Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)

EPA Method 3 Gas Analysis for the Determination of Dry Molecular Weight

EPA Method 4 Determination of Moisture Content in Stack Gases

EPA Method 5 Determination of Particulate Emissions from Stationary Sources

EPA Method 12 Determination of Inorganic Lead Emissions from Stationary Sources

EPA Method 17 Determination of Particulate Emissions from Stationary Sources (In-Stack Filtration Method)

EPA Method 29 Determination of Metals Emissions from Stationary Sources

EPA Method 101A Determination of Particle-Bound and Gaseous Mercury Emissions from Sewage Sludge Incinerators

EPA Method 301 Field Validation of Pollutant Measurement Methods from Various Waste Media

EPA SW 846 7470A Mercury in Liquid Waste—Manual Cold Vapor Technique

EPA Water and Waste 600/4-79-020 Methods for Chemical Analysis of Water and Wastes

## 3. Terminology

3.1 Definitions other than those given below in 3.2 and 3.3 are listed in Terminology D 1356.

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[1] This test method is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.03.

[4] *Annual Book of ASTM Standards*, Vol 14.03.

[5] Available from the U.S. Environmental Protection Agency's Emission Measurement Technical Information Center or Code of Federal Regulations (40 CFR Part 60, Appendix A or 40 CFR Part 61, Appendix B).

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3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *elemental mercury*—mercury in its zero oxidation state, $Hg^0$.

3.2.2 *elemental mercury catch*—mercury collected in the acidified hydrogen peroxide ($HNO_3$–$H_2O_2$) and potassium permanganate ($H_2SO_4$–$KMnO_4$) impinger solutions employed in this method. This is gaseous $Hg^0$.

3.2.3 *front half of the sampling train*—all mercury collected on and upstream of the sample filter.

3.2.4 *impinger train*—setup including only the impingers and connectors.

3.2.5 *oxidized mercury*—mercury in its mercurous or mercuric oxidation states: $Hg_2^{2+}$ and $Hg^{2+}$, respectively.

3.2.6 *oxidized mercury catch*—mercury collected in the aqueous potassium chloride (KCl) impinger solution employed in this method. This is gaseous $Hg^{2+}$.

3.2.7 *particle-bound mercury catch*—mercury associated with the particulate matter collected in the front half of the sampling train.

3.2.8 *sample train*—complete setup including nozzle, probe, probe liner, filter, filter holder, impingers, and connectors.

3.2.9 *total mercury*—all mercury (solid-bound, liquid, or gaseous) however generated or entrained in the flue gas stream (that is, summation of elemental, oxidized, and particle-bound mercury).

3.3 *Symbols*:

$A$ = cross-sectional area of stack, $m^2$ ($ft^2$)

$B_{ws}$ = water vapor in the gas stream, proportion by volume

$\Delta H$ = average pressure differential across the orifice meter, kPa (in. $H_2O$)

$Hg_{ash}$ = concentration of mercury in sample filter ash, µg/g

$Hg^{tp}$ = concentration of particle-bound mercury, µg/$Nm^3$

$Hg^0$ = concentration of elemental mercury, µg/$Nm^3$

$Hg^{2+}$ = concentration of oxidized mercury, µg/$Nm^3$

$IR$ = instrument reading from mercury analyzer, µg/L

$L_p$ = leakage rate observed during the post test leak check, $m^3$/min (cfm)

$L_a$ = maximum acceptable leakage rate

$M_s$ = molecular weight of stack gas, wet basis g/g-mole (lb/Lb-mole)

$M_w$ = molecular weight of water, 18.0 g/g-mole (18.0 lb/Lb-mole)

$N$ = Normal conditions, defined as 0°C and 101.3 kPa, (In the U.S. standard conditions 32°F and 1 atmosphere)

$P_{bar}$ = barometric pressure at the sampling site, kPa (in. Hg)

$P_s$ = absolute stack gas pressure, kPa (in. Hg)

$P_{std}$ = standard absolute pressure, 101.3 kPa (29.92 in. Hg)

$R$ = ideal gas constant, 0.008314 kPa-$m^3$/K-g-mole (21.85 in. Hg-$ft^3$/°R-lb-mole)

$T_m$ = absolute average dry gas meter temperature, K (°R)

$T_s$ = absolute stack temperature, K (°R)

$T_{std}$ = standard absolute temperature, 293 K (528°R)

$V_D$ = total digested volume, mL

$V_m$ = volume of gas sample as measured by dry gas meter, $m^3$ (dscf)

$V_{m(std)}$ = volume of gas sample measured by the dry gas meter, corrected to standard conditions, $Nm^3$ (dscf)

$V_{w(std)}$ = volume of water vapor in the gas sample, corrected to standard conditions, $m^3$(scf)

$W_{ash}$ = total mass of ash on sample filter, g

$W_{lc}$ = total weight of liquid collected in impingers and silica gel, g (lb)

$Y$ = dry gas meter calibration factor

$\theta$ = total sampling time, min

$\theta_1$ = sampling time interval, from the beginning of a run until the first component change, min

## 4. Summary of Test Method

4.1 A sample is withdrawn from the flue gas stream isokinetically through a probe/filter system, maintained at 120°C or the flue gas temperature, whichever is greater, followed by a series of impingers in an ice bath. Particle-bound mercury is collected in the front half of the sampling train. Oxidized mercury is collected in impingers containing a chilled aqueous potassium chloride solution. Elemental mercury is collected in subsequent impingers (one impinger containing a chilled aqueous acidic solution of hydrogen peroxide and three impingers containing chilled aqueous acidic solutions of potassium permanganate). Samples are recovered, digested, and then analyzed for mercury using cold-vapor atomic absorption (CVAAS) or fluorescence spectroscopy (CVAFS).

## 5. Significance and Use

5.1 The measurement of particle-bound, oxidized, elemental, and total mercury in stationary-source flue gases provides data that can be used for dispersion modeling, deposition evaluation, human health and environmental impact assessments, emission reporting, compliance determinations, etc. Particle-bound, oxidized, and elemental mercury measurements before and after control devices may be necessary for optimizing and evaluating the mercury removal efficiency of emission control technologies.

## 6. Interferences

6.1 There are no known interferences, but certain biases may be encountered (see Section 16).

## 7. Apparatus

7.1 *Sampling Train*—Similar to Test Methods D 3685, EPA Method 5/EPA Method 17 and EPA Method 29 trains, as illustrated in Fig. 1.

7.1.1 *Probe Nozzle (Probe Tip)*—Glass nozzles are required unless alternate nozzles are constructed of materials that are free from contamination and will not interact with the sample. Probe fittings constructed of polytetrafluoroethylene (PTFE), polypropylene, etc., are required instead of metal fittings to prevent contamination.

7.1.2 *Probe Liner*—If the sample train is to be in EPA Method 5 configuration (out-of-stack filtration), the probe liner must be constructed of quartz or borosilicate glass. If an EPA Method 17 (in-stack filtration) sampling configuration is used, the probe/probe liner may be constructed of borosilicate glass, quartz or, depending on the flue gas temperature, PTFE.

7.1.3 *Pitot Tube*, Type S pitot tube. Refer to Section 2.2 of EPA Method 2 for a description.

7.1.4 *Differential Pressure Gages*, inclined manometers or

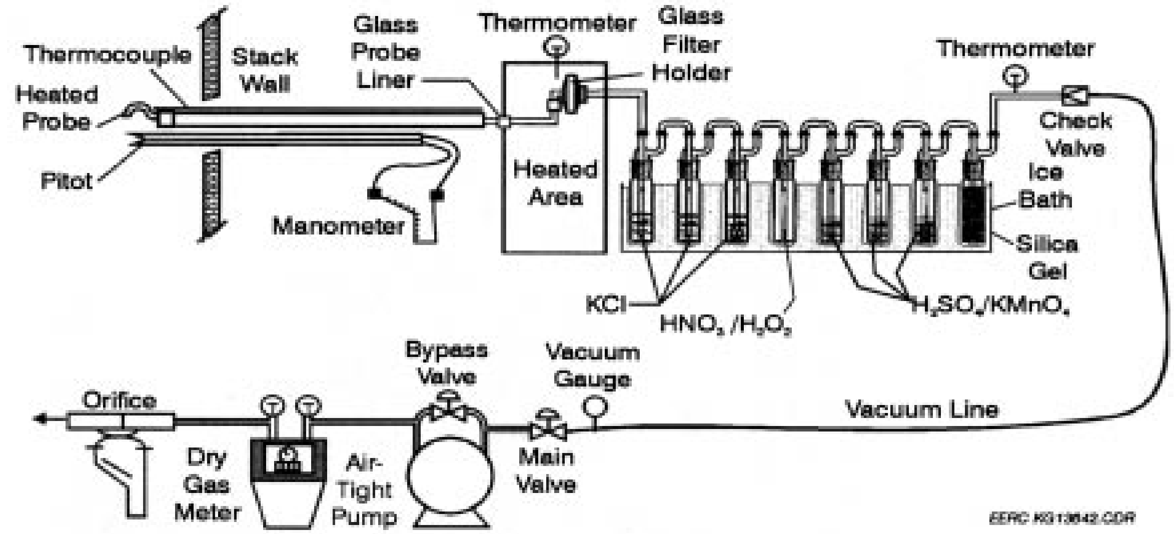

**FIG. 1 Schematic of Mercury-Sampling Train in the Method 5 Configuration**

equivalent devices. Refer to Section 2.1 of EPA Method 2 for a description.

7.1.5 *Filter Holder*, constructed of borosilicate glass or PTFE-coated stainless steel with a PTFE filter support or other nonmetallic, non-contaminating support. Do not use a glass frit or stainless steel wire screen. A silicone rubber or PTFE gasket, designed to provide a positive seal against leakage from outside or around the filter, may be used.

7.1.6 *Connecting Umbilical Tube*, heated PTFE tubing. This tube must be heated to a minimum of 120°C to help prevent water and acid condensation. (The umbilical tube is defined as any tubing longer than 0.5 m that connects the filter holder to the impinger train).

7.1.7 *Probe and Filter Heating System*:

7.1.7.1 *EPA Method 5 Configuration*—For EPA Method 5 configuration, the temperature of the flue gas, sample probe, and the exit of the sample filter must be monitored using temperature sensors capable of measuring temperature to within 3°C (5.4°F). The heating system must be capable of maintaining the sample gas temperature of the probe and exit of the sample filter to within ±15°C (±27°F) of the flue gas temperature. Regardless of the flue gas temperature, to prevent water and acid condensation, at no time must the probe temperature, sample filter exit gas temperature, or the temperature of the connecting umbilical cord be less than 120°C.

7.1.7.2 *EPA Method 17 Configuration*—For EPA Method 17 configuration, the sample filter is located in the duct and, therefore, naturally maintained at the flue gas temperature. The heating system is only required to maintain the probe and connecting umbilical cord to at least 120°C. If the flue gas temperature is less than 120°C, then EPA Method 5 configuration must be used.

7.1.8 *Condensing/Absorbing System*, consists of eight impingers immersed in an ice bath and connected in series with leak-free ground glass fittings or other non-contaminating leak-free fittings. (At no time is silicon grease or other greases to be used for this method). The first, second, fourth, fifth, sixth, and eighth impingers are of the Greenburg-Smith design modified by replacing the standard tip with a 1.3-cm (0.5-in.)-ID straight glass tube extending to about 1.3 cm (0.5 in.) from the bottom of the flask. The third and seventh impingers are also Greenburg-Smith design, but with the standard tip including the glass impinging plate. The first, second, and third impingers contain aqueous 1 N potassium chloride (KCl) solution. The fourth impinger contains an aqueous solution of $5\ \%^{V}/_{V}$ nitric acid ($HNO_3$) and $10\ \%^{V}/_{V}$ hydrogen peroxide ($H_2O_2$). The fifth, sixth, and seventh impingers contain an aqueous solution of $4\ \%^{W}/_{V}$ potassium permanganate ($KMnO_4$) and $10\ \%^{V}/_{V}$ sulfuric acid ($H_2SO_4$). The last impinger contains silica gel or an equivalent desiccant. Refer to Note 1.

NOTE 1—When flue gas streams are sampled with high moisture content (>20 %), additional steps must be taken to eliminate carryover of impinger contents from one sample type to the next. These steps must include use of oversized impinger(s) or use of an empty impinger between the KCl and $HNO_3$–$H_2O_2$. If a dry impinger is used, it must be rinsed as discussed in 13.2 of this method and the rinse added to the preceding impinger.

7.1.9 *Metering System*, vacuum gage, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), and a dry gas meter or controlled orifice capable of measuring volume to within 2 %.

7.1.10 *Barometer*, capable of measuring atmospheric pressure to within 0.33 kPa (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case, the station value (which is the absolute barometric pressure) shall be requested. An adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of negative 0.33 kPa (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

7.1.11 *Gas Density Determination Equipment*, temperature sensor and pressure gage, as described in Section 2.3 and 2.4 of EPA Method 2. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the sensor tip extends beyond the leading edge of the probe sheath and does not touch any metal. Alternative temperature sensor configurations are described in Section 2.1.10 of EPA Method 5. If necessary, a gas analyzer can be used to determine dry molecule weight of the gas (refer to EPA Method 3).

7.2 *Digestion Apparatus*:

7.2.1 *Dry Block Heater or Hot Water Bath*, a heater capable of maintaining a temperature of 95°C is required for digestion of samples, similar to that described in EPA SW 846 Method 7470A.

7.2.2 *Ice Bath*.

7.2.3 *Digestion Flasks*—Use 50- to 70-mL glass tubes or flasks with screw caps that will fit a dry block heater. For a water bath, 300-mL biological oxygen demand glass bottles for SW 846 Method 7470A are to be used. In addition, borosilicate glass test tubes, 35- to 50-mL volume, with rack are needed.

7.2.4 *Microwave or Convection Oven and PTFE Digestion Vessels*, 120 mL, or equivalent digestion vessels with caps equipped with pressure relief valves for the dissolution of ash, along with a capping station or the equivalent to seal the digestion vessel caps. Use a vented microwave or convection oven for heating. In addition, polymethylpentene (PMP) or equivalent volumetric flasks are recommended for the digested ash solutions.

7.3 *Analytical Equipment*:

7.3.1 *Mercury Analyzer*, dedicated mercury analyzer or equivalent apparatus for the analysis of mercury via CVAAS. Alternatively, CVAFS may be used. CVAAS is a method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrometer. Absorbency is measured as a function of mercury concentration. A soda-lime trap and a magnesium perchlorate trap must be used to precondition the gas before it enters the absorption cell.

7.3.2 *Pipetters*—All analysis should be performed with pipetters having accuracy $\leq$ 0.5 % and precision $\leq$ 0.5 %. A repeater pipetter is recommended to reduce the time required for sample preparation and analysis. Air displacement pipetters are not recommended.

7.3.3 *Transfer pipets*, low-density polyethylene disposable transfer pipets.

## 8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II in Specification D 1193.

8.3 *Reagents*:

8.3.1 *Boric Acid ($H_3BO_3$)*, purified reagent grade.

8.3.2 *Hydrochloric Acid (HCl)*, trace metal-grade concentrated hydrochloric acid, with a specific gravity of 1.18.

8.3.3 *Hydrofluoric Acid (HF)*, concentrated hydrofluoric acid, 48 to 50 %.

8.3.4 *Hydrogen Peroxide ($H_2O_2$)*, 30 $\%^V/_V$ hydrogen peroxide.

8.3.5 *Hydroxylamine Sulfate ($(NH_2OH)_2 \cdot H_2SO_4$)*, solid.

8.3.6 *Hydroxylamine Hydrochloride ($NH_2OH)_2 \cdot HCl$)*, 10 % solution.

8.3.7 *Sodium Chloride (NaCl)*, solid.

8.3.8 *Mercury Standard Solution*, a certified (1000 µg/mL) mercury standard.

8.3.9 *Nitric Acid ($HNO_3$)*, trace metal-grade concentrated nitric acid with a specific gravity of 1.42.

8.3.10 *Potassium Chloride (KCl)*, solid.

8.3.11 *Potassium Permanganate ($KMnO_4$)*, solid.

8.3.12 *Potassium Persulfate ($K_2S_2O_8$)*, solid.

8.3.13 *Stannous Chloride ($SnCl_2 \cdot 2H_2O$)*, solid.

8.3.14 *Sulfuric Acid ($H_2SO_4$)*, trace metal-grade concentrated sulfuric acid, with a specific gravity of 1.84.

8.3.15 *Potassium Dichromate ($K_2Cr_2O_7$)*, solid.

8.4 *Materials*:

8.4.1 *Indicating Silica Gel*, with a size of 6-16 mesh.

8.4.2 *Crushed or Cubed Ice*.

8.4.3 *Sample Filters*, quartz fiber filters, without organic binders, exhibiting at least 99.95 % efficiency (<0.05 % penetration) for 0.3-µm dioctyl phthalate smoke particles and containing less than 0.2 $\mu g/m^2$ of mercury. Test data provided by filter manufacturers and suppliers stating filter efficiency and mercury content are acceptable. However, if no such results are available, determine filter efficiency using Test Method D 2986, and analyze filter blanks for mercury prior to emission testing. Filter material must be unreactive to sulfur dioxide ($SO_2$) or sulfur trioxide ($SO_3$).[7]

8.4.4 *Filter Papers*, for filtration of digested samples. The filter paper must have a particle retention of >20 µm and filtration speed of >12 s.

8.4.5 *Nitrogen Gas ($N_2$)*, carrier gas of at least 99.998 % purity. Alternatively, argon gas may be used.

8.4.6 *Soda Lime*, indicating 4- to 8-mesh absorbent for trapping carbon dioxide.

8.4.7 *Sample Containers*, glass with PTFE-lined lids.

8.5 *Sampling Reagents*:

8.5.1 *KCl Absorbing Solution (1 mol/L)*—Dissolve 74.56 g of KCl in 500 mL of reagent water in a 1000-mL volumetric flask, swirl to mix, and dilute to volume with water. Mix well. A new batch of solution must be made prior to each field test.

8.5.2 *$HNO_3$–$H_2O_2$ Absorbing Solution (5 $\%^V/_V$ $HNO_3$,*

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[6] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

[7] Felix, L.G.; Clinard, G.I.; Lacey, G.E.; McCain, J.D. "Inertial Cascade Impactor Substrate Media for Flue Gas Sampling," U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, Publication No. EPA-600/7-77-060; June 1977, p. 83.

*10 %$^V/_V$ $H_2O_2$)*—Add slowly, with stirring, 50 mL of concentrated $HNO_3$ to a 1000-mL volumetric flask containing approximately 500 mL of water, and then add carefully, with stirring, 333 mL of 30 %$^V/_V$ $H_2O_2$. Dilute to volume with water. Mix well. A new batch of solution must be made prior to each field test.

8.5.3 *$H_2SO_4$–$KMnO_4$ Absorbing Solution (4 %$^W/_V$ $KMnO_4$, 10 %$^V/_V$ $H_2SO_4$)*—Mix carefully, with stirring, 100 mL of concentrated $H_2SO_4$ into approximately 800 mL of water. When mixing, be sure to follow standard acid to water addition procedures and safety precautions associated with strong acids. Then add water, with stirring, to make 1 L. This solution is 10 %$^V/_V$ $H_2SO_4$. Dissolve, with stirring, 40 g of $KMnO_4$ into 10 %$^V/_V$ $H_2SO_4$, and add 10 %$^V/_V$ $H_2SO_3$, with stirring, to make 1 L. To prevent autocatalytic decomposition of the permanganate solution, filter the solution through filter paper. (**Warning**—See 9.1.1). $H_2SO_4$–$KMnO_4$ absorbing Solution must be made daily.

8.5.4 *Saturated Potassium Permanganate Solution (5 %$^W/_V$)*—Mix 5 g $KMnO_4$ into water, dilute to 100 mL, and stir vigorously.

8.6 *Rinse Solutions for Sample Train*:

8.6.1 *0.1 N $HNO_3$ Solution*—A certified reagent grade 0.1 N $HNO_3$ solution can be purchased directly or can be made by slowly adding 12.5 mL of concentrated $HNO_3$ to a 2000-mL volumetric flask containing approximately 500 mL of water, then diluting with water to volume.

8.6.2 *10 %$^W/_V$ $HNO_3$ Solution*—Mix carefully, with stirring, 100 mL of concentrated $HNO_3$ into approximately 800 mL of water. When mixing, be sure to follow standard acid to water addition procedures and safety precautions associated with strong acids. Then add water, with stirring, to make 1 L.

8.6.3 *10 %$^W/_V$ Hydroxylamine Solution*—Add 100 g hydroxylamine sulfate and 100 g sodium chloride to a 1000-mL volumetric flask containing approximately 500 mL of water. After the hydroxylamine sulfate and sodium chloride has been dissolved, dilute with water to volume. As an alternative a 10 % hydroxylamine hydrochloride solution can be used in all cases as a replacement for the hydroxylamine sulfate/sodium chloride solution.

8.7 *Sample Digestion Reagents*:

8.7.1 *Boric Acid Solution (4 %$^W/_V$)*—Dissolve 4 g $H_3BO_3$ in water, and dilute to 100 mL.

8.7.2 *Aqua Regia (HCl:$HNO_3$ 3:1)*—Add 3 parts concentrated HCl to 1 part concentrated $HNO_3$. Note that this should be made up in advance and allowed to form a dark orange color. This mixture should be loosely capped, as pressure will build as gases form.

8.7.3 *Saturated Potassium Permanganate Solution (5 %$^W/_V$)*—Mix 5 g $KMnO_4$ into water, dilute to 100 mL, and stir vigorously.

8.7.4 *Potassium Persulfate Solution (5 %$^W/_V$)*—Dissolve 5 g $K_2S_2O_8$ in water, and dilute to 100 mL.

8.7.5 *Potassium Dichromate Solution (5 %$^W/_V$)*—Dissolve 5 g $K_2Cr_2O_7$ in water, and dilute to 100 mL.

8.8 *Analytical Reagents*:

8.8.1 *Hydrochloric Acid Solution (10 %$^V/_V$)*—Add 100 mL concentrated HCl to water, and dilute to 1 L. Be sure to follow all safety precautions for using strong acids.

8.8.2 *Stannous Chloride Solution (10 %$^W/_V$)*—Dissolve 100 g in 10 %$^V/_V$ HCl, and dilute with 10 %$^V/_V$ HCl to 1 L. Difficulty in dissolving the stannous chloride can be overcome by dissolving in a more concentrated HCl solution (such as 100 mL of 50 %$^V/_V$ HCl) and diluting to 1 L with water. Note that care must be taken when adding water to a strong acid solution. Add a lump of mossy tin (~0.5 g) to this solution.

8.9 *Mercury Standards*:

8.9.1 *10 µg/L Hg Stock Solution*—Dilute 1 mL of 1000 µg/L Hg standard solution to 100 mL with 10 %$^V/_V$ HCl.

8.9.2 *100 µg/L Hg Stock Solution*—Dilute 1 mL of 10 µg/L Hg stock solution to 100 mL with 10 %$^V/_V$ HCl. This solution and the Working Hg Standards described below may change concentration with time. As a minimum, stock solutions should be prepared weekly, and stored in glass or PTFE bottles.

8.9.3 *Working Hg Standards*—Prepare all working standards by digesting along with the samples. Prepare digested standards of 0.25, 0.5, 1.0, 2.5, 5.0, 7.5, and 10.0 µg/L as described in 13.4.1.1.

8.9.4 *Quality Control Standard (QC)*—A quality control standard is prepared from a separate Hg standard solution. The QC standard should be prepared at a concentration of approximately one-half the calibration range. It is recommended to prepare a QC standard at a concentration of 5.0 µg/L in the same manner as the 5.0 µg/L standard described in 8.9.3.

8.10 *Glassware Cleaning Reagents*—Prior to any fieldwork, all glassware should be cleaned in accordance with the guidelines outlined in EPA Method 29, Section 5.1.1.

## 9. Hazards

9.1 *Warning*:

9.1.1 Pressure may build up in the solution storage bottle because of a potential reaction between potassium permanganate and acid. Therefore, these bottles should not be fully filled and should be vented to relieve excess pressure and prevent explosion. Venting must be in a manner that will not allow contamination of the solution.

9.1.2 Hazards to personnel exist in the operation of the cold-vapor atomic absorption spectrophotometer. Refer to the manufacturer's instruction manual before operating the instrument.

9.1.3 Sample digestion with hot concentrated acids creates a safety problem. Observe appropriate laboratory procedures for working with concentrated acids.

9.2 *Precaution*:

9.2.1 The determination of microquantities of mercury species requires meticulous attention to detail. Good precision is generally unattainable without a high level of experience with stack-sampling procedures. Precision may be improved by knowledge of, and close adherence to, the suggestions that follow.

9.2.1.1 All glassware used in the method must be cleaned thoroughly prior to use in the field, as described in 8.10 of this method.

9.2.1.2 Use the same reagents and solutions in the same quantities for a group of determinations and the corresponding solution blank. When a new reagent is prepared or a new stock of filters is used, a new blank must taken and analyzed.

## 10. Sampling

10.1 *Preparation for Test*:

10.1.1 *Preliminary Stack Measurements*—Select the sampling site, and determine the number of sampling points, stack pressure, temperature, moisture, dry molecular weight, and range of velocity head in accordance with procedures of Test Method D 3154 or EPA Methods 1 through 4.

10.1.2 Select the correct nozzle diameter to maintain isokinetic sampling rates based on the range of velocity heads determined in 10.1.1.

10.1.3 Ensure that the proper differential pressure gage is selected for the range of velocity heads (refer to EPA Method 2, Section 2.2).

10.1.4 It is suggested that an EPA Method 17 configuration be used; however, if an EPA Method 5 setup is to be used, then select a suitable probe length such that all traverse points can be sampled. Consider sampling from opposite sides of the stack to minimize probe length when a large duct or stack is sampled.

10.1.5 *Sampling Time and Volume*—The total sampling time for this method should be at least 2 but not more than 3 h. Use a nozzle size that will guarantee an isokinetic gas sample volume between 1.0 dry cubic metres corrected to standard conditions ($Nm^3$) and 2.5 $Nm^3$. If traverse sampling is done (necessary for sampling at electric utilities), use the same points for sampling that were used for the velocity traverse as stated in 10.1.1 of this method. Each traverse point must be sampled for a minimum of 5 min.

## 11. Preparation of Apparatus

11.1 *Pretest Preparation*:

11.1.1 Weigh several 200- to 300-g portions of silica gel in airtight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container on each container. Alternatively, the silica gel can be weighed directly in the impinger immediately prior to the train being assembled.

11.1.2 Desiccate the sample filters at 20° ± 5.6°C (68° ± 10°F) and ambient pressure for 24 to 36 h, weigh at intervals of at least 6 h to a constant weight (that is, <0.5-µg change from previous weighing), and record results to the nearest 0.1 µg. Alternatively, the filters may be oven-dried at 105°C (220°F) for 2 to 3 h, desiccated for 2 h, and weighed.

11.1.3 Clean all sampling train glassware as described in 8.10 before each series of tests at a single source. Until the sampling train is assembled for sampling, cover all glassware openings where contamination can occur.

11.2 *Preparation of Sampling Train*:

11.2.1 Assemble the sampling train as shown in Fig. 1.

11.2.2 Place 100 mL of the KCl solution (see 8.5.1 of this method) in each of the first, second, and third impingers, as indicated in Fig. 1.

11.2.3 Place 100 mL of the $HNO_3$–$H_2O_2$ solution (see 8.5.2 of this method) in the fourth impinger, as indicated in Fig. 1.

11.2.4 Place 100 mL of the $H_2SO_4$–$KMnO_4$ absorbing solution (see 8.5.3 of this method) in each of the fifth, sixth, and seventh impingers, as indicated in Fig. 1.

11.2.5 Transfer approximately 200 to 300 g of silica gel from its container to the last impinger, as indicated in Fig. 1.

11.2.6 Prior to final train assembly, weigh and record the weight of each impinger. This information is required to calculate the moisture content of the sampled flue gas.

11.2.7 To ensure leak-free sampling train connections and to prevent possible sample contamination problems, use PTFE tape, PTFE-coated O-rings, or other non-contaminating material.

11.2.8 Place a weighed filter in the filter holder using tweezers or clean disposable surgical gloves.

11.2.9 Install the selected nozzle using a non-contaminating rubber-type O-ring or equivalent when stack temperatures are less than 260°C (500°F) and an alternative gasket material when temperatures are higher. Other connecting systems, such as PTFE ferrules or ground glass joints, may also be used on the probe and nozzle.

11.2.10 Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

11.2.11 Place crushed or cubed ice around the impingers.

11.2.12 *Leak-Check Procedures*—Follow the leak-check procedures given in Section 4.1.4.1 (Pretest Leak Check), Section 4.1.4.2 (Leak Checks During the Sample Run), and Section 4.1.4.3 (Post-test Leak Checks) of EPA Method 5 or 17.

NOTE 2—If the flue gas temperature at the sampling location is greater than 260°C (above the temperature where PTFE or rubber-type seals can be used), the post-test leak check is determined beginning at the front end of the probe (does not include nozzle or sample filter holder for EPA Method 17).

## 12. Calibration and Standardization

12.1 *Sampling Train Calibration*:

12.1.1 *Probe Nozzle*—Refer to Sections 2.1.1 of either EPA Method 5 or 17.

12.1.2 *Pitot Tube*—Refer to Section 4 of EPA Method 2.

12.1.3 *Metering System*—Refer to Section 5.3 of either EPA Method 5 or 17.

12.1.4 *Probe Heater*—Refer to 7.1.7.1 and 7.1.7.2 of this method.

12.1.5 *Temperature Gages*—Refer to Section 4.3 of EPA Method 2.

12.1.6 *Leak Check of the Metering System*—Refer to Section 5.6 of EPA Method 5 or Section 5.5 of EPA Method 17.

12.1.7 *Barometer*—Calibrate the barometer to be used against a mercury barometer.

## 13. Procedures

13.1 *Sampling Train Operation*:

13.1.1 Maintain an isokinetic sampling rate within 10 % of true isokinetic. For an EPA Method 5 configuration, maintain sample filter exit gas stream temperatures and probe within ±15°C of the flue gas temperature at the sampling location. Alternatively, for reasons discussed in paragraph 16.2.3, the filter and probe may be operated at 120°C. However, at no time, regardless of the sample configuration, must the sample filter, probe, or connecting umbilical cord temperature be lower than 120°C.

13.1.2 Record the data, as indicated in Fig. 2, at least once at each sample point but not less than once every 5 min.

Plant

Location

Operator

Date

Run No.

Sample Box No.

Meter Box No.

Meter ΔH @ (kPa)

C factor

Pitot tube coefficient, $C_p$

Schematic of Stack Cross Section

Ambient Temperature °C (°F)

Barometric Pressure kPa (in. Hg)

Assumed Moisture, %

Probe Length, m (ft)

Nozzle Identification No.

Average Nozzle Diameter, cm (in.)

Probe Heater Setting °C (°F)

Leak Rate, $m^3$/min (cfm)

Static Pressure, kPa (in. Hg)

Filter No.

| Traverse Point Number | Sampling Time | Vacuum | Stack Temperature ($T_s$) | Velocity Head ($\Delta P_s$) | Pressure Differential | Gas Sample Volume | Gas Sample Temperature at Dry Gas Meter | | Filter Exit Temperature | Probe Exit Temperature | Final Impinger Exit Temperature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | min | kPa (in. Hg) | °C (°F) | kPa (in. $H_2O$) | kPa (in. $H_2O$) | $m^3$ ($ft^3$) | Inlet °C (°F) | Outlet °C (°F) | °C (°F) | °C (°F) | °C (°F) |
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| Total | | | | | | | | | | | |
| Average | | | | | | | | | | | |

FIG. 2 Mercury-Sampling Field Data Report

13.1.3 Record the dry gas meter reading at the beginning of a sampling run, the beginning and end of each sampling time increment, before and after each leak check, and when sampling is halted.

13.1.4 Level and zero the manometer. Periodically check the manometer level and zero, because it may drift during the test period.

13.1.5 Clean the port holes prior to the sampling run.

13.1.6 Remove the nozzle cap. Verify that the filter and probe heating systems are up to temperature and that the pitot tube and probe are properly positioned.

NOTE 3—For an EPA Method 5 configuration, prior to starting the gas flow through the system, the sample filter exit gas temperature may not be at the hot box temperature. However, if the system is set up correctly, once flow is established, the sample filter exit gas temperature will quickly come to equilibrium.

13.1.7 Start the pump. Position the nozzle at the first traverse point with the nozzle tip pointing in the direction of flow. Seal the openings around the probe and port hole to prevent unrepresentative dilution of the gas stream. Read the pitot tube manometer, start the stopwatch, open and adjust the control valve until the isokinetic sampling rate is obtained (refer to Section 4.1.5 from either EPA Method 5 or 17 for information on isokinetic sampling rate computations), and maintain the isokinetic rate at all points throughout the sampling period.

13.1.8 When sampling at one traverse point has been completed, move the probe to the next traverse point as quickly as possible. Close the coarse adjust valve, and shut the pump off when transferring the probe from one sample port to another. Exclude the time required to transfer the probe from one port to another from the total sampling time.

13.1.9 Traverse the stack cross section, as required by EPA Method 1.

13.1.10 During sampling, periodically check and, if necessary, adjust the probe and filter exit sample gas temperatures, as well as the zero of the manometer.

13.1.11 Add more ice, if necessary, to maintain a temperature of <20°C (68°F) at the condenser/silica gel outlet.

13.1.12 Replace the filter assembly if the pressure drop across the filter becomes such that maintaining isokinetic sampling is no longer possible. Conduct a leak check (refer to EPA Method 5 or 17, Section 4.1.4.2) before installing a new filter assembly. The total particulate weight and determination of particle-bound mercury includes all filter assembly catches.

13.1.13 In the unlikely event depletion of $KMnO_4$ by means of reduction reactions with flue gas constituents other than elemental mercury occurs, it may render it impossible to sample for the desired minimum time. This problem is indicated by the complete bleaching of the purple color of the acidified permanganate solution. If the purple color is lost in the first two $H_2SO_4$–$KMnO_4$ impingers, then the sample must be repeated. If the gas stream is known to contain large amounts of reducing constituents (that is, >2500 ppm $SO_2$) or breakthrough has occurred in previous sampling runs, then the following modification is suggested: the amount of $HNO_3$–$H_2O_2$(10 %$^V/_V$) in the fourth impinger should be doubled, or a second $HNO_3$–$H_2O_2$ impinger, or both should be used to increase the oxidation capacity for reducing gas components prior to the $H_2SO_4$–$KMnO_4$ impingers.

13.1.14 Use a single train for the entire sample run, except when simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct or when equipment failure necessitates a change of trains.

13.1.15 At the end of a sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, record the final dry gas meter reading, and conduct a post-test leak check, as described in Section 4.1.4.3 of EPA Method 5. Also, leak-check the Pitot lines as described in EPA Method 2, Section 3.1. The lines must pass the leak check to validate the velocity head data.

13.1.16 Calculate percent isokinetic to determine whether the run was valid or another test run should be performed (refer to EPA Method 5 or 17).

13.2 *Sample Recovery*:

13.2.1 Allow the probe to cool before proceeding with sample recovery. When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle, and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling; a vacuum can form in the filter holder, with the undesired result of drawing liquid from the impingers onto the filter.

13.2.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train, and cap the open outlet. Be careful not to lose any condensate that may be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger, and cap the impinger. Cap the filter holder outlet and impinger inlet. Use non-contaminating caps, such as ground-glass stoppers, plastic caps, serum caps, or PTFE tape, to close these openings.

13.2.3 Alternatively, the following procedure may be used to disassemble the train before the probe and filter holder/oven are completely cooled. Initially disconnect the filter holder outlet/impinger inlet, and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet, and loosely cap the open ends. Cap the probe tip, and remove the umbilical cord as previously described.

13.2.4 Transfer the probe and filter-impinger assembly to a clean area that is protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly, and note any abnormal conditions.

13.2.5 The impinger train sample recovery scheme is illustrated in Fig. 3. All recovery operations should be completed within 4 h of the end of sampling activities.

13.2.6 *Container 1 (Sample Filter)*—Carefully remove the sample filter from the filter holder so as not to lose any ash, weigh filter and ash, and place the filter in a labeled petri dish container. To handle the filter, use either acid-washed polypropylene or PTFE-coated tweezers or clean, disposable surgical gloves rinsed with water and dried. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Transfer any particulate matter or filter fibers that adhere to the filter holder gasket to the filter in the petri dish. A dry

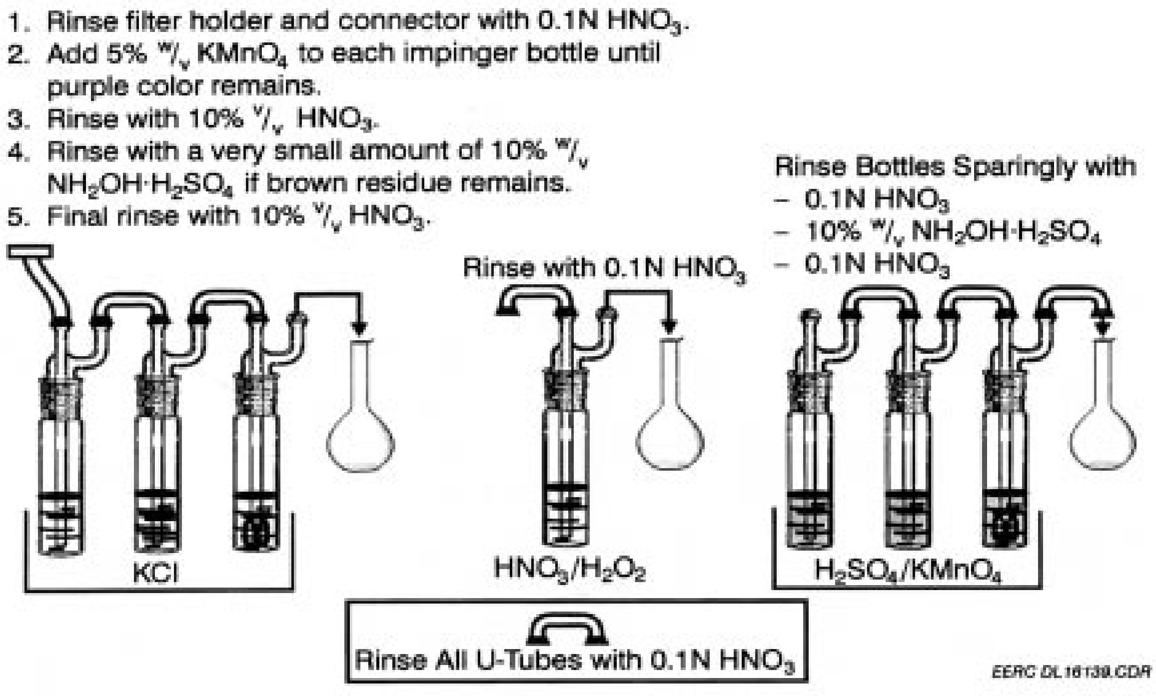

FIG. 3 Sample Recovery Scheme for the Mercury-Impinger Train

(acid-cleaned) nonmetallic bristle brush should be used to remove any remaining particulate matter. Do not use any metal-containing materials when recovering this train. Immediately cover and seal the labeled petri dish.

13.2.7 *Container 2/2a (All Rinses in Front of the Sample Filter)*:

13.2.7.1 *Case 1: Includes Gravimetric Particulate Determination in Addition to Mercury*—Quantitatively recover particulate matter and any condensate from all components prior to the sample filter. A nonmetallic brush may be used for removing particulate matter. All front-half components (all components prior to the sample filter) are then rinsed with acetone as outlined in EPA Method 5 or 17. The acetone rinse is then placed into a container (Container 2a) for which the tare weight has been recorded. Container 2a, with a ribbed watch glass over the top, is placed in a fume hood until the acetone has completely evaporated. After the front-half components have been rinsed with acetone, then rinse these components with 0.1 N $HNO_3$. The 0.1 N $HNO_3$ rinse is placed in Container 2.

13.2.7.2 *Case 2: Mercury Determination Only (No Acetone Rinse)*—Quantitatively recover particulate matter and any condensate from all components prior to the sample filter. A nonmetallic brush may be used for removing particulate matter. The front-half components are then rinsed with 0.1 N $HNO_3$, and this rinse is placed in Container 2.

13.2.8 *Container 3 (Impingers 1 through 3, KCl Impinger Contents and Rinses)*:

13.2.8.1 Dry the exterior surfaces of Impingers 1, 2, and 3. Then weigh and record the weight of each impinger (to the nearest 0.5 g).

13.2.8.2 Clean the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 0.1 N $HNO_3$. Pour the rinse into a glass sample Container 3.

13.2.8.3 Add small amounts (1 mL increments) of 5 $\%^W/_V$ $KMnO_4$ solution very slowly to each KCl impinger and gently mix the impinger solution. Continue adding $KMnO_4$ solution until a purple color is obtained. Let the impingers sit for approximately 15 min and verify that the purple color persists. The purpose of adding $KMnO_4$ is to neutralize any $SO_2$ that may be dissolved in the KCl solution. Therefore the amount of $KMnO_4$ to be added depends on the $SO_2$ concentration in the flue gas being sampled.

13.2.8.4 Pour all of the liquid from the three KCl impingers into Container 3.

13.2.8.5 Rinse the impingers and connecting glassware with 10 $\%^V/_V$ $HNO_3$. Although unlikely, if deposits remain on the impinger surfaces, remove them by doing another 10 $\%^V/_V$ $HNO_3$ rinse that has a very small amount (several drops) of 10 $\%^W/_V$ hydroxylamine solution added to the $HNO_3$ rinse solution. Rinse each of the KCl impingers with this solution until the brown stains are removed. Add these rinses to Container 3. If the solution in Container 3 becomes clear, add a small amount of the 5 $\%^W/_V$ $KMnO_4$ solution until a pink or slightly purple color is obtained. Check again after 90 min to ensure the purple color remains.

13.2.8.6 Perform a final rinse of the impingers and connecting glassware with 0.1 N $HNO_3$, and add to Container 3.

13.2.8.7 Do a final rinse of all glass components with water which is discarded.

13.2.8.8 Mark the height of the fluid level in Container 3, seal, and clearly label the contents.

13.2.9 *Container 4 (Impinger 4, $HNO_3$–$H_2O_2$ Impinger Contents and Rinses)*:

13.2.9.1 Dry the exterior surfaces of Impinger 4. Then weigh and record the weight of this impinger (to the nearest 0.5 g).

13.2.9.2 Pour the $HNO_3$–$H_2O_2$ absorbing solution into sample Container 4.

13.2.9.3 Rinse the $H_2O_2$–$HNO_3$ impinger and connecting glassware a minimum of two times with 0.1 N $HNO_3$, and pour the rinses into Container 4. Do a final rinse with water and discard water.

13.2.10 *Container 5 (Impingers 5 through 7, $H_2SO_4$–$KMnO_4$ Impinger Contents and Rinses)*:

13.2.10.1 Dry the exterior surfaces of Impingers 5, 6, and 7. Then weigh and record the weight of each impinger (to the nearest 0.5 g).

13.2.10.2 Pour all of the liquid from the three $H_2SO_4$–$KMnO_4$ impingers into a glass sample Container 5.

13.2.10.3 Rinse the $H_2SO_4$–$KMnO_4$ impingers and connecting glassware a minimum of two times with 0.1 N $HNO_3$, and pour the rinses into Container 5. A third rinse must then be done (this rinse will remove any brown stains from the surface of the impingers). This rinse consists of 0.1N $HNO_3$ and several drops of 10 $\%^W/_V$ hydroxylamine solution (either the $NH_2OH$/NaCl solution or the $NH_2OH \cdot HCl$ solution). This rinse must have enough 10 $\%^W/_V$ hydroxylamine solution such that the brown stains are easily removed. If they are not easily removed, add several more drops of 10 $\%^W/_V$ hydroxylamine solution until the stains are completely gone. Add this rinse to Container 5. If the solution in Container 5 becomes clear, add small amounts (1 mL increments) of $H_2SO_4$–$KMnO_4$ solution until a pink or slightly purple color is obtained. Finally, preserve the solution by adding 1 mL of 5 $\%^W/_V$ of dichromate solution to Container 5.

13.2.10.4 Perform a final 0.1 N $HNO_3$ rinse of the impingers and connecting glassware followed by a water rinse. The 0.1 N $HNO_3$ rinse is added to Container 5, and the water rinse is discarded.

13.2.10.5 Mark the height of the fluid level, seal the container, and clearly label the contents.

NOTE 4—As stated earlier in the warning in 9.1.1, pressure can build up in the sample storage flask because of the potential reaction of $KMnO_4$ with acid. Do not fill the container completely, and take precautions to relieve excess pressure.

13.2.11 *Container 6 (Impinger 8, Silica Gel Impinger Contents)*:

13.2.11.1 Dry the exterior surfaces of Impinger 8. Then weigh and record the weight of this impinger (to the nearest 0.5 g).

13.2.11.2 Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition. If spent, the silica gel must be either regenerated or disposed of.

13.2.12 *Solution Blanks (Containers 7-11)*—Solution blanks are taken each time new reagents are prepared. Note: The amount of solution collected for the blanks stated below is a suggested volume.

13.2.12.1 *Container 7 (0.1 N $HNO_3$ Blank)*—Place 50 mL of the 0.1 N $HNO_3$ solution used in the sample recovery process into a properly labeled container. Seal the container.

13.2.12.2 *Container 8 (1 N KCl Blank)*—Place 50 mL of the 1 N KCl solution used as the impinger solution into a properly labeled container. Seal the container.

13.2.12.3 *Container 9 (5 $\%^V/_V$ $HNO_3$–10 $\%^V/_V$ $H_2O_2$ Blank)*—Place 50 mL of the $HNO_3$-$H_2O_2$ solution used as the nitric acid impinger reagent into a properly labeled container. Seal the container.

13.2.12.4 *Container 10 ($H_2SO_4$–$KMnO_4$ Blank)*—Place 50 mL of the $H_2SO_4$–$KMnO_4$ solution used as the impinger solution in the sample recovery process into a properly labeled container. Refer to Note 4 in 13.2.10.5 of this method.

13.2.12.5 *Container 11 (10 $\%^W/_V$ Hydroxylamine Solution)*—Place 100 mL of hydroxylamine solution into a properly labeled sample container. Seal the container.

13.2.13 *Container 12 (Sample Filter Blank)*—Once during each field test, place into a properly labeled petri dish three unused blank filters from the same lot as the sampling filters. Seal the petri dish.

13.2.14 After all of the samples have been recovered, they must be analyzed within 45 days.

13.2.15 After all impingers and connectors have been properly rinsed and the solutions recovered, the glassware should be cleaned in accordance with the procedures in 8.10 or triple-rinsed with 10 $\%^V/_V$ $HNO_3$ followed by a rinsing with water. If a new source is to be sampled or if there are any brown stains on the glassware, then the glassware must be cleaned in accordance with procedures in 8.10 of this method. If multiple sites are to be sampled during a single mobilization, an exception to this procedure will be allowed. In this case, a triple rinsing of the glassware with 10 $\%^V/_V$ $HNO_3$ solution followed by a water rinse prior to sampling can be used as an alternative to the procedures in 8.10. However, if there are any brown stains on the glassware, then the glassware must be cleaned in accordance with procedures in 8.10 of this method.

13.3 *Sample Preparation*:

13.3.1 *Ash Sample (Containers 1 and 2)*:

13.3.1.1 *Case 1: Includes Gravimetric Particulate Determination in Addition to Mercury*—The gravimetric particulate loading is determined from the mass of the ash on the filter (Container 1) and the residual particulate from the acetone rinse (Container 2a), as outlined in EPA Method 5 or 17. If a large amount of ash is on the filter, carefully remove the ash to create a raw ash sample from which a representative-weighed aliquot can be taken for digestion. If the mass of ash collected on the filter is small (less than 0.5 g), digest the entire filter along with the ash. Dissolve the residual particulate from Container 2a using concentrated $HNO_3$. This solution is then added to Container 2 (0.1 N $HNO_3$ probe rinse). The ash material from Container 1 is then digested using the procedures described in 13.3.2 of this method. The same procedure is used to determine the mercury on the sample filter blank. Use a modification of EPA SW 846 7470A to digest the sample in Container 2 prior to analysis. The main modification is that the volumes of reagents and sample have been reduced tenfold to reduce waste. This reduction in reagent volume is acceptable because modern dedicated mercury analyzers do not require the large volumes that previous manual methods required.

Transfer a 10-mL aliquot of the sample to a digestion tube with a screw cap.

13.3.1.2 *Case 2: Mercury Determination Only*—The same procedures are followed as described previously in 13.3.1.1 with the exception that there is no Container 2a.

13.3.2 *Ash Digestion*—Accomplish the complete dissolution of ash by one of the following methods or an equivalent alternative method. The following methods are for the dissolution of inorganic samples, such as ash or sediments, when an analysis of trace elements including mercury is done.

13.3.2.1 *Microwave Digestion*—The use of this method assumes proper training in microwave digestion techniques. In addition, this method is tailored for a specific microwave digestion system and slight modifications may therefore be required. A 0.5-g ash sample, accurately weighed to 0.0001 g, is placed in a PTFE microwave digestion vessel with 3 mL of concentrated HF, 3 mL of concentrated $HNO_3$, and 3 mL of concentrated HCl. The vessel is sealed and placed in the microwave (along with other vessels). The vessels are slowly heated to a pressure of 347 kPa (50 psi), which is held for 5 min, followed by heating to a pressure of 550 kPa (80 psi), which is held for 20 min. The vessels are allowed to cool to room temperature before venting. 15 mL of 4 $\%^W/_V$ boric acid is added to each vessel. The vessels are sealed and placed in the microwave again. The vessels are slowly heated back to a pressure of 347 kPa (50 psi) and held for 10 min. The vessels are again allowed to cool to room temperature before venting. The contents of each vessel are quantitatively transferred to a 50-mL PMP or polypropylene (PP) volumetric flask and diluted; note that care must be taken in adding water to a strong acid solution.

13.3.2.2 *Conventional Digestion*—The use of this method assumes proper training in PTFE bomb digestion techniques. Place a 0.5-g ash sample, accurately weighed to 0.0001 g, in a PTFE digestion vessel with 7 mL of concentrated HF and 5 mL of aqua regia. Seal the vessel, and place it in an oven or water bath at 90°C for a minimum of 8 h (these may be heated overnight). Cool the vessel to room temperature before venting. Add 3.5 g of boric acid and 40 mL of water to each vessel. Seal the vessels, and place them in the oven or water bath for an additional 1 h. Cool the vessels again to room temperature before venting. Quantitatively transfer the contents of each vessel to a 100-mL PMP, PP, or glass volumetric flask and dilute. Note that care must be taken in adding water to a strong acid solution.

13.3.3 *Preparation of Aqueous KCl Impinger Solution (Containers 3 and 8)*—Confirm that the sample has retained its purple color from sample recovery procedures. Absence of a purple color may be indicative of sample degradation. This fact should be noted and reported. Clear the sample by adding 10 mL of hydroxylamine in 5 mL increments while stirring sample with a stir bar, waiting 2 min between additions. After the sample has cleared, rinse the sides of the container and lid using a transfer pipet. Transfer the cleared sample to a 500 mL volumetric flask, dilute the sample to volume with de-ionized water, and mix. If the recovered volume is greater than 500 mL then dilute the sample to 600 mL. Return the diluted sample to the jar and mix thoroughly, prior to aliquoting into digestion tubes. Use a modification of EPA SW 846 7470A to digest the sample prior to analysis. The main modification is that the volumes of reagents and sample have been reduced tenfold to reduce waste. This reduction in reagent volume is acceptable because modern dedicated mercury analyzers do not require the large volumes that previous manual methods required. Transfer a 10-mL aliquot of the sample to a digestion tube with a screw cap. Add 0.5 mL of concentrated $H_2SO_4$, 0.25 mL of concentrated $HNO_3$, and 10 mL of 5 $\%^W/_V$ $KMnO_4$ solution. Mix the solution, and allow it to stand for 15 min. Add 0.75 mL of 5 $\%^W/_V$ $K_2S_2O_8$ solution, and tightly cap the tube. Weigh the tube and record the pre-digest weight. Place the tube in a dry block heater or water bath equipped with a temperature probe, and heat to 95°C. Do not allow the temperature to exceed 95°C. Hold the sample at 95°C for 2 h before allowing it to cool to room temperature for 2 h or overnight. The purple color from the added $KMnO_4$ solution must remain throughout the digestion. Clearing of the solution during the heating indicates the depletion of $KMnO_4$. If the solution goes clear add more 5 $\%^W/_V$ $KMnO_4$ (in 1 mL increments) to the sample until a purple color persists. Weigh the tube and record the post-digest weight. If the difference between pre-digest and post-digest weights is greater than 1 % of the pre-digest weight it should be corrected, either mathematically in the dilution factor calculation, or by adding the weight back with de-ionized water. Add 10 mL of 10 $\%^W/_V$ hydroxylamine solution to the sample, in 2 mL increments, waiting 30 s between each addition. Mix the solution with a transfer pipet until clear, making sure to rinse the sides of the tube and the lid. Perform the analysis immediately after clearing the sample to avoid loss of mercury. Record the volumes of the solution additions used in the preparation procedure and adjust the *DF* factor in Eq 9 accordingly.

13.3.4 *Preparation of $HNO_3$–$H_2O_2$ Impinger Solution (Containers 4 and 9)*—This solution typically contains small amounts of mercury, so it should not be diluted. Instead, measure the volume with a volumetric cylinder and record. Treat the sample with a modified version of EPA SW 846 7470A. Modifications to the method are necessary to properly treat the $H_2O_2$-containing impinger solution before the analysis with CVAAS. The modifications include the addition of HCl, the use of an ice bath during the $KMnO_4$ addition, and the slow addition of the $KMnO_4$. Transfer a 5-mL aliquot of the sample to a digestion tube with a screw cap. Add 0.25 mL of concentrated HCl, 0.25 mL of concentrated $H_2SO_4$, place the tube in an ice bath, and allow it to cool for 15 min. The destruction of $H_2O_2$ is accomplished by slow addition of saturated $KMnO_4$ solution in 2.0-mL increments along the inside of the digestion tube. The violence of this reaction requires careful, slow addition of the $KMnO_4$ for safety reasons and to avoid loss of analyte. Cool the sample for 1 min in between additions, and mix the sample with a transfer pipet prior to each addition. Carry out the addition of $KMnO_4$ until the solution remains purple, indicating complete reaction of the $H_2O_2$. Record the volume of saturated $KMnO_4$ solution added to the sample. Add 0.75 mL of 5 $\%^W/_V$ $K_2S_2O_8$ solution to the sample, and then cap the tube tightly. Weigh the tube and record the pre-digest weight. Place the tubes in a dry block heater or water bath equipped with a temperature probe, and heat to 95°C. Do not allow the temperature to exceed 95°C. Maintain the sample at 95°C for 2 h before allowing it to cool to room temperature for 2 h or overnight. The purple color due to $KMnO_4$ must remain throughout the digestion. Clearing of the solution during the heating indicates the depletion of $KMnO_4$. If the solution clears, add more 5 $\%^W/_V$ $KMnO_4$ (in 1 mL increments) to the sample until a purple color persists. Weigh the tube and record the post-digest weight. If the difference between pre-digest and post-digest weights is greater than 1 % of the pre-digest weight it should be corrected, either mathematically in the dilution factor calculation, or by adding the weight back with de-ionized water. Add 10 mL of 10 $\%^W/_V$ hydroxylamine solution to the sample, in 2 mL increments, waiting 30 s between additions. Mix the solution with a transfer pipet until clear, making sure to rinse the sides of the tube and the lid. Perform the analysis immediately after clearing the sample to avoid loss of mercury. Record the volumes of the solution additions used in the preparation procedure and adjust the *DF* factor in Eq 13 accordingly.

13.3.5 *Preparation of $H_2SO_4$–$KMnO_4$ Impinger Solution (Containers 5 and 10)*—Confirm that the sample has retained its purple color from sample recovery procedures. Absence of a purple color may be indicative of sample degradation. This fact should be noted and reported. Clear the sample by adding 30 mL of hydroxylamine in 5 mL increments while stirring sample with a stir bar, waiting 2 min between additions. After the sample has cleared, rinse the sides of the container and lid using a transfer pipet. Transfer the cleared sample to a 500 mL volumetric flask, dilute the sample to volume with de-ionized water, and mix. If the recovered volume is greater than 500 mL then dilute the sample to 600 mL. Return the diluted sample to the jar and mix thoroughly, prior to aliquoting into digestion tubes. Add the hydroxylamine slowly because of the violence of this reaction. Transfer a 10-mL aliquot of the sample to a digestion tube with a screw cap. Add 0.75 mL of 5 $\%^W/_V$ $K_2S_2O_8$ solution, 0.5 mL of concentrated $HNO_3$, and 10.0 mL of 5 $\%^W/_V$ $KMnO_4$ solution, and tightly cap the tube. Weigh the tube and record the pre-digest weight. Mix the solution. Place the tube in a dry block heater or water bath equipped with a temperature probe, and heat to 95°C. Do not allow the temperature to exceed 95°C. Hold the sample at 95°C for 2 h before allowing it to cool to room temperature for 2 h or overnight. The purple color of the $KMnO_4$ solution must remain throughout the digestion. Clearing of the solution during the heating indicates the depletion of $KMnO_4$. If the solution clears, add more 5 $\%^W/_V$ $KMnO_4$ (in 1 mL increments) to the sample until a purple color persists. Weigh the tube and record the post-digest weight. If the difference between pre-digest and post-digest weights is greater than 1 % of the pre-digest weight it should be corrected, either mathematically in the dilution factor calculation, or by adding the weight back with de-ionized water. Add 10 mL of 10 $\%^W/_V$ hydroxylamine sulfate solution to the sample, in 2 mL increments, waiting 30 s between additions. Mix the solution with a transfer pipet until clear, making sure to rinse the sides of the tube and the lid. Perform the analysis immediately after clearing the sample to avoid loss of mercury. Record the volumes of the solution additions used in the preparation procedure and adjust the *DF* factor in Eq 12 as necessary.

13.3.6 *Simplification of the Digestion*—If an acetone rinse was not used for gravimetric particulate determination or it is very clear that there is insignificant organic material present in the sampled gas stream; then the digestion procedure for the $HNO_3$–$H_2O_2$ and $H_2SO_4$–$KMnO_4$ impinger solutions may be simplified by omitting the persulfate digest (the addition of $K_2S_2O_8$ and heating). The persulfate digest is performed for the purpose of oxidizing certain organics. Because this method is specific to coal combustion systems where organic compounds are usually insignificant[8], this digest may be omitted because the $H_2O_2$ is sufficient to oxidize most compounds. The decision to omit this procedure should be made based on the gas stream being sampled or verification that organics resistant to $H_2O_2$ oxidation are not present, or both. If unsure whether organics are present or if an acetone rinse has been used, then the total digestion procedure is required.

13.3.6.1 *Simplified Procedure for the Preparation of $HNO_3$–$H_2O_2$ Impinger Solution*—If the simplified procedure can be used for the $HNO_3$–$H_2O_2$ impinger solution, the concentrated $H_2SO_4$ and 5 $\%^W/_K$ $K_2S_2O_8$ are not added to the $HNO_3$–$H_2O_2$ aliquot sample. Also it is not necessary to heat the sample to 95°C followed by 2 h of cooling. However, it is still necessary that the concentrated HCl be added to the solution. Add 1 mL of 10 $\%^W/_V$ hydroxylamine solution to the sample, and perform the analysis as soon as possible to avoid loss of mercury. The sample should then become clear. If the simplified procedure is used, $V(K_2S_2O_8)$ and $V(H_2SO_4)$ are zero when calculating *DF* in Eq 12, Section 15.

13.3.6.2 *Simplified Procedure for the Preparation of $H_2SO_4$–$KMnO_4$ Impinger Solution*—If the simplified procedure can be used for the $H_2SO_4$–$KMnO_4$ impinger solution, the concentrated $HNO_3$ and 5 $\%^W/_V$ $K_2S_2O_8$ are not added to the $H_2SO_4$–$KMnO_4$ aliquot sample. Also it is not necessary to heat the sample to 95°C followed by 2 h of cooling. Add 1mL of 10 $\%^W/_V$ hydroxylamine solution to the sample, and perform the analysis as soon as possible to avoid loss of mercury. The sample should then become clear. If the simplified procedure is used, $V(K_2S_2O_8)$ and $V(HNO_3)$ are zero when calculating *DF* in Eq 13, Section 15.

13.3.7 *Reagent Blanks (Containers 8 through 10)*—These samples are not diluted prior to taking an aliquot. Once an aliquot is taken, the preparation steps for each of the solutions (as well as the mercury concentration calculations) are the same as described above. These are: 13.3.3 for the aqueous KCl reagent blank, 13.3.4 for the $HNO_3$–$H_2O_2$ reagent blank, and 13.3.6.2 for the $H_2SO_4$–$KMnO_4$ reagent blank.

13.3.8 *0.1 N $HNO_3$ and 10 $\%^W/_V$ Hydroxylamine Rinse Solutions (Containers 7 and 11)*—These solutions can be analyzed directly for mercury without any preparation steps.

13.4 *Sample Analysis*—Analyze all of the prepared solutions by CVAAS or CVAFS following the guidelines specified

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[8] "A Comprehensive Assessment of Toxic Emissions from Coal-Fired Power Plants: Phase I Results from the U.S. Department of Energy Study," Prepared for the U.S. Department of Energy Federal Energy Technology Center, Contract No. DE-FC21-93MC30097, Energy & Environmental Research Center, University of North Dakota, Grand Forks, ND, 1996.

by the instrument manufacturer.

13.4.1 *Atomic Absorption or Atomic Fluorescence Spectrometer Calibration*—Perform instrument setup and optimization in accordance with the manufacturer's specifications. Cold-vapor generation of mercury is performed via addition of stannous chloride solution to reduce oxidized mercury to its elemental state. The mercury-laden solution is then purged with a carrier gas into the atomic absorption cell. This procedure is used to calibrate the instrument using 3 $\%^V/_V$ HCl as the blank along with the standards described in 8.9.3. Calibration is verified by analyzing the QC standard prepared in accordance with 8.9.4 of this method.

13.4.1.1 *Preparation of Working Hg Calibration Standards*—Prepare all working standards by digesting along with the samples. Prepare digested standards of 0.25, 0.5, 1.0, 2.5, 5.0, 7.5, and 10.0 µg/L by aliquoting 100, 200, 400, 1000, 2000, 3000 and 4000 mL of the 100 µg/L Hg Stock Solution into separate digestion tubes. Bring the volume of each tube to 8.75 mL with de-ionized water. In addition, a 0.0 µg/L is prepared by adding 8.75 mL of de-ionized water to a separate tube. To each tube add 0.75 mL of 5 $\%^W/_V$ $K_2S_2O_8$ solution, 0.5 mL of concentrated $HNO_3$, and 20.0 mL of 5 $\%^W/_V$ $KMnO_4$ solution and tightly cap the tube. Weigh the tube and record the pre-digest weight. Mix the solution. Place the tube in a dry block heater or water bath equipped with a temperature probe, and heat to 95°C. Do not allow the temperature to exceed 95°C. Hold the sample at 95°C for 2 h before allowing it to cool to room temperature for 2 h or overnight. The purple color from the addition of the $KMnO_4$ solution must remain throughout the digestion. Weigh the tube and record the post-digest weight. If the difference between the pre-digest and post-digest weights is greater than 1 % of the pre-digest weight, it should be corrected by adding the weight back with de-ionized water. Add 10 mL of 10 $\%^W/_V$ hydroxylamine solution to the sample in 2 mL increments, waiting 30 s between additions. Mix the solution with a transfer pipet until clear, making sure to rinse the sides of the tube and the lid. Perform the analysis immediately after clearing the sample to avoid loss of mercury.

13.4.1.2 *Instrument Calibration*—Analyze the standards by CVAA or CVAFS following the guidelines specified by the instrument manufacturer. Construct a calibration curve by plotting the absorbances of the standards versus µg/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.

13.4.1.3 *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.

NOTE 5—If samples are shown to be less than 1.0 µg/L Hg, it is recommended that sample concentrations are recalculated using a calibration curve generated using the 0.0, 0.25, 0.5 and 1.0 µg/L standards. Most CVAA and CVAF analyzers have software that will allow you to do this without having to reanalyze the standards or samples. This is critical for achieving accurate, repeatable results in the range below 1.0 µg/L. The reason for this is that, at least for some CVAA instruments, the slope between 0.0 and 1.0 µg/L is different than the slope between 1.0 and 10.0 µg/L.

13.4.2 *Analysis Quality Assurance/Quality Control*:

13.4.2.1 *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.

13.4.2.2 *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 re-analyzed.

13.4.2.3 *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.

13.4.2.4 *Independent QA/QC Checks*—For the ash samples, a certified reference ash sample (may be purchased from NIST) is to be digested and analyzed at least once during the test program. It is also 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 (for example, re-calibration) must be taken and the samples re-analyzed.

13.4.3 *QA/QC*—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, mercury measured in either the solution or field blanks.

13.4.3.1 *Solution Blanks*—As stated in 13.2.12 of this method, solution blanks will be taken and analyzed every time a new batch of solution is prepared. If mercury 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 which ever is lower. If the solution blanks are greater than 10 % the data must be flagged as suspect.

13.4.3.2 *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 mercury detected in the field blanks cannot be subtracted from the results. Whether or not the mercury 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.

## 14. Flue Gas Calculations

14.1 *Dry Gas Volume*—Calculate the dry gas sample volume, $V_{m(std)}$, at standard conditions using Eq 1.

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m}\right)\left[\frac{P_{bar} + \Delta H}{P_{std}}\right] = K_l V_m Y \frac{P_{bar} + \Delta H}{T_m} \quad (1)$$

where:

$P_{bar}$ = barometric pressure at the sampling site, kPa (in. Hg),

$P_{std}$ = standard absolute pressure, 101.3 kPa (29.92 in. Hg),

$T_m$ = absolute average dry gas meter temperature (refer to Fig. 2), K (°R),

$T_{std}$ = standard absolute temperature, 293 K (528°R),

$V_m$ = volume of gas sample as measured by dry gas meter, $m^3$ (dscf),

$V_{m(std)}$ = volume of gas sample measured by the dry gas meter, corrected to standard conditions, $Nm^3$ (dscf),

$Y$ = dry gas meter calibration factor,

$\Delta H$ = average pressure differential across the orifice meter (refer to Fig. 2), kPa (in. Hg), and

$K_1$ = 2.894 K/kPa (17.64°R/in. Hg).

NOTE 6—Eq 1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (that is, leak checks conducted prior to component changes or following the test) exceeds the maximum acceptable leakage rate, $L_a$, equal to 0.00057 $m^3$/min (0.02 cfm) or 4 % of the average sampling rate, whichever is less. If the leakage rate observed during the post-test leak check, $L_p$, or an individual leakage rate observed during the leak check conducted prior to the "ith" component change (I = 1, 2, 3, . . .n), $L_i$, exceeds $L_a$, then Eq 1 must be modified as follows:

*Case I*—No component changes made during sampling run. In this case, replace $V_m$ with the expression:

$$[V_m - (L_p - L_a)\theta]$$

where:

$L_p$ = leakage rate observed during the post-test leak check, $m^3$/min (cfm),

$L_a$ = maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change—equal to 0.00057 $m^3$/min (0.02 cfm) or 4 % of the average sampling rate, whichever is less, and

$\theta$ = total sampling time, min.

*Case II*—One or more component changes made during the sampling run. In this case, replace $V_m$ with the expression:

$$\left[V_m - (L_l - L_a)\theta_1 - \sum_{i=1}^{n}(L_i - L_a)\theta_i - (L_p - L_a)\theta_p\right]$$

where:

$\theta_i$ = sampling time interval, from the beginning of a run until the first component change, min.

and substitute only for those leakage rates ($L_i$ or $L_p$) that exceed $L_a$.

14.2 *Volume of Water Vapor*—Calculate the volume of water vapor of the stack gas using Eq 2.

$$V_{w(std)} = \frac{W_{lc} R T_{std}}{M_w P_{std}} = K_2 W_{lc} \quad (2)$$

where:

$M_w$ = molecular weight of water, 18.0 g/g-mole (18.0 lb/Lb-mole),

$R$ = ideal gas constant, 0.008314 kPa-$m^3$/K-g-mole (21.85 in. Hg-$ft^3$/°R-lb-mole),

$W_{lc}$ = total weight of liquid collected in impingers and silica gel (refer to Fig. 2), g,

$V_{w(std)}$ = volume of water vapor in the gas sample, corrected to standard conditions, $m^3$(scf), and

$K_2$ = 0.001336 $m^3$/mL (0.04707 $ft^3$/mL).

14.3 *Volume of Moisture*—Calculate the moisture content, $B_{ws}$, of the stack gas using Eq 3.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \quad (3)$$

where:

$B_{ws}$ = water vapor in the gas stream, proportion by volume.

## 15. Calculations for Particle-Bound, Oxidized, Elemental, and Total Mercury Concentrations

15.1 *Particle-Bound Mercury*:

15.1.1 *Case 1: Amount of Ash on the Filter is Greater Than 0.5 g*—Calculate the concentration of mercury in µg/g in the ash sample ($Hg_{ash}$) using Eq 4:

$$Hg_{ash}, \mu g/g = (IR)(DF) \quad (4)$$

where:

$IR$ = instrument reading, µg/L, and

$DF$ = dilution factor = (total digested volume, L)/(mass of ash digested, g)

$$Hg_{pr}, \mu g = (IR)(V_1) \quad (5)$$

where:

$IR$ = instrument reading, µg/L, and

$V_1$ = total volume of probe rinse sample from which sample aliquot was taken, L.

Eq 5 assumes no preparation steps are needed prior to analyzing the probe rinse for mercury using CVAA. Although not required, a persulfate digest can be done on the probe rinse sample as discussed in 13.3.3. If the persulfate digest can be done, Eq 5 becomes $Hg_{pr}$, µg = $(IR)(V_1)DF$ where $DF$ is the same as Eq 9. There is no filter blank subtraction when >0.5 g of ash are collected on the sample filter or thimble. The amount of particle-bound mercury ($Hg_{fb}$) is then determined using Eq 6:

$$Hg\ (\text{particle}), \mu g = (Hg_{ash})(W_{ash}) + Hg_{pr} \quad (6)$$

where:

$W_{ash}$ = total mass of ash on filter, g.

The concentration of particle-bound mercury (µg/$Nm^3$) in the gas stream is then determined using Eq 7:

$$Hg^{tp},\ \mu g/Nm^3 = Hg\ (\text{particle})/V_{m(std)} \quad (7)$$

where:

$V_{m(std)}$ = total volume of dry gas sampled at standard (normal) conditions, $Nm^3$.

15.1.2 *Case 2: Amount of Ash on the Filter is Less Than 0.5 g*—The calculation is the same as in Case 1 except the entire sample (ash and filter) is digested; therefore, *DF* in Eq 4 is defined only by the total digested volume. In addition, a filter blank is subtracted as calculated in Eq 8.

$$Hg_{tp},\ \mu g = (IR)(V_2) \quad (8)$$

where:

$IR$ = instrument reading, µg/L, and

$V_2$ = total volume of sample filter blank digest, L.

Eq 7 for Case 2 then becomes: Hg (particle), µg = $(Hg_{ash})(W_{ash}) - Hg_{fb} + Hg_{pr}$.

15.2 *Oxidized Mercury*:

15.2.1 *KCl Solution (Impingers 1-3)*—Calculate the concentration of mercury in µg/L in the KCl impinger solutions using Eq 9:

$$Hg_{KCl},\ \mu g/L = (IR)(DF) \quad (9)$$

where:

$IR$ = instrument reading, µg/L,

$DF$ = dilution factor,

$$\frac{V_D + V(H_2SO_4) + V(HNO_3) +}{V_D}$$

$$\frac{V(KMnO_4) + V(K_2S_2O_8) + V(NH_2OH)}{V_D},$$

$V_D$ = total digested volume, 10 mL,

$V(H_2SO_4)$ = volume of added concentrated $H_2SO_4$, 0.5 mL,

$V(HNO_3)$ = volume of added concentrated $HNO_3$, 0.5 mL,

$V(KMnO_4)$ = volume of added 5 $\%^W/_V$ $KMnO_4$, 1.5 mL,

$V(K_2S_2O_8)$ = volume of added 5 $\%^W/_V$ $K_2S_2O_8$, 0.75 mL, and

$V(NH_2OH)$ = volume of added 10 $\%^W/_V$ hydroxylamine sulfate, 1.0 mL.

The amount of mercury in the KCl solution blank is calculated in the same way.

15.2.2 *Total Oxidized Mercury ($Hg_O$)* is defined by method as the mercury measured in the KCl sample minus the mercury measured in the KCl solution blanks, as shown in Eq 10:

$$Hg_O,\ \mu g = (Hg_{KCl})(V_3) - (Hg_{Ob})(V_4) \quad (10)$$

where:

$Hg_{KCl}$ = mercury concentration measured in KCl aliquot, µg/L,

$V_3$ = total volume of aqueous KCl from which sample aliquot was taken, L,

$Hg_{Ob}$ = mercury concentration measured in KCl solution blank aliquot, µg/L, and

$V_4$ = volume of aqueous KCl originally charged to the impingers, L.

The concentration of $Hg^{2+}$(µg/$Nm^3$) in the gas stream is then determined using Eq 11:

$$Hg^{2+},\ \mu g/Nm^3 = Hg_O/V_{m(std)} \quad (11)$$

where:

$V_{m(std)}$ = total volume of dry gas sampled at standard conditions, $m^3$.

15.3 *Elemental Mercury*:

15.3.1 *$HNO_3$–$H_2O_2$ Solution (Impinger 4)*—Calculate the concentration of mercury in µg/L in the $HNO_3$–$H_2O_2$ impinger solution using Eq 12:

$$Hg_{H_2O_2},\ \mu g/L = (IR)(DF) \quad (12)$$

where:

$IR$ = instrument reading, µg/L,

$DF$ = dilution factor =

$$\frac{V_D + V(HCl) + V(H_2SO_4) +}{V_D}$$

$$\frac{V(KMnO_4) + V(K_2S_2O_8) + V(NH_2OH)}{V_D},$$

$V_D$ = total digested volume, 5 mL,

$V(HCl)$ = volume of added concentrated HCl, 0.25 mL,

$V(KMnO_4)$ = volume of added saturated $KMnO_4$, mL (volume need to turn sample to a purple color),

$V(K_2S_2O_8)$ = volume of added 5 $\%^W/_V$ $K_2S_2O_8$, 0.75 mL (if used), and

$V(NH_2OH)$ = volume of added 10 $\%^W/_V$ hydroxylamine sulfate, 1.0 mL.

The concentration of mercury in the $HNO_3$–$H_2O_2$ solution blank is calculated in the same way.

15.3.2 *$H_2SO_4$–$KMnO_4$ Solution (Impingers 5-7)*—Calculate the concentration of mercury in µg/L in the $H_2SO_4$–$KMnO_4$ impinger solutions using Eq 13:

$$\text{Mercury},\ \mu g/L = (IR)(DF) \quad (13)$$

where:

$DF$ = dilution factor =

$$\frac{V_D + V(HNO_3) + V(K_2S_2O_8) + V(NH_2OH)}{V_D},$$

$IR$ = instrument reading, µg/L,

$V_D$ = total digested volume, 5 mL,

$V(HNO_3)$ = volume of added concentrated $HNO_3$, 0.5 mL, and

$V(K_2S_2O_8)$ = volume of added 5 $\%^W/_V$ $K_2S_2O_8$, 0.75 mL.

The concentration of mercury in the $H_2SO_4$–$KMnO_4$ solution blank is calculated in the same way.

15.3.3 *Total Elemental Mercury ($Hg_E$)* is defined by the method as the mercury measured in the $H_2SO_4$–$KMnO_4$ impingers plus the mercury in the $HNO_3$–$H_2O_2$ impingers minus the solution blanks as shown in Eq 14:

$$Hg_E,\ \mu g = (Hg_{H_2O_2})(V_4) - (Hg_{Eb_1})(V_5) + (Hg_{KMnO_4})(V_6) - (H_{Eb_2})(V_7) \quad (14)$$

where:

$Hg_{H_2O_2}$ = mercury concentration measured in $HNO_3$–$H_2O_2$ aliquot, µg/L,

$V_4$ = total volume of aqueous $HNO_3$–$H_2O_2$ from which sample aliquot was taken, L,

$V_5$ = total volume of aqueous $HNO_3$–$H_2O_2$ originally charged to the impinger, L,

$Hg_{Eb_1}$ = mercury concentration measured in $HNO_3$–$H_2O_2$ solution blank aliquot, µg/L,
$Hg_{KMnO_4}$ = mercury concentration measured in $H_2SO_4$–$KMnO_4$ aliquot, µg/L,
$V_6$ = total volume of aqueous $H_2SO_4$–$KMnO_4$ from which sample aliquot was taken, L,
$V_7$ = total volume of aqueous $H_2SO_4$–$KMnO_4$ originally charged to the impingers, L, and
$Hg_{Eb_2}$ = mercury concentration measured in $H_2SO_4$–$KMnO_4$ solution blank aliquot, µg/L.

The concentration of $Hg^{2+}$(µg/Nm$^3$) in the gas stream is then determined using Eq 15:

$$Hg^0,\ \mu g/Nm^3 = Hg_E/V_{m(std)} \tag{15}$$

where:
$V_{m(std)}$ = total volume of dry gas sampled at standard conditions, Nm$^3$.

15.4 *Total Mercury* is defined by the method as the sum of the particulate bound mercury, oxidized mercury, and elemental mercury as shown in Eq 16:

$$Hg(total),\ \mu g/Nm^3 = Hg^{tp} + Hg^{2+} + Hg^0 \tag{16}$$

## 16. Precision and Bias

16.1 *Precision*:

16.1.1 Formal evaluation of the Ontario Hydro method was completed with dynamic spiking of $Hg^0$ and $HgCl_2$ into a flue gas stream.[9] The results are shown in Table 1. The relative standard deviation for gaseous elemental mercury and oxidized mercury was found to be less than 11 % for mercury concentrations greater than 3 µg/Nm$^3$ and less than 34 % for mercury concentrations less than 3 µg/Nm$^3$. In all cases, the laboratory bias for these tests based on a calculated correction factor was not statistically significant. These values were within the acceptable range, based on the criteria established in EPA Method 301 (% RSD less than 50 %).

16.1.2 *Caution*—The precision of particle-bound, oxidized, and elemental mercury sampling method data is influenced by many factors: flue gas concentration, source, procedural, and equipment variables. Strict adherence to the method is necessary to reduce the effect of these variables. Failure to assure a leak-free system, failure to accurately calibrate all indicated system components, failure to select a proper sampling location, failure to thoroughly clean all glassware, and failure to follow prescribed sample recovery, preparation, and analysis procedures can seriously affect the precision of the results. Nevertheless, if suitable care is taken, a precision of 10 to 15 % is achievable.

16.2 *Bias*:

16.2.1 *Total Mercury Measurement*—Other than sample stability and preservation concerns, there are no known biases affecting the total mercury measurement.

16.2.2 *Mercury Speciation*:

16.2.2.1 Particle-bound mercury existing in the flue gas may vaporize after collection in the front half of the sampling train because of continued exposure to the flue gas sample stream and reduced pressures during the sampling period. Such vaporization would result in a negative particle-bound mercury bias.

16.2.2.2 Certain types of fly ash can catalyze oxidation of elemental mercury, causing a positive bias of the oxidized mercury and a negative bias of elemental mercury. Increases in filter temperature increase catalytic effects.

16.2.2.3 It is also possible that some fly ashes may adsorb mercury at the filter resulting in a low bias for the gaseous mercury. Adsorption typically increases at lower filter temperatures.

16.2.2.4 However, these behaviors are only expected where particle concentrations are high, and are therefore unlikely to be relevant at stack outlets following particulate control devices such as electrostatic precipitators or baghouses. Note that none of these conditions affect the total mercury measurement.

## 17. Keywords

17.1 air toxics; mercury; sampling; speciation

**TABLE 1 Results from Formal EPA Method 301 Evaluation Tests for the Ontario Hydro Method**[A]

| | Total Vapor-Phase Mercury | | | Oxidized Mercury | | | Elemental Mercury | | |
|---|---|---|---|---|---|---|---|---|---|
| Ontario Hydro Method[B] | Mean, µg/Nm$^3$ | Std. Dev. | RSD, % | Mean, µg/Nm$^3$ | Std. Dev. | RSD, % | Mean, µg/Nm$^3$ | Std. Dev. | RSD, % |
| Baseline | 23.35 | 2.05 | 8.79 | 21.24 | 2.13 | 10.02 | 2.11 | 0.65 | 30.69 |
| $Hg^0$ Spike (15.0 µg/Nm$^3$) | 38.89 | 2.00 | 5.13 | 23.32 | 2.08 | 8.94 | 15.57 | 1.09 | 6.97 |
| $HgCl_2$ Spike (19.9 µg/Nm$^3$) | 42.88 | 2.67 | 6.23 | 40.22 | 2.87 | 7.14 | 2.66 | 0.89 | 33.31 |

[A] For each mean result, there were 12 replicate samples (four quadtrains).
[B] The correction factor in all cases was not statically significant and is not shown.

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[9] EPRI, U.S. DOE NETL. "Evaluation of Flue Gas Mercury Speciation Methods," EPRI TR-108988, Electric Power Research Institute, Palo Alto, CA, Dec. 1997.

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