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METHOD 101A—DETERMINATION OF PARTICULATE AND GASEOUS MERCURY EMISSIONS FROM SEWAGE SLUDGE INCINERATORS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from methods in appendix A to 40 CFR part 60 and in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of at least the following additional test methods: Methods 1, Method 2, Method 3, and Method 5 of part 60 (appendix A), and Method 101 part 61 (appendix B).

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Mercury (Hg)	7439-97-6	Dependent upon spectrophotometer and recorder.

1.2 Applicability. This method is applicable for the determination of Hg emissions from sewage sludge incinerators and other sources as specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and are collected in acidic potassium permanganate (KMnO₄) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

3.0 Definitions. [Reserved]

4.0 Interferences

4.1 Sample Collection. Excessive oxidizable organic matter in the stack gas prematurely depletes the KMnO₄ solution and thereby prevents further collection of Hg.

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

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Nitric Acid (HNO₃). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.3 Sulfuric acid (H₂SO₄). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m³ will cause lung damage in uninitiated. 1 mg/m³ for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.3 Chlorine Evolution. Hydrochloric acid reacts with KMnO₄ to liberate chlorine gas. Although this is a minimal concern when small quantities of HCl (5-10 ml) are used in the impinger rinse, a potential safety hazard may still exist. At sources that emit higher concentrations of oxidizable materials (*e.g.*, power plants), more HCl may be required to remove the larger amounts of brown deposit formed in the impingers. In such cases, the potential safety hazards due to sample container pressurization are greater, because of the larger volume of HCl rinse added to the recovered sample. These hazards are eliminated by storing and analyzing the HCl impinger wash separately from the permanganate impinger sample.

6.0 *Equipment and Supplies*

6.1 Sample Collection and Sample Recovery. Same as Method 101, Sections 6.1 and 6.2, respectively, with the following exceptions:

6.1.1 Probe Liner. Same as in Method 101, Section 6.1.2, except that if a filter is used ahead of the impingers, the probe heating system must be used to minimize the condensation of gaseous Hg.

6.1.2 Filter Holder (Optional). 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 ± 14 °C (248 ± 25 °F) during sampling to minimize both water and gaseous Hg condensation. A filter may also be used in cases where the stream contains large quantities of particulate matter.

6.2 Sample Analysis. Same as Method 101, Section 6.3, with the following additions and exceptions:

6.2.1 Volumetric Pipets. Class A; 1-, 2-, 3-, 4-, 5-, 10-, and 20-ml.

6.2.2 Graduated Cylinder. 25-ml.

6.2.3 Steam Bath.

6.2.4 Atomic Absorption Spectrophotometer or Equivalent. Any atomic absorption unit with an open sample presentation area in which to mount the optical cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

6.2.5 Optical Cell. Alternatively, a heat lamp mounted above the cell or a moisture trap installed upstream of the cell may be used.

6.2.6 Aeration Cell. Alternatively, aeration cells available with commercial cold vapor instrumentation may be used.

6.2.7 Aeration Gas Cylinder. Nitrogen, argon, or dry, Hg-free air, equipped with a single-stage regulator. Alternatively, aeration may be provided by a peristaltic metering pump. If a commercial cold vapor instrument is used, follow the manufacturer's recommendations.

7.0 *Reagents and Standards*

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection and Recovery. The following reagents are required for sample collection and recovery:

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193-77 or 91 Type 1. If high concentrations of organic matter are not expected to be present, the analyst may eliminate the KMnO_4 test for oxidizable organic matter. Use this water in all dilutions and solution preparations.

7.1.2 Nitric Acid, 50 Percent (V/V). Mix equal volumes of concentrated HNO₃ and water, being careful to add the acid to the water slowly.

7.1.3 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received.

7.1.4 Filter (Optional). Glass fiber filter, without organic binder, exhibiting at least 99.95 percent efficiency on 0.3-µm dioctyl phthalate smoke particles. The filter in cases where the gas stream contains large quantities of particulate matter, but blank filters should be analyzed for Hg content.

7.1.5 Sulfuric Acid, 10 Percent (V/V). Carefully add and mix 100 ml of concentrated H₂SO₄ to 900 ml of water.

7.1.6 Absorbing Solution, 4 Percent KMnO₄ (W/V). Prepare fresh daily. Dissolve 40 g of KMnO₄ in sufficient 10 percent H₂SO₄ to make 1 liter. Prepare and store in glass bottles to prevent degradation.

7.1.7 Hydrochloric Acid, 8 N. Carefully add and mix 67 ml of concentrated HCl to 33 ml of water.

7.2 Sample Analysis. The following reagents and standards are required for sample analysis:

7.2.1 Water. Same as in Section 7.1.1.

7.2.2 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 HNO₃ H₂SO₄, or other strong acids for the HCl.

7.2.3 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.

7.2.4 Hydrochloric Acid, 8 N. Same as Section 7.1.7.

7.2.5 Nitric Acid, 15 Percent (V/V). Carefully add 15 ml HNO₃ to 85 ml of water.

7.2.6 Antifoam B Silicon Emulsion. J.T. Baker Company (or equivalent).

7.2.7 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 HNO₃, and adjust the volume to exactly 100 ml with water. Mix thoroughly. This solution is stable for at least one month.

7.2.8 Intermediate Hg Standard Solution, 10 µg/ml. Prepare fresh weekly. Pipet 5.0 ml of the Hg stock solution (Section 7.2.7) into a 500 ml volumetric flask, and add 20 ml of 15 percent HNO₃ solution. Adjust the volume to exactly 500 ml with water. Thoroughly mix the solution.

7.2.9 Working Hg Standard Solution, 200 ng Hg/ml. Prepare fresh daily. Pipet 5.0 ml from the "Intermediate Hg Standard Solution" (Section 7.2.8) into a 250-ml volumetric flask. Add 5 ml of 4 percent KMnO₄ absorbing solution and 5 ml of 15 percent HNO₃. Adjust the volume to exactly 250 ml with water. Mix thoroughly.

7.2.10 Potassium Permanganate, 5 Percent (W/V). Dissolve 5 g of KMnO₄ in water and dilute to 100 ml.

7.2.11 Filter. Whatman No. 40, or equivalent.

8.0 *Sample Collection, Preservation, Transport, and Storage*

Same as Method 101, Section 8.0, with the exception of the following:

8.1 Preliminary Determinations. Same as Method 101, Section 8.2, except that the liberation of free iodine in the first impinger due to high Hg or sulfur dioxide concentrations is not applicable. In this method, high 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 KMnO₄ solution. In cases where an excess of water condensation is encountered, collect two runs to make one sample, or add an extra impinger in front of the first impinger (also containing acidified KMnO₄ solution).

8.2 Preparation of Sampling Train. Same as Method 101, Section 8.3, with the exception of the following:

8.2.1 In this method, clean all the glass components by rinsing with 50 percent HNO₃, tap water, 8 N HCl, tap water, and finally with deionized distilled water. Then place 50 ml of absorbing solution in the first impinger and 100 ml in each of the second and third impingers.

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

8.3 Sampling Train Operation. In addition to the procedure outlined in Method 101, Section 8.5, maintain a temperature around the filter (if applicable) of 120 ±14 °C (248 ±25 °F).

8.4 Sample Recovery. Same as Method 101, Section 8.7, with the exception of the following:

8.4.1 Transfer the probe, impinger assembly, and (if applicable) filter assembly to the cleanup area.

8.4.2 Treat the sample as follows:

8.4.2.1 Container No. 1 (Impinger, Probe, and Filter Holder) and, if applicable, Container No. 1A (HCl rinse).

8.4.2.1.1 Using a graduated cylinder, measure the liquid in the first three impingers to within 1 ml. Record the volume of liquid present (*e.g.*, see Figure 5-6 of Method 5). 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 in Section 8.2.1.) Place the contents of the first three impingers (four if an extra impinger was added as described in Section 8.1) into a 1000-ml glass sample bottle labeled Container No. 1.

NOTE: If a filter is used, remove the filter from its holder as outlined under Section 8.4.3.

8.4.2.1.2 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, front half of the filter holder (if applicable), and impingers as follows: Rinse these components with a total of 400 ml (350 ml if an extra impinger was added as described in Section 8.1) of fresh absorbing solution, carefully assuring removal of all loose particulate matter from the impingers; add all washings to the 1000 ml glass sample bottle. To remove any residual brown deposits on the glassware following the permanganate rinse, rinse with approximately 100 ml of water, carefully assuring removal of all loose particulate matter from the impingers. Add this rinse to Container No. 1.

8.4.2.1.3 If no visible deposits remain after this water rinse, do not rinse with 8 N HCl. If deposits do remain on the glassware after the water rinse, wash impinger walls and stems with 25 ml of 8 N HCl, and place the wash in a separate container labeled Container No. 1A as follows: Place 200 ml of water in a sample container labeled Container No. 1A. Wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Pour the HCl wash carefully with stirring into Container No. 1A.

8.4.2.1.4 After all washings have been collected in the appropriate sample container(s), tighten the lid(s) on the container(s) to prevent leakage during shipment to the laboratory. Mark the height of the fluid level to allow subsequent determination of whether leakage has occurred during transport. Label each container to identify its contents clearly.

8.4.3 Container No. 2 (Silica Gel). Same as Method 5, Section 8.7.6.3.

8.4.4 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 absorbing solution. If it is necessary to fold the filter, be sure that the particulate cake is inside the fold. Carefully transfer to the 100-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 allow subsequent determination of whether leakage has occurred during transport.

8.4.5 Container No. 4 (Filter Blank). If a filter was used, treat an unused filter from the same filter lot as that used for sampling according to the procedures outlined in Section 8.4.4.

8.4.6 Container No. 5 (Absorbing Solution Blank). Place 650 ml of 4 percent KMnO_4 absorbing solution in a 1000-ml sample bottle. Seal the container.

8.4.7 Container No. 6 (HCl Rinse Blank). Place 200 ml of water in a 1000-ml sample bottle, and add 25 ml of 8 N HCl carefully with stirring. Seal the container. Only one blank sample per 3 runs is required.

9.0 *Quality Control*

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.0, 10.0	Sampling equipment leak-checks and calibration	Ensure accuracy and precision of sampling measurements.
10.2	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.3.3	Check for matrix effects	Eliminate matrix effects.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

10.0 *Calibration and Standardization*

Same as Method 101, Section 10.0, with the following exceptions:

10.1 Optical Cell Heating System Calibration. Same as in Method 101, Section 10.4, except use a-25 ml graduated cylinder to add 25 ml of water to the bottle section of the aeration cell.

10.2 Spectrophotometer and Recorder Calibration.

10.2.1 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 from a solution and, 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.

10.2.2 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. Add three drops of Antifoam B to the bottle, and then pipet 5.0 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.

10.2.3 Place a Teflon-coated stirring bar in the bottle. Add 5 ml of absorbing solution to the aeration bottle, and mix well. Before attaching 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. If conditions (1) and (2) are met, attach the bottle section to the bubbler section of the aeration cell. Add 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 seconds, 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 percent of the recorder full scale.

11.0 Analytical Procedure

11.1 Sample Loss Check. 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.

11.2 Sample Preparation. Treat sample containers as follows:

11.2.1 Containers No. 3 and No. 4 (Filter and Filter Blank).

11.2.1.1 If a filter is used, place the contents, including the filter, of Containers No. 3 and No. 4 in separate 250-ml beakers, and heat the beakers on a steam bath until most of the liquid has evaporated. Do not heat to dryness. Add 20 ml of concentrated HNO₃ to the beakers, cover them with a watch glass, and heat on a hot plate at 70 °C (160 °F) for 2 hours. Remove from the hot plate.

11.2.1.2 Filter the solution from digestion of the Container No. 3 contents through Whatman No. 40 filter paper, and save the filtrate for addition to the Container No. 1 filtrate as described in Section 11.2.2. Discard the filter paper.

11.2.1.3 Filter the solution from digestion of the Container No. 4 contents through Whatman No. 40 filter paper, and save the filtrate for addition to Container No. 5 filtrate as described in Section 11.2.3 below. Discard the filter paper.

11.2.2 Container No. 1 (Impingers, Probe, and Filter Holder) and, if applicable, No. 1A (HCl rinse).

11.2.2.1 Filter the contents of Container No. 1 through Whatman No. 40 filter paper into a 1 liter volumetric flask to remove the brown manganese dioxide (MnO₂) precipitate. Save the filter for digestion of the brown MnO₂ precipitate. Add the sample filtrate from Container No. 3 to the 1-liter 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 hr of the filtration step. Place the saved filter, which was used to remove the brown MnO₂ precipitate, into an appropriate sized container. In a laboratory hood, add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature.

11.2.2.2 Filter the contents of Container 1A through Whatman No. 40 filter paper into a 500-ml volumetric flask. Then filter the digestate of the brown MnO₂ precipitate from Container No. 1 through Whatman No. 40 filter paper into the same 500-ml volumetric flask, and dilute to volume with water. Mark this combined 500 ml dilute solution as analysis Sample No. A.2. Discard the filters.

11.2.3 Container No. 5 (Absorbing Solution Blank) and No. 6 (HCl Rinse Blank).

11.2.3.1 Treat Container No. 5 as Container No. 1 (as described in Section 11.2.2), except substitute the filter blank filtrate from Container No. 4 for the sample filtrate from Container No. 3, and mark as Sample A.1 Blank.

11.2.3.2 Treat Container No. 6 as Container No. 1A, (as described in Section 11.2.2, except substitute the filtrate from the digested blank MnO₂ precipitate for the filtrate from the digested sample MnO₂ precipitate, and mark as Sample No. A.2 Blank.

NOTE: When analyzing samples A.1 Blank and HCl A.2 Blank, always begin with 10 ml aliquots. This applies specifically to blank samples.

11.3 Analysis. Calibrate the analytical equipment and develop a calibration curve as outlined in Section 10.0.

11.3.1 Mercury Samples. Then repeat the procedure used to establish the calibration curve with appropriately sized aliquots (1 to 10 ml) of the samples (from Sections 11.2.2 and 11.2.3) until two consecutive peak heights agree within 3 percent 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 1.0 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.

11.3.2 Run a blank and standard at least after every five samples to check the spectrophotometer calibration; recalibrate as necessary.

11.3.3 Check for Matrix Effects (optional). Same as Method 101, Section 11.3.3.

12.0 Data Analysis and Calculations

NOTE: Carry out calculations, retaining at least one extra decimal significant figure beyond that of the acquired data. Round off figures only after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

$C_{(\text{filtr})\text{Hg}}$ = Total ng of Hg in aliquot of KMnO_4 filtrate and HNO_3 digestion of filter analyzed (aliquot of analysis Sample No. A.1).

$C_{(\text{filtr blk})\text{Hg}}$ = 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).

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

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

DF = Dilution factor for the HCl-digested Hg-containing solution, Analysis Sample No. "HCl A.2."

DF_{blk} = Dilution factor for the HCl-digested Hg containing solution, Analysis Sample No. "HCl A.2 blank." (Refer to sample No. "HCl A.2" dilution factor above.)

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

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

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

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

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

$V_{f(\text{blk})}$ = Solution volume of blank sample, 1000 ml for samples diluted as described in Section 11.2.2.

$V_{f(\text{filtr})}$ = Solution volume of original sample, normally 1000 ml for samples diluted as described in Section 11.2.2.

$V_{f(\text{HCl})}$ = Solution volume of original sample, 500 ml for samples diluted as described in Section 11.2.1.

10^{-3} = Conversion factor, $\mu\text{g}/\text{ng}$.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor Condensed, Moisture Content, Isokinetic Variation, and Stack Gas Velocity and Volumetric Flow Rate. Same as Method 5, Sections 12.2 through 12.5, 12.11, and 12.12, respectively.

12.3 Total Mercury.

12.3.1 For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within 3 percent of their average for the

contribution of the blank. Use the calibration curve and these corrected averages to determine the final total weight of Hg in ng in the aeration cell for each source sample.

12.3.2 Correct for any dilutions made to bring the sample into the working range of the spectrophotometer.

$$m_{(\text{HCl})\text{Hg}} = \left[\frac{C_{(\text{HCl})\text{Hg}} \text{DF}}{S} \right] - \left[\frac{C_{(\text{HCl})\text{bk}} \text{DF}_{\text{bk}}}{S_{\text{bk}}} \right] V_{f(\text{HCl})} (10^{-3}) \quad \text{Eq. 101A-1}$$

NOTE: This dilution factor applies only to the intermediate dilution steps, since the original sample volume $[(V_f)_{\text{HCL}}]$ of "HCL A.2" has been factored out in the equation along with the sample aliquot (S). In Eq. 101A-1, the sample aliquot, S, is introduced directly into the aeration cell for analysis according to the procedure outlined in Section 11.3.1. A dilution factor is required only if it is necessary to bring the sample into the analytical instrument's calibration range.

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).

$$m_{(\text{ftr})\text{Hg}} = \left[\frac{C_{(\text{ftr})\text{Hg}} \text{DF} V_{f(\text{ftr})}}{S} \right] - \left[\frac{C_{(\text{ftr})\text{bk}} \text{DF}_{\text{bk}} V_{f(\text{bk})}}{S_{\text{bk}}} \right] \quad \text{Eq. 101A-2}$$

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").

$$m_{\text{Hg}} = m_{(\text{HCl})\text{Hg}} + m_{(\text{ftr})\text{Hg}} \quad \text{Eq. 101A-3}$$

12.3 Mercury Emission Rate. Same as Method 101, Section 12.3.

12.4 Determination of Compliance. Same as Method 101, Section 12.4.

13.0 Method Performance

13.1 Precision. Based on eight paired-train tests, the intra-laboratory standard deviation was estimated to be 4.8 $\mu\text{g}/\text{ml}$ in the concentration range of 50 to 130 $\mu\text{g}/\text{m}^3$.

13.2 Bias. [Reserved]

13.3 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.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Analyzers.

16.1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) may be used as an alternative to atomic absorption analysis provided the following conditions are met:

16.1.1.1 Sample collection, sample preparation, and analytical preparation procedures are as defined in the method except as necessary for the ICP-AES application.

16.1.1.2 The quality control procedures are conducted as prescribed.

16.1.1.3 The limit of quantitation for the ICP-AES must be demonstrated and the sample concentrations reported should be no less than two times the limit of quantitation. The limit of quantitation is defined as ten times the standard deviation of the blank value. The standard deviation of the blank value is determined from the analysis of seven blanks. It has been reported that for mercury and those elements that form hydrides, a continuous-flow generator coupled to an ICP-AES offers detection limits comparable to cold vapor atomic absorption.

16.1.2 Samples may also be analyzed by cold vapor atomic fluorescence spectrometry.

17.0 References

Same as Section 16.0 of Method 101, with the addition of the following:

1. Mitchell, W.J., *et al.* Test Methods to Determine the Mercury Emissions from Sludge Incineration Plants. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/4-79-058. September 1979.
2. Wilshire, Frank W., *et al.* Reliability Study of the U.S. EPA's Method 101A—Determination of Particulate and Gaseous Mercury Emissions. U.S. Environmental Protection Agency. Research Triangle Park, NC. Report No. 600/D-31/219 AREAL 367, NTIS Acc No. PB91-233361.
3. Memorandum from William J. Mitchell to Roger T. Shigehara discussing the potential safety hazard in Section 7.2 of Method 101A. February 28, 1990.

18.0 Tables, Diagrams, Flowcharts, And Validation Data [Reserved]