Designation: D6350 – 24

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

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 gaseous fuels at concentrations down to 0.001 µg m^{-3}. It includes procedures for obtaining a representative sample and for the determination of Hg using gold amalgamation-atomic fluorescence spectrometry (AFS). The procedure detects all forms of mercury including elemental, inorganic and organic mercury and therefore reports total gaseous mercury.

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

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 for additional information. Users should be aware that selling mercury and/or mercury containing products into their 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, health, and environmental practices and determine the applicability of regulatory limitations prior to its 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]

D4150 Terminology Relating to Gaseous Fuels

D5954 Test Method for Mercury Sampling and Measurement in Gaseous Fuels by Atomic Absorption Spectroscopy

2.2 *ISO Standard*[3]

ISO 6978-2 Natural gas — Determination of mercury — Part 2: Sampling of mercury by amalgamation on gold/platinum alloy

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of general gaseous fuel 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. See 13.4.

3.2.2 *limit of quantification, n*—the lowest concentration at which the instrument can measure reliably with a defined error and confidence level. See 13.5.

3.3 *Acronyms:*

3.3.1 *AFS*—atomic fluorescence spectrometry

3.3.2 *PTFE*—polytetrafluoroethylene

4. Summary of Test Method

4.1 The sample gas is depressurized and is setup to continuously flow via speed loop bypass from which a representative sample can be obtained. Mercury from the gaseous stream is absorbed and preconcentrated onto two gold-coated silica tubes which are in series. The gold traps are heated above the dewpoint of the gas stream under reduced sample pressure

[1] This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.06.03 on Analysis by Spectroscopy.

Current edition approved May 1, 2024. Published June 2024. Originally approved in 1998. Last previous edition approved in 2014 as D6350 – 14, which was withdrawn in January 2023 and reinstated May 2024. DOI: 10.1520/D6350-24.

[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.

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

conditions. The volume of sample gas that is passed over the gold traps is measured. 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 mass of mercury in the original sample is obtained by comparison to direct injections of mercury vapor into the instrument at a specified temperature on supported gold traps. By determining the mass of mercury collected in a known volume of sample gas, the concentration of Hg can be calculated.

5. Significance and Use

5.1 This test method can be used to determine the total mercury concentration of natural gas and other sources of gaseous fuels (as defined by Terminology D4150) 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.

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

5.3 Amalgamation AFS is a pre-concentration technique, and the working range of this method can be adapted by collecting different volumes of gas. Detection limits below 0.001 μg m^{-3} can be achieved with large sample volumes (for example, >50 L) when low blanks are obtained. Using small sample volumes (for example, <1 L) the working range of the method can be extended to several thousand μg m^{-3}.

6. Apparatus and Materials

6.1 *Sampling Equipment:*

6.1.1 Sample probe, with low dead volume equipped with a ball valve connected to the sampling point is highly recommended but not essential. Wetted components should offer low adsorption of mercury. Electropolished stainless steel with glass, amorphous silicon or PTFE coating is advised.

6.1.2 Pressure regulation devices, such as two-stage stainless steel pressure regulator, capable of reducing the pressure from 20 000 kPag to 30 kPag. A heated regulator is recommended when sampling liquified gases and high-pressure streams so that Joule-Thomson cooling effect is overcome or minimized.

6.1.3 Heated enclosure to ensure that the gold tubes are maintained at least 10 °C above the dewpoint of the gas stream at the gold trap sampling conditions

6.1.4 Variable area flowmeters to control the flow of gas on bypass flows and sample flow across the gold traps.

NOTE 1—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.

6.1.5 Stainless steel 316 tubing and compression-type fittings, as required. To minimize adsorption losses of Hg, electropolished fused silica coated fittings and tubing are recommended. Alternatively, PTFE lined stainless steel braided sample hoses may be used.

6.1.6 Dry or wet flow meter which is independent of gas density to measure the total volume of the gas sample that passes over the gold traps. The meter should offer temperature and pressure output readings so that the volume measured can be corrected to standard or normal volume conditions.

6.1.7 Gold-coated fused silica tubes.

6.2 *Analytical Equipment:*

6.2.1 *Atomic Fluorescence Spectrophotometer,* equipped with an atom cell and a mercury lamp capable of irradiating at 253.652-nm wavelength. The AFS should be capable of analyzing mercury using a thermal desorption furnace to heat the sample tubes to >550 °C. The system should be based on dual amalgamation to accommodate the thermal desorption of tubes used for sampling onto a second gold tube which is used for calibration purposes. Background subtraction capabilities are required.

6.2.2 *PTFE-Fluorocarbon Tubing,* to make connections to the atomic fluorescence spectrophotometer.

6.2.3 *GC-Grade Septa,* low bleed, made of silicone used in the injection port and mercury-calibration vessel.

6.2.4 Calibration vessel with temperature readout to within ±0.05 °C, capillary vent, and septum port.

6.2.5 *Gastight Syringes,* fixed or variable volume, in the range of 10 μL to 5000 μL.

NOTE 2—Commercially available mercury calibration devices such as permeation sources or diluted saturation sources, can be used instead of gastight syringes. These systems 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.

7. Reagents and Materials

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

7.1.1 *Mercury Analytical Grade, purity* 99.995 % to 99.9995 %. **Warning—**Mercury vapor is harmful. Use proper ventilation when handling.

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

NOTE 3—Nitrogen (purity >99.995 % or Instrument air (ISO 8573-1:2010, Class 3.3.3) can also be used, however this will reduce the sensitivity of AFS by 8 and 30 times respectively. To ensure the carrier gas is free of mercury a cleanup scrubber in the form of a gold or activated carbon trap is recommended.

8. Sampling Procedure

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