Designation: D 6350 – 98 (Reapproved 2003)

Standard Test Method for Mercury Sampling and Analysis in Natural Gas by Atomic Fluorescence Spectroscopy[1]

This standard is issued under the fixed designation D 6350; 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 μg/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 Both, inch-pound and SI (metric) units of measurement are used throughout this 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 its use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 3684 Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method[2]

D 5954 Test Method for Mercury Sampling and Measurement in Natural Gas by Atomic Absorption Spectroscopy[2]

2.2 *ISO Standard:*

ISO 6978 Determination of Mercury in Natural Gas[3]

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 μg/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.

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.

4.3 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 (H_2S) 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 a 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.

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[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] *Annual Book of ASTM Standards*, Vol 05.06.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

5.1.6 Gold-coated fused silica sand traps.

NOTE 1—For details on trap preparation refer to Test Method D 5954, the procedure of vapor deposition used in scanning electron microscopy (SEM) techniques,[4] 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 gage) 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

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. (**Warning**—Mercury vapor is harmful. Use proper ventilation when handling.)

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

NOTE 3—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 something similar, to connect traps together.

7.5 Open the on/off valve again and record the time and the exact flow through the traps. 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 repeatability not exceeding a 10 % range between duplicate analyses.[5] (see also ISO 6978).

8.2 Standards are prepared by injection of different volumes of the head space from a thermostated, sealed mercury vial. Injection of the aliquots, usually in the microlitre range, should be made directly onto a mercury trapping tube, using a T-piece injection port and argon gas as carrier. See Fig. 2 for details.

8.3 All surfaces coming in contact with the mercury vapor should be passivated (except the analytical trap) before actual readings can be taken. Condition all tubing, instrument connections, as well as all syringes, by multiple injections of the gaseous mercury vapor head space contained in the temperature-controlled mercury vial.

8.4 The concentration of a particular aliquot, taken with a gastight syringe, can be calculated by the following equation of state of real gases:

$$\log(\text{ng/mL}) = (-3104/K) + 11.709 \quad (1)$$

where:

K = Mercury temperature in Kelvins.

For instance, a 100-µL withdrawal of the head space over mercury at 24°C will result in an absolute mercury concentration of 1.83 ng on the gold trap.

[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.

[5] Dumarey, R., Temmerman, E., Dams, R., and Hoste, J., "The Accuracy of the Vapour-Injection Calibration Method for the Determination of Mercury by Amalgamation/Cold-Vapor Atomic Absorption Spectrometry," *Analytica Chimica Acta*, 170, (1985), pp. 341-346.

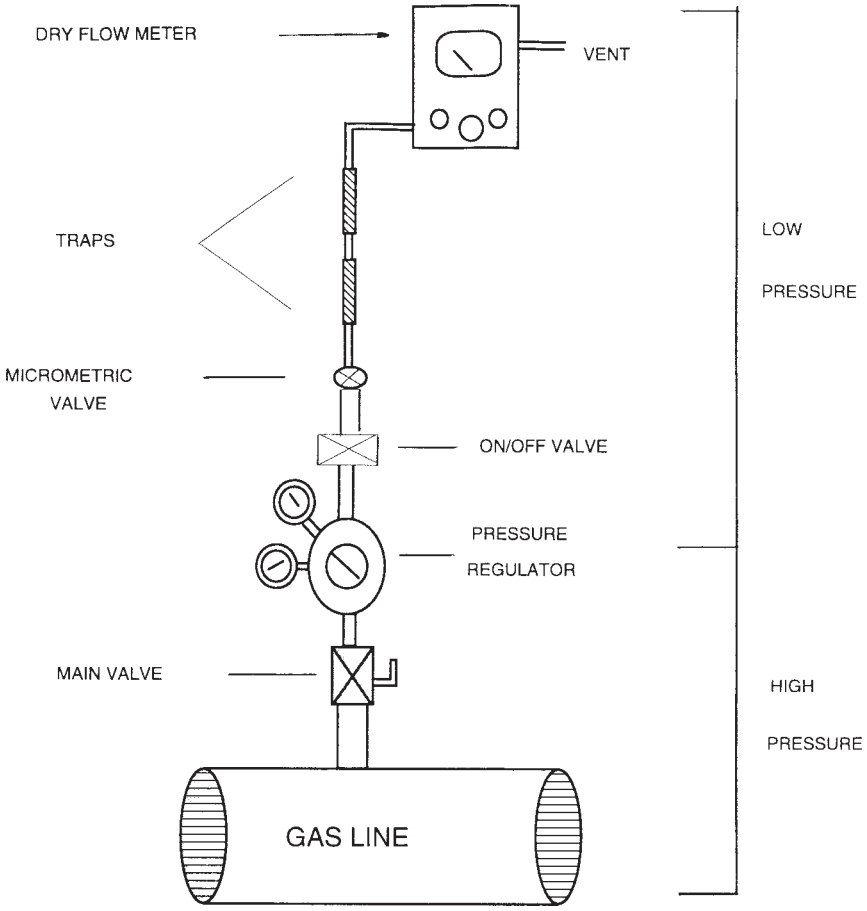

FIG. 1 Diagram of Sampling Arrangement with Gold-Coated Silica Sand Traps Installation

8.5 The analytical system should be assembled using a minimal length of high density Teflon tubing. The carrier gas flow should be carefully controlled using a rotameter, mass flow controller, or other equivalent device at 100 to 150 mL/min (see Fig. 2 and Fig. 3).

8.6 After injection of the standard, allow 2 min to elapse before starting the heating cycle. Continuously flow argon through the trap during this waiting period to establish a flat baseline.

8.7 Start the heating cycle by turning on the voltage regulator. The nichrome wire will start to heat rapidly. When properly adjusted, it can reach 550°C in less than 40 s without the risk of burning the heater wire.

8.8 A chart recorder, integrator, or computer (with appropriate peak processing software) must be connected at all times to the signal output of the fluorescence detector to obtain a hard copy of peak (see Fig. 2 and Fig. 3).

NOTE 4—The temperature of the mercury vial must be kept at a value of 25 ± 0.1°C with the use of a thermostatic bath and a certified NIST traceable thermometer. The vapor pressure of mercury is significantly impacted by small temperature changes. Therefore, sufficient thermal reequilibration time is required between headspace samplings.

9. Analytical Procedure

9.1 For sample analysis, connect the field trap on the analysis train as decipted in Fig. 2. Argon must flow through the trap into the detector inlet. Field traps must be connected to the system in the reverse direction of flow used in sampling the natural gas stream.

9.2 The trap must pass through the coiled nichrome wire, for easy in-and-out installation procedure. The coil has to fit around the trap tight enough to provide sufficient contact for acceptable heat transfer, but leave enough room for the trap to slide in and out with ease.

9.3 Set the appropriate parameters in the detector unit and on the integrator system, such as threshold, peak width, area reject, and other parameters.

9.4 Start the integrator and wait for at least 30 s, baseline should be straight and present low noise levels (noise must not exceed ⅓ the signal expected for 1-pg standard). Turn on the voltage regulator; a minimum temperature of 550°C must be achieved in 40 to 50 s. Absorbed mercury will evolve from the trap and be detected. An integrator, chart recorder, or computer software will record the detector response. Under appropriate conditions and normal concentrations, typical peaks will span 20 to 50 s.

9.5 Leave the heating filament hot for a few more seconds to ensure that all the mercury has evolved from the trap. Turn the voltage regulator and the integrator off. With an auxiliary air line rapidly cool the outside surface of the trap and filament.

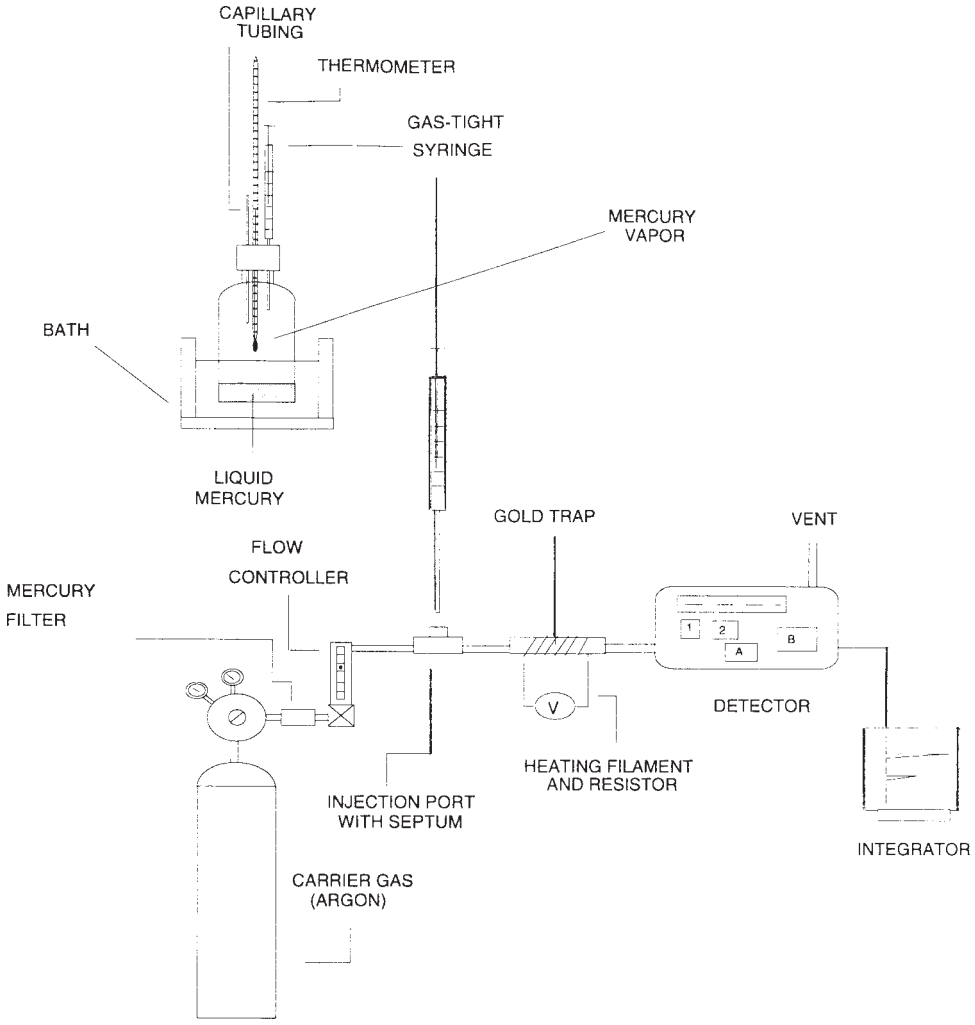

FIG. 2 Diagram of Mercury Calibration Using Syringe Injection Followed by Thermal Desorption from Gold Traps and AFS Detection

Remove the analyzed tube (which is now clean and free from mercury) and repeat Steps 1 through 5 on the remaining sample tube traps.

9.6 As part of the QA/QC program recommended for this method, a standard is introduced onto a trap used for sample analysis. After recovering mercury from a trap, a known amount of mercury vapor is introduced onto the trap and desorbed into the analytic system. Percent recoveries are calculated based upon the amount of mercury introduced onto the trap and the amount determined by this method. An acceptable recovery is typically greater than 95 % of the introduced amount.

9.7 When using the permeation injection source technique, either for routine calibration or analysis, or both, the system must be installed as depicted in Fig. 3.

10. Calculation

10.1 Sample concentration is calculated from linear calibration curve obtained experimentally from the set of standards.

10.1.1 Plot the net response (in arbitrary units) given by the integrator, for each standard, as the *y* axis versus the amount of mercury (concentration) of each standard as the *x* axis, to generate a calibration curve.

10.2 Check the correlation coefficient r^2 for the curve. The value should be at least 0.99 or higher and is calculated as follows:

$$r^2 = \frac{(\Sigma xy)^2}{(\Sigma x^2)\,(\Sigma y^2)} \tag{2}$$

where:

x = $Xi - \bar{x}$,
Xi = amount of mercury in the standard,
y = $Yi - \bar{y}$,
Yi = response value, in arbitrary units, of the standard,
$\bar{x}$ = average value for all standards, and
$\bar{y}$ = average response value of standards.

10.3 Obtain the linear least square fit equation in the form:

$$y = mx + b \tag{3}$$

where:

y = response in arbitrary units given by the integrator,
x = amount of mercury in the unknown,
m = slope of the linear equation, and
b = the y axis intercept.

The values m and b are calculated as follows:

$$m = \Sigma xy / \Sigma x^2 \tag{4}$$

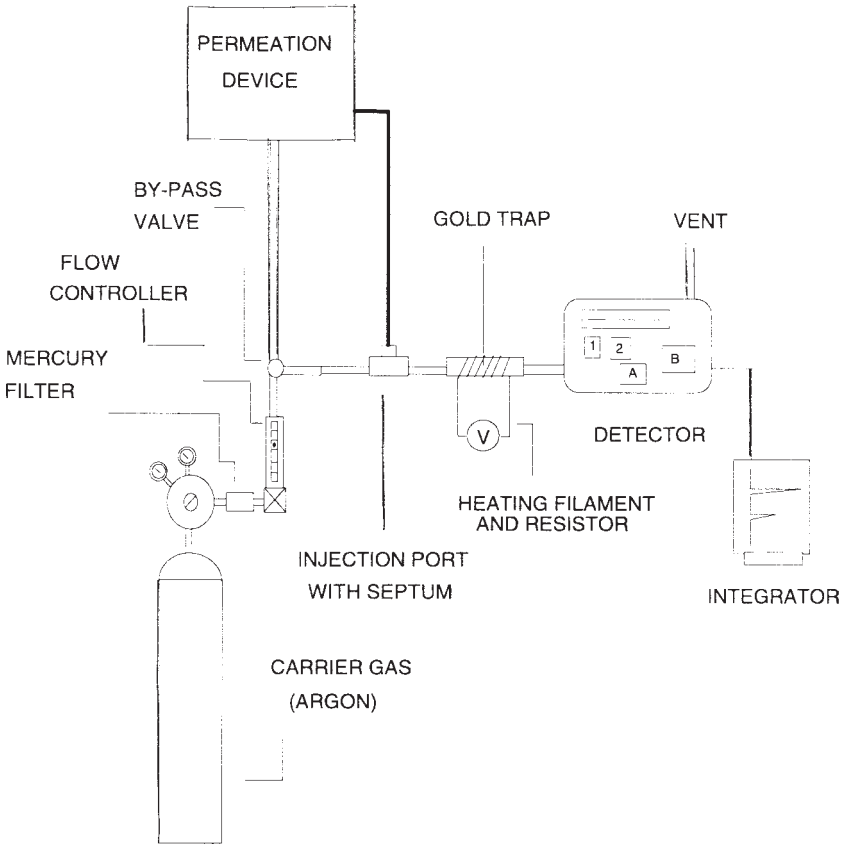

FIG. 3 Diagram of Mercury Calibration Using Permeation Injection Source Followed by Thermal Desorption from Gold Traps and AFS Detection

$$b = y - mx \quad (5)$$

10.4 Calculate the concentration of the unknown sample [*x*] from Eq 2:

$$[x] = y/m - b \quad (6)$$

10.5 Finally, calculate the mercury concentration in µg/m^3 in the gas sample:

$$\text{Mercury, } \mu g/m^3 = \frac{[x]}{V} \quad (7)$$

where:

[x] = concentration of mercury in ng from the linear regression see Eq 2 and

V = volume of sampled gas in litres.

10.6 Calculate the concentration of each individual trap separately to determine possible break through of mercury from Trap 1 to Trap 2. Final concentration is determined by the addition of both results.

10.7 Report the results to the nearest 0.001 µg/m^3.

11. Precision and Bias

11.1 *Repeatability*—The data shown in Table 1 indicate that results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would not in the normal and correct operation of the test method differ by more than 5 % of their mean value.

11.2 *Reproducibility*—Data are not available to obtain reliable reproducibility information.

11.3 *Bias*—Since there is not certified reference material suitable for determining the bias for the procedure in this test method, bias cannot be determined.

12. Keywords

12.1 atomic fluorescence spectroscopy; gold sorbent; mercury sampling; natural gas

TABLE 1 Repeatability of Five Consecutive Injections of Mercury Standards at Different Concentration Levels

NOTE—Showing mean value, standard deviation, and relative standard deviation.

Mercury, ng	Run 1[A]	Run 2[A]	Run 3[A]	Run 4[A]	Run 5[A]	Mean[A]	STD	%RSD
0.056	508 479	530 602	558 887	565 321	511 222	534 902	26 353	4.93
0.11	1 091 853	1 092 025	1 160 471	1 128 586	1 018 586	1 098 304	52 957	4.82
0.226	2 142 293	2 208 301	2 038 435	2 064 089	2 011 783	2 092 980	80 829	3.86

[A] Area counts.