



Designation: D 5954 – 98

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

This standard is issued under the fixed designation D 5954; 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 covers the determination of total mercury in natural gas at concentrations down to 1 ng/m³. It includes separate procedures for both sampling and atomic absorption spectrophotometric determination of mercury. The procedure detects both inorganic and organic forms of mercury.

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

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

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 3223 Test Method for Total Mercury in Water²

D 3684 Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method³

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis⁴

3. Summary of Test Method

3.1 Mercury in a gas stream is adsorbed onto gold-coated silica beads and subsequently directly desorbed by heat into a long path-length quartz 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.

¹ This test method is under the jurisdiction of ASTM Committee D-3 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 *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 05.05.

⁴ *Annual Book of ASTM Standards*, Vol 15.05.

4. Significance and Use

4.1 This test method can be used to measure the level of mercury in natural gas streams 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 processing and operation.

4.2 Adsorption of the mercury on gold-coated beads can remove interferences associated with the direct measurement of mercury in natural gas. 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. 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}

5. Apparatus

5.1 *Atomic Absorption Spectrophotometer*, equipped with a 10-cm-long path quartz absorption cell and a mercury source lamp (EDL or other high intensity lamp). It must be capable of collecting and integrating data over a 30- to 60-s time window. Background capabilities are strongly recommended.

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

5.2 *Rotameter or Other Flow Measurement Device* capable of attaining and regulating air at approximately 500 mL/min.

5.3 *Rotameter or Other Flow Measurement Device* capable of attaining and regulating the natural gas sample at approximately 1000 to 2500 mL/min.

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

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, June 1994.

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.

5.5 *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.

5.10 *Tube Furnace*, 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.

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

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

5.12 *Stainless Steel Tubing*, ¼- and ⅛-in outside diameter, various lengths, for connections.

5.13 *Gastight Tube Fittings*, ¼-in. nylon or TFE-fluorocarbon construction, gastight end-cap type, plus one stainless steel “T” fitting.

5.14 *Precision Gastight Syringe*, 500 µL, equipped with a needle with a side port opening.

NOTE 4—A digital syringe is recommended for better accuracy and precision in calibration.

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

5.16 *Water Bath or Constant Temperature Apparatus*, capable of regulating a sealed vial of mercury to $26 \pm 0.05^\circ\text{C}$.

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

5.18 *Thermocouple*, for monitoring tube furnace temperatures.

5.19 *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 Variac or other temperature control device may be required.

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

6. Reagents

6.1 *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.

6.2 *Reagent Water*—Reagent water, conforming to Type II of Specification D 1193, shall be used for preparation of reagents and washing of the quartz tubing.

6.3 *Gold Chloride*—Dissolve 2 g of gold chloride ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) in approximately 10 mL of water (**Warning—Poison**).

6.4 *Sulfuric Acid*, (concentrated, H_2SO_4 , relative density 1.84) (**Warning—Poison**).

6.5 *Nitric Acid*, (concentrated, HNO_3 , relative density 1.42) (**Warning—Poison**).

6.6 *Nitric Acid*, (20 %)—Mix 1 volume of concentrated nitric acid with 4 volumes of water.

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

6.8 *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.

6.9 *Mercury Standard Intermediate Solution*, (10 µg/mL)—Add 10.00 mL of the mercury standard stock solution to approximately 500 mL of water. Add 0.5 mL of concentrated nitric acid and dilute to 1 L with water. Prepare this standard solution daily.

6.10 *Mercury Standard Working Solution*, (100 ng/mL)—Add 1.00 mL of the mercury standard intermediate solution to approximately 50 mL of water. Add 0.05 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.

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

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

6.13 *Nitrogen*, PP grade.

6.14 *Sulfur Impregnated Carbon*,⁹ used to filter carrier gases.

7. Procedure for the Preparation of the Gold-Coated Beads

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

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.

⁹ HGR carbon available from Calgon Carbon Corp., Western Region, 2750-C Goodrick Ave., Richmond, CA 94801.