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/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 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.*

1.10 *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

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[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] 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 (HNO_3–H_2O_2) and potassium permanganate (H_2SO_4–$KMnO_4$) 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, 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

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

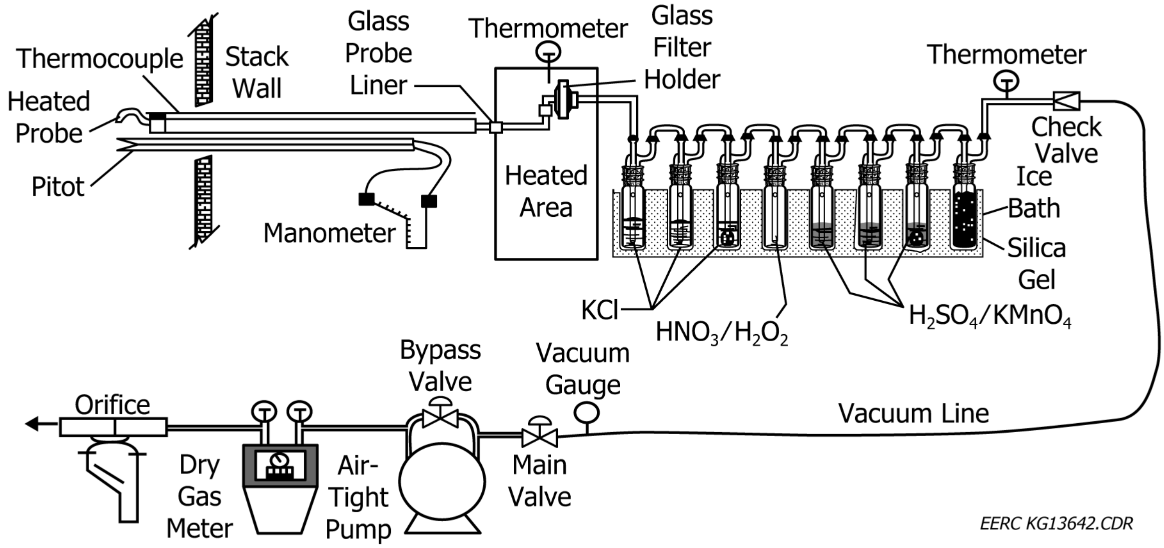

FIG. 1 Schematic of Mercury-Sampling Train in the Method 5 Configuration

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

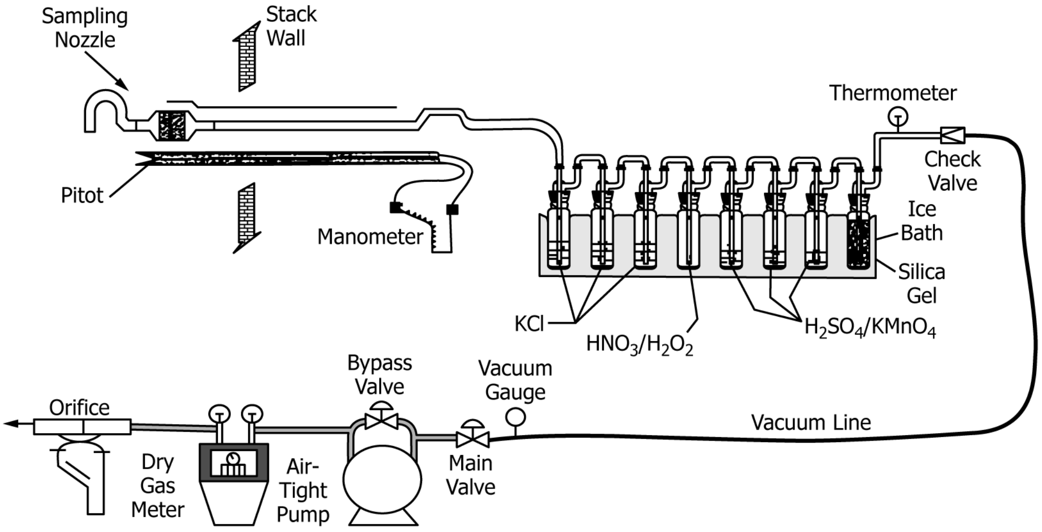

FIG. 2 Schematic of Mercury-Sampling Train in the Method 17 Configuration

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 (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 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 HNO_3–H_2O_2. 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.

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 to be within ±0.5 % of the true value, and precision ≤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.

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 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, 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. 20 %$^{V}/_{V}$ nitric acid.

8.3.10 *Potassium Chloride (KCl),* solid.

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

8.3.12 *Potassium Perchlorate ($KClO_4$),* solid.

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-µm dioctyl phthalate smoke particles and containing less than 0.2 µg/m^2 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 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 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 mol/L)*—Dissolve 74.56 g of KCl in 500 mL of reagent water in a 1000-mL volumetric

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[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.

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 (1mol/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 of 1 N KCl solution. This solution is used to charge each impinger (100 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 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 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 rises with distilled water. Soak all glassware in a 20 $\%^{V}/_{v}$ nitric acid solution for a minimum of 4 hours. Rinse three times with distilled 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 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) can cause skin irritation, serious eye damage and may damage fertility of an unborn child. 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 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 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 taken and analyzed.

10. Sampling

10.1 *Preparation for Test:*

10.1.1 *Quality Assurance Plan*—Develop a quality assurance plan (QAP) prior to conducting the tests. The basic elements of the QAP are sections that describe: (*1*) Purpose of the project, (*2*) Test methodologies, (*3*) Project organization, (*4*) Description of test logistics and schedule, (*5*) Quality objectives, (*6*) Quality control procedures, and (*7*) Documentation procedures. Each section comprises the following:

10.1.1.1 *Purpose of the Project*—Discusses why the test is being conducted and whether total or speciated mercury is to be determined.

10.1.1.2 *Project Organization*—Provides the personnel structure and identify team members and qualifications of the team leader with respect to Practice D7036. Identifies the analytical laboratory that will analyze the samples. Identifies the Quality Assurance Directors of both the test team and laboratory and their respective responsibilities in the test program.

10.1.1.3 *Test Logistics*—Details the test schedule , sampling locations, equipment to be used, role of sampling and plant personnel during sampling. Addresses communication mechanisms within the team and with the plant. A site visit prior to the testing is recommended.

10.1.1.4 *Quality Objective*—States the quality objectives for equipment calibration, test parameters, and precision and bias of the results.

10.1.1.5 *Quality Control Procedures*—Describes quality control procedures used for (*1*) equipment calibration, (*2*) glassware cleaning and handling, (*3*) Chain-of-custody describing sample management from the point of collection to analysis and final data reduction (see Guide D4840), (*4*) isokinetic sampling, (*5*) field spikes, (*6*) sample blanks, and (*7*) laboratory analysis (including spikes, blanks, replicates, and calibration procedures).

10.1.1.6 *Documentation Procedures*—Includes the format of the test report, data sheet custody and integrity, and backup for electronic files.

10.1.2 *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 D3154 or EPA Methods 1 through 4.

NOTE 7—Prior to testing, remove mercury containing devices from both staging areas and testing areas (that is, mercury manometers, broken fluorescent lamps, mercury thermometers).

10.1.3 Select the correct nozzle diameter to maintain isokinetic sampling rates based on the range of velocity heads determined in 10.1.2, and to provide adequate sample volume, without depleting the $KMnO_4$.

NOTE 8—Too high of a flow rate will cause the $KMnO_4$ to be depleted as it reacts with SO_2 in the final set of impingers; as the $KMnO_4$ is depleted, it will turn brown then clear and will lose its ability to retain mercury.

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

10.1.5 If the flue gas is stratified with respect to particulate concentrations, gas concentrations, or both, the stack crosssection is traversed, as specified by EPA Method 1. If the flue gas is not stratified, ample at a fixed, representative location where the flue gas is well-mixed. It is recommended 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 when the stack cross-section is traversed, 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.

NOTE 9—Traversing may not be necessary, depending on the objectives of the test. In coal-fired power plants, gas-phase mercury has been found to constitute on the order of 95% of the total mercury. Errors introduced by not traversing may be either positive or negative depending upon the pattern and degree of stratification. Considering low-levels of particulate adsorbed mercury, bias introduced by sampling at a single point may be negligible. For low dust applications where the flue gas is well-mixed and a sampling location representative of the stack flow can be found, single point sampling may be adequate for obtaining representative samples.

NOTE 10—Traversing the stack may affect the performance and precision of the method if not done carefully. When traversing, the apparatus should be moved in a manner to avoid leaks or breakage of the glassware.

10.1.6 *Sampling Time and Volume*—The total sampling time for this test 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 (when required), use the same points for sampling that were used for the velocity traverse as stated in 10.1.2 of this test 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 test method) in each of the first, second, and third impingers, as indicated in Fig. 1.

NOTE 11—*For Applications with High Chloride Concentrations:* Place 100 ml of the sodium thiosulfate-spiked KCl solution (see section 8.5.1) 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 test 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 test 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. When 50 kPa vacuum is applied, the leak rate must <0.01 cfm.

NOTE 12—If O-ring seal glassware is used, the leak rate should be essentially zero (<0.01 cfm).

NOTE 13—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).

11.3 *Preparation of the Field Blank*—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. See 13.4.3.2. Conduct at least one field blank for each day of testing.

11.4 *Preparation of Field Spike*—A field spike is similar to the field blank, with the addition of a predetermined amount of mercury added to each of the three impinger solution. Perform the field spike by assembling a sample train, transporting it to the sampling location during the sampling period, adding the spiked solutions and recovering it as a regular sample. These solutions are then labeled and sent to the analytical lab as if they were actual samples. See 13.4.3.3. Conduct at least one field spike for each day of testing.

12. Calibration and Standardization

12.1 *Sampling Train Calibration*—Calibrate all sampling equipment, prior to the test, according to the requirements of EPA Methods referenced below and procedures detailed in the U.S. EPA Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III Stationary Sources.

12.1.1 *Probe Nozzle*—Refer to Sections 6.1.1 of EPA Method 5.

12.1.2 *Pitot Tube*—Refer to Section 10 of EPA Method 2 or calibrate as in accordance with Practice D3796. Do not use Cp default value of EPA Method 2.

12.1.3 *Metering System*—Refer to Section 16.1.11 of either EPA Method for Dry Gas Meter calibration procedures. Prior to testing, perform a single-point calibration using a wet test meter or a critical orifice. The Dry Gas Meter Calibration Factor determined, must be with ±2 % of the original value of Y to be valid.

12.1.4 *Probe Heater*—Refer to 7.1.7.1 and 7.1.7.2 of this test method and Section 10.4 of EPA Method 5.

12.1.5 *Temperature Gages*—Refer to Section 6.3 of EPA Method 2.

12.1.6 *Leak Check of the Metering System*—Refer to Section 8.4 of EPA Method 5 or Section 8.1.4 of EPA Method 17.

12.1.7 *Barometer*—Refer to Section 10.6 of EPA Method 5.

13. Procedures

13.1 *Sampling Train Operation:*

NOTE 14—A checklist for the procedures given in this section may be found in Appendix A of EPRI Report No. 1014081.

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, regardless of the sample configuration, the sample filter, probe, or connecting umbilical cord temperature must not at any time be lower than 120°C.

13.1.2 Record the data, as indicated in Fig. 3, at least once at each sample point but not less than once every 5 min.

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 15—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 If the flue gas is stratified with respect to particulate concentrations, gas concentrations, or both traverse the stack cross section, as specified by EPA Method 1. If the flue gas is not stratified, sample at a fixed, representative location where the flue gas is well-mixed.

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 Monitor the color of the $KMnO_4$ impingers. 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*—Prepare chain-of-custody forms and sample labels prior to the test. On data sheets, provide a detailed record of custody during sampling (including all labeling information), with the initials of individuals who recover impinger contents, filters, and rinses.

NOTE 16—A checklist for the procedures given in this section may be found in Appendix A of EPRI Report No. 1014081.

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 (AP_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)
Total											
Average											

FIG. 3 Mercury-Sampling Field Data Report

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;