



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

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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.

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.

5.5 *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, 1/4-in. outside diameter, to be used for sorbent (gold-coated silica) packing.

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.

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.

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*, $\frac{1}{4}$ -in. inside diameter for connections.

5.12 *Stainless Steel Tubing*, $\frac{1}{4}$ - and $\frac{1}{8}$ -in outside diameter, various lengths, for connections.

5.13 *Gastight Tube Fittings*, $\frac{1}{4}$ -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*, $\frac{1}{8}$ 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.

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.

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 $\mu\text{g/mL}$)—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 $\mu\text{g/mL}$)—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 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.

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

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, 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) into the first sampling tube (Tube 1), followed by the second tube (Tube 2), and finally the rotameter flow control device.

9.2 The distance from the sampling point to the sampler should be minimized because mercury is easily absorbed on 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 steel tubing must be used for connections upstream of the pressure regulator. High density TFE-fluorocarbon or stainless steel tubing is preferred for connections downstream of the regulator. 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 devices should be located downstream of the sampler if possible. The entire sampling line should be heated 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.

9.4 Using a calibrated rotameter, installed upstream of the total flow measurement device, 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.

9.6 Connect the back end of the sampling tube assembly (Tube 2) to the rotameter 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 flowrate. 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 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 sorbent is much higher, 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) as “Tube 2.”

10. Calibration Procedure

10.1 *Test Method A—Calibration Using an Aqueous Standard:*

10.1.1 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.

10.1.2 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.

NOTE 7—**Caution:** All water must be removed. The presence of water in the tubes may contribute to a background absorption resulting in a sloping baseline that will be observed in the final analysis.

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

10.2 *Test Method B—Calibration Using a Gaseous Standard:*

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 natural gas streams. Laboratories that have safety concerns regarding storage of elemental mercury may use Test Method A.

10.2.2 All surfaces of the apparatus, 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 analysis 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 1000 μ L 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 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 temperature of the sealed vial of mercury should be maintained at a constant temperature that is carefully recorded and monitored. A 100- μ L aliquot of the headspace over mercury in a sealed vial is equivalent to 2.15-ng mercury at 26°C. The temperature must be closely regulated because the vapor pressure of mercury is very dependent on temperature. A change of 2°C results in a 15 % difference in the amount of mercury in the vapor sampled. Sufficient time must be allowed between headspace withdrawals to allow the mercury vapor phase to equilibrate.

10.2.7 The following table gives the amount of mercury in 100- μ L aliquots of the headspace over mercury in a sealed vial at different temperatures.

Temperature, °C	Nanogram Mercury in 100 μ L
20	1.32
22	1.56
24	1.83
26	2.15
28	2.52
30	2.95

11. Measurement Procedure

11.1 The analysis train should be assembled using minimal lengths of white silicone and 1/8-in. TFE-fluorocarbon or

stainless steel tubing. The carrier gas should flow from a rotameter flow control device into the sampling tube and subsequently into the quartz cell of the atomic absorption spectrophotometer following the same direction of flow as was used in sampling the natural gas stream. All tubing from the outlet end of the sampling tube to the inlet port of the quartz cell should be constructed of 1/8-in. TFE-fluorocarbon or stainless steel and heat traced at 50 to 60°C.

NOTE 8—**Optional:** A 6-port switching valve can be used to control gas flows. It can be used to divert the air flow from the analytical tube during a preheat stage and restore the air flow through it with minimal disruption of the flow rate.

11.2 Set the atomic absorption spectrophotometer parameters as follows.

Wavelength:	253.7 nm
Slit:	0.7 nm
Background correction:	ON
Absorption cell temperature:	100°C
Desorption furnace temperature:	720-750°C

11.3 Connect an air line to an empty tube not containing the gold-coated silica packing and adjust the flow to approximately 500 mL/min. Passivate the system with several 1-mL aliquots of mercury headspace vapor until a constant peak height or area is visually reached. Remove the empty tube.

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

11.5 Check the absorbance baseline using a recorder or the instrument’s real time display. Zero the instrument output. Set the integration time to at least 60 s. If the software allows, set a baseline offset correction to rezero the instrument reading before detection of the mercury peak. Referenced data collection times may need to be adjusted.

11.6 Quickly open the preheated furnace, place the tube into the furnace with the coated bead portion of the tube at the hot zone, close the furnace. Start collecting absorption data immediately. Lengthen the integration time, if necessary, to ensure a full integration. A spare standard tube should be used for this purpose. A typical peak will span 30 s.

NOTE 9—**Optional:** A 6-port switching valve can be used to preheat the tube with no flow for approximately 15 s. Preheating with a stopped flow will allow mercury detection with sharper and earlier peaks. Integration timing will need to be adjusted. A spare standard tube can be used to check peak timing. An ideal run time is 60 s with a typical peak width of 20 to 30 s.

11.7 Remove the tube from the furnace after the mercury peak has evolved (if any) and allow the furnace temperature to reequilibrate. Remove the used tube from the air line and repeat 11.4 on subsequent tubes containing standards and samples.

12. Calculation

12.1 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 with standards spanning the range of expected mercury concentration in the gas samples. Depending on the path length of the atomic absorption spectrometer quartz analysis cell, and the parameters of the specific instrument used, linearity up to

300-ng mercury may be achieved.

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.

$$\text{Mercury, } \mu\text{g/m}^3 = \frac{A + B}{C} \quad (1)$$

where:

A = ng mercury present in Tube 1,

B = ng mercury present in Tube 2, and

C = volume of sample gas, L (at STP).

13. Precision and Bias

13.1 The precision of this test method is not known to have

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been obtained in accordance with currently accepted guidelines. Data are still being collected to obtain reliable repeatability and reproducibility information. The relative percent standard deviation of the standard should not exceed 5 %.

13.2 Since no suitable certified reference material for mercury in natural gas is currently available, no statement on absolute bias can be made for this test method.

13.3 Multiple standards should always be prepared to improve the repeatability, and the peak areas compared to previous analyses.

14. Keywords

14.1 gaseous fuels; mercury sampling; natural gas