Section 3.19

METHOD 101A—DETERMINATION OF PARTICULATE AND GASEOUS MERCURY EMISSIONS FROM STATIONARY SOURCES

OUTLINE

SUMMARY

Method 101A, for determining particulate and gaseous mercury (Hg) emissions from stationary sources, is similar to Method 101. In 101A, however, acidic potassium permanganate ($KMnO_4$) solution is used for sample collection instead of acidic iodine monochloride. This method applies to determining particulate and gaseous mercury (Hg) emissions from sewage sludge incinerators and other sources as specified in the regulations. Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in an acidic $KMnO_4$ solution. The collected Hg (in mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry (AAS).

After initial dilution, the range of this method is 20 to 800 ng Hg/mL. The upper limit can be extended by further dilution of the sample. The sensitivity of the method depends on the recorder/ spectrophotometer combination selected. The collection efficiency of the sampling method can be affected by excessive oxidizable matter in the stack-gas that prematurely depletes the $KMnO_4$ solution.

The method descriptions given are based on the method[1,2,3] promulgated October 15, 1980, and on corrections and additions published on September 12, 1984, and September 23, 1988 (Section 3.19.10).

METHOD HIGHLIGHTS

Section 3.19 describes the procedures and specifications for determining particulate and gaseous mercury emissions from sewage sludge incinerators and other stationary sources as specified in the regulations. New procedures were added to Method 101A[3] on the basis of EPA-conducted development and evaluation of mercury sampling and analysis. The major changes for Method 101A are:

1. The impinger $KMnO_4$ absorbing solution and the 8 N hydrochloric acid (HCl) rinse are no longer combined in the field during sample recovery.
2. The impinger $KMnO_4$ absorbing solution must be filtered.
3. The filtrate must be analyzed within 24 h of filtration.
4. The residue on the filter from the filtration step must be digested with 8 N HCl.
5. The HCl digestate and the final field sample recovery rinse of HCl are combined and analyzed separately from the $KMnO_4$ filtrate.

1. Procurement of Apparatus and Supplies

Section 3.19.1 (Procurement of Apparatus and Supplies) gives specifications, criteria, and design features for the equipment and materials required for Method 101A. This section can be used as a guide for procuring and initially checking equipment and supplies. The activity matrix (Table 1.1) at the end of the section is a summary of the details given in the text and can be used as a quick reference.

2. Pretest Preparations

Section 3.19.2 (Calibration of Apparatus) describes the required calibration procedures and considerations for the Method 101A sampling equipment. Required accuracies for each component also are included. A pretest checklist (Figure 3.1 in Subsection 3.19.3) or a similar form should be used to summarize the calibration and other pertinent pretest data. The calibration section may be removed along with the corresponding sections for the other methods and made into a separate quality assurance reference manual for personnel involved in calibration activities.

Section 3.19.3 (Presampling Operations) provides testers with a guide for preparing equipment and supplies for field tests. A pretest preparation form can be used as an equipment checkout and packing list. Because of the potential for high blank levels, special attention must be paid to preparing the sampling equipment. Also, testers must ensure that any required audit samples are obtained for the test by the responsible regulatory agency.

Activity matrices for calibrating the equipment and the presampling operations (Tables 2.1 and 3.1) summarize the activities.

3. On-Site Measurements

Section 3.19.4 (On-Site Measurements) contains step-by-step procedures for sample collection, sample recovery, and sample preparation for transport. The on-site checklist (Figure 4.3, Section 3.19.4) provides testers with a quick method for checking the on-site requirements. Table 4.1 provides an activity matrix for all on-site activities.

4. Posttest Operations

Section 3.19.5 (Posttest Operations) presents the posttest equipment procedures and a step-by-step analytical procedure for determination of mercury. Posttest calibrations are required for the sampling equipment. The posttest operations form (Figure 5.9, Section 3.19.5) provides some key parameters that testers and laboratory personnel must check. The step-by-step sample preparation and analytical procedure descriptions can be removed and made into a separate quality assurance analytical reference manual for laboratory personnel.

Section 3.19.6 (Calculations) provides testers with the required equations, nomenclature, and significant digits. A calculator or computer should be used, if available, to reduce the chances of error.

Section 3.19.7 (Maintenance) provides testers with a guide for a maintenance program. This program is not required, but it should reduce equipment malfunctions. Activity matrices (Tables 5.1, 6.1, and 7.1) summarize all postsampling, calculation, and maintenance activities.

5. Auditing Procedures

Section 3.19.8 (Auditing Procedure) provides a description of necessary activities for conducting performance and system audits. The data-processing procedures and a checklist for a systems audit also are included in this section. Table 8.1 is an activity matrix for conducting the performance and system audits.

Section 3.19.9 (Recommended Standards for Establishing Traceabi-lity) provides the primary standard to which the analytical data should be traceable.

6. References

Section 3.19.10 contains the promulgated Method 101A; Section 3.19.11 contains the references cited throughout the text.

1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

Before Method 101A can yield results, it must be employed accurately. Consequently, all users are advised to read this document and to adopt its procedures. Alternative procedures should be employed only if they are outlined herein.

This section describes equipment specifications, criteria, and design features for the sampling train used for Method 101A. It is intended to help users with equipment selection. A schematic of the sampling train is shown in Figure 1.1 as an aid in the discussion that follows.

This section also describes procedures and limits, where applicable, for acceptance checks. Calibration data generated by the acceptance checks should be recorded in the calibration log book.

When procuring equipment and supplies, users should record the descriptive title of the equipment, identification number (if applicable), and the results of acceptance checks in a procurement log.

The following procedures and descriptions are provided only as guidance and may not be required for the initial ordering and check-out of the equipment and supplies. Testers should note, however, that many of these procedures are required at a later step in the sampling and analytical procedures. Instituting these or similar procedures as routine practices for checking new equipment and supplies, therefore, will prevent later problems and/or delays in test programs. At the end of this section, Table 1.1 provides a summary of quality assurance activities for procurement and acceptance of apparatus and supplies.

1.1 Sampling

The sampling train shown in Figure 1.1 is similar to the Method 5 train (Method 5 refers to 40 CFR Part 60). The Method 101A sampling train consists of the following components:

1.1.1 *Nozzle*—The nozzle shall be made of nickel, nickel-plated stainless-steel, quartz, or borosilicate glass. The tapered angle should be $\leq 30°$, with taper on the outside to preserve a constant inside diameter (ID).

A range of nozzle ID's—for example, 0.32 to 1.27 cm (0.125 to 0.5 in.)—in increments of 0.16 cm (0.0625 in.) should be available for isokinetic sampling. Larger nozzle sizes may be required if very low flows are encountered.

Upon receipt of the nozzle(s) from the manufacturer, users should inspect it for roundness, for the proper material, and for damage to the tapered edge (nicks, dents, and burrs). Check the diameter with a micrometer; calibration procedures are described in Section 3.18.2. A slight variation from exact sizes is normal. Engrave each nozzle with an identification number for inventory and calibration purposes. See Section 3.18.3 for proper cleaning procedures.

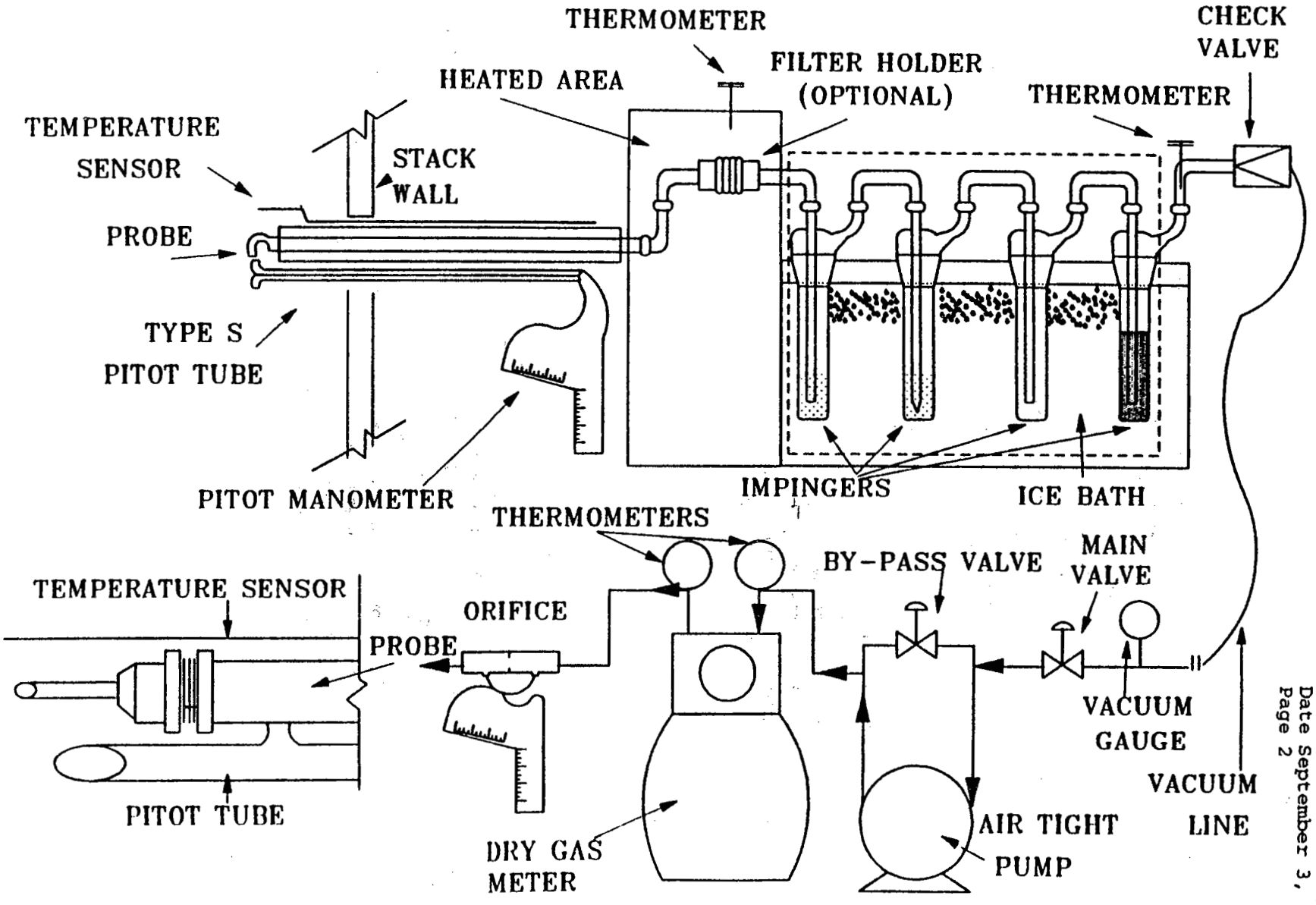


Figure 1.1. Schematic of Method 101A sampling train.

1.1.2 *Pitot Tube*—The pitot tube, preferably of Type S design, should meet the requirements of Method 2, Section 3.1.2 of this Handbook. The pitot tube is attached to the probe as shown in Figure 1.1. The proper pitot-tube/sampling-nozzle configuration to prevent aerodynamic interference is shown in figures 2.6 and 2.7 of Method 2, Section 3.1.2 of this Handbook.

The pitot tube should be inspected visually for both vertical and horizontal tip alignments. If the tube is purchased as an integral part of a probe assembly, check the dimensional clearances using figures 2.6 and 2.7 (of Method 2, Section 3.1.2). Repair or return any pitot tube that does not meet specifications. The calibration procedure for a pitot tube is covered in Section 3.4.2 of this Handbook.

1.1.3 *Differential Pressure* ΔP—The differential pressure gauge should be an inclined manometer or the equivalent, as specified in Method 2, Section 3.1.2 of this Handbook. Two gauges are required. One is used to monitor the stack velocity pressure, whereas the other is used to measure the orifice pressure differential.

Initially, check the gauge against a gauge-oil manometer at a minimum of three points: 0.64 mm (0.025 in.); 12.7 mm (0.5 in.); and 25.4 mm (1.0 in.) H_2O. The gauge should read within 5% of the gauge-oil manometer at each test point. Repair or return to the supplier any gauge that does not meet these requirements.

1.1.4 *Probe Liner*—The probe liner is made of borosilicate or quartz glass tubing. (Note: Do not use metal probe liners.) If a filter is used ahead of the impingers, testers must use the probe heating system to minimize the condensation of gaseous Hg. A heating system is required that will maintain an exit gas temperature of 120 ± 14 °C (248 ± 25 °F) during sampling. Other temperatures may be specified by a subpart of the regulations and must be approved by the Administrator for a particular application. Because the actual probe outlet temperature is not usually monitored during sampling, probes constructed in accordance to APTD-0581 and calibrated according to procedures in APTD-0576 will be acceptable.

Either borosilicate or quartz glass liners may be used for stack temperatures up to about 480 °C (900 °F), but quartz glass liners must be used from 480 to 900 °C (900 to 1650 °F). Either type of liner may be used at higher temperatures for short periods, with Administrator approval. However, the absolute upper limits—the softening temperatures of 820 °C (1508 °F) and 1500 °C (2732 °F)—for borosilicate and quartz, respectively, must be observed.

Upon receiving a new probe, users should check it visually to see whether it is the length and composition ordered. The probe also should be checked visually for breaks or cracks, and it should be checked for leaks on a sampling train (Figure 1.1). Leak checks should include a proper nozzle-to-probe connection with a Viton O-ring, Teflon® ferrules, or asbestos string.

The probe heating system should be checked as follows:

1. With a nozzle attached, connect the probe outlet to the inlet of the metering system.
2. Connect the probe heater to an outlet and turn it on for 2 or 3 min. The probe should become warm to the touch.
3. Start the pump and adjust the needle valve until it indicates a flow rate of about 0.02 m^3/min (0.75 ft^3/min).
4. Be sure the probe remains warm to the touch; the heater should be capable of maintaining an exit air temperature of 100 °C (212 °F) minimum. Failure indicates that the probe should be repaired, returned to the supplier, or rejected.

1.1.5 *Filter Holder (Optional)*—The filter holders should be made of borosilicate glass with a rigid, stainless-steel wire-screen filter support. Do not use glass frit supports. A silicone rubber or Teflon gasket is essential to provide a positive seal against leakage from outside or around the filter. Upon receipt, assemble the filter holder with a filter and conduct a leak check. There should be no leak at a vacuum of 15 in. of Hg.

1.1.6 *Impingers*—Four Greenburg-Smith impingers must be connected in series with leak-free, ground glass fittings or any similar leak-free, noncontaminating fittings. For the first, third, and fourth impingers, testers may use impingers that are modified by replacing the tip with a 13-mm ID (0.5 in.) glass tube extending to 13 mm (0.5 in.) from the bottom of the flask. The connecting fittings should form leak-free, vacuum-tight seals. See Section 3.19.3 for proper cleaning procedures.

Upon receipt of a standard Greenburg-Smith impinger, users should fill the inner tube with water. If the water does not drain through the orifice in 6 to 8 s or less, the impinger tip should be replaced or enlarged to prevent an excessive pressure drop in the sampling system. Each impinger should be checked visually for damage: breaks, cracks, or manufacturing flaws, such as poorly shaped connections.

1.1.7 *Acid Trap*—The acid trap should be a Mine Safety Appliances™ airline filter, catalog number 81857, with acid absorbing cartridge and suitable connections, or the equivalent. Upon receipt, check the part number to ensure the part is correct.

1.1.8 *Filter Heating System*—Any heating system may be used that is capable of maintaining the filter holder at 120 ± 14 °C (248 ± 25 °F) during sampling. Other temperatures may be specified by a subpart of the regulations or approved by the Administrator for a particular application. A gauge capable of measuring temperatures to within 3 °C (5.4 °F) should be provided to monitor the temperature around the filter during sampling.

Before sampling, the heating system and the temperature monitoring device should be checked. For convenience, the heating element should be easily replaceable should a malfunction occur during sampling.

1.1.9 *Metering System*—The metering system should consist of a vacuum gauge, a vacuum pump, thermometers capable of measuring ± 3 °C (5.4 °F) of true value in the range of 0 to 90 °C (32 to 194 °F), a dry-gas meter with 2% accuracy at the required sampling rate, and related equipment as shown in Figure 1.1. Other systems capable of maintaining metering rates within 10% of the isokinetic sampling rate and of determining sample volumes to within 2% of the isokinetic rate may be used if approved by the Administrator. Sampling trains with metering systems designed for sampling rates higher than those described in APTD-0581 and APTD-0576 may be used if the above specifications can be met. When the metering system is used with a pitot tube, it should permit verification of an isokinetic sampling rate through the use of a nomograph or by calculation.

Upon receipt or after construction of the system, users should perform both positive and negative pressure leak checks before beginning the system calibration procedure described in Subsection 2.1 of Section 3.19.2. Any leakage requires repair or replacement of the malfunctioning item.

1.1.10 *Barometer*—A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within ± 2.5 mm (0.1 in.) Hg is required.

A preliminary check of a new barometer should be made against a mercury-in-glass barometer or the equivalent. In lieu of a barometer check, the

absolute barometric pressure may be obtained from a nearby weather service station and adjusted for elevation difference between the station and the sampling point. Either subtract 2.5 mm Hg/30 m (0.1 in. Hg/100 ft) from the station value for an elevation increase, or add the same for an elevation decrease. If the barometer cannot be adjusted to within 2.5 mm (0.1 in.) Hg of the reference barometric pressure, it should be returned to the manufacturer or rejected.

1.1.11 *Gas Density Determination Equipment*—A temperature sensor and a pressure gauge are required as described in Method 2 (Section 3.1.2 of this Handbook). Additionally, a gas analyzer as described by Method 3 may be required. The temperature sensor should be permanently attached to either the probe or the pitot tube. In either case, it is recommended that a fixed configuration (Figure 1.1) be maintained. The sensor also may be attached just prior to field use, as described in Section 3.19.2.

1.2 Sample Recovery

1.2.1 *Glass Sample Bottles* Sample bottles should be 1000- and 100-mL without leaks and with Teflon-lined caps. Upon receipt, check visually for cracks in the glass. Ensure that the cap liners are Teflon, because other material can result in sample contamination and reaction with the $KMnO_4$. Because of the potential reaction of the $KMnO_4$ with the acid, there may be pressure buildup in the sample storage bottles. Venting is highly recommended. A No. 70-72 hole drilled in the container cap and Teflon liner has been found to allow adequate venting without loss of sample.

1.2.2 *Graduated Cylinder*—A 250-mL cylinder is required.

1.2.3 *Funnel and Rubber Policeman*—These items are used to aid in transferring silica gel to containers; they are not necessary if silica gel is weighed in the field.

1.2.4 *Funnel*—A glass funnel is needed to aid in sample recovery.

1.3 Sample Preparation and Hg Analysis

1.3.1 *Volumetric Pipets*—Class A 1-, 2-, 3-, 4-, 5-, 10-, and 20-mL pipets are required.

1.3.2 *Graduated Cylinder*—A 25-mL cylinder is required.

1.3.3 *Steam Bath*—Refers to 40 CFR, Part 60, Appendix B, Method 101A.

1.3.4 *Atomic Absorption Spectrophotometer*—Any atomic absorption unit is suitable, provided it has an open sample presentation area in which to mount the optical cell. Follow the instrument settings recommended by the manufacturer. Instruments designed specifically for measuring mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

1.3.5 *Optical Cell*—The optical cell should be of cylindrical shape, with quartz end windows and having the dimensions shown in Figure 1.2. Wind the cell with approximately 2 m of 24-gauge nichrome heating wire, and wrap with fiberglass insulation tape or the equivalent; do not let the wires touch each other. A heat lamp mounted above the cell or a moisture trap installed upstream of the cell may be used as alternatives. Upon receipt, check the dimensions and the capability of the heating system.

1.3.6 *Aeration Cell*—The aeration cell should be constructed according to the specifications in Figure 1.3. Do not use a glass frit as a substitute for the blown glass bubbler tip shown in Figure 1.3.

1.3.7 *Recorder*—The recorder must be matched to the output of the spectrophotometer described above. As an alternative, an integrator may be used to determine peak area or peak height.

1.3.8 *Variable Transformer*—This item is needed to vary the voltage on the optical cell from 0 to 40 volts.

1.3.9 *Hood*—A hood is required for venting the optical cell exhaust.

1.3.10 *Flow Metering Valve*—Refers to 40 CFR, Part 60, Appendix B, Method 101A.

1.3.11 *Flow Meter*—A rotameter, or equivalent, is required that is capable of measuring a gas flow of 1.5 L/min. Upon receipt, calibrate the flow meter at a flow rate of 1.5 L/min with a bubble meter or wet-test meter.

1.3.12 *Aeration Gas Cylinder*—The cylinder must contain nitrogen or dry, Hg-free air and must be equipped with a single-stage regulator.

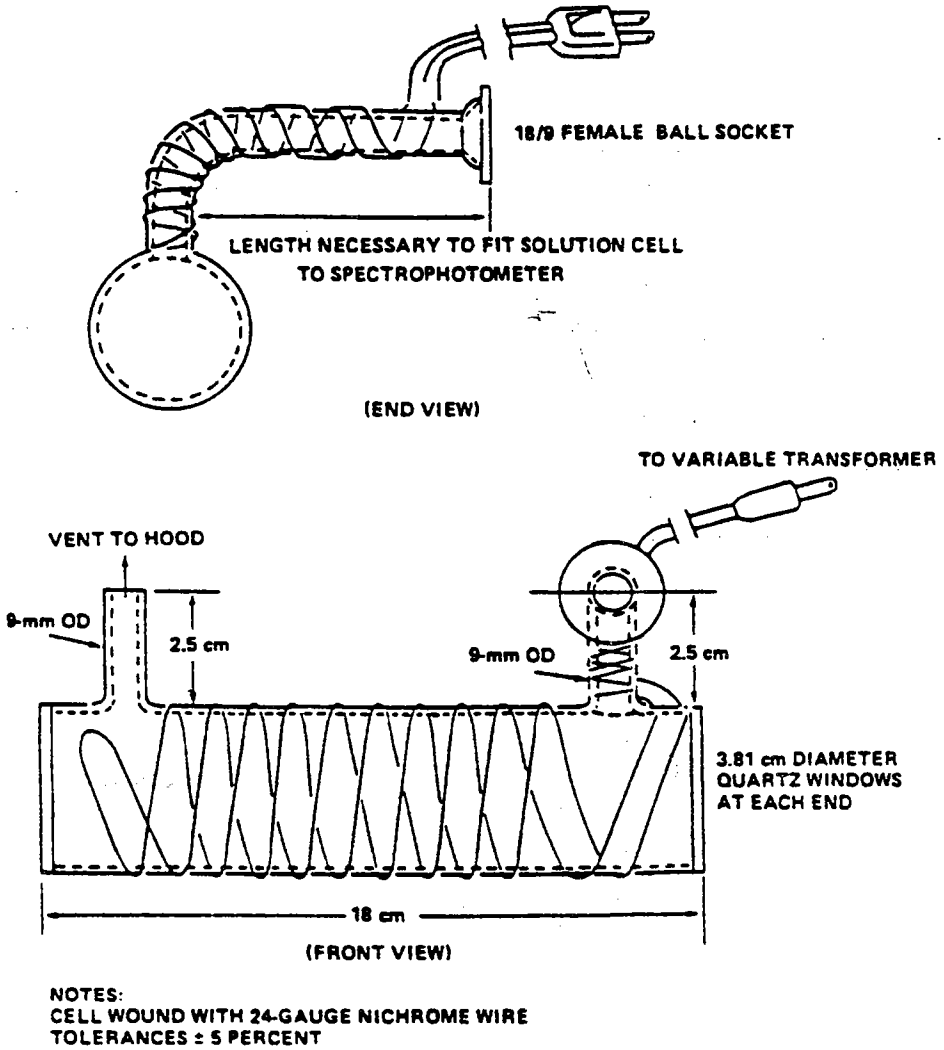


Figure 1.2. Optical cell.

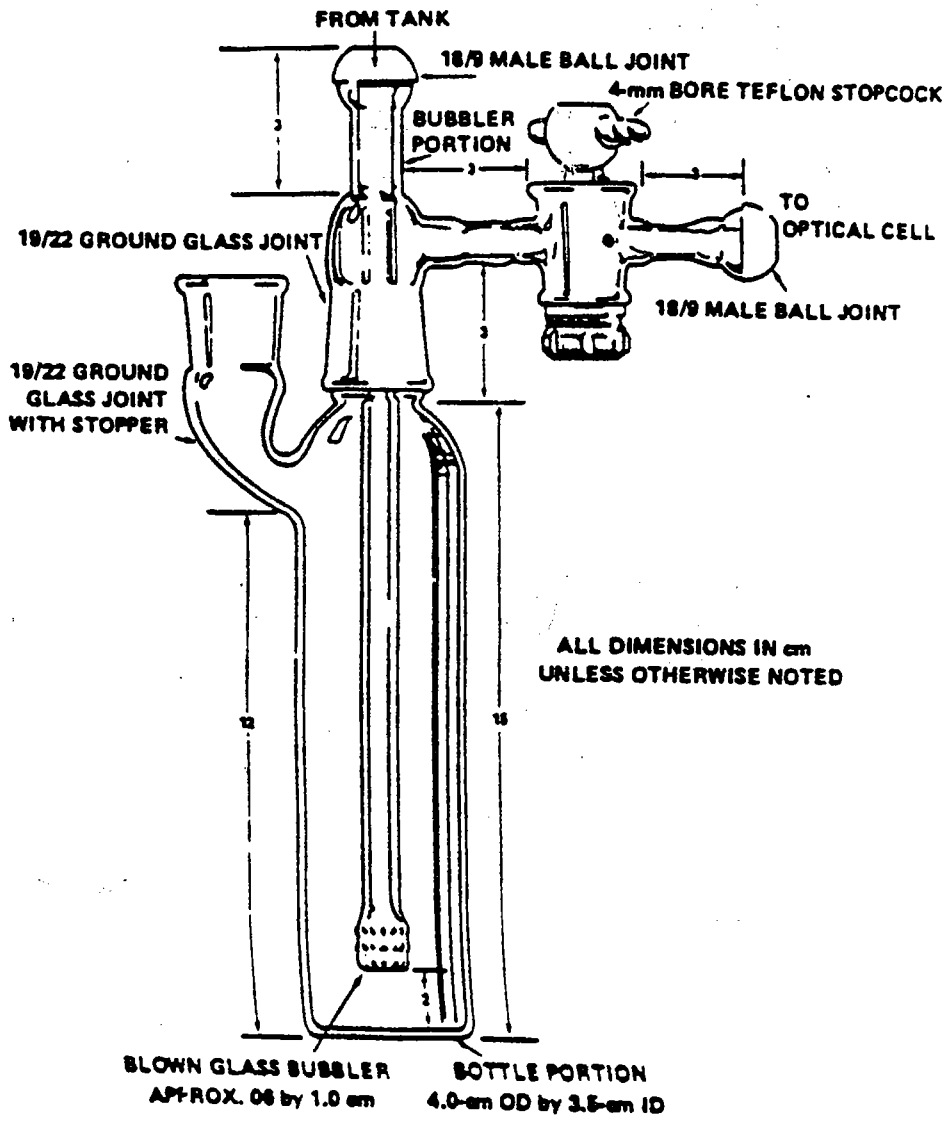


Figure 1.3. Aeration cell.

1.3.13 *Tubing*—The tubing is required for connections. Use glass tubing (ungreased ball and socket connections are recommended) for all connections between the solution cell and the optical cell; do not use Tygon tubing, other types of flexible tubing, or metal tubing as substitutes. Testers may use Teflon, steel, or copper tubing between the nitrogen tank and the flow meter valve (Section 5.3.7), and Tygon, gum, or rubber tubing between the flow meter valve and the aeration cell.

1.3.14 *Flow Rate Calibration Equipment*—This equipment consists of a bubble flow meter or a wet-test meter for measuring a gas flow rate of 1.5 ± 0.1 L/min.

1.3.15 *Volumetric Flasks*—These flasks must be Class A, with pennyhead standard taper stoppers; the required sizes are 100-, 250-, 500-, and 1000-mL.

1.3.16 *Volumetric Pipets*—These pipets must be Class A; the required sizes are 1-, 2-, 3-, 4-, and 5-mL.

1.3.17 *Graduated Cylinder*— A 50-mL cylinder is required.

1.3.18 *Magnetic Stirrer*— A general purpose laboratory-type stirrer is required.

1.3.19 *Magnetic Stirring Bar*— A Teflon-coated stirring bar is required.

1.3.20 *Trip Balance*— A trip balance capable of weighing to ± 0.5 g is required. Upon receipt, check balance with standard weights.

1.3.21 *Analytical Balance*—An analytical balance capable of weighing up to ± 0.5 mg is required. Upon receipt, check balance with standard weights.

1.4 Alternative Analytical Apparatus

If any alternative analytical apparatus is to be used, it must pass the performance criteria described in Section 3.19.5.5. Alternative Hg cold-vapor analytical systems are available commercially from most atomic absorption manufacturers and employ automated flow-injection techniques. Such systems automatically inject sample solutions into continuous reagent streams containing the reducing reagent. Mercury is usually measured as a solution concentration (e.g., mg Hg/L). An example of a typical cold-vapor AA instrument using flow injection is shown in Figure 1.4. Such systems are allowable as long as they meet the following criteria:

1.4.1 *Calibration Curve Linearity*—The system must generate a linear calibration curve, and two consecutive samples of the same aliquot size and concentration must agree within 3% of their average.

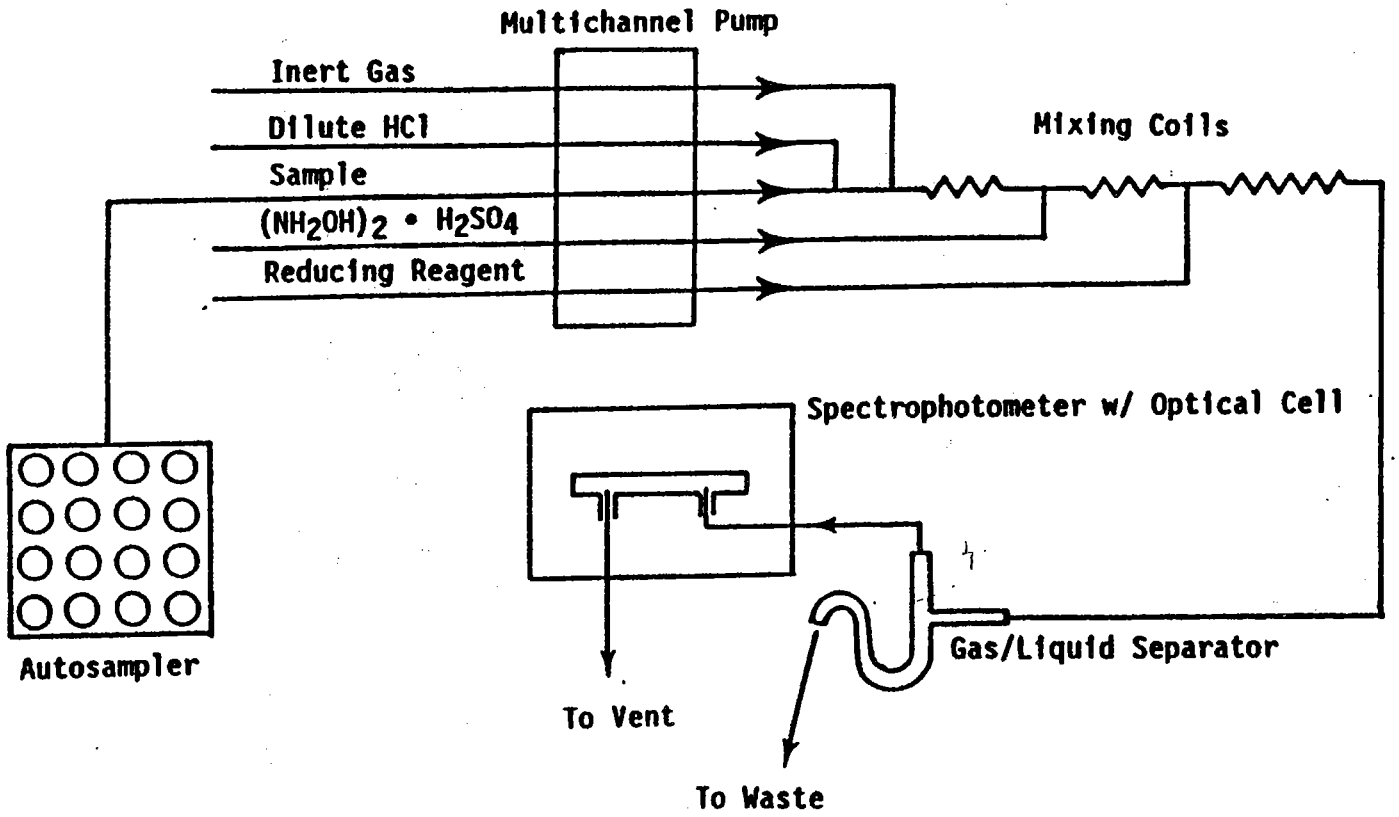


Figure 1.4. Typical Cold Vapor AA instrumentation using flow injection.

1.4.2 *Spike Recovery*—The system must allow for recovery of a minimum of 95% of the spike when an aliquot of a source sample is spiked with a known concentration of Hg (II) compound.

1.5 Reagents

1.5.1 *Sampling and Sample Recovery*—Use ACS reagent-grade chemicals or the equivalent, unless otherwise specified. The following reagents are used in sampling and recovery:

Water—Deionized distilled, meeting ASTM specifications for Type I Reagent Water—ASTM Test Method D 1193-77. If high concentrations of organic matter are not expected to be present, users may eliminate the $KMnO_4$ test for oxidizable organic matter. Use this water in all dilutions and solution preparations.

Nitric Acid (HNO_3), 50% (v/v)—Mix equal volumes of concentrated HNO_3 and water, being careful to add the acid to the water slowly.

Silica Gel—Indicating type, 6- to 16-mesh. If previously used, dry at 175 °C (350 °F) for 2 h. Testers may use new silica gel as received.

Filter (Optional)—Glass fiber filter, without organic binder, exhibiting at least 99.95% efficiency on 0.3-μm dioctyl phthalate smoke particles. Testers may use the filter in cases where the gas stream contains large quantities of particulate matter, but they should analyze blank filters for Hg content.

Sulfuric Acid (H_2SO_4), 10% (v/v)—Slowly add 100 mL of concentrated H_2SO_4 to 900 mL of water and mix cautiously.

Absorbing Solution, 4% $KMnO_4$ (w/v)—Prepare fresh daily. Dissolve 40 g of $KMnO_4$ in sufficient 10% H_2SO_4 to make 1 L. Prepare and store in glass bottles to prevent degradation.

Caution: To prevent autocatalytic decomposition of the permanganate solution, filter it through Whatman™ 541 filter paper. In addition, owing to the reaction of the $KMnO_4$ with the acid, there may be pressure buildup in the sample storage bottle. These bottles should not be filled to capacity and should be vented, both to relieve excess pressure and to prevent explosion of the container: A No. 70-72 hole drilled in the container cap and Teflon liner is recommended.

Hydrochloric Acid—Trace metals grade HCl is recommended. If other grades are used, the Hg level must be less than 3 ng/mL Hg. Upon receipt, check manufacturer's guarantee or analyze the acid for background contamination.

Hydrochloric Acid, 8 N—Dilute 67 mL of concentrated HCl to 100 mL with water (slowly add the HCl to the water).

1.5.2 *Analysis*—The reagents needed for analysis are listed below:

Tin (II) Solution—Prepare fresh daily and keep sealed when not being used. Completely dissolve 20 g of tin (II) chloride [or 25 g of tin (II) sulfate] crystals (Baker™ Analyzed reagent grade or any other brand that will give a clear solution) in 25 mL of concentrated HCl. Dilute to 250 mL with water. Do not substitute HNO_3, H_2SO_4, or other strong acids for the HCl.

Sodium Chloride-Hydroxylamine Solution—Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate (or 12 g of hydroxylamine hydrochloride) in water and dilute to 100 mL.

Hydrochloric Acid, 8 N—Dilute 67 mL of concentrated HCl to 100 mL with water (slowly add the HCl to the water).

Nitric Acid, 15% (v/v)—Dilute 15 mL of concentrated HNO_3 to 100 mL with water.

Mercury Stock Solution, 1 mg Hg/mL—Prepare and store all Hg standard solutions in borosilicate glass containers. Completely dissolve 0.1354 g of Hg (II) chloride in 75 mL of water. Add 10 mL of concentrated HNO_3 and adjust the volume to exactly 100 mL with water. Mix thoroughly. This solution is stable for at least 1 month.

Intermediate Hg Standard Solution, 10 µg/mL—Prepare fresh weekly. Pipet 5.0 mL of the Hg stock solution (Section 6.2.5) into a 500-mL volumetric flask, and add 20 mL of 15% HNO_3 solution. Adjust the volume to exactly 500 mL with water. Thoroughly mix the solution.

Working Hg Standard Solution, 200 ng Hg/mL—Prepare fresh daily. Pipet 5.0 mL from the Intermediate Hg Standard Solution (Section 6.2.6) into a 250-mL volumetric flask. Add 5 mL of 4% $KMnO_4$ absorbing solution and 5 mL of 15% HNO_3. Adjust the volume to exactly 250 mL with water. Mix thoroughly.

Potassium Permanganate, 5% (w/v)—Dissolve 5 g of $KMnO_4$ in water and dilute to 100 mL.

Filter—Use a Whatman 40, or equivalent.

TABLE 1.1 ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS AND SUPPLIES

Apparatus	Acceptance limits	Frequency & method of measurement	Action if requirements are not met
Sampling			
Probe liner	Specified material of construction; equipped with heating system capable of maintaining 120 °C ± 14°C (248 °C ± 25 °F) at the exit	Visually check and run the heating system	Repair, return to supplier, or reject
Probe nozzle	Nickel, nickel-plated stainless-steel, quartz, or borosilicate glass, tapered ≤ 30°; difference in measured diameter ≤ 0.1 mm (0.004 in.); no nicks, dents, or corrosion (Subsec. 1.1.2)	Visually check before each test; use a micrometer to measure ID before field use; after each repair	Reshape and sharpen, return to the supplier, or reject
Pitot tube	Type S (Sec. 3.1.2); attached to probe with impact (high pressure) opening plane even with or above nozzle entry plane	Visually check for both vertical and horizontal tip alignments; calibrated according to Sec. 3.4.2	Repair or return to supplier
Differential pressure gauge	Meets criteria (Sec. 3.1.2); agree, within 5% of gauge-oil manometer	Check against a gauge-oil manometer at a minimum of 3 points; 0.64 (0.025); 12.7 (0.5); 25.4 (1.0) mm (in) H_2O	Repair or return to supplier
Vacuum gauge	0-760 mm (0-30 in.) Hg, ± 25 mm (1 in.) at 380 mm in.) Hg	Check against mercury U-tube manometer upon receipt	Adjust or return to supplier

(Continued)

TABLE 1.1 (Continued)

Apparatus	Acceptance limits	Frequency & method of measurement	Action if requirements are not met
Vacuum pump	Leak free; capable of maintaining a flow rate of 0.02 - 0.03 m^3/min (0.66 to 1.1 ft^3/min) for pump inlet vacuum of 380 mm (15 in.) Hg	Check upon receipt for leaks and capacity	Repair or return to supplier
Orifice meter	ΔH@ of 46.74 ± 6.35 mm (1.84 ± 0.25 in.) H_2O at 68 °F (not mandatory)	Upon receipt, visually check for damage and calibrate against wet-test meter	Repair, if possible, otherwise return to supplier
Impingers	Four Greenburg-Smith connected in a series, leak-free, noncontaminating fittings	Visually check upon receipt; check pressure drop (Subsec. 1.1.6)	Return to supplier
Filter holder (optional)	Leak-free; borosilicate glass	Visually check before use; conduct leak check	As above
Filter support	Rigid stainless-steel wire screen	Visually check upon receipt, conduct leak check	Repair or return to manufacturer
Filter heating system	Capable of maintaining filter holder at temperature of 120 °C ± 14 °C (248 °F ± 25°F)	Visually check upon receipt and run heating system checkout	Repair or return to manufacturer
Dry-gas meter	Capable of measuring volume within 2% at a flow rate of 0.02 m^3/min (0.75 ft^3/min)	Check for damage upon receipt and calibrate (Sec. 3.4.2) against wet-test meter	Reject if damaged, behaves erratically, or cannot be properly adjusted

(Continued)

TABLE 1.1 (Continued)

Apparatus	Acceptance limits	Frequency & method of measurement	Action if requirements are not met
Acid Trap	Mine Safety Appliances air line filter acid absorbing cartridge	Visually check upon receipt	Return to supplier
Thermometers	± 1 °C (2 °F) of true value in the range of 0 to 25 °C (32 to 77 °F) for impinger thermometer and ± 3 °C (5.4 °F) of true value in the range of 0 to 90 °C (32 to 194 °F) for dry-gas meter thermometers	Check upon receipt for dents or bent stem, and calibrate (Sec. 3.4.2) against mercury-in-glass thermometer	Reject if unable to calibrate
Barometer	Capable of measuring atmospheric pressure within 2.5 mm (0.1 in.) Hg	Check against a mercury-in-glass barometer or equivalent; calibrate (Sec. 3.1.2)	Determine correction factor, or reject if difference more than ± 2.5 mm (0.1 in.) Hg
Gas density determination equipment	Meet the requirements in Sec. 3.2.1	Conduct checks shown in Sec. 3.2.1, upon receipt	Repair, replace, or return to supplier
Sample Recovery			
Glass sample bottles	Leak-free, Teflon lined caps, 1000 and 100 mL	Visually check upon receipt for cracks, ensure that caps are Teflon	Replace or return to supplier

(Continued)

TABLE 1.1 (Continued)

Apparatus	Acceptance limits	Frequency & method of measurement	Action if requirements are not met
Sample Preparation and Analysis			
Glassware	Class A	Visually check upon receipt	Replace or return to supplier
AA spectrometer	Suitable optical resolution system and detector	Perform appropriate calibrations according to Sec. 5	Return to manufacturer or repair and re-check
Recorder or electronic integrator	See owner's manual	Upon receipt, check	Repair or return to manufacturer
Optical cell	See Figure 1.2	Upon receipt, check to ensure correct dimensions, check heating system	Return to manufacturer, clean as needed
Aeration cell	See Figure 1.3	Visually check	Repair or return to manufacturer
Moisture removal system	Heated cell or moisture trap to remove condensation from optical cell	Calibrate whenever system is turned on	Calibrate heated cell or change desiccant
Regulator	Proper fittings and pressure control	Upon receipt, attach to cylinder and check	Return to manufacturer, repair, or replace fitting and re-check
Flowmeter	Capable of measuring flow of 1.5 L/min	Calibrate with bubble meter or wet-test meter upon receipt	Return to manufacturer or repair and recalibrate

(Continued)

TABLE 1.1 (Continued)

Apparatus	Acceptance limits	Frequency & method of measurement	Action if requirements are not met
Variable transformer	Capable of varying voltage from 0 to 40 volts	Visually check upon receipt	Return to manufacturer or repair
Aeration gas cylinder	Nitrogen or dry, Hg-free air equipped with regulator	Visually check upon receipt	Return to supplier
Tubing	See Sec. 1.3.13 for specifications of tubing for the connections	Visually check to ensure proper type tubing	Replace
Trip balance	Capable of measuring within 0.5 g	Check with standard weights upon receipt and before each use	Replace or return to manufacturer
Analytical balance	Capable of weighing to ± 0.5 mg	As above	As above
Alternative analytical apparatus	Capable of generating a linear calibration curve; two consecutive samples of equal size and concentration agree ± 3% of average; and ≥ 95% recovery of known concentration of spiked sample	See owner's manual	Return to supplier
Sampling and Sample Recovery			
Reagents	ACS reagent grade or Hg blank level specified	Visually check upon receipt or conduct Hg analysis	Return to supplier or replace

(Continued)

TABLE 1.1 (Continued)

Apparatus	Acceptance limits	Frequency & method of measurement	Action if requirements are not met
Water	Deionized, distilled meeting ASTM D1193-77 specifications	Check each lot or specify type when ordering	Replace or return to supplier
Silica gel	Indicating type, 6- to 16-mesh	Upon receipt, check label for grade or certification	Return to supplier
Filter (optional)	Glass fiber without organic binder; 99.95% collection efficiency for 0.3 µm dioctyl phthalate smoke particles	Manufacturer's guarantee that filters were tested according to ASTM D 2986-71; observe under light for defects	Return to supplier
Analysis			
Reagents	ACS reagent grade or equivalent; prepared as described in Sec. 1.5.3	Upon receipt, check label for grade or certification; Check stability of prepared solution and prepare when necessary	Replace or return to supplier
Filter	Whatman 40 or equivalent	Upon receipt, check label for grade	Replace or return to supplier

2.0 CALIBRATION OF APPARATUS

Calibrating the apparatus is one of the more important functions in maintaining data quality. The detailed calibration procedures for the sampling apparatus included in this section were designed for the sampling equipment specified in Method 5 and described in the previous section. Calibrating the analytical equipment is described in Section 3.19.5, which details the analytical procedures. Table 2.1, at the end of this section, summarizes the quality assurance (QA) functions for the calibrations. All calibrations, including those performed on the analytical equipment, should be recorded on standardized forms and retained in a calibration log book.

2.1 Metering System

The dry-gas meter (DGM) in the sampling system's meter console must be calibrated against a primary standard meter (wet-test meter or spirometer). An alternate procedure is to calibrate against a second reference meter (dry-gas meter or critical orifice) that has been calibrated against a primary standard meter.

2.1.1 *Wet-Test Meter*—Wet-test meters are calibrated by the manufacturer to an accuracy of ± 0.5%. The calibration must be checked initially upon receipt and yearly thereafter. A wet-test meter with a capacity of 3.4 m^3/h (120 ft^3/h) or 30 L/revolution (1 ft^3/rev) will be needed to calibrate the dry-gas meter. For large wet-test meters (>30 L/rev), there is no convenient method for checking the calibration; consequently, several methods are suggested, and other methods may be approved by the Administrator. The initial calibration may be checked by any of the following methods:

1. Certification from the manufacturer that the wet-test meter is within 1% of true value at the wet-test meter discharge, so that only a leak check of the system is then required.
2. Calibration by any primary-air or liquid-displacement method that displaces at least one complete revolution of the wet-test meter.
3. Comparison against a smaller wet-test meter that has previously been calibrated against a primary-air or liquid-displacement method, as described in Section 3.5.2 of this Handbook.
4. Comparison against a dry-gas meter that has previously been calibrated against a primary-air or liquid-displacement method.

The test-meter calibration should be checked annually. The calibration check can be made by the same method as that of the original calibration; however, the comparison method need not be recalibrated if the calibration check is within 1% of the true value. When this agreement is not obtained, the comparison method or wet-test meter must be recalibrated against a primary-air or liquid-displacement method.

2.1.2 *Dry-Gas Meter as a Calibration Standard*—A DGM may be used as a calibration standard for volume measurements in place of the wet-test meter specified in Section 5.3 of Method 5, provided that it is calibrated initially and recalibrated periodically as follows:

Standard Dry-Gas Meter Calibration—The DGM to be calibrated and used as a secondary reference meter should be of high quality and should have appropriate capacity (e.g., 3 L/rev [0.1 ft^3/rev]). A spirometer (400 L or more capacity), or equivalent, may be used for this calibration, although a wet-test meter is usually more practical. The wet-test meter should have a capacity of 30 L/rev (1 ft^3/rev) and should be capable of measuring volume to within 1.0%. Wet-test meters should be

checked against a spirometer or a liquid displacement meter to ensure accuracy. Spirometers or wet-test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. The initial calibration may be checked by any of the following methods:

1. Set up the components as shown in Figure 2.1. A spirometer, or equivalent, may be used in place of the wet-test meter in the system.
2. Run the pump for at least 5 min at a flow rate of about 10 L/min (0.35 cfm) to condition the interior surface of the wet-test meter. The pressure drop indicated by the manometer at the inlet side of the DGM should be minimized (no greater than 100 mm H_2O [4 in. H_2O] at a flow rate of 30 L/min [1 cfm]). Using large diameter tubing connections and straight pipe fittings will accomplish this minimization.
3. Collect the data as shown in the example data sheet (see Figure 2.2). Make triplicate runs at each of the flow rates and at no less than five different flow rates. The range of flow rates should be between 10 and 34 L/min (0.35 and 1.2 cfm) or over the expected operating range.
4. Calculate flow rate, Q, for each run using the wet-test meter volume (Equation 2-1), V_w, and the run time, θ. Calculate the DGM coefficient (Equation 2-2), Y_{ds}, for each run. These calculations are as follows:

$$Q = K_1 \frac{P_{bar}\ V_w}{(t_w + t_{std})\ \theta} \qquad \text{Equation 2-1}$$

$$Y_{ds} = \frac{V_w\ (t_{ds} + t_{std})\ P_{bar}}{V_{ds}\ (t_w + t_{std})\ (P_{bar} + \Delta p/13.6)} \qquad \text{Equation 2-2}$$

where:

K_1 = 0.3858 for international system of units (SI); 17.64 for English units.

V_w = Wet-test meter volume, liter (ft^3).

V_{ds} = Dry-gas meter volume, liter (ft^3).

t_{ds} = Average dry-gas meter temperature, °C (°F).

t_{std} = 273 °C for SI units; 460 °F for English units.

t_w = Average wet-test meter temperature, °C (°F).

P_{bar} = Barometric pressure, mm Hg (in. Hg).

Δp = Dry-gas meter inlet differential pressure, mm H_2O (in. H_2O).

θ = Run time, min.

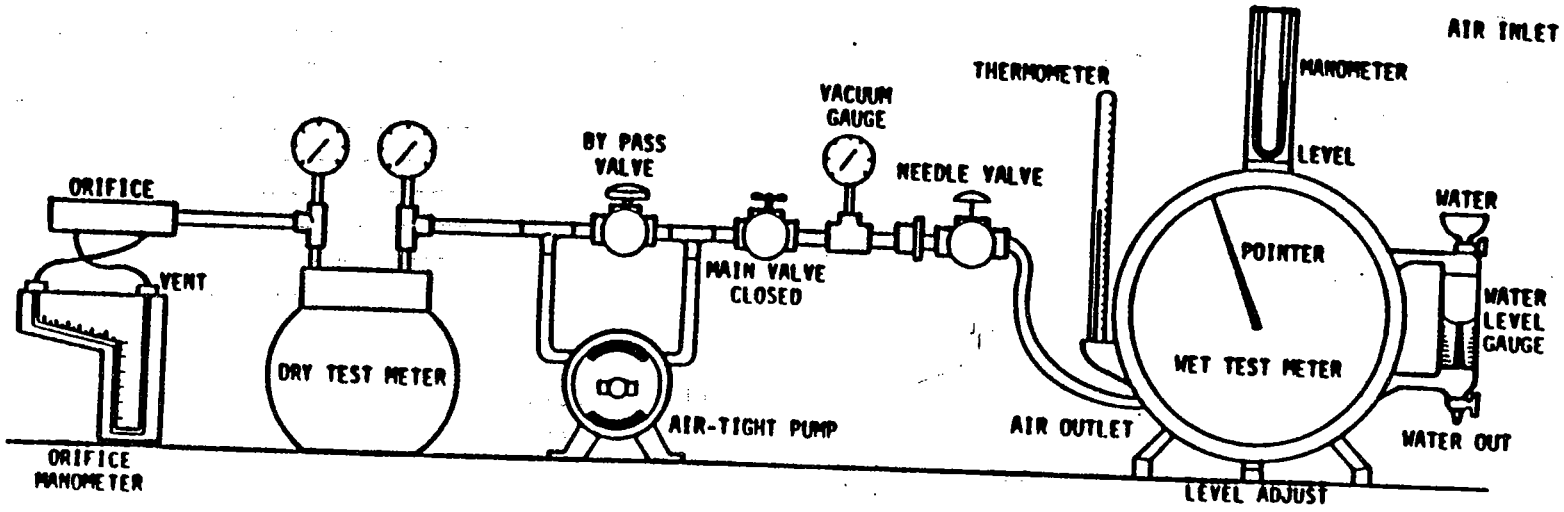


Figure 2.1. Sample meter system calibration setup.

Date: _____

Dry-gas Meter Identification: _____

Barometric Pressure (P_1): _____ in. Hg

Approximate flow rate (Q) cfm	Spirometer (wet meter) gas volume (V_s) ft^3	Dry-gas meter volume (V_{dg}) ft^3	Temperatures: Spirometer (wet meter) (t_s) °F	Temperatures: Dry-gas meter: Inlet (t_i) °F	Temperatures: Dry-gas meter: Outlet (t_o) °F	Temperatures: Dry-gas meter: Average (t_d) °F	Dry-gas meter pressure (Δp) in. H_2O	Time (θ) min	Flow rate (Q) cfm	Meter coefficient (Y_{ds})	Average meter coefficient – (Y_{ds})
0.40											
0.60											
0.80											
1.00											
1.20											

$$Q = 17.64 \frac{V_s}{\theta} \frac{P_s}{(t_s + 460)}$$

Equation 1

$$Y_{ds} = \frac{V_s}{V_{dg}} \frac{(t_i + 460)}{(t_o + 460)} \frac{P_{bar}}{\left(P_{bar} + \frac{\Delta p}{13.6}\right)}$$

Equation 2

Figure 2.2 Dry-gas meter calibration data form.

5. Compare the three Y_{ds} values at each of the flow rates and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra sets of triplicate runs may be made to complete this requirement. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications cannot be met in three sets of successive triplicate runs, the meter is not suitable as a calibration standard and should not be used as such. If these specifications are met, average the three Y_{ds} values at each flow rate resulting in five average meter coefficients, Y_{ds}.
6. Prepare a curve of meter coefficient, Y_{ds}, versus flow rate, Q, for the DGM. This curve shall be used as a reference when the meter is used to calibrate other DGM's and to determine whether recalibration is required.

Standard Dry-Gas Meter Recalibration—Recalibrate the standard DGM against a wet-test meter or spirometer annually or after every 200 hours of operation, whichever comes first. This requirement is valid provided the standard DGM is kept in a laboratory and, if transported, cared for as any other laboratory instrument. Abuse to the standard meter may cause a change in the calibration and will require more frequent recalibrations.

As an alternative to full recalibration, a two-point calibration check may be made. Follow the same procedure and equipment arrangement as for a full recalibration, but run the meter at only two flow rates (suggested rates are 14 and 28 L/min [0.5 and 1.0 cfm]). Calculate the meter coefficients for these two points and compare the values with the meter calibration curve. If the two coefficients are within 1.5% of the calibration curve values at the same flow rates, the meter need not be recalibrated until the next date for a recalibration check.

2.1.3 *Critical Orifices as Calibration Standards*—Critical orifices may be used as calibration standards in place of the wet-test meter specified in Section 5.3 of Method 5, provided that they are selected, calibrated, and used as follows:

Selection of Critical Orifices—The procedure that follows describes the use of hypodermic needles or stainless-steel needle tubing that have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used, provided the orifices act as true critical orifices (i.e., a critical vacuum can be obtained, as described in Section 7.2.2.2.3 of Method 5). Select five critical orifices of appropriate size to cover the range of flow rates between 10 and 34 L/min or the expected operating range. Two of the critical orifices should bracket the expected operating range.

A minimum of three critical orifices will be needed to calibrate a Method 5 DGM; the other two critical orifices can serve as spares, providing better selection for bracketing the range of operating flow

rates. The needle sizes and tubing lengths shown below give the following approximate flow rates:

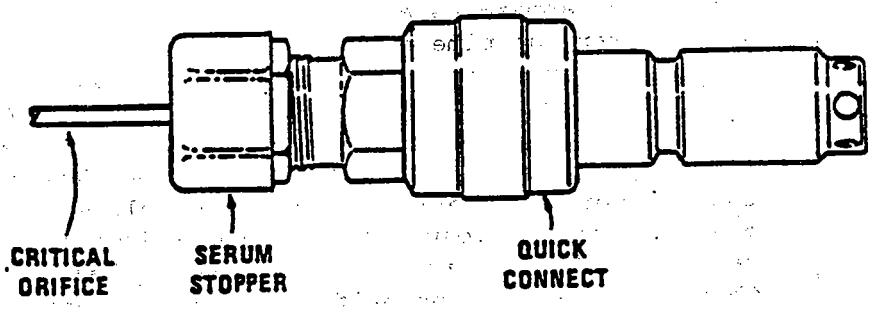
Flow rate, Gauge/cm	L/min	Flow rate, Gauge/cm	L/min
12/7.6	32.56	14/2.5	19.54
12/10.2	30.02	14/5.1	17.27
13/2.5	25.77	14/7.6	16.14
13/5.1	23.50	15/3.2	14.16
13/7.6	22.37	15/7.6	11.61
13/10.2	20.67	15/10.2	10.48

These needles can be adapted to a Method 5-type sampling train as follows: Insert a serum bottle stopper, 13- by 20-mm (0.5-in. by 75-in.) sleeve type, into a 13-mm (0.5-in.) Swagelok™ quick-connect fitting. Insert the needle into the stopper, as shown in Figure 2.3.

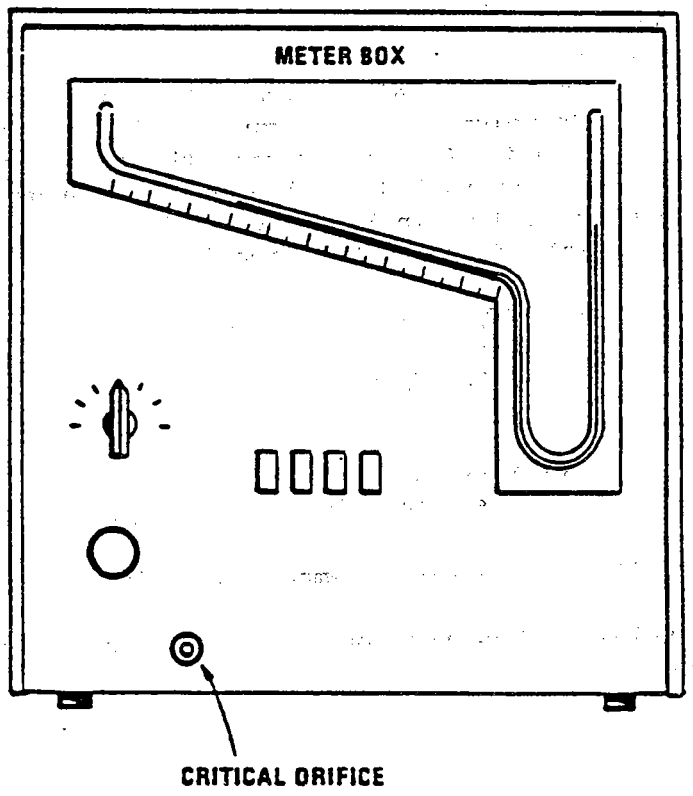
Initial Critical Orifice Calibration—The procedure described in this section uses the Method 5 meter box configuration with a DGM, as described in Section 2.1.8 of Method 5, to calibrate the critical orifices. Other schemes may be used, subject to the approval of the Administrator. The critical orifices must be calibrated in the same configuration as they will be used (i.e., there should be no connections to the inlet of the orifice).

Prior to calibrating the critical orifices, the dry-gas meter in the meter box must be calibrated. Before calibrating the meter box, leak check the system as follows:

1. Fully open the coarse adjust valve and completely close the bypass valve.
2. Plug the inlet.
3. Turn on the pump and determine whether there is any leakage. The leakage rate must be zero (i.e., no detectable movement of the DGM dial must be seen for 1 min).
4. Check also for leakages in the portion of the sampling train between the pump and the orifice meter. See Section 5.6 for the procedure; make any corrections, if necessary. If leakage is detected, check for cracked gaskets, loose fittings, worn O-rings, etc., and make the necessary repairs.



Critical orifice adaptation to Method 5-type metering system.



Apparatus setup.

Figure 2.3 Critical orifice and apparatus setup.

After determining that the meter box is leak-free, calibrate it according to the procedure given in Section 5.3. Make sure that the wet-test meter meets the requirements stated in Subsection 2.1.1. Check the water level in the wet-test meter. Record the DGM calibration factor, Y. The critical orifice is then calibrated as follows:

1. Set up the apparatus as shown in Figure 2.3.
2. Allow a warm-up time of 15 min. This step is important to equilibrate the temperature conditions through the DGM.
3. Leak check the system as described above. The leakage rate must be zero.
4. Before calibrating the critical orifice, determine its suitability and the appropriate operating vacuum as follows: Turn on the pump, fully open the coarse adjust valve, and adjust the bypass valve to give a vacuum reading corresponding to about half an atmospheric pressure. Observe the meter box orifice manometer reading, ΔH. Slowly increase the vacuum reading until the meter box orifice manometer shows a stable reading. Record the critical vacuum for each orifice. Orifices that do not reach a critical value must not be used.
5. Obtain the barometric pressure using a barometer as described in Section 2.1.9 of Method 5. Record the barometric pressure, P_{bar}, in mm Hg (in. Hg).
6. Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs must be at least 5 minutes each. The DGM volume readings must be in increments of complete revolutions of the DGM. As a guideline, the times should not differ by more than 3.0 s (this includes allowance for changes in the DGM temperatures) to achieve ± 0.5% in K'. Record the information listed in Figure 2.4.
7. Calculate K' using Equation 2-3.

$$K' = \frac{K_1 \, V_m \, Y \, (P_{bar} + \Delta H/13.6) \, T_{amb}^{1/2}}{P_{bar} \, T_m \, \theta} \qquad \text{Equation 2-3}$$

where:

K' = Critical orifice coefficient, $[(m^3)(°K)^{1/2}]/[(mm\ Hg)(min)]\{[(ft^3)(°R)^{1/2})]/[(in.\ Hg)(min)]\}$.

T_{amb} = Absolute ambient temperature, °K (°R).

Average the K' values. The individual K' values should not differ by more than ± 0.5% from the average.

Date _____ Train ID _____ Critical orifice ID _____

Critical orifice K′ factor _____

		Run number 1	Run number 2
Dry-Gas Meter			
Final reading	m^3 (ft^3)	_____	_____
Initial reading	m^3 (ft^3)	_____	_____
Difference, V_m	m^3 (ft^3)	_____	_____
Inlet/outlet temperatures			
Initial	°C (°F)	___/___	___/___
Final	°C (°F)	___/___	___/___
Avg. temperature, t_m	°C (°F)	_____	_____
Time, θ	min/s	___/___	___/___
	min	_____	_____
Orifice man. rdg., Δ H	mm (in.) H_2O	_____	_____
Bar. pressure, P_{bar}	mm (in.) Hg	_____	_____
Ambient temperature, t_{amb}	°C (°F)	_____	_____
Pump vacuum	mm (in.) Hg	_____	_____
$V_{m(std)}$ m^3 (ft^3)	_____	_____	
$V_{cr(std)}$	m^3 (ft^3)	_____	_____
DGM cal. factor, Y		_____	_____

Figure 2.4. Data sheet for determining DGM Y factor.

Using the Critical Orifices as Calibration Standards—The dry-gas meter is calibrated using the critical orifices as the secondary standard as follows:

1. Record the barometric pressure.
2. Calibrate the metering system according to the procedure outlined in Sections 7.2.2.2.1 to 7.2.2.2.5. Record the information listed in Figure 2.5.
3. Calculate the standard volumes of air passed through the DGM and the critical orifices and calculate the DGM calibration factor, Y, using the equations below:

$$V_{m(std)} = K_1 V_m [P_{bar} + (\Delta H/13.6)]/T_m \qquad \text{Equation 2-4}$$

$$V_{cr(std)} = K' (P_{bar}\ \theta)/T_{amb}^{1/2} \qquad \text{Equation 2-5}$$

$$Y = V_{cr(std)}/V_{m(std)} \qquad \text{Equation 2-6}$$

where:

$V_{cr(std)}$ = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dscm (dscf).

K' = 0.3858 °K/mm Hg for metric units
= 17.64 °R/in. Hg for English units.

4. Average the DGM calibration values for each of the flow rates. The calibration factor, Y, at each of the flow rates should not differ by more than ± 2% from the average.

Recalibration of critical orifices—To determine the need for recalibrating the critical orifices, compare the DGM Y factors obtained from two adjacent orifices each time a DGM is calibrated. For example, when checking orifice 13/2.5, use orifices 12/10.2 and 13/5.1. If any critical orifice yields a DGM Y factor differing by more than 2% from the others, recalibrate the critical orifice according to the initial calibration procedures above.

2.1.4 *Sample Meter System*—The sample meter system—consisting of the pump, vacuum gauge, valves, orifice meter, and dry-gas meter—should be calibrated by stringent laboratory methods before it is used in the field. The calibration should be re-checked after each field test series. This re-check is designed to provide testers with a method that can be used more often and with less effort, to ensure that the calibration has not changed. When the quick check indicates that the calibration factor has changed, testers must again use the complete laboratory procedure to obtain the new calibration factor. After recalibration, the metered sample volume must be multiplied by either the initial or the recalibrated calibration factor—that is, the one that yields the lower gas volume for each test run.

Date _____ Train ID _____ DGM cal. factor _____

Critical orifice ID _____

		Run number 1	2
Dry-Gas Meter			
Final reading	m^3 (ft^3)		
Initial reading	m^3 (ft^3)		
Difference, V_m	m^3 (ft^3)		
Inlet/outlet temperatures			
Initial	°C (°F)	/	/
Final	°C (°F)	/	/
Avg. temperature, t_m	°C (°F)		
Time, θ	min/s	/	/
	min		
Orifice man. rdg., ΔH	mm (in.) H_2O		
Bar. pressure, P_{bar}	mm (in.) Hg		
Ambient temperature, t_{amb}	°C (°F)		
Pump vacuum	mm (in.) Hg		
K′ factor			
Average			

Figure 2.5. Data sheet for determining K′ factor.

Before calibrating the metering system for the first time, conduct a leak check. The meter system should be leak-free. Both positive (pressure) and negative (vacuum) leak checks should be performed. The following pressure leak check procedure will check the metering system from the quick-connect inlet to the orifice outlet and will check the orifice-inclined manometer:

1. Disconnect the orifice meter line from the downstream orifice pressure tap (the one closest to the exhaust of the orifice); plug this tap (Figure 2.1).
2. Vent to the atmosphere the negative side of the inclined manometer. If the inclined manometer is equipped with a three-way valve, this step can be performed by turning the valve on the negative side of the orifice-inclined manometer to the vent position.
3. Place a one-hole rubber stopper with a tube through its hole into the exit of the orifice; connect a piece of rubber or plastic tubing, as shown in Figure 2.1.
4. Open the positive side of the orifice-inclined manometer to the "reading" position; if the inclined manometer is equipped with a three-way valve, this will be the line position.
5. Plug the inlet to the vacuum pump. If a quick-connect with a leak-free check valve is used on the control module, the inlet will not have to be plugged.
6. Open the main valve and the bypass valve.
7. Blow into the tubing connected to the end of the orifice until a pressure of 127 to 178 mm (5 to 7 in.) H_2O has built up in the system.
8. Plug or crimp the tubing to maintain this pressure.
9. Observe the pressure reading for a 1-min period. No noticeable movement in the manometer fluid level should occur. If the meter box has a leak, a bubbling-type leak check solution may aid in locating it.

After the metering system is determined to be leak-free by the positive leak check procedure, the vacuum system to and including the pump should be checked by plugging the air inlet to the meter box. If a quick-connect with a leak-free stopper system is presently on the meter box, the inlet will not have to be plugged. Turn the pump on, pull a vacuum within 7.5 cm (3 in.) Hg of absolute zero, and observe the dry-gas meter. If the leakage exceeds 0.00015 m^3/min (0.005 ft^3/min), the leak(s) must be found and minimized until the above specifications are satisfied.

Checking the meter system for leaks before initial calibration is not mandatory, but it is recommended.

Note: For metering systems with diaphragm pumps, the normal leak check procedure described above will not detect leakages within the pump. For these cases, the following leak check procedure is suggested: Make a 10-min calibration run at 0.00057 m^3/min (0.02 ft^3/min); at the end of the run, take the difference between the measured wet-test meter and the dry-gas meter volumes; divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 ft^3/min).

Initial calibration—The dry-gas meter and the orifice meter can be calibrated simultaneously and should be calibrated when first purchased and any time the posttest check yields a Y outside the range of the calibration factor Y +0.05 Y. A calibrated wet-test meter (of proper size, with +1% accuracy) should be used to calibrate the dry-gas meter and the orifice meter. The dry-gas meter and the orifice meter should be calibrated in the following manner:

1. Before its initial use in the field, leak check the metering system. Leaks, if present, must be eliminated before proceeding.
2. Assemble the apparatus, as shown in Figure 2.6, with the wet-test meter replacing the probe and impingers--that is, with the outlet of the wet-test meter connected to a needle valve that is connected to the inlet side of the meter box.
3. Run the pump for 15 min with the orifice meter differential (ΔH) set at 12.7 mm (0.5 in.) H_2O to allow the pump to warm up and to permit the interior surface of the wet-test meter to be wetted.
4. Adjust the needle valve so that the vacuum gauge on the meter box is between 50 and 100 mm (2 to 4 in.) Hg during calibration.
5. Collect the information required on the forms provided (Figure 2.7). Sample volumes, as shown, should be used.
6. Calculate Y_i for each of the six runs, using the equation in Figure 2.7 under the Y_i column, and record the results on the form in the space provided.
7. Calculate the average Y (calibration factor) for the six runs using the following equation:

$$Y = \frac{Y1 + Y2 + Y3 + Y4 + Y5 + Y6}{6}$$ Equation 2-7

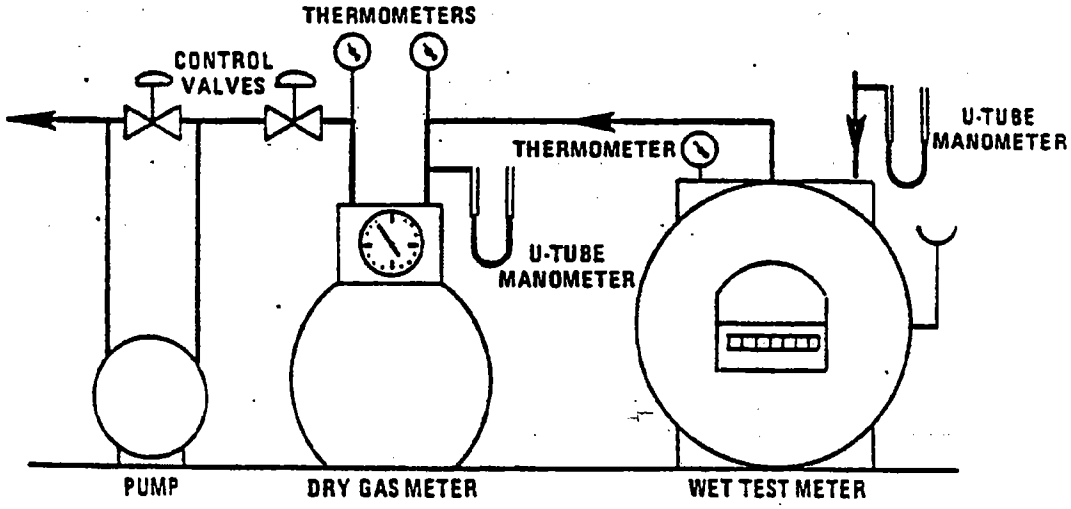


Figure 2.6. Equipment arrangement for dry-gas meter calibration.

Date _____ Meter box number _____

Barometric pressure, P_b = _____ in. Hg Calibrated by _____

Orifice manometer setting (ΔH), in. H_2O	Gas volume		Temperatures				Time (θ), min	Y_i	$\Delta H@$, in. H_2O
				Dry-gas meter					
	Wet-test meter (V_w), ft^3	Dry-gas meter (V_d), ft^3	Wet-test meter (t_w), °F	Inlet (t_{di}), °F	Outlet (t_{do}), °F	Avg[3] (t_d) °F			
0.5	5								
1.0	10								
1.5	10								
2.0	10								
3.0	10								
4.0	10								
							Avg		

ΔH, in. H_2O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 460)}{V_d \left(P_b + \frac{\Delta H}{13.6}\right)(t_w + 46)}$	$\Delta H@_i = \frac{0.0317\ \Delta H}{P_b\ (t_d + 460)} \left[\frac{(t_w + 460)\theta}{V_w}\right]^2$
0.5	0.0368		
1.0	0.0737		
1.5	0.110		
2.0	0.147		
3.0	0.221		
4.0	0.294		

[a] If there is only one thermometer on the dry-gas meter, record the temperature under t_d.

Figure 2.7. Dry-gas meter calibration data (English units, front side).

Nomenclature:

V_w = Gas volume passing through the wet-test meter, ft^3.

V_d = Gas volume passing through the dry-gas meter, ft^3.

t_w = Temperature of the gas in the wet-test meter, °F.

t_{di} = Temperature of the inlet gas of the dry-gas meter, °F.

t_{do} = Temperature of the outlet gas of the dry-gas meter, °F.

t_d = Average temperature of the gas in the dry-gas meter, obtained by the average t_{di} and t_{do} , °F.

ΔH = Pressure differential across orifice, in. H_2O.

Y_i = Ratio of accuracy of wet-test meter to dry-gas meter for each run. Tolerance $Y_i = Y \pm 0.02\ Y$.

Y = Average ratio of accuracy of wet-test meter to dry-gas meter for all six runs. Tolerance $Y = Y \pm 0.01\ Y$.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives 0.75 ft^3/min of air at standard conditions for each calibration run, in of H_2O. Tolerance = $\Delta H@ \pm 0.15$ (recommended).

$\Delta H@$ = Average orifice pressure differential that gives 0.75 ft^3/min of air at standard conditions for all six runs, in. H_2O. Tolerance = 1.84 ± 0.25 (recommended).

θ = Time for each calibration run, min.

P_b = Barometric pressure, in. Hg.

Figure 2.7. Dry-gas meter calibration data (English units, backside).

Record the average on Figure 2.7 in the space provided.

8. Clean, adjust, and recalibrate, or reject the dry-gas meter if one or more values of Y fall outside the interval Y ± 0.02 Y. Otherwise, the average Y is acceptable and should be used for future checks and subsequent test runs.
9. Calculate $\Delta H@_i$ for each of the six runs using the equation in Figure 2.7A or 2.7B under the $\Delta H@_i$ column, and record on the form in the space provided.
10. Calculate the average ΔH@ for the six runs using the following equation:

$$\Delta H@ = \frac{\Delta H@1 + \Delta H@2 + \Delta H@3 + \Delta H@4 + \Delta H@5 + \Delta H@6}{6} \qquad \text{Equation 2-8}$$

Record the average on Figure 2.7 in the space provided.

11. Adjust the orifice meter or reject it if $\Delta H@_i$ varies by more than ± 3.9 mm (0.15 in.) H_2O over the range of 10 to 100 mm (0.4 to 4.0 in.) H_2O. Otherwise, the average ΔH@ is acceptable and should be used for subsequent test runs.

Posttest calibration check—After each field test series, conduct a metering-system calibration check, as specified in Subsection 2.1.4, except for the following variations:

1. Three calibration runs at a single intermediate orifice meter setting may be used with the vacuum set at a maximum value reached during the test series. The single intermediate orifice meter setting should be based on the previous field test. A valve must be inserted between the wet-test meter and the inlet of the metering system to adjust the vacuum.
2. If a temperature-compensating dry-gas meter was used, the calibration temperature meter must be within ± 6 °C (10.8 °F) of the average meter temperature during the test series.
3. Use Figure 2.8 to record the required information.

If the calibration factor Y deviates by <5% from the initial calibration factor Y, then the dry-gas meter volumes obtained during the test series are acceptable. If Y deviates by >5%, recalibrate the metering system and use whichever meter coefficient (initial or recalibrated) yields the lowest gas volume for each test run.

Alternate procedures (e.g., using the orifice meter coefficients or critical orifices) may be used.

Date _____ Metering System ID No. _____

Barometric pressure, P_b = _____

Orifice manometer setting ΔH in. Hg	Spirometer (wet test) gas volume (V_w) ft³	Dry-gas meter volume (V_m) ft³	Temperatures: Spirometer (wet meter) (t_w) °F	Temperatures: Dry-gas meter: Inlet (t_i) °F	Temperatures: Dry-gas meter: Outlet (t_o) °F	Temperatures: Dry-gas meter: Avg (t_m) °F	Time (Θ) min

Calculations

ΔH in H_2O	Yi: $\frac{V_w P_b (t_m + 460)}{V_m [P_b + \frac{\Delta H}{13.6}] (t_w + 460)}$	ΔH@ᵢ: $\frac{0.0317 \Delta H}{P_b (t_o + 460)} [\frac{(t_w + 460)}{V_w}]^2$
Average		

Y = Ratio of reading of wet-test meter to dry-gas meter; tolerance for individual values ± 0.02 from average.

ΔH@ = Orifice pressure differential that equates to 0.75 cfm of air @ 68 and 29.92 in. of Hg, in. H_2O; tolerance for individual values ± 0.[illegible] for average.

Figure 2.8. Example data sheet for calibration of metering system (English units).

2.2 Temperature Gauges

2.2.1 *Impinger Thermometer*—The thermometer used to measure the temperature of the gas leaving the impinger train should initially be compared with a mercury-in-glass thermometer that meets ASTM E-1 No. 63C or 63F specifications. This procedure is as follows:

1. Place both the reference thermometer and the test thermometer in an ice bath. Compare readings after they stabilize.
2. Remove the thermometers from the bath and allow both to come to room temperature. Again, compare readings after they stabilize.
3. Accept the test thermometer if its reading agrees to within 1 °C (2 °F) of the reference thermometer reading at both temperatures. If the difference is greater than 1 °C (2 °F), the thermometer should be adjusted and recalibrated until the criteria are met, or it should be rejected. Record the results on Figure 3.1 of Section 3.19.3.

2.2.2 *Dry-gas Thermometers*—The thermometers used to measure the metered gas sample temperature should be compared initially with a mercury-inglass thermometer as above, using a similar procedure.

1. Place the dial type (or equivalent) thermometer and the mercury-in-glass thermometer in a hot water bath, 40 to 50 °C (104 to 122 °F). Compare the readings after they stabilize.
2. Allow both thermometers to come to room temperature. Compare readings after thermometers stabilize.
3. Users should accept the dial type (or equivalent) thermometer under the following conditions: The values must agree to within 3 °C (5.4 °F) at both points; the temperature differentials at both points are within 3 °C (5.4 °F), and the temperature differential is taped to the thermometer and recorded on the pretest sampling check form (Figure 3.1).
4. Prior to each field trip, compare the temperature reading of the mercury-in-glass thermometer at room temperature with that of the meter system thermometer. The values or corrected values should be within 6 °C (10.8 °F) of one another, or the meter thermometer should be replaced or recalibrated. Record any temperature correction factors on Figure 3.1 of Section 3.19.3 or on a similar form.

2.2.3 *Stack Temperature Sensor*—The stack temperature sensor should be calibrated upon receipt or checked before field use. Each sensor should be uniquely marked for identification. The calibration should be performed at three points and then extrapolated over the range of temperatures anticipated during actual sampling. For the three-point calibration, a reference ASTM mercury-in-glass thermometer should be used.

The following procedure is recommended for calibrating stack temperature sensors (thermocouples and thermometers) for field use.

1. For the ice-point calibration, form a slush from crushed ice and liquid water (preferably deionized, distilled) in an insulated vessel such as a Dewar flask. Taking care that they do not touch the sides of the flask, insert the stack temperature sensors into the slush to a depth of at least 2 in. Wait 1 min to achieve thermal equilibrium and record the readout on the potentiometer. Obtain three readings taken at 1-min intervals.

   Note: Longer times may be required to attain thermal equilibrium with thick-sheathed thermocouples.

2. Fill a large Pyrex beaker with water to a depth >4 in. Place several boiling chips in the water and bring the water to a full boil using a hot plate as the heat source.

   Insert the stack temperature sensor(s) in the boiling water to a depth of at least 2 in., taking care not to touch the sides or bottom of the beaker.

   Place an ASTM reference thermometer alongside the sensor(s). If the entire length of the mercury shaft in the thermometer cannot be immersed, a temperature correction will be required to give the correct reference temperature.

   After 3 min, both instruments will attain thermal equilibrium. Simultaneously record temperatures from the ASTM reference thermometer and the stack temperature sensor three times at 1-min intervals.

3. For thermocouple, repeat Step 2 with a liquid (such as cooking oil) that has a boiling point in the 150 to 250 °C (300 to 500 °F) range. Record all data on Figure 2.9. For thermometers other than thermocouples, repeat Step 2 with a liquid that boils at the maximum temperature at which the thermometer is to be used, or place the stack thermometer and reference thermometer in a furnace or other device to reach the required temperature.

   Note: If the thermometer is to be used at temperatures higher than the reference thermometers can record, the stack thermometer may be calibrated with a thermocouple previously calibrated with the above procedure.

4. If the absolute values of the reference thermometer and thermocouple(s, agree to within 1.5% at each of the three calibration points, plot the data on linear graph paper and draw the best-fit line to the three points or calculate the constants of the linear equation using the least-square method. The data may be extrapolated above and below the calibration points to cover the entire manufacturer's suggested range for the thermocouple. For the portion of the plot or equation that agrees within 1.5% of the absolute reference temperature, no correction need be made. For all portions that do not agree within 1.5%, use the plot or equation to correct the data.

   If the absolute values of the reference thermometer and stack temperature sensor (other than the thermocouple) agree to within 1.5% at each of the three points, the thermometer may be used over the range of calibration points for testing without applying any correction factor. The data cannot be extrapolated outside the calibration points.

Date _____ Thermocouple No. _____

Ambient temperature _____ °F Barometric pressure _____ in. Hg

Calibration person _____ Reference: mercury-in-glass _____ °F
other _____ °F

Reference point number	Source[a] (specify)	Reference thermometer temperature, °F	Thermocouple potentiometer temperature, °F	Temperature[b] difference, %

[a] Type of calibration system used.

[b] $\frac{(ref\ temp,\ °F + 460) - (test\ thermom\ temp,\ °F + 460)}{ref\ temp,\ °F + 460} \times 100 =$ (<1.5%)

Figure 2.9. Stack temperature sensor calibration data form.

2.3 Probe Heater

The probe heating system should be calibrated prior to field use according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the curves of APTD-0576 are used.

2.4 Barometer

The field barometer should be adjusted initially and before each test series to agree to within 2.5 mm (0.1 in.) Hg of the mercury-inglass barometer or with the station pressure value reported by a nearby National Weather Service station, corrected for elevation. The correction for elevation difference between the station and the sampling point should be applied at a rate of -2.4 mm Hg/30 m (-0.1 in. Hg/100 ft). Record the results on the pretest sampling check form (Figure 3.1 of Section 3.19.3).

2.5 Probe Nozzle

Probe nozzles should be calibrated before initial use in the field. Using a micrometer, measure the ID of the nozzle to the nearest 0.025 mm (0.001 in.). Make three measurements using different diameters each time, and obtain the average. The difference between the high and the low numbers should not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they should be reshaped, sharpened, and recalibrated before use. Each nozzle should be permanently and uniquely identified. Figure 2.10 is an example of a nozzle calibration data form.

2.6 Pitot Tube

The Type S pitot tube assembly should be calibrated using the procedure outlined in Section 3.1.2 of this Handbook for Method 2.

2.7 Trip Balance

The trip balance should be calibrated initially by using Class S standard weights and should be within 0.5 g of the standard weight. Adjust or return the balance to the manufacturer if limits are not met.

Date _____ Calibrated by _____

Nozzle ID No.	Nozzle Diameter[a] D_1 mm (in.)	D_2 mm (in.)	D_3 mm (in.)	ΔD[b] mm (in.)	D_{avg}[c] mm (in.)

where:

[a] $D_{1,2,3}$ = Three different nozzle diameters, mm (in.); each diameter must be measured within (0.025 mm) 0.001 in.

[b] ΔD = Maximum difference between any two diameters, mm (in.), $\Delta D \leq$(0.10 mm) 0.004 in.

[c] D_{avg} = Average of D_1, D_2, and D_3.

Figure 2.10. Nozzle calibration data form.

TABLE 2.1. ACTIVITY MATRIX FOR EQUIPMENT CALIBRATION

Apparatus	Acceptance limits	Frequency & method of measurement	Action if requirements are not met
Wet-test meter	Capacity ≥3.4 m^3/h (120 ft^3/h); accuracy within ± 1.0%	Calibrate initially, and then yearly by liquid displacement	Adjust until specifications are met, or turn to manufacturer
Dry-gas meter	$Y_i = Y \pm 0.02\ Y$	Calibrate vs. wet-test meter initially, and when posttest check exceeds Y ± 0.05 Y	Repair, or replace and then recalibrate
Critical	$K' = K \pm 0.03\ K'$	Calibrate vs. wet, dry, or bubble meter upon receipt and after each test	Repair and then recalibrate, or replace
Thermo-meter	Impinger thermo-meter ± 1 °C (2 °F); dry-gas meter thermometer ± 3 °C (5.4 °F) over range; stack temperature sensor ± 1.5% of absolute temperature	Calibrate each initially as a separate component against a mercury-in-glass thermometer; then before each trip compare each as part of the train with the mercury-in-glass thermometer	Adjust; determine a constant correction factor; or reject
Probe heating system	Capable of maintaining 120 °C ± 14 °C (248° ± 25 °F) at a flow rate of 20 L/min (0.71 ft^3/min	Calibrate component initially by APTD-0576; if constructed by APTD-0581, or use published calibration curves	Repair, or replace and then reverify the calibration
Barometer	± 2.5 mm (0.1 in.) Hg of mercury-in-glass barometer	Calibrate initially vs. mercury-in-glass barometer; check before and after each field test	Adjust to agree with a certified barometer

(Continued)

TABLE 2.1. (Continued)

Apparatus	Acceptance limits	Frequency & method of measurement	Action if requirements are not met
Probe nozzle	Average of three ID measurements of nozzle; difference between high and low ≤0.1 mm (0.004 in.)	Use a micrometer to measure to nearest 0.025 mm (0.001 in.)	Recalibrate, reshape, and sharpen when nozzle becomes nicked, dented corroded
Trip balance	500-g capacity; capable of measuring within ± 0.5 g	Check with standard Class S weights upon receipt	Adjust, replace or return to manufacturer

3.0 PRESAMPLING OPERATIONS

This section addresses preparing and packing sampling supplies and equipment. The pretest preparations form (Figure 3.2 of Method 5, Section 3.4.3) can be used as an equipment checklist, a status form, and a packing list for Methods 1-4 and Method 101A. The (QA) activities for the presampling operations are summarized in Table 3.1 at the end of this section.

A pretest check will have to be made on most of the sampling apparatus. Figure 3.1 should be used to record the pretest calibration checks. A schematic of the EPA Method 101A sampling train is shown in Figure 1.1. Commercial models of this system are available. Each train must be in compliance with the specifications of the reference method, Section 3.19.10.

3.1 Apparatus Check and Calibration

3.1.1 *Nozzles and Probe Liners*—The probe's heating system should be checked to see that it is operating properly. The probe should be sealed at the inlet or tip and checked for leaks at a vacuum of 380-mm (15 in.) Hg, and the probe must be leak-free under these conditions. The nozzles should be calibrated using the procedures in Subsection 2.5 of Section 3.19.2. Clean the probe and the nozzle's internal surfaces using the procedures described above in Section 3.2. The ends of the probe and the ends of the nozzle should be sealed with a Teflon film.

3.1.2 *Filter Holder, Impingers, and Other Glassware*—Ensure that all glass meets the specifications described in Subsection 1 of Section 3.19.1, has been cleaned according the procedures described below, and is sealed with a Teflon film or glass stoppers.

Clean all sample-exposed glassware with the following procedures:

1. Soak glassware in 50% HNO_3 for a minimum of 1 h.
2. Rinse with tap water.
3. Rinse with 8 N HCl.
4. Rinse with tap water.
5. Rinse with DI water.

3.1.3 *Dry-Gas Meter*—A dry-gas meter calibration check should be made using the procedure in Section 3.19.2.

3.1.4 *Filters*—Check for flaws and store.

3.1.5 *Silica Gel*—Either dry the used silica gel at 175 °C (350 °F) or use fresh silica gel and weigh several 200- to 300-g portions in airtight containers to the nearest 0.5 g. Record the total weight (silica gel plus container) for each container. The silica gel does not have to be weighed if the moisture content is not to be determined.

3.1.6 *Thermometers*—The thermometers should be compared to the mercury-in-glass reference thermometer at ambient temperature.

Date _____ Calibrated by _____
Method box number _____ ΔH@ _____

Dry-Gas Meter[a]
Pretest calibration factor Y _____ (within 2% of the average factor for each calibration run).

Impinger Thermometer
Was a pretest temperature correction used? _____yes _____no
If yes, temperature correction _____ (within 3 °C (5.4 °F) over range)

Stack Temperature Sensor[a]
Was a stack temperature sensor calibrated against a reference thermometer? _____ yes _____no
If yes, give temperature range with which the readings agreed within 1.5% of reference value _____ to _____ °K (°R).

Barometer
Was the pretest field barometer reading correct? _____yes _____no (within 2.5-mm (0.1 in.) Hg of the mercury-in-glass barometer).

Nozzle[a]
Was the nozzle calibrated to the nearest 0.025-mm (0.001 in.)?
_____yes _____no.

[a]Most significant items/parameters to be checked.

Figure 3.1. Pretest sampling checks.

3.1.7 *Barometer*—The field barometer should be compared with the mercury-in-glass barometer or the weather station reading, after making an elevation correction, prior to each field trip.

3.2 Sample Recovery Equipment and Reagents

Clean all sample exposed-glassware using the following procedures:

1. Soak glassware in 50% HNO_3 for a minimum of 1 h.
2. Rinse with tap water.
3. Rinse with 8 N HCl.
4. Rinse with tap water.
5. Rinse with DI water.

3.2.1 *Glass Sample Bottles*—The sample bottles must be leak-free, must gave Teflon-lined caps, and must be 1000 and 100 mL in size.

3.2.2 *Graduated Cylinder*—A 250-mL graduated cylinder is required.

3.2.3 *Funnel and Rubber Policeman*—These items aid in transferring the silica gel to the container; they are not necessary if the silica gel is weighed in the field.

3.2.4 *Funnel*—A glass funnel is required to aid in sample recovery.

3.3 Equipment Packing

The accessibility, condition, and functioning of measurement devices in the field depend on packing them carefully and on moving them carefully at the site. Equipment should be packed to withstand severe treatment during shipping and field operations. The material used to construct shipping cases is therefore important. The following containers are suggested, but they are not mandatory.

3.3.1 *Probe*—Seal the inlet and outlet of the probe to protect it from breakage and pack it in the container. An ideal container is a wooden case (or the equivalent) lined with foam material and having separate compartments to hold the individual probes. The case should have handles or eye-hooks that can withstand hoisting and that are rigid enough to prevent bending or twisting during shipping and handling.

3.3.2 *Impingers, Connectors, and Assorted Glassware*—All impingers and glassware should be packed in rigid containers and protected by polyethylene or other suitable material. Individual compartments for glassware will help to organize and protect each piece.

3.3.3 *Volumetric Glassware*—A sturdy case lined with foam material can contain drying tubes and assorted volumetric glassware.

3.3.4 *Meter Box*—The meter box, which contains the manometers, orifice meter, vacuum gauge, pump, dry-gas meter, and thermometers, should be packed in a shipping container unless its housing is sufficient to protect components during travel. Additional pump oil should be packed if oil is required. A spare meter box should be included in case of failure.

3.3.5 *Wash Bottles and Storage Containers*—Storage containers and miscellaneous glassware should be packed in a rigid, foam-lined container.

3.3.6 *Chemicals*—Chemicals should be packed in a rigid, foam-lined container.

As mentioned in Subsection 1.5.1.6 (Absorbing Solution, 4% $KMnO_4$), caution must be exercised for the storage and transport of $KMnO_4$. To prevent autocatalytic decomposition of the permanganate solution, filter it through Whatman 541 filter paper. The reaction of the $KMnO_4$ with the acid may cause pressure buildup in the sample storage bottle. These bottles should not be filled to capacity and should be vented to relieve excess pressure and to prevent explosion of the sample. A No. 70-72 hole drilled in the container cap and Teflon liner is recommended.

Also, caution should be exercised with the HCl reagent because it is highly corrosive.

3.3.7 *Safety Equipment for Sampling Train Preparation and Sample Recovery*—Safety glasses and protective laboratory gloves should be packed for the personnel assigned to prepare the sampling train and recover the sample. Serious injury can result from contact with HCl and $KMnO_4$.

TABLE 3.1 ACTIVITY MATRIX FOR PRESAMPLING OPERATIONS

Apparatus	Acceptance limits	Frequency & method of measurement	Action if requirements are not met
Apparatus Check and Calibration			
Nozzles and probe liners	1. Probe heating system capable of heating to 120 °C ± 14 °C at a flow rate of 20 L/min	1. Check heating system initially and when moisture cannot be prevented during testing	1. Repair or replace
	2. Probe leak free at 380-mm (15 in.) Hg	2. Visually check before test	2. Replace
	3. Nozzles calibrated (Sec. 3.19.2 Subsec. 2.4)	3. Before test to nearest 0.025-mm with micrometer	3. Recalibrate, reshape, or replace
	4. Probe and nozzle free of contaminants (Sec. 3.2)	4. Clean internally by brushing with tap water, deionized distilled water, and acetone; air dry before test	4. Repeat cleaning and assembly procedures
Impingers, filter holders, and other glassware	Meets specifications in Subsec. 1 of Sec. 3.19.1; cleaned according to Sec. 3.19.3 Subsec. 3.1.2; and sealed with Teflon or glass stoppers	Before each test	Repair or discard and replace
Dry-gas meter	Clean and readings within 2% of average calibration factor	Calibrate according to Sec. 3.19.2	Repair or replace and then recalibrate
Filters	Free of irregularities	Visually check prior to testing	Replace

(Continued)

TABLE 3.1 (Continued)

Apparatus	Acceptance limits	Frequency & method of measurement	Action if requirements are not met
Silica gel	Indicating, 6-16 mesh, use fresh- or dry-used silica gel at 175 °C (350 °F)	If moisture content is to be determined, weigh several 200- to 300-g portions of silica gel (± 0.5 g); use airtight containers; record weight of container plus silica gel	Replace or reweigh
Thermo-meters	Calibrated, within 1 °C (2 °F) for impinger thermo-meter, ± 3 °C (5.4 °F) for dry-gas meter thermometer	Calibrate against mercury-in-glass thermometer (Sec. 3.4.2) before each	Replace
Barometer	Calibrated, within 2.5-mm (0.1 in.) Hg	Calibrate against mercury-in-glass barometer (Sec. 3.7.2) before each test	Replace
Sample Recovery Equipment and Reagents			
Glass sample bottles	Clean, leakless, Teflon-lined caps	Before each field test	Replace
Graduated cylinder	Clean, glass and class A; 250 mL with ≤2 mL subdivisions	Before each field trip check for cracks, breaks, and manufacturer flaws	Replace
Funnel	Clean, glass, Class A	Same as above	Same as above

(Continued)

TABLE 3.1 (Continued)

Apparatus	Acceptance limits	Frequency & method of measurement	Action if requirements are not met
Equipment packing			
Probe	Rigid container protected by polyethylene foam	Prior to each shipment	Repack
Impingers, connectors, and assorted glassware	Rigid container protected by polyethylene foam	Prior to each shipment	Repack
Volumetric glassware	Packed in original containers, if available, or a rigid container lined with foam and marked "Fragile"	Prior to each shipment	Repack
Meter box	Meter box case and/or additional material to protect train components; pack spare-meter box	Prior to each shipment	Repack
Wash bottles and storage containers	Rigid foam-lined container	Prior to each shipment	Repack
Chemicals	Rigid foam-lined container	Prior to each shipment	Repack

4.0 ON-SITE MEASUREMENTS

On-site activities include transporting the equipment to the test site, unpacking and assembling the equipment, sampling for particulate and gaseous mercury, and recording the data. The associated QA activities are summarized in Table 4.1 at the end of this section.

4.1 Transport of Equipment to the Sampling Site

The most efficient means of transporting the equipment from ground level to the sampling site (often above ground level) should be decided during the preliminary site visit or by prior correspondence. Care should be taken to prevent damage to the equipment or injury to test personnel during the moving. A clean "laboratory type" area free of excessive dust and mercury compounds should be located and designated for preparing the nozzle, probe, filter holder, and impingers and for sample recovery.

4.2 Preliminary Measurements and Setup

A preliminary survey should be conducted prior to sampling and analysis, unless adequate prior knowledge of the source is available. Testing must be conducted at the proper sampling locations and during the proper process and control equipment operating cycles or periods. Testers should refer to Subsection 3.19.3.1 for information typically needed to establish the proper sampling and analysis protocol.

Testers should have calculated the minimum sampling run time required, unless it is known that the minimum time stated by the applicable regulations will be sufficient to provide proof of compliance.

In this method, highly oxidizable matter may make it impossible to sample for the desired minimum time. This problem is indicated by the complete bleaching of the purple color of the $KMnO_4$ solution. In these cases, testers may divide the sample run into two or more subruns to ensure that the absorbing solution will not be depleted. In cases where excess water condensation is encountered, collect two runs to make one sample.

4.2.1 *Preliminary Measurements and Setup*—The sampling site should be selected in accordance with Method 1. If the duct configuration or some other factor makes this impossible, the site should be approved by the Administrator prior to conducting the test. A 115-V, 30-A electrical supply is necessary to operate the standard sampling train. Either measure the stack and determine the minimum number of traverse points by Method 1, or check the traverse points determined during the preliminary site visit (Section 3.0). Record all data on the traverse point location form shown in Method 1. These measurements will be used to locate the pitot tube and the sampling probe during preliminary measurements and actual sampling.

4.3 Preparations for Sampling

The most common situations and problems are addressed in this section. Both required and recommended QA/control checks and procedures are provided to assist in collecting data of acceptable quality and to assess the accuracy of the sampling and analysis.

On-site sampling includes the following steps:

1. Conducting preliminary measurements and setting up the recovery area.
2. Preparing and setting up the sampling system for leaks.
3. Connecting electrical service and checking the sampling system for leaks.
4. Heating the probe and filter to the proper temperature.
5. Inserting the probe into the duct and sealing the duct.
6. Isokinetic sampling.
7. Recording data.
8. Posttest leak check of the sampling system.
9. Recovering the sample and transporting it to the laboratory.

4.3.1 *Stack Parameters*—Check the sampling site for cyclonic or nonparallel flow as described in Method 1 (Section 3.0). The sampling site must be acceptable before a valid sample can be taken. Determine the stack pressure, temperature, and the range of velocity heads encountered (Method 2). Determine the moisture content using the approximation Method 4, or its alternatives, for the purpose of setting the isokinetic sampling rate. If the identical source has been tested before or if a good estimate of the moisture content is available, this should be sufficient. The reference method (Section 3.4.10) uses the condensate collected during sampling to determine the moisture content used in final calculations. If the stack is saturated with moisture or has water droplets, the moisture content must also be determined by partial pressure with the use of a more accurate stack gas temperature sensor (Method 4).

Determine the dry molecular weight of the stack gas, as required in Method 2. If an integrated gas sample is required, follow Method 3 procedures and take the gas sample simultaneously with, and for the same total length of time, as the particulate run. The sampling and the analytical data forms for molecular weight determinations are in Method 3.

Using the stack parameters obtained by these preliminary measurements, the tester can set up the nomograph as outlined in APTD-0576 or use a calculator. An example of a nomograph data form is shown in Figure 4.1 of the Method 5, Section 3.4.4.

Select a nozzle size based on the range of velocity heads, so that it is not necessary to change the size to maintain isokinetic sampling rates during the run. Install the selected nozzle using a Viton A O-ring when glass liners are used. Other connecting systems such as Teflon ferrules may be used. Mark the probe with heat resistant tape or by some other acceptable method to denote the proper distance into the stack or duct for each sampling point. Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry so that:

1. The sampling time per point is >2 min (a greater time interval may be specified by the Administrator).
2. The sample volume corrected to standard conditions exceeds the required minimum total gas sample volume.

The latter can be based on an approximate average sampling rate. It is recommended that the number of minutes sampled at each point be either an integer or an integer plus one-half minute to avoid timekeeping errors. In some circumstances (e.g., batch cycles), it may be necessary to sample for shorter times at the traverse

points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must be obtained first.

4.3.2 *Sampling Train Preparation*—During preparation of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling commences. The glassware should have been cleaned as described in Section 3.19.3 by soaking in 50% HNO_3 and then rinsing with tap water, 8 N HCl, tap water, and finally deionized distilled water. Prepare the individual sampling train components as follows:

Impingers

1. Place 50 ml of fresh 4% $KMnO_4$ in the first cleaned impinger using a graduated cylinder that has been properly cleaned,
2. Place 100 ml of fresh 4% $KMnO_4$ in the second and third impingers using a graduated cylinder, and
3. Place 200 to 300 g of preweighed silica gel in the fourth impinger.

Precaution: It is extremely important that all sample recovery personnel wear safety glasses and gloves due to the dangers associated with impinger solutions and recovery solutions.

Record the weight of the silica gel and the container on the sample recovery data form, Figure 4.1, or other similar data form. Place the empty container in a safe place for use later in the sample recovery. If moisture content is to be determined by impinger analysis, weigh each of the first three impingers to the nearest 0.5 g, and record these weights. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

Plant _____ Sample Data _____
Sample Location _____ Run No. _____
Sample Recovery Person _____ Recovery Date _____
Filter(s) No. _____

MOISTURE

Impingers

Final volume (wt)	_____ ml (g)	Final wt	_____ g	_____ g
Initial volume (wt)	_____ ml (g)	Initial wt	_____ g	_____ g
Net volume (wt)	_____ ml (g)	Net wt	_____ g	_____ g
Total moisture	_____ g			

RECOVERED SAMPLE BLANK

Blank filter Container No. _____ $KMnO_4$ added, sealed and level marked?_____
Blank $KMnO_4$ solution (650 mL) Container No. _____ Sealed and level marked? _____
Blank HCl solution (25 mL added to 200 mL H_2O) Container No. _____
Sealed and level marked? _____

RECOVERED SAMPLE

$KMnO_4$ impinger contents and rinse (400 mL) Container No._____
Sealed and level marked? _____
Filter Container No. _____ $KMnO_4$ added, sealed and level marked? _____

HCl solution (25 mL added to 200 mL H_2O) Container No. _____
Sealed and level marked? _____

Samples stored and locked? _____
Remarks: _____
_____
Date of laboratory custody _____
Laboratory person taking custody _____
Remarks: _____
_____

Figure 4.1. Sample recovery and integrity data form.

The use of a filter is optional in Method 101A. However, because of the digestion techniques used for sample preparation, it is highly recommended that a filter be used. Assemble the filter holder as follows:

Filter (optional)

1. Using a tweezer or clean disposable surgical gloves, place a filter in the filter holder. Be sure that the filter is properly centered and that the gasket is properly placed to prevent the sample gas stream from circumventing the filter.
2. Visually check the filter for damage after the assembly is completed.
3. The filter or filter sample container should be marked.

Record the filter number on the sample recovery data form and then place the filter sample container in a clean place for later use in the sample recovery.

Assemble the probe and nozzle as follows:

Probe/nozzle assembly

1. The probe liner should be glass and cleaned using the procedures described above.
2. Place the properly sized, calibrated, and cleaned nozzle on the inlet of the probe using a Teflon ferrule or Viton O-ring connection.

The nozzle should be uniquely identified. Record the nozzle number and diameter on the sampling data form.

4.3.3 *Sampling Train Assembly*—Assemble the train as shown in Figure 1.1, using (if necessary) a very light coat of silicone grease only on the outside of all ground-glass joints to avoid contamination. The tester may find that it is beneficial to conduct a leak check of the sampling train in the assembly area prior to taking the system to the stack.

The sampling train is then transported to the stack. At the stack, place crushed ice and water around the impingers. If not already an integral part of the probe assembly, a temperature sensor should be attached to the metal sheath of the sampling probe so that the sensor extends beyond the probe tip and does not touch any metal. The sensor's position should be about 1.9 to 2.54 cm (0.75 to 1 in) from the pitot tube and the nozzle to avoid interference with the gas flow. Alternative arrangements are shown in Method 2.

4.3.4 *Sampling Train Leak Checks*—Leak checks are necessary to assure that the sample has not been biased low by dilution air. The reference method (Section 3.19.10) specifies that leak checks be performed at certain times as discussed below.

Pretest—A pretest leak check is recommended, but not required. If the tester opts to conduct the pretest leak check, follow the procedure described below:

After the sampling train has been assembled, set the filter heating system at the desired operating temperature. Allow time for the temperature to stabilize. If a Viton A O-ring or other leak free gasket is used in connecting the probe nozzle to the probe liner, leak check the train at the sampling site by plugging the nozzle and pulling a 380- mm (15 in) Hg vacuum. Note: A lower vacuum may be used if it is not exceeded during the test.

If an asbestos string is used for the probe gasket, do not connect the probe to the train during the leak check. Instead, leak check the train by first plugging the inlet to the filter holder and pulling a 380-mm (15 in) Hg vacuum (see note in the previous paragraph). Then connect the probe to the train and leak check at about 25-mm (1 in.) Hg vacuum; alternatively, the probe may be leak checked with the rest of the sampling train in one step at a 380-mm (15 in.) Hg vacuum. Leakage rates >4% of the average sampling rate or 0.00057 m^3/min (0.02 ft^3/min), whichever is less, are unacceptable.

The following leak check instructions for the sampling train are taken from APTD-05813 and APTD-0576. Start the pump with the bypass valve fully open and the coarse adjust valve closed. Open the coarse adjust valve and then slowly close the bypass valve until the desired vacuum is reached. Do not reverse the direction of the bypass valve; this will cause $KMnO_4$ solution to back up from the impingers into the filter holder. If the desired vacuum is exceeded, either leak check at this higher vacuum or end the leak check as described below and start over.

When the leak check is complete, first slowly remove the plug from the inlet to the probe or the filter holder and then close the coarse adjust valve and immediately turn off the vacuum pump. (This prevents the $KMnO_4$ in the impingers from being forced back into the filter holder and prevents the silica gel from being forced back into the third impinger.) Visually check to be sure $KMnO_4$ did not contact the filter and that the filter has no tears before beginning the sampling.

During the Sampling—If a component (e.g., filter assembly or impinger) change is necessary during the sampling run, a leak-check should be conducted before the change. The leak-check should be done according to the procedure outlined above, except that it should be at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is <0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester either should record the leakage rate and plan to correct the sample volume as shown in Section 6.3(b) of the Reference Method (Section 3.19.10), or should void the sampling run. Note: Be sure to record the dry gas meter reading before and after each leak-check performed during and after each test run so that the sample volume can be corrected.

Posttest—A leak-check is mandatory at the conclusion of each sampling run. The leak-check should be in accordance with the procedures in this section and at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is <0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester either should record the leakage rate and correct the sample volume as shown in Section 6.3(a) or 6.3(b) of the Reference Method (Section 3.19.10), or should void the sample run. Note: Be sure to record the dry gas meter reading before and after performing the leak check so that the sample volume can be corrected.

4.3.5 *Sampling Train Operation*—Just prior to sampling, clean the portholes to minimize the chance of sampling deposited material. Verify that the probe and the filter heating systems are up to the desired temperatures and that the pitot tube and the nozzle are located properly. Follow the procedures below for sampling.

1. Record the initial dry gas meter readings, barometric pressure, and other data as indicated in Figure 4.2.
2. Position the tip of the probe at the first sampling point with the nozzle tip pointing directly into the gas stream. When in position, block off the open area around the probe and the porthole to prevent flow disturbances and unrepresentative dilution of the gas stream.
3. Turn on the pump and immediately adjust the sample flow to attain isokinetic conditions. Nomographs, calculator programs, and routines are available to aid in the rapid determination of the orifice pressure drop corresponding to the isokinetic sampling rate. If the nomograph is designed as shown in APTD-0576 it can be used only with an Type S pitot tube which has a C_p coefficient of 0.85 ± 0.02 and when the stack gas dry molecular weight (Ms) is 29 ± 4. If Cp and Ms are outside these ranges, do not use the nomograph without

compensating for the differences. Recalibrate isokinetic rate or reset nomograph if the absolute stack temperature (Ts) changes more than 10%.

4. Take other readings required by Figure 4.2 at least once at each sampling point during each time increment.
5. Record the dry gas meter readings at the end of each time increment.
6. Repeat steps 3 through 5 for each sampling point.
7. Turn off the pump, remove the probe from the stack, and record the final readings after each traverse.
8. Conduct the mandatory posttest leak check (Subsection 4.2.5) at the conclusion of the last traverse (after allowing the nozzle to cool). Record any leakage rate. Also, leak check the pitot lines (Method 2, Section 2.1); the lines must pass this leak-check to validate the velocity pressure data.
9. Disconnect the probe, and then cap the nozzle and the end of the probe with polyethylene or equivalent caps.

Plant _____ Meter calibration (Y) _____ Sheet _____ of _____

City _____ Pitot tube (C_p) _____ Nozzle ID No. _____

Location _____ Probe length _____ ft Nozzle diameter _____ mm (in)

Operator _____ Probe liner material _____ Thermometer No. _____

Date _____ Probe heater setting _____ Final leak rate _____ m3/min (cfm)

Run No. _____ Ambient temperature _____ °F Vacuum during leak-check ____ mm (in) Hg

Stack dia. mm (in)_____ Barometric press (P_b) _____ mm (in) Hg Filter No(s). _____

_____ Assumed moisture _____ $\%H_2O$ Remarks:_____

Sample box No. _____ Static press. (P_s) _____ mm (in) Hg _____

Meter box No. _____ C Factor _____ _____

Meter ΔH@ _____ Reference ΔH@ _____ _____

Traverse point number	Sampling time, (θ), min	Clock time, (24 h)	Vacuum, mm (in) Hg	Stack temp (Ts) °C (°F)	Velocity head (ΔPs) mm (in) Hg	Press across orifice meter (ΔH), mm (in) Hg	Gas sample volume (Vm), m3 (ft3)	Dry gas meter temperature Inlet °C(°F)	Dry gas meter temperature Outlet °C(°F)	Gas temp leaving impinger °C(°F)	Filter temp °C(°F)
	Total		Max	Avg			Total	Avg	Avg	Max	

Figure 4.2. Method 101A field sample data form.

During the test run, a sampling rate of 10% of the isokinetic rate must be maintained unless otherwise specified by the Administrator. The sampling rate must be adjusted at any sampling point if a 20% variation in velocity pressure occurs.

Periodically during the test, observe the connecting glassware--from the probe, through the filter, to the first impinger--for water condensation. If any is evident, adjust the probe and/or filter heater setting upward until the condensation is eliminated; add ice around the impingers to maintain the silica gel exit temperature at 20 °C (68 °F).

The manometer level and zero should also be checked periodically during each traverse. Vibrations and temperature fluctuations can cause the manometer zero to shift.

4.4 Sample Recovery

The reference method (Section 3.19.10) requires that the sample be recovered from the probe, from all glassware preceding the filter, from the front half of the filter holder, from the filter, and from the impingers and connecting glassware in an area sheltered from wind and dust to prevent contamination of the sample. Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When it can be safely handled, wipe off any external particulate matter near the tip of the probe nozzle, and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling because the resultant vacuum could draw liquid out from the impingers. Before moving the sample train to the cleanup site, remove the probe from the train, wipe off the silicone grease, and cap the open outlet of the probe and the inlet of the sample train.

Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger. Use either ground-glass stoppers, plastic caps, or serum caps to close these openings. The capped-off impinger box and the capped sampling probe can be transported to the cleanup area without risk of losing or contaminating the sample. Transfer the probe, impinger assembly, and (if applicable) filter assembly to a cleanup area that is clean, protected from the wind, and free of Hg contamination. The ambient air in laboratories located in the immediate vicinity of Hg-using facilities is not normally free of Hg contamination. Inspect the train before and during disassembly, and note any abnormal conditions.

Precaution: It is extremely important that all sample recovery personnel wear safety glasses and gloves due to the dangers associated with impinger solutions and recovery solutions.

The following sample recovery sequence includes (1) recovery of the sample from the impingers using $KMnO_4$, Container 1; (2) recovery of any residual brown deposits from the impingers using water, Container 1; (3) recovery of the sample from the probe and connecting glassware using $KMnO_4$, Container No.1; (4) recovery of any residual brown deposits from the probe and connecting glassware using water, Container No.1; (5) recovery of any residual brown deposits from sample train components not removed by water with HCl, Container 1A; recovery of silica gel, Container 2; (6) recovery of the filter, Container No. 3; (7) collecting a filter blank, Container No. 4; (8) collecting an $KMnO_4$ reagent blank, Container No. 5; (9) collecting a water reagent blank, and (10) collecting a HCl reagent blank.

4.4.1 *Impinger Contents (Container Nos. 1 and 1A)*—Recover the samples follows:

1. Note the color of the reagent in each of the impingers and record the color on the Sample Recovery Data Form. If the color of the $KMnO_4$ in the last impinger has changed from the purple color, the sample run will be considered invalid and must be repeated. If all the impinger solution has been

oxidized, the tester should (1) reduce the sample time or volume if the reduced time or volume will comply with the applicable regulations, (2) add another impinger containing $KMnO_4$, or (3) use two sample trains per sample run.

2. Using a properly cleaned graduated cylinder, measure the liquid in the first three impingers to within 1 ml. Record the volume of liquid on the Sample Recovery and Integrity Data Form. This information is needed to calculate the moisture content of the effluent gas. (Use only graduated cylinders and glass storage bottles that have been precleaned as in Section 3.19.3.)
3. Place the contents of the first three impingers in a properly cleaned, 1000-ml glass sample bottle (Container No. 1). Record the data on the sample recovery data form.
4. Prior to recovering the sample, place 400-ml of fresh $KMnO_4$ in a graduated cylinder for sample recovery. This solution is used to recover sample from the probe nozzle, probe fitting, probe liner, and front half of the filter holder (if applicable) and impingers (sample-exposed surfaces). Rinse the impingers with a portion (about 100 ml) of the 400 ml of fresh 4% $KMnO_4$ solution to assure removal of all loose particulate matter from the impingers; add all washings to the 1000-ml glass sample bottle (Container No. 1).
5. To remove any residual brown deposits on the glassware following the permanganate rinse, carefully rinse all the sample-exposed glassware with approximately 100 ml of water. Add this rinse to Container No. 1. The impingers should only require about 50 ml of the 100 ml of water.
6. If no visible deposits remain after this water rinse, do not rinse with 8 N HCl. However, if deposits remain on the glassware after the water rinse, place 25 ml of 8 N HCl in a graduated cylinder. Wash impinger walls and stems with this 25 ml of 8 N HCl as follows: Place 150 ml of water in a sample container labeled Container No. 1A. Use only a total of 25 ml of 8 N HCl to rinse all impingers. Wash the impinger walls and stem with the HCl by turning and shaking the impinger so that the HCl contacts all inside surfaces. Pour the HCl wash carefully while stirring into Container No. 1A. Rinse all glassware that was exposed to HCl with 50 ml water, and add water rinse to Container No. 1A. Label the sample bottle and record the sample number on the Sample Recovery Data Form. The separate container is used for safety reasons.

4.4.2 *Probe and Connecting Glassware (Container No. 1)*—The same sample bottle (Container No. 1) as used above for the impinger contents and sample rinse is usually adequate for the collection of all the rinses. Recover the sample from the probe liner and connecting glassware as follows:

1. Clean the outside of the probe, the pitot tube, and the nozzle to prevent particulates from being brushed into the sample bottle. Take care that dust on the outside of the probe or other exterior surfaces does not get into the sample during the quantitative recovery of the Hg (and any condensate) from the probe nozzle, probe fitting, probe liner, and front half of the filter holder (if applicable).
2. Carefully remove the probe nozzle and rinse the inside surface (using a nylon bristle brush and several $KMnO_4$ rinses) into the sample bottle (Container No. 1).
3. Clean the compression fitting by the same procedure. Rinse all sampleexposed glassware components with the total of 400 ml of fresh 4% $KMnO_4$ solution as

measured above. Add these washings to the 1000-ml glass sample bottle (Container No. 1).

4. After the $KMnO_4$ rinse, use a small portion of the remaining 100 ml of water to rinse the nozzle and connecting glass after the $KMnO_4$ rinse. Add the rinses to Container 1.

The following probe rinsing procedure should be performed by two people to preclude sample loss. The rinsing procedures for the probe liner and connecting glassware is as follows:

1. Rinse the probe liner by tilting and rotating the probe while squirting fresh 4% $KMnO_4$ solution into the upper (or nozzle) end to assure complete wetting of the inside surface.
2. Allow the $KMnO_4$ solution to drain into the sample bottle (Container 1) using a funnel to prevent spillage.
3. Hold the probe in an inclined position and squirt $KMnO_4$ solution into the upper end while pushing the probe brush through the liner with a twisting motion, and catch the drainage in the sample bottle. Repeat the brushing procedure three or more times until a visual inspection of the liner reveals no particulate remaining inside.
4. Rinse the liner once more with $KMnO_4$ solution.
5. Rinse the brush with $KMnO_4$ solution into Container 1 to remove all sample that is retained by the bristles.
6. Rinse the probe liner with the remaining 100 ml of water into Container 1.
7. Wipe all the connecting joints clean of silicone grease, and clean the inside of the front half of the filter holder by rubbing the surface with a nylon bristle brush and rinsing it with $KMnO_4$. Repeat the procedure at least three times or until no particles are evident in the rinse.
8. Make a final rinse of the filter holder and brush.
9. Clean any connecting glassware which precedes the filter holder, using Steps 5 and 6.

After all washings have been collected in Container No. 1, tighten the lid on the container to prevent leakage during shipment to the laboratory. It is recommended that the lid have a No. 70-72 hole drilled in the container cap and Teflon liners for pressure relief. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents clearly, and note it on the Sample Recovery Data Form.

4.4.3 *Silica Gel (Container No. 2)*—Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition on the sample recovery data form, Figure 4.3.

1. Transfer the silica gel from the fourth impinger to its original container using a funnel and a rubber policeman, and seal the container. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall; since the weight gain is used for moisture calculations, do not use water or other liquids to transfer the silica gel.
2. Determine the final weight gain to the nearest 0.5 g, if a balance is available.

4.4.4 *Filter (Container No. 3)*—Carefully remove the filter (if used) from the filter holder, place it in a 150-ml glass sample bottle, and add 20 to 40 ml of 4% $KMnO_4$ to submerge the filter. If it is necessary to fold the filter, be sure that the particulate cake is inside the fold. Carefully transfer, to the 150-ml sample bottle, any particulate matter and filter fibers that adhere to the filter holder gasket by using a dry Nylon bristle brush and a sharp-edged blade. Seal the container. Clearly

label the container to identify its contents. Mark the height of the fluid level to determine whether leakage occurs during transport.

4.4.5 *Filter Blank (Container No. 4)*—If a filter is used for testing, initially take an unused filter for each field test series and label as a filter blank. Treat the filter blank in the same manner as described in Subsection 4.3.4 above.

4.4.6 *Absorbing Solution Blank (Container No. 5)*—For a blank, place 650 ml of 4% $KMnO_4$ absorbing solution in a 1000-ml sample bottle. If the 100 ml water rinse was used during recovery, carefully add a second 100 ml portion of water to Container No. 5. It is recommended that the lid have a No. 70-72 hole drilled in the container cap and Teflon liners for pressure relief. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container as the $KMnO_4$ blank, and seal the container.

4.4.7 *8 N HCl Blank (Container No. 6)*—If 8 N HCl was used (Container 1A) to remove any residual brown deposits remaining after rinsing sample-exposed glassware with fresh 4% $KMnO_4$ solution and water, place 25 ml of 8 N HCl used for removing the deposits in a separate sample container (Container No. 6) containing 200 ml of water. Mark container as the HCl blank, and seal the container.

4.5 Sample Logistics and Packing Equipment

Follow the sampling and sample recovery procedures until the required number of runs are completed and blank samples are labeled. Log all data on the Sample Recovery and Integrity Data Form, Figure 4.1. At the conclusion of the test:

1. Check all rinses and filters for proper labeling (time, date, location, test run number, and any other pertinent documentation). Be sure that blanks have been set aside and labeled.
2. If possible, make a copy of the field data form(s) in case the originals are lost.
3. Examine all sample containers for damage and ensure that they are properly sealed for transport to the base laboratory. Ensure that the containers are labeled properly for shipping to prevent loss of samples or equipment.
4. Review the field sampling data form and any other completed data forms to ensure that all data have been recorded and that all forms are present.

4.6 Systems Audit

A Method 101A sampling and sample recovery checklist is presented in Figure 4.3.

Date _____ Time _____ Operator _____ Observer _____

Method 101A Sampling Procedures

Probe Nozzle: stainless steel _____ glass _____
Button-hook _____elbow _____ size _____
Cleaned according to sampling protocol? _____
Sealed with Teflon tape or other cover?_____

Probe liner: borosilicate _____ quartz _____ other _____
Cleaned according to sampling protocol?_____
Openings sealed with Teflon tape?_____
Probe heating system: _____
Checked? _____ Temperature _____ Stable? _____

Pitot tube: Type S _____ Other _____
Properly attached to probe (no interference to nozzle)? ____
Modifications: _____
Pitot tube coefficient _____

Differential Pressure Gauge: Inclined manometers _____
Magnahelics _____ Ranges _____ _____ _____
Other _____ Ranges _____ _____ _____

Cyclone (inlet only): borosilicate glass _____ other _____
Cleaned according to sampling protocol? _____

Filter Holder: borosilicate glass _____ other _____
Frit material: glass _____ Teflon_____ other _____
Gasket material: silicone _____ other _____
Cleaned according to sampling protocol? _____
Sealed with Teflon tape or glass caps?_____

Filter type(s): _____
Cleaned according to sampling protocol? _____

Impinger Train: number of impingers _____
Cleaned according to sampling protocol? _____
Contents: 1st _____ 2nd _____ 3rd _____
4th _____ 5th _____ 6th _____
Impinger weights recorded?_____
Proper connections? _____
Modifications _____

Silica gel: type _____ new? _____ used? _____

Figure 4.3. Field observation of Method 101A sampling and recovery.

Date _____ Time _____ Operator _____ Observer _____

Method 101A Sampling Procedures

Procedure

Barometer: mercury _____aneroid _____ other _____

Gas Density Determination: temperature sensor _____
pressure gauge _____
Temperature sensor properly attached to probe? _____

Recent Calibrations: pitot tubes _____
meter box _____ thermocouples/thermometers _____

Filters checked visually for irregularities? _____

Filters properly centered? _____ labeled? _____

Sampling site properly selected? _____

Nozzle size properly selected? _____

Proper sampling time selected or calculated? _____

All openings of sampling train sealed (pretest
and posttest)? _____

Impingers, filter holder, probe, and nozzle assembled? _____

Cyclone attached (inlet only)? _____

Pitot lines checked for leaks and plugging? _____

Meter box leveled? _____ Manometers zeroed? _____

ΔH@ from most recent calibration _____

Nomograph setup correctly? _____ K factor _____

Pretest leak-check conducted? _____Leakage rate? _____

Care taken to avoid scraping nipple or stack wall? _____

Effective seal around probe when in-stack? _____

Probe moved to traverse points at proper time? _____

Figure 4.3. (Contined)

Date _____ Time _____ Operator _____ Observer _____

Method 101A Sampling Procedures

Nozzle and pitot tubes kept parallel to stack at all times?
_____

Filter(s) changed during run? _____
Any particulate lost during filter change? _____

Data forms completed and data recorded properly? _____

Nomograph setting changed with significant change in the stack temperature?
_____

Velocity pressure and orifice pressure recorded accurately? _____

Posttest leak-check conducted? _____ Leakage rate _____
at inches of mercury _____

Orsat analysis? _____ Stack _____ Integrated _____

Approximate stack temperature _____ Gas sample volume _____

Percent isokinetic calculated _____

Comments _____

_____

_____

Figure 4.3. (Continued)

Date _____ Time _____ Operator _____ Observer _____

Method 101A Sample Recovery

Reagents:

Brushes: Teflon bristle _____ other _____
Cleaned according to sampling protocol? _____

Wash bottles: glass _____ other _____
Cleaned according to sampling protocol? _____

Storage containers: glass? _____ other? _____
Cleaned according to sampling protocol? _____
Teflon cap liner?_____ Leak free? _____
Small hole in cap to relieve pressure? _____

Filter containers: borosilicate glass _____ other _____
Cleaned according to sampling protocol? _____

Graduated cylinder: borosilicate glass _____ other _____
Subdivisions of graduated cylinder ≤2 ml? _____
Cleaned according to sampling protocol? _____

Balance type: _____Calibrated? _____

Probe allowed to cool sufficiently? _____

Probe and sample train openings covered? _____

Clean-up area(s) used _____

$KMnO_4$ Volume: Was 400 mL of $KMnO_4$ measured for recovery? _____

Filter handling: tweezers used? _____ surgical gloves? _____
Any particulate lost? _____
$KMnO_4$ added to filter? _____

Probe handling: $KMnO_4$ rinses _____ Brushed? _____
H_2O rinses _____ Brushed? _____

Recovery of probe: probe nozzle _____ probe fitting _____
probe liner _____front half of filter holder _____

Figure 4.3. (Continued)

Date _____ Time _____ Operator _____ Observer _____

Method 101A Sample Recovery (cont)

HCl Volume: Was 25 mL of HCl measured for recovery? _____

Impinger handling: weighed? _____ volumed? _____
$KMnO_4$ rinses _____ H_2O rinse _____
HCl rinses _____

Blanks collected: filter _____
$KMnO_4$ (650 mL) _____
HCl (25 mL in 200 mL of H_2O) _____

Container No. 1: Sample No. _____ 400 mL $KMnO_4$ rinse_____
Impinger contents _____ Impinger Rinse _____
Probe rinse _____ Nozzle rinse _____

Container No. 1A: Sample No. _____ 25 mL HCl _____
Impinger rinse _____

Container No. 2 Silica gel: color? _____ condition? _____ weighed? ____

Samples labeled and stored properly? _____

Liquid levels marked? _____

Remarks:_____

Figure 4.3. (Continued)

TABLE 4.1. ACTIVITY MATRIX FOR ON-SITE MEASUREMENT CHECKS

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Preliminary determinations and measurements	Determine the moisture content of stack gas	Once each field test; use wet bulb/dry bulb thermometer, Method 4, or sling psychrometer	Complete
	Determine flow rate of stack gas	Once each field test, using Method 1	Complete
	Determine stack temperature	Prior to and during sampling	Complete
	Determine stack dimensions	Prior to sampling, using tape measure	Complete
	Determine dry molecular weight of stack gas	Once each field test, Method 2; if integrated gas sample is required, Method 3	Complete
	Select sampling time ≥ minimum total sampling time in applicable emission standard; number of minutes between readings should be an integer	Prior to sampling	Complete
Preparation of collection train	Assemble train according to specifications in Figure 1.1 and Sec. 3.18.4 Subsec. 4.3.3	Before each sampling run	Complete
	Leak-check; Leak rate < 4% or 0.00057 m^3/min (0.02 ft^3/min), whichever is less	Leak-check before sampling by plugging the nozzle or inlet to first impinger and by pulling a vacuum of 380 mm (15 in) Hg	Correct the leak

(Continued)

TABLE 4.1 (Continued)

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Sampling (isokinetically)	Within 10% of isokinetic condition	Calculate for each sample run	Repeat the test run
	Standard check for minimum sampling time and volume; sampling time/point ≥ 2 min	Make a quick calculation before each test, and exact calulation after	Repeat the test run
	Minimum number of points specified by Method 1	Check before the first test run by measuring duct and using Method 1	Repeat the procedure to comply with specifications of Method 1
	Leak-check; leakage rate ≤ 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling volume, whichever is less	Leak-check after each test run or before equipment replacement during test at the maximum vacuum during the test (mandatory)	Correct the sample volume, or repeat the sampling
Sample recovery	Sample free of contamination	Transfer sample as outlined in Sec 3.19.4, subsec 4.5 after each test run; label containers and mark level of solution in container	Repeat the sampling
Sample logistics and packing of equipment	All data recorded correctly	After completion of each test and before packing; if possible, make copies of forms	Complete data
	All equipment examined for damage and labelled for shipment	After completion of each test and before packing	Repeat sampling if damage occurred during the test
	All sample containers and blanks properly labelled and packaged	Visually check upon completion of each sampling	Correct when possible

5.0 POSTSAMPLING OPERATIONS

The postsampling operations include postsampling calibration checks of sampling equipment and analysis by atomic absorption spectrophotometry techniques. The sample analysis includes calibrations and performance checks. Checklists for monitoring the postsampling operations are provided at the end of this section. Table 5.1 at the end of this section summarizes the QA activities associated with the postsampling operations.

5.1 Calibration Checks of Sampling Equipment

Posttest checks will have to be made on most of the sampling apparatus. These checks will include three calibration runs at a single orifice meter setting, cleaning, and/or routine maintenance. Cleaning and maintenance are discussed in Section 3.19.7 and in APTD 0576. Figure 5.1 can be used to record the posttest checks.

5.1.1 *Metering System*—The metering system has two components that must be checked—the dry-gas meter and the dry-gas meter thermometer(s).

The dry-gas meter thermometer(s) should be compared with the ASTM mercury-in-glass thermometer at room temperature. If the two readings agree within 6 °C (10.8 °F), they are acceptable; if not, the thermometer must be recalibrated according to Subsection 2.2 of Section 3.19.2 after the posttest check of the dry-gas meter. For calculations, use the dry-gas meter thermometer readings (field or recalibration values) that would give the higher temperatures. That is, if the field readings are higher, no correction is necessary, but if the recalibration value is higher, add the difference in the two readings to the average dry-gas meter temperature reading.

The posttest check of the dry-gas meter is described in Section 3.19.2. The metering system should not have any leaks that were corrected prior to the posttest check. If the dry-gas meter calibration factor (Y) deviates by <5% from the initial calibration factor, the dry-gas meter volumes obtained during the test series are acceptable. If Y deviates by >5%, recalibrate the metering system (Section 3.19.2). For the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

5.1.2 *Stack Temperature Sensors*—The stack temperature sensor readings should be compared with the reference thermometer readings.

For thermocouple(s), compare the thermocouple and reference thermometer values at ambient temperature. If the values agree within 1.5% of the absolute temperature, the calibration is considered valid. If the values do not agree within 1.5%, recalibrate the thermocouple as described in Section 3.19.2 to determine the difference (ΔT_s) at the average stack temperature (T_s). NOTE: This comparison may be done in the field immediately following the tests.

For thermometers, compare the reference thermometer:

1. At ambient temperatures for average stack temperature below 100 °C (212 °F).

Plant _____ Calibrated by _____
Meter box number _____ Date _____

Dry-Gas Meter

Pretest calibration factor, Y _____ (within 2%)
Posttest check, Y* (within 5% of pretest value)
Recalibration required? _____ yes _____ no
If yes, calibration factor, Y _____ (within 2%)
Lower calibration factor, Y _____ for calculations (pretest or posttest)

Dry-Gas Meter Thermometers

Was a pretest temperature correction used? _____yes _____no
If yes, temperature correction _____ (within 5.4 °F over range)
Posttest comparison with mercury-in-glass thermometer? * (within 10.8 °F at ambient temperature) _____ °F
Recalibration required? _____yes _____no
Recalibration temperature correction? _____ (within 5.4 °F over range)
If yes, no correction necessary for calibration if meter thermometer temperature is higher, if calibration temperature is higher, add correction to average meter temperature for calculations.

Stack Temperature Sensor

Was a pretest temperature correction used? _____yes _____no
If yes, temperature correction _____°F (within 1.5% in. °R over range)
Average stack temperature of compliance test, T_s _____ °R
Temperature of reference thermometer or solution __ °R (within 10% of T_s)
Temperature of stack temperature for recalibration _____ °R
Difference between reference and stack thermometers, ΔT_s _____ °R
Do values agree within 1.5%?* _____yes _____no
If yes, no correction necessary for calculations.
If no, calculation must be done twice—once with the recorded values and once with the average stack temperature corrected to correspond to the reference temperature differential (ΔT_s). Both final results must be reported.

Barometer

Was the pretest field barometer correct? _____yes _____no
Posttest comparison?* _____ in. Hg (within 0.1 in. Hg)
Was recalibration required? _____yes _____no
If yes, no correction necessary for calculations when the field barometer has a lower readings; if the mercury-in-glass reading is lower, subtract the difference from the field data readings for the calculations.

Figure 5.1. Posttest calibration checks.

2. In boiling water for stack temperatures from 100 °C to 200 °C.
3. In a boiling liquid with the boiling point above 200 °C for stack temperatures between 200 to 405 °C. For stack temperatures above 405 °C, compare the stack thermometer with a thermocouple at a temperature within 10% of the average stack temperature. If the absolute values agree within 1.5%, the calibration is considered valid. If not, determine the error (ΔT_s) to correct the average stack temperature.

5.1.3 *Barometer*—The field barometer should be compared to a Hg-in-glass barometer. If the readings agree within 5 mm (0.2 in.) Hg, the field readings are acceptable; if not, use the lesser calibration value for the calculations. If the field barometer reads lower than the Hg-inglass barometer, the field data are acceptable. If the Hg-in-glass barometer gives the lower reading, use the difference in the two readings (the adjusted barometric value) in the calculations.

5.2 Sample Preparation

Field samples and reagent blanks should be prepared concurrently, if possible. Check the liquid level in each container to see whether liquid was lost during transport. If a noticeable amount of leakage occurred, either void the sample or use methods subject to the approval of the Administrator to account for the losses. Record the findings of the liquid level check on the sample preparation data form, Figure 5.2, or another suitable form. Then follow the procedures below.

5.2.1 *Containers No. 3 and No. 4 (Filter and Filter Blank)*—If a filter is used, the following procedures apply:

1. Place the contents, including the filter, of Container No. 3 in a separate, properly cleaned, and uniquely identified 250-mL beaker. Using three rinses of approximately 10 mL of water, complete the sample transfer from the container. Record the beaker number with the run number on the sample preparation data form.
2. Place the contents of Container No. 4 in a properly cleaned 250-mL beaker. Label it as the sample filter blank or as another suitable name. Use three rinses of approximately 10 mL of water for the sample transfer. Record the name on the sample preparation data form.
3. Heat the beakers in a laboratory hood on a steam bath until most of the liquid has evaporated. Do not take to dryness. Do not use direct heating on a hot plate. Record the completion of the step on the sample preparation data form.
4. Add 20 mL of concentrated HNO_3 to each beaker, cover each beaker with a watch glass, and heat on a hot plate at 70 °C for 2 h in a laboratory hood. Record completion of this step on the sample preparation data form.

Sample Preparation Data Form

Date _____ Plant Name _____ Sampling Location _____

Sample Preparation Checks

Sample Integrity Check: Have containers leaked?

Container 1	____	4	____
1A	____	5	____
2	____	6	____
3	____		

	Run 1	Run 2	Run 3	Blank
Place a check to indicate completion of step or record data as indicated.				
Preparation of Filter Digest: Container No. 3				
Sample No. for each 250-mL beaker	____	____	____	____
Contents added to a glass 250-mL beaker?	____	____	____	____
Heated carefully to near dryness (not dryness) using a steam bath?	____	____	____	____
Volume of HNO_3 added to beaker 25 mL?	____	____	____	____
Covered with watch glass?	____	____	____	____
Heated at 70 °C on hot plate for 2 h?	____	____	____	____
How was temperature monitored?	____	____	____	____
Filtered through Whatman 40 paper ?				
Date	____	____	____	____
Time	____	____	____	____
Rinsed beaker residue carefully through the filter?	____	____	____	____
Saved filtrate?	____	____	____	____
Preparation of Sample No. A.1:				
Are Container No. 1 contents <1000 mL?	____	____	____	____
If so, volume, mL	____	____	____	____
Are Container No. 1 contents filtered through Whatman 40 paper?	____	____	____	____
Filter saved?	____	____	____	____
Filtrate added to mL glass volumetric flask?	____	____	____	____
Filter digest (above) added to flask with Container No. 1 filtrate?	____	____	____	____
Completion of Sample No. A.1?	____	____	____	____
Date	____	____	____	____
Time	____	____	____	____

Figure 5.2. Sample preparation data form.

	Run 1	Run 2	Run 3	Blank
Preparation of Sample No. HCl A.2:				
25 mL of 8N HCl added to filter saved from preparation of Sample No. A.1?				
How was HCl added?				
Digestion started, Time				
Date				
Digestion completed, Time				
Date				
HCl digest dilution volume, mL				
Preparation of Filter Blank:				
Container 4 contents added to 250-mL beaker				
Heated carefully to near dryness (not dryness) using a steam bath?				
Volume of HNO_3 added to beaker 25 mL?				
Covered with watch glass?				
Heated at 70 °C on hot plate for 2 h?				
How was temperature monitored?				
Preparation of Sample A.1 Blank:				
Are Container No. 5 contents diluted to same volume as Container No. 1 contents?				
Filtered through Whatman 40 paper?				
Filter saved?				
Filtrate added to 1000-mL glass volumetric flask?				
Filter blank (Container No. 4) digest (above) added to same volumetric flask?				
Time of completion of Sample No. A.1				
Preparation of Sample No. HCl A.2 Blank:				
25 mL of 8N HCl added to filter saved from preparation of Sample No. A.1 blank?				
How was HCl added?				
Time 24-h digestion started?				
Date				
Time				
Time 24-h digestion completed?				
Date				
Time				
HCl digest was diluted to 500 mL using glass volumetric flask?				

Figure 5.2. (Continued)

Note: The analysts should use gloves and safety glasses and should avoid skin contact and breathing the fumes from the HNO_3.

5. Remove the beaker from the hot plate and filter the solution from the digestion of the contents of Container No. 3 through a separate Whatman 40 filter paper into a properly cleaned and identified (the same sample identification number can be used) sample container using a vacuum filtering system. Use three rinses of approximately 10 mL of water for the sample transfer. The filtration should be conducted in a laboratory hood. Record the completion of this step on the sample recovery data form.
6. Save the filtrate for addition to the Container No. 1 filtrate, as described in Subsection 5.2.2. Discard the filter.
7. Filter the solution from the digestion of the contents of Container No. 4 (sample filter blank) through Whatman 40 filter paper, as described above in Step 5, and save the filtrate for addition to the Container No. 5 filtrate, as described in Section 5.2.2. Discard the filter.

5.2.2 *Container No. 1 (Impingers, Probe, and Filter Holder) and, If Applicable, 1A (HCl Rinse)*—The $KMnO_4$ impinger solution and rinse and HCl rinse (if applicable) are prepared as follows:

Note: Because of the hazardous nature of the HNO_3 and HCl solutions, analysts must wear gloves and safety glasses and should avoid skin contact and breathing the fumes from HNO_3 and HCl. The HNO_3 and $KMnO_4$ solutions should not come in contact with oxidizable matter.

$KMnO_4$ Impinger Solution and Sample Recovery Rinse

1. To remove the brown MnO_2 precipitate, filter the contents of Container No. 1 through a Whatman 40 filter into a properly cleaned and identified 1-L volumetric flask. Use three rinses of approximately 10 mL of water for the sample transfer.
2. Save the filter for digestion of the brown MnO_2 precipitate, as described in steps 6 through 9 below, and record the date and time the filtration step was completed on the sample preparation data form.
3. Add the sample filtrate from Container No. 3 produced in Subsection 5.2.1 above to the appropriate 1-L volumetric flask from Step 1, and dilute to volume with water. If the combined filtrates are greater than 1000 mL, determine the volume to the nearest mL and record the volume on the sample preparation data form. This volume will be used to make the appropriate corrections for blank subtractions and emissions calculations.
4. Mix thoroughly. The filtrate will be referred to as Analysis Sample No. A.1.
5. The Analysis Sample No. A.1 must be analyzed for Hg within 48 h after completion of the filtration step. If the sample is not analyzed within this period, steps 1 through 4 must be repeated, the additional Whatman 40 filter paper will be digested as described below in steps 6 through 9, and the digestion will be added to the sample.

Whatman 40 Filter and MnO_2 Precipitate

6. Place the saved filter, which was used to remove the brown MnO_2 precipitate, into a container of appropriate size. Submerge the filter with 25 mL of 8 N HCl and allow it and the brown residue to digest for a minimum of 24 h at room temperature. Record the date and time for the beginning of the digestion on the sample preparation data form.

Whatman 40 Filter, MnO_2 Precipitate, and HCl Rinse

7. Filter the contents of Container No. 1A, HCl rinse (if applicable) through a Whatman 40 filter into a properly cleaned and identified 500-mL volumetric flask. Use three rinses of approximately 10 mL of water for the sample transfer. Record completion on the sample preparation data form.
8. Filter the digestion of the brown MnO_2 precipitate and Whatman filter from Step 6 into the 500-mL volumetric flask from Step 7. Use three rinses of approximately 10 mL of water for the sample transfer. Record the date and time of the filtration on the sample preparation data form.
9. Dilute to volume with water. This solution will be referred to as Analysis Sample No. HCl A.2. Save the solution for Hg analysis as described in Subsection 5.3.4 below. Discard the filters.

5.2.3 *Containers No. 5 (Absorbing Solution Blank) and No. 6 (HCl rinse blank)*—The procedures for preparing the blank solutions are described below:

Note: The same precautions should be taken with the blank solutions as were taken with the sample solutions. The sample blanks have been designed to allow easy blank subtraction from the sample. The volume of all solutions and the number of filters are identical to the field samples. Therefore, the blank sample must be prepared at the same time and in the same manner as the field samples.

$KMnO_4$ Reagent Blank Solution and Sample Recovery Blank Rinse

1. Treat Container No. 5 (650 mL of blank absorbing solution) the same as Container No. 1 (described in steps 1 through 5 in Subsection 5.2.2).

Filter Blank

2. Add the filter blank filtrate from Container No. 4 (completed in steps 1 through 7 of Subsection 5.2.1 above) to the 1-L volumetric flask (containing Container No. 5 filtrate), and dilute to volume. Mix thoroughly.
3. This solution will be referred to as Analysis Sample No. A.1 blank.
4. Analysis Sample No. A.1 blank must be analyzed for Hg within 48 h after the completion of the filtration step.

Whatman 40 Filter and $KMnO_4$ Reagent Blank Precipitate

5. Digest any brown precipitate remaining on the filter from the filtration of Container No. 5 by the same procedure described in step 6 in Subsection 5.2.2 above.

Whatman 40 Filter, $KMnO_4$ Blank Precipitate, and Blank HCl Rinse

6. Filter the contents of Container No. 6 by the same procedure described in steps 7, 8, and 9 in Subsection 5.2.2 and combine into the 500-mL volumetric flask with the filtrate from the digested $KMnO_4$ blank precipitate. The resulting 500-mL combined dilute solution will be referred to as Analysis Sample No. HCl A.2 blank. NOTE: As discussed in Subsection 5.3.4 below, when analyzing samples A.1 blank and HCl A.2 blank, always begin with 10-mL aliquots; this note applies specifically to blank samples.

5.3 Analysis

Precise and accurate analysis requires that the Hg analysis system be calibrated properly, which includes preparing calibration standards and field samples.

For Method 101A, spectrophotometer calibration is conducted in conjunction with analyzing the field samples (and QA samples). This section presents the steps for analyzing the field samples and includes preparing sample and field blanks, as well as describing how to quality control (QC) samples. It discusses the relationship between analyzing the field samples and preparing the calibration curve.

5.3.1 *Instrument Setup*—Before use, clean all glassware, both new and used, as follows: brush with soap and tap water, liberally rinse with tap water, soak for 1 h in 50% HNO_3, and then rinse with deionized distilled water.

Flow Calibration—Assemble the aeration system as shown in Figure 5.3. Set the outlet pressure on the aeration gas cylinder regulator to a minimum pressure of 500 mm Hg (10 parts per square inch [psi]); use the flow metering valve and a bubble flow meter or wet-test meter to obtain a flow rate of 1.5 ± 0.1 L/min through the aeration cell. After the flow calibration is completed, remove the bubble flow meter from the system.

Optical Cell Heating System Calibration—Using a 25-mL graduated cylinder, add 25 mL of water to the bottle section of the aeration cell. Attach the bottle section to the bubbler section of the cell. Connect the aeration cell to the optical cell and, while aerating at 1.5 L/min, determine the minimum variable transformer setting necessary to prevent condensation in the optical cell and in the connecting tubing. (This setting should not exceed 20 volts.)

Wavelength Adjustment—Set the spectrophotometer wavelength at 253.7 nm and make certain that the optical cell is at the minimum temperature needed to prevent water condensation.

Recorder Adjustment—The Hg response may be measured by either peak height or peak area. Peak height determinations may be performed manually by counting the recorder paper divisions for a given peak from a best-drawn baseline. The peak height from the baseline also may be measured conveniently using a millimeter ruler. Peak area measurements are most conveniently accomplished electronically using an integrator or similar device. For peak height determinations, set the recorder scale as follows:

Note: The temperature of the solution affects the rate at which elemental Hg is released from a solution and, consequently, it affects the shape of the generated peak as well as the peak height. Therefore, to obtain reproducible results using peak height, bring all solutions to room temperature before use.

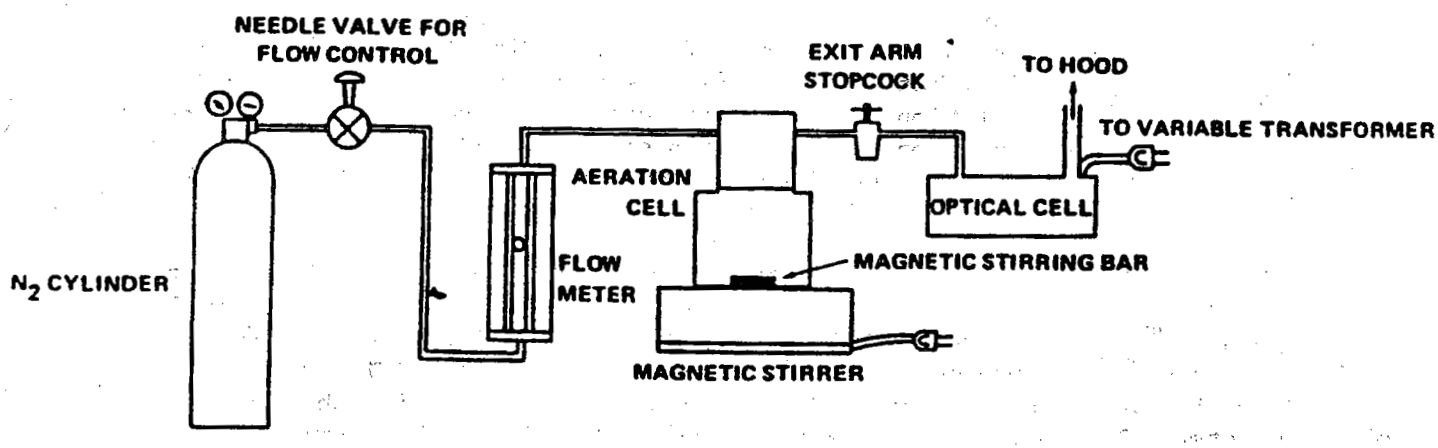


Figure 5.3. Schematic of aeration system.

1. Place a Teflon-coated stirring bar in the bottle. Using a 25-mL graduated cylinder, add 25 mL of laboratory pure water to the aeration cell bottle. Pipet 5.0 mL of the working Hg standard solution to the aeration cell.
2. Add 5 mL of the 4% $KMnO_4$ absorbing solution followed by 5 mL of 15% HNO_3 and 5 mL of 5% $KMnO_4$ to the aeration cell and mix well using a swirling motion.
3. Attach the bottle to the aerator making sure that: (1) the exit arm stopcock is closed, and (2) there is no aeration gas flowing through the bubbler.
4. Through the side arm, add 5 mL of sodium chloride hydroxylamine solution in 1-mL increments until the solution is colorless.
5. Through the side arm, add 5 mL of the Tin (II) reducing agent to the aeration cell bottle and immediately stopper the side arm.
6. Stir the solution for 15 s and turn on the recorder or integrator.
7. Open the aeration cell exit arm stopcock and initiate the gas flow.
8. Determine the maximum height (absorbance) of the standard and set this value to read 90% of the recorder full scale.

5.3.2 *Analytical Calibration Curve*—After setting the recorder scale (Section 5.3.1), the calibration is performed. To separate aeration cell bottles, add 25 mL of laboratory pure water. Then add 0.0-, 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-mL aliquots of the working standard solution using Class A volumetric pipets. This corresponds to 0, 200, 400, 600, 800, and 1,000 ng of Hg, respectively. Proceed with the calibration following steps 2 through 7 of Section 5.3.1, Recorder Adjustment. Analyze the calibration standards by measuring the lowest to the highest standard. Be sure to allow the recorder pen to return fully to the baseline before the next standard is analyzed. This step is particularly critical with peak area measurements. Repeat this procedure on each aliquot size until two consecutive peaks agree within 3% of the average.

Between sample analyses, place the aerator section into a 600-mL beaker containing approximately 400 mL of water. Rinse the bottle section of the aeration cell with a stream of water to remove all traces of the reagents from the previous sample. These steps are necessary to remove all traces of the reducing agent between samples to prevent the loss of Hg before aeration. It will be necessary, however, to wash the aeration cell parts with concentrated HCl if any of the following conditions occur: (1) a white film appears on any inside surface of the aeration cell; (2) the calibration curve changes suddenly; or (3) the replicate samples do not yield reproducible results.

Recorder or integrator responses should be documented on the analytical data form for Calibraxon Standards (Figure 5.4). Subtract the average peak height (or peak area) of the measurement blank (0.0-mL aliquot)—which should be less than 2% of recorder full scale—from the averaged peak heights of the 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-mL aliquot standards. If the blank absorbance is greater than 2% of full-scale, the probable cause is Hg contamination of a reagent or carry-over of Hg from a previous sample. Plot the corrected peak height of each standard solution versus the corresponding total Hg mass in the aeration cell (in ng).

Calculating the measured standard Hg mass (P) may be performed in two ways: a linear regression program provided by a hand calculator (or other computing device) or the manual least squares method described below:

$$P = (S)(Y) \qquad \text{Equation 5-1}$$

where:

Y = Peak height or integrator response, mm or counts.

S = Response factor, ng/mm or ng/counts (from Equation 5-2).

and

$$S = \frac{x_1y_1+x_2y_2+x_3y_3+x_4y_4+x_5y_5+x_6y_6}{y_1^2+y_2^2+y_3^2+y_4^2+y_5^2+y_6^2} \qquad \text{Equation 5-2}$$

where:

x = Standard mass value, ng.

Complete the analytical data form for analyzing calibration standards (Figure 5.4) for each standard. Calculate the deviation of each standard measurement average from the expected value (standard mass value), x. If the percent deviation from the expected value is greater than 5% for any standard measurement, the calibration must be repeated.

5.3.3 *QC Operations*—The quality of the analytical results can be assessed by analyzing a variety of standard reference solutions (SRMs) of known high accuracy, such as those available from the National Institute Standards and Technology (NIST) and other government agencies. Standard solutions prepared by commercial suppliers that meet NIST traceability criteria are also useful. If these solutions are not available, the analysis of laboratory-prepared standard solutions may be used from a source (supplier) other than the source of the calibration standards. These solutions will be known as QC solutions. For example, if the calibration standards were prepared by dilutions of a 100 mg Hg/mL solution from supplier A (or from an in-house prepared solution from the pure mercury salt), then a QC solution might be prepared from dilutions of one of the following:

1. An NIST Hg solution or other SRM.

Plant _____ Location _____
Date _____ Analyst _____

Standard Identifier	Standard mass (x) (ng Hg)	Integrator Response, Peak Height or Area (y), (mm)			Measured Standard mass (P) (ng Hg)	Deviation (%)
		1	2	Avg		
Std 1	0					
Std 2	200					
Std 3	400					
Std 4	600					
Std 5	800					
Std 6	1000					

Equation for Linear Calibration Curve, Average Response as a function of standard concentration.

$$y = mx + b = (\_\_\_\_\_)x + (\_\_\_\_\_)$$ Equation 1

where:

$$y = \text{Instrument curve slope } \frac{\text{mm or area count}}{\text{ng Hg}} = \_\_\_\_\_$$ Equation 2

$$x = \text{Standard concentration (ng Hg)} = \_\_\_\_\_$$ Equation 3

$$b = I = \text{Intercept term (mm or area count)} = \_\_\_\_\_$$ Equation 4

Measured Standard Concentration (P)

$$P(\text{ng Hg}) = \frac{\text{Average Instrument Response (y) - Intercept (I)}}{\text{Calibration Curve Slope}}$$

$$P = \frac{(\quad) - (\quad)}{(\quad)} = \_\_\_\_ \text{ ng Hg}$$ Equation 5

Deviation

$$\text{Deviation (\%)} = \frac{P\ (\text{ng Hg}) - x\ (\text{ng Hg})}{x\ (\text{ng Hg})} \times 100\%$$

$$\text{Deviation} = \frac{(\quad) - (\quad)}{(\quad)} \times 100\% = \_\_\_\_\_ \%$$ Equation 6

Figure 5.4. Analytical data form for analysis of calibration standards.

2. A commercial QC solution that has been tested against an NIST solution (or equivalent) by manufacturer A.
3. A 1,000-mg Hg/mL solution from manufacturer B.

Record analytical data for QC samples on Figure 5.5. QC solutions may be used for a variety of analytical accuracy assessments. These include three check samples (Check Sample A, B, and C):

A. *Checks of the accuracy of the calibration operations, Check Sample A*—When analyzed immediately following the calibration, the measured QC sample value must be within 5% of the expected value described in this section, or the calibration must be repeated. These QC samples are known as Initial Calibration Verification (ICVs) Check samples.

B. *Checks of the drift of the calibration, Check Sample B*—For any of a wide variety of conditions that may be related to instrument warmup or instrument component deterioration, the repeated analysis of a given sample or standard will vary over time. To ensure that the analysis is "in control," a QC solution is measured at least every five samples. If the average measured value of the QC solution has changed by more than 10% from the expected value, the causes must be identified and corrected. The calibration is then repeated, and all samples analyzed since the last successful "drift" QC sample analysis must be repeated. This "drift" QC sample is known as a CCV sample. It is worth noting that the CCV need not be a "standard" type solution; any Hg-containing solution may be used for the CCV, provided the Hg level in the aeration cell is between 200 and 1,000 ng. Again, the measured value of this solution must not vary more than 10% from the expected value.

C. *Measuring spike recovery check sample, Check Sample C*—Spiking a digested sample (a prepared sample) with a standard solution provides a means of assessing Hg recovery associated with the measurement process (sample matrix effect). The steps below must be followed to determine spike recovery:

   a. After completing all sample preparation steps in Subsections 5.2.1 and 5.2.2, spike a 10-mL aliquot of Analysis Sample No. A.1 with 10 mL of spiking solution containing a similar concentration of Hg, or with 10 mL of a spike at least 10 times greater than the detection limit, whichever is greater.
   b. Spike a 10-mL aliquot of Analysis Sample No. HCl A.2 with 10 mL of spiking solution containing a similar concentration of Hg as the field sample, or a spike at least 10 times greater than the detection limit, whichever is greater.
   c. After all samples are analyzed, subtract the results of the spiked and unspiked samples. If this spike is not within 15% of the expected value, then the Hg response may be owing to matrix effects. If so, all sample digests must be analyzed by the method of standard additions (MSA).

Date samples received _____ Date samples analyzed _____

Plant _____ Run number(s) _____

Location _____ Analyst _____

Calibration factor (S) _____ Intercept (I), if applicable _____

QC Sample Number	Analysis Number	Instrument Response (mm)	Mean Instrument Response (mm)	Percent Deviation (ng Hg)	Mean Instrument Response Blank Corrected (y)	Dilution Factor (F)	Mass QC Sample (ng Hg)

Deviation of replicate measurements, (%)

$$= \frac{(A_1 - A_2)}{\frac{A_1 + A_2}{2}} \times 100$$

$$= \frac{(\quad) - (\quad)}{\frac{(\quad) + (\quad)}{2}} 100 = \_\_\_\_\_$$

Mass of QC sample without intercept (ng Hg)

$$= S \times y \times F$$

$$= \_\_\_\_\_ \times \_\_\_\_\_ \times \_\_\_\_\_ =$$

Mass of QC sample with intercept (ng Hg)

$$= S (y - I) F$$

$$= \_\_\_\_\_ (\quad - \quad) \_\_\_\_\_ =$$

Figure 5.5. Analytical data form for analysis of QC samples.

Operations involving the use of QC samples are described in more detail below. Note that spikes always must be measured using the linear portion of the calibration curve (as with actual samples). QC samples with Hg values exceeding the linear portion of the calibration curve must be diluted and reanalyzed according to the sample analysis procedure (Subsection 5.4.3).

Preparing the ICV Solutions—If the source of the ICV is a commercial 1,000-mg/mL stock solution, it must be diluted according to the procedure described in Subsection 1.5.3 for intermediate and working standard solutions.

Measuring the ICV Solution—Analyze a 2- to 5-mL aliquot (i.e., 200-500 ng Hg) of the ICV working standard solution (some mid-point aliquot). Duplicate measurements should agree within 3% of the average. If not, determine the cause for error (consult the laboratory supervisor if necessary), correct the problem, and recalibrate the analysis system. Repeat as necessary. If the QC solution source is not a 1,000-mg Hg/mL stock solution, prepare the intermediate QC solution (QC working solution) as follows:

1. Pour about 15 mL of the solution into a clean beaker. NOTE: To avoid contamination, do not pipet directly from the bottle.
2. Pipet (using a glass pipet of at least 5-mL volume) an appropriate aliquot into a suitable clean glass volumetric flask, according to Table 5.2. Pipet 2 mL of the QC working solution for measurement. Use Table 5.2 to determine the expected values for the QC sample (ICV).

Preparing and Measuring the Initial Blank Verification (IBV) and Continuing Blank Verification (CBV)—With the conventional measurement system, these verifications may be performed merely by adding 50 mL of water, hydroxylamine sulfate solution, and stannous chloride as described in Subsection 5.3.2.

Preparing and Measuring Spiked Sample, Check Sample C—To determine whether there are sample matrix effects during the measurement, one sample digest must be analyzed in the presence of added Hg. The added (spiked) Hg recovery must be within 85-115%, or the MSA must be employed for each sample and blank digest.

TABLE 5.2 PREPARATION OF QC SOLUTIONS

Certified value of QC source solution (ng Hg/mL) C_{std}	Aliquot of QC source solution for dilution, (mL) A	Dilution Volume, mL V_d	QC working solution concentration using Eq. 1 (ng Hg/mL) C_{ws}	Volume of working solution taken for analysis, (mL) V_m	Expected Hg value, (ng) using Eq. 2 M
<1	-	---		2	
1-5	5	100		2	
5-20	5	250		2	
20-100	5	1000		2	

$$C_{ws} = \frac{C_{std} \times A}{Vd}$$ Equation 1

where:

C_{ws} = Concentration of QC "working" solution (WSQC), ng Hg/mL.

C_{std} = Concentration in ng Hg/mL of QC source solution (QC).

V_d = Dilution volume in mL.

A = Aliquot of QC source solution added to volumetric flask in mL.

$M_{Hg} = C_{ws} \times V_m$. Equation 2

where:

M_{Hg} = Expected ng Hg in aeration flask.

V_m = Aliquot of C_{ws} taken for measurement, mL.

The procedure used to determine the existence of matrix effects is described below:

1. Analyze an aliquot of the sample and record the sample aliquot size used (see Subsection 5.4.3).
2. Calculate the Hg content in ng of the sample aliquot.
3. Determine a working standard aliquot size that equals or exceeds the sample response from Step 2.
4. Add the value determined from Step 3 to an additional sample aliquot identical to that used in Step 1.
5. Analyze this spiked sample and record the response.
6. The spike recovery is calculated as follows:

$$\% \text{ Recovery} = \frac{C \text{ spiked sample} - C \text{ sample}}{C \text{ spike}} \times 100 \qquad \text{Equation 5-3}$$

where:

C spiked sample = Measured Hg in spiked sample, mg.

C sample = Measured Hg in unspiked sample, mg.

C spike = Hg added to sample, mg.

Note: To ensure the validity of the spike measurement, it is imperative that the measurement result fall within the range of the calibration.

Method of Standard Addition Analysis—If the recovery result obtained from the section above on the measurement of spiked samples falls outside the 85-115% range, then the MSA must be employed for all sample digest measurements. This procedure is described below:

1. Repeat steps 1 and 2 of spiked sample measurement above to determine the level of Hg in the sample (designated S_0).
2. To a second, identical sample aliquot, add a working standard volume that contains a Hg level that is approximately 50% of the sample Hg level. Refer to this spiked sample as S_1, and record the exact aliquot volume of sample and working standard used.
3. Analyze spiked sample (S_1).
4. To another, identical sample aliquot, add a working standard aliquot that contains an Hg level that is approximately equal to that of the sample. Refer to this spiked sample as S_2, and record the exact aliquot volume of sample and working standard used.
5. Analyze the spiked sample (S_2).
6. To another, identical sample aliquot, add a working standard aliquot that contains an Hg level that is approximately 1.5 times that at the sample. Refer to this spiked sample as S_3, and record the exact aliquot volume of sample and working standard used.
7. Analyze the spiked sample (S_3).
8. The peak intensity of each solution is determined and plotted on the vertical axis of a graph. The concentrations of the known standards are plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the

ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example is shown in Figure 5.6.

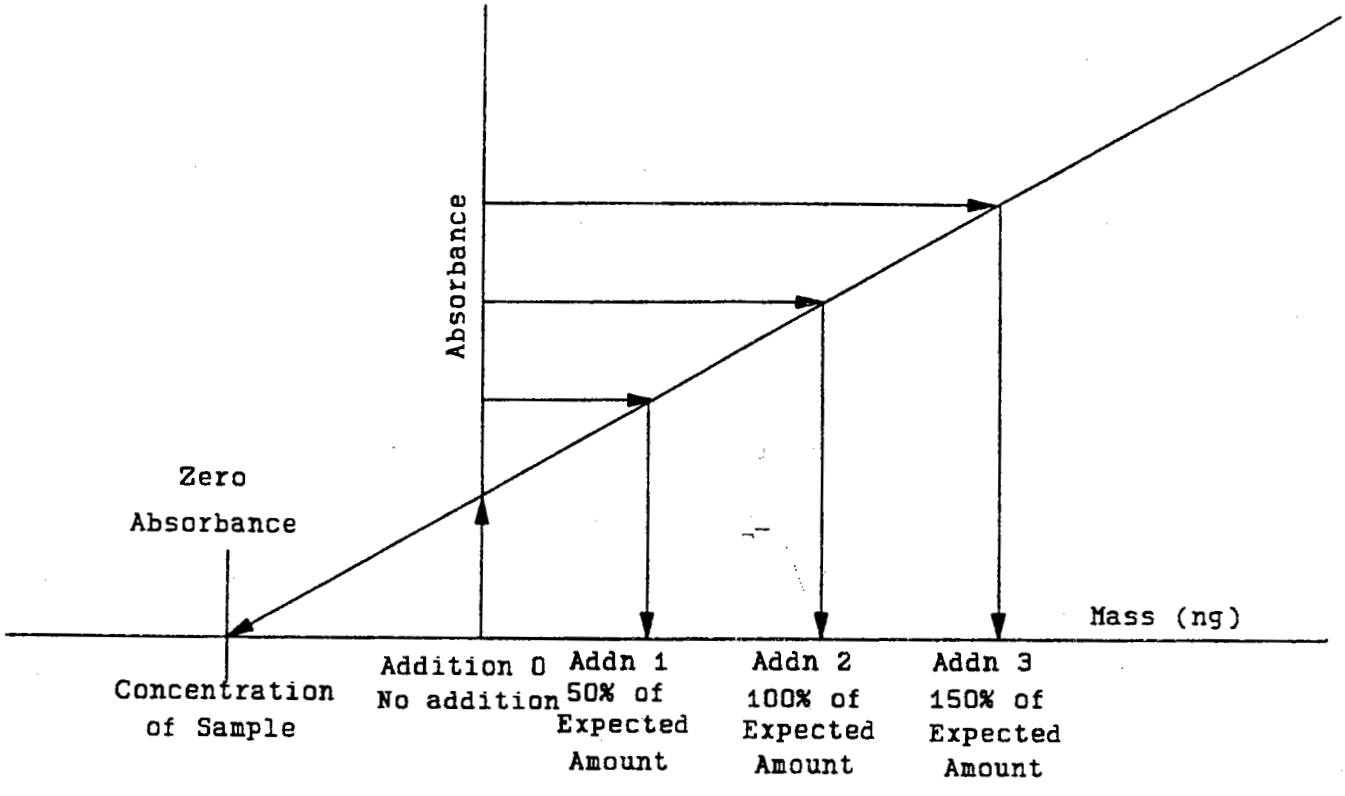


Figure 5.6. Method of standard additions for field samples.

To perform a valid MSA analysis, three criteria must be met:

1. The MSA standard curve must be linear using the criteria in Subsection 5.3.2.
2. The spiking level of Hg must be at least 50% of Hg in the sample.
3. The spiking level must be at least 10 times the detection limit (approximately 20 ng).

5.3.4 *Field Sample Analysis*—Repeat the procedure used to establish the calibration curve with an appropriately sized aliquot (1 to 5 mL) of the diluted sample until two consecutive peak heights agree as follows:

Hg mass, ng	*Limits (% deviation from average)*
<5	50
5-15	15
15-100	5
>100	3

An aliquot peak maximum (except the 5-mL aliquot) must be greater than 10% of the recorder full scale. If the peak maximum of a 1-mL aliquot is off scale on the recorder, further dilute the original source sample to bring the Hg concentration into the calibration range of the spectrophotometer.

Run a CBV and a CCV at least after every five samples to check the spectrophotometer calibration drift; recalibrate as necessary (see Subsection 5.3.3). It is recommended that at least one sample from each stack test be checked by the method of standard additions to confirm that matrix effects have not interfered with the analysis (see Subsection 5.3.3). Record all data for field sample analysis on the Method 101A field analysis data form, Figure 5.7, or similar form.

Analysis Samples No. A.1 and HCl A.2—After sample preparation of each sample run, two sample fractions must be analyzed for Hg to determine the total ng of Hg. Analysis Sample No. A.1 is the filtrate of the $KMnO_4$ absorbing solution and rinse and the digestate of the glass fiber filter, if applicable. Analysis Sample No. A.1 will be 1,000 mL or more, measured to within 1 mL. Analysis Sample No. HCl A.2 is the digestate of residue and Whatman 40 filter paper and HCl rinse, if applicable. Analysis Sample No. HCl A.2 will be 500 mL. A recommended sequence of analysis is presented in Table 5.3.

Analysis Samples No. A.1 Blank and HCl A.2 Blank—Each test series requires that a sample blank be taken. The sample blank is prepared in the same manner as the field samples. The analysis of the sample blank will have the same two fractions as each field sample. The blank will be analyzed at the same time and in the same manner as the field samples, with the exception that a 10-mL aliquot shall be used for analysis. A recommended sequence of analysis is presented in Table 5.3.

Container No. 2 (Silica Gel)—Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

Date samples received _____ Date samples analyzed _____
Plant _____ Run number(s) _____
Location _____ Analyst _____
Calibration factor (S) _____ Intercept (I), if applicable _____

Field Sample Number	Analysis Number	Instrument Response (mm)	Mean Instrument Response (mm)	Percent Deviation (ng Hg)	Mean Instrument Response Blank Corrected (y)	Dilution Factor (F)	Mass Field Sample (ng Hg)

Deviation of replicate measurements, (%) $= \dfrac{(A_1 - A_2)}{\frac{A_1 + A_2}{2}} \times 100$

$= \dfrac{(\quad) - (\quad)}{\frac{(\quad) + (\quad)}{2}} 100 =$ _____

Mass of QC sample without intercept (ng Hg)
$= S \times y \times F$
$=$ _____ x _____ x _____ =

Mass of QC sample with intercept (ng Hg)
$= S (y - I) F$
$=$ _____ (____ - ____) _____ =

Figure 5.7. Analytical data form for analysis of field samples.

TABLE 5.3 RECOMMENDED ANALYTICAL SEQUENCE[a]

Sequence No.	Sample ID	Sequence No.	Sample ID
1	IBV	21	HCl A.2, Run 1 spike
2	repeat	22	repeat
3	ICV	23	A.1, Run 2
4	repeat	24	repeat
5	CCV[b]	25	HCl A.2, Run 2
6	repeat	26	repeat
7	A.1 blank	27	A.1, Run 3
8	repeat	28	repeat
9	HCl, A.2 blank	29	HCl A.2, Run 3
10	repeat	30	repeat
11	A.1, Run 1	31	CCV
12	repeat	32	repeat
13	A.1 Spike, Run 1[c]	33	CBV
14	repeat	34	repeat
15	HCl A.2 Run 1[c]	35	Repeat Calibration
16	repeat[d]		
17	CCV		
18	repeat		
19	CBV		
20	repeat		

[a]Assuming a valid calibration has been performed.
[b]If different than ICV.
[c]Any A.1 spike from runs 1, 2, or 3.
\t this point, if the recovery is 85 to 115%, proceed to Step 26; if not, all samples must be run using MSA (Subsection 5.3.3).

5.4 Alternate Analytical Apparatus

Alternative systems are allowable as long as they meet the following criteria:

5.4.1 *Measurement Technique*—The system is based on cold vapor atomic absorption techniques.

5.4.2 *Analyte Recovery*—Eighty-five-115% of the spike is recovered when an aliquot of a source sample is spiked with a known concentration of Hg (II) compound.

5.4.3 *Calibration Curve*—A linear calibration curve is generated and two consecutive standards of the same aliquot size and concentration agree within the following limits.

Hg mass, ng/mL	*Limits (% deviation from average)*
<0.5	50
0.5-1.5	15
1.5-10	5
>10	3

5.4.4 *Sensitivity*—The system is capable of detecting 0.2 ng Hg/mL for flow-injection systems or 20 ng Hg for batch systems.

An example of a flow-injection analytical system is depicted in Figure 1.3 Note that these systems inject samples in a semicontinuous manner; consequently, the solution concentration is monitored, not the total Hg in the entire sample. Therefore, the total Hg in a given sample digest is calculated as follows:

$$M_{Hg} = C_{Hg} \times V \qquad \text{Equation 5-4}$$

where:

M_{Hg} = Total mg Hg in each sample digest from Section 5.2.

C_{Hg} = Measured concentration in mg Hg/mL.

V = Total volume in milliliters of the sample digest.

These calculations are shown in Section 3.19.6.

5.4.5 *Data Quality Assessment for Alternate Analytical Systems*—QC solutions used to determine the accuracy of the calibration may be measured directly without performing the calculations described in Subsection 5.3.3. This procedure, of course, is based on the assumption that the sample concentration value does not exceed that of the highest calibration standard, thereby requiring a dilution.

Determining matrix effects on the measurement recovery is performed as follows:

1. Determine the Hg concentration in the sample digest.
2. Remove two 10-mL aliquots of the digest and place in clean 20-mL beakers.
3. To one aliquot, add 1 mL of distilled deionized water and mix by swirling the beaker (S_0).
4. To the other aliquot, add 1 mL of a standard that is 10 to 20 times the solution concentration of the sample; mix the beaker contents (S_1).
5. Measure both solutions for Hg content.
6. The recovery of the added spike is as follows:

$$\% \text{ Recovery} = \frac{M_{S1} - M_{S0}}{M_{spike}} \times 100 \qquad \text{Equation 5-5}$$

where:

M_{S1} = mg Hg in spiked sample.

= mg Hg/mL in S_1 x 11 mL.

M_{S0} = mg Hg in sample spiked with water.

= mg Hg/mL (of spiking solution) x 1 mL.

The recovery should be between 85-115%. Otherwise, the method of additions must be employed for each sample of the sample run.

Method of Additions—In this method, equal volumes of sample are added to a DI water blank and to three standards containing different known amounts of the test element. The volume of the blank and the standards must be the same. The absorbance (peak height, counts, etc.) of each solution is determined and then plotted on the vertical axis of a graph. The concentration of the known standards are plotted on the horizontal axis. When the resulting line is extracted back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example is shown in figure 5.6.

5.5 Posttest Checklist

Posttest checklists for QC sample analysis and field sample analysis are presented in figures 5.8 and 5.9.

QC Sample Analysis Checklist

Date _____ Plant Name _____ Sampling Location _____

Calibration Standards and Matrix Checks

Mercury Stock Solution, 1 mg Hg/mL:

Prepared in-house? (Y/N) _____
Source of mercury (II) chloride _____
Commercial stock solution? (Y/N) _____
Source _____

Intermediate Mercury Standard Solution, 10 mg/mL:

Date prepared _____
Used glass pipet? (Y/N) _____
Source and grade of HNO_3 _____

Working Mercury Standard Solution, 200 ng Hg/mL:

Prepared today? (Y/N) _____
Used glass pipet? (Y/N) _____

Calibration Standards:

	mL of working standards	volume of volumetric flask, mL
#1	_____	_____
#2	_____	_____
#3	_____	_____
#4	_____	_____
#5	_____	_____
#6	_____	_____
#7	_____	_____

Instrumentation:
Spectrophotometer type _____

Moisture Removal System:
Optical cell heating system? _____ Calibrated? _____
Moisture trap used? _____ What type? _____

Data Recording System:
Recorder _____ Integrator _____ Other _____
Describe _____
Peak height _____ Peak area _____

Figure 5.8. QC sample analysis.

Cold Vapor Generation System:

Standard batch system? _____

Alternate system? _____

Describe alternate system? _____

_____

_____

Aeration gas _____ Aeration gas flow _____

Gas cylinder? _____ Peristaltic pump? _____

Standardization:

Glass pipets used? _____

mL of working standard	Standard value[a] (ng)	Reading 1	Reading 2	%Difference

[a]If using an alternate system that uses flow injection this value may be expressed as concentration, e.g., µg/L, ng/L, etc.

Calibration coefficient _____

Offset at origin (measured response of calibration blank) _____ng or % of scale.

Initial Calibration Verification (ICV):

QC check sample source _____

Certified or expected concentration _____

Measured concentration _____

% Difference _____

Initial Calibration Blank Verification (IBV):

Measured value _____

Below detection limit? _____

Matrix Interference Check:

Method of additions performed for one test site sample? _____

Spike added _____

Spike recovered _____

$$\% \text{ recovery} = \frac{\text{Spiked sample value - unspiked sample value}}{\text{spike value}} = \_\_\_\_\_$$

Figure 5.8. (Continued)

If the recovery was outside of 85-115%, were samples run using the method of standard additions? _____

Describe _____

Continuing Calibration Verification (CCV) - Check sample of standard to be reanalyzed after every five samples:

Standard used (source) _____

Expected value/unit _____

Was measured value/unit always within 10% of expected value? _____

Final Standardization:

Glass pipets used? _____

mL of working standard	Standard value[a] (ng)	Reading 1	Reading 2	%Difference

[a]Alternate analytical systems may express Hg value as a concentration (e.g., mg/L Hg).

Calibration coefficient _____

Offset at origin _____ng or % of scale.

Figure 5.8. (Continued)

Sample Analysis Checklist

Date _____ Time _____ Operator _____ Observer _____

Sample Analysis

Were all sample digests analyzed within 48 h of preparation? _____(Y/N)

Were 10 mL of samples A.1 blank and HCl A.2 blank used as a minimum? _____(Y/N)

Were duplicate measurements performed as a minimum for all blank and sample digests? _____(Y/N)

Did duplicate measurements meet the "percent difference" criteria outlined in Table 5.2 ____(Y/N)

Was the largest possible aliquot (20 mL) used when a measurement was below the detection limit? _____(Y/N)

If a sample measurement exceeded the highest calibration standard, were appropriately smaller aliquots always taken to ensure that results fell within the calibration range? ____(Y/N)

If 1-mL aliquots taken for measurement still were off scale, were sample digests diluted so that results were within the linear range of the standards? _____(Y/N)

What volumetric glassware (pipets) was used to add sample digests to the aeration flasks? _____(mL)

What volumetric glassware (pipets/flasks) was used to dilute sample digests? _____ (if necessary)

If the calibration check samples differed by greater than 10% of the expected values, was the system recalibrated? _____(Y/N)

Were CBV and CCV samples analyzed after ever five samples? _____(Y/N)

Were all samples run after the previously CBV and CCV sample analyses? _____(Y/N)

Was the full standardization performed at the end of the sample analysis? _____(Y/N)

Figure 5.9. Method 101A sample analysis checklist.

TABLE 5.1 ACTIVITY MATRIX FOR SAMPLE ANALYSIS

Characteristic	Acceptance limits	Frequency & method of measurement	Action if requirements are not met
Sample preparation	Samples and blanks prepared under same conditions	-----	Adjust dilutions, if possible; otherwise report to Administrator
All calibrations	(1) Reagents and volumes used during measurement of samples and standards are identical	Dilute samples so that matrix concentrations are are identical to original sample digest	Reanalyze samples
	(2) Perform 6-point calibration curve including calibration blank	Prepare fresh daily	Prepare fresh daily
	(3) Calibration coefficient better than 0.999	Each calibration point is the average of duplicate measurements	Repeat calibration
Calibration Verification Check Samples (ICV)	Analysis within 5% of expected or certified value	Analyze after every calibration	Ensure quality of check sample or repeat calibration
Calibration Blanks Verification (IBV)	Must be below detection limit	Analyze after every calibration	Check for potential contamination and repeat calibration
Continuing Calibration Verification Sample (CCV)	Must be within 10% of expected value	Analyze after every 5th sample	Repeat calibration and repeat all samples since last successful CCV analysis

(Continued)

TABLE 5.1 (Continued)

Characteristic	Acceptance limits	Frequency & method of measurement	Action if requirements are not met
Continuing Blank Verification (CBV)	Must be below detection limit	Analyze after every 5th sample	Repeat calibration and repeat all samples since last successful CBV analysis
Matrix check sample	Recovery of sample digest spike 85-115%	One sample digest from every stack test is spiked at a level at least equal to sample digest concentration	Analyze all samples using the method of standard additions
Duplicate measurements	See Subsec. 5.3.2	All standard and sample analyses	Repeat until agreement is achieved
Data recording	All pertinent data recorded on figs. 5.1, 5.2	Visually check	Supply missing data

6.0 CALCULATIONS

Calculation errors resulting from procedural or mathematical mistakes can be a part of total system error. Therefore, it is recommended that each set of calculations be repeated or spotchecked, preferably by a team member other than the one who performed the original calculations. If a difference greater than typical round-off error is detected, the calculations should be checked step-by-step until the source of error is found and corrected.

Calculations should be carried out to at least one extra decimal figure beyond that of the acquired data and should be rounded off after final calculation to two significant digits for each run or sample. All rounding of numbers should be performed in accordance with the ASTM 380-76 procedures.

A computer program is advantageous in reducing calculation errors. If a program is used, the original data entered should be included in the printout for review. If differences are observed, a new computer run should be made. A computer program also is useful in maintaining a standardized format for reporting results. The data shown will allow auditing the calculations.

Table 6.1 at the end of this section summarizes the QA activities for calculations.

In the next section, nomenclature and equations have been divided into two groups. The first group (Section 3.19.6.1 to 3.19.6.4) deals with sampling calculations. The second group (Section 3.19.6.5 to 3.19.6.13) deals with analytical and emissions calculations.

6.1 Sampling Nomenclature from Method 5

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

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

I = Percent of isokinetic sampling.

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

L_i = Individual leakage rate observed during the leak check conducted prior to the "i^{th}" component change (i = 1, 2, 3...n), m^3/min (cfm).

L_p = Leakage rate observed during the posttest leak check, m^3/min (cfm).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lbmole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 [(mm Hg)(m^3)]/[(°K)(g-mole)] (21.85 [(in. Hg)(ft^3)]/[(°R)(lb-mole)]).

T_m = Absolute average DGM temperature, °K (°R).

T_s = Absolute average stack gas temperature, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528R).

V_{lc} = Total volume liquid collected in impingers and silica gel, mL.

V_m = Volume of gas sample as measured by dry-gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry-gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

v_s = Stack-gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/s (ft/s).

Y = Dry-gas meter calibration factor.

ΔH = Average pressure differential across the orifice meter, mm H_20 (in. H_20).

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

θ = Total sampling time, min.

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

θ_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = S/min.

100 = Conversion to %.

6.2 Conversion Factors

From	To	Multiply by
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft^3	2.205×10^{-3}
g/ft^3	g/m^3	35.31

6.3 Average Dry-Gas Meter Temperature and Average Orifice Pressure Drop

See data sheet (Figure 4.1).

6.4 Dry-Gas Volume

Correct the sample volume measured by the dry-gas meter to standard conditions (20 °C, 760 mm Hg or 68 °F, 29.92 in. Hg) by using Equation 6-1.

$$V = V_m Y \frac{T_{std} \left(P_{bar} + \frac{\Delta H}{13.6}\right)}{T_m P_{std}}$$

$$V = K_1 V_m Y \frac{P_{bar} + \left(\frac{\Delta H}{13.6}\right)}{T_m} \qquad \text{Equation 6-1}$$

where:

K_1 = 0.3858 °K/mm Hg for metric units.

= 17.64 °R/in Hg for English units.

Note: Equation 6-1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the posttest leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 6-1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 6-1 with the expression:

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

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 6-1 by the expression:

$$[V_m - (L_i - L_a)\ \theta_1 - \sum_{i=2}^{n} (L_i - L_a)\ \theta_i - (L_p - L_a)\ \theta_p]$$

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

6.5 Volume of Water Vapor

$$V_{w(std)} = V_{lc} \frac{\rho_w R T_{std}}{M_w P_{std}} = K_2 V_{lc} \qquad \text{Equation 6-2}$$

where:

K_2 = 0.001333 m^3/mL for metric units.

= 0.04707 ft^3/mL for English units.

6.6 Moisture Content

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Equation 6-3}$$

Note: In saturated or water droplet-laden gas streams, calculate the moisture content of the stack gas in two ways: from the impinger analysis (Equation 6-3) and from the assumption of saturated conditions. The lower for B_{ws} shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note of Section 1.2, Method 4. For the purposes of this method, the average stack-gas temperature from Figure 4.2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ± 1 °C (2 °F).

6.7 Nomenclature from Method 2

A = Cross-sectional area of stack, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream (from Method 5 or Reference Method 4), proportion by volume.

C_p = Pitot tube coefficient, dimensionless.

K_p = Pitot tube constant - 34.97 for the metric system and 85.49 for the English system.

M_d = Molecular weight of stack gas, dry basis (see Section 3.6), g/g-mole (lb/lb-mole).

M_s = Molecular weight of stack gas, wet basis, g/g-mole (lb/lb-mole).

= M_d (1 - B_{ws}) + 18.0 B_{ws}

P_{bar} = Barometric pressure at measurement site, mm Hg (in. Hg).

P_g = Stack static pressure, mm Hg (in. Hg).

P_s = Absolute stack pressure, mm Hg (in. Hg),

= P_{bar} + P_g

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{sd} = Dry volumetric stack gas flow rate corrected to standard conditions, dsm^3/h (dscf/h).

t_s = Stack temperature, °C (°F).

T_s = Absolute stack temperature, °K (°R).

= 273 + t_s for metric.

= 460 + t_s for English.

T_{std} = Standard absolute temperature, 293 °K (528 °R).

v_s = Average stack gas velocity, m/sec (ft/s).

Δp = Velocity head of stack gas, mm H_20 (in. H_20).

3,600 = Conversion factor, s/h.

18.0 = Molecular weight of water, g/g-mole (lb/lb-mole).

6.8 Average Stack Gas Velocity

$$v_s = K_p\, C_p\, (\sqrt{\Delta p})_{avg} \sqrt{\frac{Ts(avg)}{P_s\, M_s}}$$ Equation 6-4

6.9 Average Stack Gas, Dry Volumetric Flow Rate

$$Q = 3600\ (1-B_{ws})\ v_s\ A\ \frac{T_{std}\ P_s}{T_{s(avg)}\ P_{std}} \qquad \text{Equation 6-5}$$

6.10 Isokinetic Variation

6.10.1 *Calculation from Raw Data—*

$$I = \frac{100\ T_s\ [K_3\ V_{lc} + (V_m\ \frac{Y}{T_m})(P_{bar} + \frac{\Delta H}{13.6})]}{60\ \Theta\ v_s\ P_s\ A_n} \qquad \text{Equation 6-6}$$

where:

K_3 = 0.003454 [(mm Hg)(m^3)]/[(mL)(°K)] for metric units.

= 0.002669 [(in. Hg)(ft^3)]/[(mL)(°R)] for English units.

6.10.2 *Calculation from Intermediate Values—*

$$I = \frac{T_s\ V_{m(std)}\ P_{std}\ 100}{T_{std}\ v_s\ \Theta\ A_n\ P_s\ 60\ (1 - B_{ws})} \qquad \text{Equation 6-7}$$

$$= K_4 \frac{T_s\ V_{m(std)}}{P_s\ v_s\ A_n\ \Theta\ (1 - B_{ws})} \qquad \text{Equation 6-8}$$

where:

K_4 = 4.320 for metric units.

= 0.09450 for English units.

6.11 Acceptable Results

If 90% ≤I ≤110%, the results are acceptable. If the PM results are low in comparison to the standard and I is over 110% or less than 90%, the Administrator may opt to accept the results. Citation 4 in the bibliography of Method 5 may be used to make acceptability judgments. If I is judged to be unacceptable, reject the results and repeat the test.

6.12 Method 101A Calculations

6.12.1 *Determining Compliance*—Each performance test consists of three repetitions of the applicable test method. For the purpose of determining compliance with an applicable national emission standard, use the average of the results of all repetitions.

6.12.2 *Total Hg*—For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agreed within 3% of their average for the contribution of the blank. Then calculate the total Hg content in µg in each sample. Correct for any dilutions made to bring the sample into the working range of the spectrophotometer.

$$m_{(HCl)Hg} = \left\{ \frac{[C_{(HCl)Hg} \quad DF]}{S} - \frac{[C_{(HCl\ blk)Hg} \quad DF_{blk}]}{S_{blk}} \right\} V_{f(HCL)} \quad 10^{-3} \qquad \text{Equation 6-9}$$

where:

$m_{(HCl)Hg}$ = Total blank corrected µg of Hg in HCl rinse and HCl digestate of filter sample.

$C_{(HCl)Hg}$ = Total ng of Hg analyzed in the aliquot from the 500-mL Analysis Sample No. HCl A.2.

$C_{(HCl\ blk)Hg}$ = Total ng of Hg analyzed in aliquot of the 500-mL Analysis Sample No HCl A.2 blank.

DF = Dilution factor for the HCl digested Hg-containing solution, Analysis Sample No. HCl A.2. This dilution factor (DF) applies only to the intermediate dilution steps because the original sample volume $(V_f)_{HCl}$ of HCl A.2 has been factored out in the equation, along with the sample aliquot, (S). In Equation 6.9, the sample aliquot, S, is introduced directly into the aeration cell for analysis according to the procedure outlined in Section 3.19.5.3.4. A dilution factor is required only if it is necessary to bring the sample into the analytical instrument's calibration range. If no dilution is necessary, then DF equals 1.0.

DF_{blk} = Dilution factor for the HCl digested solution, Analysis Sample No. HCl A.2 blank. (Note: Normal dilution factor calculations apply here.)

$V_{f(HCl)}$ = Solution volume of original Analysis Sample No. HCl A.2 and HCl A.2 blank, 500 mL for samples diluted as described in Section 5.2.2.4 of this document.

10^{-3} = Conversion factor, µg/ng.

S = Aliquot volume of sample added to aeration cell, mL.

S_{blk} = Aliquot volume of blank added to aeration cell, mL.

Note: The maximum allowable blank subtraction for the HCl is the lesser of the two following values: (1) the actual blank measured value (Analysis Sample No. HCl A.2 blank); or (2) 5% of the Hg content in the combined HCl rinse and digested sample (Analysis Sample No. HCl A.2).

$$m_{(fltr)Hg} = \left\{ \frac{[C_{(fltr)Hg} \quad DF \quad V_{f(fltr)}]}{S} - \frac{[C_{(fltr\ blk)Hg} \quad DF_{blk} \quad V_{f(blk)}]}{S_{blk}} \right\} 10^{-3} \qquad \text{Equation 6-10}$$

where:

$m_{(fltr)Hg}$ = Total blank corrected µg of Hg in $KMnO_4$ filtrate and HNO_3 digestion of filter sample.

$C_{(fltr)Hg}$ = Total ng of Hg in aliquot of $KMnO_4$ filtrate and HNO_3 digestion of filter analyzed (aliquot of Analysis Sample A.1).

$C_{(fltr\ blk)Hg}$ = Total ng of Hg in aliquot of $KMnO_4$ blank and HNO_3 digestion of blank filter analyzed (aliquot of Analysis Sample No. A.1 blank).

$V_{f(fltr)}$ = Solution volume of original sample, normally 1000 mL for samples diluted as described in Section 7.3.2 of Method 101A.

$V_{f(blk)}$ = Solution volume of blank sample, 1000 mL for samples diluted as described in Section 7.3.2 of Method 101A.

Note: The maximum allowable blank subtraction for the HCl is the lesser of the two following values: (1) the actual blank measured value (Analysis Sample No. A.1 blank); or (2) 5% of the Hg content in the filtrate (Analysis Sample No. A.1).

$$m_{Hg} = m_{(HCl)Hg} + m_{(fltr)Hg} \qquad \text{Equation 6-11}$$

where:

m_{Hg} = Total blank corrected Hg content in each sample, µg.

$m_{(HCl)Hg}$ = Total blank corrected µg of Hg in HCl rinse and HCl digestate of filter sample.

$m_{(fltr)Hg}$ = Total blank corrected µg of Hg in $KMnO_4$ filtrate and HNO_3 digestion of filter sample.

6.12.3 *Mercury Emission Rate*—Calculate the Hg emission rate R in g/day for continuous operations using Equation 101A-6 in Method 101A. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.

$$R = K \frac{m_{Hg}\, v_s\, A_s\, (86{,}400 \times 10^{-6})}{[V_{m(std)} + V_{w(std)}]\,(T_s/P_s)} \qquad \text{Equation 6-12}$$

where:

m_{Hg} = Total blank corrected Hg content in each sample, µg.

v_s = Average stack gas velocity, m/s (fps).

A_s = Stack cross-sectional area, m^2 (ft^2).

86,400 = Conversion factor, s/day.

10^{-6} = Conversion factor, g/µg.

$V_{m(std)}$ = Dry-gas sample volume at standard conditions, corrected for leakage (if any), m^3 (ft^3).

$V_{w(std)}$ = Volume of water vapor at standard conditions, m^3 (ft^3).

T_s = Absolute stack-gas temperature, °K (°R).

P_s = Absolute stack-gas pressure, mm Hg (in. Hg).

K = 0.3858 °K/mm Hg for metric units.

K = 17.64 °R/in. Hg for English units.

6.13 Determining Compliance

Each performance test consists of three repetitions of the applicable test method. For the purpose of determining compliance with an applicable national emission standard, use the average of the results of all repetitions.

6.14 Hg Calculation for Alternate Analytical Systems

For alternate analytical systems, in which Hg is measured as a concentration (mg Hg/L of sample) the Hg in mg (m_{Hg}) in the original solution is calculated as follows:

$$m_{Hg} = C_{Hg} \times (DF) \times (V_f) \qquad \text{Equation 6-13}$$

where:

C_{Hg} = Measured concentration of Hg in mg Hg/L of digested sample.

DF = Dilution factor for the Hg-containing solution used to ensure measured sample values were within the defined portion of the calibration curve.

V_f = Solution volume of sample prepared in L.

TABLE 6.1 ACTIVITY MATRIX FOR CALCULATION CHECKS

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Analysis data form	All data and calculations are shown	Visually check	Complete the missing data
Calculations	Difference between check and original calculations should not exceed round-off error	Repeat all calculations starting with raw data for hand calculations; check all raw data input for computer calculations; hand calculate one sample per test	Indicate errors on calculation form

7.0 MAINTENANCE

The normal use of emission testing equipment subjects it to corrosive gases, extremes in temperature, vibration, and shock. Keeping the equipment in good operating order requires knowledge of the equipment and a program of routine maintenance performed quarterly or after 1000 ft^3 of operation, whichever is greater. In addition to the quarterly maintenance, cleaning pumps and metering systems annually is recommended. Maintenance procedures for the various components are summarized in Table 7.1 at the end of this section. The following procedures are not required, but they are recommended to increase the reliability of the equipment.

7.1 Sampling Equipment

7.1.1 *Pump*—Several types of pumps may be used to perform Method 101A; the two most common are the fiber vane pump with in-line oiler and the diaphragm pump. The fiber vane pump requires a periodic check of the oiler jar. Its contents should be translucent; the oil should be changed if not translucent. Use the oil specified by the manufacturer. If none is specified, use SAE-10 nondetergent oil. Whenever a fiber vane pump starts to run erratically, or during the yearly disassembly, the head should be removed and the fiber vanes changed.

The diaphragm pump requires little maintenance. If the diaphragm pump leaks or runs erratically, it is normally due to a bad diaphragm or malfunctions in the valves; these parts are easily replaced and should be cleaned annually by complete disassembly of the train.

7.1.2 *Dry-Gas Meters*—The dry-gas meter should be checked for excess oil and component corrosion by removing the top plate every 3 months. The meter should be disassembled, and all components should be cleaned and checked more often if the dials show erratic rotation or if the meter will not calibrate properly.

7.1.3 *Inclined Manometer*—The fluid should be changed when it is discolored or contains visible matter and when it is disassembled yearly. No other routine maintenance is required because the inclined manometer is evaluated during the leak checks of both the pitot tube and the entire meter box.

7.1.4 *Sampling Train*—All remaining sample train components should be visually checked every 3 months, and they should be completely disassembled and cleaned or replaced yearly. Many of the items, such as quick disconnects, should be replaced only when damaged.

7.2 Analytical Instruments

7.2.1 *Spectrophotometer*—Consult the manufacturer's operation manual for specific maintenance activities.

7.2.2 *Peristaltic Pump Tubing*—Inspect pump tubing daily. The tubing should not have flat spots where it has contacted the pump rollers and should feel flexible. Replace tubing if this is not the case.

7.2.3 *Desiccant*—If a moisture trap is used instead of a heated optical cell, the desiccant should be replaced daily. Both tube ends should be filled with glass wool; the dessicant must not be packed too tightly.

7.2.4 *Optical Cell*—The windows of the optical cell should be inspected daily for any dust, dirt, or grease that will degrade light throughput and overall analytical performance. Wash gently with detergent and rinse well. Dry by blotting with a towel and wipe, if necessary, with lens paper only.

7.2.5 *Spectrophotometer Windows*—The windows of the spectrophotometer must also be inspected (at least weekly) and cleaned as described in section above.

7.2.6 *Tygon Connecting Tubing*—Connection tubing must be inspected on a daily basis (or more frequently) for condensation or dirt. Replace if necessary. The existence of moisture after the dessicant trap (if used) indicates that the dessicant needs replacing. Refer to Section 7.2.3.

TABLE 7.1 ACTIVITY MATRIX FOR EQUIPMENT MAINTENANCE CHECKS

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Sampling Equipment			
Routine maintenance	No erratic behavior	Routine maintenance quarterly, or after 1000 ft^3 of use; disassemble and clean yearly	Replace parts
Fiber vane pump	Leak-free; required flow	Periodic check of oil jar; oil changed if not translucent; change fiber vanes yearly or when running erratically	Replace as needed
Diaphragm pump	Leak-free valves functioning properly; required flow	Clean valves during yearly disassembly	Replace when leaking or when running erratically
Dry-gas meter	No excess oil, corrosion, or erratic dial rotation	Check every three months for excess oil or corrosion by removing the top plate; check valves and diaphragm when meter dial runs erratically or when meter will not calibrate	Replace parts as needed, or meter
Inclined manometer	No discoloration of or visible matter in the fluid	Check periodically; change fluid during yearly disassembly	Replace parts as needed
Sample train	No damage or leaks	Visually check every 3 months; completely disassemble and clean or replace yearly	If failure noted, use another entire control console, sample box, or or umbilical cord

(Continued)

TABLE 7.1 Checks (Continued)

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Analytical Instruments			
Spectro-photometer	See owner's manual	See owner's manual manual	See owners
Peristaltic pump tubing	Flexible; no flat spots	Visually inspect tubing daily	Replace
Desiccant	Fresh or dry used silica gel; no moisture	Inspect daily	Replace
Optical cell	Clean of dust, dirt, grease, etc.	Inspect daily	Clean gently with detergent; rinse; blot with towel
Spectro-photometer windows	Same as above	Inspect weekly	Same as above
Tygon connecting tubing	No condensation or dirt	Inspect daily	Replace

8.0 AUDITING PROCEDURES

An audit is an independent assessment of data quality. Independence is achieved when the persons performing the audit apply standards and equipment different from the standards and equipment of the regular field team. Routine QA checks by a field team are necessary to generate quality data, but they are not part of the auditing procedure. Table 8.1 at the end of this section summarizes the QA functions for auditing.

One performance audit is recommended when testing for compliance with National Emission Standards for Hazardous Air Pollutants (NESHAPs), with New Source Performance Standards (NSPS), and as required by other government agencies. A performance audit is recommended when testing for other purposes; and two other performance audits are recommended. The three performance audits are:

1. An audit of the analysis of Method 101A is recommended for NESHAPs. The use of an NIST-traceable control sample is recommended for NSPS testing and for other purposes.
2. An audit of the sampling is suggested by Method 101A and is recommended by the QA Handbook.
3. An audit of the data processing is also recommended.

It is suggested that a systems audit be conducted as specified by the QA coordinator in addition to these performance audits. The two performance audits and the systems audit are described in detail in Subsections 8.1 and 8.2, respectively.

8.1 Performance Audits

Performance audits are conducted to evaluate quantitatively the quality of data produced by the sampling, analysis, or the total measurement system (sample collection, sample recovery, sample analysis, and data processing).

8.1.1 *Performance Audit of Method 101A Analysis*—A performance audit for Method 101A analysis is recommended for NESHAPs and NSPS testing using a control sample that is NIST-traceable. Although the control sample values are known to the analyst, the successful analysis of a control sample, as described in Subsection 5.3.3, makes the results traceable to an NIST standard.

8.1.2 *Performance Audit of the Field Test*—The dry-gas meter calibration should be checked by one of the two techniques shown below (meter orifice check or critical orifice check).

Meter Orifice Check—Using the data obtained during the calibration procedure described in Section 5.3, determine the $\Delta H_@$ for the metering system orifice. The $\Delta H_@$ is the orifice pressure differential in units of in. H_2O that correlates to 0.75 cfm of air at 528 °R and 29.92 in. Hg. The $\Delta H_@$ is calculated as follows:

$$\Delta H_@ = \frac{T_m}{P_{bar}} \frac{\Theta^2}{Y^2 V_m^2} \qquad \text{Equation 8-1}$$

where:

ΔH = Average pressure differential across the orifice meter, in. H_2O.

T_m = Absolute average DGM temperature, °R.

P_{bar} = Barometric pressure, in. Hg.

Θ = Total sampling time, min.

Y = DGM calibration factor, dimensionless.

V_m = Volume of gas sample as measured by DGM, dcf.

Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (i.e., pump, volume meter, and orifice) at the $\Delta H_@$ pressure differential for 10 min. Record the volume collected, the DGM temperature, and the barometric pressure. Calculate a DGM calibration check value, Y_c, as follows:

$$Y_c = \frac{10}{V_m}\sqrt{\frac{0.0319\ T_m}{P_{bar}}} \qquad \text{Equation 8-2}$$

where:

Y_c = DGM calibration check value, dimensionless.

10 = Run time, min.

0.0319 = $(0.0567 \text{ in Hg/°R})(0.75 \text{ cfm})^2$.

Compare the Y_c value with the dry-gas meter calibration factor, Y, to determine that: $0.97Y < Y_c < 1.03Y$. If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test.

Calibrated Critical Orifice—A calibrated critical orifice, calibrated against a wet-test meter or spirometer and designed to be inserted at the inlet of the sampling meter box, may be used as a
QC check by following the procedure below:

1. Allow a warm-up time of 15 min. This step is important to equilibrate the temperature conditions through the DGM.
2. Leak check the system. The leakage rate must be zero.
3. Obtain and record the barometric pressure, P_{bar} in mm Hg (in. Hg), using a barometer.
4. Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs must be at least 5 min each. The DGM volume readings shall be in increments of complete revolutions of the DGM.
5. Record the information listed in Figure 2.4.
6. Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y, using the equations below:

$$V_{m(std)} = K_1\ V_m\ [P_{bar} + (\Delta H/13.6)]/T_m \qquad \text{Equation 8-3}$$

$$V_{cr(std)} = K' (P_{bar} \theta)/T_{amb}^{1/2} \qquad \text{Equation 8-4}$$

$$Y = V_{cr(std)}/V_{m(std)} \qquad \text{Equation 8-5}$$

where:

$V_{cr(std)}$ = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dscm (dscf).

K' = 0.3858 °K/mm Hg for metric units

= 17.64 °R/in Hg for English units.

7. Average the DGM calibration values for each of the flow rates. The calibration factor, Y, at each of the flow rates should not differ by more than ± 2% from the average.

8.1.3 *Performance Audit of Data Processing*—Calculation errors are prevalent when processing data. Data processing errors can be determined by auditing the recorded data on the field and laboratory forms. The original and audit (check) calculations should agree within round-off error; if not, all of the remaining data should be checked. Data processing also may be audited by requiring that the testing laboratory provide an example calculation for one sample run. This example calculation will include all the calculations used to determine the emissions based on the raw field and laboratory data.

8.2 System Audit

A system audit is an on-site, qualitative inspection and review of the total measurement system. Initially, a system audit is recommended for each enforcement source test, defined here as a series of three runs at a source.

The auditor should have extensive background experience with source sampling or source test observation, specifically with Method 101A or Method 5. The auditor's functions are summarized below:

1. Observe procedures and techniques of the field team during sample collection and sample recovery.
2. Check/verify records of apparatus calibration checks and QC used in the laboratory analysis.

While on-site, the auditor observes the source test team's overall performance, including the following specific operations:

1. Setting up the sampling system and checking the sample train and pitot tube for leaks.
2. Collecting the isokinetic sampling.
3. Conducting the final leak checks.
4. Sample documentation procedures, sample recovery, and preparation of the samples for shipment.

Figure 4.3 in Section 3.19.4 is a suggested field observation checklist for 101A sampling and sample recovery, and Figure 5.9 in Section 3.19.5 is a suggested checklist for 101A sample analysis.

TABLE 8.1 ACTIVITY MATRIX FOR AUDITING PROCEDURES

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Performance audit of analytical phase	Measured relative error of audit samples less than 15% (or other stated value) for both samples	Frequency: Once during every enforcement source test[a] Method: Measure audit samples and compare results to true values	Review operating technique and repeat audit
Volumetric sampling	Measured pretest volume within ± 10% of the audit volume	Frequency: Once during every enforcement source test[a] Method: Measure reference volume and compare with true volume	Review operating techniques
Data processing errors	Original and checked calculations agree within round-off error	Frequency: Once during every enforcement test[a] Method: Independent calculations starting with recorded data	Check and correct all data for the audit period represented by the sampled data
Systems audit—observance of technique	Operational technique as described in this section of the Handbook	Frequency: Once during every enforcement source source test[a] until experience gained, then every third test Method: Observation of techniques assisted by audit checklist (Fig. 4.2)	Explain to team their deviations from recommended techniques and note on Fig. 4.2

[a]As defined here, a source test for enforcement comprises a series of three runs at one source. Source test for purposes other than enforcement may be audited at the frequency determined by the applicable group.

9.0 RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY

To achieve data of desired quality, two essential considerations are necessary: (1) the measurement process must be in a state of statistical control at the time of the measurement; and (2) the systematic errors, when combined with the random variation (errors or measurement), must result in an acceptable uncertainty. Evidence of quality data results from performing QC checks and independent audits of the measurement process, documenting these data, and using materials, instruments, and measurement procedures that can be traced to an appropriate standard of reference.

Data must be routinely obtained by repeatedly measuring standard reference samples (primary, secondary, and/or working standards) and by establishing a condition of process control. The working calibration standards must be traceable to standards of higher accuracy by using a control sample or by purchasing working calibration standards that are NIST-traceable.

Performance audit samples are not required for determining compliance; however, an NIST control sample is recommended (as discussed in Section 3.19.8). A control sample is also recommended as an independent check on the measurement process when the method is performed for other purposes. This procedure makes all the compliance determination samples traceable to an NIST standard.

10.0 REFERENCE METHODS: METHOD 101A-DETERMINATION OF PARTICULATE AND GASEOUS MERCURY EMISSIONS FROM STATIONARY SOURCES

This method is similar to Method 101, except acidic potassium permanganate solution is used instead of acidic iodine monochloride for sample collection.

1.0 APPLICABILITY AND PRINCIPLE

1.1 Applicability

This method applies to determining particulate and gaseous Hg emissions from sewage sludge incinerators and other sources, as specified in the regulations.

1.2 Principle

Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in acidic potassium permanganate ($KMnO_4$) solution. The Hg collected (in mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

2.0 RANGE AND SENSITIVITY

2.1 Range

After initial dilution, the range of this method is 20 to 800 ng Hg/mL. The upper limit can be extended by further dilution of the sample.

2.2 Sensitivity

The sensitivity of the method depends on the recorder/spectrophotometer combination selected.

3.0 INTERFERING AGENTS

3.1 Sampling

Excessive oxidizable matter in the stack-gas prematurely depletes the $KMnO_4$ solution and, thereby, prevents further collection of Hg.

This section represents Method 101A and referenced procedures from Method 101. ***Text from Method 101 is shown in bold italics.***

3.2 Analysis

Condensation of water vapor on the optical cell windows causes positive interference.

4.0 PRECISION

Based on eight paired-train tests, the within-laboratory standard deviation was estimated to be 4.8 µg/mL in the concentration range of 50 to 130 µg/m³.

5.0 APPARATUS

5.1 Sampling Train and Sample Recovery

Same as in Method 101, Sections 5.1 and 5.2, respectively, except for the following variations:

5.1.1 *Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Metering System, Barometer, and Gas Density Determination Equipment*—Same as in Method 5, Sections 2.1.1, 2.1.3, 2.1.4, 2.1.8, 2.1.9, and 2.1.10, respectively.

5.1.1 *Probe Liner*—***Borosilicate or quartz glass tubing. Testers may use a heating system capable of maintaining a gas temperature of 120 ± 14 °C (248 ± 25 °F) at the probe exit during sampling to prevent water condensation. (Note: Do not use metal probe liners.)***

If a filter is used ahead of the impingers, testers must use the pr heating system to minimize the condensation of gaseous Hg. If a filter is used ahea of the impingers, testers must use the probe heating system to minimize the condensation of gaseous Hg.

5.1.2 *Filter Holder (Optional)*—The holder should be composed of borosilicate glass with a rigid stainless-steel wire-screen filter support (do not use glass frit supports) and a silicone rubber or Teflon gasket, designed to provide a positive seal against leakage from outside or around the filter. The filter holder must be equipped with a filter heating system capable of maintaining a temperature around the filter holder of 120 ± 15 °C (248 ± 25 °F) during sampling to minimize both water and gaseous Hg condensation. Testers may use a filter in cases where the stream contains large quantities of particulate matter.

5.1.3 *Impingers*—***Four Greenburg-Smith impingers are required. They should be connected in series with leak-free ground glass fittings or any similar leak-free, noncontaminating fittings. For the first, third, and fourth impingers, testers may use impingers that are modified by replacing the tip with a 13-mm ID (0.5-in.) glass tube extending to 13 mm (0.5 in.) from the bottom of the flask.***

5.2 Sample Recovery

The following items are needed for sample recovery:

5.2.1 Glass Sample Bottles—***The bottles should be leakless, with Teflon-lined caps, 1000 and 100 mL.***

5.2.2 *Graduated Cylinder*—***A 250-mL graduated cylinder is required.***

5.2.3 *Funnel and Rubber Policeman*—***These items aid in transferring silica gel to the container; they are not necessary if the silica gel is weighed in the field.***

5.2.4 *Funnel*—***The funnel should be glass; it aids in sample recovery.***

5.2 Analysis

Same as in Method 101, Sections 5.3 and 5.4, respectively, except as follows:

5.2.1 *Volumetric Pipets*—Pipets must be Class A, 1, 2, 3, 4, 5, 10, and 20 mL.

5.2.2 *Graduated Cylinder*—A 25-mL graduated cylinder is required.

5.2.3 *Steam Bath*—Same as Method 101.

5.3 Sample Preparation and Analysis

The following equipment is needed for sample preparation and analysis:

5.3.1 *Atomic Absorption Spectrophotometer*—Any atomic absorption unit is suitable, provided it has an open sample presentation area in which to mount the optical cell. Testers should follow the instrument settings recommended by the manufacturer. Instruments designed specifically for measuring Hg using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.3.2 *Optical Cell*—***The optical cell should be cylindrical, with quartz end windows and the dimensions shown in Figure 101A-2. Wind the cell with approximately 2 m of 24-gauge nichrome heating wire and wrap with fiberglass insulation tape, or equivalent; do not let the wires touch one another.*** As an alternative to the heating wire, testers may use a heat lamp mounted above the cell or a moisture trap installed upstream of the cell.

5.3.3 *Aeration Cell*—***The cell must be constructed according to the specifications in Figure 101A-3. Do not use a glass frit as a substitute for the blown glass bubbler tip shown in Figure 101A-3.*** Aeration cells, available with commercial cold-vapor instrumentation, may be used as an alternate apparatus.

5.3.4 *Recorder*—***The recorder must be matched to output of the spectrophotometer described in Section 5.3.1.***

5.3.5 *Variable Transformer*—***The transformer is necessary for varying the voltage on the optical cell from 0 to 40 volts.***

5.3.6 *Hood*—***A hood is required for venting the optical cell exhaust.***

5.3.7 *Flow Metering Valve*—***Same as Method 101.***

5.3.8 *Flow Meter*—***A rotometer, or equivalent, is required that is capable of measuring a gas flow of 1.5 L/min.***

5.3.9 *Aeration Gas Cylinder*—The cylinder must contain nitrogen or dry, Hg-free air and must be equipped with a single-stage regulator. As an alternative, aeration may be provided by a peristaltic metering pump. If a commercial cold-vapor instrument is used, follow the manufacturer's recommendations.

5.3.10 *Tubing*—***The tubing is require for making connections. Use glass tubing (ungreased ball- and socket-connections are recommended) for all connections between the solution cell and the optical cell; do not use Tygon tubing, other types of flexible tubing, or metal tubing as substitutes. Testers may use Teflon, steel, or copper tubing between the nitrogen tank and the flow meter valve (Section 5.3.7), and Tygon, gum, or rubber tubing between the flow meter valve and the aeration cell.***

5.3.11 *Flow Rate Calibration Equipment*—***This equipment consists of a bubble flow meter or a wet-test meter for measuring a gas flow rate of 1.5 ± 0.1 L/min.***

5.3.12 *Volumetric Flasks*—***These flasks must be Class A, with pennyhead standard taper stoppers; the required sizes are 100, 250, 500, and 1000 mL.***

5.3.13 *Volumetric Pipets*—***These pipets must be Class A; the required sizes are 1, 2, 3, 4, 5, 10, and 20 mL.***

5.3.14 *Graduated Cylinder*—***A 25-mL cylinder is required.***

5.3.15 *Magnetic Stirrer*—***A general-purpose laboratory-type stirring bar is required.***

5.3.16 *Magnetic Stirring Bar*—***A Teflon-coated stirring bar is required.***

5.3.17 *Balance*—***A balance capable of weighing to ± 0.5 g is required.***

5.3.18 *Steam Bath*

5.4 Alternative Analytical Apparatus

Alternative systems are allowable as long as they meet the following criteria:

5.4.1 The system must generate a linear calibration curve and two consecutive samples of the same aliquot size and concentration must agree within 3% of their average.

5.4.2 The system must allow for recovery of a minimum of 95% of the spike when an aliquot of a source sample is spiked with a known concentration of Hg (II) compound.

5.4.3 The reducing agent should be added after the aeration cell is closed.

5.4.4 The aeration bottle bubbler should not contain a frit.

5.4.5 Any Tygon tubing used should be as short as possible and should be conditioned prior to use until blanks and standards yield linear and reproducible results.

5.4.6 If manual stirring is performed before aeration, the aeration cell should be closed during the process.

5.4.7 A drying tube should not be used unless it is conditioned following the procedure for the Tygon tubing, above.

6.0 REAGENTS

Use ACS reagent-grade chemicals or equivalent, unless otherwise specified.

6.1 Sampling and Recovery

The following reagents are used in sampling and recovery:

6.1.1 *Water*—Deionized distilled, meeting ASTM specifications for Type I Reagent Water—ASTM Test Method D 1193-77. If high concentrations of organic matter are not expected to be present, users may eliminate the $KMnO_4$ test for oxidizable organic matter. Use this water in all dilutions and solution preparations.

6.1.2 *Nitric Acid (HNO_3), 50% (v/v)*—Mix equal volumes of concentrated HNO_3 and water, being careful to add the acid to the water slowly.

6.1.3 *Silica Gel*—Indicating type, 6- to 16-mesh. If previously used, dry at 175 °C (350 °F) for 2 h. Testers may use new silica gel as received.

6.1.4 *Filter (Optional)*—Glass fiber filter, without organic binder, exhibiting at least 99.95% efficiency on 0.3-µm dioctyl phthalate smoke particles. Testers may use the filter in cases where the gas stream contains large quantities of particulate matter, but they should analyze blank filters for Hg content.

6.1.5 *Sulfuric Acid (H_2SO_4), 10% (v/v)*—Add and mix 100 mL of concentrated H_2SO_4 to 900 mL of water.

6.1.6 *Absorbing Solution, 4% $KMnO_4$ (w/v)*—Prepare fresh daily. Dissolve 40 g of $KMnO_4$ in sufficient 10% H_2SO_4 to make 1 L. Prepare and store in glass bottles to prevent degradation.

6.1.7 *Hydrochloric Acid*—Trace metals grade HCl is recommended. If other grades are used, the Hg level must be less than 3 ng/mL Hg.

6.1.8 *Hydrochloric Acid, 8 N*—Dilute 67 mL of concentrated HCl to 100 mL with water (slowly add the HCl to the water).

6.2 Analysis

The reagents needed for analysis are listed below:

6.2.1 *Tin (II) Solution*—Prepare fresh daily and keep sealed when not being used. Completely dissolve 20 g of tin (II) chloride [or 25 g of tin (II) sulfate] crystals (Baker Analyzed reagent grade or any other brand that will give a clear solution) in 25 mL of concentrated HCl. Dilute to 250 mL with water. Do not substitute HNO_3, H_2SO_4, or other strong acids for the HCl.

6.2.2 *Sodium Chloride-Hydroxylamine Solution*—Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate (or 12 g of hydroxylamine hydrochloride) in water and dilute to 100 mL.

6.2.3 *Hydrochloric Acid, 8 N*—Dilute 67 mL of concentrated HCl to 100 mL with water (slowly add the HCl to the water).

6.2.4 *Nitric Acid, 15% (v/v)*—Slowly add 15 mL of concentrated HNO_3 to 100 mL of water.

6.2.5 *Mercury Stock Solution, 1 mg Hg/mL*—Prepare and store all Hg standard solutions in borosilicate glass containers. Completely dissolve 0.1354 g of Hg (II) chloride in 75 mL of water. Add 10 mL of concentrated HNO_3 and adjust the volume to exactly 100 mL with water. Mix thoroughly. This solution is stable for at least 1 month.

6.2.6 *Intermediate Hg Standard Solution, 10 µg/mL*—Prepare fresh weekly. Pipet 5.0 mL of the Hg stock solution (Section 6.2.5) into a 500-mL volumetric flask, and add 20 mL of 15% HNO_3 solution. Adjust the volume to exactly 500 mL with water. Thoroughly mix the solution.

6.2.7 *Working Hg Standard Solution, 200 ng Hg/mL*—Prepare fresh daily. Pipet 5.0 mL from the Intermediate Hg Standard Solution (Section 6.2.6) into a 250-mL volumetric flask. Add 5 mL of 4% $KMnO_4$ absorbing solution and 5 mL of 15% HNO_3. Adjust the volume to exactly 250 mL with water. Mix thoroughly.

6.2.8 *Potassium Permanganate, 5% (w/v)*—Dissolve 5 g of $KMnO_4$ in water and dilute to 100 mL.

6.2.9 *Filter*—Use a Whatman 40, or equivalent.

7.0 PROCEDURE

6.1/6

7.1. Sampling

The sampling procedure is the same as in Method 101, except for changes associated with using $KMnO_4$ instead of ICl absorbing solution and the possible use of a filter. ***Because of the complexity of this method, testers should be trained and experienced with all procedures to ensure reliable results. Because the amount of Hg collected generally is small, the method must be applied carefully to prevent sample contamination or loss.***

7.1.1 Pretest Preparation—Follow the general procedure given in Method 5, Section 4.1.1, but omit the directions on the filter.

7.1.2 *Preliminary Determinations*—The preliminary determinations are the same as those given in Method 101, Section 7.1.2, except for the absorbing solution depletion sign. In this method, high-oxidizable organic matter content may make it impossible to sample for the desired minimum time. This problem is indicated by the complete bleaching of the purple color of the $KMnO_4$ solution. In these cases, testers may divide the sample run into two or more subruns to ensure that the absorbing solution will not be depleted. In cases where excess water condensation is encountered, collect two runs to make one sample.

7.1.2 *Sampling Train Preparation*

7.1.2.1 Sampling train preparation is the same as that given in Method 101, Section 7.1.3, except for the cleaning of the glassware (probe, filter holder, if used, impingers, and connectors) and for the charging of the first three impingers. In this method, clean all the glass components by rinsing with 50% HNO_3, tap water, 8 N HCl, tap water, and finally deionized distilled water. Then place 50 mL of 4% $KMnO_4$ in the first impinger and 100 mL in each of the second and third impingers.

7.1.2.2 If a filter is used, place it with the filter holder with a pair of tweezers. Be sure to center the filter, and place the gasket in the proper position to prevent the sample gas stream from by-passing the filter. Visually check the filter for damage after assembly is completed. Be sure to set the filter heating system at the desired operating temperature after the sampling train has been assembled.

7.1.2.1 Follow the general procedure given in Method 5, Section 4.1.2, except as follows: Select a nozzle size based on the range of velocity heads to ensure that it is not necessary to change the nozzle size to maintain isokinetic sampling rates below 28 L/min (1.0 cfm).

7.1.2.2 Highly oxidizable organic content may make it impossible to sample for the desired minimum time. This problem is indicated by the complete bleaching of the purple color of the $KMnO_4$ solution. If the purple color is expended in the last (third) $KMnO_4$ impinger, the sample run is unacceptable and another run shall be conducted. In these cases, testers may divide the sample run into two or more subruns to ensure that the absorbing solution will not be depleted or a fourth impinger containing 100 mL of $KMnO_4$ may be used. In cases where excess water condensation is encountered, collect two runs to make one sample or add extra empty impinger before the first impinger containing $KMnO_4$ solution.

7.1.3 All the glass components should been cleaned in the laboratory (a hood is recommended) by soaking with 50% HNO_3 for 1 h and then by rinsing with tap water, 8 N

HCl, tap water, and finally deionized distilled water. After cleaning, openings should be covered to prevent contamination.

7.1.3.1 Place 50 mL of 4% $KMnO_4$ in the first impinger and 100 mL in each of the second and third impingers. Take care to prevent the absorbing solution from contacting any greased surfaces. Place approximately 200 g of preweighed silica gel in the fourth impinger. Testers may use more silica gel, but they should be careful to ensure that it is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, determine and record the weight of the silica gel plus impinger to the nearest 0.5 g. (Note: Contact with KMnO4 should be avoided.)

7.1.3.2 If a filter is used, place it in the filter holder with a pair of tweezers. Be sure to center the filter, and place the gasket in the proper position to prevent the sample gas stream from by-passing the filter. Check the filter for tears after assembly is completed. Be sure to set the filter heating system at the desired operating temperature after the sampling train has been assembled.

7.1.3.3 Install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260 °C (500 °F). Use a fiberglass string gasket if temperatures are higher. Other connecting systems using either 316 stainless-steel or Teflon ferrules may be used. 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. Assemble the train as shown in Figure 101A-1, using (if necessary) a very light coat of silicone grease on all ground glass joints. Grease only the outer portion to avoid contamination by the silicone grease.

Note: An empty impinger may be inserted between the filter and first impinger containing $KMnO_4$ to remove excess moisture from the sample stream.

7.1.3.4 After the sampling train has been assembled, turn on and set the probe, if applicable, at the desired operating temperature. Allow time for the temperatures to stabilize. Place crushed ice around the impingers.

7.1.4 Leak Check Procedures—***Follow the leak check procedures outlined in Method 5, Sections 4.1.4.1, 4.1.4.2, and 4.1.4.3.***

7.1.3 Sampling Train Operation—***In addition to the procedure given in Method 101, Section 7.1.5, maintain a temperature around the filter (if applicable) of 120 ± 14 °C (248 ± 25 °F).***

7.1.5 Mercury Train Operation—***Follow the general procedure given in Method 5, Section 4.1.5, maintain a temperature around the filter (if applicable) of 120 ± 14 °C (248 ± 25 °F). For each run, record the data required on a data sheet, such as the one shown in Figure 101A-4.***

7.1.6 Calculating Percent of Isokinetic Sampling—***Same as in Method 5, Section 4.1.6.***

7.2 Sample Recovery

Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When it can be handled safely, wipe off any external particulate matter near the nozzle tip and place a cap

over it. Do not cap the probe tip tightly while the sampling train is cooling because the resultant vacuum would draw liquid from the impingers. Before moving the sample train to the cleanup site, remove the probe from the train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe the silicone grease from the impinger. Use either ground-glass stoppers, plastic caps, or serum caps to close these openings. Transfer the probe, impinger assembly, and (if applicable) filter assembly to an area that is clean, protected from the wind, and free of Hg contamination.

The ambient air in laboratories located in the immediate vicinity of Hg-using facilities is not normally free of Hg contamination. Inspect the train before and during assembly and note any abnormal conditions. Treat the sample as follows:

7.2.1 *Container No. 1 (Impinger, Probe, and Filter Holder) and, if Applicable, No. 1A (HCl Rinse)*

7.2.1.1 Using a graduated cylinder, measure the liquid in the first three impingers to within 1 mL. Record the volume of liquid present (see Figure 5-3 of Method 5 in 40 CFR Part 60). This information is needed to calculate the moisture content of the effluent gas. (Use only graduated cylinder and glass storage bottles that have been precleaned as described in Section 7.1.2) Place the contents of the first three impingers into a 1000-mL glass sample bottle. Note: If a filter is used, remove the filter from its holder, as outlined under Container No. 3 below.

1.2 Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, probe liner, and front half of the filter holder (if applicable) and impingers as follows: Rinse these components with a total of 400 mL of fresh 4% $KMnO_4$ solution, carefully ensuring removal of all loose particulate matter from the impingers. Add all washings to the 1000-mL glass sample bottle. Remove any residual brown deposits on the glassware following the permanganate rinse with approximately 100 mL of water, carefully assuring removal of all loose particulate matter from the impingers, and add this rinse to Container No. 1. If no visible deposits remain after this water rinse, do not rinse with 8 N HCl. However, if deposits do remain on the glassware after the water rinse, wash impinger walls and stems with the same 25 mL of 8 N HCl and place the wash in a separate container labeled Container No. 1A. Use the following procedure: Place 200 mL of water in a sample container labeled Container No. 1A. Use only a total of 25 mL of 8 N HCl to rinse all impingers. Wash the impinger walls and stem with the HCl by turning and shaking the impinger so that the HCl contacts all inside surfaces. While stirring, pour the HCl wash carefully into Container No. 1A. The separate container is used for safety reasons.

7.2.1.3 After all washings have been collected in the sample container, tighten the lid to prevent leakage during shipment to the laboratory. Mark the height of the fluid level to help determine whether leakage occurs during transport. Label the container to identify its contents clearly.

7.2.2 *Container No. 2 (Silica Gel)*—Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal the container. A funnel may be used to pour the silica gel, and a rubber policeman may be used to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the impinger wall and are difficult to

remove. Because the weight gain is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g and record this weight.

7.2.3 *Container No. 3 (Filter)*—If a filter was used, carefully remove it from the filter holder, place it in a 100-mL glass sample bottle, and add 20 to 40 mL of 4% $KMnO_4$. If it is necessary to fold the filter, be sure that the particulate cake is inside the fold. Carefully transfer to the 150-mL sample bottle any particulate matter and filter fibers that adhere to the filter holder gasket by using a dry Nylon bristle brush and a sharp-edged blade. Seal the container. Label the container to identify its contents clearly. Mark the height of the fluid level to help determine whether leakage occurs during transport.

7.2.4 *Container No. 4 (Filter Blank)*—If a filter was used, treat an unused filter from the same filter lot used for sampling in the same manner as Container No. 3.

7.2.5 *Container No. 5 (Absorbing Solution Blank)*—For a blank, place 650 mL of 4 % $KMnO_4$ absorbing solution in a 1000-mL sample bottle. Seal the container.

7.2.6 *Container No. 6 (HCl Rinse Blank)*—For a blank, place 200 mL of water in a 1000-mL sample bottle. While stirring, add 25 mL of 8 N HCl. Seal the container. Only one blank sample per 3 runs is required.

7.3 Sample Preparation

Check the liquid level in each container to see if liquid was lost during transport. If a noticeable amount of leakage occurred, either void the sample or use methods subject to the approval of the Administrator to account for the losses. Then follow the procedures below:

7.3.1 *Containers No. 3 and No. 4 (Filter and Filter Blank)*—If a filter was used, place the contents, including the filter, of Containers No. 3 and No. 4 in separate 250-mL beakers. Heat the beakers on a steam bath until most of the liquid has evaporated. Do not take to dryness. Add 20 mL of concentrated HNO_3 to the beakers, cover them with a watch glass, and heat on a hot plate at 70 °C for 2 h. Remove from the hot plate. Filter the solution from the digestion of the contents of Container No. 3 through Whatman 40 filter paper and save the filtrate for addition to the Container No. 1 filtrate, as described below. Discard the filter. Filter the solution from the digestion of the contents of Container No. 4 through Whatman 40 filter paper and save the filtrate for addition to the Container No. 5 filtrate, as described in Section 7.3.2 below. Discard the filter.

7.3.2 *Container No. 1 (Impingers, Probe, and Filter Holder) and, if Applicable, No. 1A (HCl Rinse)*—Filter the contents of Container No. 1 through Whatman 40 filter paper into a 1-L volumetric flask to remove the brown MnO_2 precipitate. Save the filter. Add the sample filtrate from Container No. 3 to the 1-L volumetric flask and dilute to volume with water. If the combined filtrates are greater than 1000 mL, determine the volume to the nearest mL and make the appropriate corrections for blank subtractions. Mix thoroughly.

Mark the filtrate as Analysis Sample No. A.1 and analyze for Hg within 48 h after completing the filtration step. Place the saved filter, which was used to remove the brown MnO_2 precipitate, into a container of appropriate size. Add 25 mL of 8 N HCl

to the filter and allow the filter, with its brown residue, to digest for a minimum of 24 h at room temperature. Filter the contents of Container No. 1A through a Whatman 40 filter paper into a 500-mL volumetric flask. Then filter the digestion of the brown MnO_2 precipitate from Container No. 1 and the Whatman paper filter into the 500-mL volumetric flask. Dilute to volume with water. Mark this 500-mL dilute solution as Analysis Sample No. HCl A.2 and analyze for Hg. Discard the filters.

7.3.3 *Containers No. 5 (Absorbing Solution Blank) and No. 6 (HCl Rinse Blank)*—Treat Container No. 5 the same as Container No. 1, described in the previous section. Add the filter blank filtrate from Container No. 4 to the 1-L volumetric flask and dilute to volume. Mix thoroughly. Mark this as Sample No. A.1 blank and analyze for Hg within 48 h after completing the filtration step. Digest any brown precipitate remaining on the filter from the filtration of Container No. 5, using the procedure described in Section 7.3.2. Filter the contents of Container No. 6 using the procedure described in Section 7.3.2 and combine into the 500-mL volumetric flask with the filtrate from the digested blank MNO_2 precipitate. Mark this resultant 500-mL combined dilute solution as Analysis Sample No. HCl A.2 blank. Note: When analyzing blank samples A.1 blank and HCl A.2 blank, always begin with 10-mL aliquots. This note applies specifically to blank samples.

7.4 Analysis

7.4.1 Calibrate the spectrophotometer and recorder and prepare the calibration curve as described in sections 8.1 and 8.2. Then repeat the procedure used to establish the calibration curve with aliquots of appropriate size (1 to 10 mL) of the samples (from sections 7.3.2 and 7.3.3) until two consecutive peak heights agree within 3% of their average value. If the 10-mL sample is below the detectable limit, use a larger aliquot (up to 20 mL), but decrease the volume of water added to the aeration cell accordingly to prevent the solution volume from exceeding the capacity of the aeration bottle. If the peak maximum of a 1-mL aliquot is off scale, further dilute the original sample to bring the Hg concentration into the calibration range of the spectrophotometer. If the Hg content of the absorbing solution and filter blank is below the working range of the analytical method, use zero for the blank.

7.4.2 Run a blank and standard at least after every five samples to check the spectrophotometer calibration; recalibrate as necessary. It also is recommended that at least one sample from each stack test be checked by the Method of Standard Additions to confirm that matrix effects have not interfered with the analysis.

8.0 Calibration and Standards

The calibration and standards are the same as in Method 101, Section 8, except for the following variations:

8.1 Optical Cell Heating System Calibration

Same as in Method 101, Section 8.2, but use a 25-mL graduated cylinder to add 25 mL of water to the bottle section of the aeration cell.

8.2 Spectrophotometer and Recorder Calibration

8.2.1 The Hg response may be measured by either peak height or peak area. Note: The temperature of the solution affects the rate at which elemental Hg is released;

consequently, it affects the shape of the absorption curve (area) and the point of maximum absorbance (peak height). To obtain reproducible results, all solutions must be brought to room temperature before use.

8.2.2 Set the spectrophotometer wave length at 253.7 nm and make certain the optical cell is at the minimum temperature that will prevent water condensation. Then set the recorder scale as follows: Using a 25-mL graduated cylinder, add 25 mL of water to the aeration cell bottle, and pipet 5 mL of the working Hg standard solution into the aeration cell. Note: Always add the Hg-containing solution to the aeration cell after the 25 mL of water.

8.2.3 Place a Teflon-coated stirring bar in the bottle. Add 5 mL of the 4% $KMnO_4$ to the aeration bottle and mix well. Attach the bottle section to the bubbler section of the aeration cell. Make certain that: (1) the aeration cell exit arm stopcock (Figure 101-3 of Method 101) is closed (so that Hg will not prematurely enter the optical cell when the reducing agent is being added); and (2) there is no flow through the bubbler. Add 5 mL of sodium chloride hydroxylamine in 1-mL increments until the solution is colorless. Now add 5 mL of tin (II) solution to the aeration bottle through the side arm and immediately stopper the side arm. Stir the solution for 15 s, turn on the recorder, open the aeration cell exit arm stopcock, and immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard, and set this value to read 90% of the recorder full scale.

Before use, clean all glassware, both new and used, as follows: Brush with soap and tap water, liberally rinse with tap water, soak for 1 h in 50% HNO_3. Rinse with deionized distilled water.

8.1 *Flow Calibration*

Assemble the aeration system as shown in Figure 101-5. Set the outlet pressure on the aeration gas cylinder regulator to a minimum pressure of 500 mm Hg (10 psi), and use the flow metering valve and a bubble flow meter or wet-test meter to obtain a flow rate of 1.5 ± 0.1 L/min through the aeration cell. After the flow calibration is completed, remove the bubble flow meter from the system.

8.2 *Optical Cell Heating System Calibration*

Using a 25-mL graduated cylinder, add 25 mL of water to the bottle section of the aeration cell and attach the bottle section to the bubbler section of the cell. Attach the aeration cell to the optical cell; while aerating at 1.5 L/min, determine the minimum variable transformer setting necessary to prevent condensation of moisture in the optical cell and in the connecting tubing. (This setting should not exceed 20 volts.)

8.3 *Spectrophotometer and Recorder Calibration*

8.3.1 The Hg response may be measured by either peak height or peak area. (Note: The temperature of the solution affects the rate at which elemental Hg is released; consequently, it affects the shape of the absorption curve [area] and the point of maximum absorbance [peak height]. Therefore, to obtain reproducible results, bring all solutions to room temperature before use.)

8.3.2 Set the spectrophotometer wavelength at 253.7 nm and make certain that the optical cell is at the minimum temperature that will prevent water condensation. Then

set the recorder scale as follows: Using a 25-mL graduated cylinder, add 25 mL of water to the aeration cell bottle and pipet 5 mL of the working Hg standard solution into the aeration cell. (Note: Always add the Hg-containing solution to the aeration cell after the 25 mL of water.)

8.3.3 Place a Teflon-coated stirring bar in the bottle. Using a 25-mL graduated cylinder, add 25 mL of laboratory pure water to the aeration cell bottle. Pipet 5.0 mL of the working Hg standard solution to the aeration cell. Add 5 mL of the 4% $KMnO_4$ absorbing solution, followed by 5 mL of 15% HNO_3 and 5 mL of 5% $KMnO_4$ to the aeration cell, and mix well using a swirling motion. Attach the bottle to the aerator, making sure that: (1) the exit arm stopcock is closed, and (2) there is no aeration gas flowing through the bubbler. Through the side arm, add 5 mL of sodium chloride hydroxylamine solution in 1 mL-increments until the solution is colorless. Through the side arm, add 5 mL of the Tin (II) reducing agent to the aeration cell bottle, and immediately stopper the side arm. Stir the solution for 15 s and turn on the recorder or integrator. Open the aeration cell exit arm stopcock and initiate the gas flow. Determine the maximum height (absorbance) of the standard, and set this value to read 90% of the recorder full scale.

8.4 *Calibration Curve*

8.4.1 After setting the recorder scale, repeat the procedure in Section 8.3 using 0-, 1-, 2-, 3-, 4-, and 5-mL aliquots of the working standard solution (final amount of Hg in the aeration cell is 0, 200, 400, 600, 800, and 1000 ng, respectively). Repeat this procedure on each aliquot size until two consecutive peaks agree within 3% of their average value. (Note: To prevent Hg carryover from one sample to another, do not close the aeration cell from the optical cell until the recorder pen has returned to the baseline.)

8.4.2 It should not be necessary to disconnect the aeration gas inlet line from the aeration cell when changing samples. After separating the bottle and bubbler sections of the aeration cell, place the bubbler section into a 600-mL beaker containing approximately 400 mL of water. Rinse the bottle section of the aeration cell with a stream of water to remove all traces of the tin (II) reducing agent. Also, to prevent the loss of Hg before aeration, remove all traces of the reducing agent between samples by washing with water. It will be necessary, however, to wash the aeration cell parts with concentrated HCl if any of the following conditions occur: (1) a white film appears on any inside surface of the aeration cell; (2) the calibration curve changes suddenly; or (3) the replicate samples do not yield reproducible results.

8.4.3 Subtract the average peak height (or peak area) of the blank (0-mL aliquot)-which should be less than 2% of recorder full scale-from the averaged peak heights of the 1-, 2-, 3-, 4-, and 5-mL aliquot standards. If the blank absorbance is greater than 2% of full-scale, the probable cause is Hg contamination of a reagent or carry-over of Hg from a previous sample. Plot the corrected peak height of each standard solution versus the corresponding final total Hg weight in the aeration cell (in ng), and draw the best-fit straight line. This line should either pass through the origin or pass through a point no further from the origin than ± 2 % of the recorder full scale. If the line does not pass through or very near to the origin, check for nonlinearity of the curve and for incorrectly prepared standards.

9.0 Calculations

9.1 Dry-Gas Volume, Volume of Water Vapor and Moisture Content, Stack-Gas Velocity, Isokinetic Variation and Acceptable Results, and Determination of Compliance

Same as in Method 101, Sections 9.1, 9.2, 9.3, 9.6, and 9.7, respectively, but use data obtained from this test.

9.1 *Dry-Gas Volume*

Using the data from this test, calculate $V_{m(std)}$, the dry-gas sample volume at standard conditions (corrected for leakage, if necessary) as outlined in Section 6.3 of Method 5.

9.2 *Volume of Water Vapor and Moisture Content*

Using the data obtained from this test, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack-gas. Use equations 5-2 and 5-3 of Method 5.

9.3 *Stack-Gas Velocity*

Using the data from this test and Equation 2-9 of Method 2, calculate the average stack-gas velocity v_s.

9.4 *Isokinetic Variation and Acceptable Results*

Same as in Method 5, Sections 6.11 and 6.12, respectively.

9.5 *Determining Compliance*

Each performance test consists of three repetitions of the applicable test method. For the purpose of determining compliance with an applicable national emission standard, use the average of the results of all repetitions.

9.2 Total Mercury

For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agreed within 3% of their average for the contribution of the blank. Then calculate the total Hg content in µg in each sample. Correct for any dilutions made to bring the sample into the working range of the spectrophotometer.

$$m(HCl)_{Hg} = \left\{ \frac{[C(HCl)_{Hg} \; DF]}{S} - \frac{[C(HCl\ blk)_{Hg} \; DF_{blk}]}{S_{blk}} \right\} V_{f(HCl)} \; 10^{-3}$$ Equation 101A-1

where:

$m(HCl)_{Hg}$ = Total blank corrected µg of Hg in HCl rinse and HCl digestate of filter sample.

$C(HCl)_{Hg}$ = Total ng of Hg analyzed in the aliquot from the 500-mL Analysis Sample No. HCl A.2.

$C(HCl\ blk)_{Hg}$ = Total ng of Hg analyzed in aliquot of the 500-mL Analysis Sample No. HCl A.2 blank.

DF = Dilution factor for the HCl digested Hg-containing solution, Analysis Sample No. HCl A.2. This dilution factor (DF) applies only to the intermediate dilution steps because the original sample volume $(V_s)_{HCl}$ of HCl A.2 has been factored out in the equation, along with the sample aliquot, (S). In Equation 6.9, the sample aliquot, *S*, is introduced directly into the aeration cell for analysis according to the procedure outlined in Section 3.19.5.3.4. A dilution factor is required only if it is necessary to bring the sample into the analytical instrument's calibration range. If no dilution is necessary, then DF equals 1.0.

DF_{blk} = Dilution factor for the Analysis Sample No. HCl A.2 blank. (Note: Normal dilution factor calculations apply here.)

$V_{f(HCl)}$ = Solution volume of original sample, 500 mL for samples diluted as described in Section 7.3.1.

10^{-3} = Conversion factor, µg/ng.

S = Aliquot volume of sample added to aeration cell, mL.

S_{blk} = Aliquot volume of blank added to aeration cell, mL.

Note: The maximum allowable blank subtraction for the HCl is the lesser of the two following values: (1) the actual blank measured value (Analysis Sample No. HCl A.2 blank); or (2) 5% of the Hg content in the combined HCl rinse and digested sample (Analysis Sample No. HCl A.2).

where:

$$m(fltr)_{Hg} = \left\{ \frac{[C(fltr)_{Hg} \quad DF \quad V_{f(fltr)}]}{S} - \frac{[C(fltr\ blk)_{Hg} \quad DFblk \quad V_{f(blk)}]}{S_{blk}} \right\} 10^{-3} \qquad \text{Equation 101A-2}$$

$m(fltr)_{Hg}$ = Total blank corrected µg of Hg in $KMNO_4$ filtrate and HNO_3 digestion of filter sample.

$C(fltr)_{Hg}$ = Total ng of Hg in aliquot of $KMNO_4$ filtrate and HNO_3 digestion of filter analyzed (aliquot of Analysis Sample No. A.1).

$C(fltr\ blk)_{Hg}$ = Total ng of Hg in aliquot of $KMNO_4$ blank and HNO_3 digestion of blank filter analyzed (aliquot of Analysis Sample No. A.1 blank).

$V_{f(fltr)}$ = Solution volume of original sample, normally 1000 mL for samples diluted as described in Section 7.3.2.

$V_{f(blk)}$ = Solution volume of blank sample, 1000 mL for samples diluted as described in Section 7.3.2

Note: The maximum allowable blank subtraction for the HCl is the lesser of the two following values: (1) the actual blank measured value (Analysis Sample No. A.1 blank); or (2) 5% of the Hg content in the filtrate (Analysis Sample No. A.1).

$$m_{Hg} = m(HCl)_{Hg} + m(fltr)_{Hg} \qquad \text{Equation 101A-3}$$

where:

m_{Hg} = Total blank corrected Hg content in each sample, µg.

$m(HCl)_{Hg}$ = Total blank corrected µg of Hg in HCl rinse and HCl digestate of filter sample.

$m(fltr)_{Hg}$ = Total blank corrected µg of Hg in $KMNO_4$ filtrate and HNO_3 digestion of filter sample.

9.3 Mercury Emission Rate

Calculate the Hg emission rate R in g/day for continuous operations using Equation 101A-4. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.

where:

m_{Hg} = Total blank corrected Hg content in each sample, µg.

$$R = K \frac{m_{Hg}\ v_s\ A_s\ (86,400 \times 10^{-6})}{[V_{m(std)} + V_{w(std)}]\ (T_s/P_s)}$$ Equation 101A-4

v_s = Average stack-gas velocity, m/sec (fps).

A_s = Stack cross-sectional area, m^2 (ft^2).

86,400 = Conversion factor, s/day.

10^{-6} = Conversion factor, g/µg.

$V_{m(std)}$ = Dry-gas sample volume at standard conditions, corrected for leakage (if any), m^3 (ft^3).

$V_{w(std)}$ = Volume of water vapor at standard conditions, m^3 (ft^3).

T_s = Absolute stack-gas temperature, °K (°R).

P_s = Absolute stack-gas pressure, mm Hg (in. Hg).

K = 0.3858 °K/mm Hg for metric units.

= 17.64 °R/in. Hg for English units.

10.1 Bibliography

1. Same as bibliography in Method 101.

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11.0 REFERENCES

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2. Corrections to Method 101A. Federal Register, Volume 49, September 12, 1984, p. 35768.

3. Corrections to Method 101A. Federal Register, Volume 53, September 23, 1988, p. 36972.

4. Method 101 - Determination of Particulate and Gaseous Mercury Emissions from Chlor-Alkali Plants - Air Streams. Federal Register, Volume 38, May 6, 1973, p. 08826.

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