Designation: D5954 – 22

Standard Test Method for
Mercury Sampling and Measurement in Gaseous Fuels by Atomic Absorption Spectroscopy[1]

This standard is issued under the fixed designation D5954; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of total mercury in gaseous fuels at concentrations down to 0.5 ng∕m^3. It includes separate procedures for both sampling and atomic absorption spectrophotometric determination of mercury. This procedure detects both inorganic and organic forms of mercury.

1.2 *Units*—The values stated in SI units are to be regarded as the standard.

1.3 **Warning**—Mercury has been designated by many regulatory agencies as a hazardous material that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Safety Data Sheet (SDS) for additional information. Users should be aware that selling mercury or mercury containing products, or both, into your state or country may be prohibited by law.

1.4 *This standard does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D4150 Terminology Relating to Gaseous Fuels

2.2 *USEPA Document:*[3]

Method 1631, Revision E Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. EPA-821-R-02-019. U.S. Environmental Protection Agency, Office of Water, August 2002

2.3 *Other Document:*[4]

40 CFR Part 136 Appendix B Definition and Procedure for the Determination of the Method Detection Limit, Revision 2, EPA Office of Water, EPA 821-R-16-006

3. Terminology

3.1 *Definitions*—For definitions of general terms used in D03 Gaseous Fuels standards, refer to Terminology D4150.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *Detection Limit, n*—a statistically derived value representing the lowest quantity of analyte that can confidently be distinguished from background signal.

3.2.2 *Limit of Quantification, n*—the lowest value of analyte which can be quantitatively described and is represented by the lowest point on the calibration curve.

3.2.3 *sorbent, n*—a solid material that captures the analyte (mercury) from a gaseous source for quantitative analysis and is securely contained in sample tubes for sampling and analysis.

3.3 *Abbreviations:*

3.3.1 *AAS*—atomic absorption spectroscopy

3.3.2 *TFE*—tetrafluoroethylene

4. Summary of Test Method

4.1 Mercury in a gas stream is adsorbed onto gold-coated sorbent and subsequently directly desorbed by heat into a long path-length, inert cell connected to an atomic absorption spectrophotometer. Mercury atoms are detected by measuring their absorbance of light from a mercury source lamp at a characteristic wavelength. Analyte mass is determined by

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comparing the instrument response of the unknown sample to a response-versus-mass curve, generated daily from calibration standards.

5. Significance and Use

5.1 This test method can be used to measure the level of mercury in any gaseous fuel (as defined by Terminology D4150) for purposes such as determining compliance with regulations, studying the effect of various abatement procedures on mercury emissions, checking the validity of direct instrumental measurements, and verifying that mercury concentrations are below those required for gaseous fuel processing and operations.

5.2 Adsorption of the mercury on gold-coated sorbent can remove interferences associated with the direct measurement of mercury in the presence of high concentrations of organic compounds. It preconcentrates the mercury before analysis, thereby offering measurement of ultra-low average concentrations in a gas stream over a long time span. It avoids the cumbersome use of liquid spargers with on-site sampling and eliminates contamination problems associated with the use of potassium permanganate solutions.[5,6,7]

6. Interferences

6.1 The sorbent material does not retain compounds that interfere with sample analysis.

7. Apparatus

7.1 *Atomic Absorption Spectroscopy (AAS) Analyzer,* equipped with a long path-length, inert absorption cell and a mercury source lamp (electrodeless discharge lamp (EDL) or other high intensity lamp). The AAS should be capable of analyzing mercury using a thermal desorption furnace to heat the sample tubes to 550 °C. It must be capable of collecting and integrating data over a 30 to 60 s time window. Background subtraction capabilities are strongly recommended.

Note 1—Detection sensitivity may vary significantly depending on the type of spectrophotometer and its accessories.

7.2 *Dry Test Meter or Other Flow Measurement Device,* for sampling, capable of attaining, regulating, and measuring gas flow at approximately 500 to 2500 mL∕min.

7.2.1 A rotameter may be used in conjunction with a timing device to measure air flow.

7.3 *Rotameter or Other Flow Regulating Device,* for calibration/analysis, capable of attaining and regulating gas flow at approximately 500 mL/min.

Note 2—An air calibrated rotameter will not produce an accurate reading for gaseous fuel streams unless a correction factor is used, although a rotameter is suitable for controlling flow. To obtain an accurate volume reading, a dry or wet gas flow meter is preferred. The gas flow meter should be and in some applications may be required to be calibrated against a NIST-traceable reference gas flow meter, with measured volume corrected for standard or normalized conditions.

7.4 *TFE-Fluorocarbon Tubing,* to make connections to the atomic absorption spectrophotometer. The size should be appropriate for the absorption cell.

7.5 *Inert Push-to-Connect Fittings,* various sizes, for connections (materials such as perfluoroalkoxy (PFA), coated stainless steel, polypropylene, or TFE-Fluorocarbons).

7.5.1 Alternatively, silicone tubing with a ¼ in. inside diameter may be used for connections.

7.6 *Stainless Steel Tubing,* ¼ and ⅛ in. outside diameter with an inert coating on the interior (such as TFE-fluorocarbon or fused-silica), various lengths, for connections.

7.7 *Gastight Tube Fittings,* ¼ in. Nylon or TFE-fluorocarbon construction, gastight end-cap type, plus one stainless steel "T" fitting.

7.8 *Precision Gastight Syringes,* various sizes, equipped with a needle with a side port opening.

Note 3—A digital syringe is recommended for better accuracy and precision in calibration.

7.9 *Septum Material,* GC grade, low bleed type, made from silicone.

7.10 *Water Bath or Constant Temperature Apparatus,* capable of regulating a sealed vial of mercury to 26 ± 0.05 °C.

7.11 *Sealed Vial of Mercury,* prepared from a 250 mL glass bottle with a TFE-fluorocarbon septum cap and triple distilled elemental mercury.

7.12 *Heating Tape,* capable of maintaining a temperature of 50 to 60 °C, to heat trace tubing from the outlet end of the sampling tube to the inlet port of the AAS cell. A variable AC power supply or other temperature control device may be required.

7.13 *Stainless Steel 6-Port Switching Valve,* ⅛ in. for carrier gas control (optional).

7.14 *Impinger,* or equivalent sparging device with a minimum volume of 30 mL.

7.15 *Volumetric Pipettes,* micropipettes, or equivalent devices calibrated to deliver a known volume, assorted volumes.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[8] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

[5] Schroeder, W. H., "Sampling and Analysis of Mercury and its Compounds in the Atmosphere," *Environmental Science & Technology*, 16, 1982, 394A–399A.

[6] Chao, S. S., and Attari, A., "Characterization and Measurements of Natural Gas Trace Constituents—Volume II: Survey," Final Report GRI-94/0243.2.

[7] Braman, R. S., and Johnson, D. L., "Selective Absorption Tubes and Emission Technique for the Determination of Ambient Forms of Mercury in Air," *Environmental Science & Technology*, 8, 1974, pp. 996–1003.

[8] *Reagent Chemicals, American Chemical Society Specifications* , American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.2 *Reagent Water*—Reagent water, conforming to Type II of Specification D1193, shall be used for preparation of reagents and washing of the quartz tubing.

8.3 *Sulfuric Acid,* (concentrated, H_2SO_4, relative density 1.84) (**Warning**—Corrosive).

8.4 *Nitric Acid,* (concentrated, HNO_3, relative density 1.42) (**Warning**—Corrosive).

8.5 *Hydrochloric Acid,* (concentrated, HCl, relative density 1.18). (**Warning**—Corrosive).

8.6 *Mercury,* triple distilled (**Warning**—Poison).

8.7 *Mercury Standard Stock Solution,* (1000 µg/mL)—Dissolve 1.080 g of mercury (II) oxide (HgO) in a minimal amount of HCl (1 + 1). Dilute to 1 L with water.

8.8 *Mercury Standard Intermediate Solution,* (10 µg/mL)—Add 1.00 mL of the mercury standard stock solution to approximately 50 mL of water. Add 5 mL of concentrated nitric acid and dilute to 100 mL with water. This standard is stable for 1 year in a tightly sealed glass or polypropylene container.

8.9 *Mercury Standard Working Solution,* (100 ng/mL)—Add 1.00 mL of the mercury standard intermediate solution to approximately 50 mL of water. Add 5 mL of concentrated nitric acid and dilute to 100 mL with water. If micropipets are not available, this standard may be prepared by serial dilution of the mercury standard intermediate solution. Prepare this standard solution daily.

NOTE 4—Alternatively, NIST traceable mercury standards at appropriate concentrations may be purchased.

8.10 Stannous chloride solution prepared according to EPA 1631 Rev. E section 7.5. Alternatively, a concentrated stannous chloride solution may be purchased and diluted to a suitable concentration. The solution should be made fresh daily from reagents or from concentrate.

NOTE 5—If mercury is present in the stannous chloride solution, sparge the solution with a clean gas source before use.

8.11 *Air,* PP grade, or carbon filtered.

8.12 *Sulfur or Iodine Impregnated Carbon,* used to filter carrier gases.

9. Sampling Procedure

9.1 Two sampling tubes are used in series, with the second tube providing a check for breakthrough from the first tube. The gas sample should flow from the sampling point (with a pressure regulator as necessary) into the first sampling tube (Tube 1), followed by the second tube (Tube 2), and finally the flow measurement device.

9.2 The distance from the sampling point to the sampler should be minimized because mercury may be absorbed onto tubing lines and sampling equipment. The entire sampling system must be passivated with the sample gas before any sampling, especially if low levels of mercury are expected. Passivated stainless steel tubing must be used for connections upstream of the pressure regulator. High density TFE-fluorocarbon or passivated stainless steel tubing is preferred for connections downstream of the regulator. Inert push-to-connect

fittings or flexible silicone tubing may be used to make short connections to sampling tubes; although, the former is preferred. Any pumps or flow measurement devices should be located downstream of the sampler. The entire sampling line and the sample tubes should be heated above the dewpoint of the sample stream to prevent condensation, especially when a pressure reduction device is used to step down the pressure for sampling.

9.3 Ascertain that the sample can be obtained at a pressure not exceeding 15 psig (10 psig is preferable) and a flow of 0.5 to 2.5 L/min. A pressure control device may be required in addition to a flow measurement device.

9.3.1 It is possible to sample from ambient and sub-ambient pressures using an appropriately designed extractive system to measure and control flow. If sampling under these conditions, it may be necessary to sample at lower flows.

9.4 Determine an approximate flow control setting for the selected flow at the applied pressure. This will save time when setting up the sampling tubes and will condition the sampling system.

9.5 Remove the fitting on one end of each tube and join the two tubes end-to-end with a short piece of silicone tubing or inert push-to-connect fittings.

9.6 Connect the back end of the sampling tube assembly (Tube 2) to the flow measurement device and connect the front end of the sampling tube assembly (Tube 1) to the sampling point. Carefully open the sampling valve and quickly adjust the flow control (and pressure if necessary) to obtain the required flow rate. Record the time and flow data at the start of sampling. Mark the direction the sample gas flowed through the tube.

9.7 Flow the sample through the sampling tube for the desired amount of time, periodically checking that the flow is staying close to what it originally was and adjusting it if necessary. Typical volumes of gas range from 50 to 1000 L. A smaller volume of gas should be used for a sample containing a high concentration of mercury. The optimal range that should be collected is between 2 and 300 ng of mercury. The capacity of the gold-coated silica sorbent is much higher than this, approximately 7 µg, but a loading at this level should be avoided as the collection efficiency is lessened and the linearity of the atomic absorption spectrophotometer exceeded.

9.8 At the end of the sampling period, record the final time and flow data, disconnect both tubes, and replace all of the endcaps tightly on the tubes. Securely attach a label to each of the tubes, labeling the front tube as "Tube 1" and the back tube (connected to the flow measurement device) as "Tube 2."

9.9 Optionally, the sampling process can be modified to sample two pairs of sorbent tubes simultaneously and in parallel. Use a "T" fitting to divide the gas stream between two sampling trains labelled "A" and "B." By comparing the %RD of the A and B trains of the run (see 12.2), the reproducibility of the data can be assessed.

9.10 Optionally, a field recovery test can be performed to verify that the mercury in the matrix is recoverable within uncertainty and unaffected by interferents. Before sampling,

spike a known amount of mercury onto a sample tube (see 10.1 or 10.2). Prepare the sampling train as directed in 9.5 and 9.6 with the spiked tube designated as "Tube 1" and an unspiked tube as "Tube 2." Sample the spiked pair of tubes with an unspiked pair, using the train described in 9.9.

9.10.1 If sampling the spiked pair and the unspiked pair simultaneously is impossible, then sample the spiked pair immediately before or immediately after an unspiked pair and keep sampling conditions as similar as possible. It is important that the source concentration remains as close as possible between the spiked and unspiked runs because this concentration is used as a constant when determining the spike recovery (see calculation in 12.2.)

9.10.2 The amount of mercury spiked onto the sorbent tube should be within ±50 % of the expected capture.

10. Calibration Procedure

10.1 *Test Method A—Calibration Using Mercury Sparging:*

10.1.1 This test method may be used if traceable measurements are needed or if laboratories have safety concerns regarding the storage of elemental mercury.

10.1.2 Build the sparging apparatus by connecting the air inlet of the impinger to a clean gas stream (nitrogen or air passed through an activated carbon filter). Connect a baked-out sample tube to the impinger's air outlet. Place about 5 to 10 mL of water in the impinger. The impinger should have a minimum capacity of 30 mL.

10.1.3 All apparatus surfaces, including tubing, between the mercury-free gas source and the sample tube must be cleaned before standards can be prepared. This is generally accomplished by adding a small volume of stannous chloride solution to the impinger and passing the carrier gas through the system for 5 to 10 min at a flow rate of approximately 500 mL/min.

10.1.4 Calibration standards are prepared using concentrations appropriate to the level of mercury collected on the sampling tube. Different mercury loadings will require different volumes, different concentrations, or both, of the mercury working standard. Add the mercury standard and a small amount of stannous chloride solution (about 0.5 mL) to the impinger. Sparge for at least 5 min at a flow rate of approximately 500 to 1000 mL/min. After sparging, seal the ends of the tubes with gastight fittings if the tubes will not be analyzed immediately.

10.2 *Test Method B—Calibration Using Mercury Headspace:*

10.2.1 This test method is preferred because it is simple, quick, and less susceptible to contamination, especially for low-level analyses of mercury in gaseous fuel streams.

10.2.2 All apparatus surfaces, including syringes, tubing, gastight fittings, and so forth, coming into contact with the mercury vapor must be passivated before the standards can be prepared. This is generally accomplished by flushing multiple aliquots of mercury headspace vapor into the analytic system.

10.2.3 Standards are prepared by injecting aliquots of the headspace over mercury in a sealed vial onto the mercury sampling tubes using an air carrier gas at approximately 500 mL/min. Typical aliquot sizes range from 50 to 2000 μL which are delivered using a gastight syringe.

10.2.4 The gastight syringe is filled with air, and the needle pushed through the seal of the vial containing elemental mercury. The syringe is pumped several times and allowed to fill and equilibrate with mercury vapor for approximately 30 s. The syringe is withdrawn and the aliquot of mercury vapor is injected onto the gold-coated silica sampling tube.

10.2.5 The injection is made using a gastight "T" fitting equipped with a silicone septum at one end of the quartz tube. The septum is placed at a right angle with respect to the carrier gas entering directly in line with the tube. The syringe tip should extend beyond the "T" and into the stream of air flowing into the sampling tube when an injection is made. Quickly withdraw the syringe after the injection and let the air flow for 90 s. Seal the ends of the tube with a gastight fitting if the tube will not be immediately analyzed.

10.2.6 The sealed mercury vial should be maintained at a constant temperature that is carefully recorded and monitored. The temperature must be closely regulated because the vapor pressure of mercury is very dependent on temperature. It is critical that headspace temperature be at or below laboratory temperature in order to prevent condensation of mercury inside the syringe after withdrawal of an aliquot. Wait at least 2 min between headspace withdrawals to allow the mercury vapor phase to equilibrate.

10.2.7 The mass of mercury contained in an aliquot of headspace can be calculated using the Dumarey Equation:

$$C_{Hg}^{sat} = \frac{D}{T}10^{-\left(A + \left[\frac{B}{T}\right]\right)} \tag{1}$$

This equation corresponds to the least-squares best fit of results obtained for measurements of the mercury mass concentration in air at saturation between 288 and 298 K. This equation can be used to calculate mercury concentration in ng/mL. T is the temperature of the headspace gas mixture, in K, A is a constant equal to -8.134459741, B is a constant equal to 3240.871534 K, and D is a constant equal to 3216522.61 K ng mL^{-1}.[9]

10.3 *Test Method C – Calibration using an Aqueous Standard:*

10.3.1 Standards are prepared using concentrations appropriate to the level of mercury collected on the sampling tube. Different mercury loading will require different volumes or different concentrations, or both, of the mercury working standard. To prepare a 20 ng standard, slowly add a 200 μL aliquot of the aqueous working mercury standard to a gold-coated silica tube. After 15 min, or a contact time long enough to ensure adsorption of the mercury onto the gold, wash the tube interior with four 0.5 mL aliquots of water.

10.3.2 Water is removed from the standard tubes by a purge of dry nitrogen or air at approximately 400 mL/min. The purge gas, or the gold-coated silica tube, may be heated at temperatures ranging up to 60 °C to facilitate the drying.

NOTE 6—**Caution:** All water must be removed. The presence of water

[9] de Krom, I., Bavius, W., Ziel, R., Efremov, E., Meer, D., Otterloo, P., Andel, I., Osselen, D., Heemskerk, M., van der Veen, A., Dexter, M., Corns, W., and Ent, H., "Primary mercury gas standard for the calibration of mercury measurements," *Measurement*, 2020, 108351, 10.1016/j.measurement.2020.108351.

in the tubes may contribute to a background absorption resulting in a sloping baseline that will be observed in the final analysis.

10.3.3 A minimum of three to five standards should be prepared. Only repeatable results (RSD < 5 %) are to be used in calibration.

10.4 *Calibration Requirements:*

10.4.1 A calibration curve must be generated using either (*1*) three upscale calibration standards including a zero point, (*2*) three upscale calibration standards with the resulting curve forced through zero, or (*3*) four upscale calibration points (for high-range calibration curves not near the analytical MDL). Each standard measurement must come within ±10 % of the reference value.

10.4.2 A linear least squares regression (weighted or unweighted) should be used to calculate the calibration curve. TR^2 must be ≥ 0.990.

11. Measurement Procedure

11.1 It is highly recommended that the atomic absorption spectrophotometer parameters are set as follows:
 – Wavelength: 253.7 nm
 – Slit: 0.7 nm
 – Background correction: ON
 – Desorption furnace temperature: at least 550 °C.

11.2 The analysis train should be assembled using push-to-connect fittings (alternatively, minimal lengths of white silicone) and ⅛ in. TFE-fluorocarbon or coated stainless steel tubing. The carrier gas should flow from a rotameter flow control device into the sampling tube and subsequently into the analytical cell of the atomic absorption spectrophotometer using the same flow direction as was used in sampling.

11.3 The atomic absorption spectrophotometer is expected to meet the following performance criteria:
 – Detection Limit of 0.1 ng mercury
 – Limit of Quantification of 0.5 ng mercury.

11.3.1 The Detection Limit and Limit of Quantification should be verified and, if necessary, reevaluated on an annual basis using 40 CFR Part 136 Appendix B or an equivalent statistical evaluation.

11.4 Allow the system to equilibrate. If it is necessary to passivate the system, connect an air line to an empty tube not containing gold-coated sorbent packing and adjust the flow to approximately 500 mL/min. Dispense several 1 mL aliquots of mercury headspace vapor until a constant peak height or area is visually reached. Remove the empty tube.

11.5 Connect an air line to a blank tube containing gold-coated sorbent and readjust the flow to approximately 500 mL/min.

11.6 Check the absorbance baseline using a recorder or the instrument's real-time display. If necessary, zero the instrument output. If the software allows, set a baseline offset correction to re-zero the instrument reading before detection of the mercury peak. Referenced data collection times may need to be adjusted.

11.7 Place the tube into the furnace with the sorbent portion of the tube in the hot zone. Try to minimize the amount of time the system and the sample tube are exposed to ambient conditions. Start collecting absorption data immediately. Lengthen the integration time, if necessary, to ensure a full integration. A typical peak will span 30 s.

11.8 Remove the tube from the furnace after the mercury peak has evolved or after 60 s and allow the furnace temperature to equilibrate. Remove the used tube from the air line and repeat 11.4 – 11.6 on subsequent tubes containing standards and samples.

12. Calculation

12.1 On the day of analysis, construct a calibration curve for the range of mercury selected by plotting peak areas in absorbance-seconds against ng mercury. The calibration curve should be prepared in accordance with 10.3, spanning the range of expected mercury concentration in the gas samples. Each standard must measure within ±10 % of the expected value.

12.2 Determine the ng of mercury present in the sample tubes by reference to the calibration curve. The results from Tube 1 and Tube 2 are calculated separately to determine if breakthrough occurred. The final concentration is determined by addition of the two results.

$$C = \frac{M_1 + M_2}{v} \qquad (2)$$

$$\% \text{ Breakthrough} = M_2 / (M_1 + M_2)$$

$$\% \text{ Spike Recovery} = \left(\frac{(M_{1\ spiked} + M_{2\ spiked})}{V_{spiked}} - \frac{M_{1\ unspiked} + M_{2\ unspiked}}{V_{unspiked}} \right) * V_{spiked} * \frac{1}{m} * 100$$

$$\% \text{Relative Deviation} = \frac{C_{paired\ run\ a} - C_{paired\ run\ b}}{C_{paired\ run\ a} + C_{paired\ run\ b}} * 100$$

Calculating m loading value:

$$m_{lower\ limit} = C_e * V * 0.5 \qquad (3)$$

$$m_{upper\ limit} = C_e * V * 1.5$$

where:
M_1 = ng mercury present in Tube 1,
M_2 = ng mercury present in Tube 2,
V = volume of sample gas, L (at STP, defined as 1atm and 20 °C),
C = concentration of mercury ($\mu g/m^3$),
C_e = expected source concentration ($\mu g/m^3$), and
m = spiked mercury mass (ng).

12.3 See Table 1 for method criteria.

13. Precision and Bias

13.1 The precision of this test method was calculated to be 5.17 % in a single-laboratory study.

13.2 Precision of the instrument should be monitored by preparing and analyzing continuing calibration verification standards (*1*) before beginning a batch, (*2*) after every 10