

State of California
Air Resources Board

Method 101A

Determination of Particulate and Gaseous Mercury
Emissions From Sewage Sludge Incinerators

Adopted: March 28, 1986

INTRODUCTION

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

1. Applicability and Principle

1.1 Applicability

This method applies to the determination of particulate and gaseous mercury (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Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in acidic potassium permanganate (KMnO₄) solution.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.

2. 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. Interfering Agents

3.1 Sampling.

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

3.2 Analysis.

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

4. Precision

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

5. Apparatus

5.1 Sampling Train and Sample Recovery.

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

5.1.1 Probe Liner. Same as Method 101, Section 5.1.2 except that if a filter is used ahead of the impingers, the tester must use the probe heating system to minimize the condensation of gaseous Hg.

5.1.2 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 + 15°C (248 + 25°F) during sampling to minimize both water and gaseous Hg condensation. The tester may use a filter in cases where the stream contains large quantities of particulate matter.

5.2 Analysis.

The apparatus needed for analysis is the same as Method 101, Sections 5.3 and 5.4, except as follows:

5.2.1 Volumetric Pipetts. Class A: 1-, 2-, 3-, 4-, 5-, 10-, and 20-ml.

5.2.2 Graduated Cylinder. 25-ml.

5.2.3 Steam Bath.

6. Reagents

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

6.1 Sampling and Recovery.

The reagents used in sampling and recovery are as follows:

- 6.1.1 Water. Deionized distilled, meeting ASTM Specifications for Type I Reagent Water – ASTM Test Method D1193-77 (incorporated by reference – see (61.18)). If high concentrations of organic matter are not expected to be present, the analyst may eliminate the KMnO_4 test for oxidizables.
- 6.1.2 Nitric Acid (HNO_3). 50 Percent (V/V). Mix equal volumes of concentrated HNO_3 and deionized distilled water, being careful to slowly add the acid to the water.
- 6.1.3 Silica Gel. Indicating type, 6- to 16- mesh. If previously used, dry at 175°C (350°F) for 2 hr. The tester may use new silica gel as received.
- 6.1.4 Filter (Optional). Glass fiber filter, without organic binder, exhibiting at least 99.95 percent efficiency on 0.3 μm dioctyl phthalate smoke particles. The tester may use the filter in cases where the gas stream contains large quantities of particulate matter, but he should analyze blank filters for Hg content.
- 6.1.5 Sulfuric Acid (H_2SO_4). 10 Percent (V/V). Add and mix 100 ml of concentrated H_2SO_4 with 900 ml of deionized distilled water.
- 6.1.6 Absorbing Solution. 4 Percent KMnO_4 (W/V). Prepare fresh daily. Dissolve 40 g of KMnO_4 in sufficient 10 percent H_2SO_4 to make 1 liter. Prepare and store in glass bottles to prevent degradation.

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 μg of tin (II) chloride [or 25 g if 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 deionized distilled 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 deionized distilled water and dilute to 100 ml.
- 6.2.3 Hydrochloric Acid (HCl). 8 N. Dilute 67 ml of concentrated HNO₃ to 100 ml with deionized distilled water (slowly add the HCl to the water).
- 6.2.4 Nitric Acid, 15 Percent (V/V). Dilute 15 ml of concentrated HNO₃ to 100 ml with deionized distilled water.
- 6.2.5 Mercury Stock Solution. 1 mg Hg/ml. Prepare and store all mercury standard solutions in borosilicate glass containers. Completely dissolve 0.1354 g mercury (II) chloride in 75 ml of deionized distilled water. Add 100 ml of concentrated HNO and adjust the volume to exactly 100 ml with deionized distilled water. Mix thoroughly. This solution is stable for at least 1 month.
- 6.2.6 Intermediate Mercury Standard Solution. 10 ug Hg/ml. Prepare fresh weekly. Pipet 5.0 ml of the mercury stock solution (Section 6.2.5) into a 500-ml volumetric flask and add 20 ml of 15 percent HNO₃ solution. Adjust the volume to exactly 500 ml with deionized distilled water. Thoroughly mix the solution.
- 6.2.7 Working Mercury Standard Solution. 200 ng Hg/ml. Prepare fresh daily. Pipet 5.0 ml from the “Intermediate Mercury Standard Solution” (Section 6.2.6) 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 deionized distilled water. Mix thoroughly.
- 6.2.8 Potassium Permanganate. 5 Percent (W/V). Dissolve 5 ug of KMnO₄ in deionized distilled water and dilute to 100 ml.
- 6.2.9 Filter. Whatman No. 40 or equivalent.

7. Procedure.

7.1 Sampling.

The sampling procedure is the same as Method 101, except for changes due to the use of KMnO₄ instead of ICI absorbing solution and the possible use of a filter. These changes are as follows:

7.1.1 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 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, the tester may divide the sample run into two or more subruns to insure that the absorbing solution would not be depleted. In cases where an excess of water condensation is encountered, collect two runs to make one sample.

7.1.2 Preparation of Sampling Train. The preparation of the sampling train 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 the charging of the first three impingers. In this method, clean all the glass components by rinsing with 50 percent HNO_3 tap water, 8 N HCl tap water, and finally deionized distilled water. Then place 50 ml of 4 percent KMnO_4 in the first impinger and 100 ml in each of the second and third impingers.

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 proper position to prevent the sample gas stream from by-passing 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.

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 $120 \pm 14(-\text{GL}-)^\circ\text{C}$ ($248 \pm 25^\circ\text{F}$).

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 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 would 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. 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.

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 assembly, and note any abnormal conditions. Treat the sample as follows:

7.2.1 Container No. 1. (Impinger, Probe, and Filter Holder). Use 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 5-3 of Method 5 in Part 60 of 40 CFR). 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 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.) 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) as follows: Rinse these components with a total of 250 to 400 ml of fresh 4 percent KMnO_4 solution: add all washings to the 1000-ml glass sample bottle; remove any residual brown deposits on the glassware using the minimum amount of 8 N HCl required; and add this HCl rinse to this sample container.

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

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

tester may use as aids a funnel to pour the silica gel and a rubber policeman 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. Since the gain in weight 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: 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 percent 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 clearly identify its contents. Mark the height of the fluid level to 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 500 ml of 4 percent KMnO_4 , absorbing solution in a 1000-ml sample bottle. Seal the container.

7.3 Sample Preparation.

Check 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 Container 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 and 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 glass, and heat on a hot plate at 70°C for 2 hours. Remove from the hot plate and filter the solution through Whatman No. 40

filter paper. Save the filtrate for Hg analysis. Discard the filter.

7.3.2 Container No 1 (Impingers, Probe, and Filter Holder). Filter the contents of Container No. 1 through Whatman No. 40 filter paper to remove the brown MnO₂ precipitate. Wash the filter with 50 ml of 4 percent KMnO₄, absorbing solution and add this wash to the filtrate. Discard the filter. Combine the filtrates from Containers No. 1 and No. 3 (if applicable), and dilute to a known volume with deionized distilled water. Mix thoroughly.

7.3.3 Container No. 5 (Absorbing Solution Blank). Treat this container as described in Section 7.3.2. Combine this filtrate with the filtrate with Container No. 4 and dilute to a known volume with deionized distilled water. Mix thoroughly.

7.4 Analysis.

Calibrate the spectrophotometer and recorder and prepare the calibration curve as described in Sections 8.1 to 8.4. Then repeat the procedure used in establish the calibration curve with appropriately sized aliquots (1 to 10 ml) of the samples (from Sections 7.3.2 and 7.3.3) 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.

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

It is also 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 in the analysis.

8. Calibration and Standards

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

8.1 Optical Cell Heating System Calibration.

Same as Method 101, Section 8.2 except use a 25 ml graduated cylinder to add 25 ml of deionized distilled water to the bottle section of the aeration cell.

8.2 Spectrophotometer and Recorder Calibration.

The mercury 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.) 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 deionized distilled water to the aeration cell bottle and pipet 5.0 ml of the working mercury standard solution into the aeration cell. (Note: Always add the Hg-containing solution to the aeration cell after the 25 ml of deionized distilled water.) Place a Teflon-coated stirring bar in the bottle. Add 5 ml of the 4 percent KMnO_4 , absorbing solution followed by 5 ml of 15 percent HNO_3 , and 5 ml of 5 percent KMnO_4 , to the aeration bottle and mix well. Now, attach the bottle section to the bubbler section of the aeration cell and 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. 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.

9. 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 Method 101. Section 9.1, 9.2, 9.3, 9.8 and 9.7 respectively, except use data obtained

9.2 Total Mercury.

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 field blank. Then calculate the total Hg content in ug in each sample. Correct for any dilutions made to bring the sample into the working range of the spectrophotometer.

9.3 Mercury Emission Rate

Calculate the Hg emission rate R in g/day for continuous operations using Equation 101A-1. 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.

$$R = \frac{K m_{\text{Hg}} V_s A_s (86,400 \times 10^{-6})}{[V_m (\text{std.})] + V_w (\text{std.})] (T_s/P_s)} \quad \text{Equation 101A-1}$$

Where:

m_{Hg}	=	Total Hg content in each sample ug.
V_s	=	Average stack gas velocity m/sec (fps).
A_s	=	Stack cross-sectional area m^2 (ft).
86,400	=	Conversion factor, sec/day.
10^{-6}	=	Conversion factor, g/ug.
$V_m (\text{std})$	=	Dry gas sample volume at standard conditions corrected for leakage (if any), m^3 (ft^3).
$V_w (\text{std})$	=	Volume of water vapor at standard conditions, m^3 (ft^3).
T	=	Absolute average stack gas temperature °K (°R).
P	=	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. Bibliography

1. Same as Method 1101, Section 10

2. Mitchell, W.J., M.R. Midgett, J.C. Suggs, and D. Albrinck Test Methods to Determine the Mercury Emissions from Sludge Incineration Plants U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, Publication No. EPA-600/4-79-058. September 1979