



Standard Test Method for Mercury Sampling and Analysis in Natural Gas by Atomic Fluorescence Spectroscopy¹

This standard is issued under the fixed designation D6350; 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 natural gas streams down to 0.001 $\mu\text{g}/\text{m}^3$. It includes procedures to both obtaining a representative sample and the atomic fluorescence detection of the analyte. This procedure can be applied for both organic and inorganic mercury compounds.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.2.1 *Exception:* Inch-pound units are used in Sections 5.1.2 and 7.3 when discussing pressure regulator usage.

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 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, 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 its use.*

2. Referenced Documents

2.1 ASTM Standards:²

D5954 Test Method for Mercury Sampling and Measurement in Natural Gas by Atomic Absorption Spectroscopy

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 ISO Standard³

ISO 6978 Determination of Mercury in Natural Gas

3. Summary of Test Method

3.1 Mercury from the gaseous stream is absorbed and preconcentrated onto a gold-coated silica sand trap. The analyte is desorbed by raising the temperature of the trap, and a flow of inert gas carries the mercury atoms into the cell assembly of an atomic fluorescence spectrophotometer. The cell is irradiated by a low pressure mercury vapor lamp at 253.652 nm. Excitation of mercury atoms produces resonance fluorescence which reradiates at the excitation wavelength. The fluorescence radiation is detected by a photomultiplier tube and is directly proportional to the amount of mercury in the cell. The concentration of the element in the original sample is obtained by comparison to freshly prepared standards, which are analyzed by direct injection of mercury vapor into the instrument at a specified temperature on supported gold traps.

4. Significance and Use

4.1 This test method can be used to determine the total mercury concentration of a natural gas stream down to 0.001 $\mu\text{g}/\text{m}^3$. It can be used to assess compliance with environmental regulations, predict possible damage to gas plant equipment, and monitor the efficiency of mercury removal beds.

Where L_1 and L_2 are the specimen lengths at temperatures T_1 and T_2 , respectively. α is, therefore, obtained by dividing the linear expansion per unit length by the change in temperature.

4.2 The preferred sampling method for mercury collection is on supported gold sorbent, which allows the element to be trapped and extracted from the interfering matrix of the gas. Thermal desorption of mercury is performed by raising the temperature of the trap by means of a nichrome wire coiled around it.

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³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

Thermal desorption of mercury is performed by raising the temperature of the trap by means of a nichrome wire coiled around it.

4.4 Since AFS demonstrates lower detection limits approaching 0.1 pg, this test method avoids difficulties associated with prolonged sampling time. Saturation of the trap with interferants such as hydrogen sulfide (H₂S) is avoided. Average sampling can range between 15 to 30 min, or less.

5. Apparatus and Materials

5.1 Sampling Equipment:

5.1.1 Sample probe, equipped with a ball valve of the Type 316 SS, connected to the sampling point is highly recommended.

5.1.2 Pressure regulation devices, such as two-stage stainless steel pressure regulator, capable of reducing the pressure from 2000 to 30 psi.

5.1.3 On/off and micrometric-type valves capable of regulating the natural gas sample flow rate in the range of 100 to 200 mL/min.

5.1.4 Stainless steel tubing and compression-type fittings, as required.

5.1.5 Dry or wet flow meter or integrating anemometer to measure properly the total volume of the gas sample collected.

5.1.6 Gold-coated fused silica sand traps.

NOTE 1—For details on trap preparation refer to Test Method **D5954**, the procedure of vapor deposition used in scanning electron microscopy (SEM) techniques, Fitzgerald and Gill⁴, and ISO 6978, 1993.

5.2 Analytical Equipment:

5.2.1 *Atomic Fluorescence Spectrophotometer*, equipped with a quartz cell and a mercury lamp capable of irradiating at 253.652-nm wavelength.

5.2.2 *Chromatography Grade Teflon® and Silicon Tubing*, for connections between the thermal desorption system and the AFS. Length, ID, and OD are selected as appropriate.

5.2.3 *Nichrome Wire* (22 gauge) coiled (20 turns/inch) around the traps for the thermal desorption of mercury.

5.2.4 *Variable Voltage Regulator*, (rheostat) used in conjunction with the nichrome wire for the rapid heating of the traps.

5.2.5 *Temperature-Resistant Rubber Tubing*, of ¼ in. (0.06 mm), connecting the trap to the temperature desorption system.

5.2.6 *GC-Grade Septa*, low bleed, made of silicone used in the injection port and mercury-sealed vial.

5.2.7 *Constant Temperature Bath*, capable of regulating the temperature of a sealed vial of mercury to 25 ± 0.1°C.

5.2.8 *Various Stainless Steel “T” Fittings*.

5.2.9 *Gastight Syringes*, fixed or variable volume, in the range of 10 to 500 µL.

5.2.10 *A Glass Vial*, 100 mL fitted with a septum to perform as mercury container.

5.2.11 *Chart Recorder*, or integrator to process a hard copy of the data acquired by the detector.

NOTE 2—Commercially available permeation injection sources, based on the principle of permeation tubes, can be used instead of gastight syringes. Permeation devices can be used in lieu of gastight syringe-based sample introduction. A permeation system can automatically introduce an accurately known amount of mercury vapor onto a gold trap. This is particularly convenient for quantifying low pg amounts of mercury.

6. Reagents and Materials

6.1 Because of the error and contamination that may be introduced from impurities in the chemicals, the use of high purity reagents is strongly recommended.

6.1.1 *Mercury Analytical Grade*, triple distilled.

NOTE 3—**Warning:** Mercury vapor is harmful. Use proper ventilation when handling.

6.2 *Argon Gas*, ultra high purity grade (UHP 99.999 %).

NOTE 4—For the permeation injection source procedure, certified mercury permeation tubes are commercially available. Tubes can also be prepared and calibrated by comparison to syringe injection or by weight loss, over time, using an analytical balance with a resolution of ±0.01 mg.

7. Sampling Procedure

7.1 Every effort should be made to ensure that the sample is representative of the gas source from which it is taken. Select always the best and more representative sampling point for mercury trapping. Sampling will require the use of specific procedures; consult appropriate regulations.

7.2 Sampling arrangements will always use a minimum of two sampling gold tubes per location. The recommended sampling setup is shown schematically in **Fig. 1**.

7.3 Assemble the parts without connecting the gold traps, as depicted in **Fig. 1**. Open the flow of gas from the main valve and regulate the pressure down to 30 psi. Open the on/off valve and set an approximate flow of 150 mL/min with the micrometric valve adjustment. Check the flow with a dry or bubble flow meter. Let the system purge for at least 30 min. Purging is necessary, especially if the pressure regulator, tubing, and valves were used at a previous location. The longer the purging period the better.

7.4 When purging is completed, close the on/off valve and connect both gold traps to the system. Use Tygon tubing or similar to connect traps together.

7.5 Open the on/off valve again and record the time and the exact flow through the traps. Periodically check, every 15 min, that the flow remains constant throughout the duration of sampling. Best results are obtained with a 100- to 200-mL/min flow rate and an average sampling time of 15 to 30 min. Record both readings.

7.6 When sampling time has elapsed, close the on/off valve and disconnect the traps. Carefully cap and label them accordingly (Tube 1 and Tube 2). Accurately record the final time and flow data for later calculations.

8. Calibration of the Instrument (Gaseous Standard)

8.1 Calibration according to the following procedure is recommended since it is easy to perform and results in

⁴ Fitzgerald, W.F., and Gill, G.A. “Subnanogram Determination of Mercury by Two-Stage Gold Amalgamation and Gas Phase Detection Applied to Atmospheric Analysis,” *Analytical Chemistry*, 11, 1714, 1979.