Designation: 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 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
D7582 Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis
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

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.

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.

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

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 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 Method 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.

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.

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[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.

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

$$\mathrm{CRME} = \left(W\mathrm{crm}*\mathrm{CRM}+V\mathrm{standard}*0.1\right)/W\mathrm{crm} \qquad (1)$$

where:

Wcrm = 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;

Vstandard = 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 ($SnCl_2·2H_2O$) 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 $Na_2Cr_2O_7·2H_2O$ 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:*

11.1.1 Weigh a test portion of 0.15 g of the test sample into a 16- by 150-mm disposable test tube. Record the weight (*Ws*) to the nearest 0.0001 g.

11.1.2 Add approximately 0.1 g of V_2O_5, 3.5 mL of concentrated HNO_3, and 1.5 mL of concentrated H_2SO_4. Swirl to mix the contents. Place the test tube in the aluminum heating block and cover with a watch glass.

11.1.3 Adjust the temperature of the heating block so that it gradually reaches a temperature of 150°C in 4 h. Maintain heating at this temperature for 16 h.

11.1.4 After heating, carefully remove the test tube from the aluminum heating block, allow to cool, and dilute the solution to a final volume of 15 mL (*V*) with water. Securely cap the test tube and mix the contents. Centrifuge the test tube and its contents for 5 min at 1000 rpm.

11.2 *Reagent Blank*—Prepare a reagent blank by repeating the procedure in 11.1 but without the test portion of the sample.

11.3 *Quality Control Sample:*

11.3.1 Prepare a CRM coal for analysis using the procedure described in 11.1. Record the certified value as CRM.

11.3.2 Alternatively, weigh a test portion of 0.15 g of a CRM. After the addition of the nitric acid, add mercury standard solution (10.5) to the test tube. The volume of the mercury standard solution to be added should yield an amount of mercury approximately equivalent to that in the CRM coal (Note 8). Calculate the expected value CRME of mercury using Eq 1.

NOTE 8—A test portion of 0.15 g of a CRM coal with 0.11 µg/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, 0.15 mL of the mercury standard solution is added to the test tube after the addition of the nitric acid. CRME calculates to 0.21 µg/g.

11.4 *Atomic Absorption Analyses:*

11.4.1 *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.

11.4.2 *Instrument Calibration:*

11.4.2.1 Prepare 500-mL calibration standards of 0.5, 1, 3, 5, and 10 ng/mL (ppb) of mercury by diluting in water aliquots of the mercury standard solution (10.4) in 115 mL of concentrated HNO_3, 50 mL of concentrated H_2SO_4, and 10 mL of the 25 % (w/v) sodium dichromate solution. Prepare fresh calibration standards every three months.

11.4.2.2 Prepare a 500-mL dilution solution by mixing 115 mL of concentrated HNO_3, 50 mL of concentrated H_2SO_4, and 10 mL of the 25 % (w/v) sodium dichromate solution and diluting to the mark with water. Prepare dilution solution every three months.

11.4.2.3 Add a specified volume, *V*cal, not to exceed 15 mL of a calibration solution to the reduction flask or reduction system.

11.4.2.4 Either manually or by means of an autosampling device begin the analyses of the calibration solution by adding enough complex reducing solution and stannous chloride solution to ensure complete reduction of the mercury in the calibration solution.

11.4.2.5 Record the absorbance of the calibration standard (Note 9). Repeat for each calibration standard.

NOTE 9—Automated flow injection systems may have to be modified to include mixing loops when analyzing samples digested by Method B. Typical over-the-counter mixing loops are made using 4-mm outer diameter glass tubing wrapped around a 14-mm-diameter mandrel. Without the mixing loops, foaming in the gas-phase separator may occur. The foaming interferes with the transfer of mercury vapor from the gas-phase separator to the absorption cell of the cold-vapor atomic absorption spectrophotometer. Descriptions and diagrams of a manifold used for the automated generation of mercury vapor from samples digested according to Method B are given by J. G. Crock and others.[4] Automated flow injection systems that have been modified to include mixing loops can also be used to analyze samples digested by Test Method A.

11.4.3 *Analysis of Test Solution B:*

11.4.3.1 Add a volume equivalent to *V* cal of Test Solution B into the reduction flask or reduction system.

11.4.3.2 Determine the absorbance (*As*) of the Test Solution B using the procedure described in 11.4.2.

11.4.3.3 Using $3N$ H_2SO_4, 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. Record the dilution factor as DF.

11.4.3.4 *Analysis of the reagent blank*—Determine the absorbance (*Ab*) of the reagent blank using the procedure described in 11.4.2.

11.4.3.5 *Analysis of the quality control sample*—Determine the absorbance (*Aqs*) of the quality control sample using the procedure described in 11.4.2.

12. Calculation

12.1 These calculations apply to both Test Method A and Test Method B.

12.1.1 Calculate the dry weight of each test portion of sample prepared for analysis as follows

$$Wds = ((100 - Ma)*Ws)/100 \qquad (2)$$

where:

Wds = dry sample weight, g;
Ws = weight of test portion of sample; and
Ma = percent moisture in the analysis sample calculated according to Test Method D3173 or Test Method D7582.

12.2 *Quality Control:*

12.2.1 *Calculation of Mercury Concentration of the Quality Control Sample:*

12.2.1.1 *Absorbance matching*—Calculate the concentration of mercury in ppm (µg/g) in the quality control sample as

$$\text{Mercury ppm } (\mu g/g) \text{ dry basis} = \text{DF} \times (V/Vds) \times C \times [(A - Ab)/(Ac - Ab)] \qquad (3)$$

where:

A = absorbance of the quality control (Aqs) or analysis sample (A);
Ac = absorbance of the calibration standard nearest A;
Ab = absorbance of the blank;
C = concentration of the calibration standard, ng/mL;
DF = dilution factor, if any;
V = volume of the analysis solution; and
Wds = dry sample weight, g.

12.2.1.2 *Calibration curve:*

(1) Prepare a calibration curve by plotting absorbance of calibration standard minus blank response versus the concentration of the calibration solution in ng/mL. For the number of standards specified in this test method, it is recommended that a linear fit of the form $y = mx + b$ be used. Other fits can be used but can require the preparation of additional standards to ensure adequate degrees of freedom are maintained (Note 10).

NOTE 10—It is recommended that a minimum five calibration standards be used for a linear fit, six for a quadratic, seven for a cubic, and so forth. This approach allows for the rejection of a particular calibration standard for a curve while maintaining adequate degrees of freedom.

(2) Calculate the net absorbance for the quality control sample as follows

$$A\text{net} = A - Ab \qquad (4)$$

where:

A = absorbance of the quality control (Aqs) or analysis sample (A) and
Ab = absorbance of the blank.

(3) Read the concentration of the quality control sample from the calibration curve as Cs.

(4) Calculate the concentration of mercury in ppm (µg/g) in the quality control sample as follows

$$\text{Mercury ppm } (\mu g/g) \text{ dry basis} = \text{DF} \times (V/Wds) \times Cs \qquad (5)$$

where:

Cs = concentration of the quality control sample read from the calibration curve, ng/mL;
DF = is the dilution factor, if any;
V = volume of the analysis solution; and
Wds = dry sample weight, g.

12.2.2 *Calculation of Mercury Recovery in the Quality Control Sample:*

12.2.2.1 Calculate the CRM confidence factor as follows

$$\text{CRMF} = 100*(\text{mercury limits/mercury value}) \qquad (6)$$

where:

mercury limits = the confidence limits from the certificate issued by the certifying agency and
mercury value = the mercury value issued by the certifying agency.

If CRMF is greater than 30 %, then the mercury recovery limits (MLR) are:
$\text{MLR}^{+} = 100 + \text{CRMF}$
$\text{MLR}^{-} = 100 - \text{CRMF}$.

If CRMF is less than or equal to 30 %, then the MLR are:
$\text{MLR}^{+} = 130$
$\text{MLR}^{-} = 70$.

12.2.2.2 Calculate the mercury recovery from the quality control sample as follows

$$\text{Mercury recovery} = (\text{mercury ppm } (\mu g/g)/\text{CRME}) \times 100 \qquad (7)$$

where:

mercury ppm (µg/g) = the mercury value of sample calculated according to Eq 3 or Eq 5 in µg/g and
CRME = the expected value of mercury in the quality control sample in µg/g.

12.2.2.3 If the mercury recovery is between MLR^{-} and MLR^{+}, then proceed with calculation of the concentration of mercury in the analysis samples.

12.2.2.4 If the mercury recovery is not between MLR^{-} and MLR^{+}, then check one or all of the following:

(1) If absorbance matching was used to calculate the concentration of the quality control sample, recalculate the mercury recovery using two other calibration standards. If the mercury recovery calculated using both standards falls within the limits of MLR^{-} and MLR^{+}, prepare another portion of the standard upon which the original mercury recovery was based. Determine the absorbance of the new calibration standard. If the mercury recovery calculated from the absorbance of the new standard is within the MLR^{-} and MLR^{+} limits, then proceed with calculation of the concentration of mercury in the analysis samples.

(2) If a calibration curve was used to calculate the concentration of the quality control sample, examine the curve for points that deviate significantly from the curve. Recalculate the regression eliminating the suspect point(s) (Note 10). If the value for the CRM falls within the MLR^{-} and MLR^{+} limits based on the recalculated regression, then prepare another portion of the standard(s) eliminated from the regression. Determine the absorbance of the new standard(s). Recalculate the regression incorporating the new standards. If the calculated mercury recovery of for CRME is within the MLR^{-} and MLR^{+} limits, then proceed with calculation of the concentration of mercury in the analysis samples.

(3) Verify the concentration of the mercury standard solution from which the calibration standards have been prepared.

Prepare a new mercury standard solution from the mercury standard stock solution. From the new mercury standard solution, prepare a 2-ng/mL mercury solution and a 4-ng/mL mercury solution. Determine the absorbance of the two solutions and of the quality control sample. Recalculate the mercury recovery. If the recalculated values both fall within the MLR^- and MLR^+ limits, then the original mercury standard solution is suspect. Prepare fresh calibration solutions from the new mercury standard solution and reanalyze a separate aliquot of the test solutions.

12.2.2.5 If it is not possible to reconcile the mercury recovery within the limits of MLR^- and MLR^+, then discard all solutions and repeat the analysis of all samples.

12.3 *Calculations for Test Samples*—Provided the conditions in 12.2 are satisfied, calculate the mercury content of the test samples using the same equation (Eq 3, or Eq 4, Eq 5) as for the quality control sample.

13. Report

13.1 Report the results of the mercury analysis on a dry sample basis.

13.2 Procedures for converting the value obtained on the analysis sample to other basis are described in Practice D3180.

13.3 Report the recovery of mercury in the quality control sample.

13.4 Report the digestion method used.

14. Precision and Bias

14.1 *Precision*—The precision data of this test method for the determination of mercury in coal are shown in Table 1. The precision characterized by the repeatability (S_r, r) and reproducibility (S_R, R) is described in Table A1.1 in Annex A1.

14.1.1 *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 %.

14.1.2 *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 %.

TABLE 1 Concentration Range and Limits for Repeatability and Reproducibility for Mercury in Coal

	Concentration Range, ppm	Repeatability Limit r	Reproducibility Limit R
Hg	0.032–0.585	$0.012 + 0.11\ \bar{x}$	$0.003 + 0.25\ \bar{x}$

14.2 *Bias*—Certified Reference Materials NIST 1630a, NIST 2692b, and SARM 20 were included in the interlaboratory study to ascertain possible bias between reference material values and those determined by this method. A comparison of the NIST and SARM values and those obtained in the interlaboratory study are given in Table 2.

TABLE 2 Comparison of Certified Values for NIST 1630a, NIST 2692b, and SARM 20 with Interlaboratory Study Values for Total Mercury in Coal

Reference CRM	RR Value, ppm	CRM Value, ppm	Bias, ppm	Significant (95 % Confidence Level)
NIST 1630a	0.0947	0.0938	0.0009	no
NIST 2692b	0.1187	0.1333	–0.0146	yes
SARM 20	0.22	0.25	–0.03	yes

NOTE 11—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.[6]

14.3 An interlaboratory study, designed consistent with Practice E691, was conducted in 1999. Eleven labs participated. The details of the study and supporting data are given in Research Report RR: D-5 1026 filed at ASTM headquarters.

15. Keywords

15.1 coal; coal combustion residues; cold-vapor atomic absorption; mercury

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[6] ISO 5725-6:1994 Accuracy of measurement methods and results-Part 6: Use in practice of accuracy values, Section 4.2.3 Comparison with a reference value for one laboratory.

ANNEX

(Mandatory Information)

A1. PRECISION STATISTICS

A1.1 The precision of this test method, characterized by repeatability (S_r, r) and reproducibility (S_R, R) has been determined for the following materials as listed in Table A1.1.

A1.2 *Repeatability Standard Deviation (S_r)*—The standard deviation of test results obtained under repeatability conditions.

A1.3 *Reproducibility Standard Deviation (S_R)*—The standard deviation of test results obtained under reproducibility conditions.

TABLE A1.1 Repeatability (S_r, r) and Reproducibility (S_R, R) Parameters Used for Calculation of Precision Statement

Material	Average	S_r	S_R	r	R
hvAb NIST 2692b	0.118667	0.011488	0.014959	0.032166	0.041885
hvCb SARM 20	0.222542	0.015326	0.016086	0.042912	0.045041
FGD A-1	0.585	0.026418	0.057547	0.073971	0.161133
FGD A-2	0.321167	0.018197	0.023715	0.050952	0.066402
hvAb Pennsylvania	0.114292	0.007706	0.010234	0.021575	0.028656
hvBb Ohio	0.116708	0.00599	0.009411	0.016771	0.026351
hvBb Colorado	0.032	0.001772	0.003732	0.004961	0.01045
sub A Wyoming	0.087458	0.009753	0.012924	0.027309	0.036187
lig A Texas	0.111083	0.0125	0.016317	0.035	0.045688
hvAb NIST 1630a	0.09475	0.00634	0.007655	0.017752	0.021433

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