



Designation: D6784 – 16

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 sources.

1.2 This test method is applicable to elemental, oxidized, particle-bound, and total mercury concentrations ranging from approximately 0.5 to 100 µg/Nm³.

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 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 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 *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 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 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

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 A40 CFR Part 61, Appendix B.

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.

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 ($\text{HNO}_3\text{--H}_2\text{O}_2$) and potassium permanganate ($\text{H}_2\text{SO}_4\text{--KMnO}_4$) impinger solutions employed in this test 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 *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).

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

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

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

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

3.2.10 *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, $\mu\text{g/g}$

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, $\mu\text{g/L}$

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, $0.008314 \text{ kPa}\cdot\text{m}^3/\text{K}\cdot\text{g-mole}$ ($21.85 \text{ in. Hg}\cdot\text{ft}^3/^\circ\text{R}\cdot\text{lb-mole}$)

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

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). To achieve the 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

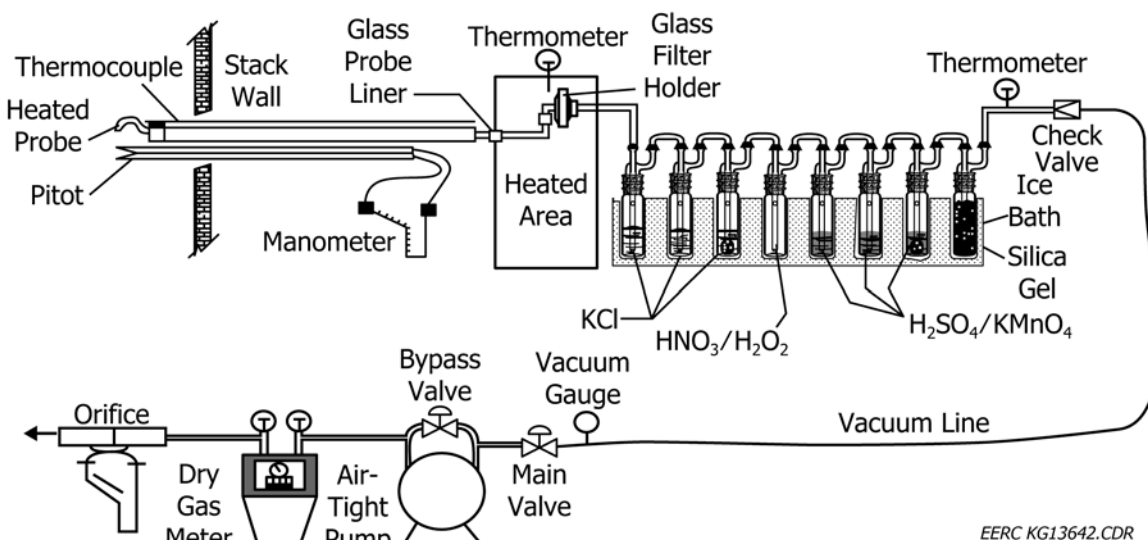


FIG. 1 Schematic of Mercury-Sampling Train in the Method 5 Configuration

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, 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 for the measurement of mercury in coal-fired power plants and has been extensively validated for that application. 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.

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 instack 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) In this case an out-of-stack filter must be used and maintained at a temperature of 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.

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 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

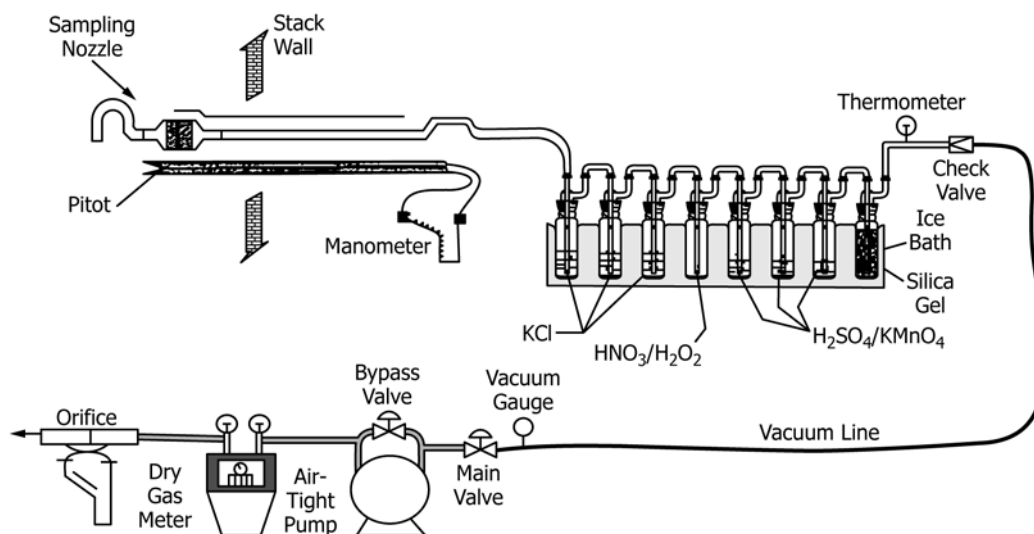


FIG. 2 Schematic of Mercury-Sampling Train in the Method 17 Configuration

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 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 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 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 %v/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, 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 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, 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.