Designation: ~~D6414 – 01 (Reapproved 2006)~~ D6414 – 14

Standard Test Methods for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption[1]

This standard is issued under the fixed designation D6414; 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 These test methods cover procedures to determine the total mercury content in a sample of coal or coal combustion residue.

1.2 The values stated in SI units are ~~regarded as the~~ to be regarded as standard. No other units of measurement are included in this 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 (SDS) 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.*

1.4 *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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D121 Terminology of Coal and Coke

D1193 Specification for Reagent Water

D2013 Practice for Preparing Coal Samples for Analysis

D3173 Test Method for Moisture in the Analysis Sample of Coal and Coke

D3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases

~~D5142~~D7582 Test Methods for Proximate Analysis of ~~the Analysis Sample of~~ Coal and Coke by ~~Instrumental Procedures~~Macro Thermogravimetric Analysis ~~(Withdrawn 2010)~~

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI): The Modern Metric System

~~E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method~~

2.2 *ISO Standard*[3]

ISO 5725-6:1994 Accuracy of measurement methods and results-Part 6

3. Terminology

3.1 For definitions of terms used in this standard, refer to Terminology D121.

4. Summary of Test Method

4.1 *Test Method A*—Mercury in the analysis sample is solubilized by heating the test sample at a specified temperature in a mixture of nitric and hydrochloric acids. The acid solutions produced are transferred into a vessel in which the mercury is reduced to elemental mercury. The mercury vapor is determined by flameless cold-vapor atomic absorption spectroscopy.

[1] These test methods are under the jurisdiction of ASTM Committee D05 on Coal and Coke and are the direct responsibility of Subcommittee D05.29 on Major Elements in Ash and Trace Elements of Coal.

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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.

[3] Available from International Organization for Standardization (ISO), 1 rue de Varembé, Case postale 56, CH-1211, Geneva 20, Switzerland.

4.2 *Test Method B*—Mercury in the analysis sample is solubilized by heating the test sample in a mixture of nitric and sulfuric acids with vanadium pentoxide.[4] The acid solutions produced are transferred into a vessel in which the mercury is reduced to elemental mercury. The mercury vapor is determined by flameless cold-vapor atomic absorption spectroscopy.

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

5. Significance and Use

5.1 The emission of mercury during coal combustion can be an environmental concern.

5.2 When representative test portions are analyzed according to one of these procedures, the total mercury is representative of concentrations in the sample.

6. Apparatus

6.1 *Apparatus for Test Method A:*

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

6.1.2 *Atomic Absorption Spectrophotometer,* with a flameless cold-vapor mercury analysis system.

6.1.3 *Digestion Vessels,* 100- to 250-mL bottles with an O-ring seal and screw cap. Bottle must be compatible for use with aqua regia. Polycarbonate and HDPE are acceptable. Bottles and cap assemblies shall be washed in 1-to-1 HCl then dried before each use.

NOTE 2—Other bottle and cap assemblies may be used provided they are compatible for use with aqua regia at a temperature of 80°C.

6.1.4 *Heat Source,* a water bath capable of maintaining a temperature of 80°C.

6.1.5 *Syringe and Filter,* a 20-cm^3 syringe and a 1-µm PTFE filter to fit syringe.

6.2 *Apparatus for Test Method B:*

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

6.2.2 *Atomic Absorption Spectrophotometer,* with a flameless cold-vapor mercury analysis system.

6.2.3 *Digestion Vessels,* 16- by 150-mm disposable glass test tubes.

6.2.4 *Heat Source,* an aluminum block with 18-mm holes to accommodate the disposable test tubes. The block shall be capable of slowly reaching and maintaining a final temperature of 150°C. The block can be heated by placing it on a hot plate or it can contain its own internal heating elements.

7. Sample

7.1 Prepare the analysis sample in accordance with ~~Method~~Practice D2013 by pulverizing the material to pass a 250-µm (No. 60) sieve.

7.2 Analyze separate test portions for moisture content in accordance with Test Method D3173 or Test ~~Methods~~Method ~~D5142~~D7582.

Test Method A for the Analysis of Mercury by Using Acid Extraction

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used. 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.[5] Other grades can 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.

8.2 *Purity of Acids*—Use trace metal purity grade acids or equivalent. Redistilled acids are acceptable.

8.3 *Purity of Water*—Use water equivalent to ASTM Type II reagent water of Specification D1193.

8.4 *Mercury Standard Stock Solution [1000 ppm (1000 µg/mL)]*—Dissolve 1.0800 g of mercury (II) oxide (HgO) in a minimum volume of HCl (1+1) and dilute to 1 L with water. Alternatively, use a commercially available stock solution specifically prepared for atomic absorption spectrometry.

8.5 *Mercury Standard Solution (100 ng/mL)*—Prepare the mercury standard solution fresh daily. Dilute 5 mL of the mercury standard stock solution to 500 mL with deionized water. Further dilute 10 mL of this intermediate solution to 1 L with deionized water.

[4] Crock, J. G., *Open-File Report*, U.S. Geological Survey, 87–84, p.19.

[5] *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.

8.6 *Nitric Acid*—Concentrated (HNO_3, sp. gr. 1.42).

8.7 *Hydrochloric Acid*—Concentrated (HCl, sp. gr. 1.19).

8.8 *Sodium Chloride/Hydroxylamine Sulfate Solution*—Dissolve 12 g ± 0.01 g of sodium chloride and 12 g ± 0.01 g of hydroxylamine sulfate in water and dilute to 100 mL.

8.9 *Potassium Permanganate Solution (5 g/100 mL)*—Dissolve 5 g of potassium permanganate ($KMnO_4$) in water and dilute to 100 mL.

8.10 *Stannous Chloride Solution (100 g/L)*—Dissolve 100 g of stannous chloride dihydrate ($SnCl_2 \cdot 2\ H_2O$) in 300 mL of concentrated hydrochloric acid (HCl, sp. gr. 1.19) and CAUTIOUSLY dilute to 1 L with water. This solution is stable for approximately one week if refrigerated.

8.11 *Certified Reference Material (CRM)*—Use Certified Reference Material (CRM) coals with dry-basis mercury values for which confidence limits are issued by a recognized certifying agency such as the National Institute of Standards and Technology (NIST). It is recommended that the user verify the value with the certifying agency before using the CRM coal for quality control purposes.

9. Procedure

9.1 *Preparation of Test Solution A (Extraction Step):*

9.1.1 Weigh a test portion of approximately 1 g of the sample into a digestion bottle. Record the weight (*Ws*) to the nearest 0.0001 g.

9.1.2 Quantitatively add 2 mL of concentrated nitric acid and 6 mL of concentrated hydrochloric acid to the digestion bottle and secure the cap.

9.1.3 Transfer the digestion bottle and contents to a water bath that has been heated to 80°C and heat for 1 h. Secure the digestion bottle in such a way as to keep the contents below the surface of the water.

9.1.4 After 1 h, remove the digestion bottle and allow to cool to room temperature.

NOTE 3—**Caution:** Carefully relieve the pressure by slowly removing the cap.

9.1.5 Add 36.5 mL of water and mix the contents.

9.1.6 Add 5 mL of 5 % potassium permanganate solution. Allow the mixture to stand for 10 min.

9.1.7 Add 0.5 mL of the hydroxylamine sodium chloride solution and mix. If a pink color persists for more than 1 min, add an additional 0.5 mL of the hydroxylamine sodium chloride solution and mix. Note the total volume and record this volume (*V*) for use in the final calculations.

9.2 *Preparation of Reagent Blank*—Prepare a reagent blank by repeating the procedure in 9.1 but without the test portion of the sample.

9.3 *Preparation of Control Sample:*

9.3.1 Prepare a test portion of a CRM coal for analysis using the procedure described in 9.1. Record the expected value of mercury, the certified value in the coal, as CRME.

9.3.2 Alternatively, weigh a test portion of 1 g of a CRM. After the addition of the nitric and hydrochloric acids to the digestion bottle, add mercury standard solution (8.5). The volume of mercury standard solution to be added should yield an amount of mercury approximately equivalent to that in the CRM coal (Note 4).

9.3.3 Calculate the expected value of mercury CRME as follows

$$\text{CRME} = (W\text{crm}*\text{CRM} + V\text{standard}*0.1)/W\text{crm} \quad (1)$$

where:

*W*crm	=	dry weight of the CRM coal used for preparation of the quality control sample, g;
CRM	=	certified value of mercury in the quality control sample;
*V*standard	=	volume of mercury standard solution added to the digestion bottle, mL; and
0.1	=	the concentration of the mercury standard solution, µg/mL.

NOTE 4—A test portion of 0.9-g dry weight of a CRM coal with 0.11 g/g (110 ng/g) of mercury is weighed out as a quality control sample. To yield an amount approximately equivalent to that present in the CRM coal, 0.9 mL of the mercury standard solution is added to the digestion bottle after the addition of the nitric and hydrochloric acids. CRME calculates to 0.21 µg/g.

9.4 *Atomic Absorption Analyses:*

9.4.1 *Instrument Conditions*—Follow the instrument manufacturers recommended procedure to align the optical cell in the beam path of the atomic absorption spectrophotometer and optimize the performance of the instrument and the flameless cold-vapor apparatus.

9.4.2 *Instrument Calibration:*

9.4.2.1 Prepare 50 mL of 0.5, 1, 3, 5, and 10 ng/mL (ppb) of mercury calibration standards in a solution of 10 % HCl by serial dilution of the mercury standard solution.

9.4.2.2 Add a specified volume (*V*cal) of a calibration solution to the reduction flask or reduction system.

NOTE 5—If an autosampler equipped with a peristaltic pump is used for delivery of both calibration and analyses sample solutions to the reduction system, a specific volume is not required.

9.4.2.3 Either manually or by means of an autosampling device begin the analyses of the calibration solution by adding enough stannous chloride solution so as to ensure complete reduction of the mercury in the calibration solution.

9.4.2.4 Record the absorbance of the calibration standard. Repeat for each calibration standard.

9.4.3 *Analysis of Test Solution A:*

9.4.3.1 Using the 20-cm^3 syringe, draw Test Solution A into the syringe.

9.4.3.2 Fit the syringe with a 1-µm filter.

9.4.3.3 Filter a volume equivalent to *V*cal of Test Solution A into the reduction flask or reduction system.

NOTE 6—A laboratory centrifuge may also be used to separate the solids from the test solution.

9.4.3.4 Determine the absorbance (*As*) of the Test Solution A using the procedure described in 9.4.2.

9.4.3.5 Using 10 % HCl, dilute test solutions with mercury absorbances greater than the highest calibration standard to give an estimated absorbance equivalent to the 3-ng/mL calibration standard and reanalyze.

9.4.3.6 Record the dilution factor as DF.

9.4.4 *Analysis of the Reagent Blank*—Determine the absorbance (*Ab*) of the reagent blank using the procedure described in 9.4.3.

9.4.5 *Analysis of the Quality Control Sample*—Determine the absorbance (*Aqs*) of the quality control sample using the procedure described in 9.4.3.

Test Method B for the Analysis of Mercury by Using Wet Oxidation Extraction

10. Reagents

10.1 *Purity of Reagents*—Reagent grade chemicals shall be used. 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.[5] Other grades can 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.

10.2 *Purity of Acids*—Use trace metal purity grade acids or equivalent. Redistilled acids are acceptable.

10.3 *Purity of Water*—Use water equivalent to ASTM Type II reagent water of Specification D1193.

10.4 *Mercury Standard Stock Solution [1000 ppm (1000 µg/mL)]*—Dissolve 1.0800 g of mercury (II) oxide (HgO) in a minimum volume of HCl (1+1) and dilute to 1 L with water. Alternatively, use a commercially available stock solution specifically prepared for atomic absorption spectrometry.

10.5 *Mercury Standard Solution (100 ng/mL)*—Prepare the mercury standard solution fresh daily. Dilute 5 mL of the mercury standard stock solution to 500 mL with deionized water. Further dilute 10 mL of this intermediate solution to 1 L with deionized water.

10.6 *Nitric Acid*—Concentrated (HNO_3, sp. gr. 1.42).

10.7 *Hydrochloric Acid*—Concentrated (HCl, sp. gr. 1.19).

10.8 *Sulfuric Acid*—H_2SO_4, sp. gr. 1.83).

10.9 *Vanadium Pentoxide, V_2O_5*—Remove traces of mercury by roasting the V_2O_5 in a fume hood at a temperature below 690°C, the melting point of V_2O_5, in a porcelain dish using a muffle furnace or a Fisher burner.

NOTE 7—**Warning:** V_2O_5 is highly toxic, an irritant, and a possible mutagen.

10.10 *Stannous Chloride Solution (100 g/L)*—Dissolve 100 g of stannous chloride dihydrate ($SnCl_2{\cdot}2H_2O$) in 300 mL of concentrated hydrochloric acid (HCl, sp. gr. 1.19) and CAUTIOUSLY dilute to 1 L with water. This solution is stable for approximately one week if refrigerated.

10.11 *Sodium Dichromate, 25 % (w/v) Solution*—Dissolve 25 g of $Na_2Cr_2O_7{\cdot}2H_2O$ in water and dilute to 100 mL.

10.12 *Complex Reducing Solution*—Dissolve 30 g of hydroxylamine hydrochloride and 30 g of sodium chloride (NaCl) in approximately 500 mL of water. Slowly add 100 mL of concentrated sulfuric acid. Allow the solution to cool, then dilute to 1 L with water.

10.13 *Certified Reference Material (CRM)*—Use Certified Reference Material (CRM) coals with dry-basis mercury values for which confidence limits issued by a recognized certifying agency such as NIST. It is recommended that the user verify the value with the certifying agency before using the CRM coal for quality control purposes

11. Procedure

11.1 *Preparation of Test Solution B:*