Standard Test Method for
Total Mercury in Crude Oil Using Combustion and Direct Cold Vapor Atomic Absorption Method with Zeeman Background Correction[1]

This standard is issued under the fixed designation D7622; 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 procedure to determine the total mercury content in a sample of crude oil. This test method can be used for total mercury determination in natural and processed liquid and oil products (gasoline, naphtha, etc.).

1.2 This test method may be applied to samples containing between 5.0 ng/mL to 350 ng/mL of mercury. The results may be converted to mass basis.

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

1.4 **WARNING**—Mercury has been designated by many regulatory agencies as a hazardous material that can cause central nervous system, kidney and liver damage. Mercury, or its vapor, may be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Material Safety Data Sheet (MSDS) for details and EPA's website—http://www.epa.gov/mercury/faq.htm—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.

1.5 *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:*[2]

D1193 Specification for Reagent Water
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4175 Terminology Relating to Petroleum, Petroleum Products, and Lubricants
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants
D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories
D7482 Practice for Sampling, Storage, and Handling of Hydrocarbons for Mercury Analysis
D7623 Test Method for Total Mercury in Crude Oil Using Combustion-Gold Amalgamation and Cold Vapor Atomic Absorption Method

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology D4175.

4. Summary of Test Method

4.1 Controlled heating following thermal decomposition of the analysis sample in air is used to liberate mercury. The sample is placed into the sample boat, which is inserted in the first chamber of the atomizer, where the sample is heated at controlled temperature at 300 °C to 500 °C (depending on the selected operation mode). The mercury compounds are evaporated and partially dissociated forming elemental mercury vapor. Mercury and all decomposition products are carried to the second chamber of the atomizer heated to about 700 °C to 750 °C (mercury reduction takes place on the surface of heating NiCr coil, thus no catalyst is required). Mercury compounds are totally dissociated, and the organic matrix of the sample is burnt out. Continuously flowing air carries mercury and other combustion products through absorbance analytical cell heated up to 750 °C positioned in the light path

---

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

Current edition approved April 1, 2015. Published June 2015. Originally approved in 2010. Last previous edition approved in 2010 as D7622 – 10$^{\varepsilon 1}$. DOI: 10.1520/D7622-10R15.

[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.

of double-wave cold vapor Zeeman atomic absorption spectrophotometer. The mercury resonance line 253.65 nm is split to several components, one of those falling within the mercury absorbance line (analytical line) profile and another one lying outside (reference line). Difference between the intensities of these compounds is proportional to number of mercury atoms in the analytical cell. Absorbance peak area or peak height is a function of the mercury concentration.

NOTE 1—Mercury and mercury salts can be volatized at low temperatures. Precautions against inadvertent mercury loss should be taken when using this test method.

5. Significance and Use

5.1 The emission of mercury during crude oil refining is an environmental concern. The emission of mercury may also contaminate refined products and form amalgams with metals, such as aluminum.

5.2 When representative test portions are analyzed according to this procedure, the total mercury is representative of concentrations in the sample.

6. Apparatus

6.1 General configuration of the instrument shall have the following functional components: temperature controlled sample heating and decomposition furnace, measuring cuvettes, mercury lamp placed in strong magnetic field, polarization modulator to separate analytical and reference lines, and detector. The following requirements are specified for all approved instruments.[3]

NOTE 2—The approval of an instrument with respect to these functions is paramount to this test method, since such approval tacitly provides approval of both the materials and the procedures used with the system to provide these functions.

6.1.1 *Zeeman Mercury Spectrometer*—Atomic absorption spectrometer with Zeeman background correction, operating with the mercury resonance absorption wavelength of 253.7 nm.

6.1.2 The atomizer shall have a decomposition tube, which shall be operated at a temperature high enough to completely decompose the sample. The suggested operating temperature is at least 600 °C.

6.1.3 The heated analytical cell shall be capable to prevent mercury loses due to deposition to cold parts and to prevent mercury recombination with chlorine. The suggested operating temperature of the analytical cell is at least 700 °C.

6.1.4 The system may contain a computer for controlling the various operations of the apparatus, for recording data, and for reporting results.

6.2 *Analytical Balance,* with a sensitivity of 0.1 mg.

6.3 *Sample Boats,* quartz, stainless steel, porcelain, or other material as recommended and convenient size suitable for use in the instrument being used.

6.4 *Micropipetters,* one or more units of variable volume to cover a range from 10 µL to 250 µL, NIST traceable. Appropriately sized tips should also be available.

6.5 *Ultrasonic Homogenizer*—A bath-type ultrasonic homogenizer is used to dissociate particulate mercury and thoroughly mix the sample.

6.6 *Glassware,* volumetric flasks of various capacities and Class A pipettes of various capacities. All glassware must be thoroughly cleaned with freshly prepared, 10 % nitric acid solution and rinsed with water. It is recommended that dedicated glassware be maintained to minimize cross-contamination.

7. Sample

7.1 Obtain the analysis sample of crude oil in accordance with Practice D4057 or D4177. Crude oil should be collected in a manner that ensures a representative of the bulk container is obtained.

7.2 To prevent loss of mercury during storage and handling of samples, follow Practice D7482. Samples should not be collected in metal containers. Precleaned, glass volatile organic analysis (VOA) vials have been found to be suitable for this purpose.

7.3 Samples should be analyzed as quickly as possible after collection. Sample containers should be kept tightly capped and stored in a cool location.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type II of Specification D1193. Water must be checked for potential mercury contamination before use.

8.3 A standard sample of mercury ions solution (concentration C_1 = 1.0 g/L).

8.4 *Certified Reference Materials (CRMs)*—Use Certified Reference Material (CRM) crude oils with mercury values for which confidence limits are issued by a recognized certifying agency such as the National Institute of Standards and Technology (NIST).

8.5 *Nitric Acid,* concentrated, Trace Metal Grade or better.

8.6 *Combustion Reagents,* activated charcoal, 30 × 50 mesh.

---

[3] The sole source of supply of the apparatus known to the committee at this time is Lumex model RA 195 available from Ohio Lumex Company, 9263 Ravenna Road, Unit A-3, Twinsburg, OH 44087. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[4] *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.

8.7 *Potassium Dichromate Solution, 4 % (mass)*—Place a 4 g portion of potassium dichromate in a volumetric flask (volume of 100 mL), dissolve in distilled water and dilute with the distilled water up to the mark. The solution is to be stored in a reservoir made of dark glass with a plug stopper. Storage time is 3 months.

8.8 *Dilution Solution*—Place 500 mL to 600 mL of distilled water in a heat-resistant glass and pour in carefully 50 mL of concentrated nitric acid (d = 1.37 g/mL). Stir constantly while pouring in the acid. Transfer to a volumetric flask of 1000 mL volume, add 5 mL of 4 % potassium dichromate solution and add up with distilled water up to the mark. The solution is to be stored in a reservoir made of dark glass with a plug stopper. Storage time is 3 months.

8.9 All CRMs, reference crude oils, or calibrating agents shall have precision values of less than or equal to method repeatability. Such CRMS, reference crude oils, or calibrating agents must be stable and must be mixed thoroughly before each use.

9. Preparation of Standards

9.1 *Working Standard Set*—Prepare a set of standards that are appropriate to the range settings on the instrument in use. An example of such a set follows:

9.1.1 Place 30 mL of a dilution solution in a volumetric flask (100 mL volume). Then place 2 mL of a standard sample of mercury ions NIST or other standard reference material issuing bodies' traceable standard solution (concentration C_1 = 1.0 g/L). Bring the contents of the volumetric flask up to the mark with the dilution solution and stir thoroughly. This results in a mercury concentration of 20 mg/L (C_2). The solution may be stored in a refrigerator during 6 months.

9.1.2 Place 30 mL of a dilution solution in a volumetric flask (100 mL volume). Then place 10 mL of a standard sample of mercury solution C_2 = 20 mg/L. Bring the contents of the retort up to the mark with the dilution solution and stir thoroughly. This makes a 2 mg/L = 2000 µg/L (C_3). The solution may be stored in a refrigerator during 3 months.

9.1.3 Place 30 mL of a dilution solution in a volumetric flask (100 mL volume). Then place 10 mL of a standard sample of mercury solution C_3 = 2.0 mg/L. Bring the contents of the retort up to the mark with the dilution solution and stir thoroughly. This makes a 200 µg/L (C_4). The solution may be stored in a refrigerator during 3 months.

9.1.4 Place 30 mL of a dilution solution in a volumetric flask (100 mL volume). Then place 10 mL of a standard sample of mercury solution C_4 = 200 µg/L.) Bring the contents of the retort up to the mark with the dilution solution and stir thoroughly. This makes a 20 µg/L (C_5). The solution may be stored in a refrigerator during 1 month.

NOTE 3—The standard preparation procedure given in Test Method D7623 is also acceptable.

10. Instrument Preparation

10.1 Assemble the instrument and check for leaks in the system in accordance with the manufacturer's instructions. Follow the instrument manufacturer's recommended procedure to optimize the performance of the instrument.

10.2 Choose the proper sample heating mode based upon the expected mercury concentration and the sample matrix.

10.3 Samples boats and charcoal should also be pretreated in the muffle furnace before initial use.

10.4 A satisfactory blank should have stable response and a signal that corresponds to the equivalent of < 3 ng/g mercury.

11. Calibration Procedure

11.1 Spread approximately 0.2 g of charcoal in the bottom of a cooled sample boat. Using a micropipetter and tip, transfer 100 µL of the dilution solution on to a charcoal media. Place the sample boat into the furnace area and start the instrument. Repeat this step four times to obtain blank value.

11.2 Spread approximately 0.2 g of charcoal over bottom of a cooled sample boat. Using a micropipetter and tip, transfer 100 µL of standard solution 200 µg/L on to a charcoal media. Place the sample boat into the furnace area and start the instrument. Repeat this step for 20 µg/L and 2000 µg/L to span the effective range of response. Create a calibration curve by assigning the appropriate mass of mercury introduced into the instrument with the corresponding response. Follow manufacturer's recommendations to use available software tools that automate the calculations.

11.3 *Periodic Calibration Verification and Recalibration*—In accordance with Practice D6792, analyze a control sample on a periodic basis. Results obtained for the control sample must be within established limits. If a control check sample result is out of control, all results obtained since the last successful control check must be rejected and the calibration procedure repeated.

12. Procedure

12.1 Place crude oil sample containers in an ultrasonic homogenizer for approximately fifteen minutes just prior to analysis. Keep the water in the bath at ambient temperature by adding a few ice chips as the temperature rises. The homogenization step dissociates particulate mercury and promotes a more stable suspension.

12.2 Remove sample boat and reagents (if required) from muffle furnace and allow to cool to room temperature in a covered container.

12.3 Spread approximately 0.2 g of charcoal over the bottom of a cooled sample boat.

12.4 Shake the sample to mix just before withdrawing an aliquot. Open the cap and quickly withdraw sample in a clean, disposable transfer pipet. Weigh approximately 0.1 g of sample into the sample boat.

12.5 Choose the appropriate instrument parameters and heating mode for crude oil based upon manufacturer's instructions.

12.6 Open the inlet cover. Insert the sample boat into the combustion area of the furnace. Close the cover and start the analysis. Analyze a test specimen of the analysis sample in accordance with the manufacturer's instructions.

12.7 After analysis is complete, remove sample boat from furnace. Allow to cool before disposing of reagent material.

13. Calculation

13.1 Calculate the concentration of mercury, on the appropriate sample basis, as follows:

$$A = \frac{(B - C) \times D}{E} \tag{1}$$

where:

A = ng/g of the analyte,
B = detector response for the analyte,
C = detector response for the reagent blank,
D = mass, ng per unit of detector response established for analyte during calibration, and
E = mass of test specimen, g.

13.2 The calculations can be provided automatically by the instrumental system used for this test method.

14. Report

14.1 Report results from the mercury determination on a ng/g (or mass-ppb) basis.

15. Precision and Bias[5]

15.1 *Precision*—The precision of this test method for the determination of mercury in crude oil based on an interlaboratory study, designed consistent with Practice D6300, was conducted in 2009. Eleven laboratories participated in analyzing eight crude oil samples. Details of this study and the supporting data are given in the ASTM Research Report RR:D02-1692 filed at ASTM Headquarters.

15.1.1 *Repeatability Limit (r)*—The value below which the absolute difference between two test results of separate and consecutive test determinations, carried out on the same sample in the same laboratory by the same operator using the same apparatus on samples taken at random from a single quantity of homogeneous material, may be expected to occur with a probability of approximately 95 %.

15.1.1.1 The repeatability limit in the 5 to 350 ng Hg/mL range in crude oil is $0.7147\ X^{0.60}$, where X is the average mercury concentration in ng/mL.

15.1.2 *Reproducibility Limit (R)*—The value below which the absolute difference between two test results, carried out in different laboratories using samples taken at random from a single quantity of material that is as homogeneous as possible, may be expected to occur with a probability of approximately 95 %.

15.1.2.1 The reproducibility limit is not known at present but will be obtained within five years after completing a new interlaboratory study.

15.2 *Bias*—Certified Reference Materials from NIST are not available in the concentration range applicable for this test method; hence, at present bias of this test method could not be determined.

NOTE 4—Whenever possible, the analysis of several reference materials, spanning the concentration range of interest, is the most meaningful way to investigate measurement bias. When a matrix match is possible the uncertainty in sample measurements can be equated to that observed in measurement of the Certified Reference Material (CRM). When such a match is not possible, but a CRM with a related matrix is available, the test sample uncertainty may be related to those observed when measuring the CRM. Different methods of measurement of a property may not be capable of equal repeatability. Accordingly, instances could arise where the method of measurement has greater variability than that or those used in certification of the CRM.

APPENDIX

(Nonmandatory Information)

X1. GENERIC QUALITY CONTROL STATEMENT FOR D02 TEST METHODS

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample that is, if possible, representative of the samples typically analyzed.

X1.2 Prior to monitoring the measurement process, the user of this test method needs to determine the average value and control limits of the QC sample (see Practice D6299 and MNL7[6]).

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total test process (see Practice D6299, Practice D6792, and MNL7). Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples is routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be periodically checked against the

---

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1692.

[6] *ASTM MNL7, Manual on Presentation of Data Control Chart Analysis*, 6th edition, ASTM International, W. Conshohocken, PA.

ASTM method precision to ensure data quality.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the sample routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions.

X1.6 Refer to relevant documents (see Practice Practice D6299, Practice D6792, and MNL7) for further guidance on QC and control charting techniques.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/