Designation: D 6414 – 01

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 D 6414; 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 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 use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 121 Terminology of Coal and Coke[2]

D 1193 Specification for Reagent Water[3]

D 2013 Method of Preparing Coal Samples for Analyses[2]

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

D 5142 Test Methods for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures[2]

IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI): The Modern Metric System[4]

3. Terminology

3.1 For definitions of terms used in this standard, refer to Terminology D 121.

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.

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.[5] 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.

[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] *Annual Book of ASTM Standards*, Vol 05.05.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 14.04.

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

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 D 2013 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 D 3173 or Test Methods D 5142.

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.[6] 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 D 1193.

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.

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

$$CRME = (Wcrm*CRM + Vstandard*0.1)/Wcrm \quad (1)$$

where:

Wcrm = dry weight of the CRM coal used for preparation of the quality control sample, g;

[6] *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.