



Designation: ~~D6784 – 16~~ D6784 – 24

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 D6784; 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 test method applies to the determination of elemental, oxidized, particle-bound, and total mercury emissions from coal-fired-stationary combustion sources.

1.2 This test method is applicable to elemental, oxidized, particle-bound, and total mercury concentrations ranging from approximately ~~0-50.5~~ 0.5 $\mu\text{g}/\text{Nm}^3$ to ~~100-100~~ 100 $\mu\text{g}/\text{Nm}^3$.

1.3 This test 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 test method is applicable ~~to~~ 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 requires users to be familiar with EPA stack-gas sampling procedures as stated in EPA Methods 1–4, Method 5, and Method 17.

1.8 The method requires a high level of experience and quality control both in the field testing and analytical procedures ~~in order~~ to obtain high quality data.

1.9 *Warning—Mercury has been designated by many regulatory agencies as a hazardous substance that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Use caution when handling mercury and mercury-containing products. See the applicable product Safety Data Sheet (SDS) for additional information. The potential exists that selling mercury or mercury-containing products, or both, is prohibited by local or national law. Users must determine legality of sales in their location.*

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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1.10 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.

1.11 This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:²

D1193 Specification for Reagent Water
 D1356 Terminology Relating to Sampling and Analysis of Atmospheres
 D3154 Test Method for Average Velocity in a Duct (Pitot Tube Method)
 D3685/D3685M Test Methods for Sampling and Determination of Particulate Matter in Stack Gases
 D3796 Practice for Calibration of Type S Pitot Tubes
 D4840 Guide for Sample Chain-of-Custody Procedures
 D7036 Practice for Competence of Air Emission Testing Bodies
 E2251 Specification for Liquid-in-Glass ASTM Thermometers with Low-Hazard Precision Liquids

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

3. Terminology

3.1 Definitions other than those given below in 3.2 and 3.3 are listed in Terminology D1356.¹

3.2 Definitions of Terms Specific to This Standard:

3.2.1 ~~elemental mercury~~—mercury, n—mercury in its ~~zero oxidation~~—zero-oxidation state, Hg⁰.

3.2.2 ~~elemental mercury catch~~—catch, n—mercury collected in the acidified hydrogen peroxide (HNO₃–H₂O₂) and potassium permanganate (H₂SO₄–KMnO₄) impinger solutions employed in this test ~~method. This method; this is gaseous Hg⁰.~~

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

3.2.4 ~~impinger train~~—train, n—setup including only the impingers and connectors.

3.2.5 ~~method detection limit~~—the minimum concentration of an analyte, when processed through the complete method, produces a signal with a 99 % probability that is different from the blank, based on a standard deviation of greater than seven replicate measurements (see Terminology D1356).

3.2.5 ~~oxidized mercury~~—mercury, n—mercury in its mercurous or mercuric oxidation states: Hg₂²⁺ and Hg²⁺, respectively.

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 EPA Methods 1 – 29 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), Method 101A in 40 CFR Part 61, Appendix B, Method 301 in 40 CFR 63 Appendix A 40 CFR Part 61, Appendix B.

3.2.6 *oxidized mercury catch—catch, n*—mercury collected in the aqueous potassium chloride (KCl) impinger ~~solutions~~ employed in this test ~~method~~. ~~This method~~; this is gaseous Hg^{2+} .

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

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

3.2.9 *total mercury—mercury, n*—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, $\mu\text{g}/\text{g}$

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

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

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

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

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 $\text{g}/\text{g-mole}$ ($\text{lb}/\text{Lb-mole}$)

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

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 $\text{kPa}\cdot\text{m}^3/\text{K}\cdot\text{g-mole}$ (21.85 in. $\text{Hg}\cdot\text{ft}^3/^\circ\text{R}\cdot\text{lb-mole}$)

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

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

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

θ = total sampling time, min

θ_1 = sampling time interval, from the beginning of a run until the first component change, min

3.3 Symbols:

3.3.1 A —cross-sectional area of stack, m^2 (ft^2)

3.3.2 B_{ws} —water vapor in the gas stream, proportion by volume

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

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

3.3.5 Hg^{ip} —concentration of particle-bound mercury, $\mu\text{g}/\text{Nm}^3$

3.3.6 Hg^0 —concentration of elemental mercury, $\mu\text{g}/\text{Nm}^3$

- 3.3.7 Hg^{2+} —concentration of oxidized mercury, $\mu\text{g}/\text{Nm}^3$
- 3.3.8 IR —instrument reading from mercury analyzer, $\mu\text{g}/\text{L}$
- 3.3.9 L_p —leakage rate observed during the post-test leak check, m^3/min (cfm)
- 3.3.10 L_a —maximum acceptable leakage rate
- 3.3.11 M_s —molecular weight of stack gas, wet basis $\text{g}/\text{g-mole}$ (lb/lb-mole)
- 3.3.12 M_w —molecular weight of water, 18.0 $\text{g}/\text{g-mole}$ (18.0 lb/lb-mole)
- 3.3.13 N —normal conditions, defined as 0 °C and 101.3 kPa (in the U.S. standard conditions 32 °F and 1 atmosphere)
- 3.3.14 P_{bar} —barometric pressure at the sampling site, kPa (in. Hg)
- 3.3.15 P_s —absolute stack gas pressure, kPa (in. Hg)
- 3.3.16 P_{std} —standard absolute pressure, 101.3 kPa (29.92 in. Hg)
- 3.3.17 R —ideal gas constant, 0.008314 $\text{kPa}\cdot\text{m}^3/\text{K}\cdot\text{g-mole}$ (21.85 in. Hg-ft³/°R-lb-mole)
- 3.3.18 T_m —absolute average dry gas meter temperature, K (°R)
- 3.3.19 T_s —absolute stack temperature, K (°R)
- 3.3.20 T_{std} —standard absolute temperature, 293 K
- 3.3.21 V_D —total digested volume, mL
- 3.3.22 V_m —volume of gas sample as measured by dry gas meter, m^3 (dscf)
- 3.3.23 $V_{m(std)}$ —volume of gas sample measured by the dry gas meter in Nm^3 (dscf)
- 3.3.24 $V_{w(std)}$ —volume of water vapor in the gas sample in m^3 (scf)
- 3.3.25 W_{ash} —total mass of ash on sample filter, g
- 3.3.26 W_{lc} —total weight of liquid collected in impingers and silica gel, g (lb)
- 3.3.27 Y —dry gas meter calibration factor
- 3.3.28 θ —total sampling time, min
- 3.3.29 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 $\pm 20^\circ\text{C}$ 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

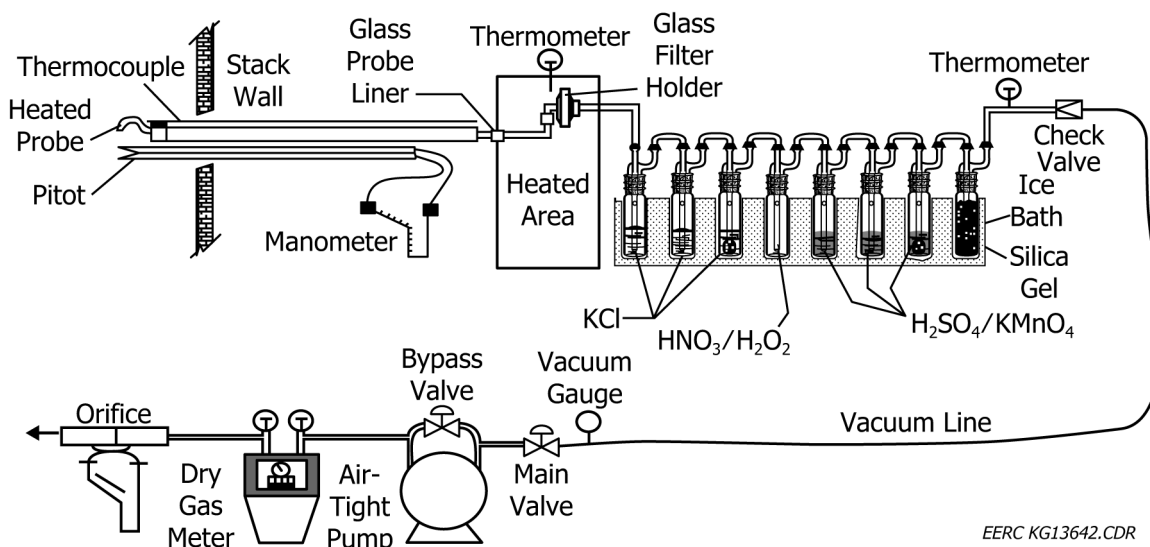


FIG. 1 Schematic of Mercury-Sampling Train in the Method 5 Configuration

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-spectrometry (CVAFS). To achieve the accuracy and precision specified in this test method, it is necessary that quality control and quality assurance procedures associated with each step of the method be scrupulously performed. Successful performance of the method by air emission testing bodies is best achieved by following the Practice D7036.

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 emissions assessments and reporting, the certification of continuous mercury monitoring systems, regulatory compliance determinations and research programs associated with dispersion modeling, modelling, deposition evaluation, human health and environmental impact assessments. 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.

5.2 This test method was developed initially for the measurement of mercury in coal-fired power plants and has been extensively validated for that application. Since the introduction of this method, it has been extensively used on other combustion sources such as cement kilns and waste incinerators. With additional procedures given in this standard, it is also applicable to sources having a flue gas composition with high levels of hydrochloric acid, and low levels of sulfur dioxide (Section 16).

6. Interferences

6.1 Chlorine and particulate matter will interfere in speciating flue gas samples for oxidized and elemental mercury concentrations. These biases are addressed further in Section 16 of this test method.

7. Apparatus

7.1 *Sampling Train*—Similar to Test Methods D3685/D3685M, EPA Method 5/EPA Method 17 and EPA Method 29 trains, as illustrated in Fig. 1 and Fig. 2.

NOTE 1—It is recommended that an in-stack filter method (Method 1, Figure 2) be used if possible. The requirement of the method, that the filter be maintained at the temperature of the flue gas, is ensured in this configuration. In addition, the in-stack filter method has the added advantage that, only a small portion of the probe/nozzle collects ash that needs to be brushed onto the filter. Method 5 procedures must be used when the temperature of the flue gas is below the water dew point (wet stack stack). In this case an out-of-stack filter must be used and maintained at a temperature of $\pm 20^{\circ}\text{C}$, 120°C .

NOTE 2—If sampling is conducted in a wet stack where water droplets are present, and the nozzle is positioned into the flow, water droplets will be collected, and mercury contained in the droplets will be measured. When water droplets are present, the isokinetic sampling rate and percent isokinetic must be calculated accordingly.

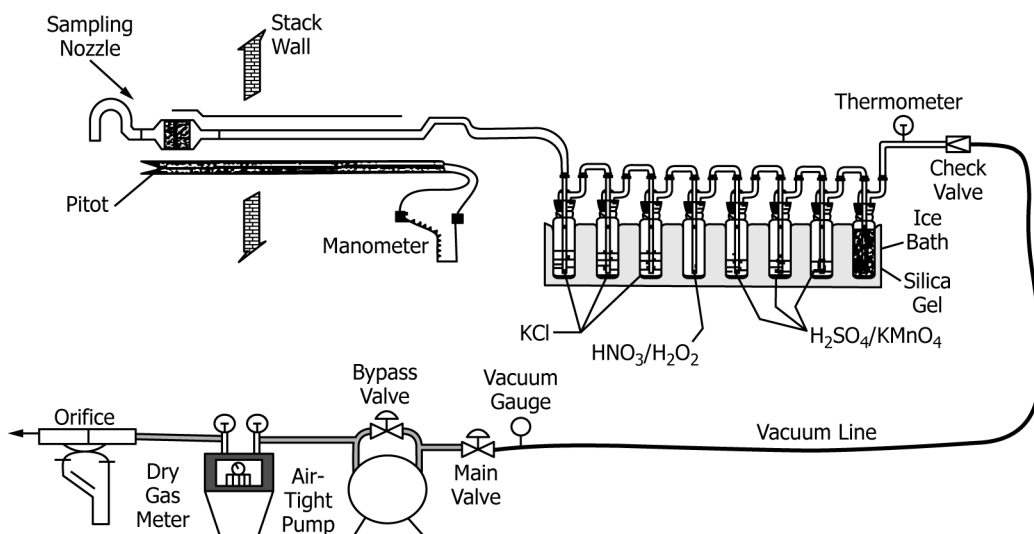


FIG. 2 Schematic of Mercury-Sampling Train in the Method 17 Configuration

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, fluorinated ethylene propylene (FEP), etc., are required instead of metal fittings to prevent contamination; surface losses of mercury and contamination. Coated metal fittings that overcome adsorption losses of mercury may be used.

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, for example, 260 °C for 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/Gauges*, 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-stainless-steel with a PTFE filter support or other nonmetallic, non-metallic, non-contaminating support. Do not use a glass frit or stainless-steel-stainless-steel wire screen. A silicone rubber-rubber, viton, 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 $\pm 20^{\circ}\text{C}$: 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): 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 $\pm 15^{\circ}\text{C}$ ($\pm 27^{\circ}\text{F}$): $\pm 15^{\circ}\text{C}$ ($\pm 27^{\circ}\text{F}$) of the flue gas temperature. Regardless of the flue gas temperature, to prevent water and acid condensation, the probe temperature, sample filter exit gas temperature, or the temperature of the connecting umbilical cord shall at no time be less than $\pm 20^{\circ}\text{C}$: 120°C .

7.1.7.2 *EPA Method 17 Configuration*—For EPA Method 17 configuration, the sample filter is located in the duct and, 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 $\pm 20^{\circ}\text{C}$: 120°C . If the flue gas temperature is less than $\pm 20^{\circ}\text{C}$: 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 ~~silicone~~ silicone grease or other greases to be used for this test 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~~ 1.3 cm (0.5 in.)-ID straight glass tube extending to about ~~1.3-cm~~ 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 (7.46 %^{w/v}) 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 4**.

NOTE 3—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 test method and the rinse added to the preceding impinger.

7.1.9 *Metering System*, vacuum ~~gage,gauge~~, leak-free pump, thermometers capable of measuring temperature to within ~~3°C (5.4°F)~~ 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 *Thermometers*, Precision digital thermometers based on resistance temperature detectors (RTDs), thermistors, thermocouples, or organic liquid-in-glass thermometers (such as Thermometer S18C in Practice **E2251**) meeting the requirements of specific applications in this test method may be used.

7.1.12 *Gas Density Determination Equipment*, temperature sensor and pressure ~~gage,gauge~~, 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 ~~moleculer~~ molecular 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~~ 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~~ 50 mL to 70 mL glass tubes or flasks with screw caps that will fit a dry block heater. For a water bath, ~~300-mL~~ 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~~ 35 mL 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. CVAFS is a technique based on the absorption and re-emission of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and ~~aerated~~ sparged from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption ~~spectrometer~~. Absorbency or fluorescence spectrometer. Absorbance or fluorescence 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. Alternatively, a hygroscopic membrane to precondition the gas can be used.

7.3.2 *Pipetters*—All analysis should be performed with pipetters having accuracy ~~to be~~ within $\pm 0.5\%$ of the true value, 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.

7.3.4 *Balance*, analytical grade, capable of weighing ~~the filter and sample beakers to within 0.1 g.~~ to within 0.1 μg .

7.4 *Ancillary equipment*, depending upon the application, other flue gas parameters may need to be obtained to convert the mercury measurements into appropriate units. This equipment may include sampling equipment and O_2 or CO_2 analyzers.

7.5 *Spare Parts*—Enough sampling equipment must be brought to the site so that common spare parts are available. Arrangements should be made so that, if necessary, parts can also be shipped ~~next day~~ next day to the site.

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 **D1193**.

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, 4848 % to 50 %.

8.3.4 *Hydrogen Peroxide* (H_2O_2), 30 % v/v hydrogen peroxide.

8.3.5 *Hydroxylamine Sulfate* ($(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$), solid.

8.3.6 *Hydroxylamine Hydrochloride* ($(\text{NH}_2\text{OH})_2 \cdot \text{HCl}$), 10 % solution.

8.3.7 *Sodium Chloride* (NaCl), solid.

8.3.8 *Mercury Standard Solution*, a certified (1000 $\mu\text{g/mL}$) mercury standard.

8.3.9 *Nitric Acid* (HNO_3), trace metal-grade concentrated nitric acid with a specific gravity of 1.42. 20 % v/v nitric acid.

8.3.10 *Potassium Chloride* (KCl), solid.

8.3.11 *Potassium Dichromate* ($\text{K}_2\text{Cr}_2\text{O}_7$), solid.

8.3.12 *Potassium Perchlorate* (KClO_4), solid.

⁴ “*Reagent Chemicals, American Chemical Society Specifications*,” *Am. ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see “*Reagent Chemicals and Standards*,” by *Analar Standards for Laboratory Chemicals*, Joseph Rosin, D. Van Nostrand Co., Inc., BDH Ltd., Poole, Dorset, U.K., and the *New York, NY, and the United States Pharmacopeia and National Formulary*, States Pharmacopeia—U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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

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

8.3.15 *Soda Lime* ($Ca(OH)_2$, $NaOH$, KOH), solid.

8.3.16 *Sodium Thiosulfate* ($Na_2S_2O_3 \cdot 5H_2O$) (for high chloride applications).

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

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

8.3.19 *Tin* (Sn) Mossy.

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- μ m~~ 0.3 μ m dioctyl phthalate smoke particles and containing less than 0.2 μ g/m² of mercury. Test data provided by filter manufacturers and suppliers stating filter efficiency and mercury content are acceptable. 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 μ 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~~ 4 mesh to 8 mesh absorbent for trapping carbon dioxide.

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

NOTE 4—It is recommended that glass amber bottles be used to prevent possible deterioration by ultraviolet (UV) light.

8.5 *Sampling Reagents:*

8.5.1 *KCl Absorbing Solution 1 N (1 mol/L)*—Dissolve 74.56 g of KCl in 500 mL of reagent water in a ~~1000-mL~~ 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.

NOTE 5—For applications with ~~High Chloride Applications: KCl Absorbing Solution spiked with Sodium Thiosulfate (1 mol/L)~~ high chlorine concentrations: KCl absorbing solution spiked with sodium thiosulfate (1 mol/L) KCl, 0.5 %w/v $Na_2S_2O_3 \cdot 5H_2O$ – 5 g $Na_2S_2O_3 \cdot 5H_2O$ is dissolved in ~~1 litre~~ 1 L of 1 N KCl solution. This solution is used to charge each impinger (100 ~~mL~~ mL per impinger). This solution should be made daily.

8.5.2 *HNO_3 - H_2O_2 Absorbing Solution (5 %v/v HNO_3 , 10 %v/v H_2O_2)*—Add slowly, with stirring, 50 mL of concentrated HNO_3 to a ~~1000-mL~~ 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,

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.

with stirring, 40 g of KMnO_4 into 10 % v/v H_2SO_4 , and add 10 % v/v H_2SO_{34} , 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 Rinse 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~~2000 mL volumetric flask containing approximately 500 mL of water, then diluting with water to volume.

8.6.2 *10 % v/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~~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,~~water and dilute to 100 mL.

8.7.2 *Aqua Regia ($\text{HCl}:\text{HNO}_3$ 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 $\text{K}_2\text{S}_2\text{O}_8$ in ~~water,~~water and dilute to 100 mL.

8.7.5 *Potassium Dichromate Solution (5 % w/v)*—Dissolve 5 g $\text{K}_2\text{Cr}_2\text{O}_7$ 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,~~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~~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~~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 $\mu\text{g}/\text{mL}$ Hg Stock Solution*—Dilute 1 mL of ~~1000~~1000 $\mu\text{g}/\text{mL}$ Hg standard solution to 100 mL with 10 % v/v HCl .

8.9.2 *100 $\mu\text{g}/\text{L}$ Hg Stock Solution*—Dilute 1 mL of ~~10~~10 $\mu\text{g}/\text{mL}$ 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, 0.25 µg~~ ~~0.5 µg~~, ~~1.0 µg~~, ~~2.5 µg~~, ~~5.0 µg~~, ~~7.5 µg~~, and ~~10.0 µg~~ 0.25 µg/L, 0.5 µg/L, 1.0 µg/L, 2.5 µg/L, 5.0 µg/L, 7.5 µg/L, 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 must be cleaned in accordance with the guidelines outlined in EPA Method 29, Section 8.1.1 if the stated precision of this test method is to be met. This procedure requires that the sampling train glassware first be rinsed with hot tap water and then washed in hot soapy water. Then, rinse the glassware three times with tap water, followed by three additional rinses with distilled water. Soak all glassware in a ~~20%~~ 10% v/v nitric acid solution for a minimum of 4 ~~hours~~. Rinse three times with distilled ~~water~~, water and rinse a final time with acetone. Allow the glassware to air dry and cover all glassware openings where contamination can occur until the sampling train is assembled for sampling.

NOTE 6—There are two ways to ensure clean glassware. The first is to bring enough glassware into the field to construct all needed sampling trains. The second, is to clean the glassware in the field. This requires a large enough space to soak the glassware. In addition, depending on the scope of the sampling program, an extra person may be required on site.

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 is safe and 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. Hydrofluoric acid used in the sample digestion procedures is highly corrosive and is very toxic by inhalation or contact with the skin. Avoid exposure by contact with the skin or eyes, or by inhalation of HF vapor. It is essential to use suitable personal protective equipment, including impermeable gloves and eye protection when working with HF. Use a fume hood when working with concentrated HF and when carry out open-vessel dissolution with HF.

9.1.4 Mercury standards at high concentrations (1000 µg/mL) are toxic and can cause skin irritation, serious eye damage and may damage fertility of an unborn child. ~~irritation and serious eye damage.~~ Suitable safety equipment (gloves, goggles, etc.) should be used when working with standards and samples containing mercury, or where exposure to mercury vapors is a concern.

9.1.5 Acetone is hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, and of inhalation. Acetone is highly flammable in the presence of open flames or sparks.

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 and accuracy 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,~~ field use, as described in 8.10 of this test 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.