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Standard Test Method for Total Mercury in Crude Oil Using Combustion-Gold Amalgamation and Cold Vapor Atomic Absorption Method[1]

This standard is issued under the fixed designation D7623; 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 procedures to determine the total mercury content in a sample of crude oil.

1.2 The test method may be applied to crude oil samples containing between 5 ng/mL to 400 ng/mL of mercury. The results may be converted to mass basis, and reported as ng/g of mercury.

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

D7622 Test Method for Total Mercury in Crude Oil Using Combustion and Direct Cold Vapor Atomic Absorption Method with Zeeman Background Correction

3. Terminology

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

4. Summary of Test Method

4.1 Controlled heating of the analysis sample in oxygen is used to liberate mercury. The sample is heated to dryness in the instrument and then thermally (at about 700 °C) and chemically decomposed. The decomposition products are carried by flowing treated air to the catalytic section of the furnace (at about 850 °C), where oxidation is completed. The decomposition products are carried to a gold amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any remaining decomposition products other than mercury, the amalgamator is rapidly heated to about 600 °C, releasing mercury vapor. Flowing oxygen carries the mercury vapor through absorbance cells positioned in the light path of single wavelength cold vapor atomic absorption spectrophotometer. Absorbance peak height or peak area, as a function of mercury concentration, is measured at 253.65 m.

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.

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[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.

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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.

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 There are several configurations of the instrumental components that can be used satisfactorily for this test method.[3] Functionally, the instrument shall have the following components: sample heating furnace, decomposition furnace, gold amalgamator, amalgamator furnace, measuring cuvettes, mercury lamp, and detector. The following requirements are specified for all approved instruments.

NOTE 2—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 The instrument shall be capable of drying the sample once it is weighed and introduced.

6.1.2 The instrument 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 700 °C.

6.1.3 The catalyst shall be capable of completing the oxidation of the sample and trapping halogens as well as nitrogen and sulfur oxides. The suggested operating temperature of the catalytic tube is 850 °C.

6.1.4 The instrument shall contain one or more gold amalgamator fixed to an inert material and shall be capable of trapping all mercury.

6.1.5 The amalgamator shall contain a furnace capable of rapidly heating the amalgamator to release all trapped mercury.

6.1.6 The instrument shall have an absorption cell through which the elemental mercury released from the gold amalgamator flows. The cell shall be heated to avoid any condensation of water or other decomposition products.

6.1.7 The light source for the atomic absorption process shall be a low pressure mercury lamp.

6.1.8 A narrow bandpass interference filter or monochromator, capable of isolating the 253.65 nm mercury line, shall be used.

6.1.9 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 Combustion Boats,* porcelain, quartz, or other material as recommended and of convenient size suitable for use in the instrument being used.

6.4 *Crucibles,* porcelain, high-form, 40 mL capacity or suitable size for heating reagent in furnace.

6.5 *Micropipettes,* one or more units of variable volumes to cover a range of 10 µL to 250 µL. Appropriately sized tips should also be available.

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

6.7 *Electric Muffle Furnace,* capable of maintaining 750 °C ± 25 °C and sufficiently large to accommodate the sample boats and reagent containers.

6.8 *Glassware,* class A, volumetric flasks and 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 sample from the bulk container is obtained.

7.2 To prevent loss of mercury during storage and handling of samples, follow Practice D7482. Sample 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 free from direct sunlight.

8. Reagents

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 *Air or Oxygen*—Filtered, purified air or high purity oxygen, as specified by the instrument manufacturer, shall be

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[3] The sole source of supply of the apparatus known to the Committee at this time is Nippon SP3D model available from Nippon Instrument Corp., 14-8, Akaoji-cho, Takatsuki-shi, Osaka 569-1146, Japan. 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, 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.

used. The air must be mercury-free. Some instruments process incoming combustion air with filters and driers before it is used for the analysis.

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).

8.4.1 All CRMs, reference crude oils, or calibrating agents must 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.

8.5 *L-cysteine,* 99+ % purity. Reagents must be evaluated for mercury content by checking blank solutions for response on the instrument.

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

8.7 *Mercuric Chloride,* 99.99+ % purity. A commercially prepared mercury stock standard may be used.

8.8 *Phosphate Buffer,* pH 7.2. Some phosphate buffers use mercury compounds as preservative. The buffer must be mercury-free. Check with the instrument manufacturer for sources of suitable buffer.

8.9 *Combustion Reagents:*

8.9.1 *Additive 1 or B (Aluminum Oxide),* ground, available from instrument manufacturer.

8.9.2 *Additive 2 or M,* 40/60 m % mixture of calcium hydroxide and sodium carbonate available from instrument manufacturer.

8.9.3 *Calcium Hydroxide,* 99.5 % minimum purity.

8.9.4 *Sodium Carbonate,* 99.99 % minimum purity.

8.10 *Glassine Weighing Paper.*

9. Preparation of Mercury Standards

9.1 *L-cysteine Solution, 0.001 m %*—Weigh approximately 0.010 g of L-cysteine to the nearest milligram onto a glassine weighing paper. Quantitatively transfer the contents of the paper to a 1 L volumetric flask. Add approximately 800 mL of water. Add 2 mL of nitric acid into the flask with a pipette. Swirl to dissolve the solids. Fill to the mark with water. The L-cysteine solution stabilizes the ionic mercury and is used to prepare working standards.

9.2 *Mercuric Chloride Stock Solution*—Weigh 0.0677 g of mercuric chloride onto weighing paper. Quantitatively transfer the material to a 500 mL volumetric flask using the L-cysteine solution prepared in accordance with 9.1. Fill to the mark with L-cysteine solution and mix. This results in a mercury concentration of 100 mg/kg.

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

9.3.1 With a 5 mL pipette, transfer an aliquot of the mercuric chloride stock solution to a 100 mL volumetric flask. Fill the flask to the mark with L-cysteine solution and mix. This makes a 5 mg/kg standard.

9.3.2 With a 1 mL pipette, transfer an aliquot of the mercuric chloride stock solution to a 100 mL volumetric flask and fill up to the mark with L-cysteine solution. Mix. This makes a 1 mg/kg standard.

9.3.3 Perform appropriate dilutions of the 1 mg/kg standard with L-cysteine solution to prepare 0.1 mg/kg and 0.01 mg/kg mercury standards.

10. Instrument Preparation

10.1 Assemble the instrumental 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 sensitivity range and sample heating mode based upon the expected mercury concentration and the sample matrix.

10.3 Reagents used for the analysis of hydrocarbon samples should be placed in the 750 °C muffle furnace overnight prior to use. Sample boats should also be pretreated in the muffle furnace before initial use.

10.4 The instrument should be run through several heating cycles after being powered up to attain a new blank signal. A satisfactory blank should have stable response and a signal that corresponds to the equivalent of <0.1 ng/g mercury in the sample.

11. Calibration Procedure

11.1 Choose the working standard to match the sensitivity range to which the instrument is set. For example, a sensitivity range with a maximum of 2 ng of mercury would require using the nominal 0.01 mg/kg standard solution. A sensitivity range of 20 ng would use the 0.1 mg/kg standard and so on.

11.2 After the instrument has cycled several times and a stable response has been attained, initiate the analysis with no sample boat in the furnace and record the blank value.

11.3 Using a micropipetter and tip, transfer 50 µL of standard solution to a cooled sample boat. Place the sample boat into the furnace area and start the instrument. Repeat this step for 100 µL, 150 µL, and 200 µL aliquots 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 the manufacturer's instructions to use available software tools that automate the calculations.

11.4 A reagent blank is subtracted from the response of the samples to compensate for trace mercury signal associated with the sample boat and combustion reagents.

11.4.1 Remove a sample boat and treated reagent(s) from the muffle furnace and allow to cool in a container that is purged of ambient mercury.

11.4.2 Prepare the reagent blank by adding the cooled reagent(s) in the recommended portions to a sample boat.

11.4.3 Open the inlet cover. Place the sample boat into the instrument's combustion furnace and run on the same heating cycle as that used for samples. Record the reagent blank for subtraction from the mercury response of the samples. The data handling software of the instrument may perform this calculation for each sample in the batch.

NOTE 3—An indicated problem with linearity of the instrument during calibration can result from contamination of the CRM or calibrating agent as the container becomes depleted. It is therefore recommended that the CRM or calibrating agent be discarded when less than five grams remain in the container.

11.5 Analyze, as samples, portions of a CRM, reference crude oil, or calibrating agent chosen to represent the level of mercury in the samples to be tested. Use the mercury values for calibration. These values must have been calculated previously from the certified mercury values. Continue analyzing until the results from five consecutive determinations fall within the repeatability interval of the test method. Calibrate the instrument according to the manufacturer's instructions using these values. Analyze, as samples, two CRM reference crude oils or calibrating agents that bracket the range of values to be tested. The results obtained for these samples must be within the stated precision limits of the CRM, reference crude oil, or calibrating agent or the calibration procedure shall be repeated. Record all calibrations.

11.6 *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, or all results obtained since the last successful control check must be rejected and the calibration procedure repeated.

12. Procedure

12.1 Place the crude oil sample containers in an ultrasonic homogenizer for approximately 15 min 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 the sample boat and reagents (if required) from the muffle furnace and allow to cool to room temperature in a covered container.

12.3 If required for the analysis, spread approximately 1 g of Reagent 1 (aluminum oxide) in 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 pipette. Weigh approximately 0.1 g of the sample into the sample boat, spreading the liquid over Reagent 1 already in the boat. Cover the sample evenly with another 1 g of Reagent 1.

12.5 Evenly spread approximately 3.5 g of Reagent 2 in the sample boat over the layer of Reagent 1 and sample.

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

12.7 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.

12.8 After the analysis is complete, remove the sample boat from the furnace. Allow to cool before disposing the reagent material. Rinse the residue from the sample boat with water and return it to muffle furnace to condition the boat for the next analysis.

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 ng/g (or mass-ppb) basis.

15. Precision and Bias[5]

15.1 *Precision:*

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 400 ng Hg/g range in crude oil is $0.4396\ X^{0.5864}$ where X is the average mercury concentration in ng/g.

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 5 years after completing a new interlaboratory study. At that point the standard will be revised.

15.2 *Bias*—At present time the bias of this test method could not be determined since Standard Reference Materials in concentrations of interest are not yet available from NIST.

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

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

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.

15.3 An interlaboratory study, designed consistent with Practice D6300, was conducted in 2009. Nine laboratories participated using 8 samples of crude oils. The details of the study and supporting data are given in ASTM Research Report RR:D02-1692 filed at ASTM headquarters.

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 are 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 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 D6299, Practice D6792, and MNL7) for further guidance on QC and control charting techniques.

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