



Designation: ~~D5954 – 98 (Reapproved 2014)~~^{ε1} D5954 – 22

Standard Test Method for Mercury Sampling and Measurement in ~~Natural Gas~~ Gaseous Fuels by Atomic Absorption Spectroscopy¹

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.

^{ε1} NOTE—Mercury caveat was added editorially to the Scope in April 2014.

1. Scope

1.1 This test method covers the determination of total mercury in ~~natural gas~~ gaseous fuels at concentrations down to $\pm 0.5 \text{ ng ng/m}^3$. It includes separate procedures for both sampling and atomic absorption spectrophotometric determination of mercury. ~~The~~ 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~~—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. ~~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 and/or mercury containing products into your state or country may be prohibited by law.~~

1.4 *This standard does not purport to address all of the safety concerns, if any, concerns associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and ~~health~~ 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](#)

¹ This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.05 on Determination of Special Constituents of Gaseous Fuels.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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 silica beads sorbent and subsequently directly desorbed by heat into a long path-length quartz 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. The mercury concentration is obtained from the absorbance peak area by comparison to standards prepared at the time of analysis. Analyte mass is determined by 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 natural gas streams 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 natural gas gaseous fuel processing and operation operations.

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

³ Available from United States Environmental Protection Agency (USEPA), 1200 Pennsylvania Ave., NW, Washington, DC 20460, <https://www.epa.gov>.

⁴ Available from <https://www.ecfr.gov>.

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

⁶ Chao, S.S., S. S., and Attari, A., "Characterization and Measurements of Natural Gas Trace Constituents—Volume II: Survey," Final Report **GRI-94/0243.2, June 1994**, GRI-94/0243.2.

⁷ Braman, R.S., R. S., and Johnson, D.L., 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.

6. Interferences

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

7. Apparatus

7.1 Atomic Absorption Spectrophotometer, Spectroscopy (AAS) Analyzer, equipped with a ~~10-cm-long path quartz~~ long path-length, inert absorption cell and a mercury source lamp (~~EDL~~ (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 ~~30-30~~ to ~~60-60~~ 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 Rotameter-Dry Test Meter or Other Flow Measurement Device, for sampling, capable of ~~attaining and regulating air~~ attaining, regulating, and measuring gas flow at approximately 500 mL/min 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 Measurement Device Regulating Device, for calibration/analysis, capable of attaining and regulating the ~~natural-gas sample~~ flow at approximately ~~1000 to 2500~~ 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.

5.4 Dry or Wet Positive Displacement Test Meter, or other calibrated total flow measurement device for measuring the volume of the sample.

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

5.6 Quartz Tubing, 12 cm long, ¼-in. outside diameter, to be used for sorbent (gold-coated silica) packing.

NOTE 2—All glass and plastic ware coming into contact with the sample must be acid washed with 20 % nitric acid and thoroughly rinsed with water.

5.7 Quartz Tubing, approximately 24 in. long and 1-in. outside diameter, to be used for the preparation of the gold-coated silica.

5.8 Quartz Wool to be used for sorbent (gold-coated silica) packing.

5.9 Fused Silica or Quartz Beads, 60/80 mesh, to be used for the preparation of the gold-coated silica.

7.5 Tube Furnace, Inert Push-to-Connect Fittings, approximately 8 to 10 cm in length, to be used for the preparation of the gold-coated silica and the mercury desorption. It must be capable of maintaining temperatures up to $750 \pm 25^\circ\text{C}$ over a 4-cm length. A Variac or other temperature control device may be required. various sizes, for connections (materials such as perfluoroalkoxy (PFA), coated stainless steel, polypropylene, or TFE-Fluorocarbons).

NOTE 3—A shorter sampling tube and a shorter tube furnace may be used as long as the specified temperature can be maintained.

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

5.11 Silicone Tubing, ¼-in. inside diameter for connections.

7.6 ~~Stainless Steel Tubing, 1/4- and 1/8-in outside diameter,~~ 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, 1/4-in. nylon~~ Nylon or TFE-fluorocarbon construction, gastight end-cap type, plus one stainless steel “T” fitting.

7.8 ~~Precision Gastight Syringe, Syringes, 500 µL, 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.~~ 0.05 °C.

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

~~5.18 Thermocouple, for monitoring tube furnace temperatures.~~

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

7.13 ~~Stainless Steel 6-Port Switching Valve, 1/8-in.~~ 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.

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.

~~6.3 Gold Chloride~~—Dissolve 2 g of gold chloride (HAuCl₄·3H₂O) in approximately 10 mL of water (**Warning—Poison**).

8.3 ~~Sulfuric Acid, (concentrated, H₂SO₄, relative density 1.84) (Warning—CorrosiveWarning).~~—**Poison**).

8.4 ~~Nitric Acid, (concentrated, HNO₃, relative density 1.42) (Warning—CorrosiveWarning).~~—**Poison**).

8.5 ~~Nitric~~ Hydrochloric Acid, (20%)—Mix 1 volume of concentrated nitric (concentrated, HCl, relative density 1.18). (**Warning—Corrosiveacid with 4 volumes of water.**)

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.

8.6 *Mercury*, triple distilled (~~Warning—Poison~~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 ~~10.00~~1.00 mL of the mercury standard stock solution to approximately ~~500~~50 mL of water. Add ~~0.5 mL~~5 mL of concentrated nitric acid and dilute to ~~1 L~~100 mL with water. ~~Prepare this standard solution daily.~~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~~1.00 mL of the mercury standard intermediate solution to approximately ~~50 mL~~50 mL of water. Add ~~0.05 mL~~5 mL of concentrated nitric acid and dilute to ~~100 mL~~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.

6.12 *Hydrogen*, PP grade (~~Warning—Flammable~~).

6.13 *Nitrogen*, PP grade.

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

7. Procedure for the Preparation of the Gold-Coated Beads 9a-4da9-44fa-b478-12b6d806d8b4/astm-d5954-22

7.1 Soak the silica beads in concentrated sulfuric acid overnight to remove any coating or contamination. Silica beads used for GC operations are often deactivated by silanization and this coating must be removed. Wash thoroughly with reagent water and dry.

7.2 Add 50 g of acid washed silica beads to 10 mL of gold chloride solution. This will result in a 2 % loading of gold on the silica substrate. Add a minimal amount of water, if necessary, to form a slurry. Heat on a hot plate with stirring until most of the water evaporates. Let the beads air-dry until the apparent moisture is evaporated. The color may change from yellow to a yellowish orange.

7.3 Pack the coated beads into the 1-in. outside diameter quartz tube with quartz wool plugs at either end and begin heating using a tube furnace with a nitrogen purge. Slowly raise the temperature from ambient to 170°C to dry thoroughly. A heat gun may be used to remove condensed moisture downstream of the furnace. The color of the beads will begin to turn orange and then purplish. This may take 1 to 2 h to complete depending on how much moisture is present.

NOTE 5—**Caution:** Moisture and oxygen must be removed and the beads completely dry before hydrogen gas is introduced.

7.4 Switch the gas to hydrogen and slowly raise the temperature to 250°C to reduce the gold ion to metallic gold. As the temperature rises, HCl vapors are generated from the tube and may appear as a smoky haze. A yellowish haze may be seen on the inside walls of the quartz tube. The reaction is complete when this haze either disappears or does not change over a 15- to 20-min period. Do not allow the temperature of the furnace to rise above 250°C since gold chloride will sublime at 265°C. This procedure may take 2 to 3 h to complete.

Note 6—Caution: The gas stream exiting from the tube furnace should be directed into a flask containing water to absorb the HCl gas generated as the gold ion is reduced.

7.5 Raise the furnace temperature to approximately 400°C over a 10-min period. Switch the gas to nitrogen and continue heating up to 500 to 550°C for an additional 10 min. Remove the quartz tube from the furnace and allow to cool under the nitrogen purge.

8. Procedure for the Preparation of the Sampling Tubes

8.1 Wash each ¼-in. outside diameter quartz tube with 20 % HNO₃, rinse with water, and dry in an oven at 105°C.

8.2 Place a 1-cm length of quartz wool at one end of a tube.

8.3 Add 0.5 g of the gold-coated beads to a quartz tube (oriented vertically) and gently tap the contents to eliminate air spaces. The final length of gold-coated beads should be approximately 2.5 cm and centered within the tube.

8.4 Add a final 1-cm length of quartz wool to the opposite end of the tube.

8.5 Bake out each tube using an air purge at 800°C at approximately 500 mL/min for at least 15 min. The air should be filtered through HGR carbon and a clean tube packed with gold-coated beads to remove any traces of mercury that may be present.

8.6 Seal the end of each tube with a gastight fitting.

9. Sampling Procedure

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

9.2 The distance from the sampling point to the sampler should be minimized because mercury is easily 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. Stainless 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. Flexible Inert push-to-connect fittings or flexible silicone tubing may be used to make short connections to sampling tubes. Any pumps, metering valves, and so forth or other flow- and pressure-controlling tubes; although, the former is preferred. Any pumps or flow measurement devices should be located downstream of the sampler if possible. 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 1 to 2.5 L/min (2 L/min is preferable). Pressure- and flow-control devices may be required. A total flow volume measurement device, such as a dry test meter, can be used to record the exact amounts of gas sampled for more accurate sampling. 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 Using a calibrated rotameter, installed upstream of the total flow measurement device, determine 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 tubing or inert push-to-connect fittings.

9.6 Connect the back end of the sampling tube assembly (Tube 2) to the rotameter 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 ~~100~~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~~, 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 ~~rotameter~~) 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 interferences. 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 an Aqueous Standard: 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 Standards—Calibration standards are prepared using concentrations appropriate to the level of mercury collected on the sampling tube. Different mercury ~~loadings~~ will require different ~~volumes or volumes~~, 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. 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. 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/min. After sparging, seal the ends of the tubes with gastight fittings if the tubes will not be analyzed immediately.~~

10.1.2 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.