



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 approval. 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/Nm³.

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:²

D 1193 Specification for Reagent Water

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres

D 2986 Practice for Evaluation of Air-Assay Media by the Monodisperse DOP (Diocetyl Phthalate) Smoke Test

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

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

E 1 Specification for ASTM Thermometers

2.2 Other Standards:³

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

¹ This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ 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).

3. Terminology

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

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

ΔH = average pressure differential across the orifice meter, kPa (in. H_2O)

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

Hg^{pb} = concentration of particle-bound mercury, $\mu g/Nm^3$

Hg^0 = concentration of elemental mercury, $\mu g/Nm^3$

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

IR = instrument reading from mercury analyzer, $\mu g/L$

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 $0^\circ C$ and 101.3 kPa, (In the U.S. standard conditions $32^\circ F$ 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- $ft^3/^\circ R$ -lb-mole)

T_m = absolute average dry gas meter temperature, K ($^\circ R$)

T_s = absolute stack temperature, K ($^\circ R$)

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

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

θ = total sampling time, min

θ_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 $120^\circ C$ 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,

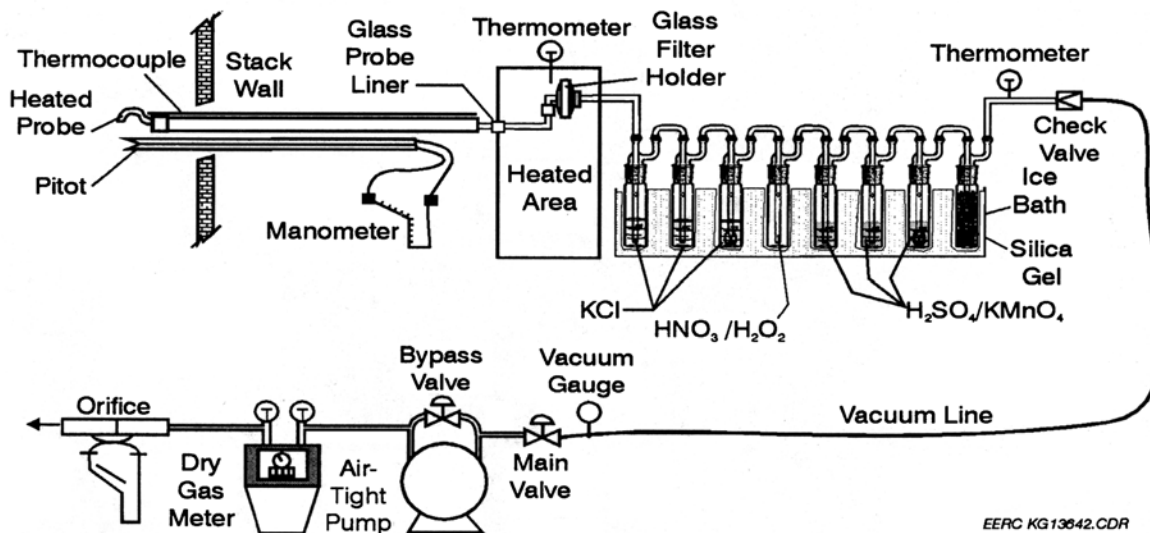


FIG. 1 Schematic of Mercury-Sampling Train in the Method 5 Configuration

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 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 (HNO₃) and 10 %^{v/v} hydrogen peroxide (H₂O₂). The fifth, sixth, and seventh impingers contain an aqueous solution of 4 %^{w/v} potassium permanganate (KMnO₄) and 10 %^{v/v} sulfuric acid (H₂SO₄). 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 HNO₃-H₂O₂. 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 *Pipettors*—All analysis should be performed with pipettors 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 pipettors 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.⁴ 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 $\mu g/mL$) 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).⁵

8.4.4 *Filter Papers*, for filtration of digested samples. The filter paper must have a particle retention of $>20\ \mu m$ 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.

⁴ "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."

⁵ 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.

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 *HNO₃–H₂O₂ Absorbing Solution (5 %^{V/V} HNO₃, 10 %^{V/V} H₂O₂)*—Add slowly, with stirring, 50 mL of concentrated HNO₃ to a 1000-mL volumetric flask containing approximately 500 mL of water, and then add carefully, with stirring, 333 mL of 30 %^{V/V} H₂O₂. Dilute to volume with water. Mix well. A new batch of solution must be made prior to each field test.

8.5.3 *H₂SO₄–KMnO₄ Absorbing Solution (4 %^{W/V} KMnO₄, 10 %^{V/V} H₂SO₄)*—Mix carefully, with stirring, 100 mL of concentrated H₂SO₄ 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} H₂SO₄. Dissolve, with stirring, 40 g of KMnO₄ into 10 %^{V/V} H₂SO₄, and add 10 %^{V/V} H₂SO₃, 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). H₂SO₄–KMnO₄ absorbing Solution must be made daily.

8.5.4 *Saturated Potassium Permanganate Solution (5 %^{W/V})*—Mix 5 g KMnO₄ into water, dilute to 100 mL, and stir vigorously.

8.6 *Rinse Solutions for Sample Train*:

8.6.1 *0.1 N HNO₃ Solution*—A certified reagent grade 0.1 N HNO₃ solution can be purchased directly or can be made by slowly adding 12.5 mL of concentrated HNO₃ to a 2000-mL volumetric flask containing approximately 500 mL of water, then diluting with water to volume.

8.6.2 *10 %^{W/V} HNO₃ Solution*—Mix carefully, with stirring, 100 mL of concentrated HNO₃ 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 H₃BO₃ in water, and dilute to 100 mL.

8.7.2 *Aqua Regia (HCl:HNO₃ 3:1)*—Add 3 parts concentrated HCl to 1 part concentrated HNO₃. 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 KMnO₄ into water, dilute to 100 mL, and stir vigorously.

8.7.4 *Potassium Persulfate Solution (5 %^{W/V})*—Dissolve 5 g K₂S₂O₈ in water, and dilute to 100 mL.

8.7.5 *Potassium Dichromate Solution (5 %^{W/V})*—Dissolve 5 g K₂Cr₂O₇ 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 be 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 $20^\circ \pm 5.6^\circ\text{C}$ ($68^\circ \pm 10^\circ\text{F}$) and ambient pressure for 24 to 36 h, weigh at intervals of at least 6 h to a constant weight (that is, $<0.5\text{-}\mu\text{g}$ 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 $\text{HNO}_3\text{-H}_2\text{O}_2$ 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 $\text{H}_2\text{SO}_4\text{-KMnO}_4$ 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 $\pm 15^\circ\text{C}$ of the flue gas temperature at the sampling location.